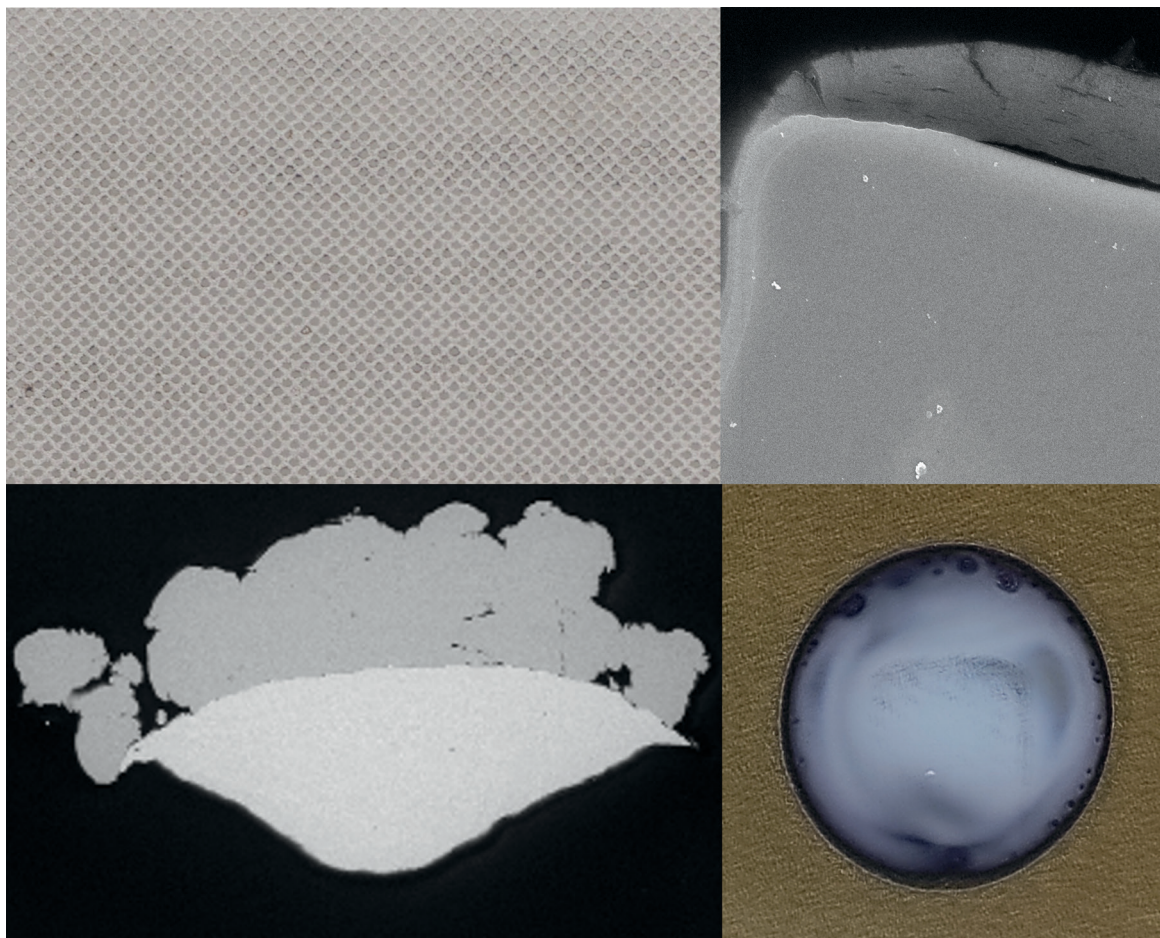




Reducing the noble metal and titanium content of anode PTLs in PEM water electrolysis – performance and degradation

Sarah Zerressen

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Abstract

Among the industrialized processes of water electrolysis, proton exchange membrane water electrolysis (PEMWE) has been demonstrated to exhibit high efficiency, thus contributing to the production of green hydrogen and playing a crucial role in decarbonizing the production of fundamental chemicals such as ammonia and methanol. Additionally, PEMWE can contribute to the electrification of our energy system, a pivotal step in the transition to a low-carbon economy. Nonetheless, the financial outlay required for this undertaking is substantial, primarily due to the employment of noble metal catalysts and noble metal-coated titanium porous transport layers (PTLs). Therefore, this work investigated two approaches to reduce the use of precious metals on PTLs and the reduction of titanium as a base material.

The first approach involved noble metal free coating materials for the anode PTL, which have not yet been researched as PTL coatings or have been investigated with inconsistent results. The materials involved titanium nitride, tungsten, indium tin oxide, niobium, tantalum and titanium-niobium and titanium-tantalum alloys. Their deposition was carried out by the institute IMD-2 using physical vapor deposition (magnetron sputtering) and thermal spray techniques (atmospheric and vacuum plasma spraying as well as cold gas spraying). While magnetron sputtering provided dense and thin coatings of just a few micrometers, thermal spray processes yielded thicker coatings between 30 μm and 60 μm . The coated PTLs were investigated for their stability in PEMWE single cell operation using electrochemical impedance spectroscopy (EIS), ex-situ resistance measurements and scanning electron microscopy (SEM) with elemental analysis via energy dispersive X-ray spectroscopy (EDX). The experiments revealed, that almost all materials underwent oxidation, resulting in increased ohmic resistances and decreased cell performances. Only coatings consisting of a mixture of 6 at.% niobium or tantalum and 94 at.% titanium provided a significant enhanced stability over 144 h. However, also pure magnetron-sputtered Ti layers enabled stable PEMWE performance close to the alloy coating. Hence, the influence of niobium and tantalum in the titanium layer on the preservation of the conductivity of the forming oxide scale has not yet been conclusively proven. Due to the insufficient oxidation stability of the materials that were selected based on their reported corrosion stability under simulated PEMWE conditions in the literature, additional investigations addressed the question to what extent ex-situ corrosion tests can reflect the oxidation and corrosion stability of anode PTL coatings. For rapidly oxidizing TiN coatings, it was found that the conditions set in the corrosion cell (pH 1.16 and potentials of 1.4 V and 1.6 V vs. RHE) led to stronger oxidation than for coatings in PEMWE experiments at 1.5 V and 2.0 V cell voltage. Consequently, it was found, that ex situ tests under the conditions most commonly used in the literature to date (sulfuric acid and potentials up to 2.0 V) are not adequate for simulating the oxidation of PTL coatings.

The second approach aiming for reduction of the amount of Ti used consisted of titanium-reduced and stainless steel-based anode PTLs as an alternative to full titanium PTLs. As stainless steel requires a corrosion protection layer, magnetron sputtered (PVD) layers with a thickness $<10\text{ }\mu\text{m}$ were deposited on stainless steel meshes and felts and cold gas sprayed (CGS) Ti layers with a thickness between $33 \pm 14\text{ }\mu\text{m}$ and $60 \pm 12\text{ }\mu\text{m}$ on meshes. The results with thin coatings on the two different substrates differed greatly. While the mesh showed extensive pitting corrosion, the felt PTL was only subject to surface corrosion with increasing cell performance even after more than 1000 h of operation, whereby membrane thinning could not be ruled out, explaining a substantial part of the performance improvement. As the two substrates were provided by different suppliers, they exhibited slightly different proportions of alloying elements. Consequently, the results indicate a correlation between stainless steel composition and corrosion resistance, requiring further systematic research.

Sufficient corrosion protection of the 316L mesh-based PTLs was only achieved with a $60 \pm 16 \mu\text{m}$ thick CGS titanium coating (CG-60). During the experiments, the effluent water from the anode and cathode sides was screened for emission of stainless steel components via inductively coupled plasma mass spectrometry (ICP-MS). With thinner CGS Ti layers ($48 \pm 16 \mu\text{m}$ and $33 \pm 16 \mu\text{m}$), increased emission of stainless steel components was observed, underscoring superior corrosion protection provided by the thicker coating. All Ti-coated stainless steel substrates had to be sputtered with an additional 38 nm Pt contact layer to prevent titanium oxidation, enabling the CG-60 PTLs to achieve comparable performance and stability over 1000 h at 2.0 V cell voltage to commercial Pt-coated Ti felt PTLs while saving approximately 25 % titanium.

Finally, performance data were extracted from dynamic wind profile operation of PEMWE single cells with state-of-the-art PTLs, providing a starting point for the analysis of PEMWE cells with new components. The methods developed for this purpose allow characterization during dynamic operation without having to interrupt the operation to record I-V curves or impedance spectra. The extracted performance indicators include cell voltage changes, I-V curves and ohmic resistances as well as indications of changes in catalyst activity.

Kurzfassung

Die Protonenaustauschmembran Wasserelektrolyse (engl. PEMWE) ist unter den industrialisierten Verfahren zur Wasserelektrolyse die effizienteste Technik und trägt somit zur Erzeugung von grünem Wasserstoff bei. Damit spielt sie eine entscheidende Rolle bei der Dekarbonisierung der Produktion grundlegender Chemikalien wie Ammoniak und Methanol. Darüber hinaus trägt die PEMWE zur Elektrifizierung unseres Energiesystems bei, einem entscheidenden Schritt auf dem Weg zu einer emissionsarmen Wirtschaft. Allerdings sind die Investitionskosten dieser Technologie hoch, was auf den Einsatz von Edelmetallkatalysatoren und mit Edelmetallen beschichteten porösen Transportschichten (PTLs) aus Titan zurückzuführen ist. Daher wurden in dieser Arbeit zwei Ansätze zur Reduktion des Edelmetalleinsatzes auf der PTL und der Reduktion von Titan als Basismaterial untersucht.

Der erste Ansatz umfasste edelmetallfreie Beschichtungsmaterialien für die Anoden-PTL, welche zu Beginn der Arbeit noch nicht als PTL Beschichtung erprobt waren oder zu welchen keine eindeutigen Ergebnisse vorlagen. Die Materialien umfassten Titannitrid, Wolfram, Indiumzinnoxid, Niob und Tantal sowie Legierungen aus Niob und Titan und Tantal und Titan. Die Beschichtungen wurden vom Institut IMD-2 mittels physikalischer Gasphasenabscheidung (engl. PVD) sowie thermischen Spritzprozessen (Atmosphärisches- und Vakuumplasmaspritzen sowie Kaltgasspritzen) aufgebracht. Während mittels PVD dichte, nur wenige Mikrometer dicke Schichten abgeschieden werden können, konnten über die thermischen Spritzprozesse Schichtdicken zwischen 30 μm und 60 μm realisiert werden. Die so beschichteten PTLs wurden in PEMWE-Einzelltests mit elektrochemischer Impedanzspektroskopie (EIS) sowie ex-situ-Widerstandsmessungen und Rasterelektronenmikroskopie (REM) mit Elementanalyse mittels energiedispersiver Röntgenspektroskopie (engl. EDX) auf ihre Stabilität untersucht. Die Versuche zeigten, dass fast alle Materialien oxidierten, was zu einem Anstieg des ohmschen Widerstands und damit einer verminderten Zelleistung führte. Nur Beschichtungen, die aus einer Mischung von 6 at.% Niob oder Tantal und 94 at.% Titan bestanden, zeigten eine deutlich höhere Stabilität über 144 h. Mit reinen über PVD abgeschiedene Titabeschichtungen konnten jedoch auch Stabilitäten nahe an der mit Legierungsbeschichtungen beobachteten Performance beobachtet werden. Folglich konnte der Einfluss der Dotierungsmittel Niob und Tantal auf den Erhalt der Leitfähigkeit des sich im Betrieb bildenden Oxids nicht abschließend geklärt werden.

Aufgrund der unzureichenden Oxidationsstabilität der Materialien, die aufgrund ihrer in der Literatur angegebenen Korrosionsstabilität unter simulierten PEMWE-Bedingungen ausgewählt wurden, wurden zusätzliche Untersuchungen durchgeführt, um zu untersuchen, inwieweit ex-situ-Korrosionstests die Oxidations- und Korrosionsstabilität von Anoden-PTL Beschichtungen widerspiegeln können. Mit schnell oxidierende Titannitridbeschichtungen wurde festgestellt, dass die in der Korrosionszelle eingestellten Bedingungen (pH 1,16 und Potentiale von 1,4 V und 1,6 V vs. RHE) zu einer stärkeren Oxidation führten als bei Beschichtungen in PEMWE-Versuchen bei 1,5 V und 2,0 V Zellspannung. Daher kann geschlossen werden, dass ex-situ tests unter den in vielen bisherigen Studien meist eingestellten Bedingungen (Schwefelsäure und Potentiale von bis zu 2,0 V) die Oxidation von PTL Beschichtungen nicht adäquat abbilden können.

Der zweite Ansatz zur Reduktion des Einsatzes von Titan bestand in titanreduzierten und edelstahlbasierten Anoden-PTLs als Alternative zu Volltitan-PTLs. Da Edelstahl eine Korrosionsschutzschicht erfordert, wurden magnetrongesputterte (PVD) Schichten mit einer Dicke von $<10\text{ }\mu\text{m}$ und kaltgasgesprühte (CGS) Ti-Schichten mit einer Dicke zwischen $33 \pm 14\text{ }\mu\text{m}$ und $60 \pm 12\text{ }\mu\text{m}$ aufgebracht. Die Ergebnisse mit dünnen Beschichtungen auf zwei verschiedenen Substraten, einem Edelstahl-Streckmetall und einem Edelstahlvlies, unterschieden sich stark. Während das Streckme-

tall Lochfraßkorrosion aufwies, wurde auf der Vlies-PTL nur Oberflächenkorrosion beobachtet und die Zelleistung nahm mit diesen PTLs bei einer Betriebsdauer von über 1000 h zu, wobei Membranausdünnung nicht gänzlich ausgeschlossen werden konnte, welche zu einem großen Teil zur Performanceverbesserung beigetragen hat.

Da die beiden Substrate von unterschiedlichen Lieferanten stammten, wiesen diese leicht unterschiedliche Anteile an Legierungselementen auf, wodurch ein Zusammenhang zwischen der Zusammensetzung des Edelstahls und dessen Korrosionsbeständigkeit vermutet wird. Ein ausreichender Korrosionsschutz der 316L Streckmetall PTLs konnte nur mit einer $60 \pm 16 \mu\text{m}$ dicken kaltgasgesprühten Titanbeschichtung (CG-60) erreicht werden. Während der Versuche wurde das Abwasser von der Anoden- und Kathodenseite mittels induktiv gekoppelter Plasma-Massenspektrometrie (ICP-MS) auf Emission von Edelstahlkomponenten untersucht. Bei dünneren kaltgasgesprühten Ti-Schichten ($48 \pm 16 \mu\text{m}$ und $33 \pm 16 \mu\text{m}$) wurde eine erhöhte Emission von Edelstahlkomponenten beobachtet, was den überlegenen Korrosionsschutz der dickeren Beschichtung unterstreicht. Alle Ti-beschichteten Edelstahlsubstrate mussten mit einer zusätzlichen 38 nm Pt-Kontaktschicht beschichtet werden, um Titanoxidation zu verhindern. Dadurch erreichten die CG-60-PTLs bei einer Zellspannung von 2,0 V über 1000 h eine vergleichbare Leistung und Stabilität wie kommerzielle Pt-beschichtete Ti-Vlies-PTLs, wobei mit diesen PTLs etwa 25 % Titan eingespart werden kann.

Abschließend wurden Leistungsdaten aus dynamischem Windprofilbetrieb von PEMWE Einzelzellen mit kommerziellen PTLs extrahiert. Die zu diesem Zweck entwickelten Methoden ermöglichen eine Charakterisierung während des dynamischen Betriebs, ohne dass dieser unterbrochen werden muss, um I-V-Kurven oder Impedanzspektren aufzuzeichnen. Zu den extrahierten Leistungsindikatoren gehören Zellspannungsänderungen, I-V-Kurven und ohmsche Widerstände sowie Hinweise auf Veränderungen der Katalysatoraktivität. Die dabei erarbeiteten Methoden stellen somit einen Ausgangspunkt für die Analyse von PEMWE-Zellen mit neuen Komponenten dar.

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List of contributions to scientific publications

Title	Journal	DOI	Contribution
Performance data extraction from dynamic long-term operation of proton exchange membrane and alkaline water electrolysis cells	International Journal of Hydrogen Energy	10.1016/ j.ijhydene.2025.03.387	Writing – original draft, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization
Cold gas spraying of titanium on stainless steel to enhance corrosion protection inside proton exchange membrane water electrolyzers	Surface & Coatings Technology	10.1016/ j.surfcoat.2025.132486	Investigation, Data curation, Writing – review and editing
Nb-Ti alloy coatings for anode PTLs in PEM water electrolyzers	Review in progress	/	Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation, Visualization, Writing – original draft, Writing – review and editing

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1. Introduction

Hydrogen allows the storage of electricity from renewable energy sources and is an essential component in the chemical industry for the production of basic chemicals like methanol and ammonia. Beyond that, hydrogen offers the potential to bring down CO₂ emissions of the steel production [1] and through hydrogen, sector coupling can be achieved, being an important building block for the security of our energy supply [2]. However, at present, hydrogen is largely obtained from fossil sources, also referred to as gray hydrogen. To decarbonize our primary energy consumption and large parts of the chemical industry, it is of decisive importance to produce hydrogen in a more climate-friendly way. Reducing the climate impact of hydrogen production can be achieved by water electrolysis, with the electricity required provided by renewable energy sources, also referred to as green hydrogen. It is estimated, that in 2023, hydrogen production by polymer electrolyte membrane water electrolysis (PEMWE), driven by electricity from wind turbines, offered a reduction of greenhouse gas emissions by 82 % compared to conventional steam reforming [2]. However, as the production of green hydrogen is currently more expensive, in 2021, the share of hydrogen produced by water electrolysis was only 4 % [3]. Among all mature water electrolysis techniques, PEMWE is considered to be the prevailing electrolysis technology by 2030 [4], as the hydrogen produced exhibits a purity of 99.999 % [5] and compared to alkaline electrolysis higher current densities and consequently higher production rates can be achieved.

The price of green hydrogen depends on the one hand on the price of electricity and on the other hand on the investment costs of the electrolyzer and system. For PEMWE, iridium, platinum and titanium are used. As these materials are costly and classified as rare and critical materials [2], research is currently carried out to reduce the amount of precious metals and titanium required. In particular, the cost reduction of porous transport layers (PTLs) can contribute to reduce stack costs, as they account for about 17-35 % of stack costs and are, together with bipolar plates and the anode catalyst material, considered to be the most critical and costly component in PEMWE stacks [6, 7].

1.1. Motivation and approach

One aim of the work was to investigate and evaluate precious metal-free coatings for the PTL on the anode side of PEM water electrolyzers. For this purpose, selected materials were coated by the institute of Materials Synthesis and Processing (IMD-2) on titanium felts, titanium expanded meshes and titanium sintered bodies and tested for their corrosion, oxidation and long-term stability in PEMWE single cells. For ex-situ evaluation of the PTL resistance, a setup for the measurement

1. Introduction

of the contact resistance was built.

Furthermore, the conditions at the interface between the PTL and anode catalyst layer were investigated to refine the search for new materials that can withstand the acidic vicinity of the proton conducting membrane and anode overpotentials.

Another approach to reduce the costs of anode PTLs in PEMWE that was pursued within this work is considered to be the replacement of titanium by stainless steel. Therefore, it was investigated whether the titanium content of PTLs can be reduced by partial replacement with stainless steel AISI 316L. 316L belongs to the austenitic stainless steels with high corrosion resistance [8]. Its specification allows for the following composition: 60-70 wt% Fe, 17-21 wt% Cr, 9-13 wt% Ni, 0-1.5 wt% Mn, 2-3 wt% Mo, and 0-1.5 wt% Si [8]. After an introduction to all relevant fundamentals related to this work and methods and measurement techniques used, the work is structured as follows:

Chapter 1 introduces the intention, gives context of the work and an overview of the methodology followed.

Chapter 2 presents the scientific fundamentals and identifies open questions based on previous research findings.

Chapter 3 provides information about all materials, methods and measurement techniques used.

Chapter 4 examines with standard PEMWE cells the extend of performance differences that are to be expected at the five cell places of the 5-fold test bench used to enable a performance assessment of new PTLs in the further course of the work. Hence, this chapter provides an overview of the reproducibility of the PEMWE single-cell measurements.

Chapter 5 presents the single cell performance with state-of-the-art platinum coated titanium PTLs, serving as a basis for performance comparisons with new PTLs. Apart from commercially available titanium felt PTLs, titanium expanded meshes and titanium sintered bodies were used in subsequent chapters to investigate new coatings. Beyond that, all titanium PTLs were investigated with regards to their performance without Pt coating, defining the performance range that can be achieved with the test cells used with uncoated and Pt coated PTLs.

Chapter 6 represents one core part of the work. Within this chapter, noble-metal free coating materials that were identified from literature research as promising candidates are investigated regarding their oxidation- and corrosion stability. PEMWE single cell tests including the recording of I-V curves and electrochemical impedance spectra are accompanied by SEM, EDX analysis and ICR measurements of the PTLs prior to cell tests and post mortem.

Chapter 7 presents the second core part the work, where the second approach for cost-reduction of PTLs was pursued, involving the reduction of the titanium content by partial replacement with stainless steel. Also here various analytical techniques are used and in addition ICP-MS analysis for the monitoring of impurities in water samples.

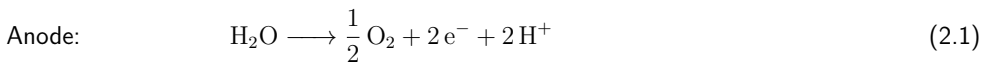
Chapter 8 presents the extraction of performance data from dynamic wind profile operation. The method development was carried out in cooperation with Pape et al. [9]. Background to this work was that new PTLs and coatings must also be able to withstand dynamic operation. The method development was carried out with standard materials (Pt-coated titanium PTLs), as no non-precious metal coating with sufficient long-term stability was readily available when the methods were developed. Thus, the method development serves as a basis for further research with novel cell components.

2. Scientific Fundamentals and State of the Art

2.1. Proton exchange membrane water electrolysis

Currently, five main electrolysis techniques are available with different technology readiness levels: Alkaline Water Electrolysis (AWE), Proton exchange membrane water electrolysis (PEMWE), Anion exchange membrane water electrolysis (AEMWE), solid oxide electrolysis (SOEC) and proton conducting ceramic electrolysis (PCCEL). The first three technologies are classified as low-temperature electrolysis, as they work below 90 °C, while SOEC and PCCEL involve higher temperatures of 700 °C to 850 °C and 300 °C to 600 °C [10]. Due to their advantages and disadvantages, the various technologies cover a range of different application areas, with particularly strong overlaps in the area of low-temperature electrolysis and AWE and PEMWE being the most mature technologies that are developed to an industrial scale.

Compared to AWE, PEMWE is able to operate at a higher power input and is thus able to produce larger amounts of hydrogen and additionally with higher purity than AWE, where expensive treatment of product gases is necessary [11]. Furthermore, the use of a perfluorinated sulphonic acid (PFAS) copolymer membrane as a proton conductor and solid electrolyte allows a zero-gap design with a high system efficiency of 71 % excluding hydrogen compression [12]. However, investment costs for PEM electrolyzers are high due to the use of precious metals catalysts for the water splitting and hydrogen evolution reactions as well as noble metal coatings for metallic components. Therefore, research is continuing to increase the efficiency and reduce the investment costs of PEM electrolyzers to reduce the levelized cost of hydrogen [13]. Furthermore, it is estimated that the immense quantities of green hydrogen required cannot be produced by means of the other technologies, particularly not at the dynamic power input levels that occur when coupled with renewable energies [11]. Therefore, continued development of PEM electrolyzers is an important building block for scaling up the production of green hydrogen.



2. Scientific Fundamentals and State of the Art

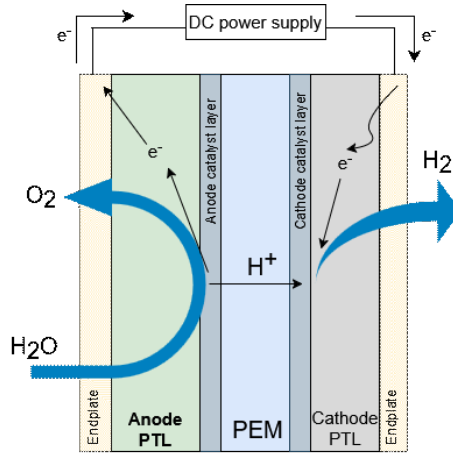


Figure 2.1. Schematic illustration of the working principle of PEM water electrolysis. Proportions are not to scale.

Figure 2.1 presents a schematic illustration of the design of PEM electrolyzers. The principle of operation is that at a sufficiently high voltage difference between the anode and cathode side, or when current is applied, the supplied water is split into oxygen, protons and electrons (Equation 2.1). The water splitting reaction, also referred to as oxygen evolution reaction (OER) takes place at the anode side, as the half cell potential is higher there (see section 2.2). Due to the concentration gradient and the electric field between the anode and cathode side, the protons migrate through the membrane to the cathode. Therefore, the membrane consists of a proton-conducting sulfonated tetrafluoroethylene-based copolymer (NafionTM). At the cathode catalyst, platinum catalyst supported on carbon, the protons recombine with the electrons arriving via the external electric circuit and hydrogen is produced. Both gases can thus be produced in separate reaction chambers. As the product gases are saturated with water, they must be dried in several stages. In addition, hydrogen must be further compressed for storage. Oxygen is usually not used and released into the atmosphere. On an industrial scale, PEM electrolyzers are often operated under pressure to reduce the number of further compression stages, although efficiency decreases as a result of the higher pressure [14].

The heart of the electrolyzer consists of a membrane electrode assembly (MEA), also known as a catalyst-coated membrane, as the electrodes are hot-pressed with the membrane. As the protons produced by water splitting have to reach the cathode side, not only an electrically conductive, metallic catalyst is needed in the catalyst layer, but also a proton-conducting phase. Therefore, the catalyst layers contain a proportion of ionomer of the membrane polymer, enabling the chemical connection between the catalyst layer (CL) and membrane during hot pressing. To realize the elec-

trical connection of the catalyst layers, they are in direct contact with so-called porous transport layers (PTLs) that consist of porous and electrically conducting materials like titanium at the anode and carbon at the cathode side. Due to the focus of the work, the PTLs are described in more detail in section 2.3.

The use of a solid polymer electrolyte enables a zero-gap design with low ohmic losses and no gap between the catalyst and the current collector. Iridium oxide is typically used as the anode catalyst material, and platinum as the cathode catalyst material. One of the current research priorities is to reduce the loading of iridium, as the metal is expensive [15–20] and its annual production rate is limited to 7.25 t [19]. Some research is also being carried out on the cathode catalyst [21].

2.2. Thermodynamics and kinetics of water electrolysis

The standard potential, also referred to Nernst potential, for the water splitting reaction at 25 °C is 1.229 V. However, for electrolysis operation, higher cell voltages are required as further contributions add to the overvoltage like charge transfer (CT) of the half-cell reactions and ohmic losses. The latter occur mainly due to the resistance of the proton transport [22]. All metallic components usually have a negligible contribution to the overvoltage caused by ohmic resistances, unless insulating oxide layers form. The thermoneutral cell voltage at 80 °C is 1.479 V [23], where the cell neither consumes nor emits any heat. However, at this point, only small current densities are reached (c.f. Figure 2.2), and therefore only a very small amount of hydrogen is produced. Therefore, electrolyzers are operated above the thermoneutral cell voltage to remain economically viable.

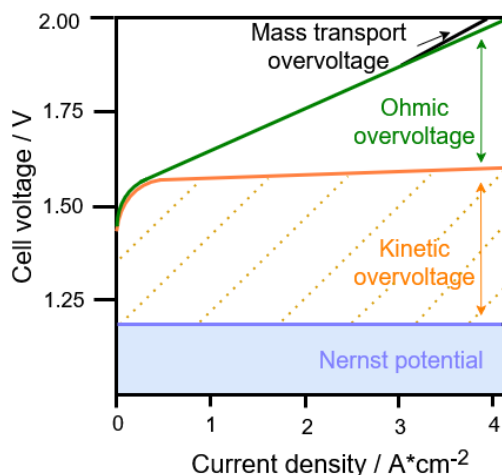


Figure 2.2. Contributions to the overvoltage in PEM water electrolysis as a function of current density.

The appearance of overvoltage due to hindered mass transport, here exemplarily shown above approximately 3 A cm^{-2} , highly depends on the PTL, CL, water management and contact pressure distribution at the PTL/CL interface. In an ideal system with efficient water transport and gas removal, mass transport losses do not occur. Exceeding the upper limit of 2.0 V is often prevented, as according to the Pourbaix diagram of iridium, at pH 0 and approximately 2.0 V IrO_4^{2-} can form, which is a soluble complex [24].

2.3. The anode porous transport layer

Together with the membrane electrode assembly, the porous transport layers (PTLs) are crucial parts of PEM electrolyzers, as they are in direct contact with the catalyst layers and therefore influence the amount of active sites. At the anode side, the main functions of the PTL are "collecting" the current from the water splitting reaction (Equation 2.1), allowing the water to reach the catalyst layer and enabling the evolving gas-water mixture to escape from the cell as quickly as possible. It is particularly important to ensure the effective removal of the oxygen produced to avoid the blockage of active catalyst centers by gas bubbles. Consequently, the anode PTL has to be porous, electrical conductive and mechanical stable. Therefore, typically titanium felts, sintered bodies or meshes [25] are used, whereas sintered bodies potentially offer more triple phase contact boundaries (TPCB) compared to fiber (felt) PTLs, as they can exhibit a lower porosity and can be denser packed at the surface [18]. In addition, a lower porosity can also lead to higher thermal conductivity, as Schuler et al. [26] found that a sintered body with lower porosity provided better thermal conductivity than a fiber-based material ($2 \text{ W m}^{-1} \text{ K}^{-1}$ to $6 \text{ W m}^{-1} \text{ K}^{-1}$ vs. $10 \text{ W m}^{-1} \text{ K}^{-1}$). More TPCBs are also favorable for mass transport. As the porosity of the PTL and the water uptake of the membrane and consequently the proton conductivity of the membrane are crucial for the cell performance [27], a lot of studies investigated an optimal thickness, pore size [28] and porosity for anode PTLs [29–33]. Two studies agreed on an optimal pore size of around $10 \mu\text{m}$ [33, 34] and Grigoriev et al. [32] reported an optimal mean pore diameter of $12 \mu\text{m}$ to $13 \mu\text{m}$ when sintered spherical Ti particles with a distribution of $50 \mu\text{m}$ to $75 \mu\text{m}$. With these parameters, ohmic losses and mass transport limitations were as small as possible, as a higher pore diameter increases the ohmic resistance [35]. Rakousky [36] compared the cell performance of two PTLs from sintered powder beds with $3 \mu\text{m}$ and $10 \mu\text{m}$ titanium particles, and found that the overvoltage at 2 A cm^{-2} was 200 mV higher with the sintered body of smaller particle size, probably as it allows for a more dense packaging, leading to a lower porosity and a smaller pore diameter. An analysis of porosity and pore diameter was not carried out, but water droplets were observed not to soak into the sintered body with $3 \mu\text{m}$ particles, in contrast to that with $10 \mu\text{m}$ particles, indicating poorer wettability and thus potential contributions to the ohmic resistance or mass transport limitation.

The influence of the pore opening and porosity on ohmic losses was also studied by Weber et

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al. [37]. They observed a strong increase of the high frequency resistance (HFR) with increasing current density with pore openings of 200 μm and 400 μm as well as with lower porosities of 29 % and 9 %. Apart from ohmic losses, more pronounced mass transport limitation was also observed with low porosities and large pore openings. Both effects are assumed to occur due to strong membrane dry-out and or in combination with trapped oxygen under the PTL. At low current densities no performance differences could be observed, indicating that in the low current density region, catalyst utilization is not limited by the PTL/CL interface. They conclude that a pore size of 5 μm to 10 μm might be optimal. Lopata et al. [31] also explained mass transport limitation with coverage of gas bubble or dry-out of the CL and membrane, but did not define a prevalent cause. For sintered titanium PTLs, optimal porosities are reported ranging between 30-50 % [32] or 27-30 % [38]. Some studies used commercially available titanium felt with a porosity of about 68 % and achieved similar or better performances than with sintered PTLs [39, 40]. In terms of compressibility, both sintered and titanium felt PTLs are assumed to be incompressible or to exhibit negligible compressibility [41, 42]. Ito et al. [34] found for Ti felt PTLs, that the performance does not change significantly when the porosity is increased from 50 % to 75 % which might explain the good performance with Ti felts with 68 % porosity. Also Nara et al. [43] found an improved performance with 78 % over 56 % porosity with Ti felt PTLs. In addition to higher porosities, felt PTLs typically possess lower tortuosities [44]. Consequently, when selecting the PTL porosity, it is necessary to consider whether a sintered or felt PTL is used, as optimal porosities of approximately 30 % have been found for sintered bodies, while the optimal porosity for felt PTLs is reported to be around 70 %.

Another approach to improve the removal of oxygen is a gradient pore structure with lower porosity facing the bipolar plate side and higher porosity facing the MEA side [33]. In terms of the PTL thickness, most studies report an improved performance with thinner PTLs [45–47], while only few studies reported a different trend [48].

Furthermore, the hydrophilicity, influencing the wettability of the PTL is important for the effective detachment and removal of gas bubbles. In hydrophobic PTLs, gas bubbles remain longer leading to increased overvoltage and consequently performance losses [49].

On the cathode side, PTLs are used for the same functions as on the anode side, but as the potential at the cathode is close to a standard hydrogen electrode and therefore around zero or slightly negative, carbon felts can be used. Apart from their lower costs compared to titanium, carbon felts are compressible and thus can compensate for irregularities of other components. Additionally, depending on the chosen gasket thickness of the carbon PTL, a defined compression of the PTL can be adjusted, as the level of compression influences the conductivity of the PTL and hydrogen permeation through the MEA [42].

2.3.1. The PTL/CL interface

To investigate new coating materials for anode PTLs, it is of decisive importance to know as precisely as possible the conditions influencing the thermodynamic and kinetic stability of the PTL coating. In general, the thermodynamic stability of a material depends on the temperature, the pH of the surrounding medium as well as the electrochemical potential to which the material is exposed. Therefore, these three influencing factors on the stability of PTLs are briefly summarized in the following and subsequently another research aspects of this interface.

1. Temperature

PEM water electrolyzers are typically operated between 50 °C to 80 °C [10], as the ionic conductivity of the membrane increases with the temperature [50, 51] and the reaction rate increases according to Arrhenius, but no further performance increase can be achieved at 90 °C [52], as above 80 °C chemical degradation of the proton exchange membrane accelerates [53, 54]. As explained in section 2.2, electrolyzers typically operate above the thermoneutral cell voltage (> 1.5 V) for an economical hydrogen production rate and therefore generate waste heat. Consequently cooling would be necessary when operating at lower temperatures below 50 °C, thereby requiring additional energy. As metallic coatings are stable in this temperature window, the mild temperatures in low-temperature electrolysis play a minor role for the stability of the coating. In addition, it is expected that temperature fluctuations of a few degree Celsius will have no effect on the stability of the coatings.

2. pH

As the MEA consist of an acidic, proton-conducting sulfonated tetrafluoroethylene-based copolymer, it can be assumed that acidic conditions prevail where the PTL is in direct contact with the electrode. Various data on the pH value of Nafion™ are given in the literature. Brightman et al. [55] calculated a pH value of less than 2. A recent study by Cho et al. [56] reported that the local pH at the anode catalyst interface can drop to <1 due to the accumulation of protons, but they used a modified setup without anode catalyst layer and HClO_4 as feedstock to exclude iridium dissolution from the catalyst layer and to reach significant current densities that would not be possible just with deionized water. The acid strength (pK_a) of the functional sulfonic acid groups is given as approximately -6 [57].

Concerning the circulating water, Langemann [8] detected a drop in the pH value to 3.5 on the anode side and 4.5 on the cathode side after 50 h of operation. As he detected chloride ions in the water, he attributed the decrease in pH to the leaching of hydrochloric acid impurities from the catalyst material, e.g. stemming from the synthesis of the platinum catalyst. As these impurities in the catalyst material are subject to fluctuations, M. Langemann's result might not be applicable to

all PEMWE cells. Therefore, investigations of the pH of the anode and cathode circulating water were also carried out as part of the work (chapter 7).

3. Cell voltage

The local electrode potential of the anode CL and the question to what extent the PTL surface is affected by this potential are important parameters, particularly for the thermodynamic stability of a material. Although the local potential difference may vary due to an uneven distribution of active catalyst sites and the possible presence of different iridium species, it is conceivable that, on average, the anode potential approximately corresponds to the iR-free cell voltage, as the iR-free cell voltage is adjusted for the ohmic voltage drop caused by the membrane. This assumption is supported by the following consideration: The cell voltage with a thinner membrane is lower than with a thicker membrane due to a lower membrane resistance, but not due to a lower CT resistance. Consequently, the iR-free cell voltages with different membranes are expected to be similar, as the overvoltages for CT at the catalyst are independent of the membrane thickness. Consequently, it can be anticipated, that the anode potentials will correspond approximately to the iR-free cell voltages. The cathode potential does not equal 0 V vs. SHE in practice, but is slightly negative up to approximately -0.3 V [58] due to the CT of the HER.

The effect of the anodic polarization of the electrode on the PTL was experimentally and theoretically studied by Becker et al. [59]. Due to the low ionic conductivity of the circulating water, about $20\text{ }\mu\text{S cm}^{-2}$ for deionized and osmosis-cleaned but CO_2 -dissolved water, they found that the ionic potential of the electrode drops through the PTL to the resting potential of the PTL within $200\text{ }\mu\text{m}$. Consequently, they concluded that the zone of anodic polarization drops away from the catalyst layer and in sufficient distance to the anode, it might theoretically be possible to use less expensive materials like stainless steel or carbon. Sorsa et al. [60] measured anode and cathode potentials with in-situ reference electrodes and found that the half cell voltage of the anode stays below 1.25 V vs. SHE, while the cathode potential dropped to almost -0.5 V vs. SHE at a cell voltage of 2.0 V while recording an I-V curve. However, after 10 min at 1 A cm^{-2} and a cell voltage of 2.0 V , the anode potential stabilizes at approximately 1.49 V and the cathode potential at approximately -0.49 V , which is in accordance with experimental results from Böhre et al. [61], who connected a salt bridge reference electrode to a NafionTM coated anode PTL and measured a potential of approximately 1.49 V to 1.51 V over the entire cell voltage range up to 2.0 V . Also Wallnöfer-Ogris et al. [58] display the anode potential at maximum 1.62 V . Consequently it can be assumed, that the maximum potential where the PTL coating has to be stable approximately amounts for 1.6 V vs. SHE.

Apart from the impacts on the stability of the PTL, two studies report the growth of iridium clusters in the membrane [62, 63], which might be influenced by the contact with the PTL. One of the

two studies suggests that this growth occurs at contact points with the PTL where high current densities prevail. The proposed mechanism suggests that dissolved Ir(III) ions migrate through the membrane to the cathode, where they are reduced by permeating hydrogen to metallic iridium, which remains in the membrane [63]. As this phenomenon is likely to occur particularly in the case of an inhomogeneous current density distribution, in which the reaction zone shifts strongly towards the contact points with the PTL, the PTL must be equipped with as many contact points as possible and the CL with the highest possible in-plane conductivity to achieve a current density distribution that is as homogeneous as possible.

2.3.2. Anode PTL materials

As mentioned in section 2.3, different PTL geometries have been investigated by a lot of studies. Concerning the base material of anode PTLs, titanium is the state of the art, as titanium is corrosion resistant under the operating conditions [3]. The stability of titanium stems from its characteristic to form a stable oxide layer on the surface, which prevents or at least significantly slows down further oxidation of the metal. However, depending on the layer thickness, titanium oxide is a semiconductor or even an insulator and thus reduces the electrical conductivity between the PTL and CL. This additional resistance on the PTL surface causes less energy to be available for electrolysis. As a result, the efficiency of the water splitting reaction decreases. Therefore, titanium PTLs are typically protected with a thin layer of platinum or iridium [64]. State of the art coatings and surface treatments for PTLs are summarized in the next subsection 2.3.3.

As titanium is a comparatively expensive material [65], efforts are made to replace titanium by carbon [66] or stainless steel [67]. However, more studies are available on bipolar plates as they are subject to less oxidizing conditions due to the decreasing ionic potential away from the CL as the pores of the PTL are only filled with water with a low conductivity [8, 68–71]. Gago et al. [71] and Lettenmeier et al. [70] demonstrated stable cell performance with 316L bipolar plates protected by a 50 μm to 60 μm Ti vacuum plasma sprayed (VPS) coating and 1.5 μm Pt coating. Concerning PTLs, Becker et al. [59] presented almost stable PEMWE single cell operation with a carbon coated 316L PTL for 30 days at 2 A cm^{-2} (1.9 V), whereby the thickness of the carbon coating amounted for 130 nm. In the same year Stiber et al. [67] published a study about a 316L mesh PTL with a layered coating consisting of Ti and Nb by VPS that enabled almost stable cell performance for 1500 h without any signs of corrosion or MEA poisoning and a degradation rate of approximately $270\text{ }\mu\text{V h}^{-1}$. Even though these studies achieved promising results, the question remains whether pure contact with ultrapure water and the oxygen produced over longer periods of time would attack the stainless steel surface and lead to surface corrosion, as this degradation mechanism is known from other applications [72].

2.3.3. Anode PTL coating materials

Noble metals

As mentioned above, platinum or iridium coatings on anode PTLs are the standard materials in PEMWE to avoid oxidation of the titanium PTL. Even if the surface of the titanium PTL is not pre-treated and the precious metal layer is coated on the natural titanium oxide layer (approximately 5 nm [73]), the contact resistance between the PTL and CL is significantly reduced. The reason why the addition of a platinum coating on titanium is increasing the PTL conductivity might be due to the electronic interaction between the native titanium oxide layer and platinum. For slightly sub-stoichiometric $\text{TiO}_{1.9}$ particles coated with Pt catalyst, strong metal support interactions are reported [74]. These interactions are possible when oxygen vacancies are present in TiO_{2-x} , which produce energy levels in the band gap 0.5 - 1.0 eV underneath the conduction band of the oxide leading to population of surface electrons that are available for conduction. This effect is even stronger with fluorine doped stoichiometric TiO_2 [74]. Theoretically, also a Schottky junction could be established due to a higher work function of polycrystalline Pt (5.6 - 5.8 eV vs. 3.2 - 4.8 eV for TiO_2 [74, 75]). Choi et al. [76] conducted a Mott-Schottky analysis and report that a Pt coating on TiO_{2-x} increases the donor-density by 2 to 12 times, narrowing down the depletion zone and thus lowering the barrier for an electron transfer and increasing the conductivity. However, Hope et al. [77] found a Schottky barrier only when the titanium surface was etched prior to the platinum coating process. Additionally, they reported that an ohmic, low-resistivity contact is established when Pt diffuses into the rutile structure of the oxide. Without diffusion, rectifying properties are dominating.

If the improved conductivity of Pt coated Ti-PTLs, compared to pure Ti PTLs, is established due to a Schottky junction between both materials, any metallic coatings that aim to replace Pt should also exhibit a larger work function than TiO_x . Considering the findings on the interaction of the band structures of TiO_x and Pt, an improvement in conductivity by a Pt coating seems to be particularly effective when the natural oxide layer, on which the platinum layer is deposited, is slightly sub-stoichiometric. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) by Liu et al. [39] revealed that the native oxide layer on a titanium PTL is sub-stoichiometric ($\text{Ti}_{84}\text{O}_{16}$). Therefore, it is likely, that band interactions between titanium PTLs and noble metal coatings take place.

Despite their stability, Pt and Ir or IrO_2 coatings on anode PTLs are also affected by corrosion processes [56]. Research from PEM fuel cells reports the formation of PtO multilayers above 0.6 V vs. SHE [78]. However, for PEMWE, Liu et al. [39] postulated, that Pt oxidation does not affect the cell performance, as the amount of conductive area on the Pt coating before and after the 4000 h of operation were comparable. Although Pt is thermodynamically not stable at the potentials prevailing on the anode side, dissolution rates are very low, as its oxidation is kinetically inhibited [78, 79] and

with a slow reaction rate slow with a time constant of about 10 s [80]. Furthermore, the passive oxide film on Pt prevents the metal from further dissolution [79].

Although iridium is more expensive and more rare than platinum, it can, in contrast to Pt, contribute as a catalyst for water splitting [16, 81] and one study found that membrane degradation proceeds more slowly with Ir-coated anode PTLs [81]. Furthermore, another study observed detachment of Pt from the PTL surface after 1940 h of electrolysis operation above 2 A cm^{-2} (between 1.9 V to 2.1 V) within the last 800 h. Also Alia et al. [82] reported detachment of a platinum coating. Consequently, one could conclude that iridium might provide an enhanced stability, but it is not confirmed by further studies if Pt detachment is a general phenomenon or only occurred due to the combination of the specific PTL and coating used.

Most coating processes for PTLs are line-of-sight processes in which the surface and in most cases, depending on the process, also deeper, unshielded areas are coated. Although the degree of coating is not specified in most publications, it can be assumed that, using spray or sputter processes, large parts of the PTL surface that are not facing the spray nozzle or the target remain uncoated. An approach for coating the entire surface of a titanium felt PTL was recently presented [83]. The approach involved a three-step process involving electrochemical etching for the removal of surface oxides, electrostriking to create an Au bonding layer and electroplating to deposit an Au toplayer. With the so prepared PTL, the cell voltage was reduced by 124 mV at 2 A cm^{-2} . Although this approach seems promising to increase the electrolyzers efficiency, it is necessary to consider whether the higher manufacturing costs due to the use of precious metal and the multi-stage coating process can be compensated by the lower overvoltage. Furthermore, long term testing would be important with gold coated PTLs, as Liu et al. [39] found that with gold-coated PTLs, the current density decreased by 35 % after 4000 h of operation.

Titanium heptoxide

As Pt, Au and Ir are expensive materials, a lot of studies began to investigate alternative noble metal free coating materials. Wakayama [84] for example recently presented a Ti_4O_7 coating for anode PTLs. However, when they applied Ti_4O_7 on the MEA-facing side, the cell voltage sharply increased and the ICR was elevated after 100 h at 3 A cm^{-2} . Stable cell operation for 100 h was only possible with a Pt coating on the MEA-facing side. Consequently, although the conductivity of the heptoxide is promising, oxidation during electrolysis to pure titanium oxide, observable from Raman shifts [84] renders its use as a PTL coating impractical.

Nitrides

Another possible coating material for anode PTLs is titanium nitride as it is reported to be corrosion resistant with excellent conductivity [85]. So far, there is only one publication that successfully

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introduced TiN as a contact layer on the anode PTL for corrosion protection against the anode catalyst layer [46]. In this study, the TiN layer was produced via a thermal nitride surface treatment of a titanium PTL and enabled a performance close to that of a gold coating, but without any investigation on long-term stability. Another recent publication reports long-term operation with a TiN_x-coated Ti PTL by magnetron sputtering for 2000 h with a high degradation rate of 387 $\mu\text{V h}^{-1}$ within the first half and 32 $\mu\text{V h}^{-1}$ in the second half resulting in a total cell voltage rise from 1.196 V to 2.42 V at 3 A cm⁻² [86]. The degradation rate in the second half of the test was probably one order of magnitude lower than the aging rate within the first 1000 h, as the oxidation of the coating was most likely already nearly complete in the first half and then progressed only slowly in the second half. Studies on TiN-coated bipolar plates for fuel cell [87–91] or electrolysis application [92] are more numerous. Toops et al. [92] reported the oxidation of TiN on separator plates in PEMWE, which was not detrimental for the cell performance. Langemann et al. [68] found TiN to undergo fast oxidation under simulated PEMWE conditions in sulfuric acid. Also earlier reports from corrosion of TiN in different concentrations of H₂SO₄ exist [93] and Milosev et al. [94] reported electrochemical oxidation of TiN PVD coatings to oxynitrides between 0 V to 1.0 V vs. SHE and oxidation to TiO₂ above 1.1 V vs. SHE under neutral conditions. Due to the proximity to the catalyst layer and the potential applied to it, it seems likely, based on the experiments on the oxidation behavior of titanium nitride, that TiN coatings oxidize on the anode PTL.

A further potential candidate for anode PTL coatings close to TiN is titanium oxynitride as it exhibits a better corrosion resistance than titanium [95]. So far titanium oxynitride coatings are only tested under simulated conditions for bipolar plate coatings for fuel cell application where the corrosion resistance could be improved compared to TiN coatings [96], but the test conditions are not comparable to a PEMWE environment. Therefore, it is possible that oxynitrides, analogous to TiN, will oxidize further to pure oxides.

Other nitrides like TaN were applied magnetron on anode PTLs by Ye et al. [97]. However during PEMWE operation, the coatings oxidized and increased the contact resistance. As a similar oxidation behavior can be expected for NbN, it can be concluded that nitrides are not suitable as protective coatings for anode PTLs. Niobium nitride has so far only been investigated as a bipolar plate coating, where it provided corrosion protection [98]. However, as already shown by the comparison of studies on bipolar plate and PTL coatings, these studies do not allow conclusions to be drawn from one to the other.

Niobium

Close to titanium in the periodic table, niobium became subject to investigations as coating material for PEMWE. As mentioned above, Stiber et al. [67] ran a 316L mesh PTL with a layered Ti and Nb coating (VPS) for 1500 h with an aging rate of approximately 270 $\mu\text{V h}^{-1}$, but no signs of corrosion or MEA poisoning. With regards to the aging rate it is likely, that the resistance of the Nb coating increased. Another study by Kellenberger et al. [99] developed a 30 μm thick Nb corrosion

protection coating applied via APS on copper bipolar plates. Although they observed the formation of a passive oxide layer of around 10 nm, predominantly composed of Nb_2O_5 , the cell resistance did not increase. It might be possible that the electrical conductivity of niobium oxide, which is higher than that of titanium oxide [100] (c.f. Table 6.1) was high enough to enable a sufficient electrical conductivity. Additionally, a higher resistance against fluoride compared to titanium turns niobium into an attractive coating material [101]. However, it must be noted that niobium is classified as a critical raw material by the European Union, while the supply with platinum group metals (PGMs) is classified as moderately endangered without specifically addressing the availability of iridium [102]. Therefore, the usage of Nb as a coating material can be only recommended if an equal or superior performance over noble-metal coatings can be achieved.

Alloys

Another approach that has not yet been pursued with regard to metallic coatings for BPP and PTLs in PEMWE, but is conceivable and will be addressed in this work, is the doping or alloying of titanium with other refractory metals. Similar to substoichiometric titanium oxides, the conductivity of titanium oxides can be increased by doping with higher valence refractory metals [103]. In 2000, Pérez et al. [104] reported about Ti-Nb alloy coatings with 4 at.% Nb in titanium and assumed that the transport of oxygen might be impeded due to the incorporation of niobium in the titanium lattice, which could help to protect against oxidation. Furthermore, Frisch et al. [103] calculated that Nb is the most auspicious dopant to improve the electrical conductivity of TiO_2 and found experimentally an increased conductivity of $\text{Nb}_x\text{Ti}_{1-x}\text{O}_2$ with up to 35 mol% Nb of more than three orders of magnitude compared to pure TiO_2 due to an increased occupation of 3d-orbitals of titanium. This increased orbital occupation contributes to the conductivity by increasing the states at the Fermi level and shifting the Fermi level to higher energies as the electron density increases. However, with higher fractions of Nb, e.g. 50 mol%, the sheet conductivity decreased again due to a lower crystallinity and the transition to a solid solution with more Nb-Nb interactions. The formation of a solid solution is likely as Ti_4^{+} and Nb_5^{+} exhibit comparable ionic radii (0.68 Å and 0.69 Å) [105]. Aukland et al. [106] investigated 1 % to 3 % Nb in Ti and Ta in Ti alloys and found that the surface conductivity of the alloys was higher compared to pure titanium oxide. They investigated the stability in H_2SO_4 (pH 4.66 to 3.18) between -0.4 V to 1.0 V vs. SCE, as the study aimed to simulate PEM fuel cell conditions. They suggested that the conductivity of the alloy is enhanced when the dopant exhibits a valence state above +IV, as e.g. Nb^{5+} or Ta^{5+} force Ti^{4+} ions to the oxidation state Ti^{3+} to maintain electrical conductivity. Consequently, electrical conductivity is maintained by electron hopping between Ti^{3+} and Ti^{4+} ions. Apart from the improvement of the electric conductivity, there are also reports on the usage of Nb-doped TiO_2 as support for the OER IrO_2 catalyst enhancing the catalytic activity compared to titania supports or unsupported iridium oxide [107].

Tantalum

Although tantalum has not yet been implemented as a PTL coating, the element is described in the literature as corrosion-resistant [108]. However, this corrosion protection effect has, in the context of water electrolysis, so far only been demonstrated under simulated conditions in a three-electrode setup [109].

Surface treatment of titanium PTLs

A further approach to increase the stability of Ti PTLs without an additional coating is the etching with hydrochloric acid to form $TiHx$, leading to a decreased contact resistance [40]. Bautkinova et al. [110] further showed, that apart from a decreased ohmic resistance, the reproducibility of the experiments could be improved by acid etching. However, in order to achieve sufficient long-term stability of the PTL surface, deposition of a noble-metal coating on the etched titanium surfaces is still required.

Other coating materials have not yet been tested as coatings for the anode PTL, but under so-called simulated conditions of the anode environment in the PEMWE, that will be discussed in section 2.6.

2.4. Electrochemical impedance spectroscopy

Impedance spectroscopy analyzes the frequency-dependent sinusoidal current or voltage response of a system to a periodic disturbed voltage or current by applying an AC potential or current with a small amplitude. Thereby, impedance refers to the resistance of an electrical component to alternating current within a range of different frequencies [111]. In electrochemical impedance spectroscopy (EIS), the “components” and processes of the half-cell reactions are described simplified by an equivalent circuit based on the properties of electrical components such as resistances, capacitances and inductances, as different processes in the cell contribute to the total impedance, dependent on the frequency. Therefore, EIS was carried out to gain deeper insights into phase boundaries (capacitances), CT- and mass transport processes inside the cell as well as the ohmic cell resistance. However, when using equivalent circuits to fit impedance spectra, it must be noted that more than one equivalent circuit might be applicable and that for fitting the ideal prerequisites would be if the following conditions are met [112]:

- Causality: The system’s response must only stem from the applied perturbation.
- Linearity: Disturbance and response must be describable with linear differential equations.
- Stationarity: The system must be in a steady state.

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- **Stability:** The system must be stable over time and has to return to its original state before the perturbation was applied.

In particular, the last two conditions can not be fulfilled with PEMWE cells, as aging processes can occur during the recording of spectra and the system does not exactly return to its initial state, e.g. due to changes of the oxidation state of the iridium catalyst or oxidation processes on the PTL surface. At low frequencies, gas formation and the associated discontinuous release of gas bubbles lead to periodic changes in the system [113]. Consequently, the evaluation of the low-frequency range at high current densities is particularly susceptible to instationarity and is therefore subject to error. However, the focus in the context of this work was on the ohmic resistance at high-frequencies, which depends on the proton transport of the membrane and on the electrical conductivity of the PTL and the contact resistances between the cell components. In case the resistances of all electrically conductive components are negligibly small, the resistance is dominated by the resistance of proton transport through the membrane. In case of the formation of an insulating oxide layer on the surface of the PTL or the flowfield plate, the ohmic resistance increases. The opposite effect of a decreasing HFR can be observed in case of e.g. membrane thinning or when the MEA adapts to the PTL [36].

To extract the resistances, an alternating current or voltage (sinusoidal signal) with a small amplitude is applied to the system with different frequencies. The system's response is then analyzed, as the excited signal returns with a different magnitude (amplitude) or phase shift depending on the system and frequency. Different than with pure electronic components like ohmic resistances, in electrochemical systems, additional processes like CT or ion diffusion take place, exhibiting different time constants and are therefore frequency dependent.

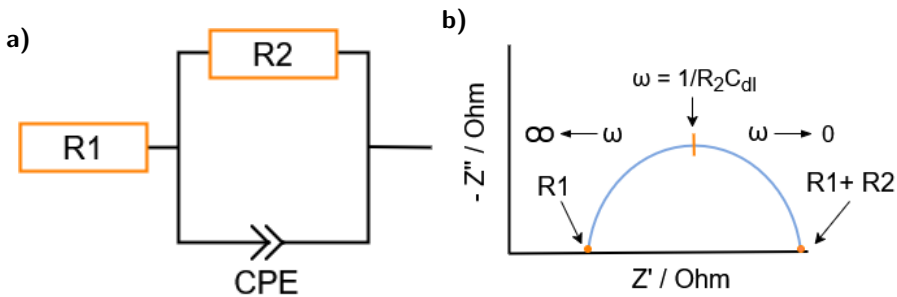


Figure 2.3. a) Simple equivalent circuit (Randles circuit) describing electrochemical systems with electrolyte resistance (R_1), CT resistance (R_2) and CPE containing a double layer capacitance (C_{dl}); b) Corresponding Nyquist plot with indication of the high frequency region ($\omega \rightarrow \infty$) and low frequency region ($\omega \rightarrow 0$).

In electrochemistry, impedance spectra are often displayed as so called Nyquist plots, also referred to as Guassian plane, showing the imaginary part of the impedance on the y-axis in relation to the

real part of the impedance on the x-axis (Figure 2.3b). Where the imaginary part becomes 0 at high frequencies, the recorded resistances are purely ohmic. Furthermore, a semicircle visible in a Nyquist plots can be interpreted as a CT process through a phase boundary, as it forms due to a combination of capacitances and ohmic resistances. The corresponding equivalent circuit for this reaction is a resistor in parallel with a capacitance [111], as the CT must overcome both an ohmic resistance and a double layer is formed at the phase boundary, with the properties of a capacitor. In real electrochemical systems, a classic capacitor cannot be assumed due to the mostly porous structure of electrodes. Therefore, a constant phase element (CPE) is often used.

For a more detailed analysis of the phase shift and magnitude in dependence of the frequency, Bode plots are used. Features at low frequencies are usually occurring due to mass transport limitation of the reactant ions, as diffusion process take place on magnitudes above CT. For example, Lopata et al. [31] reported mass transport limitation, visible by an emerging Warburg impedance at low frequencies and an increased HFR with a pore diameter of the PTL larger than $150\text{ }\mu\text{m}$ and a catalyst loading of 0.085 mgcm^{-2} , as oxygen accumulated in the pores of the PTL, hindering the mass transport of water to the CL.

2.5. Influences on aging mechanisms in PEM electrolysis cells

This subchapter provides an overview of the main influences on aging in PEMWE that are important in the context of this work. More detailed review articles, which in particular deal with membrane and catalyst degradation in more depth, can be found e.g. by Walln  fer-Ogris et al. [58]. Within the scope of this work, a comparatively thick membrane (N117) and moderate catalyst loadings were used, reducing the impact of membrane and catalyst aging effects compared to studies with thin and low-loaded MEAs below 0.4 mgIr,cm^{-2} [15, 18]. Therefore, only catalyst losses attributable to general dissolution pathways of iridium and platinum catalysts are mentioned in the course of this work, and effects attributable to low catalyst loading are omitted.

2.5.1. Mode of operation

The mode of operation mainly influences aging of the membrane and catalyst layers [15, 21, 82]. Start and stop cycles for example are increasing performance losses as the iridium catalyst is changing its redox state, additionally under the influence of hydrogen crossover [82].

Alia et al. [15] investigated the influence of different load profiles during 90 d (2160 h) operation at potential hold, triangle-wave, square-wave, sawtooth up, and sawtooth down and square-wave jumping from 1.4 V to 2.0 V with different frequencies of 10 s, 30 s, 60 s and 120 s and found that

performance losses and consequently degradation were more pronounced at high frequencies and higher cell potentials. Consequently, wind and solar profiles resulted in smaller losses than triangle and square wave operation, as they exhibit lower cycling frequencies. Loss mechanisms appeared to be of a kinetic nature for all profiles, as polarization resistances increased, but ohmic losses did not change.

Whether and to what extent aging is caused or accelerated by dynamic operating profiles additionally depends on the materials and components used. For example, Rakousky [36] could not detect any difference in the aging rate between dynamic and static operation with highly loaded catalyst layers of $2.25 \text{ mg}_{\text{Ir}}/\text{cm}^2$ and $0.8 \text{ mg}_{\text{Pt}}/\text{cm}^2$ and Pt-coated PTLs. However, increased degradation can occur at current densities above 3 A cm^{-2} , especially at a low the water flow rate of 2 mL min^{-1} [114]. Therefore, any study on aging analysis must always be evaluated in the context of the MEA (thickness of the membrane and catalyst loadings) used and the operating parameters. In addition, dynamic operation often includes periods of open-circuit potential (OCP). Although brief removal of the load can lead to short-term recovery of the cell performance when the voltage drops below 1.5 V [115], also referred to as reversible degradation [36, 115], frequent potential drops can lead to the dissolution of unstable iridium species due to the transition between oxidation states with different stabilities, especially when the potential drops to or below the OCP [116]. Krenz et al. [115] found that the HFR remained unchanged after a recovery phase of 15 min. Consequently, the reversible fractions of aging observed are attributable to kinetics. This is supported by their finding, that the recovery effect occurs when the cell voltage drops below 1.5 V , but is even more pronounced when the cell voltage drops to 0.8 V , as Ir(V) reduces to Ir(IV) below 1.5 V vs. RHE and further to Ir(III) below 0.8 V vs. RHE.

In addition, platinum loss can occur on the cathode side during periods of open-circuit voltage in case of a rising potential at the cathode side above 0.85 V vs. NHE due to oxygen crossover [21]. Brightman et al. [117] even reported, that during shut-down, the cathode contributes more to changes of the OCP than the anode potential by rising up to 1.0 V during 1 h of OCP. Furthermore they found, that the electrochemical surface area (ECSA) of the platinum catalyst decreased due to intermittent operation, which might be caused by dissolution, Ostwald ripening or agglomeration. The influence of dynamic operation on aging of PEMWE single cells used within this work will be investigated in chapter 8.

2.5.2. Oxidation and corrosion of the anode PTL

Under anodic polarisation above 2.0 V vs. SHE in 0.5 M sulfuric acid close to room temperature, titanium is reported to grow an oxide scale with a thickness of 2.75 nm V^{-1} . [118]. Also during PEMWE, uncoated titanium PTLs oxidize at and below 2.0 V potential difference between the anode- and cathode side [64], as the standard potential for the equilibrium between Ti and TiO_2

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(see Equation 2.3) is -0.86 V vs. SHE [119]. The respective equilibrium reactions are given in Equation 2.3.



Apart from the increasing resistivity of the titanium oxide layer compared to pure titanium, the thermal conductivity of TiO_2 is three times lower than that of pure Ti (c.f. Table 6.1). Consequently, heat produced by the OER that is not dissipated can lead to local hotspots where the proton conductivity and thus membrane resistance decreases locally, but can also lead to accelerated degradation of the ionomer and the membrane [120]. This phenomenon is also reflected by a decreasing HFR with increasing current density. Another cause of HFR shifting can be nonuniform contact of the PTL and CL, as the formation of poorly conductive oxides due to the uneven contact pressure distribution of the PTL on the MEA due to the land and channel structure of the flow field also does not proceed homogeneously. Consequently, the contact to the MEA also becomes more inhomogeneous due to the uneven oxide formation.

The assumption that titanium oxidation is not only detrimental for the cell performance with regards to the rising cell resistance, but also in terms of MEA degradation, was supported by experiments from Liu et al. [81], where an iridium coating on PTLs reduced MEA degradation, probably due to a reduction of ionomer loss and maintenance of higher conductivity of the CL.

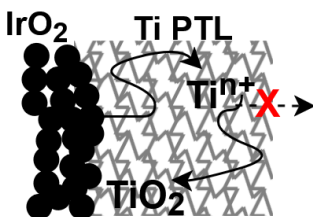


Figure 2.4. Schematic representation of titanium dissolution and precipitation on the anode catalyst layer. Adapted from Cho et al. [56]

While the oxidation of anode titanium PTLs is well known, Cho et al. [56] also reported the dissolution of Ti above 1.0 V vs. RHE , monitored by inductively coupled plasma mass spectrometry (ICP-MS) directly coupled with an electrolysis cell operated with HClO_4 . They found that Ti dissolution increases with the potential and that hydrolyzed Ti ions form surface oxides that protect the bulk and decrease the rate of dissolution. However, the passivation layers formed during operation are not resistant against corrosion. Additionally, Ti was found at the anode and cathode side, indicating the dissolution and movement of Ti from the anode to the cathode. According to the Pourbaix diagram of titanium, Ti ions precipitate under the neutral conditions of the circulating water to $\text{TiO}_2 \cdot \text{H}_2\text{O}$ [24]. Consequently, it is more likely that titanium oxide particles will remain in the cell and not be

emitted, as shown schematically in Figure 2.4. It was also investigated that significantly lower Ti dissolution rates of 39 ng/g_{Ti} and 4 ng/g_{Ti} vs. 125 ng/g_{Ti} were found with Pt and IrO₂ coated Ti PTLs compared with a pure Ti PTL [56]. Furthermore, Tan et al. [121] proved migration of titanium ions dissolved from the PTL to the cathode side, increasing the resistance of proton transfer and adding overvoltage to the CT reactions of the HER. Thereby, they proposed a dissolution process of titanium involving fluoride ions released from the membrane or Nafion™ within the catalyst. They further elucidated evolving resistances through a distribution of relaxation times (DRT) investigation, as upon poisoning with Ti, two distinct semicircles in the Nyquist plot were visible, pointing to a separation of time constants of different CT processes, possibly caused by an increased resistance of the CT of OER or HER reactions. For uninhibited OER and HER reactions at the electrodes, usually only one semicircle appears, which can be only separated into two semicircles by fitting the spectrum to a model, indicating that the time constant of one reaction dominates, while the faster reaction “disappears under” the slower one. If the CT resistance of one reaction increases significantly, two semicircles may become visible. Through their analysis, they found a minor influence on the OER, while the HER was significantly influenced by Ti⁺ ions occupying H⁺ sites.

2.5.3. Cation contamination

Cation contamination can either stem from system components, impurities in the catalyst layers, contaminated feed water or from the production of Nafion™ membranes [122]. Upon anode-side formation or introduction of cations into PEMWE cells, the electric field and drag cause a migration of cations from the anode to the cathode side [123–125]. The cations then either remain in the membrane or cathode catalyst layer or are discharged from the cell [126]. Thereby, cationic impurities influence MEA aging in three different ways:

1. Catalysis of radical reactions: Some metal cations, e.g. Fe²⁺, Cu²⁺, TiO₂⁺, Pt²⁺, Ni²⁺ and Al³⁺ catalyze peroxide radical formation on the cathode side, with the catalytic activity decreasing from iron to aluminum [127]. The metal cations catalyze the formation of hydroxyl radicals from hydrogen peroxide, whereby peroxide formation can take place if oxygen permeates to the cathode side. Then radicals attack the polymer backbone of the membrane and accelerate thinning of the membrane, whereby the thinning rate depends on the temperature. Frensch et al. [128] found that the extent of membrane thinning doubles with a temperature increase of 10 K from 80 °C to 90 °C, emphasizing that in presence of cationic contamination, the thermal conductivity of the PTL has a decisive influence on the stability of the MEA and that the heat generated at high current densities must be well dissipated. Furthermore, as oxygen is involved in the formation of hydrogen peroxide and eventually in the formation of hydroxyl radicals, the oxygen permeation rate has an influence on membrane degradation

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(c.f. Figure 7.24). Trinke et al. [129] found that oxygen crossover increases with increasing current density due to supersaturation and the electro-osmotic drag. Fenton reactions are also catalyzed by Cr^{2+} . However, Kinumoto et al. [130] found that Cr impurities contributed less to membrane degradation than Fe.

2. Blockage of acid sulfate groups: Primarily alkaline and alkaline earth metals block proton transport through the membrane. Padgett et al. [124] report the appearance of "S"-shaped I-V curves in presence of cation impurities (Na^+ , K^+ , Ca^{2+} and Fe^{3+}) in the ascending scan and hysteresis in the descending scan. They explain the S-shape of the curve with a depletion of protons on the cathode side. As the cations present at the anode move towards the cathode due to the electric field, a concentration gradient develops across the cell, as the cation contaminants are not consumed like the protons. This depletion of protons leads to kinetic losses increasing the CT resistance, especially at high current densities. If the overvoltage is sufficiently high, a switch to the alkaline HER mechanism, that does not require protons, can occur ($E^0 = -0.828 \text{ V}$), resulting an upper plateau of the curve. Zhang et al. [125] showed that the pH at the cathode side increases when sodium cations are introduced in the cell, supporting the assumption of a switch to the alkaline pathway at higher cell voltages. They also observed a bending of the I-V curve, but no plateau at higher current densities, as the current densities reached probably were not high enough for observing a plateau. Although they only present impedance spectra at a low cell voltage of 1.45 V, it is visible, that the low-frequency resistance is significantly higher for contaminated cells, whereas the high-frequency resistance increases only slightly, suggesting that the influence of the contamination on the kinetics is significantly greater than on the proton conductivity of the membrane. They further measured the cathode and anode potentials with an external reference electrode and observed an increase of the cathode overpotential. Additional impedance spectra in the supplementary information from Padgett et al. [124] show in the event of contamination with $5 \mu\text{mol Ca}^{2+}$, that the low-frequency resistance shifts to higher resistances at 4 A cm^{-2} , contrary to the usual shift of the LFR to smaller resistances at higher current densities. Furthermore, Becker et al. [131] reported an influence of cation impurities on the membrane conductivity by displacing protons in the NafionTM membrane, as multivalent cations like Na^+ , Ca^{2+} , Ni^{2+} and Fe^{3+} possess higher affinities to the $-\text{SO}_3^-$ end groups than protons [132].
3. Influence on the water content: With Na^+ and Ca^{2+} impurities, it was found that the water content of the membrane decreases, because the water transfer coefficient is higher for cations with a larger hydration shell [133, 134].

In terms of performance recovery from cation contamination, Li et al. [126] found, that recovery from Cu^{2+} was not possible, as Cu^{2+} adsorbed in the membrane and tended to stay there. In

contrast, recovery from Fe^{3+} was possible, as iron ions did not stay in the membrane, but exited the electrolyzer continuously. The latter is supported by another study, where only minor traces of Fe were found in a MEA that was subject to operation with Fe contaminated water [123].

2.6. Corrosion studies under simulated PEMWE conditions

Apart from the coating materials summarized in subsection 2.3.3, more materials have not yet been tested as coatings for the anode PTL, but under so-called simulated conditions imitating the anode environment of PEM water electrolysis cells. The setup usually consists of a three-electrode setup with the material or coating under investigation acting as working electrode, a reference electrode, often reversible hydrogen electrodes (RHE) or silver-silver chloride electrodes (Ag/AgCl), and a counter electrode, in most cases a platinum sheet or mesh. As NafionTM is used in PEMWE as solid electrolyte, studies that aim to simulate its acidic environment work with diluted H_2SO_4 , Na_2SO_4 or a combination of both in various concentrations. Sometimes fluoride or chloride ions are added to mimic fluoride emission from the membrane or chloride emission from the catalyst. Often the electrolyte is heated to the operating temperature of PEMWE between 60 °C to 80 °C.

So far, there exist no official targets for the corrosion stability of coatings in PEMWE, but for bipolar plates in fuel cells, the U.S. Department of Energy defined technical targets, that aim for corrosion current densities below $1 \mu\text{A cm}^{-2}$ and an interfacial contact resistance (ICR) below $10 \text{ m}\Omega \text{ cm}^2$ [135]. Even though these targets are not defined for BPPs in PEMWE, they provide an indication of the order of magnitude acceptable for corrosion currents and resistances as the environment in fuel cells and electrolyzers is close except for the cell potentials, and, depending on the educts used, also the chemical environment.

For example tungsten was investigated regarding its suitability as BPP material by Lædre et al. [136] under simulated PEMWE conditions in 0.1 M Na_2SO_4 , adjusted to pH 5.5 with sulfuric acid at 70 °C. After polarization for 1 h at 2.0 V vs. SHE, the ICR slightly decreased from $13 \text{ m}\Omega \text{ cm}^2$ to $11 \text{ m}\Omega \text{ cm}^2$. Combined with the observation that only a small fraction of the measured current stemmed from corrosion, as the weight loss was lower than expected from the measured current, they concluded, that tungsten might be, next to titanium and tantalum, a promising (coating) material for BPPs. However, due to its high melting point [137], tungsten may require more energy during the coating process than titanium and platinum.

Indium tin oxide (ITO) is another n-type semiconductor with high electrical conductivity used in solar cells [138], flat panel displays [139] and for other applications where optical transmittance and electrical conductivity is required. Lædre et al. [140] presented a bi-layer coating composed of tantalum and ITO deposited on titanium with magnetron sputtering, intended to be applied as

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coating for bipolar plates. They conducted ex-situ corrosion testing with different pH (3, 5.5 and 8), potential (1.4 V to 2.6 V vs. RHE) and polarization duration up to 72 h. In all experiments, the ICR increased after polarization, indicating the formation of a less conductive oxide layer. X-ray photoelectron spectroscopy (XPS) revealed that the oxygen content increased with increasing potential. However, as the ICR remained stable after 24 h ($30 \text{ m}\Omega \text{ cm}^2$), the corrosion currents below 1.7 V vs. RHE were around $20 \mu\text{A cm}^{-2}$, SEM images showed no changes on the surface and no weight loss was observed, they concluded that the coating might be a promising coating for application in PEMWE. Apart from this, ITO has so far only been mentioned in association with PEMWE as a carrier for iridium catalysts [141, 142], with one of the studies mentioning leaching of indium and tin in solutions with a low pH without further specification of a critical pH range. Therefore, it remains questionable whether ITO would be stable enough on anode PTLs.

When evaluating corrosion studies under simulated PEMWE conditions, it is not elucidated yet to what extent the results can be transferred to real PEMWE operation, as no studies exist concerning the comparability of simulated PEMWE conditions in a three electrode setup and PEMWE operation. Consequently, only implications can be made through a comparison between findings from the same materials that were studied under simulated conditions and in PEMWE. Messing et al. [66] reported for example high corrosion rates of carbon based BPP in sulfuric acid at pH 1 and 80°C , while the implementation of BPPs of the same material was possible in PEMWE cells. Consequently, there was a gap between the ex-situ and in-situ results. However, it should be noted that ex-situ testing for BPPs within this study was carried out under very harsh and too acidic conditions that are likely not relevant for BPPs, as the acidic environment only prevails in contact with NafionTM.

As the knowledge gap regarding the transfer of ex-situ and in-situ testing still existed, experiments were carried out in a corrosion cell with several possible coating materials. However, the question about the extent to which these experiments can predict the actual oxidation and/or corrosion behavior of a material as an anode coating came up more with every experiment, leading to the decision to focus on this emerging question within section 6.8.

3. Materials, methods and measurement techniques

The following chapter provides an overview over all experimental setups, raw and processed materials, coating techniques as well as electrochemical, physical and physico-chemical analysis methods used.

3.1. Proton exchange membrane water electrolysis

3.1.1. PEMWE cells

For PEMWE single cell testing, in-house built test cells were used [36]. The end plates consist of stainless steel (1.4571) and are in contact to the back side of titanium flowfield plates (FF) that are platinum-plated at the anode side and gold-plated on the cathode side. A single-meander flowfield (42 mm x 42 mm, see Figure 3.2) is milled into the flowfield plates, ensuring the water supply for the cell from inlet to outlet. A scheme of the test cells is shown in Figure 3.1.

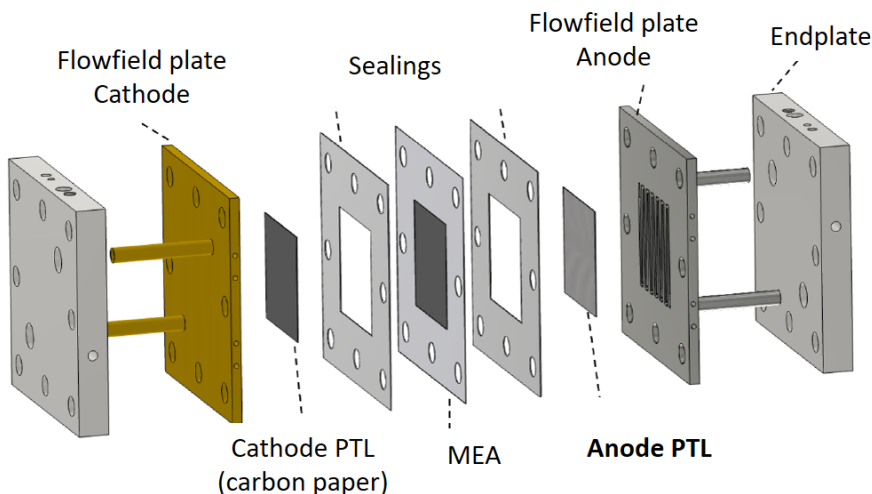


Figure 3.1. Illustration of a standard PEM electrolysis test cell at IET-4, adapted from [143].

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that enough space was available for mounting during the coating process. In these cases, a 15 μm thin subgasket was placed between the PTL and MEA, which exhibited an opening of 17.64 cm^2 to ensure, that the CL-facing side of the PTL was only in contact with the active area of the MEA. When assembling the cell, the nine screws on the edges of the end plates were tightened to a target torque of 4 N m.

3.1.2. Pressure-sensitive films

To characterize the different test cells used, their contact pressure distribution was determined with pressure-sensitive films from Fujifilm (Prescale). Two different films were needed for each measurement: a color-producing foil containing colorant in microcapsules that burst under pressure and a second foil that reacts with the colorant. The resulting color density with different shades of red is proportional to the pressure. Three types of Fujifilm films were used in this work, classified as low pressure (LW), super low pressure (LLW) and ultra super low pressure (LLLW). The working range of the respective film types are: 2.5 MPa to 10 MPa (LW), 0.5 MPa to 2.5 MPa (LLW) and 0.2 MPa to 0.6 MPa (LLLW). The measurement accuracy specified by the manufacturer is $\pm 10\%$ or less for measurements at a temperature of 23 °C and a relative humidity of 65 % [144]. The humidity could not be maintained exactly for all measurements, but all measurements within this work were carried out under the same conditions in an air-conditioned room with a constant temperature of 23 °C. To determine the pressure distribution of PEMWE single cells, the foils were stamped out in the shape of the cell geometry and were placed inside instead of the MEA. Experiments were carried out with only the flow fields and the pressure-sensitive film, as well as with cathode (carbon fleece) and anode PTLs (titanium felt). After two minutes, the cell was disassembled and the red-colored film used for post-processing using the “FPD-8010E” mapping software from Fujifilm. The films with the shades of red were scanned with a conventional scanner with a resolution of 0.125 mm per pixel. With a calibration sheet, the software assigns pressure values to the different intensities of red and visualizes them as a colored image (see Figure A.5).

3.1.3. PEMWE test bench

At the in-house-built test bench for PEMWE single cell testing [36], five cells could be run simultaneously. Each cell is connected to a power supply, temperature and voltage senses, heating rods and water supply via a peristaltic pump (Ismatec ISM832C). One pump delivers water separately for the anode and cathode of one cell. The average water flow rates were $25.0 \pm 1.5 \text{ mL min}^{-1}$ on the anode and $24.0 \pm 2.5 \text{ mL min}^{-1}$ on the cathode sides. With these flow rates, water consumption ratios (λ) of 82 ± 7 are achieved. An example for the calculation of λ is given in the appendix (Equation A.1 and A.2). Deviation between the flow rates for different places on the testbench may occur due to

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different compression of the tubes by the roller cassette. However, there are minor deviations in the flow rate for every experiment, as pumps had to be changed in the event of failures and regular calibrations were carried out. The water was purified to a conductivity of $0.055\ \mu\text{S cm}^{-1}$ and a total organic carbon content (TOC) of less than 3 ppb by a water treatment system (Merck Millipore), before it was filled into the storage tanks by a semi-automatic refilling system. Each cell is supplied from two water tanks, one for the anode and one for the cathode circuit. Also the excess water from the cell outlets returns to the tanks. Glass tubes with frit with ion exchange resin (Amberlite® IRN-150) are installed between the water storage tank and the cell inlet to ensure that no impurities enter the cells. Before being delivered to the cell, the water is heated via glass heat exchangers for a water input temperature of $80\ ^\circ\text{C}$. The cell temperature of the end plates is measured by two NiCr-Ni thermocouples and controlled at $80\ ^\circ\text{C}$ by an in-house built temperature control. The measurement accuracy of the thermocouple is given as $\pm 1\ ^\circ\text{C}$ by the manufacturer. As the water of all five cells is preheated by glass heat exchangers, which are fed by one thermostat (Lauda Eco Silver), the water inlet temperature deviates by about $1.6\ ^\circ\text{C}$. The temperature difference between the cells was experimentally determined to be $1.16\ ^\circ\text{C}$. A TDK Lambda GEN-20-76 DC power supply was used as current source (accuracy of voltage output: 10 mV; current output: 152 mA; readback current: 228 mA). Cell voltages were recorded using a Keithley model 2701 multimeter with an accuracy readback voltage of 10 mV. The power supplies were controlled via LabVIEW-based software and the sample rate was 10 s, unless otherwise stated. Impressions of the cell and test bench and cell are given in Figure 3.3 and Figure A.1.

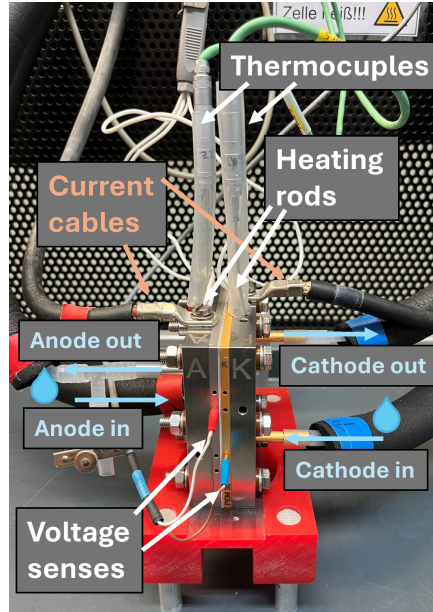


Figure 3.3. PEMWE test cell installed in the test bench.

3.1.4. Conditioning, I-V curves, static and dynamic operation

Before applying any voltage or current to the PEMWE cells, they were heated up to 80 °C for 1 h and conditioned for 15 h at 1.7 V as proposed by Lickert et al. [145]. Therefore, the cells were ramped up from 1.5 V to 1.7 V in 50 mV-steps every minute. The polarisation curves were then recorded potentiostatically in 50 mV-steps from 1.3 V to 2.0 V, whereby the intervals between the voltage steps were chosen closer in the low voltage range where activation overvoltages predominate (between 20 mV to 30 mV). Each voltage step was held for 5 min. The I-V curves were then generated from the mean values of the last 10 measuring points of a voltage step. I-V curves after conditioning are referred to as BOT (begin of test)-curves and the ones that were recorded last as EOT (end of test). Further electrochemical investigations involved impedance spectroscopy (see subsection 3.1.5) and either static or dynamic testing. Figure 3.4 provides an overview of the typical steps involved in PTL characterization. Unless otherwise stated, all electrochemical characterization steps (I-V curves, long term experiments and EIS) were carried out at 80 ± 1 °C. With TiN-coated PTLs used in section 6.8, the conditioning step was omitted, as the focus of these experiments was not on stable cell performance but rather exact polarization times.

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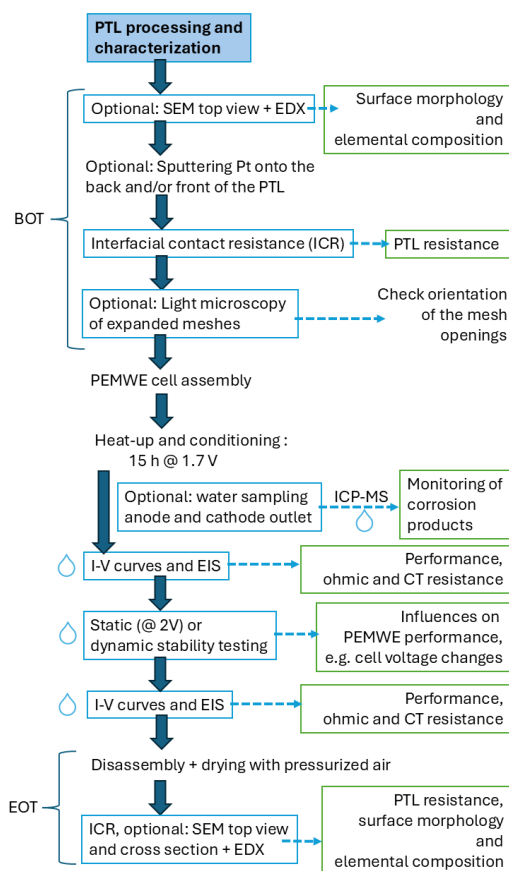


Figure 3.4. Process route for PTL characterization with analysis methods used. Dependent on the research question, water samples were taken from the cell outlets and water tanks and analyzed by ICP-MS during the characterization steps marked with water droplets.

3.1.5. Electrochemical impedance spectroscopy

As described in section 2.4, impedance spectroscopy analyzes the frequency-dependent reaction of a system to a periodic disturbed voltage or current by applying a sinusoidally varying potential or current with a small amplitude. To record impedance spectra, the power supply from the test bench had to be interrupted and disconnected to connect the cell to a Biologic HCP 1005 potentiostat, including a booster unit to allow currents up to 100 A. Furthermore, the sense lines of the test bench were also removed to connect the potentiostat's sense lines. In case multiple cells were tested, each cell that was not connected to the potentiostat and subject to EIS stayed at open circuit potential (OCP). Spectra were recorded potentiostatically at 1.45 V, 1.5 V, 1.55 V, 1.6 V, 1.65 V, 1.7 V, 1.8 V, 1.9 V and 2.0 V in a frequency range between 100 mHz and 10 kHz and an amplitude of 5 mV.

High-frequency resistances, representing the ohmic cell resistance, were derived from equivalent circuit fitting using the software ZView® from Scribner. In some cases, e.g. in particular in the presence of impurities, severe aging or instationarity before or during the recording of the spectra, it was not possible to fit the spectra with the presented model. In these cases, the HFR was determined either graphically at the intersection of the imaginary axis where no imaginary impedance was measured, or, if no intersection was available, the intersection was generated by linear interpolation of the high-frequency part of the spectrum. Both methods introduce an error by over- or underestimating the HFR, whereby Heimerdinger et al. [146] reported within investigations about the ohmic resistance of membranes, that even through linear interpolation, the HFR can be accurately determined, but additionally, that the frequency range considered influences the result.

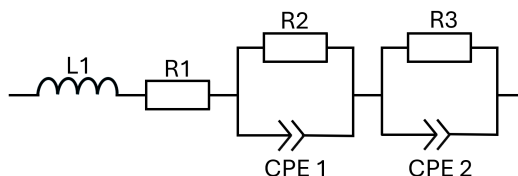


Figure 3.5. Equivalent circuit for fitting of impedance spectra.

Figure 3.5 displays a simple equivalent circuit for fitting of impedance data from electrochemical cells based on the Randles circuit [147], which is frequently used in water electrolysis research. As the water is circulated with a sufficient lambda of at least 67 (calculation see Equation A.1 and A.2), no Warburg impedance is included as no significant frequency-dependent resistance contribution by mass transport limitation due to diffusion was expected. Furthermore, due to the rough electrode surface and porosity vertical to the surface, the catalytic activity of the electrode is expected not to be uniform and the electrochemical double layer not to be uniformly distributed [148]. Consequently, charge transfer processes might take place with different time constants and capacitances

might deviate. To model electrochemical systems with rough and porous electrodes with a distribution of time constants, a constant phase element (CPE) is often used instead of a capacitor [149], as a capacitor only describes a perfect phase boundary. The equivalent circuit contains two R/CPE-elements, one for each half-cell reaction. An inductance is added to the model to account for possible inductive contributions from the current cables or other system components like the heating rods in the end plates. With the setup used, the inductive contribution was typically in the range of 1.3×10^{-7} H. However, when using equivalent circuits to fit impedance spectra, it must be noted that more than one equivalent circuit might be applicable and that for fitting the ideal prerequisites discussed in section 2.4 should be met. Using the simple equivalent circuit presented, the HFR could be determined with a fit error of less than 1 %. Further uncertainties in determining the HFR can be introduced by the phase error of the potentiostat, introducing higher uncertainties exceeding 1%. Although there are uncertainties in determining resistances and capacitances, no other techniques are available to determine the same parameters with higher accuracy that do not depend on potentiostats as well.

Most software for modelling and fitting of impedance data offer various iteration methods and modes for weighting of the data. As the HFR did not differ by more than 0.5 % with all weightings methods available in ZView®, it was assumed that the weighting had no influence on the result of the high-frequency resistance, provided that the spectrum contains no outliers, little non-stationarity at low frequencies and little inductance at high frequencies. For spectra with higher non-stationarity, inductance or outliers, a different weighting could possibly yield more precise results for the HFR. Nevertheless, to treat all spectra equally, the “Calc-Modulus” with 100 iterations was used throughout the work, which normalizes each data point by its magnitude. In addition, extraction of the ohmic series resistance with spectra of standard cells was also carried out using the THALES software from Zahner for comparison. Both software provided the same result for the HFR.

3.2. Anode PTLs and coatings

There are two main titanium grade 1 PTLs that were used for this work: Commercially available titanium felts (TiF) from the company Bekaert (NV Bekaert SA, Belgium) with a thickness of $363 \pm 8 \mu\text{m}$, a porosity of 68 % and a fiber diameter of $20 \mu\text{m}$, which are referred to as standard (reference) PTL and titanium expanded meshes (TiEM) from Bender GmbH Maschinenbau & Streckmetallfabrik. Expanded meshes were used in addition to titanium felt PTLs, as their large pores allow to coat the meshes with new dense coatings, while large enough openings remain to ensure water supply to the catalyst. The pores from the felt could possibly become clogged when coated by thermal spray processes where the particle size of the feedstock powder is in the range of several micrometers. Furthermore, the expanded metals are easy to cut due to their low thickness and are very uniform in thickness, enabling to achieve a uniform distribution of contact pressure

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on the MEA. In addition, titanium sintered bodies (TiS) from GKN Powder Metallurgy were used for a comparison between Pt coated and uncoated titanium PTLs as well as investigations about atmospheric plasma sprayed (APS) coatings (section 5.3 and subsection 6.4.2).

With regard to stainless steel-based PTLs, two substrates were used, 316L expanded meshes from Bender with a geometry close to the titanium ones and 316L felts on 316L expanded meshes (SMF) from GKN Powder Metallurgy.

All PTLs used for this work are listed with their properties in Table 3.1 and Table 3.2 and Figure 3.7 illustrates the main PTL substrates used. 3D X-Ray tomograms from the back sides of TiS and SMF are given in Figure A.3.

The thickness of all PTLs and gaskets were determined using a thickness gauge DM2010 from Wolf Messtechnik GmbH, with a resolution of $1\text{ }\mu\text{m}$ and an accuracy of $4\text{ }\mu\text{m}$ [150], whereby nine points were measured and averaged per sample. All PTLs were cleaned before they were coated or installed in the cell using a $95\text{ }^{\circ}\text{C}$ oil removing program in a laboratory dishwasher from Miele Professional PG (8583). Afterwards the samples were then dried using compressed air.

Figure 3.6 visualizes the most important parameters to describe the geometry of an expanded metal. The values for the opening in the tables correspond to the distances colored in green.

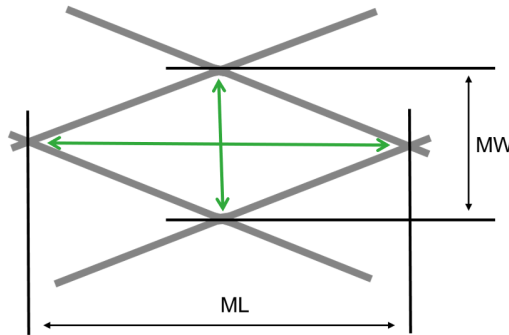


Figure 3.6. Schematic illustration of expanded metal with indication of the mesh length (ML) and mesh width (MW) as well as the mesh opening (length and width) in green.

Table 3.1. Overview of titanium grade 1 PTLs used.

Type	Porosity / %	Thickness / μm	Opening / μm	Manufacturer	Label
Felt	67 ¹	361 ± 13	/	Bekaert	TiF
Expanded metal	24.9 ± 2.5 ²	136.5 ± 3.5	$336 \pm 10 \times 190 \pm 15$ ³	Bender	TiEM
Sintered body on expanded metal	57 ¹	1148 ± 312	$50\text{-}75$ ⁴	GKN	TiS

¹Porosities determined from X-ray tomography; ²Open area according to the manufacturer; ³Mesh opening determined from SEM images; ⁴Biggest pore according to the manufacturer.

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Table 3.2. Overview of 316L PTLs used.

Type	Porosity / %	Thickness / μm	Opening / μm	Manufacturer	Label
Expanded metal	36 ± 2.5^1	129 ± 11	$344 \pm 9 \times 223 \pm 6.5^2$	Bender	316LEM
Felt with $8 \mu\text{m}$ fibres on EM	88^1	$1100 \mu\text{m}^1$	75^3	GKN	SMF8
Felt with $22 \mu\text{m}$ fibres on EM	86^1	$1060 \mu\text{m}^1$	93^3	GKN	SMF22

¹Open area according to the manufacturer; ²Mesh opening determined from SEM images; ³Biggest pore according to the manufacturer.

As indicated in the tables 3.1 and 3.2, the titanium expanded mesh (TiEM) and 316L expanded mesh (316LEM) differ by an average of $77 \mu\text{m}$ in the length of the mesh opening and $85 \mu\text{m}$ in the width of the mesh opening. Thus the mesh openings (pores) of the 316L expanded metal are larger. Furthermore, the manufacturer of the expanded metal always allows for a tolerance of 10 % for all production parameters.

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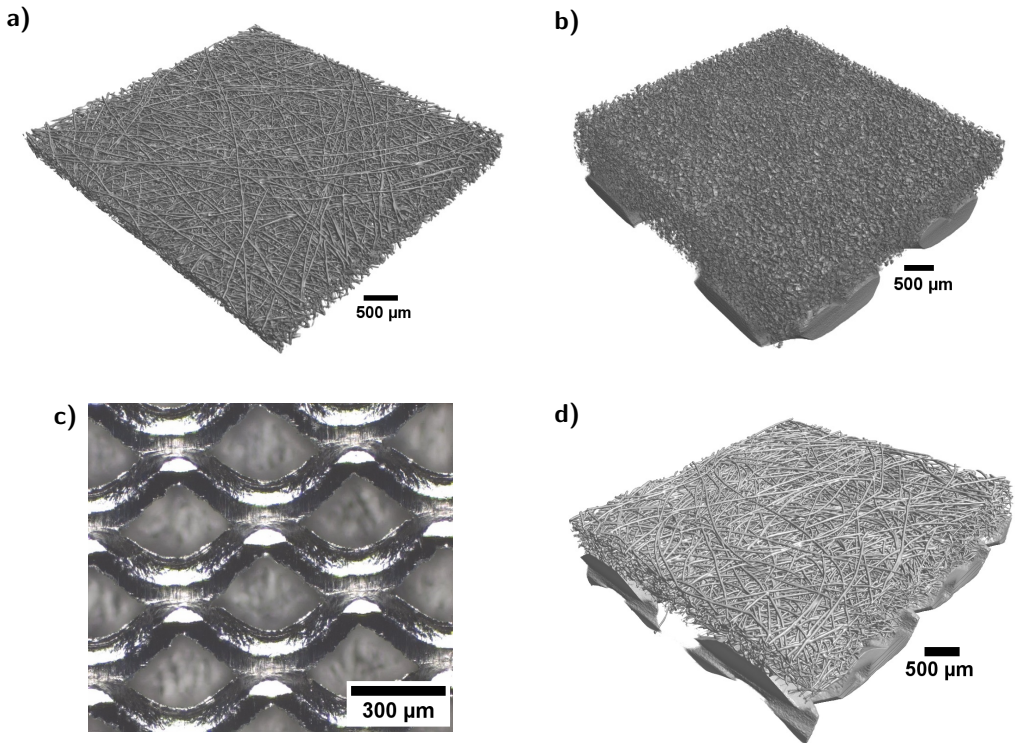


Figure 3.7. 3D X-Ray tomograms of a) titanium felt from Bekaert (Reference), b) titanium sintered body on titanium expanded mesh from GKN (TiS), c) Light microscopy image of titanium expanded mesh from Bender (TiEM) and d) 316L felt on 316L expanded metal from GKN (SMF).

In the following, all technologies used for the deposition of coatings on PTLs are briefly introduced. All coatings, except for Pt PVD layers, were deposited at and by the institute of materials synthesis and processing (IMD-2) at the research center Jülich.

3.2.1. Magnetron sputtering (PVD) at IET-4 and IMD-2

For thin PTL coatings, magnetron sputtering was used, which is a physical vapor deposition (PVD) process, where atoms from a target made of the coating material are sputtered on the substrate with noble gas ions that originate from a plasma. At impact of the ions on the target, an energy transfer takes place. If the transferred kinetic energy is higher than the binding energy of the atom, atoms are released from the target and move to the substrate, where they condense. The process takes place in vacuum to allow the atoms released from the target to fly long enough to reach the substrate. Without a vacuum, these atoms would collide with ambient atoms in the air and not reach the substrate. Furthermore, the vacuum ensures, that no oxidation or contamination with impurity ions takes place. As no other PVD process than sputtering was used, all coatings deposited by sputtering are referred to as "PVD" coatings.

Magnetron sputtering of platinum at IET-4

Platinum coatings on PTLs were applied with a sputter coater Quorum Q150T ES (Quorum Technologies Ltd) with an accelerating current of 30 mA and a vacuum of 10 mbar under Argon.

The sputter time was 360 s and the resulting loading $0.060 \pm 0.008 \text{ mg}_{\text{Pt}}\text{cm}^{-2}$. The thickness of the platinum coating was determined on silicon wafers using a lithographic and lift-off process. For this purpose, Pt was sputtered for 30 s, 90 s, 180 s, 270 s and 360 s on pre-treated silicon wafers coated with a photosensitive resist for lift-off. To create a step for the determination the coating thickness, the coated wafer pieces were treated twice in an ultrasonic bath in acetone for approximately 1 min to remove parts of the resist. The wafer pieces were then cleaned with 2-propanol. The coating thicknesses were measured using atomic force microscopy, ellipsometry and profilometry at the Helmholtz Nano Facility at Forschungszentrum Jülich. Three methods were used, as it was not possible to determine the coating thickness after the shortest sputtering time of 30 s using profilometry with a Dektak device. Additionally, by using different methods it was ensured that systematic errors in one method did not distort the determination of the coating thickness. For a sputtering time of 360 s, the average layer thickness was $37.5 \pm 0.2 \text{ nm}$. As a coating thickness of approximately 37 nm was also reported by Liu [64] in 2021, it is assumed, that the deposition of platinum was reproducible and was not susceptible to measurable changes.

As platinum or iridium coatings on anode PTLs are state of the art in PEMWE, platinum coated PTLs are used as reference PTLs. Thus, whenever the term "reference" or "benchmark" PTL is

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used in the course of the work, it refers to a titanium felt from Bekaert (Figure 3.7a) with a thin Pt coating of 37.5 ± 0.2 nm. The Pt PVD coating of one 316L expanded metal PTL (section 7.2), as well as the PTLs Ti-CG-33 and Ti-CG-48 (subsection 7.4.2) were carried out by an external coating company, where additional steps were realized, which were not possible with the sputter system at IET-4. These included a preheating step for 30 min at 150 °C to remove surface water and a plasma cleaning step to remove the native titanium oxide layer. This should serve to compare whether the corrosion stability of the 316L expanded metal could be improved with a potentially better adhesion of the platinum layer on the 316L substrate and minimize potential Pt loss from the titanium cold gas sprayed layers. The layer thickness applied by the external company was 40 nm.

Magnetron sputtering at IMD-2

Noble metal free niobium, titanium, tantalum and alloy PVD-coatings of niobium or tantalum with titanium were deposited by the institute IMD-2 on different PTL substrates. Table 3.3 gives an overview of the substrates and coatings. Details about the coating process are given by Sievert [151].

Table 3.3. Noble metal free PVD coatings prepared by IMD-2.

Coating material	Substrate	Coating thickness ¹ / μm	Label	Pt top coating	Corresponding chapter
Niobium	TiEM and 316LEM	$3.6 \pm 0.1 \mu\text{m}$	TiEM_Nb_PVD and 316L_Nb_PVD	no	6.4.3
Titanium	316LEM	$3.80 \pm 0.08 \mu\text{m}$	316LEM_Ti_PVD	yes	7.3.1
Titanium	TiEM	$5.1 \pm 0.5 \mu\text{m}$	TiEM_Ti_PVD	no	6.5
3 at.% Nb - 97 at.% Ti	TiEM	$5.1 \pm 0.5 \mu\text{m}$	TiEM_Ti ₉₇ Nb ₃	no	6.5
6 at.% Nb - 94 at.% Ti	TiEM	$4.5 \pm 0.1 \mu\text{m}$	TiEM_Ti ₉₄ Nb ₆	no	6.5
28 at.% Nb - 72 at.% Ti	TiEM	$5.1 \pm 0.5 \mu\text{m}$	TiEM_Ti ₇₂ Nb ₂₈	no	6.5
3 at.% Nb - 97 at.% Ti	TiF	$5.1 \pm 0.5 \mu\text{m}$	TiF_Ti ₉₇ Nb ₃	no	6.5
6 at.% Nb - 94 at.% Ti	TiF	$4.5 \pm 0.1 \mu\text{m}$	TiF_Ti ₉₄ Nb ₆	no	6.5
28 at.% Nb - 72 at.% Ti	TiF	$5.1 \pm 0.5 \mu\text{m}$	TiF_Ti ₇₂ Nb ₂₈	no	6.5
Tantalum	TiEM	$1.4 \pm 0.1 \mu\text{m}$	TiEM-Ta_PVD	no	6.6.2
6 at.% Nb - 94 at.% Ti	TiEM	$1.0 \pm 0.1 \mu\text{m}$	TiEM_Ti ₉₄ Ta ₆	no	6.6.2
ITO	TiEM	$1.00 \pm 0.02 \mu\text{m}$	TiEM_ITO	no	6.5

1: Determined by Sievert [151] (IMD-2) from SEM cross sections using the software imageJ.

316L expanded mesh PTLs with Ti PVD coating (316LEM_Ti_PVD) were additionally coated with Pt for a comparison with Ti coated 316L meshes by means of cold gas spraying (see subsection 7.3.1 and section 7.4). While PVD can produce ideal dense coatings on flat surfaces, deposition on bended surfaces can cause cracks at edges due to the thin coating thickness.

Reactive sputtering of titanium nitride at IMD-2

TiN PVD layers on titanium felts from Bekaert and titanium grade 1 sheets from Bender were deposited by means of reactive sputtering of titanium under nitrogen atmosphere. The resulting mean coating thickness on silicon wafers was 1.7 μm . The process of reactive sputtering works similar to pure metallic PVD coatings described above, except that titanium nitride is formed due to the presence of nitrogen.

3.2.2. Thermal nitration at IMD-2

Titanium expanded metal were nitrided for 3 h at 850 °C in nitrogen atmosphere for a comparison of their oxidation stability with the coatings deposited by reactive sputtering (PVD).

3.2.3. Atmospheric and Vacuum Plasma Spraying at IMD-2

Atmospheric and Vacuum Plasma Spraying (APS and VPS) use a feedstock powder and therefore deposit thicker layers than PVD. The working principle for both methods is the same, with the difference that the VPS process takes place in a vacuum chamber. As the deposition of tungsten by means of cold gas spraying (CGS) was not possible, W was deposited by means of APS and VPS. Furthermore, Nb was deposited on a Ti sintered body by means of APS.

Vacuum plasma spraying (VPS) or also referred to as low pressure plasma spraying takes place in a low-pressure chamber, sometimes filled with an inert gas such as argon where oxide free layers can be deposited. The layer thickness of the tungsten coating was 24 μm and no oxide phase was detected by X-ray diffraction analysis at IMD-2 [151].

3.2.4. Cold Gas Spraying at IMD-2

Niobium, tantalum and titanium coatings were deposited on titanium and 316L expanded meshes by means of CGS by the institute IMD-2 with an impact Innovations GmbH cold spray system with nitrogen as propellant and feedstock carrier gas to avoid oxidation of the coating material [151]. CGS yields thicker coatings than PVD, which was of special interest for the development of corrosion-protection layers for stainless steel expanded meshes. As the coating material is a powder, the surface properties, layer thickness and, to a certain extent, the porosity of the coating can be influenced by the particle size and particle size distribution of the powder. Additionally, CGS requires no vacuum and is therefore suitable to scale up [152]. The deposition principle is to achieve adhesion of the powder on the substrate through plastic deformation by enhancing the kinetic energy of the particles

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through acceleration of the feedstock powder to supersonic velocity. This acceleration is achieved by heating and pressurizing a propellant gas up to 1100 °C and 50 bar before the gas expands through a convergent-divergent nozzle and transits to ambient pressure. Within the convergent section of the nozzle, the powder is introduced to the gas stream. Upon impact on the surface of the substrate, the particles deform and adhere to the substrate. The deposition takes place efficiently with 90 % of the starting material being deposited on the substrate, provided the substrate does not contain any holes. The feedstock powders were purchased from TLS Technik GmbH & Co. Spezialpulver KG.

Details about the system and coating process are available here [151]. Table 3.4 gives an overview of the deposition temperature, particle size distribution of the feedstock powder and average layer thickness. All layers remained free from oxygen below the detection limit of X-ray diffraction (XRD).

Table 3.4. Overview of deposition temperatures and properties of the feedstock powders used for CGS [151].

Type	Deposition temperature / °C	Range particle size ¹ / μm	Average particle size ² / μm	Layer thickness ³ / μm
Niobium	500	not determined	40 $\pm$ 18	40 $\pm$ 23
Tantalum	500	15 - 45	25 $\pm$ 20	72 $\pm$ 17
Titanium	900	20 - 53	35 $\pm$ 13	33-60

1: Specification from manufacturer; 2: Determined by IMD-2; 3: Determined by T. Sievert (IMD-2) from SEM cross sections using the software imageJ.

The layer thicknesses of all samples used are described in more detail in Table 3.5. Due to the particle size distribution and inhomogeneous growth rates of the layer due to the curvature of the PTL, no uniform layer thickness can be specified for the cold gas sprayed layers, which becomes evident by the range. The layer thickness distribution can be determined using SEM cross-sections. This is considered to be the most accurate method, although the result depends on the number of samples taken and the locations at which samples were taken. Furthermore, the layer thickness can be determined by subtracting the thickness of the PTL substrate from the total PTL thickness, reflecting the maximum layer thickness rather than the average. Subtraction of the thickness of the expanded mesh from the total PTL thickness for the determination of the maximum layer thickness is feasible, as the expanded metal exhibits a comparatively homogeneous thickness distribution (see Table 3.2). Therefore, this subtracted thickness is given in the table to show that, due to the inhomogeneity of the coating and possible deflection of the PTL, there is a discrepancy between the measured total thickness of the PTL and the theoretical total thickness of the PTL (thickness of the expanded metal and the thickness of the coating). Due to the large range of layer thicknesses, an approximate weight per unit area of the expanded metal was also determined, whereby the open area of the mesh was subtracted beforehand.

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Table 3.5. Coating thickness of titanium CGS coatings on PTLs discussed in section 7.4 determined from SEM cross sections and subtraction of the coated PTL thickness and expanded mesh.

PTL	Coating thickness ¹ / μm	PTL thickness ² / μm	PTL thickness minus expanded mesh / μm	Layer weight [151] / gcm^{-2}
CG-33	33 $\pm$ 14	196 $\pm$ 5	67 $\pm$ 6	0.0084
CG-48_1	48 $\pm$ 15	226 $\pm$ 7	97 $\pm$ 7	0.0164
CG-48_2	48 $\pm$ 15	242 $\pm$ 17	113 $\pm$ 10	0.0164
CG-60_1	60 $\pm$ 12	300 $\pm$ 39	171 $\pm$ 20	0.0216
CG-60_2	60 $\pm$ 12	319 $\pm$ 51	190 $\pm$ 26	0.0216
CG-60_3	60 $\pm$ 12	307 $\pm$ 58	178 $\pm$ 30	0.0216
TiEM_TiCG	38 $\pm$ 16	196 $\pm$ 8	67 $\pm$ 7	0.009

1: Determined by T. Sievert (IMD-2) from SEM cross sections using the software imageJ; 2: Measured using a thickness measuring device at IET-4, see section 3.2.

Table 3.6 shows an overview of the average mesh openings after the coating process. Furthermore, the minimum and maximum measured length and width of the coated expanded meshes are given to illustrate that mesh openings exhibit tolerances due to the CGS coating.

Table 3.6. Measured opening of CGS coated expanded meshes for section 7.4.

PTL	Min./Max. opening length ¹ / μm	Av. opening length ¹ / μm	Min./ Max. opening width ¹ / μm	Av. opening width ¹ / μm
CG-33	291/359	325 $\pm$ 24	204/224	214 $\pm$ 7
CG-48	286/318	298 $\pm$ 23	142/230	193 $\pm$ 23
CG-60_1	117/317	268 $\pm$ 23	92/239	211 $\pm$ 28
CG-60_2	232/308	280 $\pm$ 23	159/312	242 $\pm$ 45
CG-60_3	232/331	274 $\pm$ 31	155/216	180 $\pm$ 21
TiEM_TiCG	305/347	325 $\pm$ 13	154/225	188 $\pm$ 10

1: Determined from SEM top view images using the software imageJ.

3.3. Light microscopy

To ensure that the expanded metals were always placed in the same orientation with the mesh length along the direction of the meander flow, they were inspected under an optical light microscope (Axio Imager.M1m from Carl Zeiss MicroImaging GmbH) before cell assembly.

3.4. X-ray computer tomography

For a 3D visualisation of the PTLs used, a computer tomograph (XCT) Xradia Versa 410 from Carl Zeiss AG was used where the sample rotates by 360° during the measurement. The respective measurement setups are given in Table 3.7.

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Table 3.7. Parameters for XCT measurements.

PTL	Accelerating voltage / <i>kV</i>	Resolution / $\mu\text{m} * \text{pixel}^{-1}$	Filter	Exposure time / <i>s</i>	Number of projections	Magnification
TiF (Figure 3.7a)	60	3.94	LE4	5	1601	4X
TiS (Figure 3.7b)	80	4.18	LE6	5	3001	4X
SMF (Figure 3.7d)	80	4.16	LE6	15	1601	4X

LE: low energy filter.

3.5. Scanning electron microscopy and energy dispersive X-ray spectroscopy

Cross sections and top views of PTLs and MEAs were imaged under a scanning electron microscope Gemini Ultra Plus from Carl Zeiss NTS GmbH (Gemini Ultra Plus) at IET-4. The measurements were carried out with a working distance of 8.5 mm and an accelerating voltage of 20 keV. To gain information about the elemental composition of the surface under investigation, energy-dispersive X-ray (EDX) analysis was carried out with an ULTIM MAX detector (Oxford instruments), whereby the excitation and hence the depth and radius of the receiving signal and therefore information reaches approximately up to 500 nm below the material surface. For cross-sections of PTLs or MEAs, the samples were embedded in resin. To prevent membrane cross-sections, which exhibit a poor electrical conductivity from becoming charged, these cross-sections were sputtered with gold for 40 s at 20 mA (sputter device Q150T from Quorum). However, as gold tends to form agglomerates, which interfere with high-resolution imaging, in some cases sputtering with Pt was carried out, with the drawback of complicating the tracking of possible Pt migration.

Back scattered electrons (BSE) were detected to visualize different materials, as the heavier a nucleus is, the more electrons are backscattered and the respective element appears brighter. In all InLense images, it should be noted that edges might appear brighter than the bulk due to the effect of deflection. At edges, excited electrons are less absorbed by the material as in the bulk. As a result, more electrons reach the detector than are emitted from the bulk of the PLT. Therefore, bright edges can only be attributed to a change in the material composition by means of EDX or by a comparison between InLense and BSE images.

When EDX is used to analyze titanium oxide, it must be noted that the absorption peak of oxygen overlaps with the shoulder of the absorption peak of titanium. Consequently, up to approximately 5 % of oxygen can be misinterpreted due to the shoulder of a titanium peak. Furthermore, the penetration depth of the electrons and consequently analysis depth is reported to range between 0.02 μm to 5 μm [153–155], depending on the acceleration voltage of the electron beam and material density. Consequently, the thickness of most thin oxide layers like the native oxide layer on titanium of only a few nanometer can hardly be determined by EDX. Additionally, the quantification of

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iridium is difficult in the presence of platinum, e.g. in the case of iridium migration from the anode to the cathode side, as platinum and iridium peaks overlap. In contrast, iron, for example, can be quantified in smaller concentrations, as there is no superimposition of another element with iron that are expected in the samples used. For standard specimens, a minimum detectable concentration of approximately 1 at.% was specified by Shindo et al. [156] or 0.1 at.% to 0.5 at.% by Marie et al. [155]. Unless otherwise stated, the SEM images shown were acquired at IET-4. Images taken at the IMD-2 are marked as such in the caption.

3.6. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is an analytical method that was used to determine the surface composition of selected coatings on PTLs with significantly lower depth (1 nm to 10 nm) and lateral resolution than EDX spectroscopy. The measurements were conducted at IET-4 with a Phi5000 VersaProbeII spectrometer (ULVAC-Phi Inc.) and an Al K-alpha monochromatic source. Survey spectra were performed with 187.5 eV pass energy in 0.8 eV steps and 100 ms/step. Detail spectra were performed with 23.5 eV pass energy with 0.8 eV steps and 100 ms/step. The spectra were analyzed using the CasaXPS software (Casa Software Ltd., U.K.). For quantification of the Ti and Nb oxidation states at the surface of TiNb alloy-coated PTLs (samples with 6 at.% Nb discussed in section 6.5), peaks were fit to experimental data using a Gaussian/Lorentzian (GL) line shape with a Shirley-type background.

3.7. Interfacial contact resistance

Interfacial contact resistances of PTLs and TiN coated titanium sheets were determined before and after the experiments using an in-house built 4-wire measurement. The setup consisted of a pneumatic cylinder (compact cylinder CQMB80TF-20 with a piston of 80 mm from SMC Deutschland GmbH) to which an exchangeable gold-plated copper block can be fastened. A copper block with an elevation of 42 mm x 42 mm x 4 mm was used for measurements with PTLs, and a block with an elevation of 10 mm x 10 mm x 4 mm for measurements with metal plates before and after corrosion testing. A scheme of the setup is given in Figure 3.8a and a photograph and CAD drawing in Figure A.4. For the measurement, the sample was placed between two gold-coated copper blocks and the PTLs additionally between two carbon PTLs (Torays, TGP-H120). The carbon PTLs served to compensate for unevenness in the sample PTL, as the carbon PTLs are compressible [27]. For the PTLs, 5.8 bar were applied by means of a pneumatic cylinder, which operates in a pressure range up to 10 bar. The pressure applied (operating pressure) to the pneumatic cylinder was measured using a pressure transducer and displayed on a digital display on an in-house built control box. According to the manufacturer, the accuracy of the pressure transmitter is specified as 0.5 % of the span,

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which corresponds to 0.05 bar. The carbon PTLs were initially pre-compressed six times without the sample PTL and their resistance value was determined as the system resistance. At the beginning of each measurement, the system resistance was determined at least twice, and between each PTL when several PTLs were measured in succession. The resistance was determined by measuring the voltage drop between the copper blocks at a current of 100 mA, 200 mA, 300 mA, 400 mA, 500 mA, 600 mA, 700 mA and 790 mA, whereby the copper blocks are connected a SP-150 potentiostat from Biologic with four wires: two current cables and two voltage sensing cables. This setup ensures, that the result is not influenced by the cable resistance. The I-V data is then fitted using linear regression where R^2 always amounted to at least 0.99 with the slope corresponding to the through plane resistance. To calculate an approximation of the interfacial contact resistance (ICR) of the PTL, the previously determined system resistance of the two carbon PTLs is subtracted from the resistance measured of the sandwich carbon PTL-sample PTL-carbon PTL. This is based on the assumption that the contact resistance between the two carbon PTLs is negligibly low due to the similarity of the material and that the contact resistances of the carbon PTLs are low as there is no oxide layer with a higher resistance compared to the bulk on the surface of the carbon PTLs. The resulting resistance is a combination of the contact resistances between the carbon PTLs against the gold plated copper blocks as well as the contact resistance between carbon PTL and sample PTL and the bulk resistances of the carbon PTLs and sample PTL. As the bulk resistance of the materials used (carbon, titanium, stainless steel) is assumed to be negligibly low compared to the contact resistances, the resistance determined here approximates closely to the contact resistance of the sample PTL and is often referred to as such [64].

Figure 3.8b gives an overview of the contact pressure on the PTL dependent on the applied pressure. The experimental contact pressure was determined with a load cell from Burster with a working range up to 2 kN (gray curve) and the orange curve shows the theoretical pressure values calculated with the theoretical forces given by the manufacturer. With the 17.64 cm² stamp, 1.4 kN were reached at an operating pressure of 3.2 bar. Consequently, only the first three points at 1.3 bar, 2.3 bar and 3.2 bar are experimentally determined and all other pressures displayed stem from linear interpolation. Unless otherwise specified, ICR measurements of the PTLs were carried out at an operating pressure of 5.8 bar, where the contact pressure on a 17.64 cm² PTL is 1.53 MPa and consequently close to 1.2 MPa, corresponding to the average contact pressure in in-house built PEMWE cells reported by Holtwerth [143]. An increasing ICR indicates an increase in PTL resistance. However, as the setup is not comparable with the assembly situation in the electrolysis cell, the ICR cannot predict or be directly compared to the cell resistance (HFR from impedance measurements), but serves to qualitatively compare different PTLs, coatings and their resistance changes during electrolysis.

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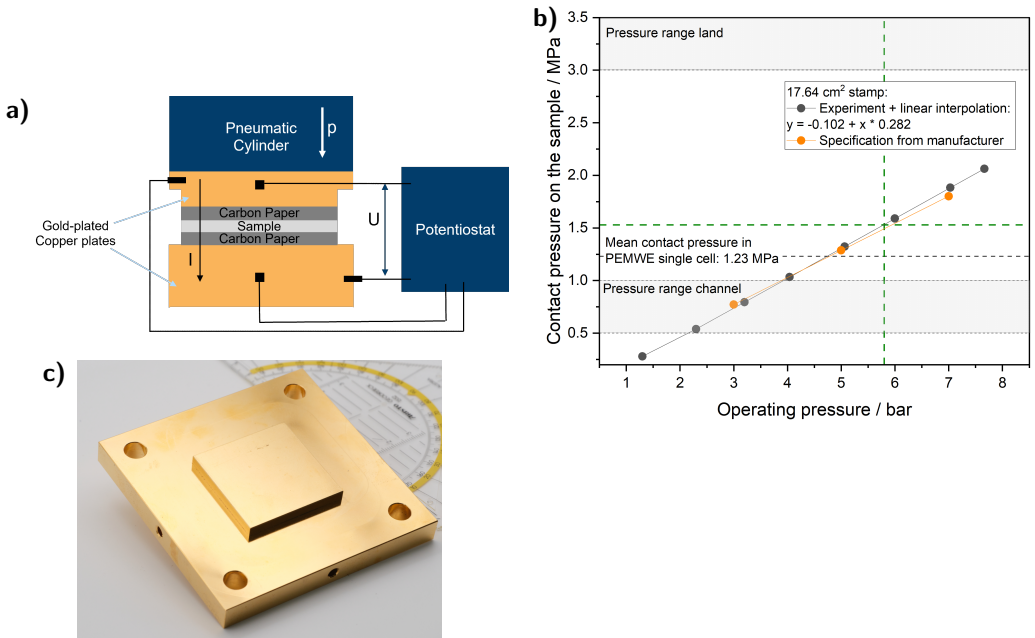


Figure 3.8. a) Scheme of the setup for ICR measurements, proportions not to scale; b) Contact pressure on the sample with a 17.64 cm² stamp in dependence of the operating pressure of the pneumatic cylinder with indication of the relevant pressure ranges in PEMWE single cells according to [143] and in bold green the pressure used for ICR measurements of PTLs at 5.8 bar corresponding to 1.53 MPa; c) Photography of the top stamp.

3.8. Inductively coupled plasma mass spectrometry

Water samples from the anode and cathode outlet of the cell and the storage tanks were taken prior and during PEMWE single cell tests for selected experiments, e.g. for experiments with 316L based PTLs as indicated in the respective results section and analyzed via inductively coupled plasma-mass spectrometry (ICP-MS), as ICP-MS allows the detection of metal concentrations in the sub-ppb-range. Measurements were performed by the institutes ZEA-3 and IET-4 at the research center Jülich. The measurements at ZEA-3 were carried out with a single quadrupole ICP mass spectrometer 7900 from Agilent, where three parallel dilutions of each sample (10-fold) were prepared and analyzed. Measurements at IET-4 were performed with an Nexlon® 2000 ICP mass spectrometer from PerkinElmer®.

3.9. Inductively coupled plasma optical emission spectroscopy

Inductively coupled plasma optical emission spectroscopy (ICP-OES) was used to analyze the composition of the two stainless steel 316L PTLs used in section 7.1. The measurements were carried out at the institute of central analytics at the research center Jülich. For the digestion of the metal samples, 2 aliquots of approximately 50 mg per sample were dissolved with 3 mL HCl, 1 mL HNO₃ and 0.2 mL HF at approximately 80 °C for 2 h. Each digestion was filled to 50 mL with Milli-Q water. 2 parallel dilutions of each digestion solution (200-fold and 10-fold) were prepared with 1 % HNO₃ and analyzed with an iCAP 7600 ICP-OES device.

3.10. pH measurements

For pH measurements, a Multi 3620 IDS pH electrode from WTW (Xylem Analytics Germany Sales GmbH & Co. KG) was used, with an operating pH range between 0 and 14. For calibration, buffer solutions of pH 4.0, 7.0 and 10.0 (Certipur®, Merck) were used. The pH value of the water samples leaving PEMWE cells with Pt coated titanium felt PTLs (reference) and Nafion™ 117 and Nafion™ 212 membranes were measured while operated without load and at cell voltages of 1.5 V and 2.0 V. Water samples were taken directly from the cell outlets and collected in 100 mL polypropylene bottles. pH measurements were carried out as soon as possible after sampling in a laboratory air-conditioned to 23 °C. Furthermore, pH measurements were carried out to determine the pH of the electrolyte for three-electrode corrosion experiments.

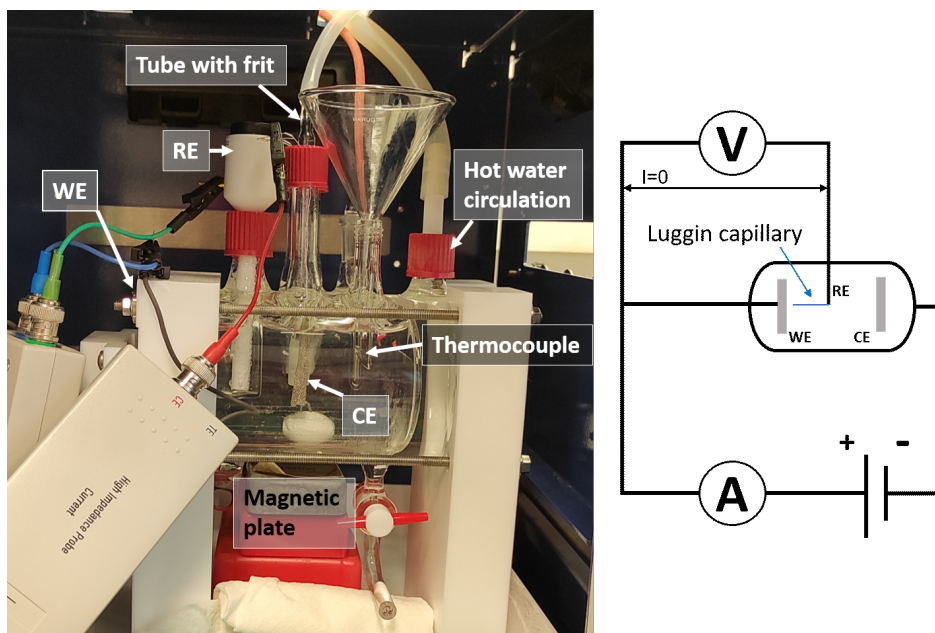


Figure 3.9. Three-electrode corrosion cell setup with schematic illustration, illustration adopted from Langemann [8].

3.11. Three-electrode corrosion cell

A three-electrode setup was used for an evaluation of corrosion studies under simulated PEMWE conditions using titanium nitride to compare with the oxidation behavior of similarly coated PTLs through electrolysis operation (section 6.8). The corrosion cell (Figure 3.9) consists of a glass chamber equipped with openings for the Pt mesh counter electrode (CE), a luggin capillary for the reference electrode (RE) next to the opening for the working electrode (WE), an insert for temperature sensing with a PT 100 thermocouple, a tube with frit for oxygen injection and an opening for filling with electrolyte. One side of the cylindrical glass chamber exhibits a circular opening for a flat sample (WE). The sample was pressed by a stamp on a PTFE block and sealed with a ring gasket (Viton®), which exhibits a circular opening of 2.54 cm², ensuring that the sample was only in contact with the electrolyte in the area of the circular opening. The inner reaction chamber, filled with electrolyte, is surrounded by a glass jacket through which tempered water can flow, allowing an electrolyte temperature of 80 °C to be set.

A Zennium Pro potentiostat from Zahner was used together with HiZ probes from Zahner for high impedance measurements, as the resistance of the samples (WE) were expected to rise and consequently the currents to drop in the range of some micro Ampere. Furthermore, the setup

3. Materials, methods and measurement techniques

was placed in a Faraday cage to shield against any disturbances. The reference electrode was a reversible hydrogen electrode (RHE) (HydroFlex®, Gaskatel GmbH) and the electrolyte consisted of 0.045 M H₂SO₄, resulting in a pH of 1.16 ± 0.01 at room temperature. Sulfuric acid was chosen, as Nafion™ contains sulfuric acid groups. However, the pK_a of Nafion™ was calculated by Chaabane et al. [57] to be approximately -6, while the first dissociation stage of sulfuric acid in H₃O⁺ and HSO₄⁻ exhibits a pK_{a1} of -3.0 and the second stage (dissociation of HSO₄⁻ to SO₄²⁻, pK_{a2}) of +1.96, resulting in almost complete dissociation in HSO₄⁻ and H₃O⁺ in aqueous solutions, while HSO₄⁻ only protolyses about 1 % in the second stage [137]. Consequently, the acid strength of the sulfonic acid groups within the polymer is higher due to the electron-withdrawing fluorine substituents, but in the liquid electrolyte of the corrosion cell, hydronium ions H₃O⁺ exhibit a higher mobility than the protons which remain near the sulfonic acid groups of the polymer. To simulate the oxygen evolution reaction, the electrolyte was gassed with oxygen at a flow rate of 0.15-0.16 standard liter per minute (SLPM). Furthermore, the temperature of the heating water flowing through the outer glass jacket was set to 82 °C to maintain an electrolyte temperature of 80 °C. The Pt-mesh electrode and oxygen purge tube were cleaned in an ultrasonic bath in deionized water twice for 15 min prior to and after each experiment and the electrolyte chamber rinsed with deionized water. For oxidation experiments with TiN PVD coatings on titanium sheets, the polarization time had to be adapted exactly to the time of the corresponding samples in PEMWE cells. Therefore, the test protocol consisted of the following steps:

1. EIS at OCP from 100 kHz to 0.01 Hz with an amplitude of 10 mV without stirring and oxygen supply to prevent disturbance of the EIS measurement
2. Chronoamperometry (CA) either at 1.4 V or at 1.6 V vs. RHE for either 15 min, 1 h, or 6 h with stirring to prevent the development of a concentration gradient on the surface of the WE and trapping of oxygen bubbles at the electrodes
3. 15 min OCP
4. EIS at OCP from 100 kHz to 0.01 Hz with an amplitude of 10 mV without stirring and oxygen supply

4. Repeatability of PEMWE single cell testing

As different PEMWE cells, PTLs and MEAs were used within this work and the testbench consisted of five places, a series of experiments was carried out to quantify the differences in performance that occur due to differences of standard cell components like end- and flow field plates, MEAs and PTLs and the test bench.

With regard to the test cells (pairs of end- and flow field plates), their pressure distribution on the active surface is a decisive factor influencing PEMWE performance [143]. Differences of the pressure distribution are caused by tolerances of the end- and flow field plates and changes to these metallic components due to their service life. Although the flow field plates and the end plates were manufactured plane-parallel, frequent screwing of the cells can lead to slight deformations of the components, leading to inhomogeneous pressure distributions within the cells. Therefore, the pressure distributions of the active- and gasket area of the test cells were determined using pressure-sensitive films from Fujifilm (principle see 3.1.2) and the results are displayed in the appendix (Figure A.5, Figure A.6 and Figure A.7). The pictures show, that the pressure in the channel area is between 1.0 MPa to 1.5 MPa (type LLW, Figure A.7) and between 2.5 MPa to 7.0 MPa in the land areas with most points between 3.0 MPa to 5.0 MPa, dependent on the cell. The trends are a bit above, but in accordance with findings by Holtwerth [143], were up to 3.5 MPa below the land and 0.5 MPa to 1.0 MPa in the channel areas were found with a similar cell. The most homogeneous pressure distribution and on average the highest pressures on the active area were found in the cells 41, 21 and 29, while the pressures in the cells 14 and 39 were weaker (see type LW, Figure A.5). However, all pressure distributions determined with the pressure sensitive foil will change during cell operation due to an additional swelling pressure of the MEA and it is not known how the pressure distribution determined in the dry state without MEA is an indicator for cell performance, as the MEA swelling will also affect the carbon PTL compression, influencing its conductivity and consequently cell performance [143]. Nevertheless, the pressure distribution on the active area is an important factor [42] and was therefore investigated qualitatively.

In addition to cell components like end- and flowfield plates, that are reused over long periods of time, cell components, that are only used for one experiment can introduce further performance differences like the PTLs and MEA. However, the standard deviation of the thickness of the titanium felt PTLs used for this chapter was maximum 2 μm and therefore negligibly small. As described in 3.2.1, the thickness of the Pt coating for PTLs was analogous to a work published in 2021 and weight determinations of PTLs before and after the sputter process always yielded the same Pt loadings

4. Repeatability of PEMWE single cell testing

within the measurement uncertainty of the weight measurement. Moreover, the contact resistances of the Pt-coated Bekaert PTLs were all in the same range within the measurement accuracy. Therefore, it is assumed that possible performance differences are not primarily caused by the anode PTL. Furthermore, the anode loading of the five cells used for this chapter was $0.94 \pm 0.05 \text{ mg}_{\text{Ir}}\text{cm}^{-2}$ and the cathode loading $0.24 \pm 0.02 \text{ mg}_{\text{Pt}}\text{cm}^{-2}$, corresponding to loading fluctuations of 5.5 % and 10 %. Whether and to what extent these fluctuations affect cell performance can be approximated by comparing iR-free I-V curves. However, it must be noted that the determination of the HFR is subject to device-related uncertainties, such as the phase error of the potentiostat (specified as 1° for Biologic HCP-1500), affecting the calculation of the iR-free curves. In addition, the kinetic overvoltage is not only influenced by the catalyst loading, but also by other factors such as the oxidation state of iridium and morphology of the catalyst layers. As the catalyst layers were produced from the same catalyst batch, no significant performance differences are to be expected from these either.

To investigate the repeatability of PEMWE single cell experiments with the test bench used for this work, five PEMWE test cells, number 41, 39, 24, 29 and 14, were assembled as described in 3.1.1 with similar Pt coated titanium felt anode PTLs. Each cell was operated on three different places of the test bench and each "cycle" consisted of an 1-hour heat-up, a short-circuit test of 7 min at 0.2 A cm^{-2} and conditioning for 20 h at 1.7 V. After that, impedance spectra were recorded at 1.45 V, 1.5 V, 1.55 V, 1.6 V, 1.65 V, 1.7 V and 1.8 V and at 1 A cm^{-2} and 6 I-V curves were recorded from 1.45 V to 2.0 V. Each voltage point was held for 1 min and for 5 min for 3 curves each, to additionally examine whether the duration of the hold of one operating point has an influence on the resulting I-V curve. In cycle 5, only 3 I-V curves were recorded with 5 min hold time for each voltage point. Consequently, a total of 27 I-V curves were recorded from each cell. From cycle 1 to 2 and 2 to 3, the cells were shifted by one cell place. Between cycles 3 and 4, the cells were only cooled down to examine the effect of cool-down on cell performance. From cycle 4 to 5, the cells were shifted to their places from cycle 2.

4. Repeatability of PEMWE single cell testing

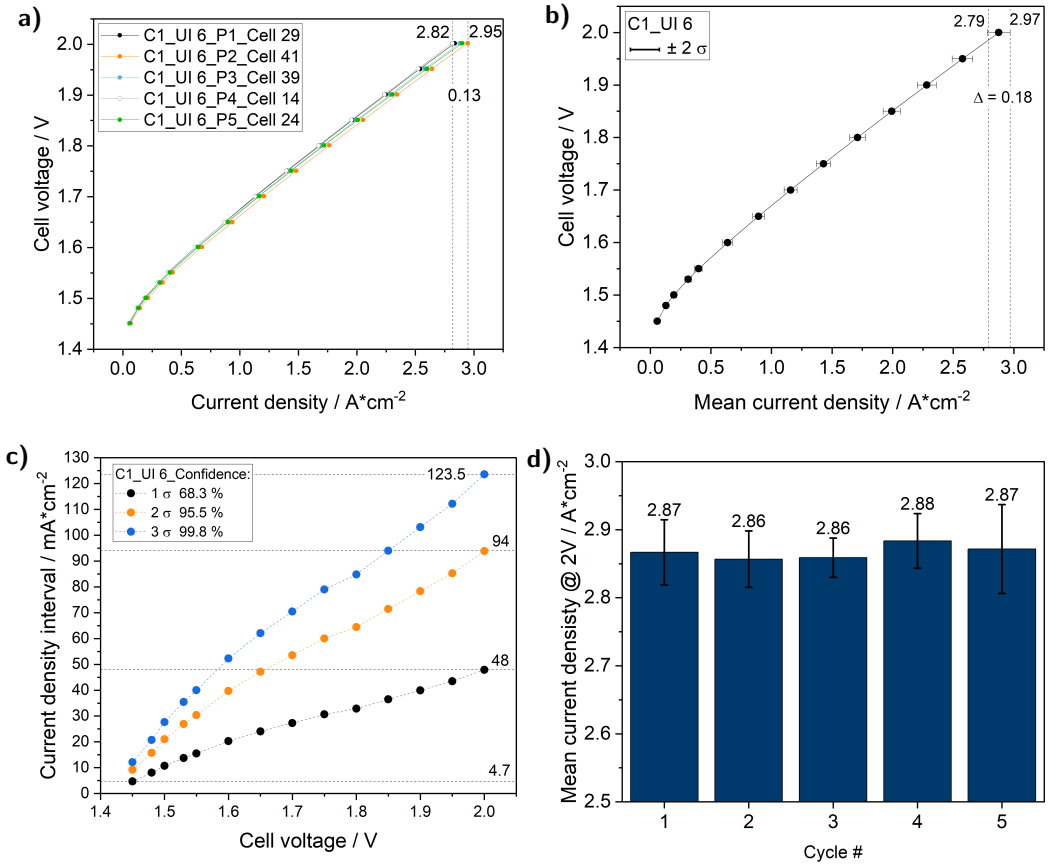


Figure 4.1. Results from the 6th I-V curves of the 1st cycle of repeatability testing: a) All I-V curves with indication of the minimum and maximum current density at 2.0V and the deviation between them; b) Mean I-V curve with 2 σ current density interval; c) Comparison of the 1 σ , 2 σ and 3 σ current density intervals as a function of the cell voltage, whereby 1 σ includes 68.3% , 2 σ 95.5% and 3 σ 99.8% of the current density range at 2.0V; d) Mean current density at 2.0V of every cycle with sample standard deviation (1 σ).

4. Repeatability of PEMWE single cell testing

Figure 4.1a exemplary shows the last I-V curves from the first cycle after conditioning. The current density at 2.0 V ranged from 2.82 A cm^{-2} to 2.95 A cm^{-2} , resulting in a difference of 130 mA cm^{-2} . In most cycles, the difference between the weakest and highest performing cell at 2.0 V was between 70 mA cm^{-2} to 90 mA cm^{-2} and the largest difference in current density observed was in cycle 5 with 170 mA cm^{-2} (Figure A.10a). Figure 4.1b additionally shows the mean I-V curve from the 6th I-V curves of the first cycle and the respective standard deviations. Considering the standard deviations at 2.0 V with a confidence level of 95.5 % (2σ , Figure 4.1c), a performance difference between cells with different PTLs in the subsequent chapters can only be reliably distinguished if their difference is outside the 2σ -interval, which was highest in cycle five with $\pm 144 \text{ mA cm}^{-2}$ (Figure A.10b), corresponding to approximately 5 %. An even more reliable difference would be outside the 3σ interval (190 mA cm^{-2}). The mean current density considering all cycles stayed around $2.87 \pm 0.01 \text{ A cm}^{-2}$ (Figure 4.1d), indicating that upon averaging over all cells and places, the different test cells and places cause only a minor influence on cell performance of 0.01 A cm^{-2} at 2.0 V. However, to achieve such a low standard deviation, at least five experiments on all bench places would be necessary. Furthermore, no difference could be observed between I-V curves recorded with 1 min or 5 min per operating point. During the exchange between cell places, the cells had to be disconnected from the water supply and the heating cartridges for a short time, resulting in a cool down to minimum 31°C . The effect of cooling was studied within cycle 4, where the cells were not switched, but only cooled down to 38°C and reheated. The cool down was not harmful to the cells as the last I-V curves from cycle 3 and the first I-V curves from cycle 4 were almost identical (see Figure A.8). Four out of five cells even showed an improvement in performance after cooling down and heating up again and the HFRs (Figure 4.2a) stayed almost constant before and after the cool down. The increase in performance likely occurred less due to the temperature changes but rather due to changing oxidation states of Ir. When the load is switched off, the potential on the anode side decreases, leading to reduction of the iridium oxide catalyst to metallic Ir. Once the load is switched on again, iridium will be oxidized to an amorphous hydrous $\text{Ir}(\text{OH})_x$ [116]. This species is more active towards the OER [157], initially leading to an increase in performance after the load is switched back on. The performance drops after an initial peak, as $\text{Ir}(\text{OH})_x$ oxidizes back to crystalline IrO_2 . However, it remains unclear why this effect of increased performance upon shutdown could only be observed with four out of five cells.

4. Repeatability of PEMWE single cell testing

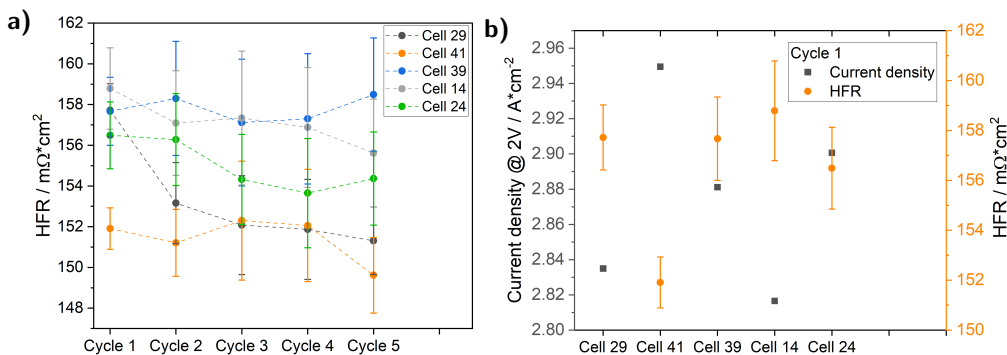


Figure 4.2. a) Development of the mean high frequency resistances of all cells with error from EIS fitting; b) Comparison between current density at 2.0 V of the last I-V curves and high frequency resistances from EIS of the first cycle.

While in cycle 1 the high-frequency resistances of cells 29, 39, 14 and 24 coincided within the error deviation of the HFR determination (Figure 4.2a), current densities deviated by about 100 mA cm^{-2} (Figure 4.2b), supporting that not only the cells, but also the cell places lead to slight differences in performance, e.g. due to different water supply rates ($24.0 \pm 2.5 \text{ mL min}^{-1}$) or water inlet temperatures ($80.0 \pm 1.6 ^\circ\text{C}$). In all other cycles, the HFR and current density corresponded well (Figure A.9), implying that the current density achieved corresponds to the relative ranking of the cell resistance and that the influence of the cell positions decreases after an extended conditioning period beyond the first cycle. This furthermore emphasizes, that the conditioning process needs to be long enough to allow for a stable performance comparison.

4. Repeatability of PEMWE single cell testing

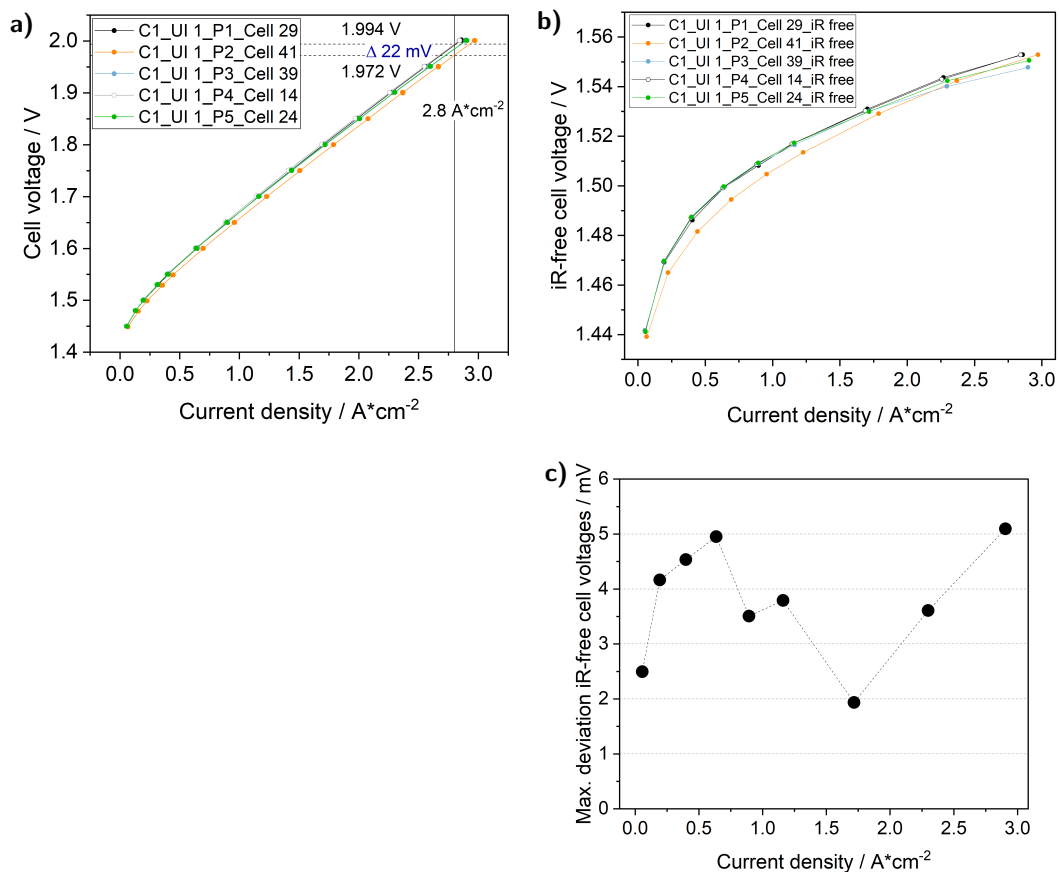


Figure 4.3. a) First I-V curves of the first cycle with indication of the minimum and maximum cell voltage at 2.8 A cm^{-2} and the cell voltage difference between the upper and lower boundaries; b) First I-V curves of the first cycle, compensated by the ohmic overpotential and c) the maximum deviation of the iR-compensated overpotentials.

4. Repeatability of PEMWE single cell testing

Figure 4.3a compares exemplarily the cell voltage difference of the first I-V curve at 2.8 A cm^{-2} , accounting for 22 mV (Figure 4.3). The largest observed cell voltage difference was in cycle 5 with 30 mV at 2.78 A cm^{-2} . Consequently, performance differences between different PTLs can only be reliably assumed if their mean cell voltages differ by more than 30 mV at 2.8 A cm^{-2} .

The slope of I-V curves that are compensated by the ohmic overvoltage (iR-free curves) display charge transfer resistances and other residual resistances like mass transport [36]. Among the iR-free curves (Figure 4.3b and c), the difference of the overvoltage was significantly lower with a maximum of 5 mV. Thus the variability introduced by the MEAs can be assumed to be minor and a larger part of the difference in cell voltages can be attributed to ohmic resistances. These can be caused by differences in the contact pressure distribution, temperature or the removal of gas and thus the water flow rate.

In a round robin test with PEMWE single cells conducted at three different laboratories, cell voltages deviated by maximum 20 mV at 2.5 A cm^{-2} and the deviations within individual laboratories were <5 mV to 10 mV [145], whereby it should be noted that a slightly thinner membrane (Nafion™ N115, 125 μm) was used, but similar current densities of about 3 A cm^{-2} at 2.0 V cell voltage were achieved compared to the standard test cells presented here. The cell voltage deviation at 2.5 A cm^{-2} from the I-V curves presented in Figure 4.1 was 20.5 mV and thus within the range from cross-laboratory testing. A higher deviation was present in cycle 5 with 29 mV. That the results are closer to the deviations of the cross-laboratory comparison rather than to the deviations of a single laboratory could be due to the fact that, similar to the use of different test facilities, the water inlet temperatures and water flow rates of every test place on the test bench used slightly vary, thus behaving more like different test benches.

The deviation of the water inlet temperature was determined by randomly measuring the water inlet temperature and found to be 1.6 °C. This deviation occurs, as the water of all five cells is preheated by two glass heat exchangers per cell, one for the anode and one for the cathode circuit and all ten glass heat exchangers are heated by one thermostat. Consequently, the temperature control influences the reaction rate and ohmic resistances. In addition, unlike cross-laboratory testing, not just one but different test cells with slightly different pressure distributions were used. Another factor with unknown extend is the ambient temperature, as the building heats up in summer and cools down in winter. Due to the comparatively thick end plates that represent a large thermal mass, it is assumed that the end plates can compensate for temperature differences to an unknown extent. To quantify this effect, experiments would have to be carried out with and without thermal insulation of the cell in winter and summer, whereby the cell components should not be subject to aging.

As the deviations between iR-free cell voltages were significantly smaller than those between full cell voltages (5 mV vs. 30 mV), it can be concluded that deviations in performance were mainly caused by influences on the ohmic cell resistance. Summarized, three main factors influencing the ohmic cell

4. Repeatability of PEMWE single cell testing

resistance can be identified that influence the performance among the cells and at different places on the test bench, whereby it was not possible to quantify each factor:

- Pressure distribution on the active area: The cell with the least pressure on the active surface (meander flowfield of number 14, Figure A.6) achieved in almost all experiments the weakest cell performance together with cell number 39, both cells with the highest HFR (Figure 4.2a). In contrast, cell number 41 with the lowest average HFR also achieved the highest current densities in almost all cycles.
- Water inlet temperature: The water for all five cells is preheated by glass heat exchangers, which are fed by one thermostat, resulting in a deviation of the water inlet temperature of 1.6 °C.
- Water flow rates: Fluctuations of the water flow rates ($24.3 \pm 1.1 \text{ mL min}^{-1}$ on the anode and $24.3 \pm 1.6 \text{ mL min}^{-1}$ on the cathode side) potentially lead to slightly different bubble detachment which might influence the ohmic resistance.

Influenced by the above-mentioned factors, the following relevant deviations for PEMWE single cell measurements on I-V curves and high-frequency resistances were determined:

- 2σ current density interval at 2.0 V: $\pm 144 \text{ mA cm}^{-2}$, corresponding to approximately 5 %
- Maximum cell voltage difference at 2.8 A cm^{-2} : 30 mV
- Maximum 2σ HFR interval: $11 \text{ m}\Omega \text{ cm}^2$

When evaluating results with new PTLs and coatings in the following chapters, it must be considered, that differences in current density $< 0.01 \text{ A cm}^{-2}$ at 2.0 V between different experiments are not attributable to the performance of the PTLs, but rather to the test cells and the test bench. Despite these deviations, the average performance distribution of $2.87 \pm 0.01 \text{ A cm}^{-2}$ at 2.0 V is considered to be narrow enough to conduct further PEMWE single cell tests with new components with cells 24, 29, 39 and 41. Only cell number 14 will not be used in the further course of the work due to the insufficient contact pressure on the active surface and the associated weak cell performance. In addition to the five cells that were compared in this chapter, two further cells are used in the course of the work (18 and 21), which were not part of this chapter, but which, based on their contact pressure distribution (Figure A.5), are expected to perform similarly to cells 24, 29, 39 and 41.

For subsequent studies it can be derived, that the pressure distribution of the cells and the precision of the control of the water inlet temperature and water flow rates should be optimized, as the

4. Repeatability of PEMWE single cell testing

maximum observed cell voltage deviation of 30 mV is above the deviation found in a round robin test involving three laboratories (20 mV [145]).

In contrast, the maximum voltage differences of iR-compensated curves amounted for only 5 mV and were thus below the deviations of iR-free curves within the round robin test (26 mV). Therefore, as already mentioned above, the observed performance differences can be attributed to a greater extent to influences that determine the ohmic resistance. Consequently, when optimizing the reproducibility of PEMWE single cell measurements, care must be taken to ensure that the pressure distribution on the active cell surface is as uniform as possible, that the water inlet temperature is kept constant, and that the water flow rate is precisely adjusted and not subject to temporal fluctuations. In addition, constant catalyst quality and loading are important for single-cell measurements, but for the MEAs used in this work (Figure 4.3b), the reproducibility of this component was given.

5. PEMWE performance with titanium PTLs

Before titanium PTLs with noble metal free coatings are investigated in the next chapter, this chapter will address the cell performance with the three titanium grade 1 PTLs used in the course of the work: titanium felts, that were already used in the previous chapter for assessing the reproducibility of single-cell tests, titanium expanded meshes and titanium sintered bodies on expanded mesh. The PTLs were investigated with and without Pt coating, as Pt is a standard coating material for anode PTLs and the performance without coating corresponds to the minimum achievable performance with the respective PTL, which should not be below with new coatings.

5.1. Titanium felt

As the cell performance with commercially available titanium felts coated with Pt on the CL-facing side has already been presented in the previous chapter 4, the average performance with titanium felts coated not only on the MEA side, but also on the BPP side will be briefly discussed. Titanium felts coated on both sides with Pt are also referred to as reference or benchmark PTL, abbreviated by "Ref" in the course of the work or "TiF_2Pt" in this chapter. Results with an uncoated titanium felt PTL are discussed together with long-term experiments in the next subsection 5.1.1.

Figure 5.1a displays the average cell performance with TiF_2Pt PTLs. The same performance range was observed in repeatability experiments reported in chapter 4, where Ti felt PTLs that were only coated with Pt on the MEA-facing side were used. However, the distribution among the experiments with TiF_2Pt PTLs was broader, as the results with TiF_2Pt PTLs originated from different experiments that followed the same protocol spread over a longer time than the experiments for repeatability testing that were one consecutive set of experiments. The 2σ interval at 2.0 V with TiF_2Pt PTLs amounted for $\pm 200 \text{ mA cm}^{-2}$ vs. maximum $\pm 144 \text{ mA cm}^{-2}$ with TiF_1Pt PTLs. Figure 5.1b shows the average high frequency resistance, ranging from $151.0 \pm 8.6 \text{ m}\Omega \text{ cm}^2$ at 2.0 V to $153.0 \pm 7.0 \text{ m}\Omega \text{ cm}^2$ at 1.7 V, the same range that was observed with Ti PTLs that were only coated with Pt on the MEA-facing side (Figure 4.2a). According to the cell performance and HFRs, there was no identifiable difference between the cells operated with titanium PTLs coated with Pt only towards the CL or additionally coated towards the FF, which is in accordance with findings from Stein et al. [86]. However, the difference between the minimum and maximum iR-free cell voltages at 2.5 A cm^{-2} with TiF_2Pt PTLs was 20 mV, while the difference of the iR-free cell voltage within the

5. PEMWE performance with titanium PTLs

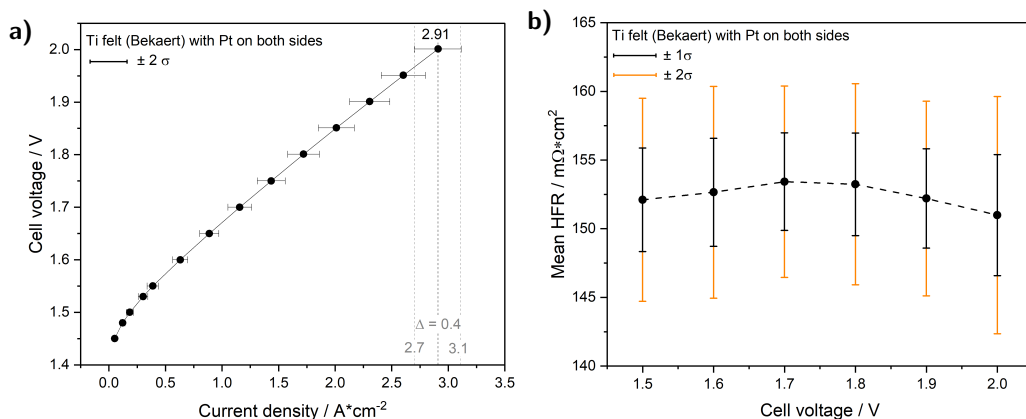


Figure 5.1. a) Mean first I-V curve recorded after conditioning from six PEMWE cell tests with TiF_2Pt PTLs and marking of the current density range at 2.0 V by gray dashed lines; b) Mean high frequency resistances at the begin of test from the same experiments.

repeatability experiment was only 5 mV (Figure A.11), indicating a variation in kinetic overvoltages. Activation overvoltages were consequently not as narrow as found in the chapter before (Figure 4.3b and c). Considering full I-V curves, the cell voltage difference at 2.5 A cm⁻² was only on third higher (30 mV), than found for iR-free curves. Consequently, the higher share (2/3) of overvoltage difference between the reference measurements can to be attributed to kinetic overvoltages. The main reason for deviations between the measurements thus differs between the two comparisons in chapter 4 and this chapter. While in the previous chapter influences on ohmic resistances were identified to account for a larger part of the performance differences, in this series of experiments it is primarily the kinetic overvoltage that led to different cell voltages. It can therefore be concluded that, despite using the same catalyst charge, greater differences between the catalyst layers can occur over longer periods of time, e.g., due to minor differences in catalyst loading.

5.1.1. Long-term stability

The longest potentiostatic experiment with a TiF_Pt PTL at 2.0 V ran for 457 h and with an uncoated TiF PTL for 1005 h, whereby during the experiment with an uncoated titanium felt, some unplanned interruptions occurred (current curve see Figure A.17a). With Pt coating, from begin to the end of test, the current density increased from 2.87 A cm⁻² to 2.91 A cm⁻² (Figure 5.2a). Consequently, no aging but performance improvement was observed with the benchmark PTL. Corresponding EIS spectra are displayed in Figure A.15, where after 457 h a slight decreased HFR and also a slightly decreased charge transfer resistance (CTR) are visible at small current densities at 1.5 V. Furthermore, the PTL resistance from another experiment with a TiF_Pt measured ex-situ post

5. PEMWE performance with titanium PTLs

mortem at 5.8 bar amounted for $2.1 \pm 0.1 \text{ m}\Omega \text{ cm}^2$ at the end of test (Figure A.12a), representing a negligible contribution to the total cell resistance compared to the membrane resistance.

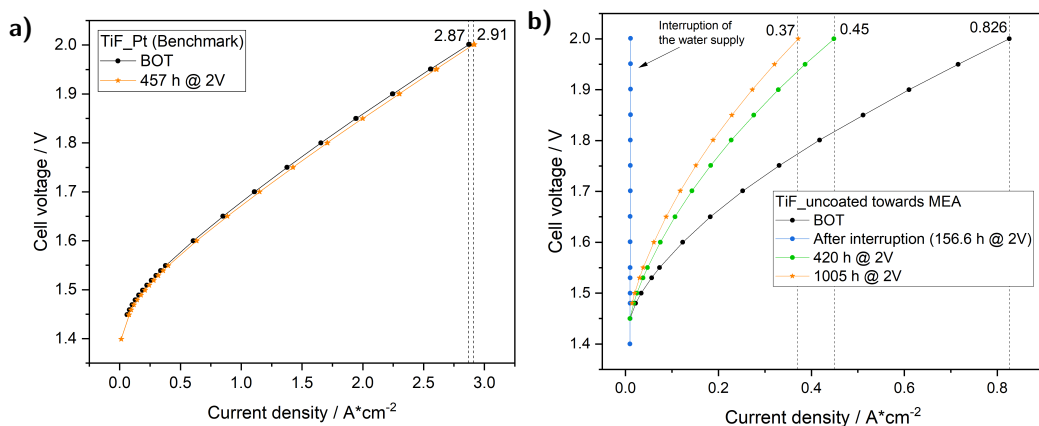


Figure 5.2. a) I-V curves of a PEMWE cell with Pt coated titanium felt anode PTL (Benchmark) after conditioning (BOT) and after 457 h of operation; b) I-V curves of a PEMWE cell with uncoated titanium felt anode PTL (TiF) after conditioning (BOT), interruption after 156.5 h, 420 h and 1005 h at 2.0 V.

Without Pt coating on the CL-facing side, the initial current density was significantly reduced and decreased by 0.456 A cm^{-2} after 1005 h at 2.0 V, corresponding to a drop of 55 %, see Figure 5.2b. The performance decline could be partly attributed to an interruption of the water supply, but also to the growth of an oxide layer on the titanium surface [64], which is reflected by a high cell resistance that ranged approximately between $430 \text{ m}\Omega \text{ cm}^2$ to $600 \text{ m}\Omega \text{ cm}^2$ at the begin of test and increased to $1005 \text{ m}\Omega \text{ cm}^2$ to $1250 \text{ m}\Omega \text{ cm}^2$ after 1005 h with an additional feature at high frequencies (Figure A.13). CTRs increased, pointing to performance loss that can partly be attributed to MEA degradation. The observed initial current density with an uncoated TiF PTL here was significantly lower compared to the initial current density reported by Liu [64] with similar uncoated Ti felt PTLs, where 1.75 A cm^{-2} at 2.0 V were measured. Liu also reported an HFR of $275 \text{ m}\Omega \text{ cm}^2$ at 0.5 A cm^{-2} with the uncoated Ti felt while the HFR determined here lay above $430 \text{ m}\Omega \text{ cm}^2$. It is conceivable that the oxidation state and thickness of the titanium oxide layer on the PTL surface differed depending on the storage time and therefore resulted in different resistances and electrolysis performance. Additionally, the surface states of the the felt PTL and expanded mesh PTL are expected to be different, as the mesh is cut in cold state, while the felt is sintered at high temperatures around 1000°C [100], whereby the sintering process takes place under high vacuum for the prevention of titanium oxidation. Furthermore, the higher surface area of the felt offers more exposed area for oxidation. An illustration of the current density during operation for 1005 h at 2.0 V with an uncoated TiF PTL is given in Figure A.17a, where a calculation of an aging rate is difficult, as

5. PEMWE performance with titanium PTLs

several unintended interruptions occurred, but a general loss was observed as reflected by the I-V curves (Figure 5.2b).

A degradation process of IrO_2 in combination with uncoated Ti PTLs contributing to impeded CT was suggested by Liu et al. [73]: The transfer of oxygen from IrO_2 to titanium might lead to the formation of unstable iridium species, whereby this hypothesis is not experimentally validated. Furthermore, an increasing imaginary impedance at high frequencies was also reported by Siracusano et al. [22] and attributed to capacitive behaviour caused by a high contact resistance and junction effect between the electrode and bipolar plate. In addition, this capacitive effect at high frequencies due to charge accumulation of the TiOx-layer causes that the imaginary impedance does not become zero and consequently the Z' -axis is not reached in the Nyquist plot, unlike with Pt-coated PTLs, where an ohmic contact between the PTL and the CL is present. Furthermore, where the TiOx layer is in contact with NafionTM, a so-called pinch-off effect can occur [158], describing band bending when semiconductors are in mixed contact with an electrolyte and catalyst particles. The more contact points between the TiOx-layer and the ionomer are established, the larger becomes the band bending of TiOx. Additionally, the Pt coating might influence the electronic properties of the native TiOx layer by strong metal-support interactions. Lewera et al. [159] found for Pt deposited on TiO_2 , that lower binding energies are present in titanium, possibly enabling charge transfer and increasing the electron density of Pt. Consequently, in addition to the rising resistance, this effect is absent without Pt coating.

Another set of experiments investigated aging under dynamic wind profile operation with TiF_2Pt PTLs for up to 1452 h, where the ohmic cell resistance remained nearly constant (chapter 8), indicating no remarkable changes of the metallic components including the PTL. Both long-term experiments, static and dynamic, proved, that the PEMWE cells with standard materials and Pt coated Ti felts are not susceptible to aging within the analyzed time frames that would have a measurable effect on the PEMWE cell performance, which is in accordance with previous findings [64].

5.2. Titanium expanded metal

In addition to titanium felts, titanium expanded metals (see specifications in section 3.2) were used to test new coating materials. As expanded metals are cheaper and easier to manufacture than metal felts, they are additionally a potentially cost-effective alternative. In order to choose which mesh size is suitable for further experiments, the cell performance with different titanium expanded metals was investigated first. As only one of the three expanded metals (TiEM3) will be used in the subsequent chapters, the other two expanded metals were not included in the experimental part and the respective mesh geometries are listed in Table 5.1.

Table 5.1. Overview of titanium grade 1 expanded metals provided by Bender GmbH with different mesh openings.

Label	Thickness / μm	Mesh length / mm	Mesh width / mm	Bridge width / mm
TiEM1	410 ± 2	1.5	3	0.3
TiEM2	264 ± 1	1	2	0.2
TiEM3	136.5 ± 3.5	0.5 - 0.6	0.5	0.15 - 0.25

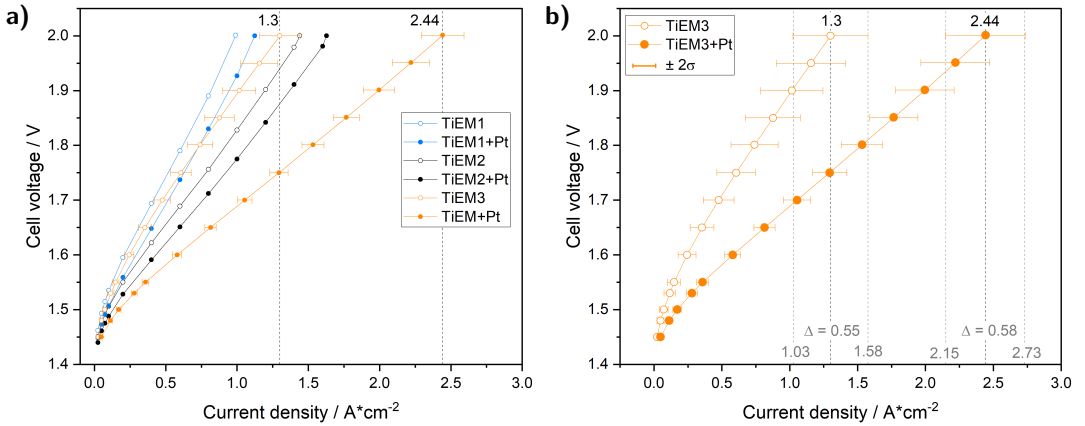


Figure 5.3. a) I-V curves at the beginning of test with PEMWE single cells with three titanium mesh PTLs of different geometries, each with and without Pt coating on the MEA-facing side. The CLs used in conjunction with TiEM1 and 2 deviated from the standard catalyst loadings described in subsection 3.1.1 and were $2.0 \pm 0.1 \text{ mg}_{\text{Ir}} \cdot \text{cm}^{-2}$ and $0.7 \text{ mg}_{\text{Pt}} \cdot \text{cm}^{-2}$. The confidence intervals with TiEM3 and TiEM3+Pt stem from three measurements each. b) I-V curves only with TiEM3 with and without Pt coating and indication of $\pm 2\sigma$ current density interval.

From the I-V curves in Figure 5.3, it can be derived that the cell performance with the Pt coated meshes is not as high with titanium felt PTLs. The trend with Pt coated expanded metals is that smaller mesh openings enable higher current densities, as the current density increases from $\text{TiEM1+Pt} < \text{TiEM2+Pt} < \text{TiEM3+Pt}$. Smaller mesh openings offer more contact points with

5. PEMWE performance with titanium PTLs

the CL and thus enabling a higher share of catalyst utilization [25]. However, the trend without Pt coating is not as clear as with Pt coating, as the performance with the finest uncoated expanded metal TiEM3 is expected to be higher than with the two coarser uncoated meshes, but ranges between them. The measurement protocols with TiEM1 and TiEM2 and TiEM3 contained one difference. While the protocol with TiEM3 was carried out as described in subsection 3.1.4 with 15 h conditioning, conditioning with the PTLs TiEM1 and TiEM2 consisted of recording five I-V curves. Consequently, the conditioning process could not yet be completed with TiEM1 and TiEM2. Another possible explanation for the performance with uncoated TiEM2 at the upper end of the performance with uncoated TiEM3 could be the higher catalyst loading of the MEA used in conjunction with TiEM2 that potentially compensated for the larger mesh openings of TiEM2 due to a better in-plane conductivity in the CL. This could additionally explain why the overvoltage of the cell with TiEM1+Pt at low current densities (approximately up to 0.5 A cm^{-2}) is smaller as with TiEM3. Furthermore, experiments with uncoated Ti PTLs involve the additional factor that each of the PTLs differs in terms of the thickness of the native titanium oxide scale, thereby causing greater variation in the initial resistances than with PGM-coated PTLs.

However, regardless of the mesh size and catalyst loading, the current densities at 2.0 V are higher when the PTL is coated with platinum as expected and similar to the results with Ti felts.

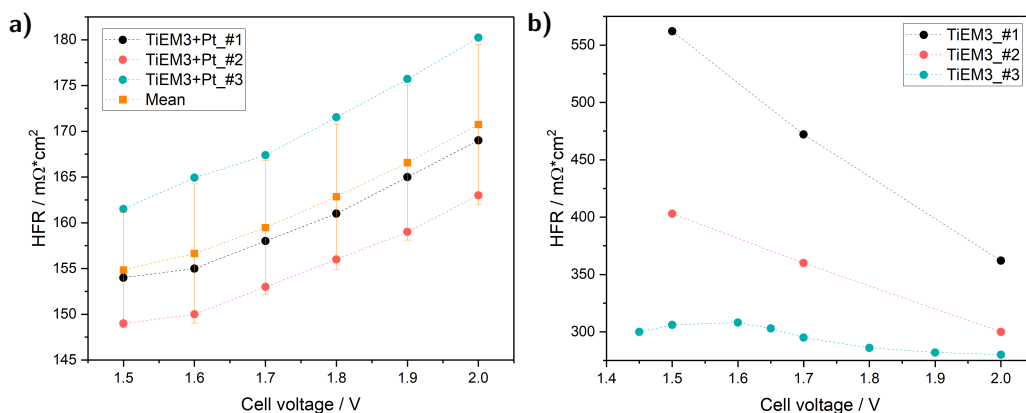


Figure 5.4. High frequency resistances from EIS spectra after conditioning with TiEMs; a) With Pt coating; b) Pt coatings only on the BPP-facing side.

Compared to experiments with TiF+Pt, the high-frequency resistances of the cells with TiEM3+Pt PTLs were on average $3 \text{ m}\Omega \text{ cm}^2$ to $16 \text{ m}\Omega \text{ cm}^2$ higher (c.f. Figure 5.4a and Figure 5.1b). Thereby, it is noticeable that in all three experiments the HFR increased with the cell voltage and the scattering was greater than with TiF PTLs. The cell resistances with uncoated TiEM from repeated measurements were further apart than would be expected from the I-V curves, as the 2σ interval of the I-V curve with uncoated TiEM PTLs were only slightly broader than from repetition with

5. PEMWE performance with titanium PTLs

Pt-coated TiEM PTLs (580 mA cm^{-2} vs. 400 mA cm^{-2} , see Figure 5.3b and Figure 5.1a). Also the HFRs from experiments with TiF+Pt were distributed more narrowly (Figure 5.1b).

To contextualize the results, it should be noted that in case of large pores, like with the expanded meshes, the conductivity of the catalyst layer becomes increasingly important. Consequently, the shown performance with the meshes might be different in case of lower loaded iridium oxide layers as the conductivity of the catalyst layer decreases with a decreasing metal content. Overall and as expected, the highest current densities can potentially be achieved with the finest expanded metal TiEM3. Therefore, only this expanded metal will be used in the further course of the work for the investigation of coatings and long-term experiments. Thus, whenever the term "titanium expanded metal" is used in the course of the work, it always refers to the finest mesh under investigation TiEM3 and will be abbreviated by "TiEM".

5.2.1. Long-term stability

Analogous to the stability test with a TiF_Pt PTL (Figure 5.2a), the longest experiment with TiEM3+Pt_#4 was carried out for 457 h and without Pt coating for 1005 h at 2.0 V.

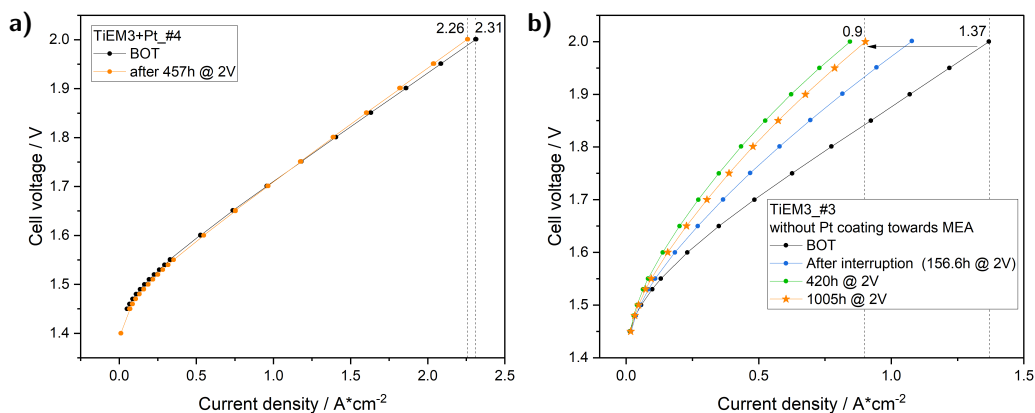


Figure 5.5. a) I-V curves of a PEMWE cell with TiEM3+Pt PTL number four after conditioning (BOT) and after 457 h of operation at 2.0 V; b) I-V curves of a PEMWE cell with TiEM3 without Pt coating after conditioning (UI 1), after 165 h where a short interruption occurred, after 420 h and 1005 h of operation at 2.0 V.

With the TiEM3+Pt PTL, only a slight decrease in current density of 50 mA cm^{-2} at 2.0 V was observed after 457 h (Figure 5.5a). Furthermore, comparing EIS spectra with TiEM3+Pt_#4 at the begin of test reveal, that the HFRs remained constant (Figure A.15b), indicating a stable cell resistance and consequently no PTL degradation. Additionally, the PTL resistance from another

5. PEMWE performance with titanium PTLs

experiment with TiEM_Pt measured ex-situ post mortem at 5.8 bar amounted for $3.1 \pm 0.1 \text{ m}\Omega \text{ cm}^2$ at the end of test (Figure A.12a).

The initial current density with uncoated TiEM was 1.37 A cm^{-2} at 2 V and decreased to 1.08 A cm^{-2} after 156.6 h of operation and further down to 0.845 A cm^{-2} after 420 h. The performance decrease was dominated by an increasing PTL resistance, as the PTL resistance measured at a contact pressure of 5.8 bar (section 3.7) increased from initially $11.3 \pm 1.4 \text{ m}\Omega \text{ cm}^2$ to $104.6 \pm 12.8 \text{ m}\Omega \text{ cm}^2$ post mortem. From 420 h until the end of test (1005 h), the performance recovered slightly to 0.9 A cm^{-2} . In this second part of the experiments, titanium oxidation does not appear to progress further or at a slower rate. Another cause for a performance recovery could be the dissolution of TiO_x , particularly in the case of fluoride emissions [121].

Furthermore, the samples TiEM3_#1 and TiEM3_#2 were subject to 40 h polarization at 2.0 V cell voltage and exhibited a more pronounced performance decrease.

Figure A.16 displays the aging rates at 2.0 V from three experiments with the finest uncoated titanium expanded meshes TiEM3_#1, TiEM3_#2 and TiEM3_#3 from 10 h to 40 h, amounting for $-0.7 \text{ mA cm}^{-2} \text{ h}^{-1}$, $-1.1 \text{ mA cm}^{-2} \text{ h}^{-1}$ and $-2.1 \text{ mA cm}^{-2} \text{ h}^{-1}$. With uncoated TiF PTLs, Liu [64] reported smaller aging rates between $-0.32 \text{ mA cm}^{-2} \text{ h}^{-1}$ to $-0.35 \text{ mA cm}^{-2} \text{ h}^{-1}$. The rates reported by Liu might be smaller as the first 250 h were excluded from the analysis, even though oxidation of the titanium surface and thus the resistance increase progress most rapidly during this initial period. Considering the entire experiment with TiEM3_#3 conducted for 1005 h, the current density at 2.0 V decreased by 17 % and the averaged rate of current decrease was even smaller as reported for the uncoated TiF PTL ($-0.17 \text{ mA cm}^{-2} \text{ h}^{-1}$, see Figure A.17b). As already mentioned, different aging rates of uncoated PTLs can be attributed to different oxidation rates and different passivation behavior.

In summary, both the commercial titanium felts and novel titanium expanded metals with Pt coating allowed long-term experiments at high cell voltages without losses. Electrolysis was also possible without Pt coating on the PTLs, but significantly lower current densities were achieved and the aging rates lead to uneconomical hydrogen production rates. Another important result of this chapter is, that with the fine titanium grade 1 expanded metals with Pt coating unexpected high current densities with an average of $2.44 \pm 0.15 \text{ A cm}^{-2} \text{ h}^{-1}$ could be achieved, despite its large openings compared to felt PTLs and the resulting less efficient use of the catalyst. Furthermore, such high current densities with mesh PTLs in conjunction with 1 mg Ir cm^{-2} coated N177 membrane have not been reported in the literature so far. Furthermore, as the expanded metals are significantly thinner than felt or sintered PTLs, the amount of titanium used could be reduced, even when an additional MPLs for an improved performance would be deposited on top. In addition, expanded metals can be manufactured quickly and continuously and are therefore suitable for a fast scale-up.

5.3. Titanium sintered bodies on expanded metal

Titanium sintered bodies on expanded mesh provided by GKN (specification see Table 3.1 and XCT image Figure 3.7) are used less frequently in the course of the work than TiF and TiEM PTLs. Nevertheless they provided a further inside in the stability of an uncoated titanium PTL, as their stability turned out to be superior to the other two titanium substrates, thus providing an explanatory approach for differing stabilities of non-precious metal-free PTL coatings. As no reproducibility measurements could be carried out with uncoated TiS PTLs, this section summarizes performance and long-term stability.

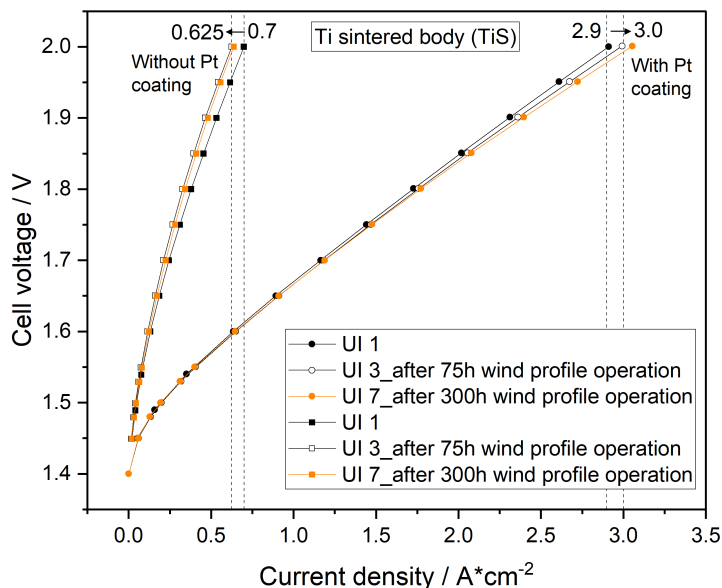


Figure 5.6. I-V curves from two PEMWE single cells with TiS PTLs; dots: with Pt coating, squares: without Pt coating.

While the cell performance with TiS_Pt was similar to the performance with benchmark TiF_Pt PTLs (c.f. Figure 5.1a), two differences compared to a TiF PTL (without Pt coating) could be distinguished with the TiS PTL without Pt coating: On the one hand, the initial maximum current density at 2.0 V was 126 mA cm^{-2} lower with TiS (0.7 A cm^{-2} vs. 0.826 A cm^{-2} , c.f. Figure 5.2b). On the other hand, the performance decrease was less pronounced.

As the performance with Pt coated TiF and TiS was the same and thus independent from the PTL geometry, the differences observed with Ti PTLs without Pt coating imply two conclusions:

The thickness of the native oxide layers might be different. Furthermore, it is possible that due to different surfaces morphologies and states, further oxide growth during PEMWE operation proceeded at different rates and with varying homogeneity. In addition, TiS was not operated constantly as

5. PEMWE performance with titanium PTLs

in previous experiments, but in wind profile operation (Figure 8.1c), hence the average cell voltage was below 2.0 V. Consequently, only the first I-V curves are directly comparable.

Nevertheless, the observations indicate that reproducible measurements with noble-metal free coating materials in the further course of the work might be more difficult to achieve than with noble-metal coatings due to potential different native oxide layers and different oxidation behavior in case the surface properties of the samples differ. One way to reduce these irregularities would be to treat the surface by acid etching, hydrogenation or plasma treatment, whereby oxidation processes are immediately restarted upon contact with the atmosphere. Due to the different results and broader scattering with uncoated titanium PTLs, it can be concluded that in general interpretations from studies using uncoated titanium PTLs are less reproducible.

6. Noble metal free anode PTL coatings

Eight noble-metal free coating materials were tested as a replacement for platinum or iridium coatings on anode PTLs: titanium nitride (TiN), tungsten, indium tin oxide (ITO), niobium, titanium-niobium alloys, tantalum and a titanium-tantalum alloy. Following the results obtained with these materials, at the end of the chapter the question was addressed if it is possible to experimentally approach the conditions (pH and potential) that prevail at the PTL/CL interface with a three-electrode corrosion-cell setup, as the materials were selected among other criteria based on studies that tested their stability in sulfuric acid in such setups.

Titanium, niobium, tantalum and tungsten belong to the group of transition metals and more specifically, refractory metals, whereas niobium and tantalum are considered to be rare [102, 160]. The name of this group is derived from the Latin word "refractarius", meaning stubborn, referring to their resistant character. There is no clear definition of refractory metals, but often a high melting point, e.g. above that of iron (1535 °C), is given as a criterion [160]. Furthermore, they have in common, that their d-shell is unfilled [160], resulting in similar chemical properties. Refractory metals were selected due to their known resistance and reports about their (electrochemical) stability in acid in the literature.

6.1. Titanium nitride - magnetron sputtered (PVD) and thermally nitrided

As the results with TiN as a protective layer for the anode PTL were contradictory in the literature (subsection 2.3.3) at the beginning of the work, TiN PVD coatings on titanium felt (3.2.1) and one thermally nitrided titanium expanded metal (subsection 3.2.2) were investigated with regard to their oxidation and corrosion stability during PEMWE operation. During the course of this work, another study was published investigating a titanium felt PTL coated with a 473 nm TiN PVD layer, with which electrolysis operation was demonstrated for 2000 h at 3 A cm^{-2} , whereby the cell voltage increased from approximately 1.96 V to 2.46 V [86]. Although electrolysis operation was possible at high current density, this increase represents an aging rate too high for commercial applications.

For the nitride layers, two preparation techniques were used, as there was only one report about a thermally nitrided PTL [46] and according to other publications introduced in subsection 2.3.3, the stability of TiN towards oxidation seems to depend on the structure of the coating and consequently the deposition or synthesis process.

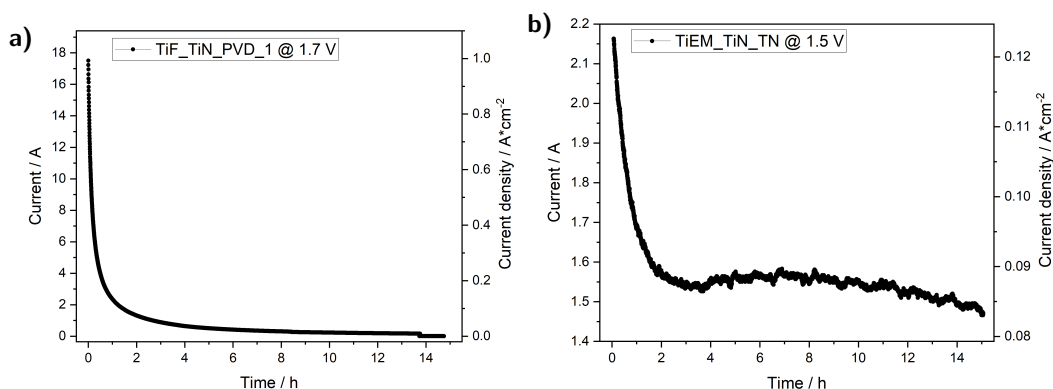


Figure 6.1. Current curves of PEMWE single cells at a) 1.7 V with PVD TiN-coated anode PTL and Nafion™ 212 membrane and b) 1.5 V with thermally nitrided titanium expanded metal anode PTL with Nafion™ 117 membrane.

Current curves of one cell with a TiN coated PTL during conditioning at 1.7 V and of one cell with a thermally nitrided titanium expanded metal anode PTL at 1.5 V are shown in Figure 6.1. The polarization lasted for 15 h, but after 13.7 h the current dropped below 160 mA with the PVD coating and from then on could no longer be measured by the test bench. As no electrolysis was possible after the conditioning period, no I-V curves could be recorded and no corresponding EIS data are available, but more experiments with TiN coated anode PTLs in section 6.8 showed a clear increase of the HFR already after 15 min of operation at 1.5 V or 2.0 V. Due to the rapid oxidation

6. Noble metal free anode PTL coatings

of the PVD coating, for testing of the nitrided PTL, it was chosen to apply milder conditions and conduct the experiment at a lower cell voltage of 1.5 V. The initial current was comparable to TiEM_Pt PTLs as around 3 A at 1.5 V were achieved, but the performance loss was also rapid with the thermally nitrided PTL, although cell operation with this PTL was still comparatively stable at a low cell voltage even after 15 h. Contrary to the first experiment, within the second experiment with a thermally nitrided PTL it was possible to run electrolysis at a very low current density of 0.08 A cm^{-2} . This could be due to the lower load caused by anodic polarization at a cell voltage of 1.5 V instead of 1.7 V. This result indicates that the oxidation behavior of the PTL surface depends on the cell voltage. This dependence is examined in more detail in section 6.8. The reason for the slight increase between 4 h and 12 h (Figure 6.1b) cannot be analyzed based on the available data. However, as the increase was very small, temperature fluctuations in the environment are conceivable.

However, the results reported in literature with a thermally nitrided titanium PTL or TiN PVD coating could not be reproduced [46, 86]. Additionally, the thermally nitrided PTL was operated for another 24.5 h at 1.5 V, during which the current dropped to 0.683 A in a continued decreasing trend (Figure A.18). After cell operation, a significant change of the coating could be observed. The typical golden color of the nitride turned into gray on the side facing the MEA and into blue on the side facing the bipolar plate (see Figure A.19) due to oxidation of the nitride layer.

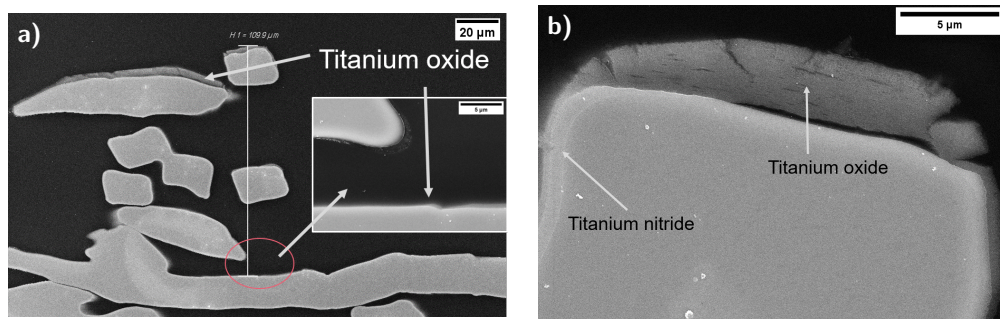


Figure 6.2. SEM cross sections of a) oxidized TiN coated titanium felt PTL; b) oxidized TiN coated titanium fibre after polarization with remaining TiN at the side of the fibre, which presumably was not in contact with the catalyst layer.

SEM images revealed that the TiN PVD layer oxidized on titanium fibers up to a depth of around $110 \mu\text{m}$ (Figure 6.2a), which was confirmed by EDX spectra. Becker et al. [59] found experimentally and conducted calculations which predicted the polarization of the anode extending approximately $200 \mu\text{m}$ into the PTL [59]. Therefore it is likely that the oxidation of the nitride layer approximately $110 \mu\text{m}$ away from the catalyst layer was driven by the polarization from the anode. However, it remains unclear if the oxidation process $110 \mu\text{m}$ away from the CL was electrochemically or

6. Noble metal free anode PTL coatings

thermodynamically driven. Figure 6.2b shows the expansion of the layer by up to three times its original size, indicating the transition from nitride to oxide [161]. On the sides of the titanium fibers, the titanium nitride layer was partially preserved, as also visible in Figure 6.2b. Consequently, the surface of the PTL, which is not in contact with the catalyst layer, is exposed to either a lower non-oxidizing potential or the duration of the polarization was too short to completely oxidize the nitride coating. However, why the nitride layer on the side of the fiber, that was presumably not in contact with the CL, did not oxidize, while the coating 110 μm away from the catalyst layer, which was likely also not in contact with the catalyst layer, did oxidize remains a question for further research about the potential map inside PEMWE cells.

6.2. Tungsten - plasma sprayed (APS and VPS)

As mentioned in subsection 2.3.3, tungsten coatings have so far only been investigated under simulated PEMWE conditions in a three-electrode setup as a potential coating for bipolar plates in 0.1 M Na_2SO_4 , adjusted to pH 5.5 with sulfuric acid [136]. Therefore, the oxidation behavior of tungsten coatings on TiEM anode PTLs will be discussed in the following. Tungsten was deposited with two different techniques: atmospheric plasma spraying (APS) and vacuum plasma spraying (VPS) at the institute of materials synthesis and processing, IMD-2 (subsection 3.2.3). VPS was used in addition to APS, as the initial current density achieved with the APS coatings were very low (Figure 6.4a) due to oxide formation during the coating process, lowering the conductivity of the coating. Therefore, VPS was chosen, where the deposition takes place under non-oxidizing conditions.

Different from Lædre et al. [136], who found tungsten to be stable against corrosion under neutral conditions, the formation of tungsten oxides after PEMWE single cell operation was observed, which was confirmed with EDX analysis, where the W:O ratio was around 1:3, indicating the formation of WO_3 crystals (Figure 6.3). The formation of WO_3 is also expected from the Pourbaix diagram of tungsten at a potential above 1.25 V and at pH 0 (at 25 °C) [162]. In addition, the coating was yellowish after the experiment, also indicating tungsten oxide and the crystals displayed in SEM images exhibited a similar shape compared to those presented by Mineo et al. [163].

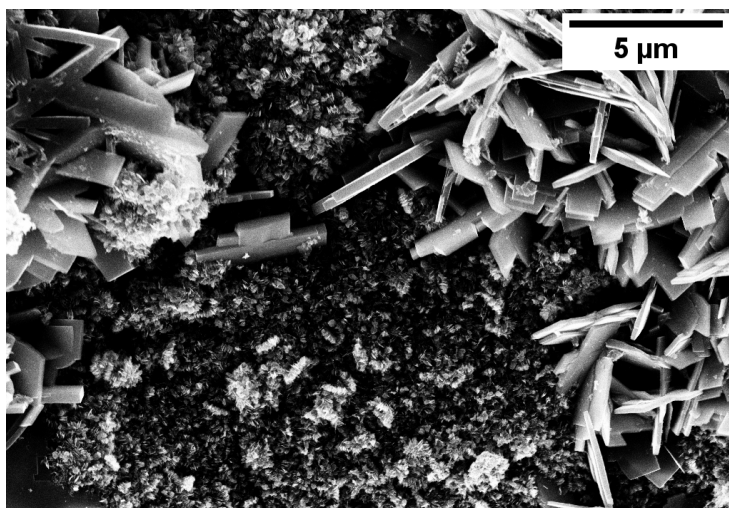


Figure 6.3. Scanning electron microscopy (SEM) image of APS tungsten coating on anode PTL (Ti expanded metal) after PEMWE single cell operation for 15 h at 1.7 V cell voltage.

6. Noble metal free anode PTL coatings

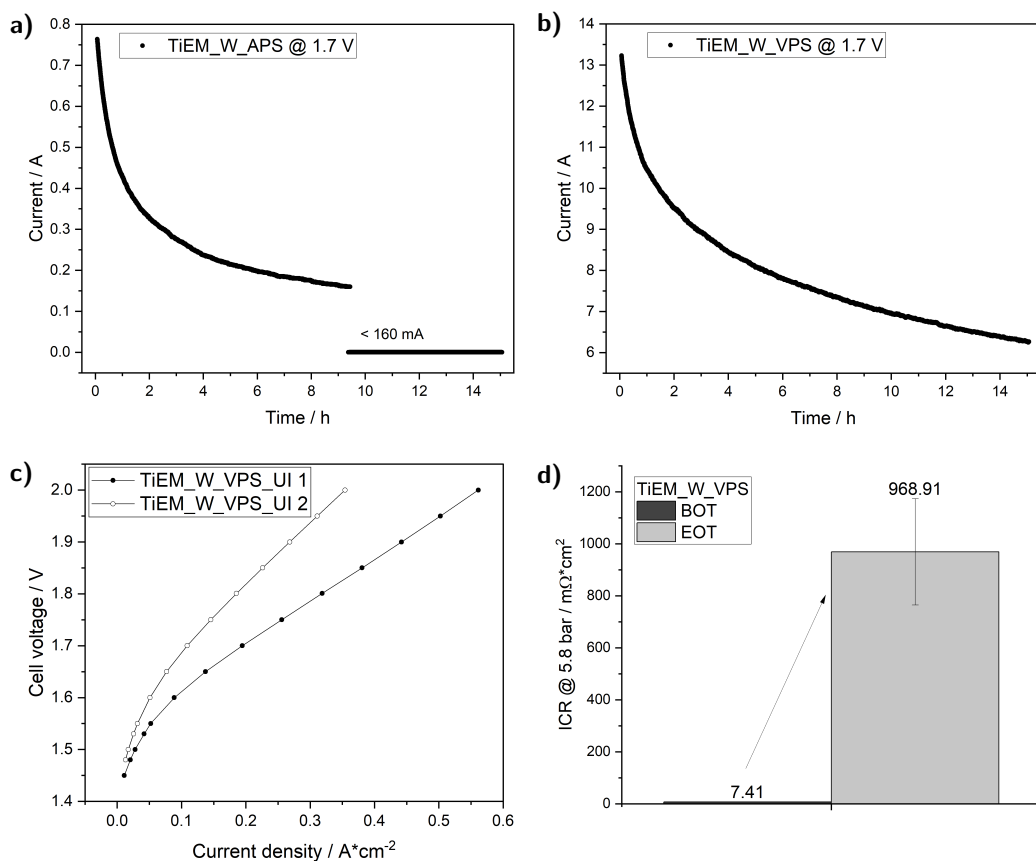


Figure 6.4. Current curves during conditioning at 1.7 V of PEMWE single cells with the anode PTLs: a) TiEM with APS tungsten coating and b) TiEM with VPS tungsten coating. c) I-V curves with W VPS coating after the conditioning. d) Resistance of the expanded metal with VPS tungsten coating before and after PEMWE operation measured between two gold-plated copper blocks and two carbon PTLs at 5.8 bar and RT.

6. Noble metal free anode PTL coatings

PEMWE single cell testing with the tungsten coated anode PTLs began with a 15 h conditioning at 1.7 V. With the APS coating, cell operation was almost not possible (Figure 6.4a) and the current dropped within 9.4 h to 160 mA. Currents below could not be recorded by the test bench. In the pristine APS coating, 4 % WO_3 was present [151], as the coating process took place under atmospheric conditions. Consequently, it is likely that due to the oxide layer, the initial limited conductivity was high enough to impede the current flow to the MEA significantly already in the beginning of the experiment [164]. In contrast, the VPS coating was free from oxygen after deposition [151] and the current obtained with the VPS coating was 13.2 A at the beginning of the test at 1.7 V. However, oxidation proceeded rapidly, as the current dropped to 6.3 A after 15 h at 1.7 V. Subsequently, two I-V curves were recorded directly one after the other. During the recording of the I-V curves, oxidation progressed further, as the slope of the second I-V curve was higher (Figure 6.4c). Also the contact resistance of the PTL increased (Figure 6.4d), causing the observed current losses. Due to the oxidation of the tungsten coating and the associated increased contact resistances, tungsten cannot be classified as a suitable coating material for anode PTLs. Whether it is possible to maintain conductivity of the coating by adding alloying metals remains to be the subject of future investigations.

6.3. Indium tin oxide - magnetron sputtered (PVD)

A thin ITO layer ($1.00 \pm 0.02 \mu\text{m}$) was deposited by means of PVD on TiEM by IMD-2 [151].

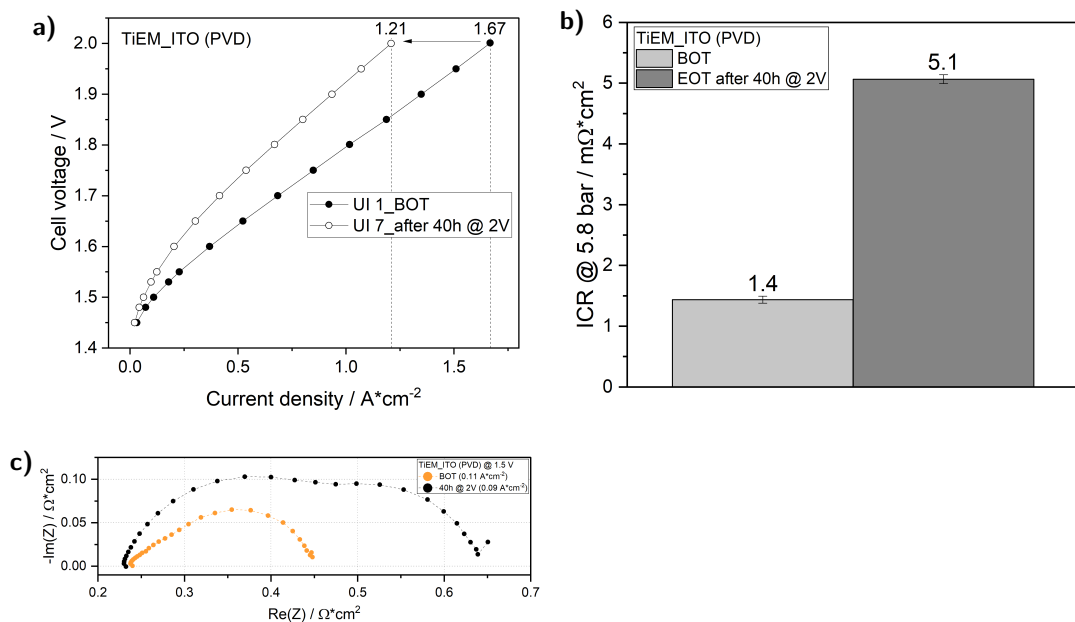


Figure 6.5. Results from PEMWE single cell operation with TiEM_ITO. a) I-V curves; b) Interfacial contact resistance determined at 5.8 bar according to 3.7; c) EIS spectra at 1.5 V at the begin of test after conditioning and after 40 h at 2.0 V

Despite a fast performance loss with the ITO coating (Figure 6.5a), the ICR increase was moderate (Figure 6.5b), demonstrating that the ex-situ measured ICR of the PTL can provide an indication of the cell performance, but can not predict the performance, as other effects such as dissolution of the coating and catalyst inactivation can contribute to performance losses. Furthermore, the HFR stayed between $225 \text{ m}\Omega \cdot \text{cm}^2$ and $240 \text{ m}\Omega \cdot \text{cm}^2$, indicating that the origin of performance loss here does not stem from an increased resistance, but from catalyst inactivation. This is supported by increasing CT resistance visible from Nyquist plots (Figure 6.5c), possibly stemming from catalyst inactivation from Sn or In dissolution. Due to the rapid loss of performance, a more detailed analysis of the reasons and further optimization were not carried out at this point.

6.4. Niobium

As a VPS niobium coating on a titanium coated stainless steel mesh PTL was presented to enable almost stable PEMWE single cell operation over 1500 h [67], Nb coatings deposited by Sievert [151] using CGS, APS and PVD were investigated with regards to their performance and degradation. CGS Nb layers will be discussed first, followed by APS and PVD coatings.

6.4.1. Cold Gas Sprayed

CGS niobium coatings were applied by the institute IMD-2 on titanium expanded mesh (TiEM_Nb-CG, see Table 3.4) and on 316L expanded mesh with an additional CGS titanium inter-layer (316LEM_Ti_Nb-CG). The titanium layer was deposited because previous stability tests in a three-electrode setup [165] and a study by another research group found that Nb adheres better to titanium than to 316L [166]. The same effect was observed with Pt coatings on 316L [71].

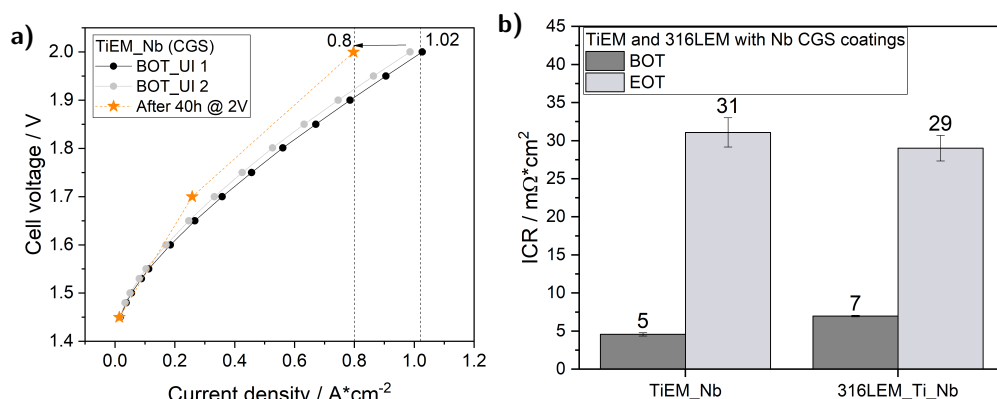


Figure 6.6. a) I-V curves with TiEM anode PTL coated with a niobium CGS layer. b) Resistances of two Nb CGS coated PTLs before and after PEMWE operation measured between two gold-plated copper blocks and two carbon PTLs at 5.8 bar and RT.

Figure 6.6a illustrates that a performance decrease was observed with TiEM_Nb-CG after 40 h of electrolysis operation at 2.0 V. A similar performance decrease was observed with 316LEM_Ti_Nb-CG. With the 316L mesh PTL after 40 h, only one current density point was recorded at 1.7 V, thus the corresponding I-V curves are not displayed. With 316LEM_Ti_Nb-CG, the initial current density amounted for 0.88 $A \cdot cm^{-2}$. The ICR of TiEM_Nb-CG increased by $26 \pm 1 m\Omega \cdot cm^2$ and the ICR increase of 316LEM_Ti_Nb-CG was close with $22 \pm 1 m\Omega \cdot cm^2$, supporting that the ICR increase was caused by the top Nb coating and not the underlying Ti or 316L substrate. Kellenberger [167] also reported the formation of an oxide layer on Nb under simulated PEMWE conditions in a three electrode setup upon exposure to O_2 saturated 0.05 M H_2SO_4 at 90 °C and polarization at 2.0 V

for 6 h. Although they found the oxide layer to be very stable, the ICR increased by a factor of 2.5. Thus, a similar trend compared to Figure 6.6b was observed with regard to the through-plane conductivity of the Nb coated PTLs. However, the stability during electrolysis operation reported by Stiber et al. [67] could not be reproduced. In addition, with TiEM_Nb-CG a strong dependence of the the current density on the HFR was observed, as the HFR after 40 h ranged from $802 \text{ m}\Omega \text{ cm}^2$ at 1.45 V, over $630 \text{ m}\Omega \text{ cm}^2$ at 1.7 V to $441 \text{ m}\Omega \text{ cm}^2$ at 2.0 V. Shifting of the HFR to lower resistances at higher current densities was also observed with uncoated Ti felt PTLs (see Figure A.13) and reported by Kang et al. [120] with uncoated titanium PTLs. They explained this observation by heterogeneous heat production and distribution of the oxidized surface. Due to the lower thermal conductivity of the oxide compared to pure Nb (Table 6.1), the local temperature can rise particularly at higher current densities. If the heat produced cannot be dissipated by the material above the thermoneutral voltage, local hotspots form, causing the proton conductivity of the ionomer and the membrane to increase, but degradation may also progress more rapidly. With 316LEM_Ti_Nb-CG, it was not possible to determine a HFR as the high frequency resistances contained large proportions of imaginary impedance. Furthermore, despite a total thickness of the CGS layers of $40 \pm 16 \mu\text{m}$ and a short duration of the experiment, corroded areas were present on the surface of the FF-facing side of the 316L expanded metal, whereby it is assumed that only surface corrosion occurred, as no pitting corrosion was observed. Further investigations on 316L based PTLs will follow in chapter 7.

Table 6.1. Overview of thermal conductivities and electrical resistivities of Ti, Nb, their respective oxides and Pt at RT collected from literature.

	Thermal conductivity / $\text{W m}^{-1} \text{K}^{-1}$	Electrical resistivity / $\mu\Omega \text{ cm}$
Nb	54 [168]	15 - 16 [169, 170]
NbO	7 [171]	21 [170]
NbO ₂	3 - 4 [172]	1E^{10} [170]
Ti	2 - 22.5 [26, 120]	43-57.5 [120, 173]
TiO ₂	4.8 - 11.8 [120]	1E^{19} - 1E^{24} [120]
Pt	71.6 [120]	10.5 [120]

6.4.2. Atmospheric Plasma Sprayed

APS was investigated because the process does not involve a vacuum and is therefore considered to be cost-effective. In addition, vacuum-free processes are better suited for the implementation in continuous processes. However, the coating exhibited considerable oxide scales as the composition resulted in 68 % Nb, 23 % NbO and 8 % NbO₂ [151].

Nb was applied by means of APS (subsection 3.2.3) on a titanium sintered body (section 5.3). The initial performance was similar to that observed with an uncoated TiS PTL (Figure 6.7), but the performance decay was more pronounced. One reason for the different decay might stem from different modes of operation. The uncoated TiS PTL was subject to wind profile operation with an

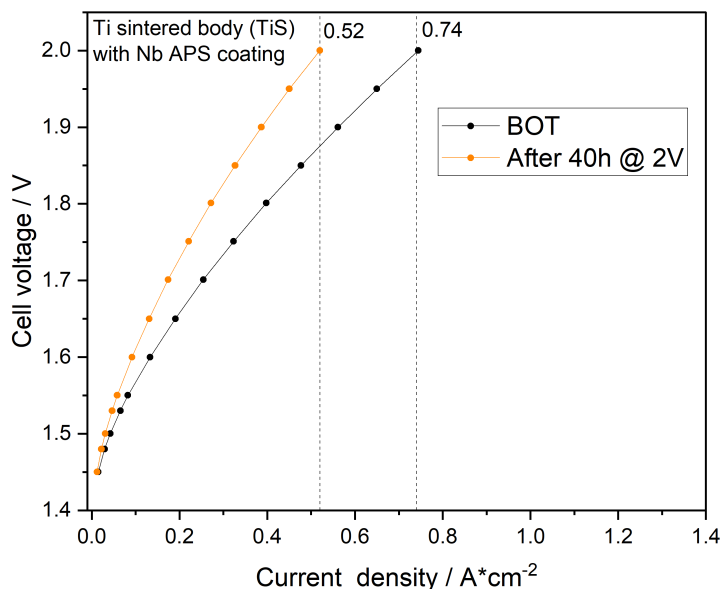


Figure 6.7. I-V curves from PEMWE single cell operation with TiS PTLs coated with Nb by means of APS.

average cell voltage below 2.0 V for 300 h, while the PTL with Nb coating was operated constantly at 2.0 V but only for 40 h. Consequently, it is not known whether aging driven by a higher cell voltage at shorter operating times and longer operation at a lower cell voltage might offset each other. Nevertheless, the low current densities achieved with the Nb APS coating do not allow economical electrolysis operation.

6.4.3. Magnetron sputtered (PVD)

As PVD coatings can be applied to almost any substrate, including those with small pore openings, Nb PVD coatings with a layer thickness of $3.6 \pm 0.1 \mu\text{m}$ were applied on Ti and 316L expanded meshes as well as a 316L felt PTL [151]. The results of the latter will be discussed in subsection 7.3.2, as the focus with this sample was on investigating its corrosion stability.

The initial current density with Nb PVD coated expanded metal anode PTLs was slightly higher than with the CGS Nb coating (above vs. below 1 A cm^{-2} , c.f. Figure 6.8 and Figure 6.6). The highest current density with an improved Nb PVD coating in terms of the density of the coating [151] on TiEM amounted for 1.43 A cm^{-2} . For the sake of clarity, the corresponding I-V curves are displayed in the appendix, see Figure A.20. However, a performance decay after 40 h of operation at 2.0 V was observed with all Nb PVD coatings. The decline in current density at 2.0 V was observed to be within

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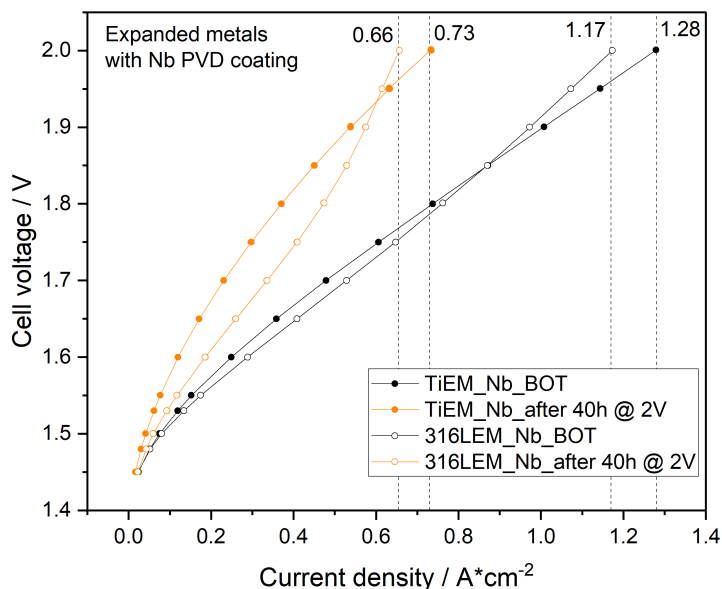


Figure 6.8. I-V curves with Nb coated anode PTLs (titanium and 316L expanded mesh) by means of PVD (Table 3.3).

the same range for both expanded metal substrates amounting for 510 mA cm^{-2} with the TiEM and 550 mA cm^{-2} with the 316LEM. However, a notable distinction emerged in the upper cell voltage range with the 316L expanded metal, where mass transport limitation became evident. The cell voltage degradation rates at 0.6 A cm^{-2} were $4625 \text{ } \mu\text{V h}^{-1}$ and $5125 \text{ } \mu\text{V h}^{-1}$ and consequently higher than observed by Stein et al. [86], where the degradation rate within the first 30 h of operation amounted for approximately $1300 \text{ } \mu\text{V h}^{-1}$ at 3 A cm^{-2} . No ICR measurements are available from these PTLs, but the HFRs increased with both Nb PVD coated expanded meshes. Furthermore, EDX spectra of the PTL surfaces were taken post mortem. The average oxygen content found in spectra that only contained niobium and oxygen, and maximum 0.5 at.% impurities, was $23 \pm 3 \text{ at.}\%$, whereas the absence of oxygen in the pristine coating was confirmed by Sievert [151]. Furthermore, it must be noted, that the post mortem oxygen content at the surface is likely to be higher than the average ratio of 3.3:1 (Nb:O), as the depth of information from EDX spectra stems from a few micrometers below the surface [155]. Thus the uppermost few nanometer may contain more oxygen, with the oxygen content decreasing below the surface.

Summarized, Nb coatings were deposited on different PTL substrate by means of CGS, APS and PVD as a potential replacement for Pt coatings. The initial cell performance with Nb coated PTLs ranged from 0.74 A cm^{-2} to 1.28 A cm^{-2} at 2.0 V and a significant increase in PTL and cell resistance was observed, leading to strong performance decreases even after 40 h. Consequently results from

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the literature with VPS coatings could not be reproduced [67], but are in accordance with Stein et al. [86], who also observed high degradation rates with Nb PVD coated PTLs. Furthermore, although the costs for Nb are lower compared to Pt, it must be noted that niobium is classified as a critical raw material by the European Union [102] and can therefore, also with regards to the observed oxide formation, not be considered as an alternative to platinum according to the current state of research.

6.5. Titanium-niobium alloys - magnetron sputtered (PVD)

In the following, mixed Ti-Nb PVD anode PTL coatings deposited by Sievert [151] with 3 at.% Nb (TiF and TiEM_ $\text{Ti}_{97}\text{Nb}_3$), 6 at.% Nb (TiF and TiEM_ $\text{Ti}_{94}\text{Nb}_6$) and 28 at.% Nb (TiF and TiEM_ $\text{Ti}_{72}\text{Nb}_{28}$) will be investigated. These ratios were selected as Aukland et al. [106] found the lowest surface resistance for $\text{Ti}_{97}\text{Nb}_3$ coatings on bipolar plates and Frisch et al. [103] reported a maximum conductivity of Nb doped mesoporous titanium oxide ($\text{Nb}_x\text{Ti}_{1-x}\text{O}_2$) with a Nb mole fraction of 33 at.%. To quantify if the alloying metals have an influence on the conductivity of the coating, additionally pure titanium PVD coatings on titanium expanded meshes were investigated (TiEM_Ti).

Compared to uncoated titanium PTLs (Figure 5.2b and Figure 5.5b), the initial performance and long-term stability with TiF and TiEM coated with $\text{Ti}_{97}\text{Nb}_3$ was superior (Figure 6.9a and b). In addition, the performance and performance development were similar with the felt and expanded mesh, indicating that the performance was determined by the properties of the coating rather than the PTL geometry. As the current densities were comparatively low and stayed below 2 A cm^{-2} , the transport properties of the PTLs were not yet decisive. However, compared to Pt coated PTLs (Figure 5.2a and Figure 5.5a), the performance was significantly reduced. Furthermore, the performance and performance losses with pure Ti PVD coatings were in the same range as with 3 at.% Nb. Thereby, the oxygen content determined from top view EDX point spectra of the samples TiEM_Ti-PVD_1-3 amounted for 13.4 ± 3.4 at.% and increased to 18.5 ± 3.8 at.% at the end of test (Figure A.21). The contact resistances of the PTLs with pure Ti coating and with 3 at.% and 6 at.% were close and the increase in resistance after 144 h was less pronounced without Nb additive. Consequently, no increased conductivity of the PTL surface could be observed upon addition of 3 at.% or 6 at.% Nb. One reason for the close performance between the pure and alloyed coating could be the deposition method of the mixed coatings where three Ti targets and one Nb target were used while the sample was rotated [151]. It is therefore possible that the coating surface contained few or no Nb leading to similar oxidation and resistance increase compared to a pure Ti coating. This hypothesis is corroborated by XPS measurements, as the composition of the coating surface determined by means of XPS exemplary for pristine and post mortem samples of TiF_ $\text{Ti}_{94}\text{Nb}_6$ PTLs revealed, that there were no or only trace amounts of Nb on the surface with a maximum ratio of 1.00:0.04 (Ti:Nb). The inhomogeneous distribution of Nb in Ti could be prevented by using pre-alloyed Ti-Nb targets.

Another assumption from the performance comparison of the uncoated TiEM PTL and TiEM PTL coated with Ti PVD was already drawn from the performance comparison of uncoated titanium felt and titanium sintered body PTLs. Both the experiments with uncoated Ti PTLs and Ti PVD-coated TiEM PTLs showed that pure titanium surfaces lead to less reproducible measurements. Furthermore, there appears to be a greater difference between PTLs with an uncoated titanium

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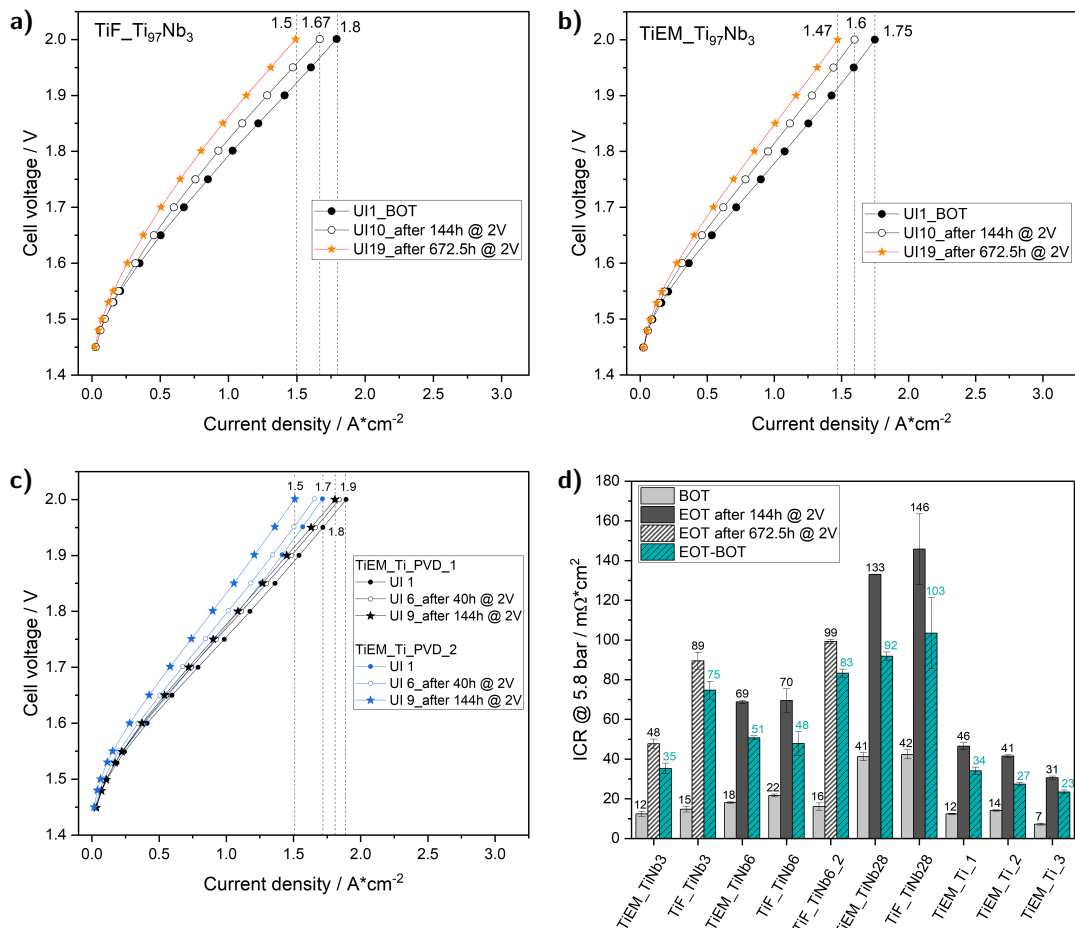


Figure 6.9. a) and b): I-V curves with TiF and TiEM PTLs with PVD coating consisting of 97 at.% Ti and 3 at.% Nb (TiEM_Ti₉₇Nb₃). c) I-V curves with Ti PVD coated TiEM without Nb (TiEM_Ti). A third experiment yielded a current density of 1.8 A cm⁻² at 2.0 V; d) ICR of all investigated Ti-Nb and Ti PVD coated Ti PTLs at 5.8 bar corresponding to a contact pressure of 1.53 MPa (c.f. Figure 3.8b). All PTLs are Pt PVD coated on the FF-facing side.

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surface and TiEM_Ti-PVD PTLs, as higher current densities could be achieved with Ti PVD coated expanded metal. Additionally, ICRs of the PTLs with Ti PVD coating with and without 3 at.% Nb were close ($7 \text{ m}\Omega \text{ cm}^2$ to $15 \text{ m}\Omega \text{ cm}^2$, see figure Figure 6.9c). The development of the HFR over time in dependence of the cell voltage with TiEM_Ti₉₇Nb₃ is displayed in Figure A.22, where two trends are visible. One trend is a decreasing HFR with increasing cell voltages. This observation supports the assumption of the formation of pure titanium oxide, as TiO₂ exhibits a lower thermal conductivity than the pure metal (Table 6.1). At higher power input where heat is produced by the reactions, less conductive oxides favor the formation of local hot spots, leading to a reduction of the membrane resistance and accelerating proton transport. The second trend is an increasing average HFR with progressing time from BOT $255 \text{ m}\Omega \text{ cm}^2$ to $224 \text{ m}\Omega \text{ cm}^2$ (ranging from 1.45 V to 2 V) to $324 \text{ m}\Omega \text{ cm}^2$ to $250 \text{ m}\Omega \text{ cm}^2$ after operation for 521 h at 2.0 V.

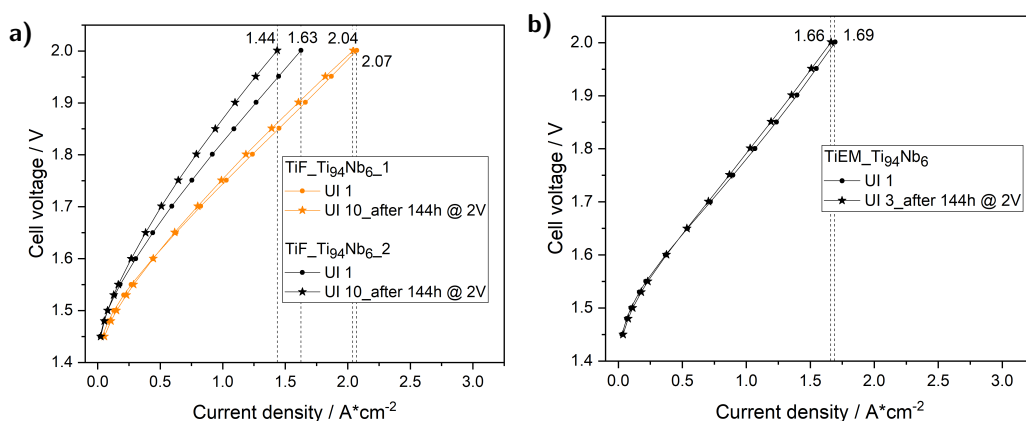


Figure 6.10. I-V curves with titanium felt and mesh PTLs with 6 at.% niobium in the Ti PVD coating; a) two Ti felt PTLs with Ti-Nb alloy PVD coating; b) Ti expanded metal PTL with Ti-Nb alloy PVD coating. All PTLs were Pt PVD coated on the FF-facing side.

Also with Ti coatings containing 6 at.% Nb, higher current densities were achieved compared to uncoated Ti PTLs. The initial resistances of the PTLs with 6 at.% Nb coating were on average slightly higher than with 3 at.% Nb (Figure 6.9d). This might be caused by a thinner Pt coating on the FF-facing side (2 nm instead of 37 nm) due to breakdown of the sputter coater. However, the ICR increase of TiEM_Ti₉₄Nb₆ and TiF_Ti₉₄Nb_{6_1} were closeby, from about $20 \text{ m}\Omega \text{ cm}^2$ of the pristine samples to $70 \text{ m}\Omega \text{ cm}^2$ post mortem. In addition, the performance decrease with both PTLs was very low. The ICR increase with TiF_Ti₉₄Nb_{6_2} was higher than with the first sample, but the experiment was also conducted longer with this PTL. However, as evident from the results with TiF_Ti₉₄Nb_{6_1} and 2, the performance with alloy coatings was not yet reproducible. While the current density with sample 1 decreased only by 30 mA cm^{-2} after 144 h, the decrease with

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sample 2 was a bit more than six times higher (190 mA cm^{-2}). Hence, these findings require further investigation beyond this work about the surface properties and oxidation mechanisms of the titanium surfaces of the expanded mesh and the surface of the PVD coating.

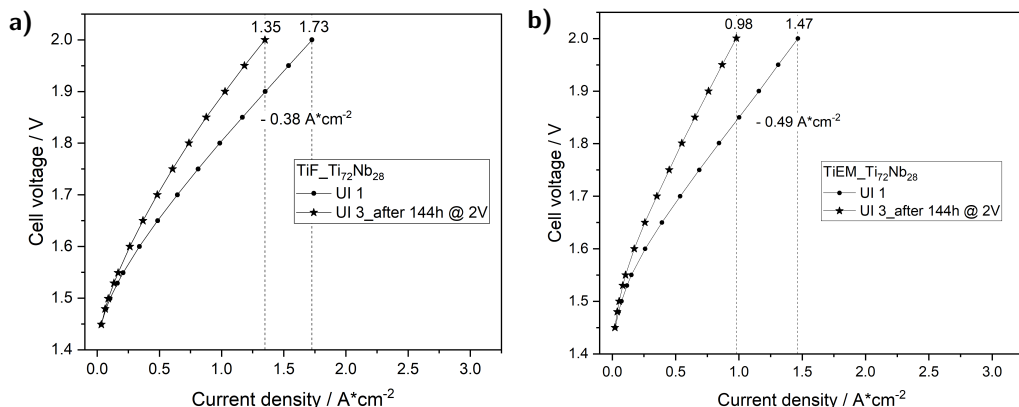


Figure 6.11. I-V curves with titanium felt and mesh PTLs with 28 at.% niobium content in the Ti PVD coating; a) with felt PTL; b) with Ti expanded metal PTL; All PTLs are Pt PVD coated on the FF-facing side.

Compared to the results with 3 and 6 at.% Nb, the achievable current density with 28 at.% Nb was lower and the performance loss more pronounced, which was also reflected by an initial higher ICR as well as the highest observed post mortem ICRs among the alloy coatings. The significantly lower performance of the coatings with 28 at.% Nb could be due to the structure of the coating. Cross sections of the coatings revealed that these coatings in particular consisted of a layered structure with Nb and Ti-rich phases. Figure A.23 shows a SEM cross section of TiEM_Ti₉₄Nb₆. The same layered structure was also visible with TiEM_Ti₇₂Nb₂₈ [151]. This insufficient mixing could have caused the coating to perform more like a pure Nb coating. Furthermore, the Ti₇₂Nb₂₈ coating on TiEM contained more cracks and defects than the coatings with less Nb (Figure A.23c and d). However, the same coating on TiF contained less cracks, consequently the coating defects are likely not to be the decisive factor for the performance decay.

Summarized, the results achieved represent a starting point for the further development of alloy coatings. PTLs coated with Ti₉₄Nb₆ showed improved stability compared to uncoated or Nb-coated titanium PTLs. However, the results were not yet reproducible, as sputtering with three Ti and one Nb target while rotating the sample did not result in a homogeneous distribution of Nb in the bulk and on the surface, as confirmed by XPS and SEM in combination with EDX. Furthermore, the absence of Nb on the surface of some samples can be inferred from the results obtained with pure Ti-PVD coatings, as the stabilities over 144 h of operation at 2.0 V with pure Ti PVD coatings were close to

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the results with coatings that contained on average 3 or 6 at.% Nb. Consequently, the fraction on the surface of some samples amounted for less than 6 at.%, resulting in a close performance between the doped and pure Ti coating leading to non-reproducible results. Therefore, new methods or sputtering with a pre-alloyed target would have to be developed to ensure a homogeneous distribution of Nb in Ti. Furthermore, it is conceivable that a thin alloy coating under a low-loaded noble metal coating covering the native oxide layer of a Ti PTL offers the possibility of lower precious-metal loadings on the anode PTL, as the alloy potentially maintains a higher conductivity than the pure titanium oxide surface of the uncoated PTL. A coating system consisting of a Ti-Nb alloy coating with Pt on top or the simultaneous sputtering of Ir or Pt with Ti and Nb could be considered to achieve a distribution of Nb and Ir or Pt in Ti.

6.6. Tantalum

The last element investigated as a potential replacement for PGM coatings on PTLs was tantalum, deposited via CGS (3.2.4) and PVD (3.2.1). Additionally and parallel to the Ti-Nb alloy coatings investigated in the previous subchapter, a sputtered alloy coating with titanium and 6 at.% tantalum (3.2.1) on titanium expanded mesh was investigated. First results with cold gas sprayed coatings will be discussed followed by results with sputtered coatings.

6.6.1. Cold Gas Sprayed

Tantalum was first tested as a CGS coating. If these coatings provided sufficient stability, they could potentially also be used as a corrosion protection layer on stainless steel PTLs.

From XRD spectra it was confirmed that no oxides were present in the tantalum cold gas layer [151], providing a promising starting point. However, the maximum current density at the begin of test at 2.0 V amounted only for 0.32 A cm^{-2} (Figure 6.12a). Similarly, the current density at 1.7 V at the beginning of the conditioning phase was comparatively low with 0.218 A cm^{-2} , decreased to 0.118 A cm^{-2} at the end of conditioning and decreased even further after 40 h at 2.0 V to 0.063 A cm^{-2} . For the 4th I-V curve only three points derived from the potential hold before recording impedance spectra (subsection 3.1.5) could be extracted. Nevertheless, a strong performance decay was visible. Impedance spectra at the end of test are shown in Figure A.24. The ohmic resistances at high frequencies ranged approximately from $2 \Omega \text{ cm}^2$ to $3.5 \Omega \text{ cm}^2$. However, ohmic resistances could only be estimated as no intercept with the x-axis (real impedance) was visible which could be caused by charge accumulation due to oxide formation at the Ta interface, as a similar effect on impedance was observed by Doo et al. [158] with ultralow catalyst loadings in combination with an insulating oxide layer on titanium PTLs. Additionally, the ICR of the PTL increased fourfold (Figure 6.12c), supporting the assumption of the formation of an oxide layer on the surface of the tantalum layer. Although the initial resistance of the PTL was in a range where an average cell performance could be expected, no application-relevant cell performance could be achieved with this coating due to an increased resistance during operation.

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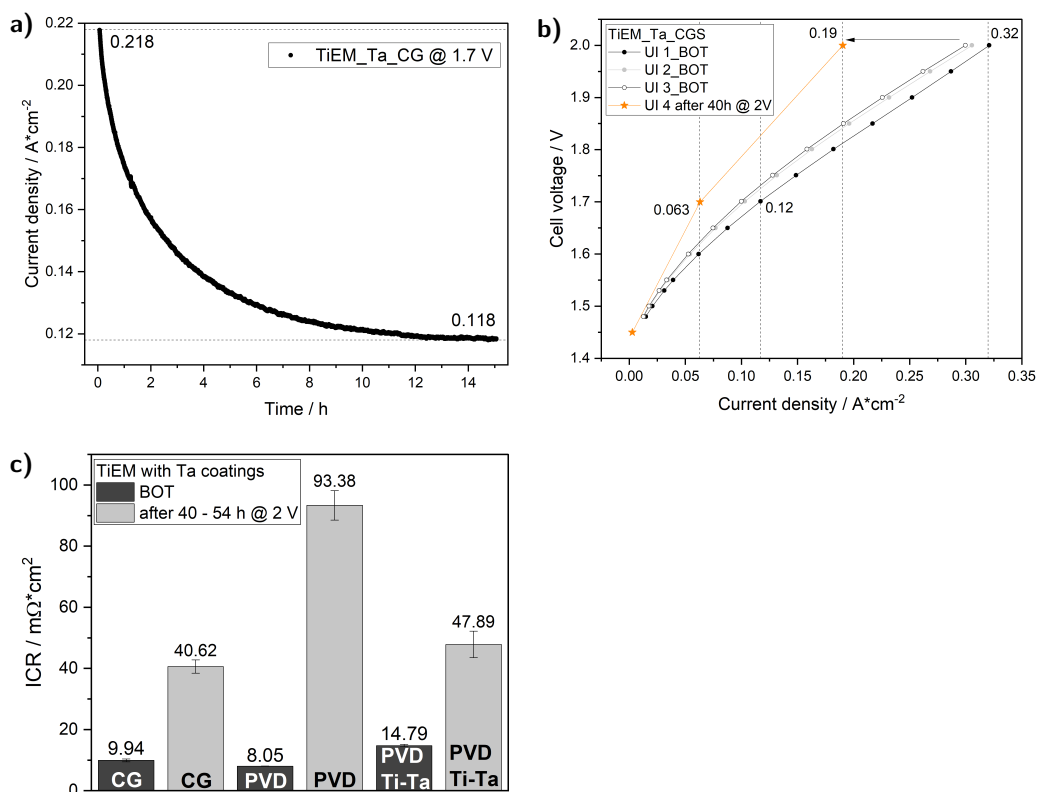


Figure 6.12. a) and b): Results from PEMWE single cell operation with a TiEM with tantalum CGS coating on the CL-facing side and Pt coating on the FF-facing side; a) Current density during conditioning at 1.7 V; b) I-V curves 1-3 after conditioning and 4th I-V curve prior to EIS; c) Resistances of all tantalum coated PTLs under investigation before and after PEMWE operation measured according to section 3.7 at 5.8 bar and RT. ICR values with the CGS coating were obtained after 40 h and ICR values with the PVD coatings after 54 h.

6.6.2. Magnetron sputtered (PVD)

As better results were achieved with PVD coatings than with thermal spraying processes for Nb coatings, magnetron sputtered coatings were also tested for tantalum.

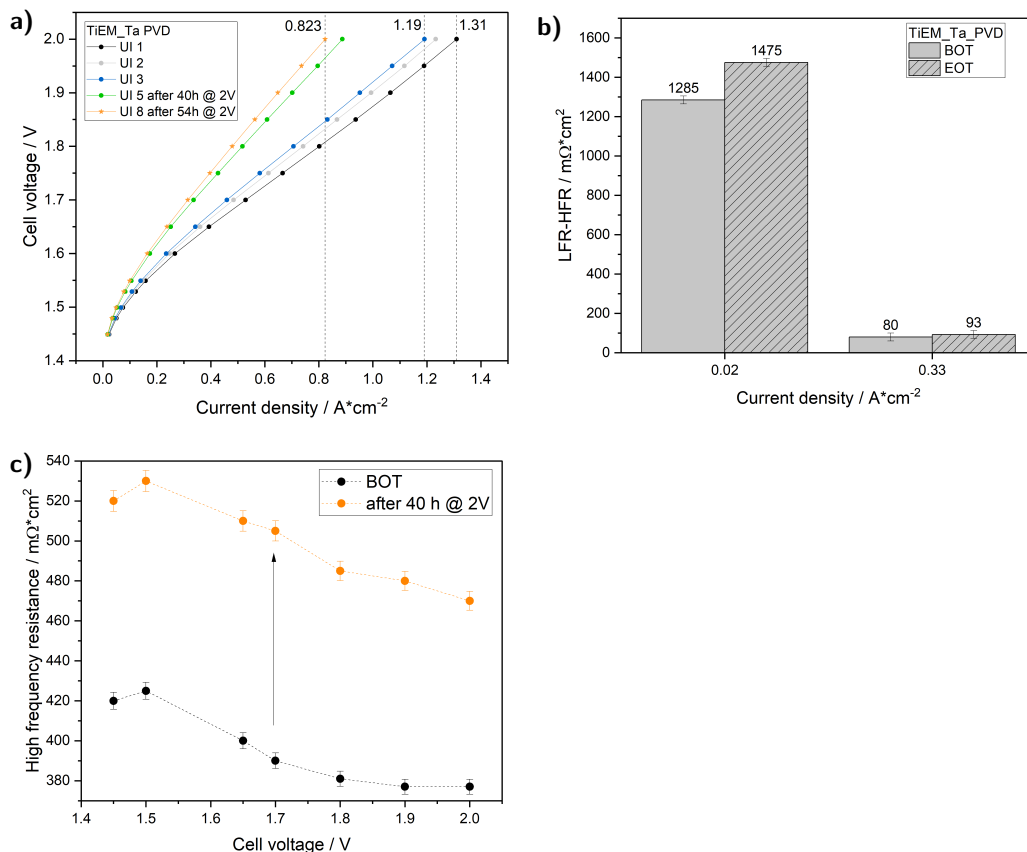


Figure 6.13. Results from PEMWE single cell operation with a TiEM with PVD tantalum coating on the CL-facing side and Pt coating on FF-facing side; a) I-V curves 1-3 after conditioning, 5th I-V curve after 40 h at 2.0 V and 8th I-V curve after 54 h at 2.0 V; b) Difference between low- and high-frequency resistance (LFR-HFR) at 0.2 $A \cdot cm^{-2}$, 0.35 $A \cdot cm^{-2}$ from EIS spectra at the begin of test and after 40 h at 2.0 V; c) HFRs at different cell voltages.

With the tantalum PVD coating at 2.0 V an initial current density of 1.31 $A \cdot cm^{-2}$ was observed, being 1 $A \cdot cm^{-2}$ higher compared to the CGS coating and close to the initial current density reached with a niobium PVD coating on titanium expanded mesh (1.43 $A \cdot cm^{-2}$, see Figure A.20). The reasons for this difference in performance could be differences in contact pressure distribution,

surface morphology, or a combination of both. However, the reasons remain unclear and were not further investigated due to the formation of high resistances leading to a non application-relevant performance. Although there were no visible changes on the PTL surface of TiEM_Ta_PVD (Figure A.25), the current density decreased with this PTL to 0.823 A cm^{-2} at 2.0 V after 54 h of operation at 2.0 V (Figure 6.13a). This decline corresponds to a degradation rate of 9 mA cm^{-2} per hour or 3.48 mV h^{-1} when comparing the cell voltages at 0.8 A cm^{-2} . These degradation rates are far beyond what is accepted according to the targets set by the U.S. Department of Energy (DOE) [174].

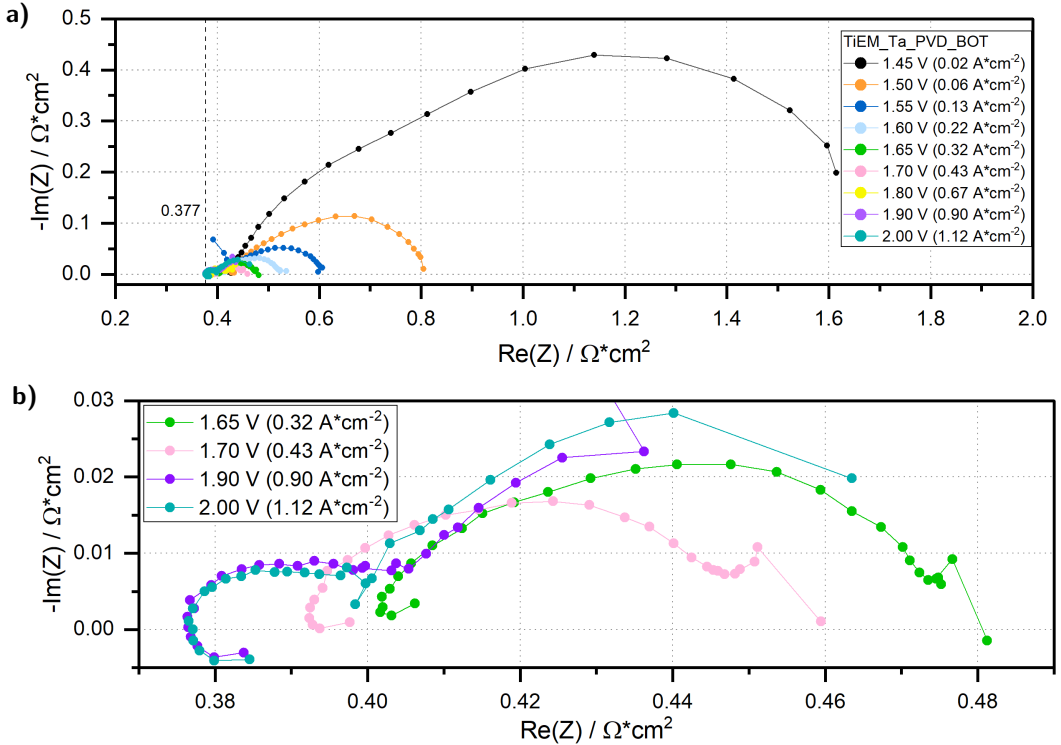


Figure 6.14. Impedance spectra of a PEMWE single cell with a TiEM coated with a Ta PVD layer as anode PTL at the begin of test after conditioning. a) Whole spectra; b) Zoom in the HFR region for selected spectra, for clarity only for spectra at 1.65 V, 1.70 V, 1.90 V and 2.0 V.

Impedance spectra at the begin of test and after 40 h at 2.0 V are displayed in Figure 6.14 and Figure 6.15. A comparison of the spectra reveals that the HFR increased by around $100 \text{ m}\Omega \cdot \text{cm}^2$. Additionally, the ICR of the PTL increased nearly twelvefold after PEMWE operation (Figure 6.12c), supporting that the HFR increase is related to the increased PTL resistance. However, the slope of the I-V curve after 40 h cannot be fully explained by an increase of the HFR. While the slope of the

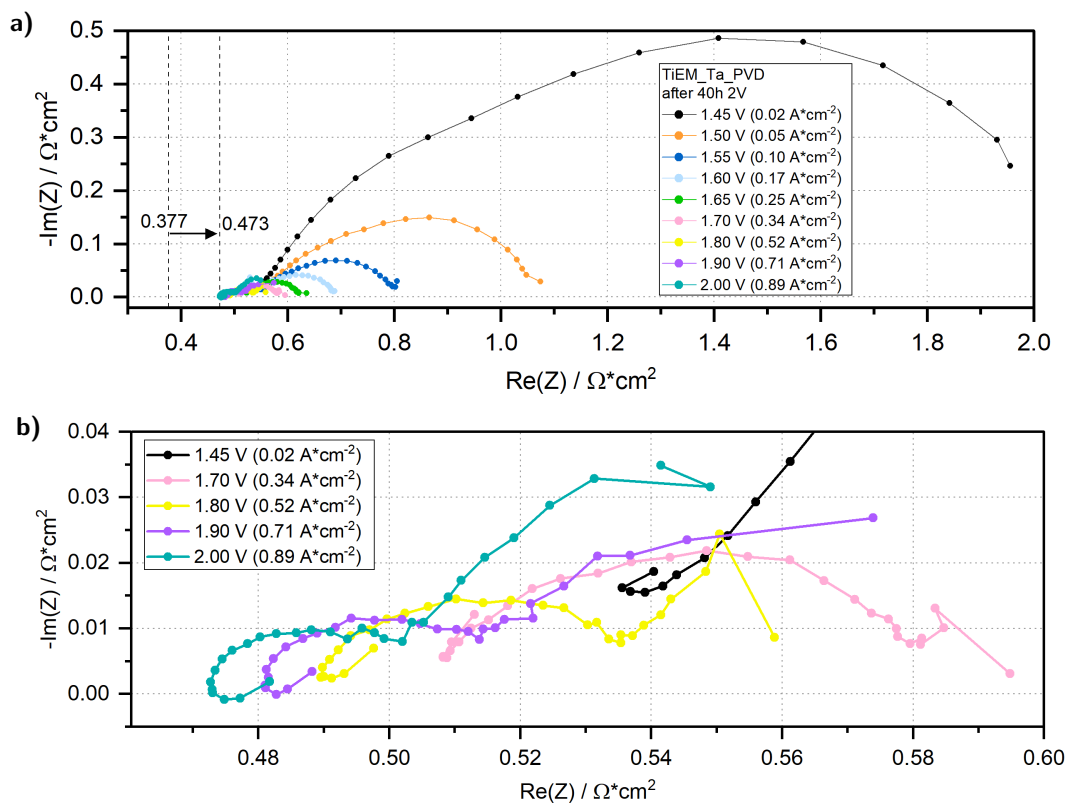


Figure 6.15. Impedance spectra of a PEMWE single cell with a TiEM coated with a Ta PVD layer as anode PTL after 40 h at 2.0 V; a) Whole spectra; b) Zoom in the HFR region for selected spectra, for clarity only for spectra at 1.45 V, 1.70 V, 1.80 V, 1.90 V and 2.0 V.

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I-V curve was $388 \text{ m}\Omega \text{ cm}^2$ within the linear domain between 1.75 V and 2.0 V at the beginning of the experiment, being close to the HFR of $377 \text{ m}\Omega \text{ cm}^2$ within the error range of the HFR determination, the difference between the resistance from the slope of the I-V curve and the HFR after 40 h was more pronounced. After 40 h the slope of the I-V curve between 1.75 V to 2.0 V amounted for $541 \text{ m}\Omega \text{ cm}^2$ while the HFR from impedance spectra was only $473 \text{ m}\Omega \text{ cm}^2$. An additional contribution to the overvoltage by charge transfer is therefore likely, implying that changes on the PTL surface can affect kinetics of the OER. However, this potential effect remains a task for further research as so far in literature only the effect of an increased ohmic resistance due to oxide formation is reported [175]. Figure 6.13b compares the LFR-HFR, also referred to as charge transfer resistances obtained from EIS measurements at 0.02 A cm^{-2} and $0.33 \pm 0.01 \text{ A cm}^{-2}$. For both current densities the CT resistance increased, indicating an increased overvoltage due increased activation energy required for the OER. Furthermore, the noise in the low-frequency range increased with increasing cell voltage, complicating the determination of the low-frequency resistance at and above 1.8 V, where in addition, the formation of a second incomplete semicircle could be discerned. In both spectra, at the begin of test and after 40 h, the HFR shifted towards lower resistances at higher current densities (Figure 6.13c), which is not expected for a stable system without temperature variations where the HFR should be independent of the current density. Kang et al. [120] also observed a shifting HFR with increasing current densities with uncoated titanium PTLs. Their assumption is that at higher current densities, the proton conductivity of the NafionTM phase locally increases due to the development of an uneven heat distribution with local hotspots within the catalyst layer caused by uneven thermal conductivity of the PTL. The thermal conductivity of tantalum is given in the literature to be around $60 \text{ W m}^{-1} \text{ K}^{-1}$ [108], whereas the thermal conductivity of tantalum oxide is reported to be below $1 \text{ W m}^{-1} \text{ K}^{-1}$ [176]. Therefore, it is likely that the oxidation of the coating causes a HFR shift, which is also supported by the observed ICR increase (Figure 6.12c). Also reported in literature is a decreased thermal conductivity of tantalum with increasing oxygen content [176], indicating that HFR shifting can become more evident with progressing oxidation.

As the titanium niobium alloy coatings exhibited a superior stability over pure titanium PTLs and niobium coatings, the stability of Ti-Ta alloy coatings with 6 at.% tantalum were investigated analogous to the alloy coatings with niobium. The results revealed that the alloy coating was much more stable as performance losses after 54 h at 2.0 V (Figure 6.16a) were less pronounced compared to the pure sputtered tantalum coating. The initial maximum current density of 1.6 A cm^{-2} dropped by 40 mA cm^{-2} to 1.56 A cm^{-2} after 54 h of cell operation at 2.0 V. Although the initial ICR of the alloy coating was a bit higher than the pure sputtered tantalum coating, the ICR increase of the alloy coating was significantly less pronounced (Figure 6.12c).

6. Noble metal free anode PTL coatings

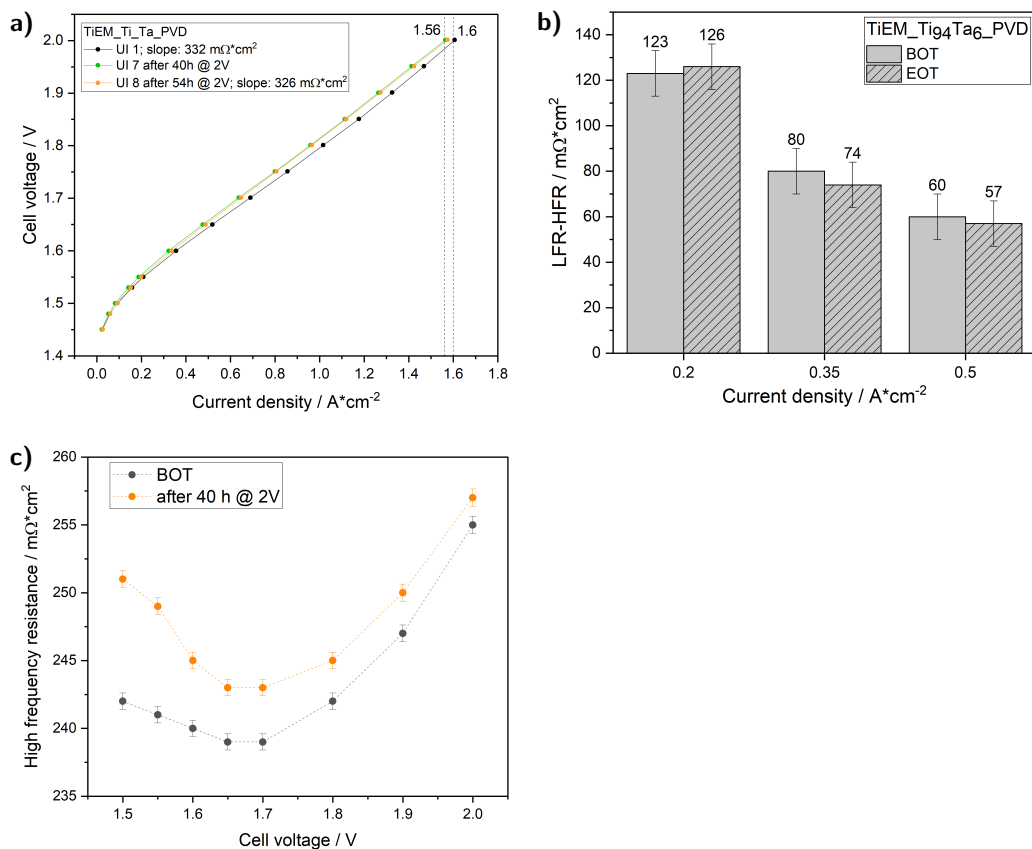


Figure 6.16. Results from PEMWE single cell operation with TiEM_Ti₉₄Ta₆: a) I-V curves after conditioning, 7th I-V curve after 40 h at 2.0 V and 8th I-V curve after 54 h at 2.0 V; b) Charge transfer resistances (LFR-HFR) at 0.02 A cm⁻², 0.33 ± 0.01 A cm⁻² and 0.5 A cm⁻² from EIS spectra at the begin of test and after 40 h at 2.0 V; c) HFRs at different cell voltages.

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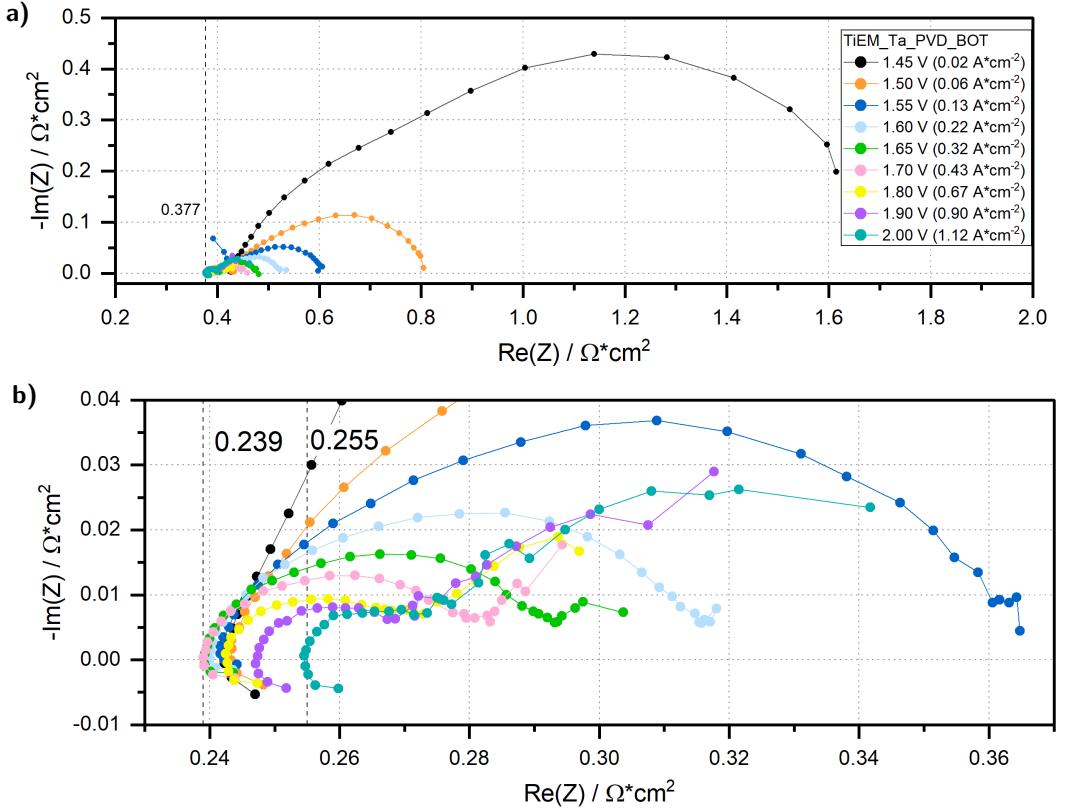


Figure 6.17. Impedance spectra of a PEMWE single cell with TiEM_Ti₉₄Ta₆ at the begin of test after conditioning; a) Whole spectra; b) Zoom in the high frequency region.

As expected from the I-V curves, the HFRs remained almost in the same ranges between 239 mΩ cm² to 255 mΩ cm² after the conditioning step and 243 mΩ cm² to 257 mΩ cm² after 40 h at 2.0 V (Figure 6.17b and Figure 6.18b). Different from the impedance spectra with pure tantalum coatings, the HFR shifted less pronounced and in the opposite direction towards lower resistances with increasing current density (Figure 6.17b and Figure 6.18b). The HFR shift between 1.65 V and 1.7 V and 1.9 V and 2.0 V was around 15 mΩ cm² (BOT) and 12 mΩ cm² (after 40 h), see Figure 6.16c. As the HFR shift was almost the same at the BOT and after 40 h and therefore remained unaffected by cell operation, it can be assumed that the shifting was caused by a systematic effect. Furthermore, it is noticeable that the CT resistances stayed constant (Figure 6.16b), which was not the case with a purely tantalum-coated PTL, indicating that no catalyst inactivation or degradation took place.

As mentioned before, there was also a strong low-frequency noise with the alloy coated PTL, hence the LFRs above 1.65 V could only not be determined. Additionally, the formation of a second

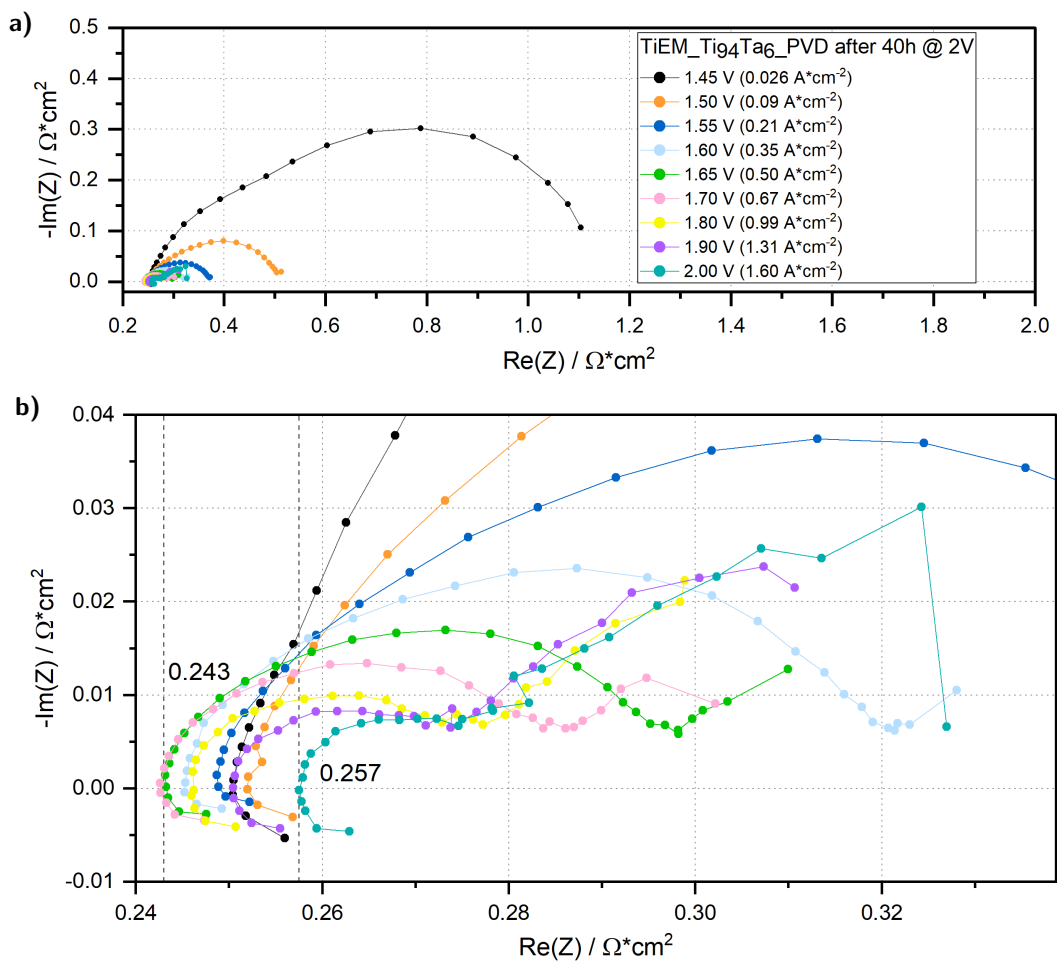


Figure 6.18. Impedance spectra of a PEMWE single cell with TiEM_Ti₉₄Ta₆ after 40 h at 2.0 V; a) Whole spectra; b) Zoom in the high frequency region.

6. Noble metal free anode PTL coatings

incomplete semicircle could be discerned. This noise was already observed at the beginning of the test after conditioning, indicating that the underlying phenomenon was independent from aging. Gas bubbles can accumulate more easily in the large pores of the expanded metal compared to smaller pores of sintered bodies or felt PTLs. Lee et al. [177] report that the bubble growth time in pores of commercial PTLs (pore size not mentioned) is more than 2.88 s and the bubble detachment time is about 11 s, corresponding to frequencies between 350 MHz and 90 MHz that fall in the low-frequency range of impedance spectroscopy, which covers frequencies down to 100 MHz. Nouri-Khorasani et al. [28] found that drag-driven bubbles and buoyancy-driven bubbles remain for 2.5 s and 20 s (400 MHz and 50 MHz) on the catalyst surface. As the detachment of the gas bubbles takes place discontinuously, the criterion of stationarity cannot be fulfilled at low frequencies with relatively longer measurement times compared to high frequencies. The observation that the noise is more pronounced with the alloy coating than with the pure Ta layer is probably only indirectly related to the properties of the coating, as higher current densities could be achieved with the alloy coating, which in turn leads to more gas evolution and consequently more scattering at low frequencies. Although a slight performance decrease was observed after the first 40 h of operation at 2.0 V, the cell performance remained stable thereafter, indicating that similar effects to those observed with Ti-Nb alloys lead to better maintenance of conductivity compared to pure Ti, Nb or Ta coatings. Longer experiments would have to elucidate if this stability can be maintained also over longer time periods.

6.7. Summary noble metal free anode PTL coatings

Table 6.2 provides an overview of the begin of test performance and after 15 h, 40 h or 144 h of operation with all tested noble free coating materials. The samples are sorted according to their appearance in the work. The coating techniques, conducted by IMD-2 [151], involved PVD, thermal nitration, APS, VPS and CGS.

Table 6.2. Current densities at the begin of test and after operation at 1.5 V, 1.7 V or 2.0 V with all noble metal free coated PTLs.

Sample	Current density BOT at 2.0 V ¹ after conditioning / A cm ⁻²	Current density after operation at 2.0 V ¹ , time indicated in brackets / A cm ⁻²	Related section
TiF_TiN_PVD_1 ²	1.0 (@ 1.7 V)	< 0.01 (15h @ 1.7 V)	6.1
TiEM_TiN_TN ²	0.12 (@ 1.5 V)	0.08 (15h @ 1.5 V)	6.1
TiEM_W_APS ²	0.01 (@ 1.7 V)	< 0.01 (15h @ 1.7 V)	6.2
TiEM_W_VPS ²	0.75 (@ 1.7 V)	0.36 (15h @ 1.7 V)	6.2
TiEM_ITO_PVD	1.67	1.21 (40h)	6.3
TiEM_Nb_CGS	1.02	0.80 (40h)	6.4.1
TiS_Nb_APS	0.74	0.52 (40h)	6.4.2
TiEM_Nb_PVD	1.28	0.73 (40h)	6.4.3
316LEM_Nb_PVD	1.17	0.66 (40h)	6.4.3
TiF_Ti ₉₇ Nb ₃	1.80	1.67 (144h)	6.5
TiEM_Ti ₉₇ Nb ₃	1.75	1.60 (144h)	6.5
TiEM_Ti_PVD_1	1.90	1.80 (144h)	6.5
TiEM_Ti_PVD_2	1.70	1.50 (144h)	6.5
TiF_Ti ₉₄ Nb ₆ _1	2.07	2.04 (144h)	6.5
TiF_Ti ₉₄ Nb ₆ _2	1.63	1.44 (144h)	6.5
TiEM_Ti ₉₄ Nb ₆	1.69	1.66 (144h)	6.5
TiF_Ti ₇₂ Nb ₂₈	1.73	1.35 (144h)	6.5
TiEM_Ti ₇₂ Nb ₂₈	1.47	0.98 (144h)	6.5
TiEM-Ta_CGS	0.32	0.19 (40h)	6.6.1
TiEM-Ta_PVD	1.31	0.87 (40h)	6.6.2
TiEM-Ti-Ta_PVD	1.60	1.56 (144h)	6.6.2

1: lower cell voltages are noted in brackets, 2: Without conditioning.

Although PTLs with TiN (PVD), W (VPS) and Nb (PVD and CGS) coatings exhibited sufficiently low resistances ranging from $<1 \text{ m}\Omega \text{ cm}^2$ to $10 \text{ m}\Omega \text{ cm}^2$ prior to PEMWE operation, all materials were subject to oxidation during PEMWE operation, leading to an increase of the contact resistance between PTL and anode CL and decreasing cell performance. With ITO, the ICR increase was moderate (Figure 6.5b), but nevertheless the cell performance decreased significantly (Figure 6.5a), which could be attributed to an increasing charge transfer overvoltage visible from Nyquist plots (Figure 6.5c). It can therefore be assumed that the aging pathway with ITO was different from all other coatings, as presumably leaching of indium or tin lead to inactivation of the catalyst, increasing the overvoltage. Consequently, the ex-situ measured contact resistance of a PTL can provide an indication of the cell performance, but can not predict it, as other effects such as dissolution of coating components and catalyst inactivation can contribute to performance loss. APS coatings (W and Nb) lead to higher overvoltages from the begin of test, due to oxidation during the coating process, thereby rendering APS unsuitable as a process for PTL coatings.

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Solely PVD alloy coatings with the composition $\text{Ti}_{94}\text{Nb}_6$ and $\text{Ti}_{94}\text{Ta}_6$ enabled stable PEMWE operation compared to pure Nb and pure Ta PVD coatings as well as uncoated titanium PTLs, tested for maximum 144 h to 672.5 h at 2.0 V. The initial current density at 2.0 V with $\text{TiF_Ti}_{94}\text{Nb}_6$ of 2.07 A cm^{-2} stayed at 2.04 A cm^{-2} after 144 h, proving an improved stability over pure Nb coatings or uncoated Ti PTLs, where the HFR increased significantly. However, comparable cell performance to noble metal coatings could not be achieved and the performance with these alloy coatings was not yet reproducible, as the initial current density with a second Ti felt PTL coated with 94 at.% Ti and 6 at.% Nb decreased from BOT to the EOT from 1.625 A cm^{-2} to 1.44 A cm^{-2} . One reason for a lack of reproducibility could be that the composition of the coating surface was different between the two samples. XPS spectra revealed that there was little to no Nb present on the surface of $\text{Ti}_{94}\text{Nb}_6$ coatings. These findings additionally explain why the performance with Ti PTLs with pure Ti PVD coatings were in the same range as with the mixed coatings. Deposition of more homogeneous mixed coatings could be achieved with pre-alloyed targets. A homogeneous distribution of Nb in Ti is important as the alloy coating, like a pure titanium surface, oxidizes during operation. In contrast to pure titanium oxide, it is assumed that the presence of higher-valent niobium atoms, which act as donor sites, maintain the electrical conductivity of the mixed oxide.

In summary, it can be concluded that among non-precious metal coating materials, alloy coatings are the most promising class to date due to the introduction of donor atoms and should be the subject of future research.

Furthermore, a significantly better performance could be achieved in the future with an additional thin Pt contact layer of 1 nm to 2 nm on top of the alloy coating. In the event of defects in the Pt coating, the conductivity of the PTL surface could be maintained by the underlying alloy coating, thereby significantly reducing the use of Pt.

6.8. Investigations of the pH and potential at the PTL/CL interface

In the previous subchapters, it was shown that materials, that were considered to be promising coating materials according to the literature after corrosion testing under simulated PEMWE conditions, were not stable and conductive enough in PEMWE operation. For example, tungsten was reported to be stable at pH 5.5, but oxidized during PEMWE operation within a few hours. Based on these results, it can be assumed that the pH value for stability testing of PEMWE coatings in a corrosion cell should be below 5.5. Furthermore, it is conceivable that it is not possible to realize a suitable proton activity of the electrolyte under simulated conditions due to the different local mobilities and activities of sulfonic acid groups bound to the polymer backbone with limited mobility in the PEM and an electrolyte with a dissociate acid. Besides, studies comparing ex-situ corrosion tests and PEMWE experiments have earlier on raised doubts about the comparability of the two setups [66, 86].

Therefore, the last section of this chapter deals complementary with the question of whether it is possible to experimentally approach the conditions to which the PTL coating is exposed and to what extent corrosion cell experiment can simulate PEMWE. As described in 2.3.1, the electrochemical potential stemming from overpotential for the OER at the catalyst layer and the pH value are particularly important parameters. To simulate the conditions at the PTL/CL interface for testing PTL materials, often electrochemical stability tests in a three-electrode setup (corrosion cell as described in section 3.11) are used with H_2SO_4 solutions as electrolyte. In some studies, fluoride and/or chloride ions are added to simulate fluorine emission from the MEA and potential chloride emission from the catalyst layers.

For comparative experiments between the two setups PEMWE and corrosion cell, titanium nitride was chosen as a model coating, as the oxidation of the nitride progresses comparatively quick (c.f. Figure 6.1). Hence the formation of an analyzable oxide scale was assumed to be possible within a few hours. Furthermore, upon transition from nitride to oxide, the volume increases by a factor of approximately three [161], resulting in a more pronounced structural change compared to oxidation of a titanium surface. TiN coated TiF PTLs were prepared by IMD-2 by means of reactive sputtering (PVD, see 3.2.1). As the corrosion cell setup requires a dense sample (WE) to prevent electrolyte leakage, TiN was coated on titanium sheets in the same manner as the PTLs. Furthermore, a potential window between 1.4 V to 1.6 V was considered to be relevant for the corrosion stability of PTL coatings (see 2.3.1). Therefore, these two “limit potentials” were used for CA experiments with the corrosion cell. For PEMWE cell tests, a lower cell voltage limit of 1.5 V was chosen, as during prolonged operation at lower voltages a higher hydrogen permeation rate is to be expected and an upper limit of 2.0 V cell voltage was chosen, as this potential limit was also chosen for

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other experiments within this work. Both types of experiments were carried out at 80 °C. Although heat production by the OER is higher at 2.0 V than at 1.5 V due to an increased reaction rate, it was already observed in section 6.1 that with TiN coated anode PTLs the current density dropped below 0.15 A cm^{-2} after 1 h, leading to the assumption that local temperature differences between the two cell voltages are negligible and therefore have a minor influence on the oxidation of the nitride. The electrolyte in the corrosion cell was gassed with O_2 and the experimental procedure for corrosion cell testing is given in section 3.11. Experiments were conducted for 15 min, 1 h, and 6 h to investigate whether oxidation progresses similarly in both setups. Prior to and between PEMWE single cell tests with TiN-coated TiF PTLs, reference measurements were performed with TiF_Pt PTLs consisting of the heat-up and conditioning step described in subsection 3.1.4 as well as one I-V curve to determine the state of health of the MEA. If a MEA showed a drop in performance, it was discarded. On average three oxidation experiments with different TiF_TiN PTLs were carried out with each MEA. I-V curves from the reference measurements are displayed in Figure A.27.

Due to the expected increase in volume from nitride to oxide, it was initially planned to analyze and compare cross sections of all samples. However, this proved challenging due to the coating peeling off during cutting or embedding.

However, post mortem examination of the samples already revealed changes to the surfaces. Figure 6.20 shows photographs of the samples from the corrosion cell (a) and the PTLs (b) and Figure 6.19 results from EDX point measurements of the sample surface. Due to the design of the corrosion cell, only a circular section of the sample is in contact with the electrolyte and becomes polarized, hence the changes are only visible in this area of the photographs. The peripheral area around the circular oxidized area corresponds to the pristine TiN coating.

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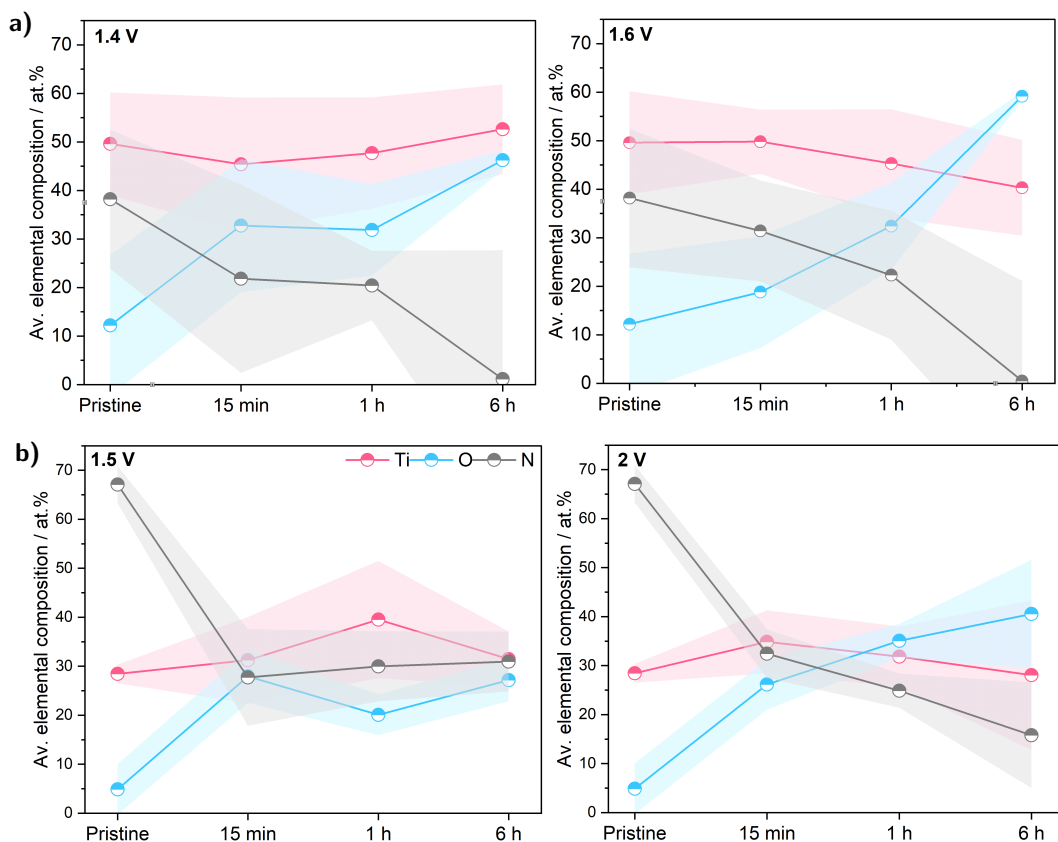


Figure 6.19. Average elemental composition from top view EDX spectra of TiN coated samples in dependence on the duration of polarization: a) Ti sheets coated with TiN (PVD) polarized in a corrosion cell at 1.4 V and 1.6 V vs. RHE; b) TiF_TiN (PVD) anode PTLs polarized in a PEMWE cell at 1.5 V and 2.0 V.

6. Noble metal free anode PTL coatings

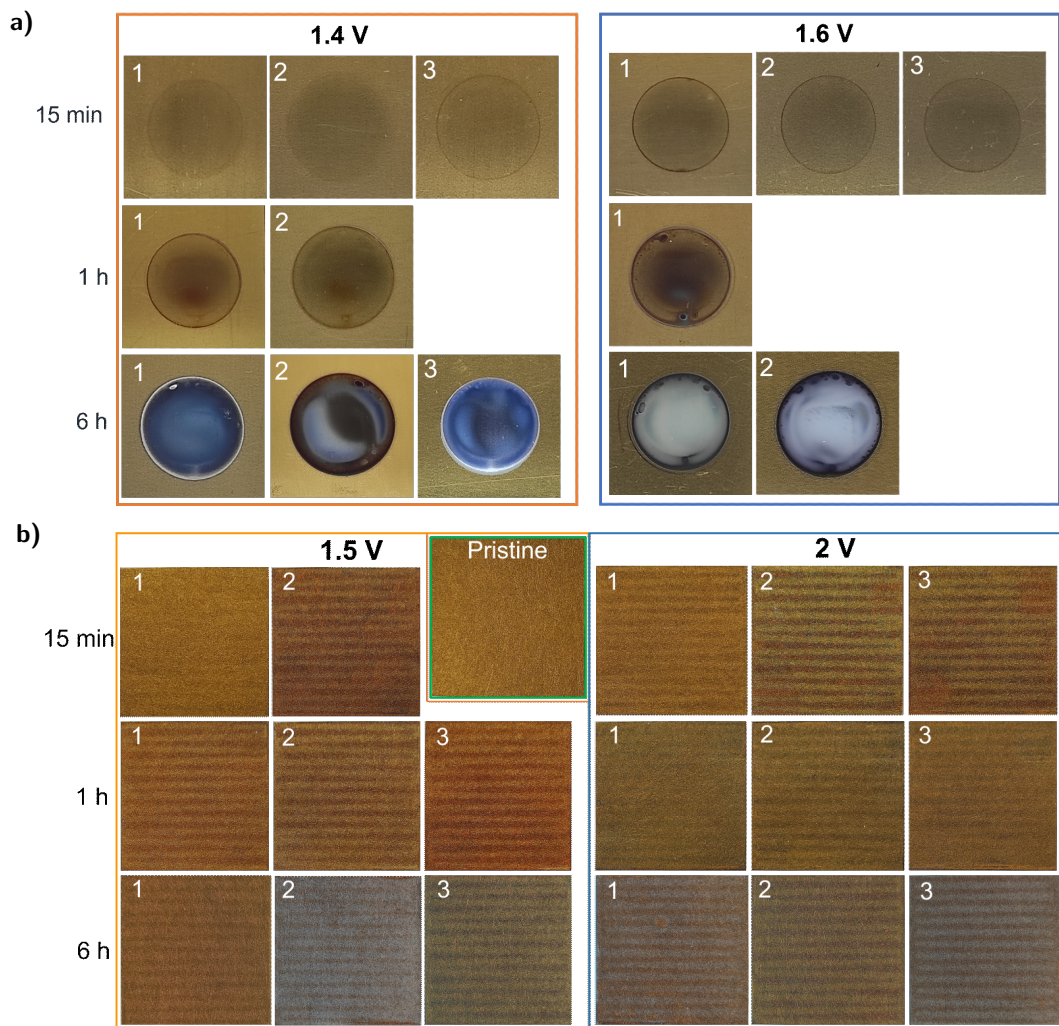


Figure 6.20. Photographs of a) TiN coated Ti sheets after polarization in the corrosion cell for 15 min, 1 h and 6 h at 1.4 V vs. RHE (left) and 1.6 V vs. RHE (right), where only the circular areas in the center of the sample were in contact with the electrolyte and became oxidized; b) TiN coated TiF PTLs after PEMWE operation for 15 min, 1 h and 6 h at 1.5 V (left) and 2.0 V cell voltage (right).

6. Noble metal free anode PTL coatings

Results from EDX measurements (Figure 6.19) as well as the color change of the samples after polarization (Figure 6.20) indicate that oxidation proceeded completely to TiO_2 after 6 h polarization in the corrosion cell, regardless of the potential (Figure 6.19a and Figure 6.20a), while a titanium oxynitride phase was still present on the PTL. Accordingly, the conditions simulated in the corrosion cell tended to be stronger oxidizing than in the PEMWE cell. Although the nitrogen content of the coatings in the corrosion cell dropped to almost zero during oxidation at both potentials, the oxygen content tended to be slightly higher after polarization at 1.6 V. Scattering of element analyses using EDX was significantly higher with the samples from the corrosion cell, which is also reflected by the photos shown in Figure 6.20, where especially after 6 h the oxide scales were not grown uniformly. Within the first 15 min of PEMWE operation, the increase in oxygen content and decrease in nitrogen content were similar at 1.5 V and 2.0 V (Figure 6.19). However, the further progression differed. While at 1.5 V, the oxygen and nitrogen content remained almost constant after 1 h and 6 h compared to the concentrations after 15 min, at 2.0 V the nitrogen content continued to decrease and the oxygen content continued to increase. Consequently, it is conceivable that the overvoltage at the PTL surface was lower at 1.5 V cell voltage and that an initially forming oxide layer protected the nitride from further oxidation. Furthermore, these observations imply, that the cell voltage has an influence on the stability of the PTL coating and that the PTL is exposed to a greater driving force for oxidation at higher cell voltages. This is also supported by the photographs shown in Figure 6.20b, where the characteristic golden color of the nitride diminished significantly at higher voltages and with increasing test duration. Additionally, a more pronounced decrease in current density was observed with increasing potential and longer polarization time. After 15 min at 1.5 V, the current density dropped by around 20 % and by around 50 % at 2.0 V. After 6 h the decline amounted for 70 % and 90 % (see Figure A.28). In contrast, the current drop during the corrosion cell experiment was over 90 %, regardless of the potential and time (Figure A.29). Although the currents from the PEMWE experiments and the currents measured from the corrosion cell are not comparable due to the different contributions of OER and oxidation, it can be assumed that oxidation had progressed so far at the end of the corrosion cell experiments that either the nitride layer was completely oxidized or a similar thick oxide layer had formed on each sample, preventing further oxidation into deeper coating layers. However, due to the color differences (see Figure 6.20), indicating different oxide thicknesses, the latter is less likely.

Inhomogeneity of the oxidation on the PTL was primarily caused by the meander flow field, which was particularly evident in the samples polarized for 6 h. The channel areas (gray areas) showed a higher degree of oxidation. On the one hand, it is possible that local overvoltages differed between experiments due to MEA aging (Figure A.27), resulting in the variance of oxidation patterns and degrees of oxidation despite formally identical experiments. On the other hand, it is conceivable that, although the TiN coatings were deposited in the same run, locally minor differences in the surface structure were present among the samples. Furthermore, the results are influenced by the

6. Noble metal free anode PTL coatings

contact pressure distribution, which also might be slightly different with different PTLs. Furthermore, the higher degree of oxidation in channel areas reveals that not contact with the MEA alone drives oxidation, but rather OER overvoltage. Also the coatings that were polarized in the corrosion cell did not oxidize homogeneously. While the white color after polarization 6 h at 1.6 V is an indication of TiO_2 , the blue color after polarization at 1.6 V is an indication of Ti_2O_3 [137]. However, clear changes on the surface from pristine over 15 min, 1 h and 6 h were visible. In EIS spectra acquired at OCP, evolving semicircles could be observed, where in the Nyquist plots the diameters increased with increasing polarization time and from Bode plots, a shift of the maximum phase angle to higher frequencies could be observed with increasing reaction time, as described by Kellenberger et al. [99] for oxidizing Nb coatings. Consequently, EIS spectra also reflected the progressive oxidation of the nitride layer. In accordance, water analyses of the electrolyte (ICP-MS) revealed increasing titanium dissolution with increasing polarization time. A dependency of the potential on the amount of Ti dissolution was not observed. In contrast, water analyses from PEMWE experiments did not find increased titanium dissolution, representing another difference between the results of the two experimental setups.

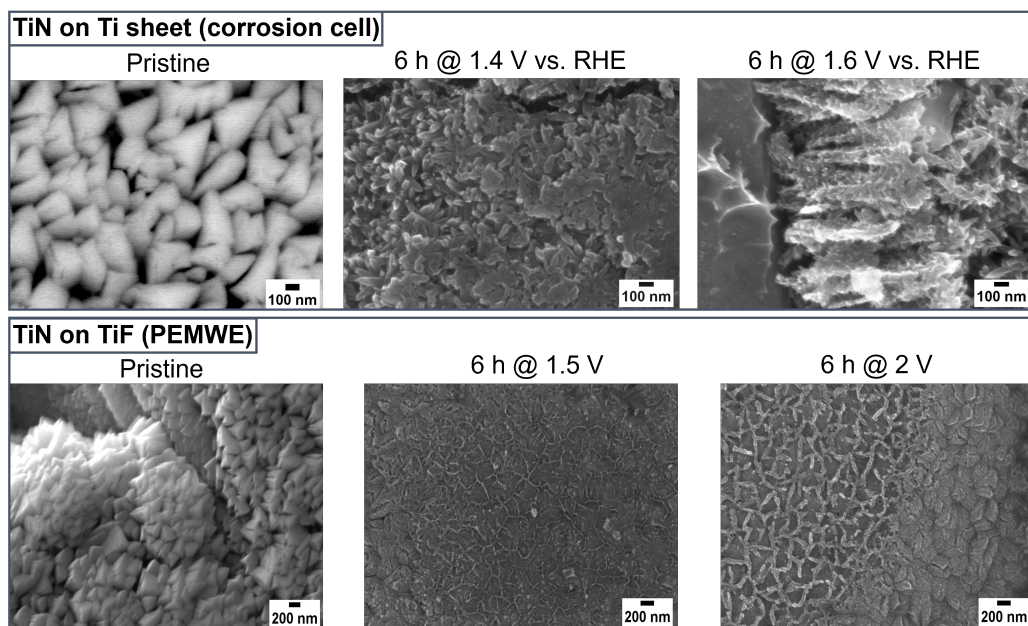


Figure 6.21. SEM top view pictures of TiN coated Ti sheets pristine, after polarization in the corrosion cell for 6 h at 1.4 V vs. RHE and 1.6 V vs. RHE in 0.045 M H_2SO_4 (pH 1.16 ± 0.01 at RT) and TiN coated TiF PTLs after PEMWE operation for 6 h at 1.5 V and 2.0 V cell voltage.

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Apart from the photographs, where surface changes on a macroscopic scale are visible, SEM images reveal changes on a microscopic scale. After both experiments, a structural change from crystalline to a more amorphous structure of the coating was observed, see Figure 6.21.

Summarized, the fast proceeding oxidation of TiN coatings on anode PTLs was successfully used to compare the transferability of corrosion studies in a three electrode setup and liquid electrolyte to the oxidation behavior of the same material as anode PTL coating in PEMWE. Post mortem analyses revealed that the degree of oxidation of the coatings polarized in the corrosion cell was more advanced compared to the coatings on the MEA-facing side of PTLs, as they fully oxidized after 6 h, whereas on the PTL surface nitrogen was still present. Consequently, the conditions set in the corrosion cell (0.045 M H₂SO₄, corresponding to pH 1.16 ± 0.01 at RT) and potentials of 1.4 V and 1.6 V vs. RHE lead to a higher oxidation rate. Furthermore, as the liquid electrolyte in the corrosion cell can penetrate into the pores of the coating and the oxide phase that forms, and thus accelerate the oxidation processes, it remains questionable whether it is at all possible to reproduce the conditions at the PTL/CL interface with a three-electrode setup and acidic electrolyte. Consequently, in addition to the possibility that the potential was chosen too high and/or the electrolyte too acidic, it is possible that the set of the test parameters in the corrosion cell that simulate the oxidation behavior of PTL coatings during PEMWE operation is difficult to identify due to different proton activities of the PEM and the liquid electrolyte with dissociated acid. In any case, further extensive testing of pH and potential combinations would be required to further assess the potential and pH at the PTL/CL interface.

An additional finding from PEMWE operation was that the oxygen content increased by around 15 % more and the nitrogen content decreased by around 10 % more when operating at 2.0 V compared to operating at 1.5 V, supporting that the PTL surface is influenced by the cell voltage and, secondly, that stability tests for PTLs at a high cell voltage of 2.0 V are appropriate.

7. Titanium-reduced and stainless steel-based anode PTLs

In addition to the approach pursued in the previous chapters of reducing the material costs of anode PTLs by replacing the precious metal coating by noble metal free coating materials, a second approach to reduce investment costs discussed in the literature (subsection 2.3.2) involves replacing the base material titanium with less expensive raw materials such as stainless steel.

As stainless steel corrodes quickly in contact with the anode catalyst layer [178], protection against anodic polarization and the acidic NafionTM environment must be realized by a sufficiently thick corrosion protection layer. However, the question remains if the bulk of the PTL is exposed to an acidic environment and whether stainless steel corrosion could be initiated by the water flowing through the cell, also in areas without contact to the anode CL. As the sulfonic acid groups in NafionTM are bound to the polymer backbone and the protons produced during water splitting do not pass into the water due to the concentration gradient across the cell moving them to the cathode side, it can be assumed that the water flowing through the cell on the anode side has a neutral to slightly acidic pH. As mentioned in 2.3.1, Langemann [8] observed a drop in pH from 5.6 to 4.5 and 3.5 on the cathode and anode side after 50 h with a PEMWE single cell setup similar to one used within this work. By analyzing chloride in the effluent water using ion chromatography (IC), he was able to show that the drop in pH was caused by hydrochloric acid contaminants from the catalyst layers, presumably stemming from the synthesis of the platinum catalyst. As impurities in raw materials are subject to fluctuations, the pH of the anode and cathode water was examined in the course of this work and the results briefly discussed in the following.

A series of experiments was carried out where the pH of samples from the circulating water of the anode and cathode sides from different cells with NafionTM 117 and NafionTM 212 membranes were measured while operated without load and at cell voltages of 1.5 V and 2.0 V. A description of the pH measurement is given in section 3.10. No decrease in pH was observed, regardless of the operating point of the cell. The pH of the effluent water was 5.6 ± 0.4 and thus within the measurement uncertainty at the same level as the pH value of the water from the storage tanks, where the pH amounted for 5.7 ± 0.4 . The pH lies a bit below 7, as the water is at equilibrium with the surrounding air and thus saturated with CO₂. It might be that no impurities were present in the catalyst that would have led to a lowering of the pH value.

Furthermore, these results support the assumption that the NafionTM phase and membrane are acidic, but that the protons stay in the vicinity of the sulfonic acid groups and thus do not influence the pH of the circulating water. If protons would be released into the circulating water, in addition counter

7. Titanium-reduced and stainless steel-based anode PTLs

anions would have to be released from the polymer. Possible is, that fluoride ions are dissolved out of the MEA, a process that depends on the temperature [179] and the mode of operation [54]. When Fouda-Onana et al. [53] investigated the release of fluoride ions, they found fluoride only at the cathode side, as peroxide formation and the formation of radicals preferably take place at the cathode. Therefore, the water from PEMWE cell tests was additionally tested for fluoride and chloride ions using IC as part of this work, but neither of the two anions could be detected. It can therefore be assumed that the catalyst materials used in this work did not contain the same level of impurities as found by Langemann [8]. However, it must be noted that a direct comparison is not possible, as within Langemann's study, no ion exchange resins were used, leading to an accumulation of impurities in the system.

Nevertheless, from the experiments elucidating the pH value of the anode and cathode effluent water, it can be concluded that the part of the PTL that is not in contact with the Nafion™ phase is only exposed to a neutral, tending slightly acidic, but not strongly acidic environment. Consequently, for investigations about bipolar plates or the base material of anode PTLs, which are not in contact with the catalyst layer, an exposure of pH 5.5 can be assumed. However, the pH is not the only factor influencing the stability of 316L. As water with a conductivity of less than $1 \mu\text{S cm}^{-1}$ is used for PEMWE, the oxide layer of stainless steel might become destabilized due to the low concentration of dissolved ions in ultrapure water [180]. On the other hand, evolving oxygen from water splitting stabilizes the oxide layer. Whether and which effect has a stronger influence on the stability of 316L in PEMWE has not been investigated yet.

Therefore, this chapter investigates two different types of 316L stainless steel based PTLs: Expanded meshes (316LEM) with a geometry similar to the titanium meshes (TiEM) used in the previous chapters, both provided by Bender GmbH, and a stainless steel felt supported on a coarser expanded metal (SMF) provided by GKN Sinter Metals (specification and details see Table 3.2). Both PTLs are produced of 316L stainless steel, also referred to as AISI 316 or 1.4404, as this type of stainless steel is one of the most corrosion resistant ones [68]. As the PTLs are provided by different suppliers, the first subchapter will discuss the elemental composition of the PTLs. Thereafter, the following results are discussed from PEMWE single cell testing with:

- 316LEM and SMF coated with platinum (PVD) and galvanically platinized to investigate the influence of corrosion products on the performance and impedance spectra with coatings $<1 \mu\text{m}$.
- 316LEM and SMF coated with titanium (PVD) and platinum (PVD) to investigate the ability of a thin Ti coating with a thickness of $3.80 \pm 0.08 \mu\text{m}$ to protect against corrosion.
- 316LEM coated with titanium by CGS and platinum (PVD) to investigate the ability of thicker Ti coatings $>10 \mu\text{m}$ to protect against corrosion.

7.1. Elemental composition of 316L expanded mesh and felt

The mass fractions of the expanded mesh and felt of Fe, Mn, Cr, Mo, Ni, Si and P were determined via inductively coupled plasma optical emission spectroscopy (ICP-OES, section 3.9) and the fractions of C, S and N via a combustion process. The results are presented in Figure 7.1. While the shares of C, S, N, Fe, Si, Cr, Ni and P are in the same range, fractions of Mn and Mo are slightly different. The Mn content is 0.87 wt% higher in the mesh and the Mo content 0.37 wt% higher in the felt. In addition, the Mo content of the mesh (1.93 wt%) is slightly below the range specified for stainless steel 316L (2 - 2.5 wt%) [181]. While Mo increases the corrosion stability of 316L, the formation of manganese sulfide promotes pitting corrosion [182]. Consequently the corrosion stability of both PTL substrates might deviate due to their composition.

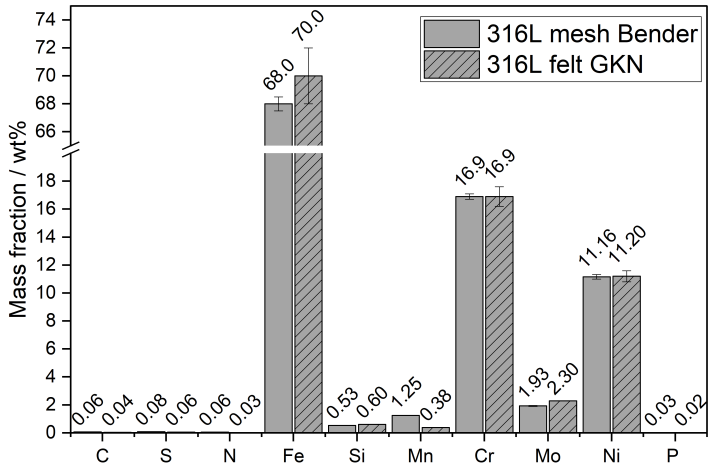


Figure 7.1. Mass fractions of C, S, N, Fe, Si, Mn, Cr, Mo, Ni and P of the two investigated 316L substrates, mesh and a stainless steel felt.

7.2. PVD and galvanic platinum coating

As demonstrated by Mo et al. [178], pure stainless steel PTLs are subject to rapid corrosion, rendering electrolysis impossible. However, before corrosion protection of coatings will be investigated within the next chapters, the influence of stainless steel corrosion on cell performance and impedance spectra needs to be investigated. For this purpose, a first experiment consisted of a cell with an uncoated 316L expanded metal. Without any coating, corrosion progressed rapidly as expected and it was not possible to record I-V curves or impedance spectra. Hence, further experiments were carried out with Pt coatings on the same type of expanded metal and 316L felt, as the Pt layer was intended to provide sufficient corrosion protection to slow down corrosion processes to such an extent that electrolysis would be possible long enough to record one I-V curve and one impedance spectrum. Results with Pt coated 316L expanded meshes will be discussed first, followed by results with Pt coated 316L felts.

7.2.1. 316L expanded metals

Pt coatings on 316L expanded metals were deposited using two techniques: physical vapor deposition (PVD at IET-4 for samples #1 and #2 and PVD by an external coating company with additional steps for surface cleaning of sample #3, see 3.2.1) and the second technique was electrodeposition by Precors GmbH. 316L felt PTLs were only coated by means of PVD. While the PVD coatings amounted for around 40 nm (3.2.1), electrodeposited layers were much thicker with 450 ± 98 nm.

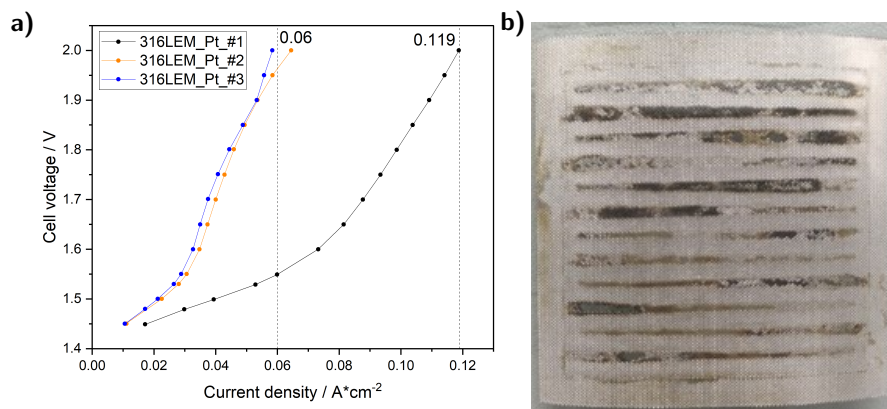


Figure 7.2. a) I-V curves of three PEMWE single cells with 316L Pt coated mesh PTLs after conditioning; b) Sample #1 after electrolysis operation with visible pitting corrosion.

With Pt coated 316L expanded meshes, corrosion was slowed down compared to uncoated meshes as intended, but electrolysis operation was, as expected, also only possible for a short time. Pitting

7. Titanium-reduced and stainless steel-based anode PTLs

corrosion was observed after conditioning, recording of one I-V curve and one impedance spectrum at 400 mA. An image of the corroded expanded mesh is given in Figure 7.2b. Figure 7.2a shows strongly distorted I-V curves, two of them with a beginning S-shape as described by Padgett et al. [124] in presence of cation impurities at cell voltages beyond 2.0 V. After the I-V curve, one impedance spectrum was recorded galvanostatically at 400 mA, corresponding to 22.7 mA cm^{-2} , to keep the rate of corrosion, and in consequence the change of the system during EIS, as low as possible.

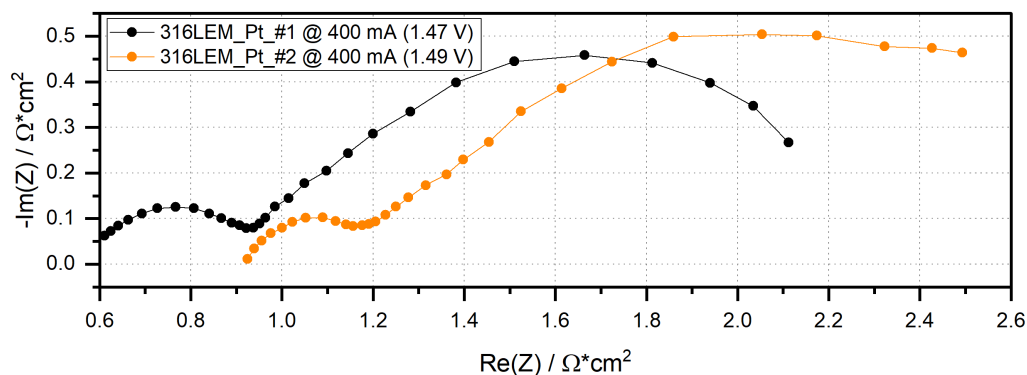


Figure 7.3. EIS spectra at 400 mA (22.7 mA cm^{-2}) of two PEMWE single cells with samples 316LEM_Pt_#1 and 316LEM_Pt_#2.

EIS spectra show two distinct semicircles in the Nyquist plot (Figure 7.3), either due to strongly inhibited kinetics or processes taking place along an additional phase boundary. The EIS spectrum with sample #3 is not shown, as the resistances were higher compared to the first two samples. Furthermore, no difference could be observed between a PVD coating with and without an additional cleaning step of the substrate surface on the basis of the I-V curves (see Figure 7.2a sample #1 and #2 vs. sample #3). The fact that the EIS spectra with the samples #1 and #2 and #3 differ greatly could be due to the rapid degradation of the stainless steel PTLs, complicating reproducible measurements. With the meshes coated by electrodeposition, no I-V curves could be recorded because the current densities were below those shown in Figure 7.2a. With corroding expanded meshes, clear influences on the cell resistance and kinetics could be observed which will help to evaluate new 316L based PTLs with regards to their corrosion stability. A brief summary of the observed influences is given at the end of this subchapter (see page 117).

7.2.2. 316L felts

In addition to 316L expanded meshes, 316L felts on 316L expanded meshes (SMF) from GKN were Pt coated by PVD (37.5 ± 0.2 nm) to investigate whether with 316L felt PTLs, similar to Ti felt PTLs, similarly higher current densities can be achieved compared to expanded metals.

Two felts with an average fiber diameter of $8\text{ }\mu\text{m}$ (SMF8_Pt_1 and SMF8_Pt_2) and one with an average fibre diameter of $22\text{ }\mu\text{m}$ were tested in PEMWE single cells. Results with the PTL with an average fiber diameter of $22\text{ }\mu\text{m}$ (SMF22) are not included in the following, as they were analogous to the results obtained with SMF8_Pt_1 and SMF8_Pt_2. The sample SMF8_Pt_1 was only coated with Pt on the top side facing the MEA and SMF8_Pt_2 with Pt on the MEA- and FF-facing sides. While the protocol for sample SMF8_Pt_1 consisted of static operation for 525 h, SMF8_Pt_2 was subject to dynamic operation with the wind profile discussed in chapter 8 and a total operation time of 1393 h. Furthermore, the cell operated with SMF8_Pt_1 was disassembled after one day to monitor whether the PTL showed any signs of corrosion. As no corroded spots were visible on the PTL surface, the cell was assembled again with the PTL and a new carbon paper on the cathode side to re-establish the targeted compression and restart the experiment. However, reddish deposits were visible on the first carbon paper used, pointing to iron corrosion. Hence it is likely that iron dissolved from the surface of bulk fibers from the felt or underlying mesh. As the carbon PTL on the cathode side of the cell with SMF8_Pt_2 was not replaced, but a similar performance curve to SMF8_Pt_1 was observed, it can be assumed, that the replacement of the cathode PTL was not crucial to the improvement in performance with SMF8_Pt_1. Padgett et al. [124] reported, that cation contaminations can be removed from the cell at high current densities. As the cells were either constantly or periodically supplied with high current densities. This effect of "washing out" of cation impurities might have taken place within both experiments.

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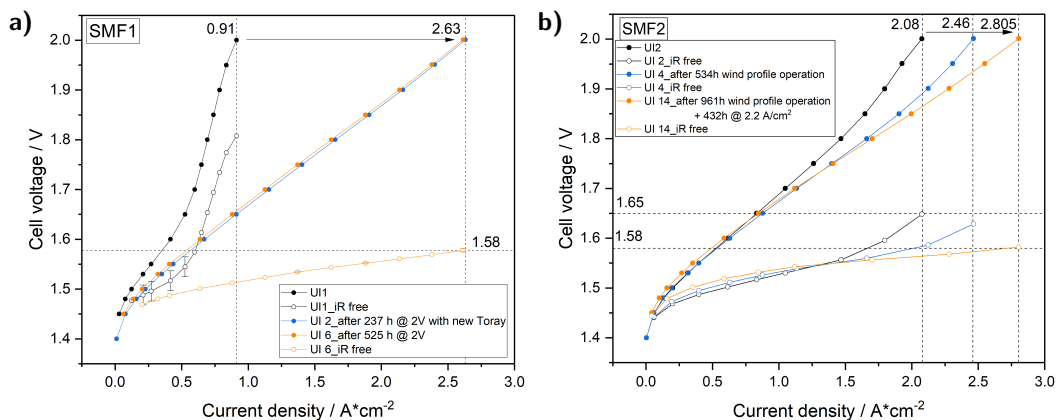


Figure 7.4. I-V curves and iR-free I-V curves of two PEMWE single cells with 316L anode felt PTLs (SMF) with Pt coating; a) sample number one (SMF8_Pt_1), constantly operated at 2.0 V and b) sample number two including wind profile operation (SMF8_Pt_2, see chapter 8).

Figure 7.4 displays the I-V curves and iR compensated I-V curves with Pt coated 316L felt anode PTLs. The first I-V curves of both cells after conditioning exhibit steep slopes, almost shaping an "S". With SMF8_Pt_1, after exchange of the carbon PTL (Toray) at the cathode side, a restart and 237 h of operation at 2.0 V, the cell performance improved (UI 2_SMF1) and was stable for another 288 h. I-V curves compensated by the ohmic resistance reveal, that at the beginning of test the overvoltage stemming from the reaction kinetics and mass transport were high, as even the iR-compensated curve exhibited a steep slope while the iR-free cell voltage at the end of test dropped to 1.58 V at 2.6 A cm^{-2} (Figure 7.4), the same range as was observed with standard cells (cf. Figure A.11). Consequently, losses were mainly generated by contamination of the membrane with corrosion products leading to increasing ohmic losses than by impeded kinetics. The same trend of initially high overvoltages due to reaction kinetics or mass transport occurred with SMF8_Pt_2. As the EIS spectra with SMF8_Pt_1 (Figure 7.5) only reveal an increase in low-frequency resistance and no second semicircle, it can be assumed that mass transport accounts only for a minor or no proportion of the overvoltage. However, at the begin of the experiment with SMF8_Pt_2, a contribution from mass transport limitation cannot be excluded, as beginnings of a second semicircle at low frequencies can be seen in the spectra above 1.7 V (Figure 7.6a).

With SMF8_Pt_2, long-term operation was also possible and the same trend in the course of performance was observed as with SMF8_Pt_1, from an initially weaker performance with maximum 1.55 A cm^{-2} at 2.0 V and indications of mass transport limitations at the begin of test to 2.8 A cm^{-2} at 2.0 V after 1393 h. The evolution of the current density at 2.0 V with SMF8_Pt_2 is shown in Figure A.33.

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High current densities might be possible with 316L based PTLs, although Fe was found post mortem in MEAs that were operated with both PTLs. Operation close to 3.0 A cm^{-2} might be possible in case dissolved metal impurities are not detrimental until a certain threshold.

In one linescan, more Fe was found on the anode side (Figure A.32), while in a second scan, a distribution of Fe in the MEA (Figure A.31) was visible and in a third one more Fe on the cathode side (Figure A.30). The latter confirms, together with rust-colored deposits at the cathode outlet by the end of the test, a migration of metal cations from the anode to the cathode side.

High local Fe and Pt concentrations in close vicinity to the anode catalyst layer can stem from fibers of the PTL that adhere to the catalyst layer when the cell is disassembled. Adhesion of 316L fibers on the anode catalyst layer was observed with the 316L felt PTL with a fiber thickness of $22 \mu\text{m}$ (SMF22, see Figure A.37).

Except for Fe, no other stainless steel elements were detected by EDX, but in addition to iron, Ca and K (Figure A.30) and in one case Cu (Figure A.31) were found on the cathode side with approximate fractions of 3.5 at.%, 4.5 at.% and 1 at.%, which might also affect cell performance. A source of Ca could be the production of Nafion™ membranes, as Ca^{2+} or Na^{+} may be used to stabilize the dispersion [122]. Furthermore, K and Ca were also found in MEA cross sections with standard PTLs, supporting exclusion of the PTLs as a source of these impurities. The source of Cu remains unidentified.

Impedance spectra at the begin of test (BOT) and end of test (EOT) with SMF8_Pt_1 and SMF8_Pt_2 are displayed in Figure 7.5 and Figure 7.6. The data presented in both figures indicate a decrease of high frequency and charge transfer resistances from BOT (Figure 7.5a and Figure 7.6a) to the end of the test (Figure 7.5b and Figure 7.6b), suggesting that the cell performance enhanced, which was not anticipated with a platinum-coated 316L PTL. A mechanism that might improve the cell resistance and catalyst use, especially during the conditioning process is the adaption of the membrane to the PTL, increasing the contact area between the PTL and anode catalyst layer. This process might take longer as with standard PTLs, as the 316L felt PTL is more compressible than Ti felt PTLs. The effect of an additional feature at low frequencies caused by cation impurities described by Padgett et al. [124] was visible in spectra with Pt coated 316L felt PTLs. As visible from the Nyquist plots in Figure 7.5 recorded at the begin of test, the diameters of the semicircles are unusually wide and the low frequency resistances high. These features are also visible in the spectra after 527 h above 1.65 V, but less pronounced than at the begin of test.

This additional feature at low frequencies is a strong indicator of contamination by corrosion products and will be an indicator also for the interpretation of further impedance spectra with coated 316L mesh PTLs.

Tan et al. [121] investigated the influence of titanium corrosion from the anode PTL and found that dissolved titanium ions influence the HER, presumably by occupying H^{+} sites and in consequence increasing the charge transfer for hydrogen evolution. As a result, the HFR and LFR increase and

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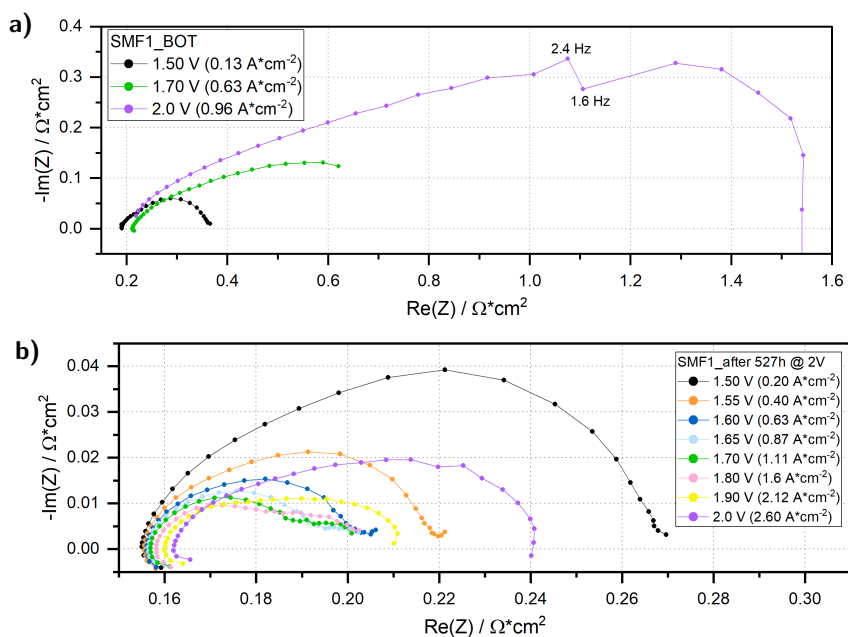


Figure 7.5. Impedance spectra with SMF8_Pt_1; a) Recorded at the begin of test with indication of the frequencies 2.4 Hz and 1.6 Hz at which unknown artifacts occurred, possibly caused by the potentiostat; b) Recorded after 527 h operation at 2.0 V.

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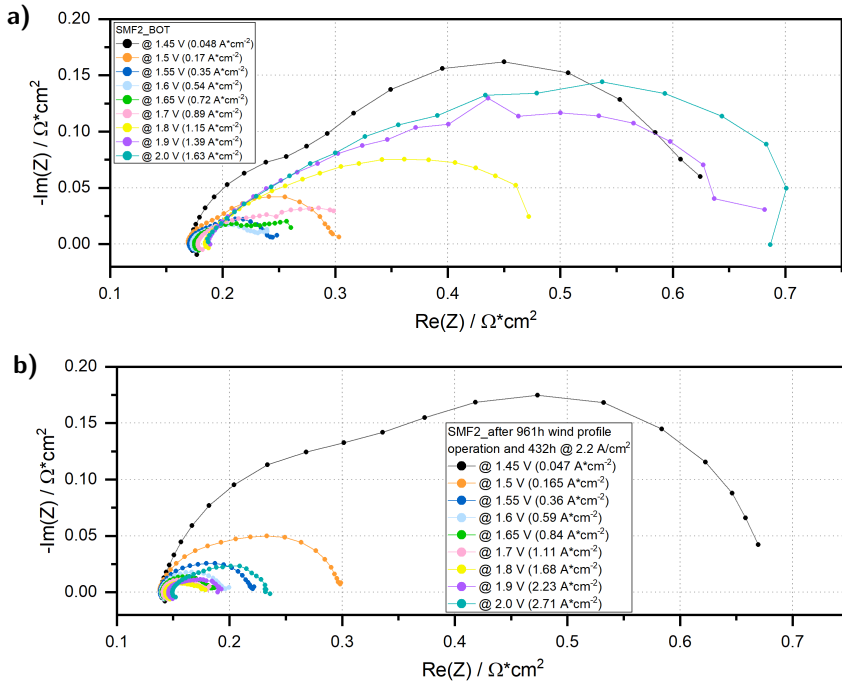


Figure 7.6. Impedance spectra with SMF8_Pt_2; a) Recorded at the begin of test; b) Recorded after 961 h wind profile operation and 432 h at 2.2 $\text{A} \cdot \text{cm}^{-2}$.

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two almost distinct semicircles become visible in the Nyquist plot, indicating a separation of time constants. Although titanium corrosion can be excluded within these experiments, it is conceivable that other metal cations lead to a similar influence.

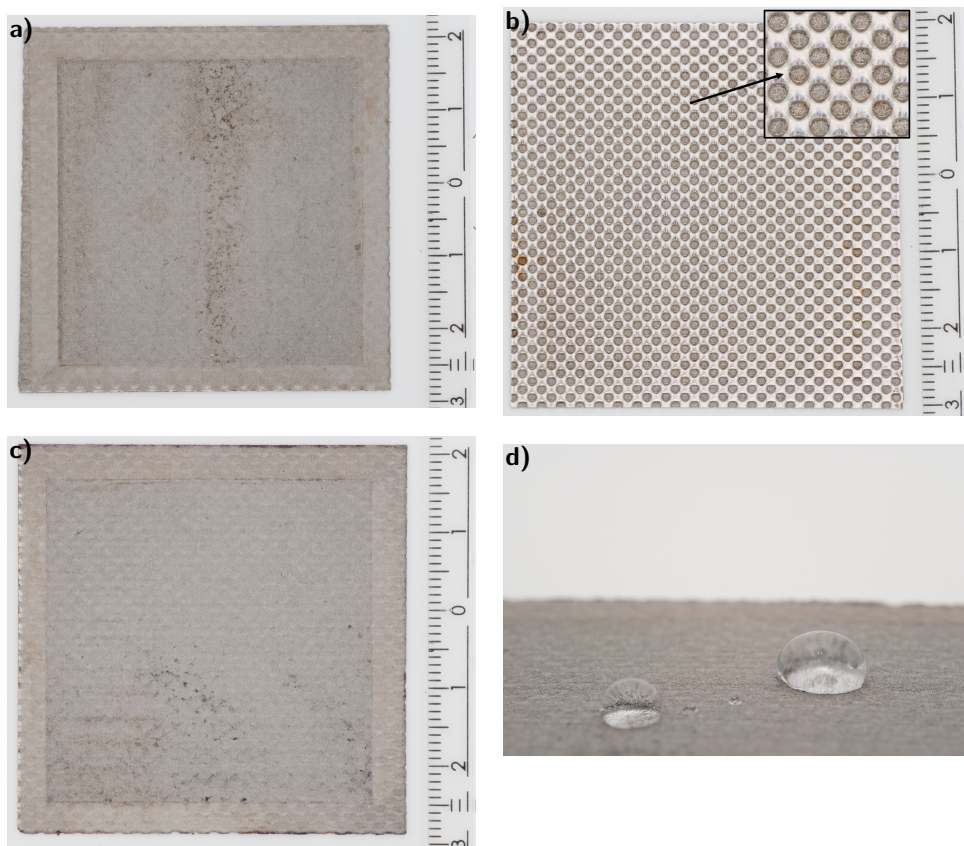


Figure 7.7. Post mortem photographs of: a) SMF8_Pt_1 CL-facing side with visible imprint of the active area; b) FF-facing side of SMF8_Pt_1; c) SMF8_Pt_2 CL-facing side with visible imprint of the active area; d) SMF8_Pt_2 with water drops.

Corrosion took place at the PTL/CL and PTL/FF interface, as small rust-colored spots were visible on the PTL surfaces and on the back of the supporting expanded metal, whereby the biggest spots were located at the edges of the PTL, which were not in contact with the flow field, as well as at the outer cut edges, regardless of whether the PTL was coated on the FF-facing side with Pt or not. Furthermore, corrosion in the bulk of the PTL cannot be precluded. High resolution photographs of the PTLs after the experiments revealed rust-colored spots also on the back side of the felt (see Figure 7.7b). These discolorations might be an effect that is referred to as “rouging”, a form of surface corrosion which can, among other environments, occur through contact with ultrapure

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water [180], as it contains scarcely any ions and is therefore more aggressive towards stainless steel surfaces than water with a higher ion concentration. Preventing this kind of surface corrosion would only be possible through a complete coating of the surface, an approach that was recently presented by Singh et al. [83] for titanium PTLs. However, if exposure to ultrapure water resulted in surface corrosion, this phenomenon would also appear on the cathode side, where the potential is around 0 V or slightly negative. Further experiments with 316L expanded meshes on the cathode side would be necessary to clarify this question.

ICP-MS analysis of the effluent water from dynamic long-term testing with SMF8_Pt_2 revealed low concentrations of iron emission ($< 0.83 \mu\text{g L}^{-1}$, see Figure A.36a), mainly from the cathode outlet. Linescans of post mortem SEM cross sections from the MEA revealed iron being present in the anode catalyst layer (Figure A.34 and Figure A.35). Ni concentrations in the effluent water stayed below $0.85 \mu\text{g L}^{-1}$ except for three samples where $2.3 \mu\text{g L}^{-1}$, $2.4 \mu\text{g L}^{-1}$ and $1.3 \mu\text{g L}^{-1}$ were detected (Figure A.36c). The highest chromium concentrations were found in the samples at the beginning of the test without electrolysis operation during heating (samples SMF2_A0 and SMF2_K0 in Figure A.36c). This implies either a low corrosion rate during electrolysis or that stainless steel elements became most likely mainly trapped within the CL or the membrane during electrolysis operation due to the electric field and formation of a concentration gradient. Emissions of Zn and Cu were significantly higher during electrolysis operation than under idle conditions (Figure A.36e, samples A0 and K0 vs. A and K 1-6). As these two elements were not detected in the storage tanks, it is deduced that they were washed out of the cell, with higher concentrations from the anode. Kinumoto et al. [130] report that apart from iron, copper accelerates membrane degradation because of its catalytic activity for radical formation via Fenton reactions, while alkali and alkaline metal ions do not catalyze radical formation. However, different from one MEA linescan with SMF8_Pt_1, no copper was detected in SEM cross sections from the MEA operated with SMF8_Pt_2.

Future investigations should be carried out with different levels of impurities at higher current densities to investigate whether the level of impurities considered to be acceptable for electrolysis operation here would have a stronger effect in the higher power range, as a slight bending of the I-V curves was visible at the end of test, indicating either the onset of mass transport limitation or, as reported in case of cation contamination, overvoltage caused by losses due to the contamination appearing like mass transport limitation [124].

Furthermore, due to the emission of Fe and the occasional presence of Cu, it is possible that membrane thinning occurred. The mean thicknesses at the end of the test of the MEA used with SMF8_Pt_1 was $203 \pm 10 \mu\text{m}$ and the MEA used with SMF8_Pt_2 was $162 \pm 20 \mu\text{m}$. The thickness of membranes that were used with standard Ti PTLs after the same wind profile measurements as those with SMF8_Pt_2 exhibited mean post mortem thicknesses between $200 \mu\text{m}$ to $240 \mu\text{m}$ (see Table A.1), which is in the range reported by Heimerdinger et al. [146] for swollen Nafion™ 117

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membranes. Thus, the thickness of the MEA used with SMF8_Pt_2 lay below the thickness of MEAs operated with Ti PTLs that were operated with the same wind profile. When determining the membrane thickness, it must be taken into account that due to the channel-ridge structure of the flowfield, more and less compressed zones are present, resulting in a thickness distribution and the determination of an average membrane thickness depends on the location of thickness determination. Consequently, although attention was paid during the analysis to ensure that both land and channel areas were taken into account equally, it cannot be ruled out that one of the two areas has been included with a higher proportion in the calculation of the membrane thickness.

However, considering the results with Pt coated 316L meshes, the stability of the Pt coated 316L felt PTLs was not expected and requires further investigations. Stable electrolysis operation could be feasible in case the PTL surface passivates, thus interrupting the corrosion process and preventing the further release of metal cations. One reason for the superior stability of the stainless steel felt compared to the 316L mesh could be its composition. The Mo content of the felt was higher (approximately 0.4 wt% more than the mesh) and Mo is known to increase the corrosion resistance of stainless steel, especially in the presence of Cl^- ions. Additionally, the Mn content of the mesh was more than three times higher (0.38 wt% vs. 1.25 wt%, see Figure 7.1) than of the felt and Mn is reported to decrease the corrosion resistance [182], but also contributes to a smoother surface. Although it could be assumed that a higher Mn content and thus a smoother surface could be beneficial for corrosion resistance, the Mo content might have a higher impact according to the results. Consequently, further systematic investigations about the influence of the alloying elements of 316L on the corrosion resistance of anode PTLs are of great interest. Furthermore, the question remains whether the different stabilities of these two 316L PTLs occurred due to their composition, or whether other factors such as the composition of surface elements, other surface properties or the thickness of the PTLs also had an influence, as the 316L expanded metal was significantly thinner with $130\text{ }\mu\text{m}$ than the expanded metal-felt combination with $1100\text{ }\mu\text{m}$. Hence, it is possible that the back of the thin expanded metal is more affected by corrosion, as the back is still within the presumably corrosive zone of $200\text{ }\mu\text{m}$, where polarization from the anode catalyst layer is still assumed to be present [59].

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In summary, the following **influences of corrosion products** on the position and shape of I-V curves and impedance spectra could be observed:

- In the case of **severe pitting corrosion affecting the cell performance** with 316L expanded metals with Pt coating:
 - Significantly reduced performance of maximum 1.1 A at 2.0 V.
 - Significantly distorted shape of the I-V curve (Figure 7.2), possibly due to progressive corrosion during recording of the I-V curve and blockage of proton channels by metal cations.
 - Appearance of two distinct semicircles in the Nyquist plot (Figure 7.3), either generated by strongly inhibited kinetics or processes taking place along an additional phase boundary.
- In the case of **less severe corrosion with minor impact on cell performance** with 316L felt PTLs with Pt coating and stable long-term performance for 1393 h close to titanium PTLs:
 - Initially strong bending of the I-V curves above 1.6 V, also when compensated by the ohmic resistance indicating initially high activation and/or mass transport overvoltage.
 - In accordance with I-V curves: increasing CT resistances at higher current densities visible from Nyquist plots, especially at the beginning of the experiment.
 - Improved and stable performance after a, compared to titanium PTLs, longer conditioning process with a duration between 50 h and less than 237 h.
 - iR compensated curve at the end of test without any signs of mass transport limitation.
 - Decrease of CT resistances in the course of the experiment, but still comparatively high CT resistances in the higher power range visible from Nyquist plots.
 - Decrease of HFR in the course of the experiment, most likely due to overlapping effects caused by the adaptation of the MEA to the PTL and thinning of the membrane.

In case of less severe corrosion, a further observation includes that surface corrosion of the PTLs covered only isolated areas.

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These observations about the impact on cell performance and EIS are in accordance with other studies that investigated the influence of cation impurities on PEMWE performance (subsection 2.5.3) and serve to interpret further experiments with different corrosion protection coatings on 316L-based PTLs.

However, long-term experiments with stainless steel-based PTLs with a low corrosion rate have not been covered in the literature yet. Additionally, the different stabilities of the expanded metal and felt indicate, that the stability of a 316L based PTL is influenced by unknown parameters. It is conceivable, that variation in the composition of stainless steel 316L within its specification, in particular Mo and Mn, could be crucial for the corrosion stability under PEMWE conditions. Furthermore, is not yet been examined to what extend processing and pre-treatment of the PTL influences corrosion-related surface properties.

7.3. PVD titanium and platinum coating

Although it is assumed that polarization from the anode catalyst layer extends up to 200 μm into the depths of the PTL [59], leading to the conclusion that a protective coating for 316L anode PTLs may also have to be 200 μm , the corrosion protection properties of 3 μm thick Ti PVD coatings were investigated, as the stability of the 316L felts was, as reported in the previous subsection 7.2.2, already unexpectedly high with a thin 38 nm Pt coating that was not designed for corrosion protection. Given that these PTLs have already withstood electrolysis for up to 1452 h at 2.0 V, it is conceivable that a thinner corrosion protection layer below 200 μm could be sufficient to protect the PTL from corrosion. Solely surface corrosion from the bulk triggering membrane thinning could not be ruled out so far with these PTLs. Furthermore, the application of thicker coatings, such as by CGS, was not possible with the felt PTLs due to their smaller pore openings compared to meshes and no reports of stainless steel PTLs with thin corrosion protection layers were available to date. For a comparison with full titanium expanded mesh PTLs, PVD titanium coatings were also deposited on 316L expanded metals, that were already used in the previous subchapter. First, results with 316L expanded metal PTLs and then with 316L felt PTLs are discussed. To avoid oxidation of the titanium coatings, all PTLs were additionally sputtered with a 38 nm platinum layer, also on the FF-facing side to maintain consistency with the experiments using Ti PTLs. Ti PVD coatings were deposited at and by the institute IMD-2 [183], see subsection 3.2.1.

7.3.1. 316L expanded meshes

Unlike with 316L meshes coated only with platinum (cf. 7.2.1), electrolysis with Ti and Pt PVD coated stainless steel expanded meshes was possible beyond the recording of one I-V curve and one impedance spectrum, although the $3\text{ }\mu\text{m}$ PVD coating is considered to be too thin to shield the PTL substrate from polarization of the anode catalyst layer [59].

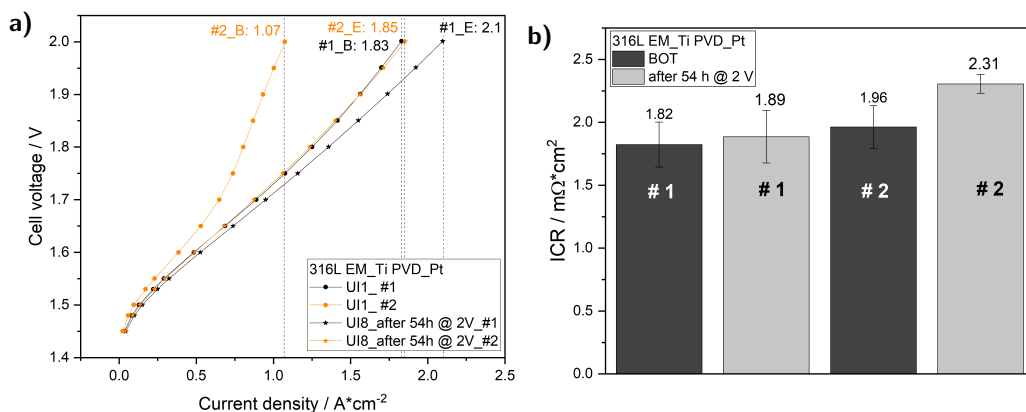


Figure 7.8. a) I-V curves at the begin of test after conditioning (#1_B and #2_B) and at the end of test after 54 h at 2.0 V (#1_E and #2_E) of two PEMWE single cells with titanium and platinum PVD coated 316L mesh anode PTLs; b) Interfacial contact resistances of PTLs #1 and #2 before the cell test (BOT) and after 54 h at 2.0 V.

As shown in Figure 7.8a, the performance of two cells with similar Ti and Pt PVD coated 316L mesh PTLs differed significantly. While sample #2 started with $1.07\text{ A}\cdot\text{cm}^{-2}$ at 2.0 V and the I-V curve showed a clear inflection above $0.5\text{ A}\cdot\text{cm}^{-2}$, the initial current density with sample #1 was $1.83\text{ A}\cdot\text{cm}^{-2}$ at 2.0 V. The performance differences might be influenced by the pressure and current density distribution or the expanded metals, caused by production-related variances on the surface, such as grain boundaries, where corrosion preferentially occurs. The inflection in the I-V curve with sample #2 corresponds with results from impedance spectra at 1.8 V, 1.9 V and 2.0 V, where the resistances at low-frequencies are higher than expected (Figure 7.8b) as was observed before with Pt coated 316L felt PTLs (Figure 7.5a and Figure 7.6a).

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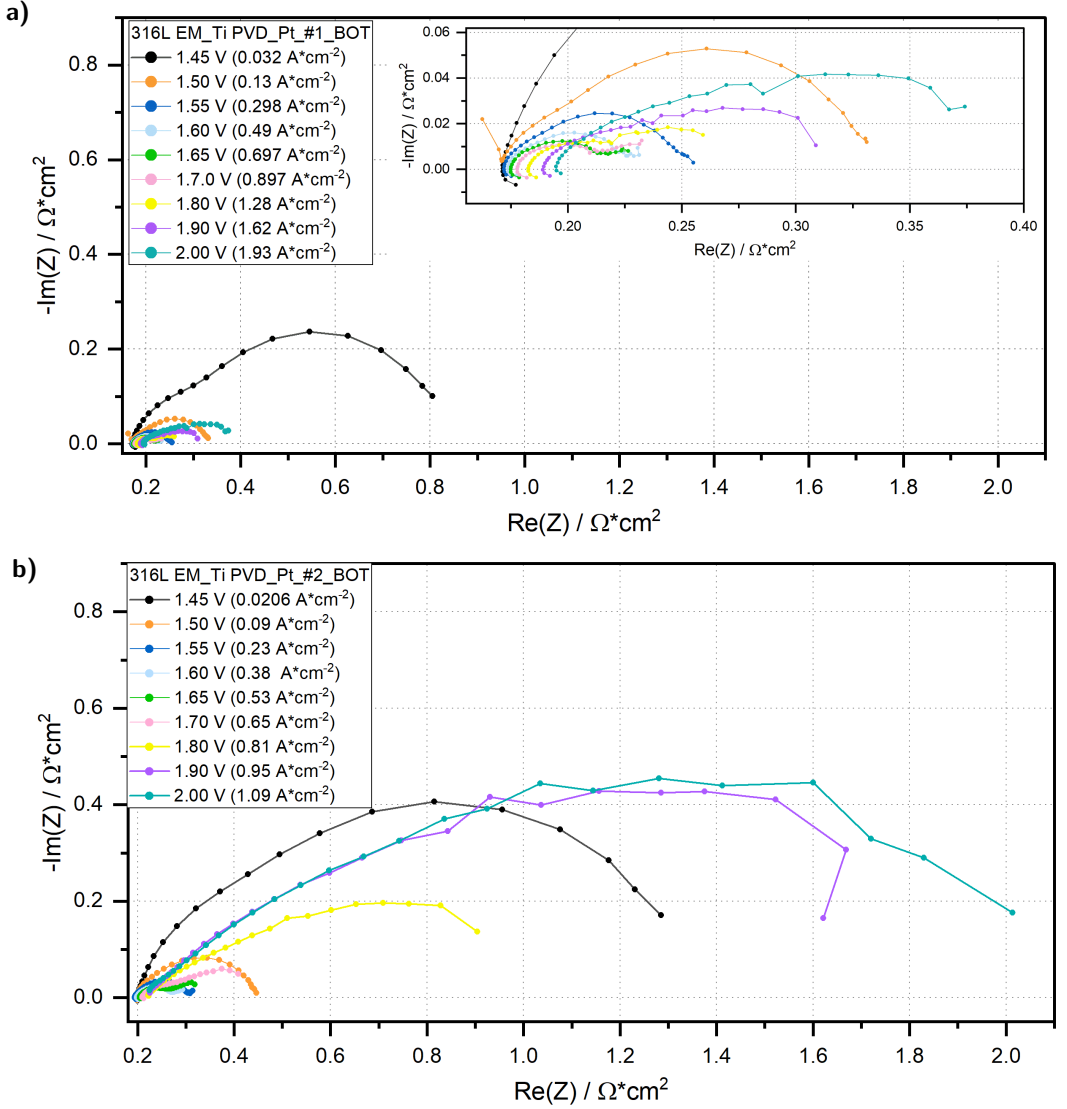


Figure 7.9. Impedance spectra of two PEMWE single cells with titanium and platinum PVD coated 316LEM PTLs; a) Cell with sample #1 with inset at the top right with zoom in the high-frequency range; b) Cell with sample #2.

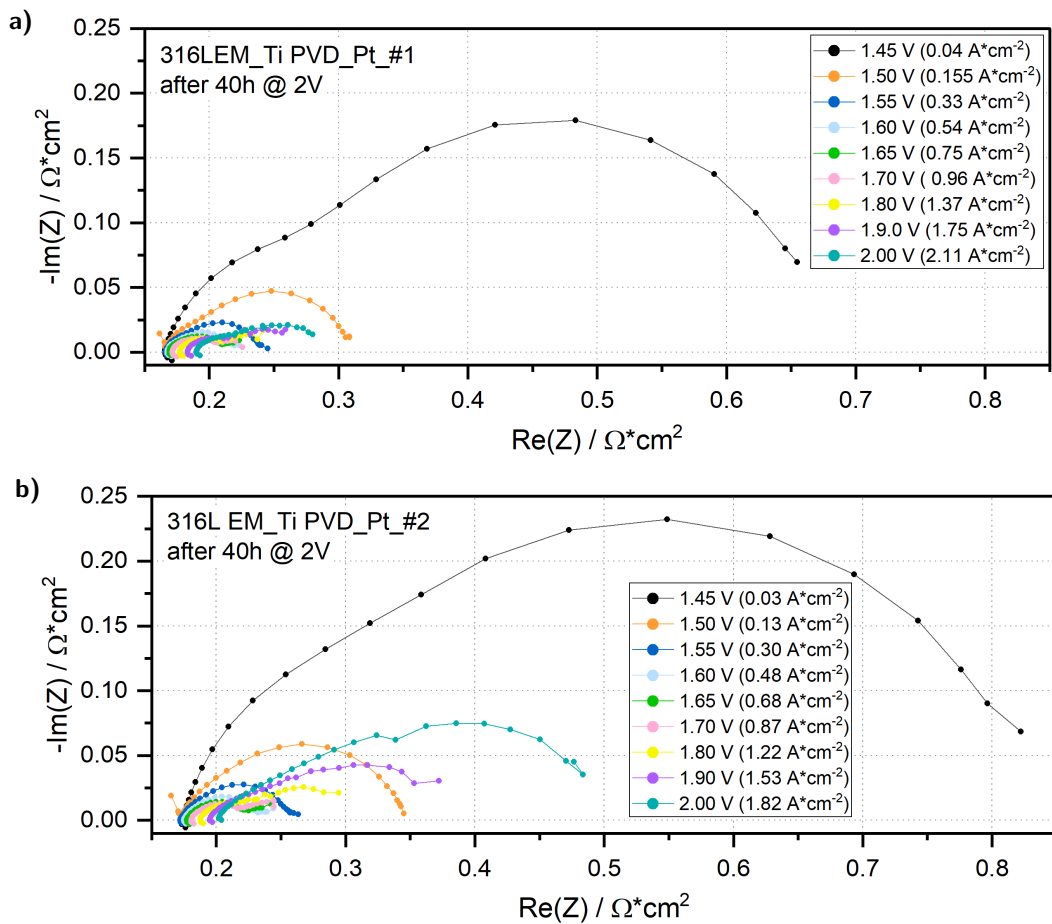


Figure 7.10. Impedance spectra of two PEMWE single cells with Ti and Pt PVD coated 316LEM PTLs after 40 h at 2.0 V.

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Although in stable PEMWE cells where the OER kinetics are slower than the HER, consequently having a higher impact on CT resistances [67], from the spectra alone, it can not be elucidated which of the two half-cell reactions contributes more to a higher CT resistance. Furthermore, as also seen in the previous subchapter with Pt coated 316L felt PTLs, and as evident from the I-V curves #1_E and #2_E, the performance of both cells improved after 54 h at 2.0 V and the bending of the I-V curves became less pronounced, which is further reflected by the EIS spectra recorded after 40 h (Figure 7.10). These similar performance developments to the results of the previous subchapter with a different stainless steel substrate indicate that initially high overvoltages possibly occurred less due to mass transport limitation and thus due to the geometry of the PTL, but due to increased overvoltages of the charge transfer due to contamination with corrosion products.

SEM post mortem analysis of a cross section from the MEA, that was operated with sample #2 revealed thicker and thinner areas with an average thickness of $222 \pm 15 \mu\text{m}$ and $175 \pm 6 \mu\text{m}$, possibly caused by imprinting of the expanded metal. Similarly strong differences in membrane thickness were not observed with the MEA operated with sample #1, as the thickness distribution was $202 \pm 15 \mu\text{m}$. Nevertheless, as the MEA cross sections were randomly selected, it cannot be excluded that similar MEA deformation and locally thinner regions were present at other parts of both MEAs, whereby it is not certain whether thinner regions formed due to compression by the PTL or due to iron ion catalyzed radical formation.

A comparison with other MEA thicknesses (Table A.1) indicates that on average no membrane thinning might have taken place, but could not be confirmed by the available amount of MEA cross sections. As the investigated cross sections only represent minor parts of the entire MEA, membrane thinning can only be reliably detected if the membrane thickness is below the range of MEA thicknesses without contamination.

The high frequency resistances of both cells ranged from $170 \text{ m}\Omega \text{ cm}^2$ to $195 \text{ m}\Omega \text{ cm}^2$ and $197 \text{ m}\Omega \text{ cm}^2$ to $220 \text{ m}\Omega \text{ cm}^2$ (see Figure 7.9). Consequently, the difference in overvoltage caused by the different ohmic resistances of the cells account for approximately 45 mV at 1.07 A cm^{-2} (left dashed line in Figure 7.8a), indicating that other contributions to overvoltage such as charge transfer overvoltages contributed with a higher share to differences of the performance curves. Moreover, it must be noted that a direct comparison of EIS measurement and I-V curve is not entirely feasible for fast-changing systems, as the state of the system may differ during the two measurements. Furthermore, the assumption that performance differences of overvoltages did not stem from a contribution of ohmic resistances is supported by the fact that the ICRs of the PTLs remained constant and were similar within the margin of measuring inaccuracy (see Figure 7.8b). The increase of the ICR of sample #2 was slightly higher, but as the current density after 54 h also increased, this slight ICR increase is considered not to influence the cell performance. Furthermore, the influence of the ICR on cell performance is negligible, as with $2 \text{ m}\Omega \text{ cm}^2$, the ICR lies two orders of magnitude below the cell resistance of around $200 \text{ m}\Omega \text{ cm}^2$.

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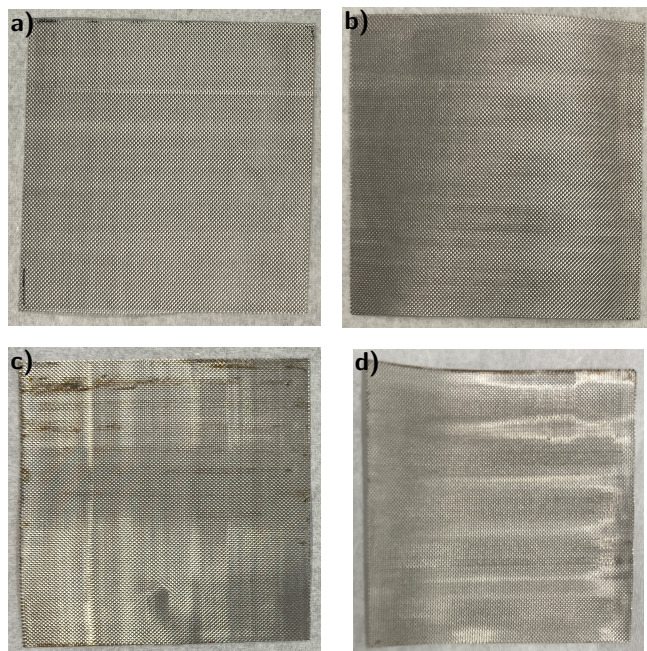


Figure 7.11. Photographs of: a) and b) CL-facing side of 316LEMs with Ti and Pt PVD coating after operation for 54 h at 2.0 V. a) 316LEM_TiPVD_Pt_1 with slight traces of the catalyst layer at the edge of the PTL; b) 316LEM_TiPVD_Pt_2. c) and d) FF-facing side of 316LEM with Ti and Pt PVD coating after 54 h at 2.0 V; c) 316LEM_TiPVD_Pt_1; d) 316LEM_TiPVD_Pt_2.

While the front sides of both expanded meshes remained unchanged after the cell test (Figure 7.11a and b), some small rust-colored areas, mainly at the edges of the mesh and along the contact area with the ribs of the flowfield, were visible on the back side of both samples after 54 h at 2.0 V (Figure 7.11c and d), with the PTL 316LEM_TiPVD_Pt_2 containing more discolored areas. As mentioned in the previous subchapter, the occurrence of corrosion on the back of the PTL is conceivable due to two reasons: Either a corrosion protection layer is also needed on the side facing the FF regardless of the applied potential or thickness of the PTL due to exposure to the flowing ultrapure water or the back side is not sufficiently protected from anodic polarization. The latter could be solved by a thicker corrosion protection layer on the MEA-facing side, increasing the distance between the CL and the back side of the PTL. As thicker coatings can be achieved by thermal spray processes, stainless steel mesh with thicker titanium CGS coatings will be investigated in the next chapters. However, to protect against the surrounding ultrapure water, only coating the entire surface would provide sufficient protection.

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Table 7.1. Elements detected in the effluent water by ICP-MS from PEMWE single cell testing with 316LEM_TiPVD_Pt_1 and 316LEM_TiPVD_Pt_2 and impurities found in MEA cross sections.

	316LEM_TiPVD_Pt_1	316LEM_TiPVD_Pt_2
Elements in the effluent water (anode) ¹	Fe, Cr, Mo, Mn, Cu, Zn, K, Ca	Fe, Cr, Mo, Mn, Cu, Zn, K, Ca
Elements in the effluent water (cathode) ¹	Fe, Cr, Ni, Mo, Mn, Cu, Zn, K, Ca	Fe, Cr, Ni, Mo, Mn, Cu, Zn, K, Ca
Impurities in the anode CL ²	Fe, K, Ca, Cu	Fe, Cr, Cu
Impurities in the cathode CL ²	/	Si, K, Ca, Cr, Fe, Cu
Impurities in the membrane ²	K, Ca, Mg, Fe, Cu	Na, Mg, Fe, Ca, Cu

1: Analyzed via ICP-MS, see Figure A.41 and Figure A.42, 2: Analyzed via EDX.

Based on ICP-MS analysis of the effluent water (see Figure A.41 and Figure A.42) and EDX analysis of MEA cross sections, it can be inferred that the titanium layer remained stable, as Ti was neither detected in the water ($DL < 0.05 \mu\text{g L}^{-1}$) nor in the MEAs. However, stainless steel elements were found in the MEAs with both 316L based PTLs, summarized in Table 7.1. Effluent water samples contained Fe, but without trend regarding concentrations of Cr, Ni and Mn compared to water samples taken from the cell with SMF8_Pt_2, except that corrosion products were present more often (c.f. Figure A.36 and Figure A.41).

EDX analysis of MEA cross sections detected small amounts of Fe in both MEAs with one spot within the anode catalyst from sample #1 containing 8.5 at.% of Fe, where on the same spot also slightly increased potassium and calcium concentrations occurred, both around 2.5 at.%. Apart from one spot with higher concentrations of impurities, the concentrations of Fe in the MEAs ranged from 0.3 at.% to 0.5 at.%, indicating that iron was present in the MEAs, but as the fractions were small, a quantification is not possible. The same applied for chromium, as Cr was found with fractions between 0.14 at.% and 0.17 at.%. As Cu and Zn were not detected in the storage tanks, but in almost all samples taken from the cells, it is deduced that these elements were released from the cell. Copper and zinc were also detected in a previous experiment with SMF8_Pt_2, but the concentrations were higher (Figure A.36 and Figure A.41). Further impurities included potassium and calcium (Figure A.42), which were also present in the storage tank and therefore might be introduced by the surrounding. As mentioned before, another source of earth alkali metals can stem from the membrane, as Ca^{2+} and Na^+ might be used in the production of Nafion™ membranes to stabilize the dispersion [122]. Also in EDX-Spectra, Ca, Cu, K, and in some cases Na and Mg were detected, all below 0.9 at.%.

In summary, the Ti PVD coating was able to significantly improve the corrosion stability of the 316L expanded mesh substrate compared to a thin Pt coating. However, the emission of stainless steel elements could not be reliably prevented, as stainless steel elements were detected in the effluent water and post mortem in MEA cross sections. Most of the corroded areas were not in contact with the CL, but were found on the FF-facing side or at the edge of the PTL. Furthermore, investigations over longer periods of more than 54 h at maximum cell voltage would be insightful to determine whether thin corrosion protection coatings would also provide long-term protection.

7.3.2. 316L felts

Analogous to the results presented in the previous chapter with Pt-coated 316L felt PTLs (SMF8_Pt_1 + SMF8_Pt_2), similar PTLs with a fiber diameter of 8 μm (SMF8_Ti) and 22 μm (SMF22_Ti), were coated with Ti via PVD at the institute IMD-2 (see Table 3.3) and sputtered with Pt at IET-4 (see 3.2.1). The cells were operated for 691 h at 2.0 V and the development of the current density with indication of all interruptions is displayed in Figure A.43.

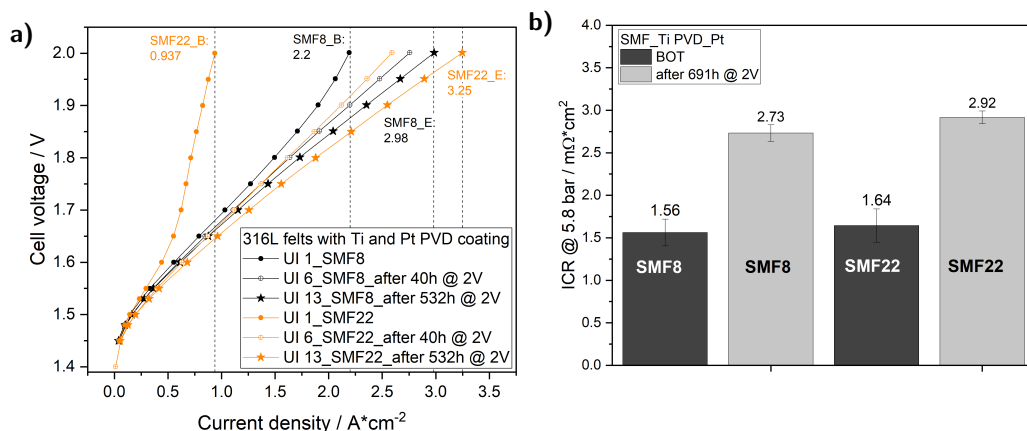


Figure 7.12. a) I-V curves of two PEMWE single cells with 316L Ti and Pt PVD coated anode felt PTLs with a mean fiber diameter of 8 μm (SMF8) and 22 μm (SMF22); b) Interfacial contact resistances of PTLs SMF8_Ti and SMF22_Ti before the cell test (BOT) and after 532 h at 2.0 V.

Figure 7.12 shows the I-V curves with Ti and Pt PVD-coated 316L expanded metal felt PTLs. Similar to the 316L felt PTLs with Pt coating (Figure 7.4), the initial performance ranged from around 0.9 A cm⁻² to 2.2 A cm⁻² and a strong shift to higher current densities was observed between the begin of the test and after 40 h. This was also reflected by decreasing cell resistances (Figure 7.13). While the Pt coated SMFs reached 2.6 A cm⁻² at 2.0 V after 525 h and 1452 h, the current density achieved with SMF8_Ti and SMF22_Ti after 532 h (2.9 A cm⁻² and 3.25 A cm⁻²) were at the upper end of the current densities measured with standard cells. Whether the current density achieved with SMF22_Ti after 532 h contains fractions of unknown side reactions or whether an improved PTL/CL interface lead to the increased cell performance, can not be elucidated. The low HFR at the end of the experiment of $132.0 \pm 0.6 \text{ m}\Omega \text{ cm}^2$ suggests thinning of the membrane, as the cell resistances with reference cells with Pt-coated titanium PTLs operated for 457 h did not decrease below 151 mΩ cm² and also the cell resistances after 550 h long-term wind-profile experiments did not drop below 151 mΩ cm² either (chapter 8).

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Thinning of the membrane is problematic not only in terms of pinhole formation, but also because the dissolution of the fluoropolymer is accompanied by the emission of fluorinated organic compounds. Furthermore, thinner membranes are more vulnerable to the formation of Ir clusters in the membrane from dissolved iridium, leading to short circuits between the electrodes where parasitic currents can flow and in consequence decrease the hydrogen production rate [62, 63]. However, membrane thinning could not be confirmed, as the post mortem membrane thickness from MEA cross-sections revealed an average membrane thickness of $238 \pm 9 \mu\text{m}$ (operated with SMF22_Ti) and $187 \pm 15 \mu\text{m}$ (operated with SMF8_Ti). Due to the thinner membrane with SMF8_Ti, a lower ohmic resistance and thus higher current densities would be expected for SMF8_Ti, but I-V curves and impedance measurements do not confirm a lower ohmic resistance. This emphasizes, that conclusions from MEA cross sections can only be drawn with a high number of samples to be sufficiently representative, and that local thickness differences occur due to different compression and indentation of the PTL. Similar to the results with SMF_Pt PTLs, no differences in PTL resistance (ICR) between the two samples were identified and the increase in resistance from BOT to EOT was negligible at around $1 \text{ m}\Omega \text{ cm}^2$ (Figure 7.12b), indicating that the differences in cell performance are attributable not to the PTL resistance but to activation overvoltage and/or mass transport limitation, as was also found with SMF_Pt PTLs (subsection 7.2.2). Additionally, the ICRs meet the DOE targets of maximum $10 \text{ m}\Omega \text{ cm}^2$ for BPPs in fuel cells [174].

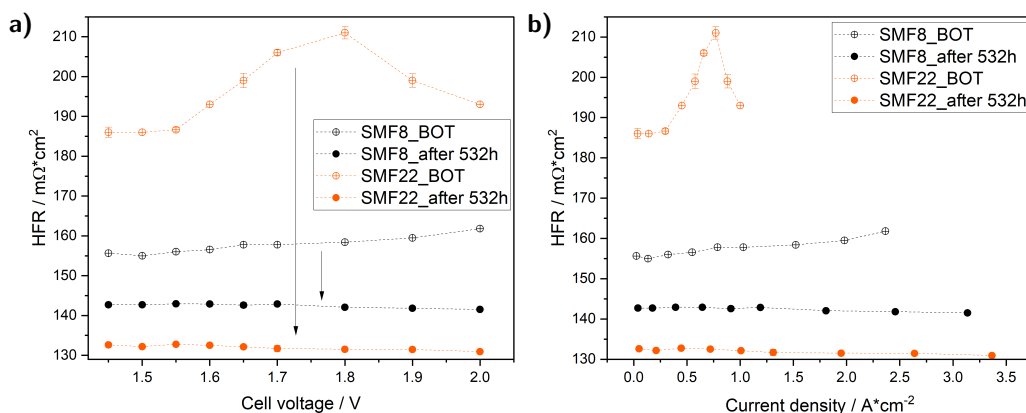


Figure 7.13. High frequency resistances with SMF8_Ti and SMF22_Ti at the beginning of test and after 532 h of operation at 2.0 V in dependence of the a) cell voltages; b) Current density.

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Table 7.2. Elements detected in the effluent water from PEMWE single cell testing with SMF and impurities found in MEA cross sections.

	SMF8_Ti-PVD_Pt	SMF22_Ti-PVD_Pt
Elements in the effluent water (anode) ¹	Fe, Cr, Ni, Na, Mg, Ca	Fe, Cr, Ni, Na, Mg, Ca
Elements in the effluent water (cathode) ¹	Fe, Ni, Na, Mg, Ca	Fe, Ni, Na, Mg, Ca
Impurities in the anode CL ²	Fe, Mg, K, Ca, Cu	Fe, Ni, Ca, Na
Impurities in the cathode CL ²	K, Ca, Cu	Mg, Ca, Na
Impurities in the membrane ²	Mg, K, Ca, Na	Mg, K, Ca, Na

1: Analyzed via ICP-MS, see Figure A.44, 2: Analyzed via EDX, see Figure A.45, A.46, A.47, A.48, A.49, A.50 and A.51.

Compared to effluent water samples from SMF8_Pt_2, iron concentrations were slightly higher (Figure A.44a), whereby ICP-MS measurements for the two experiments were carried out at two different institutes, resulting in preparative differences and detection limits (DLs). Additionally, in the cathode storage tanks for SMF22_Ti, the same concentration of iron was detected as in the effluent water.

Furthermore, trapped Fe in the MEAs was detected (up to 0.6 at.%), without any significant difference between the MEA used with SMF8_Ti and SMF22_Ti.

Regarding the water samples that contained chromium, it is noticeable that the highest concentrations occurred at the beginning of the experiment (see "0" samples in Figure A.44b), when the cells were not under load, but only heated while the water circulated, indicating that chromium dissolved from the stainless steel surface without any influence from the OER. The same applied for Mn (Figure A.44d). Furthermore, higher Cr concentrations were found from the anode than at the cathode outlet, implying that either only a small proportion of chromium migrated from the anode to the cathode side or was bound to the MEA. Presence or accumulation of Cr in the MEA could not be confirmed on the basis of EDX spectra, supporting the assumption that the source of chromium is the uncoated surface of the bulk of the PTL, as it is more likely that chromium ions, which are dissolved from the bulk of the PTL distant to the CL, are carried out of the cell with the water flow instead of migrating through the MEA. Additionally, Ni was washed out without any water splitting taking place (samples A0 and K0 in Figure A.44c) and the concentrations were only slightly below, but in the same range as with Pt coated SMF8_Pt_2. The corrosion rate was presumably higher when the 316L felts were only coated with Pt, as not only on the FF-side and in the bulk, but also at the interface to the CL corrosion took place (photographs see Figure 7.7 and Figure A.37). However, nickel concentrations were not much higher in the experiment with SMF8_Pt_2 than with SMF8_Ti and SMF22_Ti. If Ni was trapped in the MEA, the quantities were too small to be detected by EDX spectroscopy, as Ni was only found in two line spectra from the MEA used with SMF22_Ti with a maximum concentration of 0.6 at.%. As the concentration of dissolved Ni seemed to be independent from the corrosion protection layer and consequently independent from the corrosion rate, it might be possible, that Ni is not predominantly dissolved due

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to anodic polarization, but due to contact with ultrapure water.

Dissolution of stainless steel elements upon contact with ultrapure water was demonstrated in an experiment wherein an uncoated stainless steel mesh was placed in 100ml of water for 90 h at $80.0 \pm 1.0^\circ\text{C}$ and 80 h at room temperature (ICP-MS analysis see Figure A.38). Although the residence time of the water was magnitudes longer than in the PEMWE cell, the results demonstrate, that stainless steel elements dissolve into the surrounding medium without the influence of acid or potential.

Copper and zinc were detected with mean concentrations of $0.52 \pm 0.15 \mu\text{g L}^{-1}$ and $4.7 \pm 0.8 \mu\text{g L}^{-1}$, but differently from previous measurements not only in the effluent water, but also in the storage tanks, implying accumulation from previous experiments. Before the water is supplied from the storage tanks to the cell, it is purified using an ion exchange resin. Consequently, it is assumed that all impurities present in the storage tanks are not affecting the cell performance. Despite, water samples from the tanks were examined for monitoring purposes before the experiments.

Other occasional impurities included sodium, magnesium, aluminum, potassium and calcium. All these impurities found by ICP-MS were also found in EDX spectra of MEA cross sections with concentrations below 0.7 at. %.

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Figure 7.14. Photographs of a) FF-facing side of SMF8_Ti post mortem; b) FF-facing side of SMF8_Ti post mortem; c) Anode flowfield used in conjunction with SMF8_Ti post mortem; d) CL-facing side of SMF8_Ti post mortem.

As in previous experiments with stainless steel-based PTLs, spots of orange discoloration on the FF-side were observed post mortem on SMF22_Ti and SMF8_Ti, in particular in the edge areas and especially with SMF8_Ti (Figure 7.14a and b). Additionally, deposits were visible at the edge of the flow field where the FF-facing side of the PTL was in direct contact with the flow field plate (Figure 7.14c). Deposits can emerge in this area, as the PTL was chosen to be larger than the active area (42 mm x 42 mm) at 50 mm x 50 mm to ensure that enough space is available for mounting during the coating process. To prevent the MEA from coming into contact with uncoated edge areas, a 15 μ m thin subgasket with an opening of the size of the active area was placed between the PTL and MEA, allowing the CL-facing side of the PTL being only in contact with the active area of the MEA. The front sides of the PTLs remained unchanged (see Figure 7.14d exemplary for SMF8_Ti). Although there were fewer areas affected by surface corrosion on the back of SMF22_Ti, discoloration was observed at the cathode outlet, in contrast to the experiment with SMF8_Ti. Therefore, it can be assumed that an unknown part of the iron deposits were released

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from the surface of bulk fibers. EDX analysis of a tube at the cathode outlet confirmed that the reddish deposits were iron.

As a potential replacement for the Pt coating, electrolysis operation with Nb PVD coated PTLs was investigated as described in the previous chapter section 6.4. In the course of these experiments, a layered coating of Ti and Nb PVD was also applied to an SMF22 PTL (coating parameters see Table 3.3) and operated at 2.0 V. After 165 h, a pump failure occurred and in contrast to the SMF8_Ti and SMF22_Ti PTLs, massive pitting corrosion was observed after removal. The results are shown in the appendix (Figure A.40) and illustrate that unsolved questions remain concerning the stability of 316L based PTLs. As pitting corrosion had formed a band through the PTL, the contact pressure may have been higher at the points where the felt was corroded due to inhomogeneities in the PTL and/or the flow fields. Furthermore, it is conceivable that the formation of niobium oxide led to a (local) temperature increase, as the thermal conductivity of NbO₂ is lower than that of Nb, Ti, TiO₂ and Pt (see Table 6.1). In addition, the pump failure and the resulting lack of water supply could have contributed to a local increase in temperature.

In summary, it was demonstrated that although both types PTLs, the expanded metals and the felts with two different fiber thicknesses supported on expanded metal, were subject to corrosion, electrolysis was possible at a maximum cell potential of 2.0 V and current densities between 1.8 A cm⁻² to 3.25 A cm⁻², even with a very thin corrosion protection layer consisting of 3 μm titanium PVD coating and a 38 nm contact layer of platinum. However, especially within longer experiments with 316L felt PTLs (SMF8 and SMF22), membrane thinning could not be ruled out.

Corrosion was not observed on the titanium-coated CL-facing side of the PTL, but on the platinum-coated FF-side. Furthermore, as found previously with 316L PTLs, indications about corrosion on the surface of the bulk of the PTL were found in high-resolution photographs of SMF22_Ti post mortem and corrosion products were visible at the cathode outlet. However, the FF-facing side of the PTL showed, in contrast to the PTL SMF8_Ti, almost no signs of corrosion, demonstrating that the corrosion behavior can differ even among similar PTLs and is therefore difficult to predict. The following chapters will therefore investigate if thicker coatings can, through potentially enhanced shielding against anodic polarization, protect against corrosion in the bulk and on the back of the PTL and increase the reproducibility of measurements.

7.4. CGS titanium and PVD platinum coating

The following subchapter is based on findings with a 38 μm thick Ti CGS coated 316L expanded mesh PTL within a study that was acquired and published together with T. Sievert [183] (DOI: 10.1016/j.surfcoat.2025.132486). This work has contributed with the following contributions: conceptualization of the study, electrochemical stability testing with PEMWE single cells and the associated analysis of I-V and impedance data and review and editing of the original draft.

Thin PVD coatings may provide corrosion protection for 316L-based PTLs to a limited extent as shown in the previous section 7.3, but uncoated areas of the PTL were still affected by corrosion and long term testing as well as electrolysis in a higher power range with thinner membranes and lower catalyst loadings are pending.

To protect uncoated areas of the PTL against corrosion, one approach is to coat the entire surface through an electroplating process, e.g. with gold [83]. However, this requires the use of an increased amount of precious metal. Hence a second way to improved corrosion protection is considered be the deposition of a thicker coating of several tens of micrometers on the CL-facing side to prevent the inside of the PTL from being exposed to anodic polarization.

To deposit thicker coatings than PVD, CGS was proposed by the institute IMD-2, as CGS not only enables thicker coatings (subsection 3.2.4), but additionally yields a rougher surface morphology, increasing the contact area with the CL and thus the amount of catalyst sites used. Furthermore, CGS is a scalable process for deposition of coatings beyond the laboratory scale. As this coating technique uses a powder, 316L felt PTLs could not be used as substrate, as the pore openings of the felt of a few micrometers would be closed by the coating (particle size distribution and average particle size see Table 3.4). Therefore, CGS coatings were only applied on 316L meshes.

There are indications about a minimal thickness required for a corrosion protection layer of around 200 μm in the literature [59]. As the amount of closed openings in the expanded metal increases with thicker coatings, a coating thickness of $60 \pm 12 \mu\text{m}$ (CG-60) was chosen to ensure that the openings stayed open. Further experiments with the aim of reducing the thickness and consequently the amount of titanium used, involved coatings with $48 \pm 15 \mu\text{m}$ (CG-48) and $33 \pm 14 \mu\text{m}$ (CG-33) titanium layers. To investigate the influence of the stainless steel expanded mesh, a comparative experiment was carried out with a Ti CGS coated Ti expanded mesh layer (TiEM_Ti-CG with Pt). Due to the particle size distribution of the titanium powder, the standard deviation of the thickness of the coating results on average in 16 μm . Detailed information fluctuations of the layer thickness can be found in Table 3.5.

Figure 7.15 displays top view and cross section SEM images of the coated expanded meshes and Figure 7.16 provides an overview of the ICR changes of all the PTLs discussed within this chapter. The discussion and interpretation of the ICRs follows in the subsequent subchapters.

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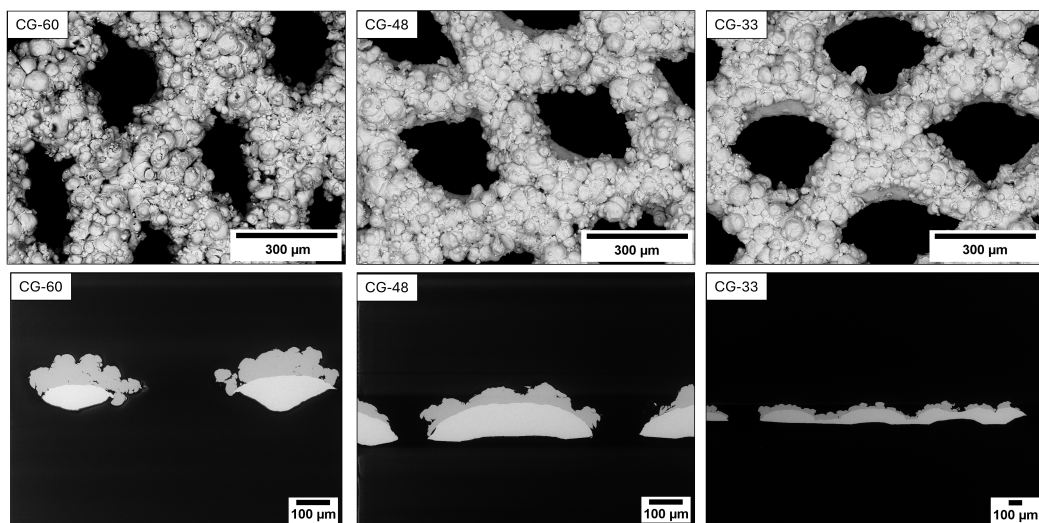


Figure 7.15. SEM top view and cross section images provided by Sievert [151] (IMD-2) of 316L expanded metals with CGS titanium coatings.

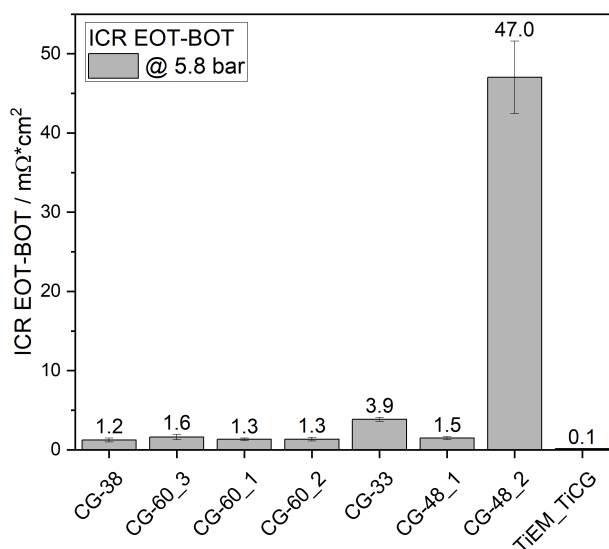


Figure 7.16. Increase of the interfacial contact resistance determined at a pressure of 5.8 bar between two gold plated copper plates (section 3.7) before and after PEMWE single cell testing of 316L mesh PTLs with $33 \pm 16 \mu\text{m}$, $48 \pm 16 \mu\text{m}$ and $60 \pm 16 \mu\text{m}$ titanium CGS and Pt PVD coatings and one titanium expanded mesh with titanium CGS coating and Pt PVD coating (TiEM_TiCG). The maximum operation times at 2.0 V amounted for 1006 h with CG-60 PTLs, 1004 h with CG-48 PTLs, 362 h with the CG-33 PTL and more than 514 h with TiEM_TiCG.

7.4.1. 60 μm titanium on 316L expanded meshes

With CG-60 PTLs, two parallel experiments were conducted. The results are presented in Figure 7.17, including the development of mean I-V curves and the high frequency resistances from two parallel experiments with $60 \pm 16 \mu\text{m}$ coated 316L mesh PTLs (CG-60).

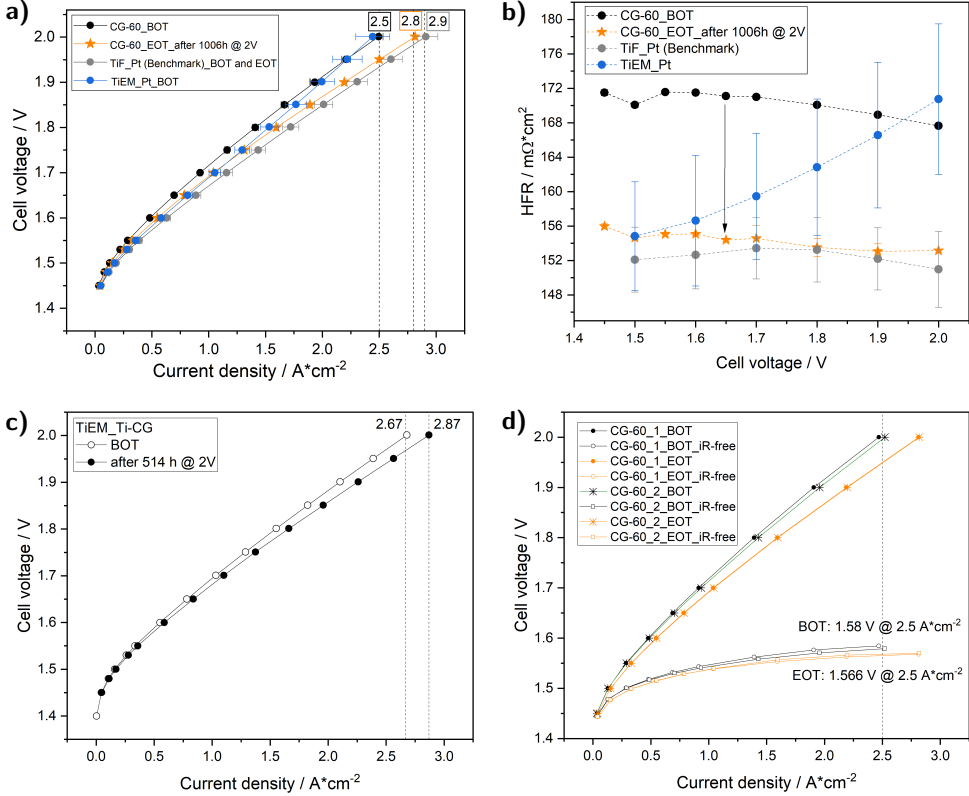


Figure 7.17. a) Mean I-V curves with two 316LEM_CG-60_Pt PTLs compared with benchmark Pt coated TiF PTLs and TiEM_Pt; b) Corresponding HFRs from impedance spectra in dependence of the cell voltage. HFRs with Benchmark and TiEM_Pt PTLs after 457 h are not shown as there was no significant change (Figure 5.2a and Figure 5.5a); c) I-V curves of a PEMWE single cell with TiEM_CG-38_Pt PTL for comparison with 316L based PTLs; d) I-V and iR-free curves with CG-60_1 and CG-60_2.

Both, the I-V curves and the development of the HFRs reflect an increased cell performance after 1006 h at 2.0 V, with a performance at the end of test being close to the performance with a benchmark Pt coated TiF PTL. The current profile during the potentiostatic long-term test at 2.0 V with CG-60 PTLs is provided in Figure A.52.

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At the beginning of the test, no performance difference could be seen within the margin of error between a TiEM_Pt and 316LEM_CG-60_Pt PTL. Differences occurred only after long-term operation. While the performance without CGS coating remained stable after 457 h (Figure 5.5a), an increase in performance was observed with the CG-60 PTLs. Also with the full Ti PTL TiEM_Ti-CG, a performance increase was visible after 514 h (Figure 7.17c) and the HFR decreased from $156 \pm 1 \text{ m}\Omega \text{ cm}^2$ to $146 \pm 1 \text{ m}\Omega \text{ cm}^2$ after 536 h (Figure A.53).

Consequently, the performance increase can be attributed to the properties of the CGS coating and is not a result of membrane thinning due to iron emission, as was observed previously with corroding 316L based PTLs.

Post mortem membrane thicknesses were on average between $218 \pm 15 \mu\text{m}$ to $229 \pm 10 \mu\text{m}$, which is in the range of membrane thicknesses measured with titanium PTLs after long-term experiments, confirming that no measurable membrane thinning took place.

As with the stainless steel felt PTL, adaptation of the MEA to the non-uniform structure of the CGS layer can lead to better contact between the PTL and the catalyst layer. These adaptation process can take several hundred hours [184]. While the increase of the current density at 2.0 V was 0.04 A cm^{-2} for the benchmark after 457 h (Figure 5.2), the increase with CGS coated PTLs was 0.4 A cm^{-2} after 1006 h, supporting that the adaption of the MEA to the PTL surface might be more pronounced for the CGS coated PTLs than for PTLs with a smoother surface that are coated via PVD. The performance with a Pt coated TiEM even decreased slightly (Figure 5.5).

Another factor contributing to the enhanced performance of CGS coated PTLs compared to pure mesh PTLs might be an improved mass transport due to the combination of the large mesh opening with smaller pores of the coating, as Lee et al. [177] found that the gas saturation is reduced and hence mass transport improved, if pores with a significantly larger pore diameter than the average pores are present in the PTL. Compared to an uncoated mesh, the CGS coating potentially provides pores with a high capillary pressure where water invades easily. Impedance spectra revealed no signs of mass transport limitations (Figure A.54a and Figure A.55a). Furthermore, no features were identifiable at low frequencies, as was the case with corroding PTLs, indicating that the CG-60 PTLs exhibit a significant enhanced corrosion stability over 316L PTLs with thin PVD coatings.

Performance improvement due to an increase in catalyst activity was negligible, as the iR-free cell voltage at 2.5 A cm^{-2} only dropped by about 1.4 mV (Figure 7.17d), indicating that a higher share of performance improvement was caused by decreasing ohmic resistances, reflected by the HFR (Figure 7.17b). In addition, ICP-MS was used to monitor if any corrosion products like Fe, Cr, Ni, Mn or Mo were released from the PTLs. For this purpose, water samples were taken directly from the anode and cathode outlets of the cells during operation (effluent water, see Figure 7.18a) and samples from the storage tanks before and after the experiment. In the storage tanks (volume: 15 L to 20 L), no stainless steel components were detected (DL Fe, Cr and Ni: $0.3 \mu\text{g L}^{-1}$, DL Mo: $0.05 \mu\text{g L}^{-1}$, DL Mn: $0.1 \mu\text{g L}^{-1}$).

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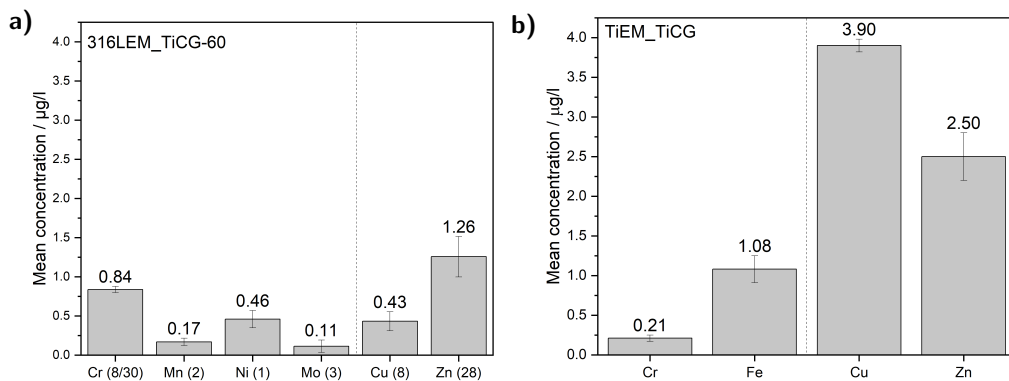


Figure 7.18. a) Mean concentrations derived from ICP-MS analysis of Cr, Fe, Mn, Ni, Mo, Zn and Cu from the anode and cathode outlet during 1006 h PEMWE single cell tests at 2.0 V with 316LEM_TiCG-60 PTLs. The number of samples in which the respective analyte was found are indicated in brackets. b) Water sample from the anode side during PEMWE operation with TiEM_TiCG-38 (full titanium PTL) for comparison.

During electrolysis operation, no iron and only small amounts of chromium in 8 out of 30 samples ($0.84 \pm 0.04 \mu\text{g L}^{-1}$), Mn in 2 out of 30 samples ($0.17 \pm 0.05 \mu\text{g L}^{-1}$) and Ni in one sample ($0.46 \pm 0.01 \mu\text{g L}^{-1}$) were detected in the effluent water, whereby the 1σ error bars given for the Cr and Ni concentrations correspond to the variance among the samples illustrating their distribution, while the deviation given for the Ni concentration corresponds to the measurement uncertainty. The sample with Ni was from the anode side of CG-60_2. Mn was only detected at the cathode during conditioning in one sample of each cell. Hence, it can be assumed that no continuous corrosion of manganese took place, as Mn was dissolved by the water flow without influence of anodic polarization. Furthermore, detecting chromium is probable, as it is the most abundant element at the surface of 316L [185].

Except for Cr, all concentrations were below what was found in Milli-Q water exposed to an uncoated 316L expanded mesh for about 90 h at 80°C and 80 h at room temperature (c.f. Figure A.38). In addition to the slightly different limits of detection for each measurement due to calibration, it must be noted that the residence time of the water in the cell is short due to the high flow rate and the concentrations are therefore in the ppb range. Nevertheless, in case of a higher corrosion rate, as seen with PVD coated stainless steel based PTLs, occasionally much higher concentrations occurred (c.f. Figure A.36 and Figure A.41). Furthermore, the absence of iron points to a low to negligible corrosion rate. Figure 7.18b shows the results from the analysis of water samples with a similar full titanium PTL consisting of a Ti expanded mesh with Ti CGS layer (TiEM_TiCG) for comparison. Within this experiment, $0.21 \mu\text{g L}^{-1}$ chromium and $1.08 \mu\text{g L}^{-1}$ iron were found in the effluent water. As components of the test bench can be excluded as a source of Fe and Cr and stainless steel PTLs

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were tested only in other test places on the bench, it is possible that during sampling impurities in the test hall were introduced via the air by steel pillars that were present during renovation work. Therefore, it must be assumed that at least the analysis of Cr and Fe from the cell outlets cannot be fully attributed to the emission of stainless steel from the PTL.

Additionally, within EDX analysis of 404 spectra from MEA cross sections that were operated with CG-60_1 and CG-60_2, no Fe, Cr and Ni were detected in the anode and cathode CL as well as the membrane, but Ti was present in some samples, indicating titanium dissolution from the coating at the anode side and migration to the cathode side, while no Ti was detected in water samples by ICP-MS (DL: $0.2 \mu\text{g L}^{-1}$). Titanium dissolution at the anode and migration to the cathode was also reported by Tan et al. [121], especially in the presence of F^- ions. As no thinning of the membranes was observed, it can be assumed that fluoride emission was negligible and that titanium dissolution was not accelerated by F^- ions. Additionally shown in Figure 7.18 are Cu and Zn impurities, which occasionally occurred during PEMWE single testing without any recognizable pattern. However, considering EIS spectra and I-V curves, the amount of impurities here seem not to influence cell performance, although Cu is reported to impact the HER, but can also be removed from the cell [131]. Research about the impact of Zn impurities in PEMWE is not available.

Based on I-V curves, impedance spectra and EDX analysis of membrane cross-sections, it can be concluded that the stainless steel base of the PTL did not negatively impact PEMWE operation, despite occasional low concentrations of Cr, Mn and Ni in the effluent water. The observation that a $60 \pm 16 \mu\text{m}$ CGS layer can sufficiently protect a stainless steel PTLs against corrosion is consistent with the results from Stiber et al. [67], who also found no signs of corrosion with stacked vacuum plasma sprayed (VPS) Ti and Nb coatings on 316L meshes with a cumulative thickness of about $24 \mu\text{m}$ to $94 \mu\text{m}$.

With the $60 \pm 16 \mu\text{m}$ Ti-coated 316L mesh based layered PTLs, a titanium saving of 25 % can be achieved compared the conventional full titanium felt PTL used within this work. The calculation is based on the assumption that the area-specific weight of the TiF PTL, calculated with a thickness of $360 \mu\text{m}$, an average porosity of 68 % and titanium density of 4.5 g cm^{-3} , amounts for $52 \text{ mg}_{\text{Ti}} \text{ cm}^{-2}$. The area-specific weight of the CGS coating is $21.6 \text{ mg}_{\text{Ti}} \text{ cm}^{-2}$ (c.f. Table 3.5) and over spraying is taken into account yielding an estimated deposition efficiency of around 55 % [183]. The detailed calculation of the titanium savings is given in the appendix in Equation A.3 to Equation A.9.

7.4.2. Reduction of the titanium layer thickness

As the experiments with $60 \pm 16 \mu\text{m}$ coated stainless steel expanded metals enabled stable performance for 1006 h at 2.0 V, the thickness of the titanium CGS layer was reduced to $48 \pm 16 \mu\text{m}$ (CG-48) and $33 \pm 16 \mu\text{m}$ (CG-33). Experiments with CG-48 PTLs ran for 1004 h at 2.0 V, whereby

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the ion exchangers were removed after 420 h to accumulate possible corrosion products in the water tanks with the intention to potentially increase the concentrations of impurities above the DLs of ICP-MS analysis and decrease standard deviations. During the experiments with CG-48 and CG-33, a short interruption occurred after 156.5 h. The results with two cells with $48 \pm 16 \mu\text{m}$ coated PTLs (CG-48_1 and CG-48_2) will be discussed first. CG-48_2 was not coated with Pt on the FF-facing side, as was conducted as standard with most other PTLs. By that it was intended to examine whether corrosion increases without a coating on the FF-facing side. Furthermore, the results from CG-48_1 and CG-48_2 were not averaged as the results were slightly different.

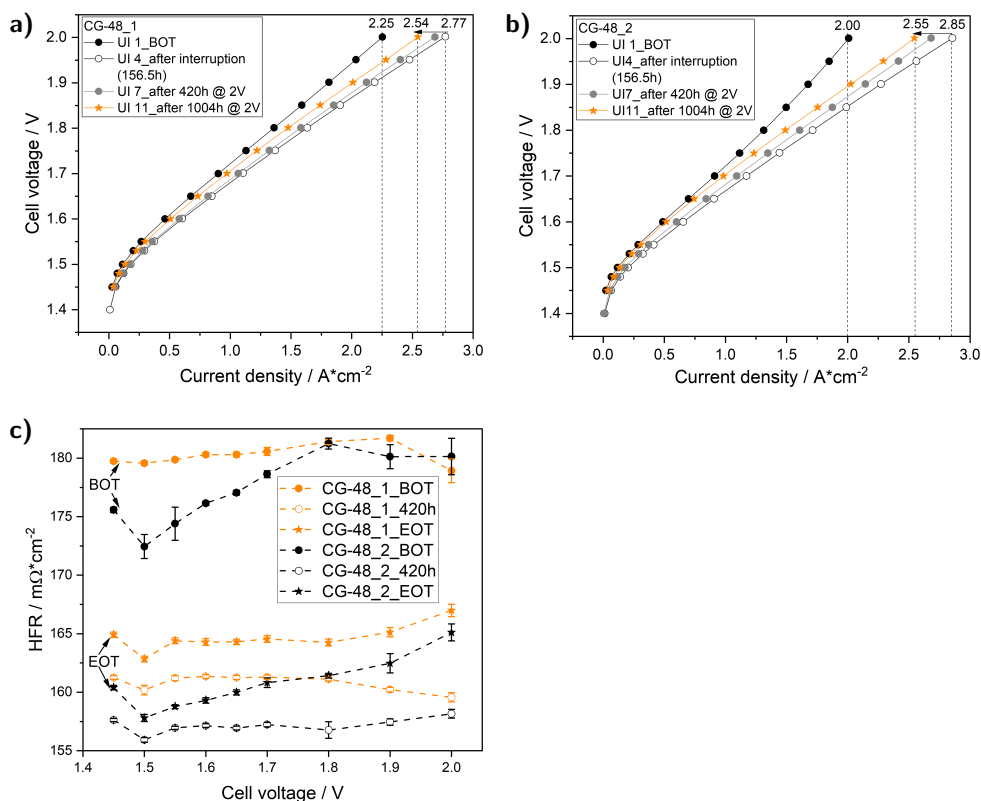


Figure 7.19. a) and b) I-V curves of two PEMWE single cells with 316LEM_CG-48 PTLs. The temperature with CG-48_2 (b) was unintentionally elevated to 81 °C to 86 °C within the last 450 h of operation; c) Corresponding HFRs from impedance spectra in dependence of the cell voltage.

Although an initial increase in performance was also visible with thinner Ti layers after an interruption after 156.5 h, the cell performance dropped until 420 h and furthermore until the end of test (Figure 7.19a and b). The development of the high frequency resistances showed a similar

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trend (Figure 7.19c). The cells started with mean HFRs of $180.3 \pm 0.1 \text{ m}\Omega \text{ cm}^2$ (CG-48_1) and $177.3 \pm 0.3 \text{ m}\Omega \text{ cm}^2$ (CG-48_2). After 420 h, the cell resistance dropped to $161 \pm 1 \text{ m}\Omega \text{ cm}^2$ and $157 \pm 1 \text{ m}\Omega \text{ cm}^2$ respectively and slightly increased again to $165 \pm 1 \text{ m}\Omega \text{ cm}^2$ and $161 \pm 2 \text{ m}\Omega \text{ cm}^2$ after 1004 h. At the end of test, the HFR at 1.9 V and 2.0 V was slightly higher than at lower potentials, indicating the blockage of proton channels, as more pathways for protons are needed at high current densities. A higher HFR at higher current densities in presence of $5 \mu\text{g L}^{-1} \text{ Ca}^{2+}$ contamination was also reported by Padgett et al. [124]. Until 420 h, the CT resistance exhibited a decreasing trend and an increasing trend from 420 h until the end of the test, as visible from Nyquist plots displayed in the appendix (Figure A.57 and Figure A.58).

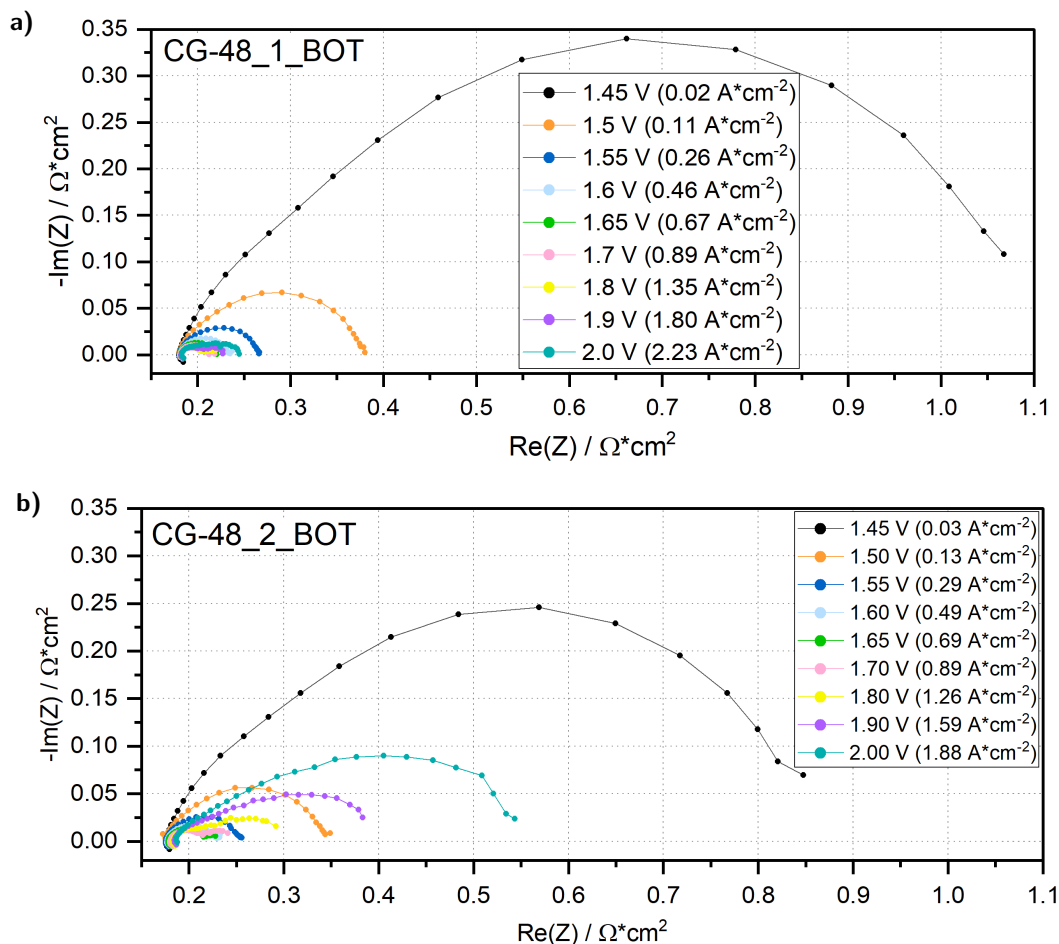


Figure 7.20. Impedance spectra between 100 mHz and 10 kHz of PEMWE single cells with CG-48_1 and CG-48_2 at the begin of test.

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Impedance spectra at the begin of test are displayed in Figure 7.20, as with CG-48_2, an additional feature at low frequencies above 1.8 V was most pronounced in the spectra at the begin of test after conditioning. Also with CG-48_1, increased low-frequency resistances were observed above 1.9 V. Increased low frequency resistances, resulting in "widening" of the semicircle at higher current densities, were also observed and discussed in previous chapters where corrosion took place and was described by Padgett et al. [124] as an additional feature at high current densities, most likely related to a depletion of protons on the cathode side and thereby increasing the overvoltage for the hydrogen evolution reaction (HER). However, unlike Padgett et al., no "S-shaped" I-V curves were observed, which they observed in conjunction with Na^+ concentrations above $50 \mu\text{g L}^{-1}$, when the cathode is depleted of protons to such an extent that hydrogen evolution can no longer take place via a reduction of protons and changes to the alkaline HER at a cell voltage beyond 2.0 V [125]. Consequently, the level of contaminants from corrosion was probably low enough to influence the reaction at the cathode side, but to a limited extent. Likewise, the iR -free cell voltage decreased slightly after 420 h, indicating a small increase in catalyst activity, but increased towards the end of test, thus changed only minimally throughout the experiment (Figure A.56). Consequently, with iR -free curves, inactivation of the catalysts could not be proven, while it is possible that parts of active catalyst sites were permanently blocked.

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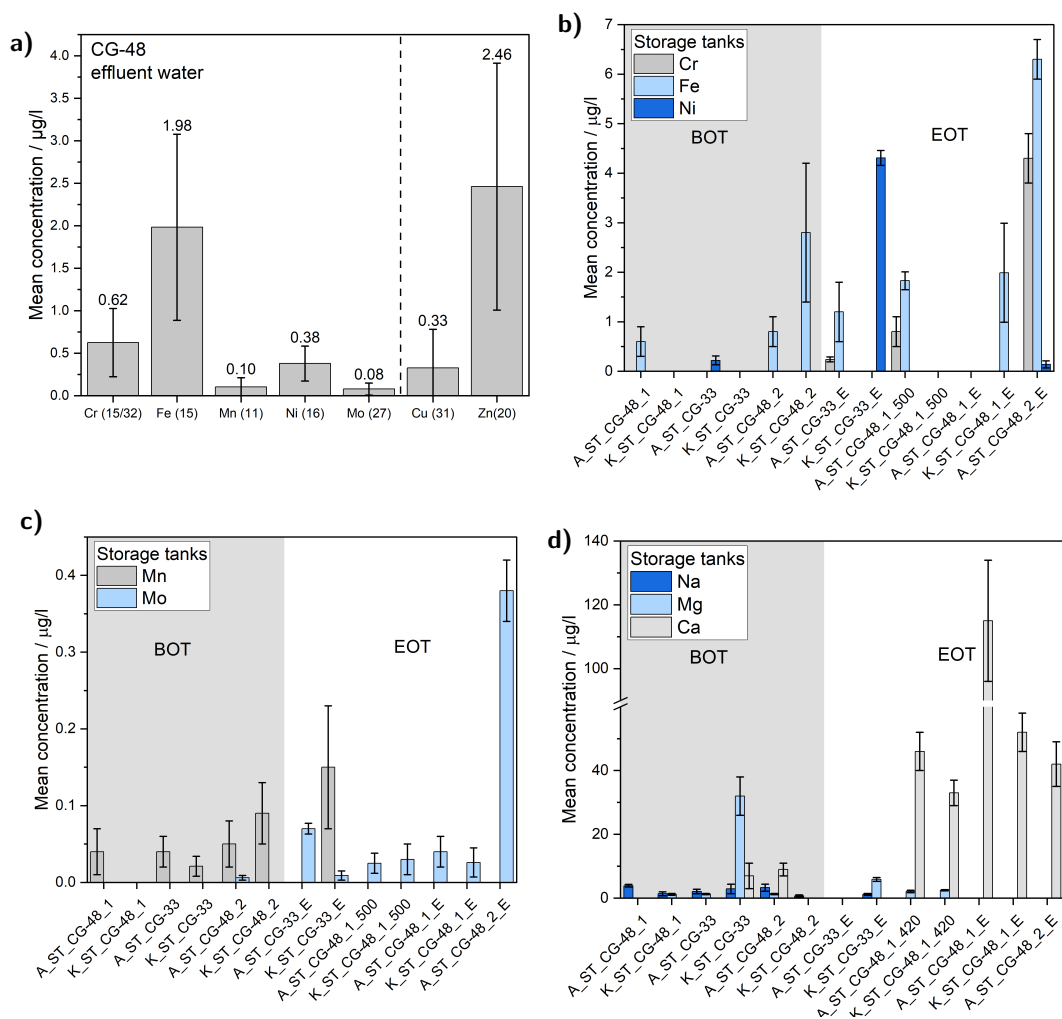


Figure 7.21. ICP-MS analysis from the anode and cathode outlet from PEMWE single cell testing. a) Mean concentrations during 1004 h at 2.0 V with CG-48. The number of samples in which the respective analyte was found are indicated in brackets. For the mean concentration of Zn in the effluent water, 3 samples were excluded as they amounted for $11.2 \pm 0.7 \mu\text{g L}^{-1}$ (anode CG-48_1), $9.4 \pm 1.2 \mu\text{g L}^{-1}$ (anode CG-48_2) and $50 \pm 30 \mu\text{g L}^{-1}$ (cathode CG-48_1). b-d) ICP-MS analysis of samples from the storage tanks (ST) used for PEMWE single cell testing with CG-48_1, CG-48_2 and CG-33; A= anode tank, K= cathode tank, 420= after 420 h of operation before removal of the ion exchange resins, E= EOT, marked with a white background. Samples taken prior to the experiment (BOT) are marked with a gray background.

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Compared to the experiments with $60 \pm 16 \mu\text{m}$ Ti CGS coatings, iron was present in the effluent water with $48 \pm 16 \mu\text{m}$ Ti CGS coated PTLs (Figure 7.21a vs Figure 7.18a). However, further impurities like Ca were found in some samples, hence iron emission cannot be clearly identified as the only cause for a decreasing performance. As standard, the water is filtered using ion exchangers before it is delivered to the cell. To investigate if any corrosion products accumulate during the experiment and to simplify water analysis with CG-33 and CG-48 PTLs, the ion exchange resins were removed after 420 h of operation. While the concentrations of impurities like Na, Mg, K and Al did not increase, the concentration of Ca significantly increased from maximum $12 \pm 7 \mu\text{g L}^{-1}$ to an average of $56 \pm 5 \mu\text{g L}^{-1}$ and maximum of $115 \pm 19 \mu\text{g L}^{-1}$ (Figure 7.21d). Thus the cell performance might be additionally affected by Ca^{2+} poisoning. However, the amount of Ca in the MEA detected by EDX (up to 1 at.% with one exception of 2.4 at.% at one point in an anode CL) was not higher as found in previous experiments with SMF+Pt samples with ion exchange resin (Figure A.30 to Figure A.32, Figure A.34 and Figure A.35). Additionally, as the cells were constantly operated at high current density and Ca^{2+} ions are known to get removed from the cell when operated at high current densities [124], the influence of Ca^{2+} on the cell performance can not be quantified. However, compared to Ca concentrations with long-term operated standard cells with Pt coated Ti felt anode PTLs (chapter 8), where Ca concentrations did not exceed 0.35 at.% in the MEA, the calcium concentrations found with 316L-based PTLs were higher. However, it must be noted that the atomic fractions obtained from different measurements cannot be directly compared, as the proportions depend on the presence of other elements. Whether or not there is a connection between the use of 316L-based anodes PTLs and accumulation of Ca^{2+} in the MEA can neither be confirmed nor ruled out. With SMF8_Pt_1, high concentrations of Fe, Ca and K were found at the cathode (see spectra in Figure A.30) while in all other spectra with SMF8_Pt_1 PTLs more Ca was found in the membrane than in the CL, while the Fe concentration in the CL was higher than in the membrane (Figure A.31, Figure A.32, Figure A.34 and Figure A.35). Consequently, the reasons and patterns of calcium distribution in the MEA cannot be solved on the basis of the data collected and would require further research. Based on the low Ca concentrations in the MEAs, it is assumed that Ca is more likely to be transported out of the cell than trapped in the MEA. Concentrations of all other 316L elements like Cr, Mn, Ni and Mo were in the same range as with experiments with CG-60 PTLs, but were present in more samples, the latter pointing to a higher rate of corrosion. Chromium was not present in the storage tanks before the experiment, but in three samples from storage tanks between $0.24 \pm 0.05 \mu\text{g L}^{-1}$ to $4.3 \pm 0.5 \mu\text{g L}^{-1}$ after the experiment (Figure 7.21b). The iron concentration in the storage tanks increased from $0.6 \pm 0.3 \mu\text{g L}^{-1}$ to $2.8 \pm 1.4 \mu\text{g L}^{-1}$ to $1.2 \pm 0.6 \mu\text{g L}^{-1}$ to $6.3 \pm 0.4 \mu\text{g L}^{-1}$. Mn was only detected in one storage tank after the experiment ($0.15 \pm 0.08 \mu\text{g L}^{-1}$), but was detected in the tanks before the cell tests with concentrations near the detection limit ($0.021 \pm 0.013 \mu\text{g L}^{-1}$ to $0.09 \pm 0.04 \mu\text{g L}^{-1}$, DL: $0.02 \mu\text{g L}^{-1}$), as the limit of quantification was lower in the analysis BOT and first half of the experiment. The concentration of

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Ni was only elevated in the storage tank from the cell with a pump failure (CG-33), where visible corrosion took place ($4.31 \pm 0.14 \mu\text{g L}^{-1}$) and Ni was only detected in one storage tank prior to the experiment at a low level of $0.22 \pm 0.09 \mu\text{g L}^{-1}$. The levels of Mo were a bit higher in the tanks after than prior to the test, but still at a low level between $0.009 \pm 0.006 \mu\text{g L}^{-1}$ to $0.38 \pm 0.04 \mu\text{g L}^{-1}$. A comparison of the metal ion concentrations in the storage tanks before and after the cell tests can provide information about the emission of stainless steel elements, but it should be noted that the water levels and thus the concentrations in the storage tanks fluctuate due to the consumption and refilling of water. Furthermore, an influence of ions in the water tanks affecting electrolysis can only be assumed for the test part without ion exchanger. While the concentrations of Mn and Ni showed no clear trends, ICP-MS results from the analysis of Fe, Cr and Mo reflect, that surface corrosion took place presumably mainly on the uncoated surface of the 316L substrates. Although the cell with CG-48_2 operated at elevated temperatures between 81°C to 86°C over the last 450 h, the concentrations of stainless steel elements were in a similar range than with CG-48_1, either indicating that the elevated temperature did not accelerate corrosion or that the corrosion rates were close enough not to become reflected by analysis of the effluent water. The latter is assumed, as also in EDX spectra of the MEAs the amount of iron was close with both PTLs. However, as the FF-facing side of CG-48_2 showed stronger changes in form of discoloration compared to the FF-facing side of CG-48_1 (see photography Figure 7.22c), a higher corrosion rate can not be ruled out.

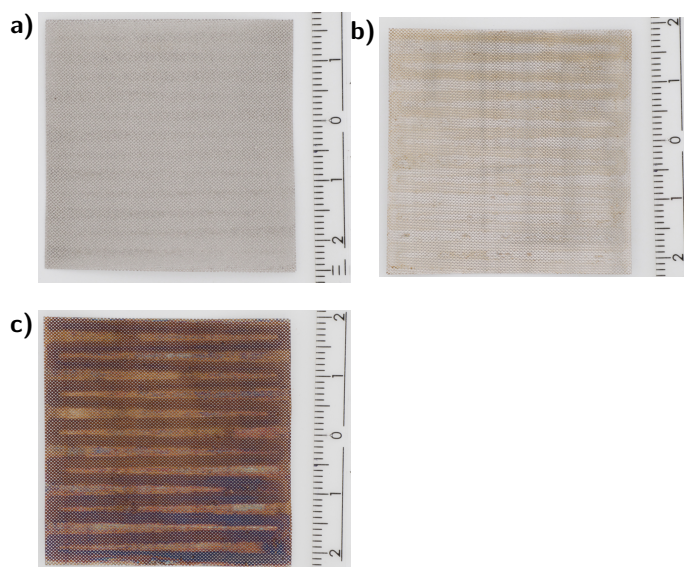


Figure 7.22. Post mortem photographs of: a) CL-facing side of CG-48_1, b) FF-facing side of CG-48_1 and c) FF-facing side of CG-48_2.

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EDX analysis of MEA cross sections revealed small amounts of 0.1 at.% to 0.6 at.% Fe and 0.1 at.% to 0.3 at.% Mo being present on or in the anode CL layers. In the anode CL from the MEA used with CG-48_2, Cr fractions of around 0.4 at.%, Mn fractions of around 0.55 at.% and Fe fractions of 0.6 at.% were present. Furthermore, in some spectra, titanium was detected up to 1.9 at.% at the anode side. Additionally, within two spectra from the cathode CLs maximum 2.26 at.% Ti was found, indicating that titanium was released from the coating at the anode side and migrated through the membrane, which has also been observed with CG-60 PTLs. Ni and Ir were detected in one spectrum at the cathode side (0.1 at.% and 0.7 at.% to 3.1 at.%, c.f. Pt fractions: 3.1 to 7.1 at.%), indicating nickel and iridium dissolution. Similar to the interpretation of ICP-MS results, it must be noted that the results from EDX measurements are only representative of random samples and therefore cannot provide a complete picture of the emission and distribution of corrosion products. Furthermore, the concentrations found were low, thus it can be assumed that the contaminants found are present in the MEAs, though a quantification is not possible.

Further randomly occurring trace impurities detected by EDX in the MEA included Na (up to 0.9 at.%), Mg (up to 0.8 at.%), K (up to 0.18 at.%) and Cu (up to 0.85 at.%). One further aspect pointing to a higher corrosion rate with CG-48 PTLs compared to CG-60 PTLs is the membrane thickness. While the post mortem membrane thickness with CG-60 PTLs and full titanium PTLs was $224 \pm 15 \mu\text{m}$ and $223 \pm 14 \mu\text{m}$, the membrane thickness with CG-48 PTLs was approximately $40 \mu\text{m}$ thinner (see Table A.1). Apart from the MEAs, cathode PTLs were analyzed via EDX mapping where one iron particle was present on the carbon paper used together with CG-48_1 and some iron in nine more spectra.

Another indicator of changed PTL surface properties is the interfacial contact resistance (ICR), which was determined before and after the experiments. While the increase of the ICR of all PTLs with $60 \mu\text{m}$ and $48 \mu\text{m}$ CGS coatings were between $1.23 \text{ m}\Omega \text{ cm}^2$ and $1.61 \text{ m}\Omega \text{ cm}^2$, the ICR increase of CG-48_2 without Pt coating on the FF-facing side and a temporary higher cell temperature was significantly higher, as the resistance increased by $47 \text{ m}\Omega \text{ cm}^2$ (Figure 7.16) and tarnish colors on the back side were visible (Figure 7.22). Unfortunately, the unplanned superimposition of two effects, the missing coating on the FF-facing side and increased temperature, impedes identifying the cause for the more pronounced changes to the FF-facing side of CG-48_2. However, the ohmic resistance (HFR) did not increase more with CG-48_2 than with CG-48_1. Consequently, the ICR can give an indication of changes in PTL surface conductivity, but cannot predict the ohmic resistance during operation. Other factors, which are not part of the ICR measurement setup, such as the contact pressure between components or the in-plane conductivity of the MEA might lead to these deviations.

CG-33

The experiment with CG-33 was shortened to 362 h, as the corrosion of iron was visible in form of reddish deposits at the cell outlets after an unplanned interruption of the water supply after 201.5 h of operation. As mentioned before, another interruption of the test bench occurred after 156.5 h.

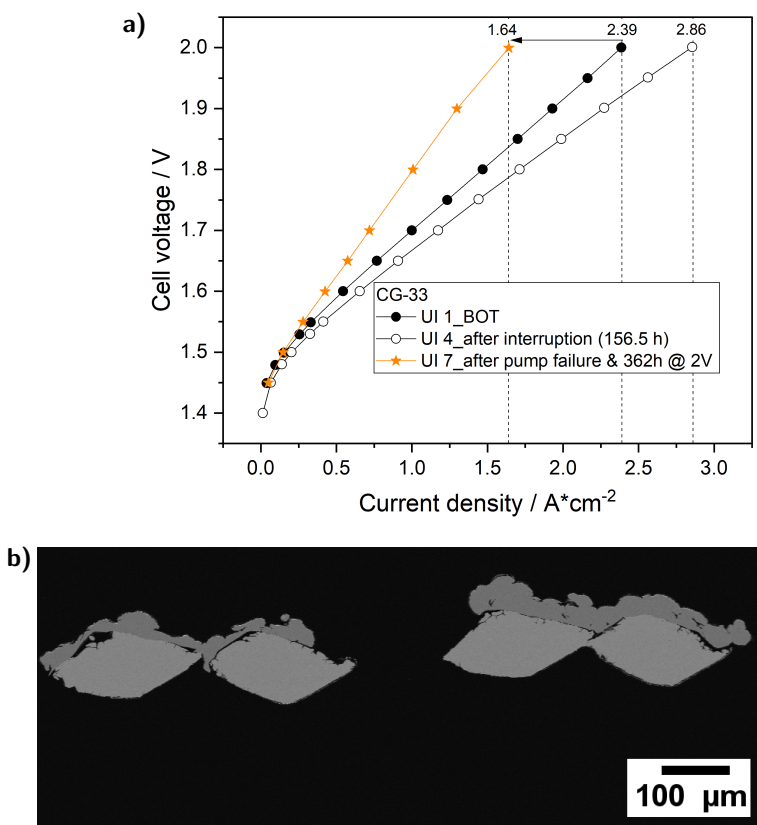


Figure 7.23. a) I-V curves with 316LEM_CG-33; b) Post mortem SEM cross section of CG-33 provided by Sievert [151].

The initial performance of the cell with a $33 \pm 16 \mu m$ Ti coated 316L mesh anode PTL (CG-33) was in the the same range as all other Ti coated 316L mesh anode PTLs ($2.39 A \cdot cm^{-2}$ vs. $2.1 A \cdot cm^{-2}$ to $2.5 A \cdot cm^{-2}$). Also with CG-33, an initial performance increase was visible (Figure 7.23a), but after 201.5 h at 2.0 V, the pump stopped working and the water supply was interrupted for 62.5 h. After 62.5 h (264 h total operating time), the water supply was re-established and the cell operated for another 98 h at 2.0 V. As the cell voltage was limited to 2.0 V, the pump failure did not lead to an increased cell voltage, but it is likely, that the membrane and the catalyst layers dried out. During the period of interrupted water supply, a total current below 1 A was recorded, as the remaining

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water in the pipes was possibly enough to run electrolysis at a small rate for a certain period of time. However, the cell performance dropped after dry running and reddish discoloration at the cathode outlet became visible. Therefore, the experiment was terminated after 362 h operating hours at 2.0 V.

The post mortem cross section of the PTL showed that corrosion had also occurred under the corrosion protection layer, see Figure 7.23b. As this was not observed with the PTLs with thicker coatings, it can be inferred that a coating thickness of 17 μm to 49 μm is not sufficient for corrosion protection. In one water sample from the effluent water at the cathode side before the pump failure, increased iron and nickel concentrations occurred ($170 \pm 20 \mu\text{g L}^{-1}$ and $12.7 \pm 0.3 \mu\text{g L}^{-1}$, see Figure A.59). Apart from this temporary increase, the concentrations of stainless steel elements with CG-33 were similar compared to the experiments with CG-48 PTLs. Consequently, also with regards to ICP-MS analysis with a pure titanium PTL, corrosion or roughing processes might not occur continuously. Furthermore, this supports, that the detection of stainless steel elements might be dependent on whether or not dissolution occurs during sampling and if the metal ions are adsorbed within the MEA. Consequently, for a reasonable interpretation of ICP-MS results, further analytics, such as EDX spectroscopy of MEA cross sections and the carbon PTL, are necessary to detect stainless steel elements remaining in these components.

The ICR increase of CG-33 was only slightly higher than with PTLs without incident ($3.85 \text{ m}\Omega \text{ cm}^2$ vs. around $1.4 \text{ m}\Omega \text{ cm}^2$, Figure 7.16). However, impedance spectra with CG-33 indicated degradation of the catalyst. At the begin of test after conditioning, the difference between low- and high frequency resistance, also referred to as charge transfer resistance (R_{CT}), possibly with an unknown fraction of resistance due to mass transport, only decreased up to 1.65 V, stayed constant between 1.65 V to 1.8 V and increased above 1.8 V (Figure A.60a). High charge transfer resistances were even more pronounced in the spectra at the end of test, where the R_{CT} only decreased up to 1.6 V and stayed constant up to 2.0 V (Figure A.60b). Although the slope of the I-V curve was steeper at the end of the test than at the beginning (Figure 7.19), no strong bending can be noted, hence the loss of performance cannot be attributed solely to an increased overvoltage of the redox reactions. As described above, these features at low frequencies and increased charge transfer overvoltage at high current densities are associated with cation poisoning of the membrane leading to proton depletion at the cathode side [124]. Although the beginning of visible corrosion coincided with the failure of the water supply and thus the dehydration of the cell, it can nevertheless be concluded that a $33 \pm 16 \mu\text{m}$ coating is not sufficient to protect the stainless steel mesh in the event of incidents such as a pump failure.

In summary, stable electrolysis operation close to the performance of standard Pt-coated titanium PTLs was confirmed with 316L expanded mesh PTLs coated with a $60 \pm 16 \mu\text{m}$ CGS titanium layer and thin Pt PVD layer on top (CG-60) by I-V curves, SEM and EDX analysis of the MEAs, as well as ICP-MS analysis of water samples from anode and cathode outlets. Furthermore, from Nyquist

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plots with CG-60, no features were identifiable at low frequencies, as was the case with corroding 316L felt PTLs that were coated with thin PVD coatings, underlining no poisoning of the CL or blocking of proton channels. Consequently, thicker CGS coatings provide improved corrosion protection compared to thin PVD layers.

During experiments with slightly thinner titanium CGS layers ($48 \pm 16 \mu\text{m}$), the ion exchange resin prior to the cell inlet was removed after 420 h to accumulate possible corrosion products in the storage tanks. Increased iron concentrations were found in the effluent water from the anode and cathode outlets compared to experiments with CG-60 PTLs. However, concentrations of all other stainless steel elements were in similar ranges, but the number of contaminated samples was higher. Consequently, based on ICP-MS analyses, a slight trend towards a higher corrosion rate with decreasing coating thickness could be identified. However, traces of Cr and Fe were found in water samples with a full titanium PTL for comparison (TiEM_TiCG). Therefore, it must be assumed that at least the analysis of Cr and Fe from the cell outlets cannot be fully attributed to the emission of stainless steel from the PTL.

Complementary EDX spectra of MEA cross sections and the catalyst surfaces revealed that higher concentrations of stainless steel elements were present post mortem in the MEAs operated with CG-48 PTLs. Consequently, ICP-MS analysis is not sufficiently indicative for a comparison of corrosion rates due to corrosion products remaining in the MEA. In addition, a higher corrosion rate compared to experiments with CG-60 PTLs is assumed, as the experiments with CG-48 PTLs showed a slight decrease in performance. However, also higher concentrations of Ca were identified upon removal of the ion exchanger, with an unknown influence on cell performance, complicating a conclusive evaluation of the experiments with CG-48 PTLs.

Nevertheless, from EDX analysis of the MEAs, it can be derived, that the coating thickness should be at least $60 \pm 16 \mu\text{m}$ to achieve sufficient corrosion protection of the PTL bulk, whereby thicker coatings could possibly provide even better protection against corrosion.

A higher corrosion rate of the CG-48 PTLs can further be confirmed based on the post mortem thickness of the membranes. While no membrane thinning was observed with CG-60, the post mortem thickness of the membranes operated with CG-48 was approximately $40 \mu\text{m}$ reduced, pointing to degradation of the polymer through radical reactions catalyzed by iron ions.

Furthermore, it can be concluded that corrosion was assumed not to occur on the CL-facing side of the PTLs CG-60 and CG-48, as the titanium- and platinum-coated CL-facing sides appeared to be unchanged post mortem. In contrast, corrosion was observed under the titanium coating with PTLs coated with the thinnest CGS coating (CGS-33). Furthermore, all PTLs showed discolored spots on the FF-facing side, mainly at contact points with the plate, and partly on the cutting edges without MEA contact, as these were protected by a subgasket. Isolated Ti particles were found by EDX analysis in all MEAs at at least one point at the cathode side, indicating that titanium dissolution of the anode PTL coating and migration to the cathode side occurred, whereby no impact on the

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cell performance could be identified. Apart from CG-60 PTLs, a Ti expanded metal coated with Ti by CGS and sputtered with the standard Pt contact layer (38 nm) was also successfully tested for a comparison with 316L mesh based PTLs. Although this PTL is a full Ti PTL, Ti could nonetheless be saved compared to thicker titanium sintered bodies or felt PTLs, as the CGS layer must not be as thick as possible to provide corrosion protection, as the purpose of a CGS coating on titanium expanded metal is to improve the properties of the PTL surface by increasing the contact area with the CL.

7.5. Summary titanium-reduced and 316L based PTLs

To investigate the strength of corrosion protection in dependence of the layer thickness, coatings in the order of magnitude

- $< 1 \mu\text{m}$ (Pt PVD at IET-4)
- $3.8 \mu\text{m}$ (Ti PVD at IMD-2 [151] with Pt PVD at IET-4)
- and $> 10 \mu\text{m}$ (Ti CGS at IMD-2 [151] with Pt PVD at IET-4)

were deposited on 316L PTLs. An overview of the current densities at 2.0 V and the current density after operation at 2.0 V are summarized in Table 7.3. Furthermore, it is indicated whether membrane thinning was observed in SEM cross sections, provided corresponding measurements were available. As membrane thinning occurs due to the attack of radicals, which are produced by iron-catalyzed Fenton reactions (see Figure 7.24), membrane thinning is an indicator of stainless steel corrosion.

Table 7.3. Current densities at 2.0 V at the BOT and the current density after operation at 2.0 V for the time indicated in brackets with all 316L based PTLs.

Sample	Current density BOT at 2.0 V / A cm^{-2}	Current density after operation at 2.0 V, time indicated in brackets / A cm^{-2}	Membrane thinning ¹	Related section
316LEM_Pt_1	0.119	no data due to instability	not determined	7.2.1
316LEM_Pt_2	0.064	no data due to instability	not determined	7.2.1
316LEM_Pt_3	0.058	no data due to instability	not determined	7.2.1
SMF8_Pt_1	0.91	2.63 (525 h)	not certain based on available data	7.2.2
SMF8_Pt_2	1.55	2.57 (1452 h ²)	yes	7.2.2
316LEM_Ti-PVD_Pt_1	1.83	2.1 (54 h)	not certain based on available data	7.3.1
316LEM_Ti-PVD_Pt_2	1.07	1.85 (54 h)	not certain based on available data	7.3.1
SMF8_Ti-PVD_Pt	2.2	2.98 (532 h)	not certain based on available data	7.3.2
SMF22_Ti-PVD_Pt	0.94	3.25 (532 h)	not certain based on available data	7.3.2
316LEM_Ti-CGS-60_Pt_1+2	2.50 ± 0.04	2.82 ± 0.004 (1006 h)	no	7.4.1
TiEM_Ti-CGS-38_Pt	2.67	2.87 (514 h)	not determined	7.4.1
316LEM_Ti-CGS-48_Pt_1	2.25	2.54 (1004 h)	yes	7.4.2
316LEM_Ti-CGS-48_Pt_2	2.00	2.55 (1004 h)	yes	7.4.2
316LEM_Ti-CGS-33_Pt	2.39	1.64 (362 h ³)	not determined	7.4.2

1: determined using SEM analysis of MEA cross sections (see Table A.1), 2: including 1115 h wind profile operation (see Figure 8.1c) and 337 h at 2.2 A cm^{-2} , 3: with temporary interruption of the water supply.

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As visible from Table 7.3, a thin Pt coating on 316L expanded mesh PTLs was not sufficient to prevent rapid corrosion (316LEM_Pt_1+2), as no recording of I-V curves beyond the first one was possible. In contrast, Pt-coated 316L felt PTLs (SMF8_Pt_1+2) exhibited superior corrosion stability. Corrosion could be observed also with these PTLs, leading to membrane thinning, but experiments could be carried out for up to 1452 h. It remains unexplained where the different stabilities between the mesh and felt originate, but it can be anticipated that different Mo contents, other surface properties or the different thicknesses of the PTLs contributed to different corrosion properties.

With an additional Ti-PVD interlayer between PTL and thin Pt coating (316LEM_Ti-PVD_Pt_1+2), the stability of 316LEM-PTLs was significantly enhanced. However, already during the short test duration of 54 h, iron contamination was found in the anode CL and membrane thinning was observed. Consequently the PVD layers were too thin to provide sufficient corrosion protection. Additionally, with Ti-PVD interlayers on 316L felt PTLs with 8 μm and 22 μm fibers (SMF8_Ti-PVD_Pt and SMF22_Ti-PVD_Pt), higher current densities of up to 3.25 A cm^{-2} were achieved. However, also after these experiments (532 h), membrane thinning could not be ruled out.

With thicker CGS coated 316L mesh PTLs, high current densities compared to benchmark PTLs (up to 2.9 A cm^{-2}) could be achieved without membrane thinning (c.f. Figure 7.24). This was particularly noticeable with $60 \pm 16 \mu\text{m}$ titanium coatings (CG-60), as these coatings provided the best corrosion protection. Thereby, the current density increased from the BOT to 1006 h of operation, as presumably the conditioning phase was not completed after the standard conditioning time of 15 h. A prolonged conditioning time might stem from the fact that the surface of this powder coating is significantly more uneven and rough compared to PVD coatings, requiring the MEA to swell into its structure over a longer period of time.

Consequently, the surface structure of the CGS coating allows for the formation of more three-phase boundaries compared to pure expanded meshes or PVD coated PTLs, increasing the number of catalyst centers utilized and thus improving performance.

Current densities above 2 A cm^{-2} could be also achieved with thinner CGS coatings of $48 \pm 16 \mu\text{m}$ titanium (CG-48) and $33 \pm 16 \mu\text{m}$ titanium (CG-33), but the performance gain was lower due to corrosion and catalyst poisoning. Additionally, membrane thinning was observed for the MEAs used with CG-48. MEA analyses with CG-33 were not carried out due to an interruption at the test bench and the associated drying out of the MEA. However, post mortem cross sections of CG-33 PTLs showed that corrosion had also occurred under the Ti CGS coating on the PTL surface.

Titanium PVD and CGS layers with a thin 38 nm Pt coating facing the anode CL remained unchanged from the top and no holes or pitting corrosion were observed. However, on the FF-facing sides, surface corrosion, visible in form of small rust-discolored spots, also referred to as "roughing", occurred at the edges and most likely also on the surface of bulk fibers. Consequently, corrosion

7. Titanium-reduced and stainless steel-based anode PTLs

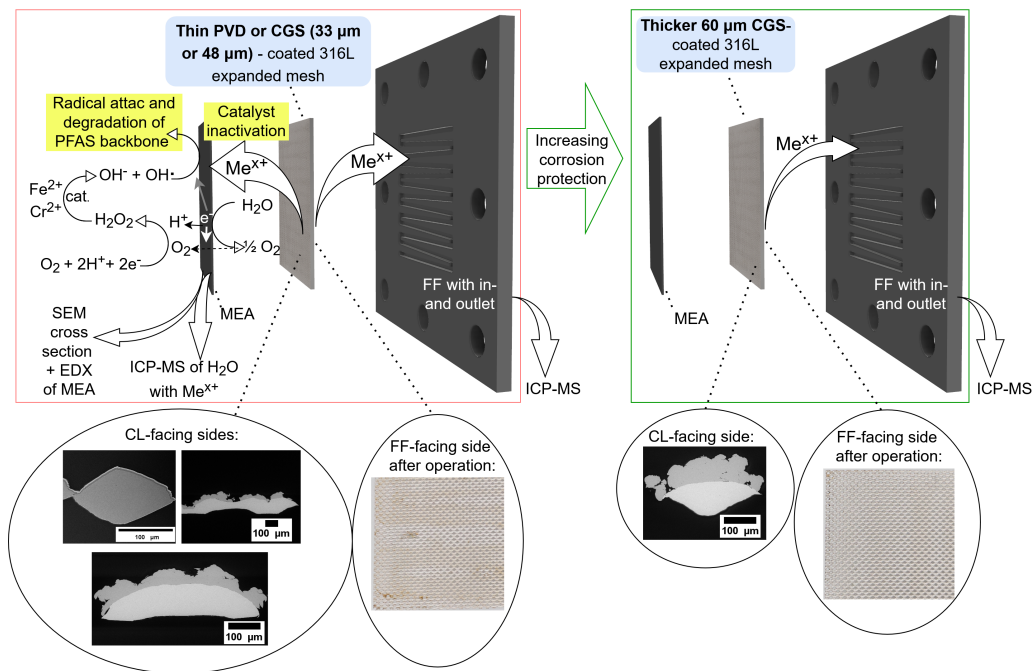


Figure 7.24. Schematic overview of pathways and reactions followed by stainless steel corrosion products such as iron, chromium and nickel. While surface corrosion in the bulk and on the FF-facing side occurred with all 316L based PTLs, increased amounts of corrosion products were found for 316L based PTLs with coatings $< 50 \mu\text{m}$ leading to catalyst inactivation and membrane thinning (left side).

processes can occur at parts of the PTL that are not in contact with the catalyst layer and are not expected to be exposed to anodic polarization, such as the edges or surface of PTL fibers in the bulk, just by contact with ultrapure water.

As mentioned above, surface corrosion on the FF-facing side had no effect on cell performance with CG-60 PTLs. With these PTLs, it is assumed that ions dissolved from the PTL surface on the FF-facing side are carried out of the cell by the water flow faster than they can migrate to the CL (c.f. Figure 7.24). However, for optimal corrosion protection, the entire surface of the stainless steel PTL would have to be coated with a protective coating and the layer thickness on the CL-facing side should be at least $60 \mu\text{m}$. However, further tests need to be carried out to determine a threshold for the layer thickness.

Furthermore, as the cells were operated at a maximum cell voltage of 2.0 V , corrosion products are forced out of the cell [124]. Consequently, further investigations about stainless steel-based PTLs would have to include long-term experiments at lower current densities to examine whether

7. Titanium-reduced and stainless steel-based anode PTLs

an accumulation of corrosion products occurs.

ICP-MS analyses of water samples screening for Cr, Ni, Mn and Mo in the effluent water identified a slight trend of increasing corrosion rates with decreasing coating thickness. Only a comparison of Fe concentrations revealed a trend of higher Fe concentrations with thinner coatings towards the CL-facing side. Additionally, with thinner coatings (PVD and CG-48), the number of samples in which stainless steel components were found was higher, indicating a higher corrosion rate. In addition, individual outliers of higher concentrations of Fe, Mn and Ni occurred during the experiments with the thinnest investigated titanium CGS coating, pointing to a higher corrosion rate than with 316L meshes with a thicker CGS titanium layer. As ICP-MS analysis is less reliable to compare the extent of corrosion of differently coated PTLs due to the short residence time of the water in the cell and possible binding or adsorption of dissolved metal cations in the MEA, causing part of corrosion products to be inaccessible for ICP-MS analysis, EDX spectra of MEA cross sections or CL top views completed the analysis for a qualitative comparison.

While no stainless steel elements were found in 404 spectra of MEA cross sections with CG-60 PTLs, in MEAs from the experiments with CG-48 PTLs, small amounts of Fe, Cr, Mn and Mo were found in the anode CL, Fe in the membrane, and Ni in the cathode CL. Consequently, a slightly higher corrosion rate can be assumed with the CG-48 PTLs compared to CG-60 PTLs. However, it should be noted that EDX spectroscopy, even in the case of several samples per MEA, only covers a very small area of the entire sample. Another indicator of an increased corrosion rate upon the reduction of the Ti CGS thickness was the membrane thickness, as the membrane thickness of the MEAs that were operated with CG-48 samples were on average 42 μm thinner than MEAs operated with CG-60 samples or full titanium PTLs where no Fe contamination was present (c.f. Table A.1).

Based on the results from I-V curves, ICP-MS analysis, impedance spectroscopy and EDX of the MEAs used with the PTLs, an increasing corrosion rate in the order CG-60_Pt < CG-48_Pt < CG-33_Pt < 316LEM_Ti_Pt PVD $\approx$ SMF_Ti_Pt PVD < SMF_Pt < 316L_Pt is assumed. For further research, two conditions can be identified under which the use of stainless steel PTLs in PEMWE single cells and stacks might be possible:

1. Coating of the entire PTL surface, as recently presented by Singh et al. [83] for Ti PTLs, in addition with a thicker coating on the CL-facing side to shield against anodic polarization.
2. Deposition of a sufficiently thick protective layer on the CL facing side with a minimum thickness of 60 μm , as membrane thinning due to corrosion and emission of iron ions could only be prevented with this coating thickness. Nonetheless, with this approach, surface corrosion in the bulk could be unavoidable. However, the results obtained so far show that traces of surface corrosion in the bulk and FF-facing side of the PTL, far enough away from the CL,

7. Titanium-reduced and stainless steel-based anode PTLs

does not affect the catalyst material, as the ions emitted are removed from the cell with the water flow (c.f. Figure 7.24, right side).

As the first path in the literature was pursued with gold, it would be necessary to investigate whether less costly coating materials such as carbon coatings could also be used as a bulk coating, as carbon was already successfully introduced for BPP materials [66]. In addition, as there is evidence from the experimental results that stainless steel elements are dissolved by contact with ultrapure water, it is possible that path 2 cannot provide full protection against the emission of stainless steel elements regardless of the thickness of the coating. To clarify whether pure contact with ultrapure water leads to surface corrosion, further studies should investigate whether surface corrosion would also occur with stainless steel expanded metals on the cathode side between the carbon PTL and flowfield where no oxidizing conditions prevail like at the anode side.

However, as the results demonstrated that stable electrolysis operation is possible even in case of dissolution of trace amounts of stainless steel elements, it is necessary to verify for thinner membranes, lower catalyst loadings and longer test times whether stable operation is also possible with these systems and whether the faradaic current and the amount of hydrogen produced align. Furthermore, future studies should investigate the dissolution of titanium from the CGS layers in more detail, as titanium particles were found occasionally in EDX spectra of cathode CLs from experiments with CG-60 PTLs. However, as no clearly recognizable influence of sparsely titanium migration on the cell performance was visible, its dissolution rate can be considered to be uncritical. Whether titanium dissolution could become detrimental over longer test periods or whether the losses could be extensive enough after several tens of thousands of hours to expose the stainless steel base should be subject of future research.

8. Dynamic operation

The results and research achieved and conducted summarized in this chapter were published in more detail in the International Journal of Hydrogen Energy by S.-V. Pape, S. Zerresen and F. Seidler as joint first authors [9] (DOI: 10.1016/j.ijhydene.2025.03.387). This work has contributed with the following contributions: conceptualization of the study, method development for data analysis, wind profile measurements with PEMWE single cells and the associated analysis of I-V and impedance data and writing of the original draft.

By running wind profile measurements, it was intended to investigate aging of newly developed PTLs in dynamic operation, but as sufficiently stable PTLs were not available towards the end of the work, this chapter provides an overview over results with one of the two methods applied to wind profile operation with benchmark cells. The methods, named the trigger and surface fit method enable the extraction of performance data from dynamic operation, providing a basis for future development of PTLs and other components. As the surface fit includes all data points and enables the extraction of ohmic cell resistances, which is not possible with the trigger method, results from the latter will be omitted in this chapter. However, the trigger method is better suited for an online implementation, as only the interpolation of a previously determined current density levels is considered, thus not all data in the data set needs to be processed and less computing power is required.

The potentiodynamic wind profile within boundary cell voltages of 1.45 V and 2.0 V, consisting of a repeating sequences of 8.33 h with a step interval of 1 s is displayed in Figure 8.1c. Galvanodynamic operation is also possible, but as described in previous chapters about stability testing, the potentiodynamic profile was chosen to not exceed the potential limit of 2.0 V. The experiments were conducted with three benchmark cells for 961 h, but results will be shown from one cell as an example, as trends and magnitudes were the same for all three.

8. Dynamic operation

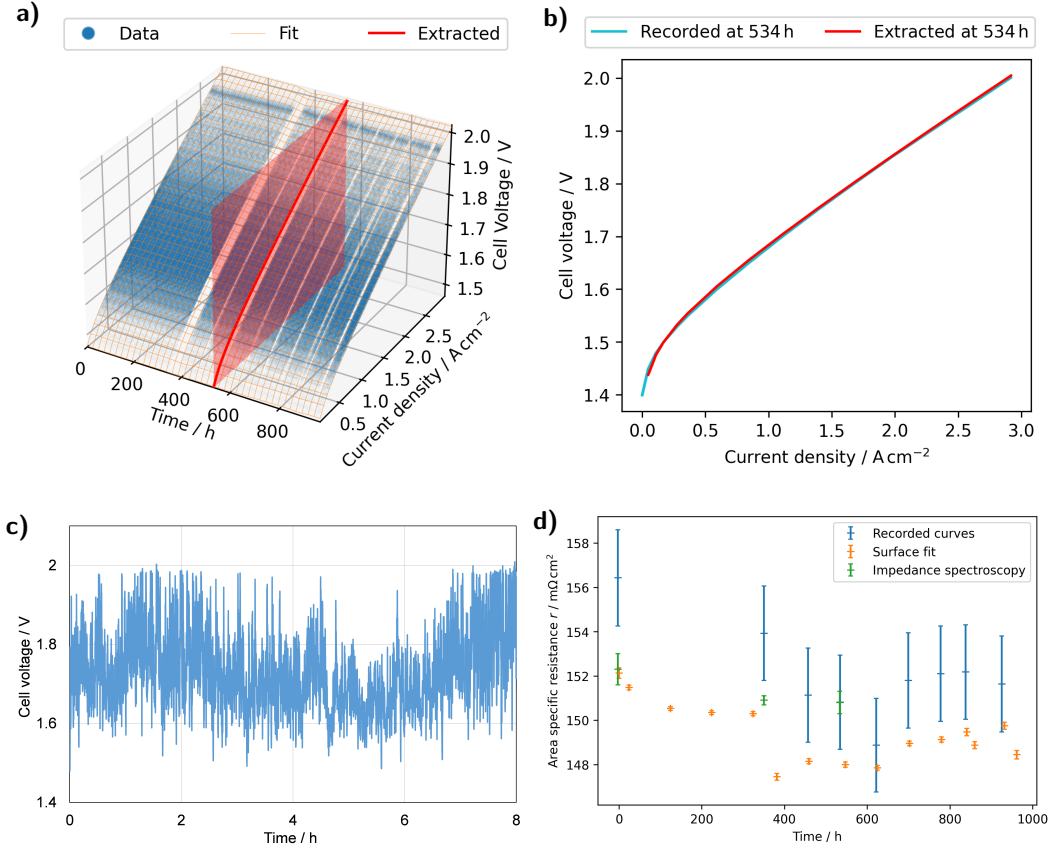


Figure 8.1. a) Surface fit from 961 h of wind profile operation with benchmark cell; b) Comparison of recorded and extracted I-V curves; c) Potentiodynamic wind profile with a step interval of 1 s; d) Development of the ohmic cell resistances derived from EIS compared with extracted resistances from recorded curves and the surface fit from Equation 8.1; All graphs are reprinted with permission from Pape et al. [9].

8. Dynamic operation

Figure 8.1a displays all corresponding I-V datapoints from 961 h of wind profile operation as a function of time. Gaps visible in the second part of the experiment from around 350 h onwards occur due to interruptions for recording impedance spectra or I-V curves. The I-V curves were recorded in the second part of the experiment to compare them with the curves extracted from the surface fit. A comparison of the extracted and recorded I-V curves is shown in Figure 8.1b, where the overvoltage at low current densities $< 0.1 \text{ A cm}^{-2}$ of the extracted curve lies slightly below the recorded curve, while the overvoltages for current densities $> 0.1 \text{ A cm}^{-2}$ are slightly higher within the extracted curve. Lower overvoltage in the activation regime of the extracted curve cannot be explained by the data available, but it is possible that fitting of the activation regime requires further optimization. Lower overvoltages of the recorded curve over the larger part of the I-V curve could stem from the regeneration of reversible overvoltages. As the cell remained in OCP for 10 s before recording the I-V curve, the short recovery time may have resulted in lower overvoltage compared to the extracted curve from continuous dynamic operation. The surface fit was created with Equation 8.1 [9], providing time-dependent parameter sets of r , b , n , with the current density dependent cell voltage $U(j, t)$, the area-specific resistance $r(t)$, an approximation of the Tafel slope $b(t)$, the reference current density j_{ref} (1 mA cm^{-2} here for a unitless argument of the logarithm) and the j -independent parameter $n(t)$ containing the exchange current density j_0 , the reversible cell voltage and any further, unknown overvoltage. Furthermore, the recorded I-V curves were fitted with the same equation without time dependence to extract resistances for comparison, displayed in Figure 8.1d.

$$U(j, t) = r(t)j(t) + b(t) \log \left(\frac{j(t)}{j_{\text{ref}}} \right) + n(t) \quad (8.1)$$

8. Dynamic operation

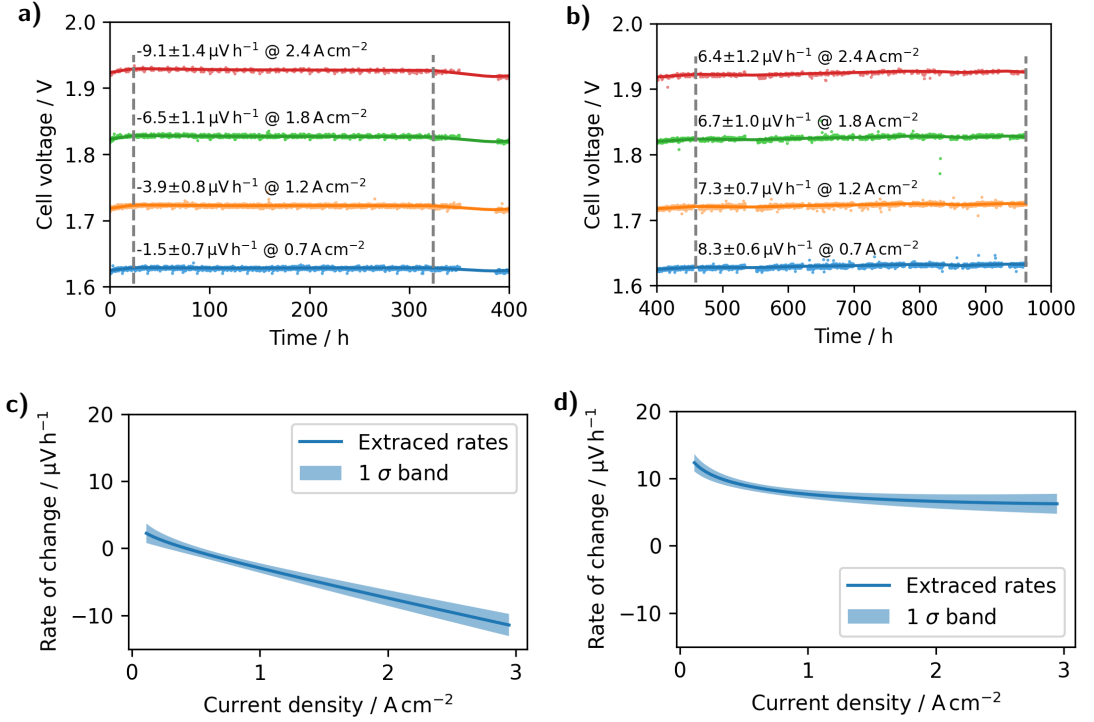


Figure 8.2. a) Cross sections of four selected current densities during uninterrupted dynamic operation; b) Cross sections of four selected current densities during interrupted dynamic operation; c) and d) corresponding overview of the rates of change over the entire current density range.

8. Dynamic operation

Voltage changes at four current densities obtained from cross-sections from the surface fit are shown in Figure 8.2a and b, but extraction of voltage changes for any current density within the power range of the respective cell are possible. In Figure 8.2c and d, voltage changes are shown as a function of the current densities for the respective time periods. Voltage changes in the first test section were positive for low current densities but negative over a larger current density range, thus performance-enhancing effects prevailed in this part. These findings are in accordance with Alia et al. [15], where more pronounced cell voltage degradation at higher current densities was found. They observed a cell voltage increase during 90 d (2160 h) of dynamic operation with a wind profile, which was more pronounced at 2 A cm^{-2} (62 mV) than at lower current densities (45 mV at 0.02 A cm^{-2}), corresponding to rates of cell voltage increases of $2.87 \mu\text{V h}^{-1}$ (62 μV) and $2.08 \mu\text{V h}^{-1}$ (45 μV). In contrast, the cell voltage changes in the second part of the test were positive over the entire current density range. Considering measured and extracted cell resistances that showed a decreasing trend (c.f. Figure 8.3), the degradation rate observed in the second part of the experiment is likely attributed to catalyst degradation rather than contributions to the ohmic overvoltage.

To distinguish between MEA aging and PTL degradation, within another experiment, the MEA of a cell was replaced by a new one after repeatability experiments (chapter 4) and dynamic operation for 42.3 h, consisting of switching between 0 V and 2.0 V every 20 s. In the course of the MEA replacement, a new Toray was also used on the cathode side to achieve the desired compression. Figure A.61 shows the I-V curve before and after dynamic operation and with a new MEA. The I-V curve after dynamic operation exhibits a steeper slope, reflected by the HFR from EIS spectra. As the I-V curve after MEA exchange exhibits a similar slope as the curve before dynamic operation, it can be assumed that the MEA was more affected by degradation than the PTL. This result is in accordance with Weiß et al. [41], who as also described the changes of oxidation states of the iridium catalyst change during potential switching in dynamic operation, leading to catalyst detachment.

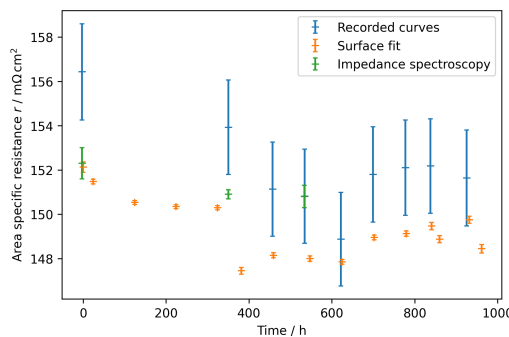


Figure 8.3. Development of the ohmic resistance from fit to the recorded curves (blue), surface fit (orange), and high frequency resistances from impedance spectra (green).

8. Dynamic operation

In case of mass transport limitation, the model needs to be extended. Furthermore, a further extension of the model taking into account increasing temperatures at higher current densities needs to be extended for PEMWE cells with thinner membranes, where more heat is produced at current densities above 3 A cm^{-2} . In general, it is possible to transfer the method to wind profile operation or any other kind of dynamic profile with repeating sequences covering a wide range of performance with new types of PTLs or other cell components.

9. Summary and conclusion

Comparative measurements with benchmark cells at the five places of the test bench in **chapter 4** revealed that the average performance between different places and cells was narrow with an average of $2.87 \pm 0.01 \text{ A cm}^{-2}$ at 2.0 V. However, a comparison of individual experiments showed that the cell performance was subject to differences of up to 170 mA cm^{-2} at 2.0 V. As the reproducibility of iR-free curves with a maximum deviation of 5 mV was significantly lower, it was concluded that the performance of the MEAs could be considered constant. Consequently, the main factors leading to performance differences could be attributed to influences on ohmic losses such as the pressure distribution of the cells, the water inlet temperature and the water flow rate. Precise control of these variables is therefore crucial for single cell measurements and should be particularly taken into account when manufacturing test cells and designing test benches.

After quantification of the reproducibility of single cell experiments and performance evaluation of titanium PTLs that were used in the course of the work (**chapter 5**), eight noble-metal free coating materials were tested as a replacement for noble metal coatings on anode PTLs in **chapter 6**: titanium nitride, tungsten, indium tin oxide, niobium, titanium-niobium alloys, tantalum and a titanium-tantalum alloy.

All pristine and oxide free pure metallic coatings as well as ITO exhibited low resistances, the majority meeting DOE targets. However, except with the titanium-niobium/tantalum alloy coatings, electrolysis performance decreased after operation at 2.0 V for 40 h or longer. All pure metallic coatings including niobium, tantalum and tungsten as well as the nitride underwent oxidation, leading to increased ohmic resistances and decreased cell performance. As the ICR of the ITO coating exhibited a minor $3.7 \text{ m}\Omega \text{ cm}^2$ increase, it is assumed that the degradation pathway involving ITO comprises of tin or indium dissolution, leading to catalyst inactivation, as evidenced by augmented charge transfer resistances. In addition, different aging rates were observed among the materials. While the current densities decreased to almost zero within 15 h of operation with TiN, W, and Ta (CGS), electrolysis was still possible after 40 h with decreased performance with Nb coatings and Ta PVD coatings. With Ti-Nb alloy coatings ($\text{Ti}_{97}\text{Nb}_3$), the performance loss after 673 h was 300 mA cm^{-2} at 2.0 V and consequently lower as observed with pure Nb PVD coatings after shorter experiments that were conducted for 40 h where losses amounted for 510 mA cm^{-2} to 550 mA cm^{-2} at 2.0 V. However, even with pure Ti PVD coatings, almost stable electrolysis operation was possible after 144 h with a current density loss ranging between 100 mA cm^{-2} and 200 mA cm^{-2} . After the same time span of 144 h, a decline in current density was observed with $\text{Ti}_{97}\text{Nb}_3$ coatings ranging between 130 mA cm^{-2} and 150 mA cm^{-2} . With $\text{Ti}_{94}\text{Nb}_6$ an even enhanced stability could be observed with reduced losses of 30 mA cm^{-2} after 144 h. Losses with $\text{Ti}_{94}\text{Ta}_6$ likewise amounted to

9. Summary and conclusion

40 mA cm⁻². In case of a homogeneous distribution of Nb or Ta in Ti, it is assumed that the electrical conductivity of the mixed oxide forming upon electrolysis operation is maintained by the presence of higher valence niobium or tantalum atoms, which act as donor sites. Consequently, the similar results with Ta and Nb indicate that the underlying mechanism responsible for maintaining conductivity is the same for both elements and can therefore be attributed to the valence of the atoms. However, it must be noted that the results with the alloy coatings have not been replicated. An analysis of the surface via XPS revealed that Nb was not distributed evenly on the surface, suggesting the possibility of non-reproducible titanium oxidation. An increase in the Nb content to 28 at.% (Ti₇₂Nb₂₈) led to a significantly faster increase in resistance and losses ranging from 380 mA cm⁻² to 490 mA cm⁻². These losses are likely attributable to the composition of the coating, as the distribution of Ti and Nb was found to be non-uniform, resulting in the formation of Ti- and Nb-rich layers. Thus, pure Nb and Ti oxides may have formed instead of mixed oxides. Consequently, the influence of Nb and Ta alloying with Ti must be investigated further. Moreover, the investigation of Nb-Ta mixed coatings would be a topic of interest. In consideration of the observed oxide formation and performance decrease, the use of TiN, W, Nb, and Ta as pure coatings can, according to the current state of research, not be regarded as an alternative to platinum, while alloy coatings could offer a viable approach and should be further developed in future studies.

The fast oxidation of TiN PVD coatings on PTLs was used in **section 6.8** to investigate whether the oxidation of the PTL coating progresses in the same way in a three-electrode setup that is often used for stability tests of new materials as in PEMWE operation. For this purpose, TiN coated PTLs were analyzed after PEMWE operation at 1.5 V and 2.0 V for 15 min, 60 min and 6 h, as well as after polarization of similar TiN coatings on Ti sheets in O₂-saturated 0.5 M H₂SO₄ at 1.4 V and 1.6 V vs. RHE for the same test duration. While the analysis of cross sections from PTLs and Ti sheets proved challenging, top view EDX spectra revealed that the coatings polarized in the corrosion cell completely oxidized after 6 h and contained an average of 18 at.% more oxygen, whereas after 6 h of PEMWE operation, approximately 5-40 at.% N was still present. Thus, it can be concluded, that either the acidic environment or the applied potential or the combination of both parameters set in the corrosion cell represented stronger oxidizing conditions than in PEMWE cells. Consequently, other pH values and potential combinations have to be investigated for the further development of ex-situ corrosion tests. However, it is possible that the proton activity of the NafionTM membrane cannot be simulated, as in a liquid electrolyte protons move freely with their hydrate shell, while in the polymeric acid, the proton will remain close to the bound anion. Furthermore, electrolyte within the corrosion cell can penetrate into defects and cracks of the coating, providing additional pathways for oxidation and corrosion processes that are not accessible on the PTL surface. In addition, although the potential distribution of the anode CL is not known, it can be assumed that potential differences vary locally, which likewise cannot be simulated in a three-electrode setup. Another observation was made during PEMWE with TiN coated anode PTLs: After 6 h at a cell voltage of 2.0 V, the

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oxygen content of the coating was higher and the nitrogen content lower compared to operation at 1.5 V, indicating that the oxidation rate at the PTL surface is influenced by the OER overpotential and is not decoupled from it. Consequently, the experiments comparing the two setups additionally provided valuable insights into the influence of the cell and thus anode potential during PEMWE operation and their impact on oxidation of the PTL. Furthermore, the comparison of the results from PEMWE operation at 1.5 V and 2.0 V emphasizes that stability testing of PTLs should be carried out at a cell voltage of 2.0 V.

Investigations about stainless steel based PTLs in **chapter 7** started with the determination of the pH of the effluent water from the anode and cathode outlet, revealing that the pH remained constant at 5.6 ± 0.4 . Consequently, the environment surrounding the PTL where no contact with Nafion™ is established can be considered neutral. As neutral conditions are considered to be suitable for austenitic stainless steel, two different 316L substrates with coatings of different thicknesses were tested as anode PTLs. The coatings consisted of 38 nm Pt deposited by PVD, 3.8 μm Ti deposited by PVD and Ti deposited by CGS. All Ti coatings were additionally coated with 38 nm Pt. The thickness of the CGS layers amounted for $33 \pm 16 \mu\text{m}$ (CG-33), $48 \pm 16 \mu\text{m}$ (CG-48) and $60 \pm 16 \mu\text{m}$ (CG-60). As Pt does not provide corrosion protection for 316L, but slows down the corrosion process, experiments with Pt-coated 316L PTLs were carried out to observe the influence of corrosion products on I-V curves and impedance spectra and thus enabled the evaluation of corrosion in subsequent experiments with thicker coatings. A 316L expanded mesh from Bender and a 316L felt on expanded metal from GKN were used as substrates.

With the mesh solely coated with Pt four indicators of corrosion and thus cation contamination were observed: two distinct semicircles, compared to uncontaminated cells increased high frequency- and charge transfer resistances in Nyquist plots above $500 \text{ m}\Omega \text{ cm}^2$ and $1500 \text{ m}\Omega \text{ cm}^2$ from impedance spectra as well as almost S-shaped I-V curves.

With the Pt coated 316L felt PTL, in contrast, stable electrolysis operation was possible over 1393 h. IR-free I-V curves at the end of test revealed no signs of inhibited charge- or mass transfer, providing a superior stability compared with the expanded mesh. However, low frequency resistances increased above 1.6 V, indicating inhibited kinetics in the upper power range and iron and chromium were found in the catalyst layers. The emission of iron caused two overlapping effects: the reduction of the ohmic resistance due to membrane thinning and an increasing charge transfer overvoltage due to cation contamination. Although the reduction in ohmic resistance caused by membrane thinning and by the adaptation of the MEA to the PTL cannot be separated from each other, membrane thinning cannot be ruled out, as the membranes operated with Pt-coated 316L felt PTLs were post mortem on average 10 % to 27 % thinner than membranes with titanium PTLs after comparable test durations.

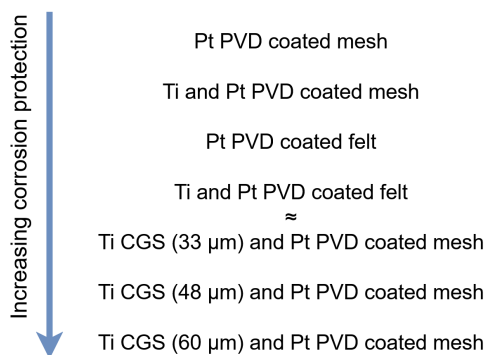
The different degrees of stability of the two 316L substrates may be influenced by their composition, as the Mo content of the felts was higher and Mo increases the corrosion stability of stainless steel.

9. Summary and conclusion

However, other factors such as the composition and roughness of the surfaces could also influence the adhesion of the Pt coating and corrosion stability. With Ti coatings deposited by means of PVD (3.8 μm), corrosion protection of the 316L expanded mesh substrate was increased compared to the thin Pt coating (38 nm). However, the emission of stainless steel elements could not be prevented, as stainless steel elements were detected in the effluent water and post mortem in MEA cross sections. Most of the corroded areas were not in contact with the CL, but were found on the FF-facing side or at the edge of the PTL. Similar results were obtained with Ti PVD coated 316L felt PTLs. However, also after these experiments, membrane thinning could not be ruled out, as the HFR decreased to $137.5 \pm 5.5 \text{ m}\Omega \text{ cm}^2$ after 532 h of operation at 2.0 V.

While CG-48 and CG-60 coatings were able to protect the 316L mesh on the CL-facing side from corrosion, corrosion occurred under the titanium coating of CG-33, implying that for the mesh a coating thickness of more than $33 \pm 16 \mu\text{m}$ is required. Surface corrosion occurred at the FF-facing side of all 316L based PTLs. Nevertheless, the performance achieved after a prolonged conditioning phase with all CGS coated PTLs was competitive to the benchmark, as $2.8 \pm 0.6 \text{ A cm}^{-2}$ were reached at 2.0 V. The performance developed differently depending on the thickness of the PTL coating. While an increase in performance over 1000 h could be observed with CG-60, a decrease in performance after 420 h was visible with CG-48, and an even more pronounced decrease in performance was observed with CG-33 due to corrosion affecting the cell performance.

In summary, among all experiments with 316L-based PTLs, a decreasing corrosion rate was observed in the following order:



This rating is based on the development of I-V curves, EIS and analysis of the water and the MEA, whereas no 316L based PTL reached a corrosion rate of zero.

However, surface corrosion observed on CG-60 did not have any effect on the blockage or inactivation

9. Summary and conclusion

of active catalyst centers or ion channels. It is possible that the concentrations of stainless steel components dissolved by surface corrosion were low enough not to affect the reactions. It is also conceivable that cations dissolved in the vicinity of the FF are carried out of the cell with the water flow before they can reach the CL. In this case, an unknown concentration level of cation impurities could remain harmless for electrolysis operation. However, it would be necessary to verify where this concentration limit lies and whether beginning surface corrosion within 1000 h extends to a harmful level after several tens of thousands of operating hours. Furthermore, a full Ti PTL consisting of a TiEM coated with a similar Ti CGS layer than was deposited on 316L meshes and sputtered with Pt served to compare the performance with 316L based PTLs. As the performance with both base materials closely approximated the benchmark, it can be concluded, that the observed performance improvement with CGS coated meshes compared to solely Pt coated Ti meshes stems from properties of the CGS coating rather than the mesh. Nevertheless, further investigation is necessary to ascertain the competitive potential of mesh PTLs with Ti CGS coatings at higher current densities. Furthermore, as long as uncoated areas of stainless steel based PTLs are in contact with ultrapure water, surface corrosion will occur.

It therefore remains a debatable discussion whether the lower investment costs of stainless steel as a raw material outweigh the occurrence of surface corrosion compared to titanium. In addition, when selecting materials, it must be taken into consideration that, depending on the production rate and number of quantities, the decisive factor for the investment costs of PTLs is not the raw material, but the manufacturing costs [186]. CG-60 PTLs with the smallest corrosion rate could save approximately 25 % titanium compared to Ti felt PTLs used within this work.

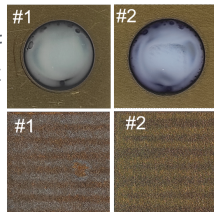
Chapter 8 presents a collaborative work about the extraction of performance data from dynamic wind profile operation. The methods developed enable the examination of cell voltage changes, I-V curves and ohmic resistances during dynamic operation without interruption. As interrupting dynamic operation can lead to conditions that may influence these parameters, the methods provide the advantage that interruptions are no longer necessary. With benchmark cells, average aging rates of approximately $6 \mu\text{V h}^{-1}$ were observed during wind profile operation. Thereby, it was found that low current densities were more affected by an increase in overvoltage than high current densities. At high current densities even negative change rates were obtained. In addition, a decrease in ohmic resistance was observed. Therefore, it is assumed that the increase in overvoltage was caused by an increase of the activation overvoltage and consequently driven by degradation of the catalyst rather than the PTL. In the future, the methods developed can be used and expanded to investigate new cell components. Figure 9.1 summarizes the most important highlights and findings.

9. Summary and conclusion

Advancements in comprehension of **ex-situ corrosion testing**

→ oxidation with TiN in H_2SO_4 not transferable to oxidation under anode PEMWE conditions
→ milder conditions, $\text{pH} > 1.16$ and/or potential $< 1.4 \text{ V}$ vs. RHE should be applied

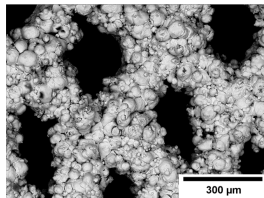
Corrosion cell:
6 h @
1.6 V vs. RHE



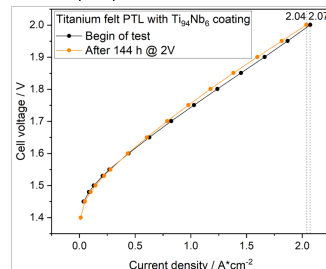
PEMWE:
6 h @ 2 V

Investigation of **stainless steel based PTLs**

→ stable performance at 2.8 A/cm^2 (2 V) for 1006h with Ti cold gas spray coated 316l expanded mesh



Discovery of **Nb-Ti and Ta-Ti alloy coatings** as potential replacement for PGM-coatings on the anode PTLs
→ 6 at.% Nb in Ti (PVD) on titanium felt PTL enabled stable operation at 2 A/cm^2 (2 V) for at least 144h



Development of methods for the **extraction of performance data from dynamic wind power profile operation**
→ extraction of I-V curves, degradation rates and cell resistances without interruption of the dynamic measurement

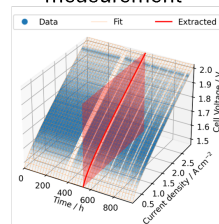


Figure 9.1. Overview of the most important findings and recommendations.

10. Outlook

The water supply in stacks is provided via graded expanded metal layers. In contrast, only one layer of expanded metal was used within this work. To achieve a more accurate representation of the stack performance on single cell scale, further experiments could involve single cell testing with multiple welded layers of graded expanded metal.

Furthermore, it is highly probable that the geometry and porosity of the PTLs used within this work has to be adjusted when using anode catalyst layers with lower loadings or when higher current densities are applied with thinner membranes. Furthermore, electrolysis under pressure is relevant for industrial application. Due to the large openings of the expanded metals compared to conventional felt PTLs or sintered bodies, subsequent investigations should also consider the intrusion of the MEA into the expanded metal openings under pressure and its effects on membrane aging and cell performance.

As Zn and Cu were found in various water and/or MEA samples post mortem without any recognizable pattern, fundamental studies should investigate the source and influence of these two elements. An understanding of these two questions would be important for further studies to avoid attributing effects that occur due to these impurities to other interpretations and thus to prevent false conclusions. In addition to the above-mentioned possible directions for further research, three main paths regarding PTL development are of particular interest:

1. Investigations about alloy coatings for PTLs involving mixtures of Ti, Ta, Nb and low Pt loadings.
2. The investigation of different titanium surfaces, as the experiments with titanium PVD coated PTLs showed an improved stability up to 144 h compared to uncoated titanium PTLs. Further investigations of these surfaces, oxide layers, oxide growth and longer test times are relevant here.
3. Development of bulk coatings for 316L based PTLs and investigation of the stainless steel composition, as illustrated in Figure 10.1. If a bulk coating proves to be too complex or expensive to provide optimum corrosion protection, it would be necessary to examine whether the concentrations emitted by surface corrosion on stainless steel components would lead to a decline in performance even after tens of thousands of operating hours, as until now, 316L can not be regarded as viable PTL material.

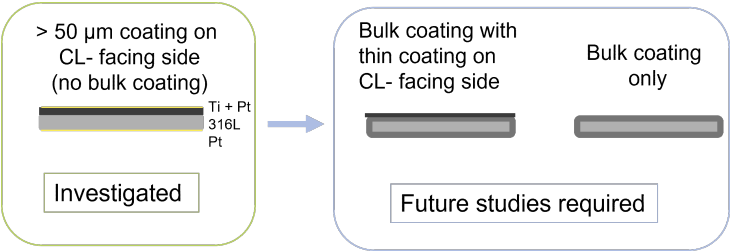


Figure 10.1. Illustration of coatings for 316L based PTLs: Right: the coating system investigated on 316L PTLs and left: possible future coating systems consisting of a coating on the entire PTL surface and optional additional coating on the CL-facing side.

Nomenclature

Abbreviations

<i>316L</i>	Stainless steel 316L
<i>316LEM</i>	316L Expanded Metal
<i>APS</i>	Atmospheric Plasma Spraying
<i>at.%</i>	Atomic percent
<i>AWE</i>	Alkaline Water Electrolysis
<i>BPP</i>	Bipolar Plate
<i>BSE</i>	Back Scattered Electrons
<i>CA</i>	Chronoamperometry
<i>CAD</i>	Computer-Aided Design
<i>CE</i>	Counter Electrode
<i>CGS</i>	Cold Gas Spraying/Sprayed
<i>CL</i>	Catalyst Layer
<i>CPE</i>	Constant Phase Element
<i>CT</i>	Charge Transfer
<i>CTR</i>	Charge Transfer Resistance
<i>DL</i>	Detection Limit
<i>DRT</i>	Distribution of Relaxation Times
<i>ECSA</i>	Electrochemical Surface Area
<i>EDX</i>	Energy-Dispersive X-Ray Spectroscopy
<i>EIS</i>	Electrochemical Impedance Spectroscopy
<i>FF</i>	Flow Field

Nomenclature

<i>HAADF – STEM</i>	High-angle Annular Dark-Field Scanning Transmission Electron Microscopy
<i>HER</i>	Hydrogen Evolution Reaction
<i>HFR</i>	High Frequency Resistance
<i>ICP – MS</i>	Inductively Coupled Plasma-Mass Spectrometry
<i>ICP – OES</i>	Inductively Coupled Plasma-Optical Emission Spectroscopy
<i>ICR</i>	Interfacial Contact Resistance
<i>LFR</i>	Low Frequency Resistance
<i>LLLW</i>	Ultra Super Low Pressure
<i>LLW</i>	Super Low Pressure
<i>LW</i>	Low Pressure
<i>MEA</i>	Membrane Electrode Assembly
<i>NHE</i>	Normal Hydrogen Electrode
<i>OCF</i>	Open-Circuit Potential
<i>OER</i>	Oxygen Evolution Reaction
<i>PCCCL</i>	Proton Conducting Ceramic Electrolysis
<i>PEM</i>	Polymer Electrolyte Membrane
<i>PEMWE</i>	Polymer Electrolyte Membrane Water Electrolysis
<i>PFAS</i>	Per- and polyfluoroalkyl Substances, here: perfluorinated sulphonic acid
<i>PTFE</i>	Polytetrafluoroethylene
<i>PTL</i>	Porous Transport Layer
<i>PVD</i>	Physical Vapor Deposition
<i>RE</i>	Reference Electrode
<i>RHE</i>	Reversible Hydrogen Electrode
<i>RT</i>	Room Temperature
<i>SCE</i>	Standard Calomel Electrode

Nomenclature

<i>SEM</i>	Scanning Electron Microscopy
<i>SHE</i>	Standard Hydrogen Electrode
<i>SLPM</i>	Standard Liter Per Minute
<i>SMF</i>	316L Stainless steel expanded Metal with 316L Felt
<i>SOEC</i>	Solid Oxide Electrolysis
<i>TiEM</i>	Titanium Expanded Metal
<i>TiF</i>	Titanium Felt
<i>TiS</i>	Titanium Sintered body
<i>TPCB</i>	Triple Phase Contact Boundaries
<i>VPS</i>	Vacuum Plasma Spraying
<i>WE</i>	Working Electrode
<i>XCT</i>	X-ray Computer Tomography
<i>XPS</i>	X-ray Photoelectron Spectroscopy
<i>XRD</i>	X-Ray Diffraction

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A. Appendix

A.1. Post mortem membrane thicknesses

Table A.1. Membrane thickness (without catalyst layers) after PEMWE cell tests with different PTLs, graphically determined from SEM cross sections using the software ImageJ. As the values were determined using a limited number of samples, the true distributions are likely to be broader.

PTL	Mean thickness / μm	Minimum thickness / μm	Maximum thickness / μm	Membrane thinning ¹	Related chapter or section
SMF8_Pt_1	203 $\pm$ 10	184	220	not certain based on available data	7.2.2
SMF8_Pt_2	162 $\pm$ 20	124	186	yes	7.2.2
TiF_2Pt_1	216 $\pm$ 14	180	234	no	8
TiF_2Pt_2	236 $\pm$ 12	212	261	no	8
TiF_2Pt_3	218 $\pm$ 12	198	239	no	8
316LEM_TiPVD_1	202 $\pm$ 15	181	229	not certain based on available data	7.3.1
316LEM_TiPVD_2	198 $\pm$ 15	166	231	not certain based on available data	7.3.1
SMF8_TiPVD	187 $\pm$ 15	152	210	not certain based on available data	7.3.2
SMF22_TiPVD	238 $\pm$ 9	219	253	not certain based on available data	7.3.2
CG-60_1	218 $\pm$ 15	202	232	no	7.4.1
CG-60_2	224 $\pm$ 15	216	251	no	7.4.1
CG-60_3	229 $\pm$ 10	218	242	no	7.4.1
CG-48_1	176 $\pm$ 12	139	202	yes	7.4.2
CG-48_2	188 $\pm$ 19	150	213	yes	7.4.2

1: determined using SEM analysis of MEA cross sections.

A.2. Appendix for 3.1.3 Experimental - PEMWE test bench

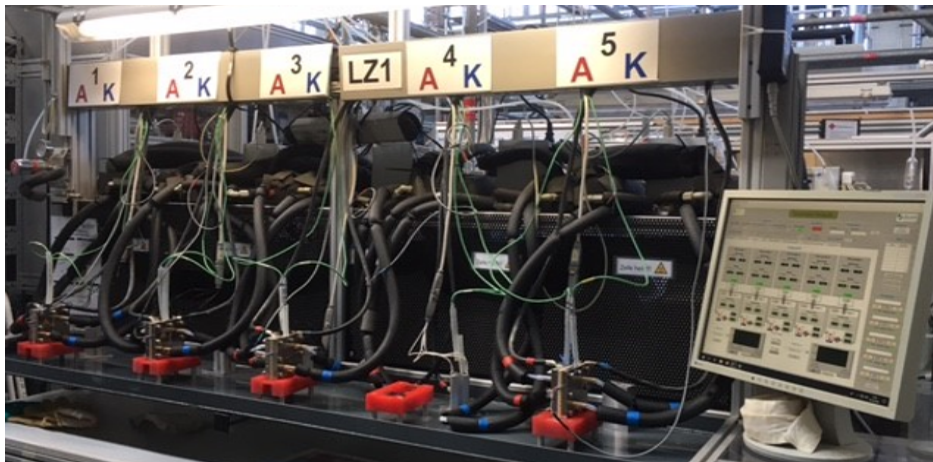


Figure A.1. Test bench for five PEMWE single cells.

Calculation of the water consumption ratio lambda

The amount of water consumed can be determined according to Faraday's law:

$$m = \frac{M \cdot I \cdot t}{z \cdot F} \quad (\text{A.1})$$

m : mass, g

M : molar mass, g mol^{-1}

I : current, A

With: t : time, s

z : number of electrons transferred, dimensionless

F : Faraday constant, $96\,485.34 \text{ C mol}^{-1}$

λ : consumption ratio, dimensionless

Amount of water consumed at a maximum current density of 3 A cm^{-2} :

$$\begin{aligned} m &= \frac{18 \text{ g mol}^{-1} \cdot 52.92 \text{ A} \cdot 60 \text{ s}}{2 \cdot 96\,485 \text{ C mol}^{-1}} \\ &= 0.3 \text{ g} \triangleq 0.3 \text{ mL} \end{aligned} \quad (\text{A.2})$$

With the set flow rate of the water supply, the consumption factor λ results:

$$\lambda = \frac{20 \text{ mL min}^{-1}}{0.3 \text{ mL min}^{-1}} = 67$$

A.3. Appendix for 3.1.1 Experimental - PEMWE test cells

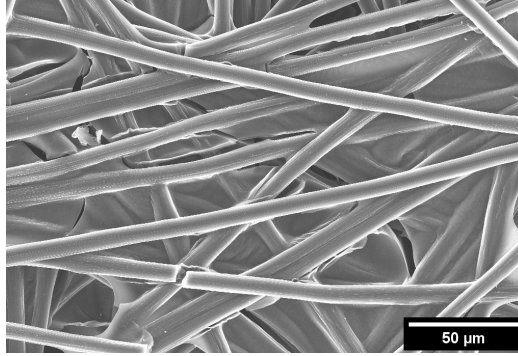


Figure A.2. SEM image of carbon paper cathode PTL from Toray.

A.4. Appendix for 3.2 Experimental - Anode PTLs and coatings

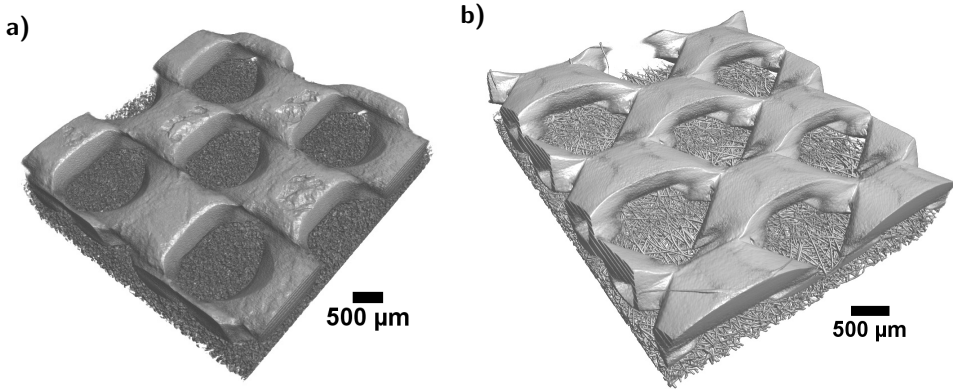


Figure A.3. 3D X-Ray tomograms of a) FF-facing side of TiS; b) FF-facing side of SMF.

A.5. Appendix for 3.7 Experimental - Through plane and interfacial contact resistance

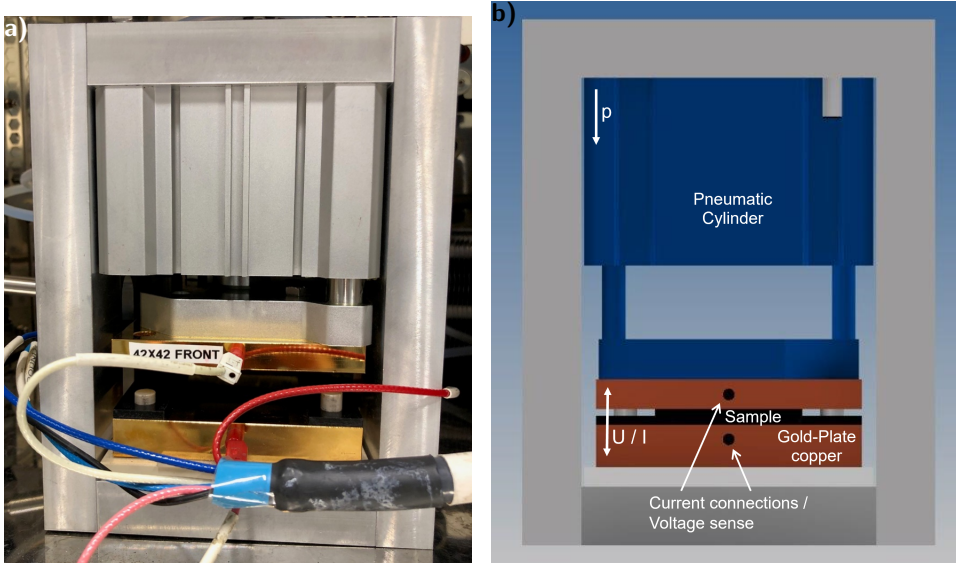


Figure A.4. a) Photograph of setup for ICR measurements; b) CAD drawing of setup for ICR measurements.

A.6. Appendix for 4 Results - Repeatability of PEMWE single cell testing

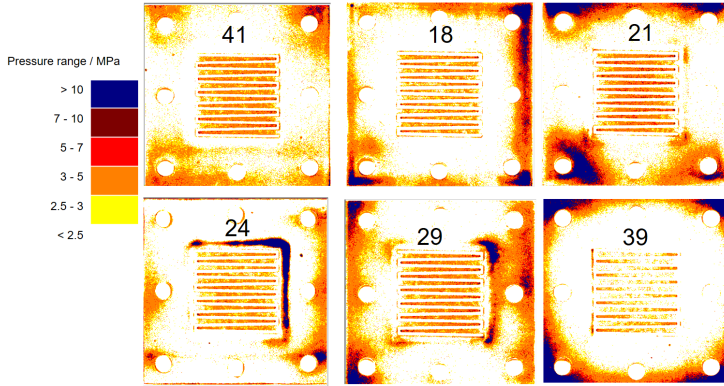


Figure A.5. Pressure distribution of 6 different PEMWE cells (number 41, 18, 21, 24, 29 and 39) determined with a pressure-sensitive film from Fujifilm (type LW). The cells were assembled with a Toray paper and a PTFE gasket.

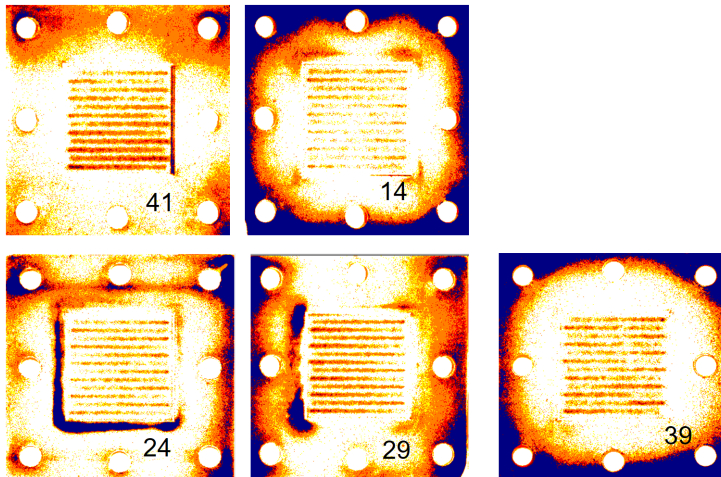


Figure A.6. Pressure distribution of 5 different PEMWE cells (number 41, 14, 24, 29 and 39) determined with a pressure-sensitive film from Fujifilm (type LW). The cells were assembled with a Toray paper, one Bekaert PTL and two gaskets.

A. Appendix

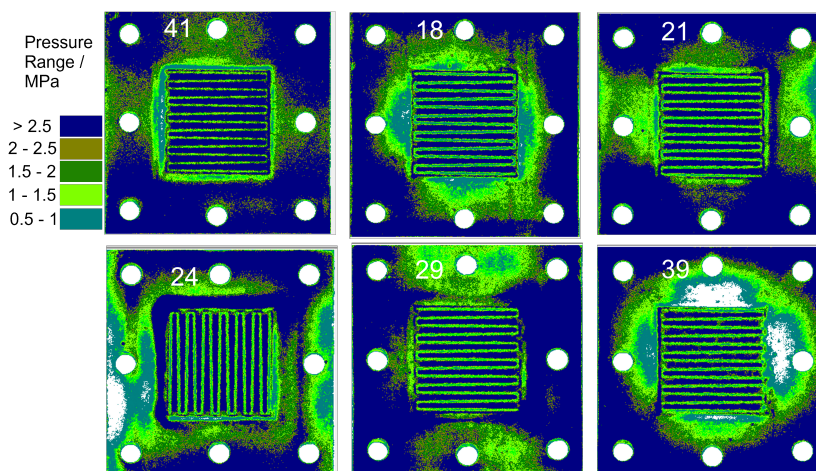


Figure A.7. Pressure distribution of 6 different PEMWE cells (number 41, 18, 21, 24, 29 and 39) determined with a pressure-sensitive film from Fujifilm (type LLW). The cells were assembled with a Toray paper and a PTFE gasket.

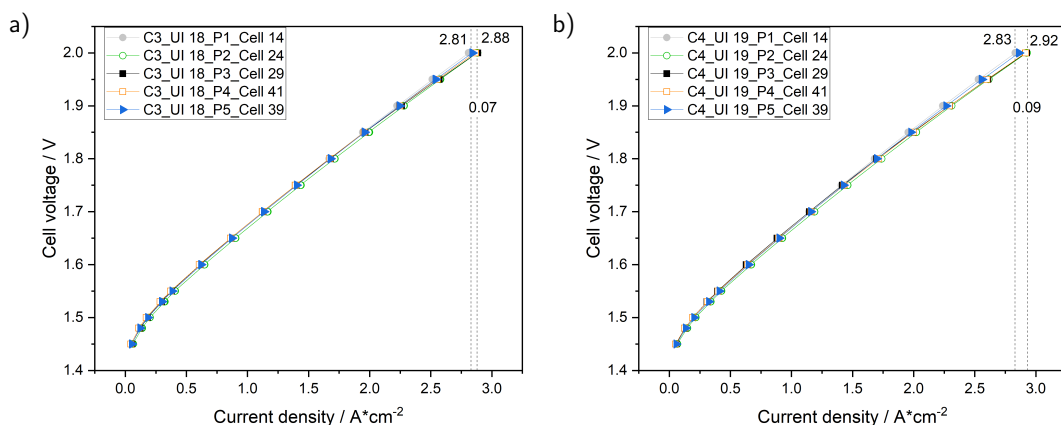


Figure A.8. a) Last I-V curves of the third cycle. b) First I-V curves of the fourth cycle.

A. Appendix

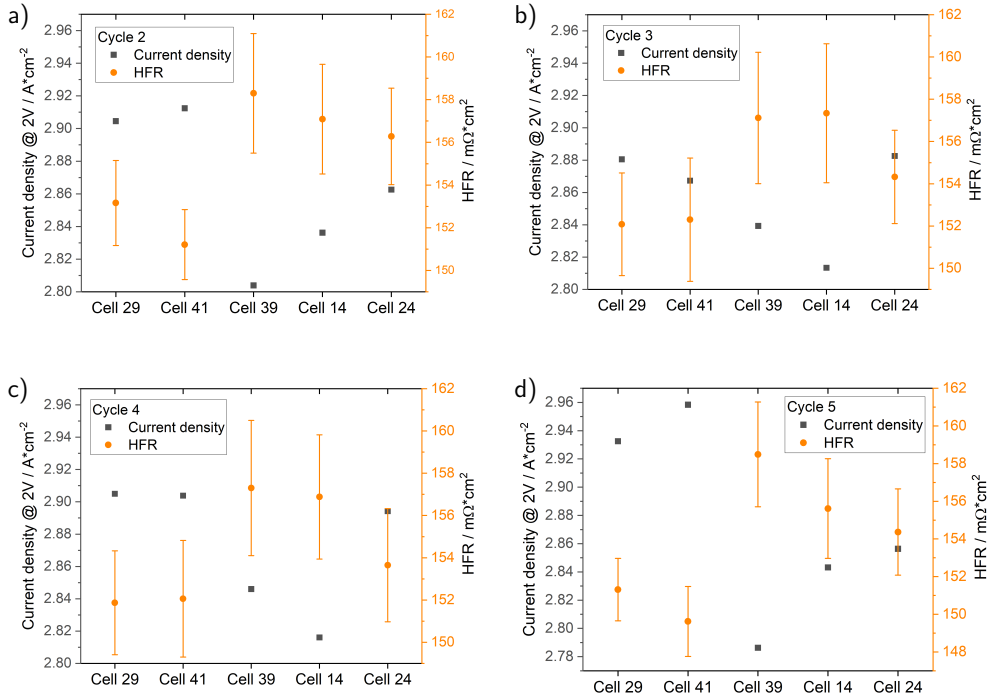


Figure A.9. Current density at 2.0V of the last I-V curves and HFRs from EIS of the cycles 2 - 5 with standard single cells rotating between different places of the test bench. a): Cycle 2; b): Cycle 3; c): Cycle 4 (only cool down); d): Cycle 5 (same places as cycle 2).

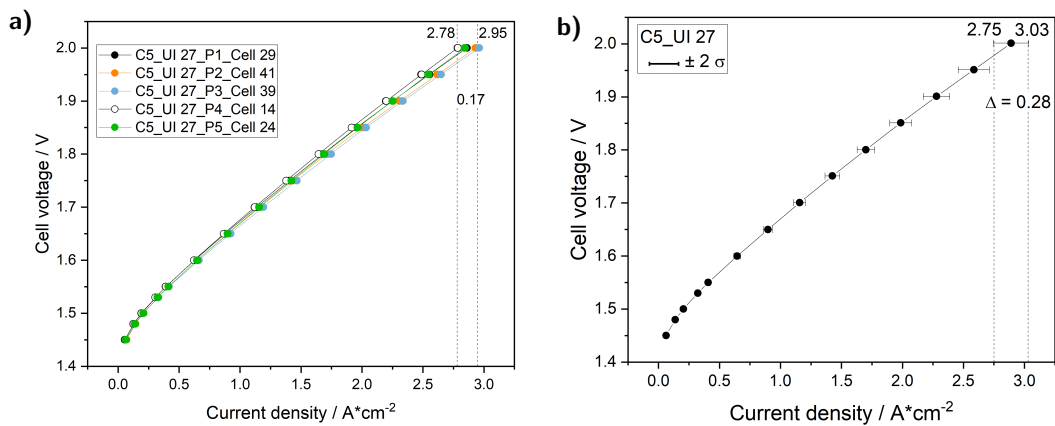


Figure A.10. Results from the 27th I-V curves of the fifth cycle of repeatability testing (chapter 4):
a) All I-V curves with indication of the minimum and maximum achieved current density at 2.0 V and the difference between them; b) Mean I-V curve with 2σ current density interval.

A.7. Appendix for 5 Results - PEMWE performance with titanium PTLs

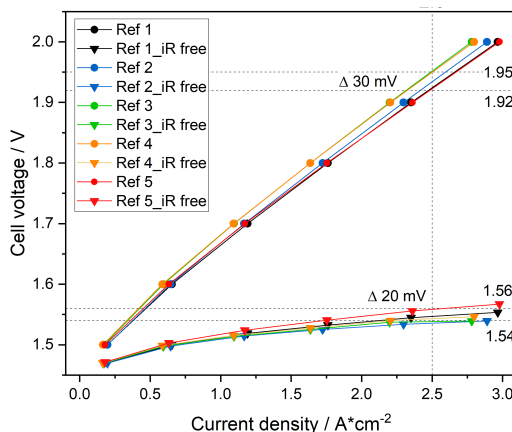


Figure A.11. I-V curves of five PEMWE cells with Pt coated TiF anode PTLs (Reference) after conditioning and corresponding iR -free I-V curves compensated by the ohmic overvoltage calculated with the HFR from EIS and indication of the minimum and maximum cell voltages at $2.5 A \cdot cm^{-2}$ for full and iR compensated curves as well as the maximum cell voltage differences at $2.5 A \cdot cm^{-2}$.

A. Appendix

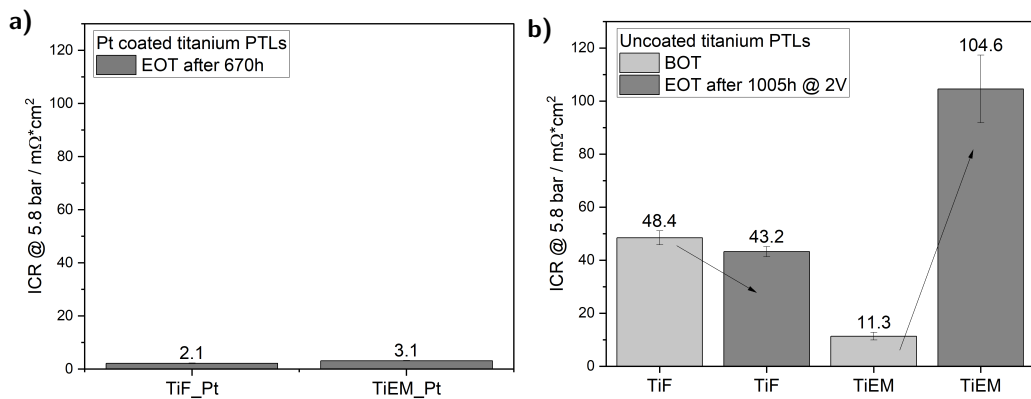


Figure A.12. PTL resistances before and after PEMWE operation measured between two gold-plated copper blocks and two carbon PTLs at 5.8 bar and RT. a) Pt coated TiEM and TiF PTLs; b) Uncoated TiEM and TiF PTLs.

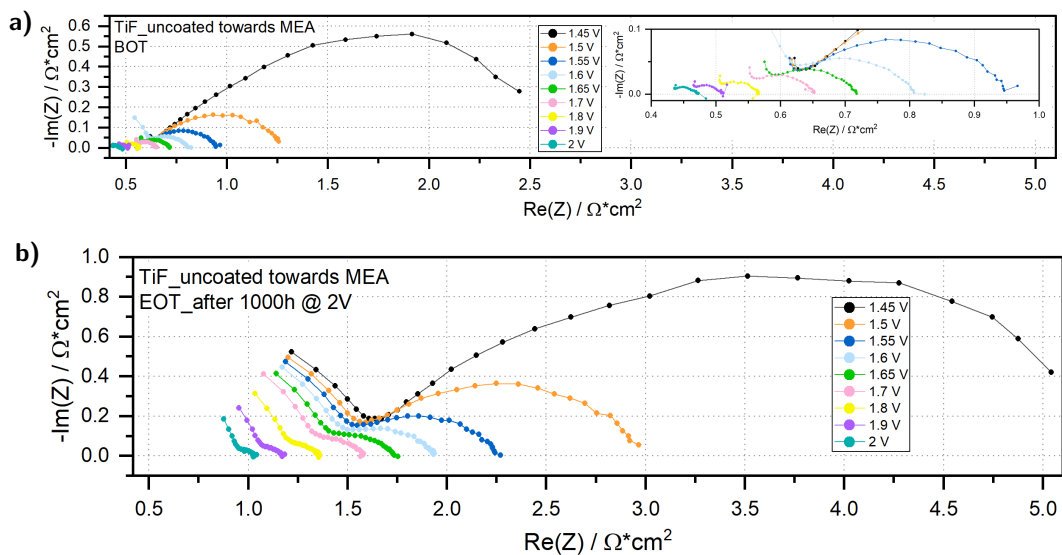


Figure A.13. Impedance spectra of a PEMWE single cell with TiF PTL without coating towards CL; a) Begin of test (BOT) after conditioning with zoomed-in inset of spectra above 1.55 V; b) End of test (EOT) after 1005 h at 2.0 V.

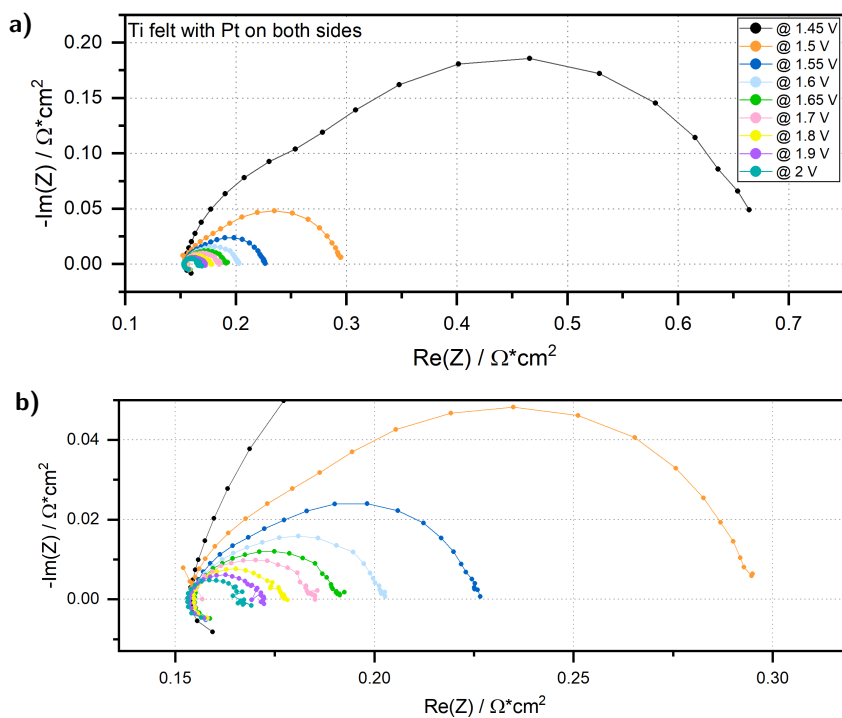


Figure A.14. Impedance spectra of a PEMWE single cell with TiF PTL (Bekaert) wit Pt coating towards CL and FF; b) Zoomed-in spectra above 1.5 V.

A. Appendix

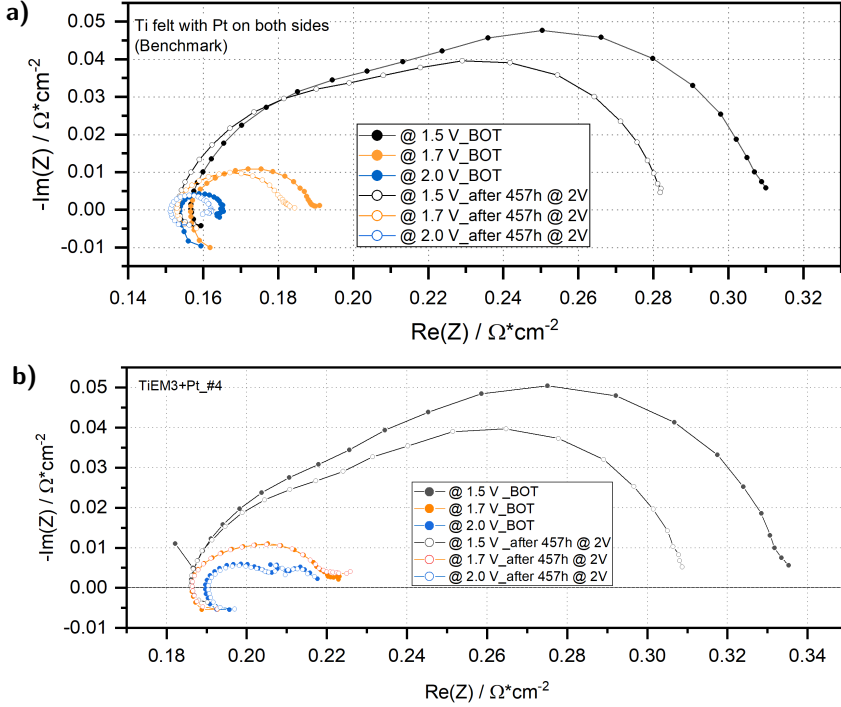


Figure A.15. a) EIS spectra from a PEMWE cell with Pt coated TiF anode PTL (Benchmark) after conditioning (BOT) and after 457 h of operation, corresponding to Figure 5.2; b) EIS spectra from a PEMWE cell with Pt coated TiEM anode PTL after conditioning (BOT) and after 457 h of operation.

A. Appendix

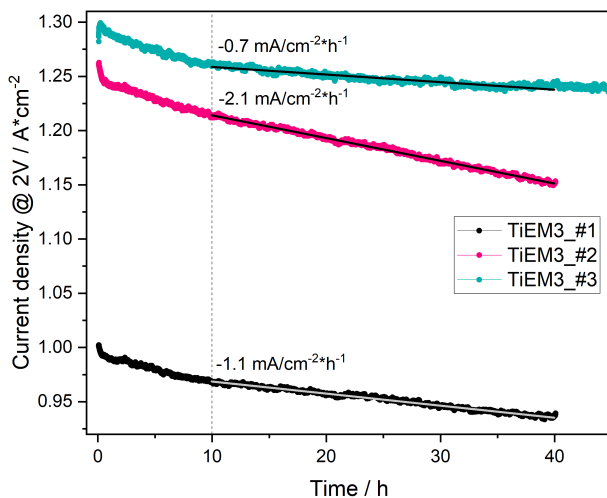


Figure A.16. Current density of three PEMWE single cells at 2.0V with titanium expanded mesh PTLs (TiEM3) without Pt coating and current density slopes from 10h to 40h from linear fitting. The first 10h were excluded from the linear fit as the initial rate of change is higher, especially with sample number 3, and may overlap with a conditioning process.

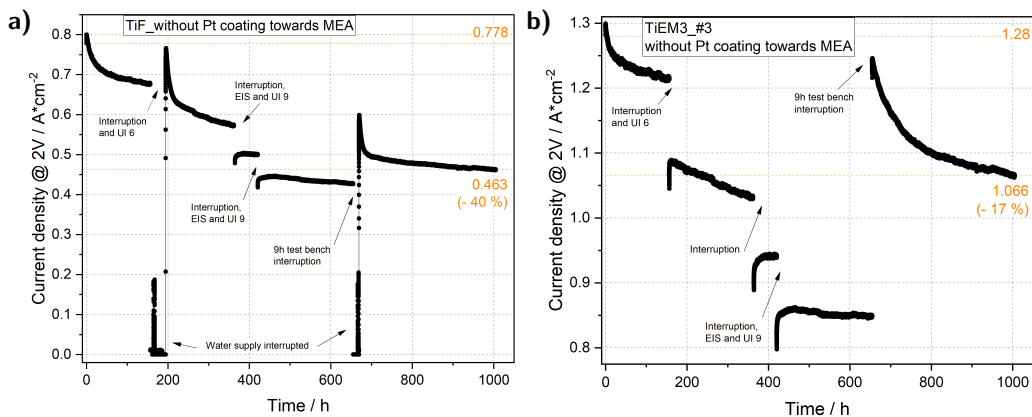


Figure A.17. Current density at 2.0V with pure, uncoated titanium PTLs over 1000h. The current density at the end of test is marked by a dashed line; a) with TiF PTL; b) with TiEM2_#3. The resulting rates of current density decrease are $-0.315 \text{ mA cm}^{-2} \text{ h}^{-1}$ (TiF) and $-0.17 \text{ mA cm}^{-2} \text{ h}^{-1}$ (TiEM).

A.8. Appendix for 6.1 Results - Noble metal free anode PTL coatings: TiN

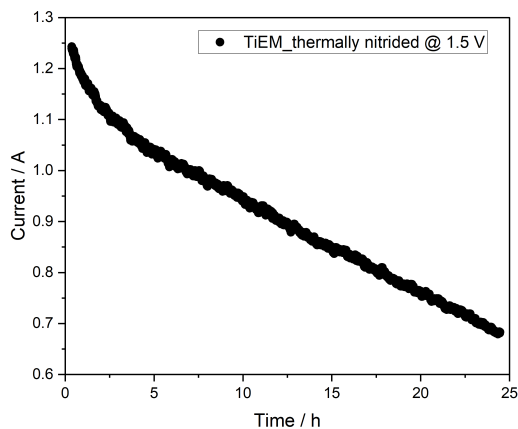


Figure A.18. Current curve of PEMWE single cell at 1.5 V with a thermally nitrided TiEM anode PTL after conditioning for 15 h at 1.5 V.

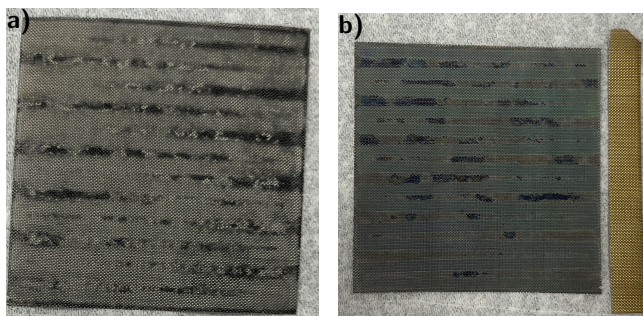


Figure A.19. Thermally nitrided TiEM anode PTL after 39.5 h at 1.5 V and two I-V curves; a: CL-facing side. b: FF-facing side and a piece of pristine nitrided PTL on the right in the picture.

A.9. Appendix for 6.4 Results - Noble metal free anode PTL coatings: Nb

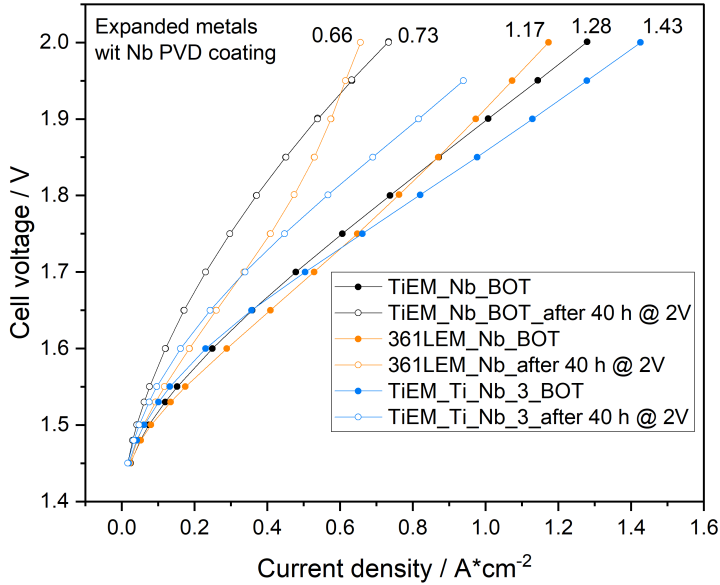


Figure A.20. I-V curves with Nb coated anode PTLs (Ti and 316L EM) by means of PVD with TiEM_Ti_Nb_3 being the third improved Nb PVD generation. The latter PTL consisted of a TiEM with a Ti PVD coating and Nb PVD coating on top.

A.10. Appendix for 6.5 Results - Noble metal free anode PTL coatings: Ti Nb alloys

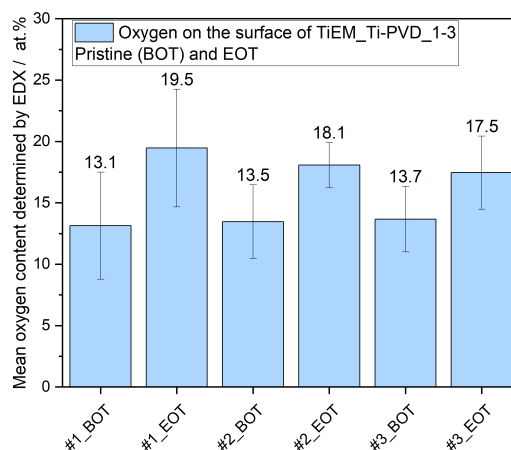


Figure A.21. Oxygen content determined from point spectra on the surface of TiEM_Ti-PVD samples 1-3 pristine (BOT) and after disassembly (EOT).

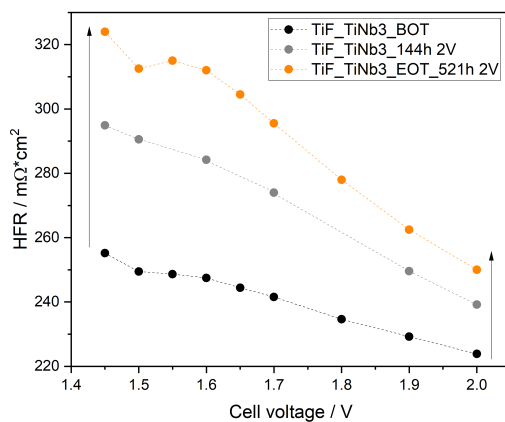


Figure A.22. HFR in dependence of the cell voltage at the begin of test, after 144 h at 2.0 V and after 521 h at 2.0 V with a TiEM PTL coated with a Ti(97 %)-Nb(3 %) alloy coating by means of PVD. The mesh is Pt PVD coated (37 nm) on the FF-facing side.

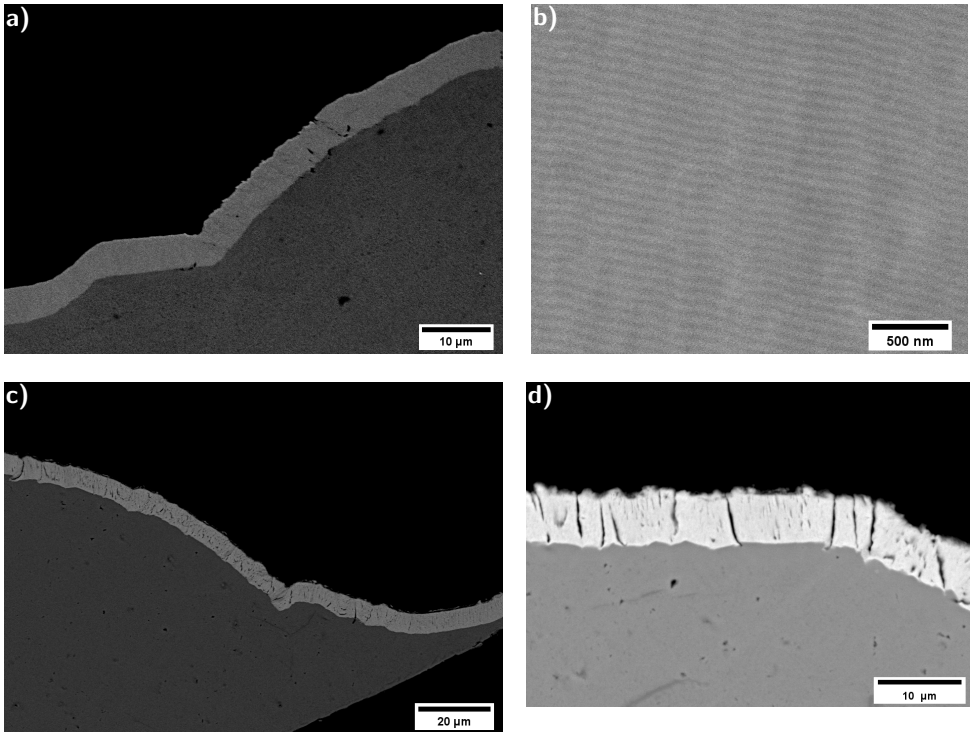


Figure A.23. SEM cross sections acquired and provided by Sievert [151] with a high definition BSE detector (HDBSD) at a working distance of 8.5 mm. a) TiEM_Ti₉₄Nb₆ with a magnification of 3.83 kX and an acceleration voltage of 10.000 keV; b) TiEM_Ti₉₄Nb₆ with a magnification of 72.83 kX and an acceleration voltage of 10.000 keV; c) TiEM_Ti₇₂Nb₂₈ with a of magnification 2.01 kX and an acceleration voltage of 1500 keV; d) TiEM_Ti₇₂Nb₂₈ with a of magnification 5.05 kX and an acceleration voltage of 1500 keV.

A.11. Appendix for 6.6 Results - Noble metal free anode PTL coatings: Ta

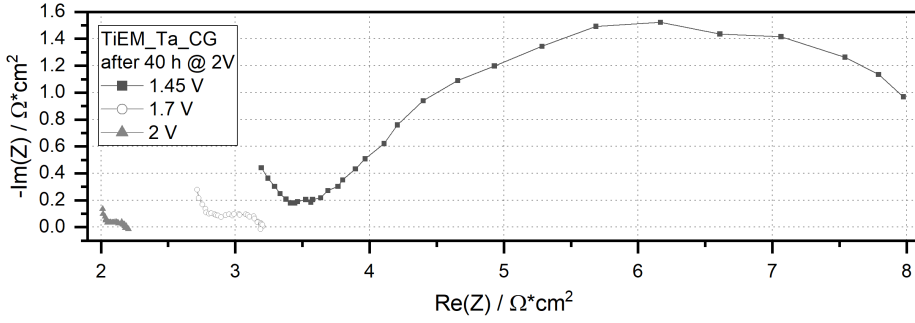


Figure A.24. Impedance spectra of a PEMWE single cell with an tantalum CGS coated TiEM anode PTL after conditioning, two I-V curves and 40 h at 2.0 V.

A. Appendix

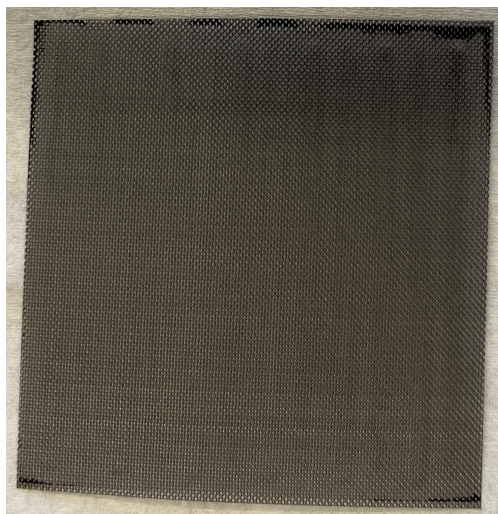


Figure A.25. TiEM with tantalum PVD coating after operation for 54 h at 2.0 V. Black traces on the edges of the PTL stem from the catalyst layer.

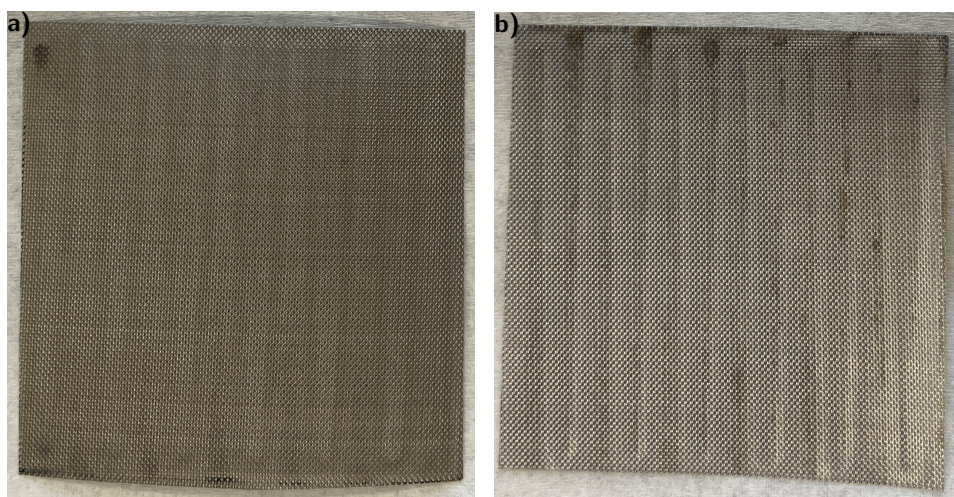


Figure A.26. Titanium expanded metal with PVD titanium alloy coating with 6 % tantalum and 94 % titanium after operation for 54 h at 2.0 V cell voltage. a) CL-facing side. b) FF-facing side

A.12. Appendix for 6.8 Results - Noble metal free anode PTL coatings: Investigations of the pH and potential at the PTL/CL interface

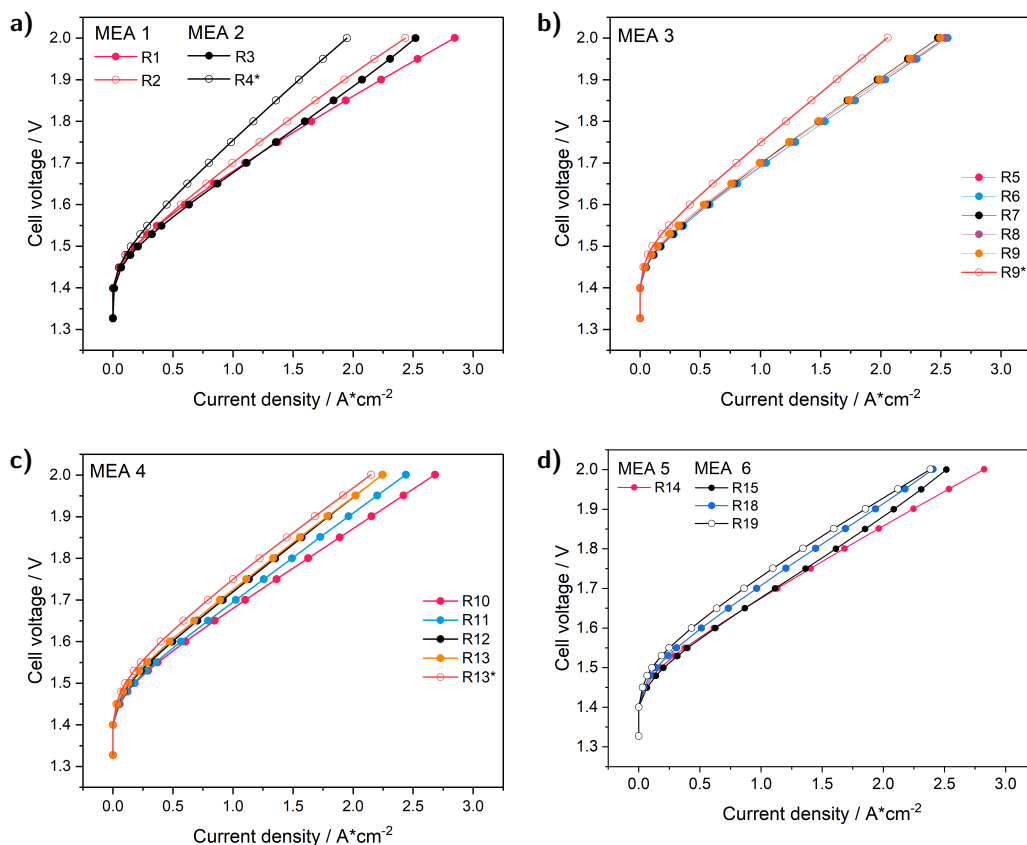


Figure A.27. I-V curves with TiF_Pt PTLs between oxidation experiments with TiN PVD coated TiF PTLs. The reference experiments were performed in ascending order, starting with R1 and ending with R19. All curves marked with * indicate the last curve recorded with a MEA, after which the MEA was discarded.

A. Appendix

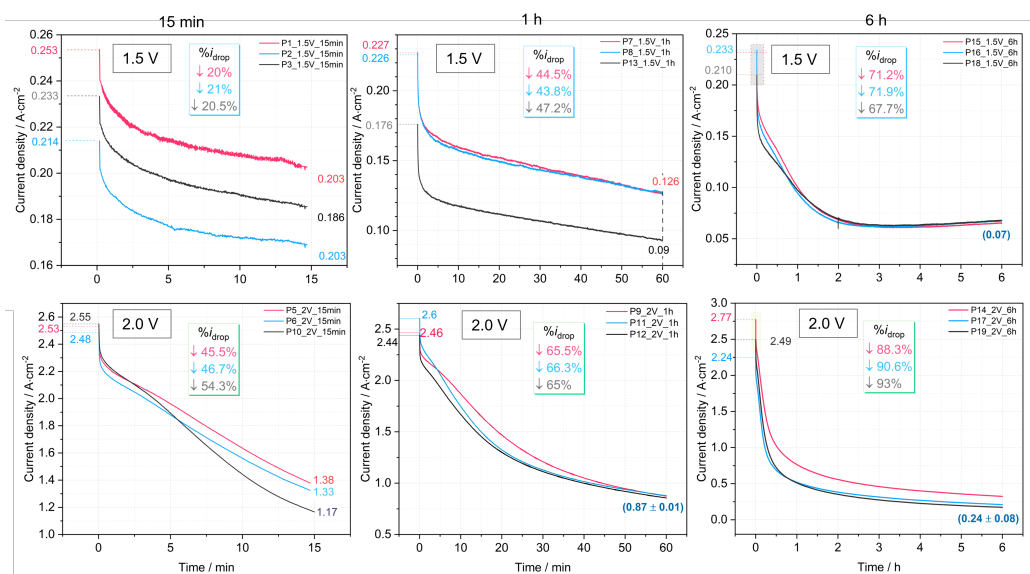


Figure A.28. Current densities during oxidation experiments with TiF_TiN PTLs during 15 min, 1 h and 6 h PEMWE single cell operation at 1.5 V and 2.0 V. Three repetitions are shown per experiment with percentage decrease in current density.

A. Appendix

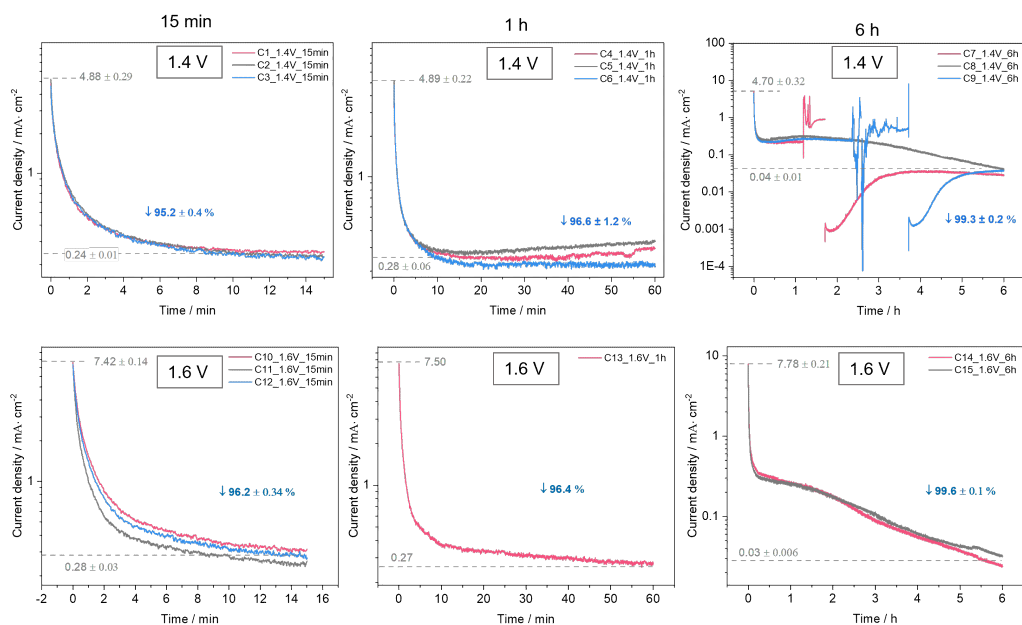


Figure A.29. Current densities during oxidation experiments with Ti-TiN during 15 min, 1 h and 6 h polarization in 0.45 M sulfuric acid at 1.4V and 1.6V vs. RHE. Repetitions are shown with average percentage decrease in current density.

A.13. Appendix for 7.2 Results - Titanium-reduced and stainless steel-based anode PTLs: Pt PVD

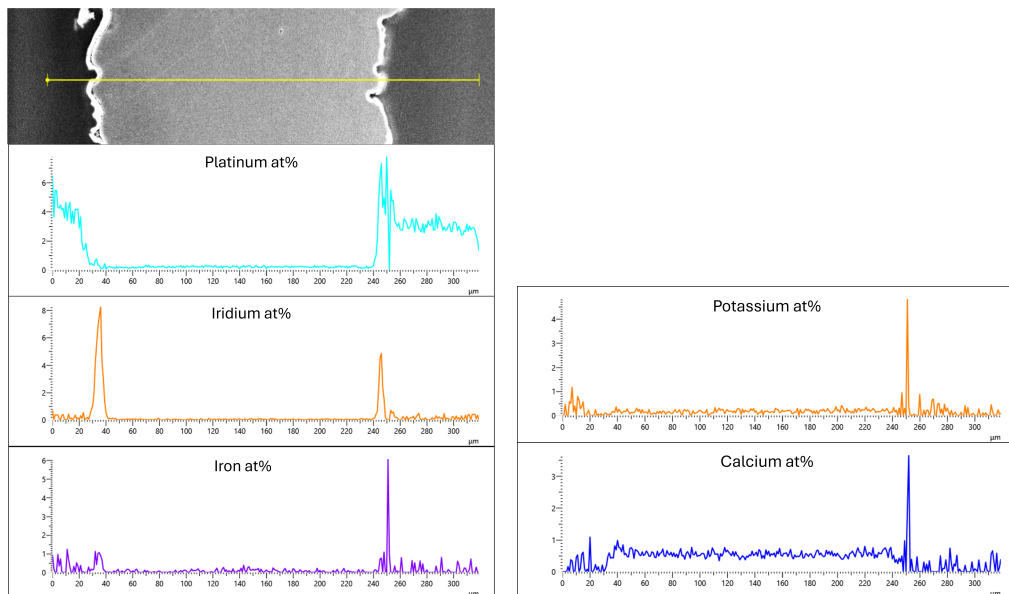


Figure A.30. Post mortem MEA cross section (SEM linescan 1) after 525 h at 2.0 V PEMWE single cell testing with SMF8_Pt_1 anode PTL with analysis of the distribution of Pt, Ir, Fe, K and Ca by means of EDX. Pt detected in the membrane originates from sputtering the cross-section with Pt to prevent the membrane from becoming charged.

A. Appendix

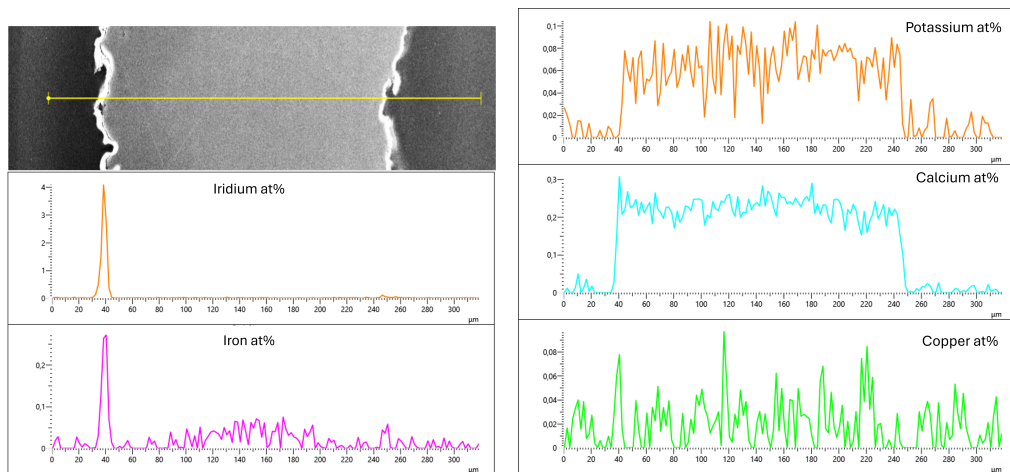


Figure A.31. Post mortem MEA cross section (SEM linescan 2) after 525 h at 2.0 V PEMWE single cell testing with SMF8_Pt_1 anode PTL with analysis of the distribution of Ir, Fe, K, Ca and u by means of EDX. Counts are given in atomic percent.

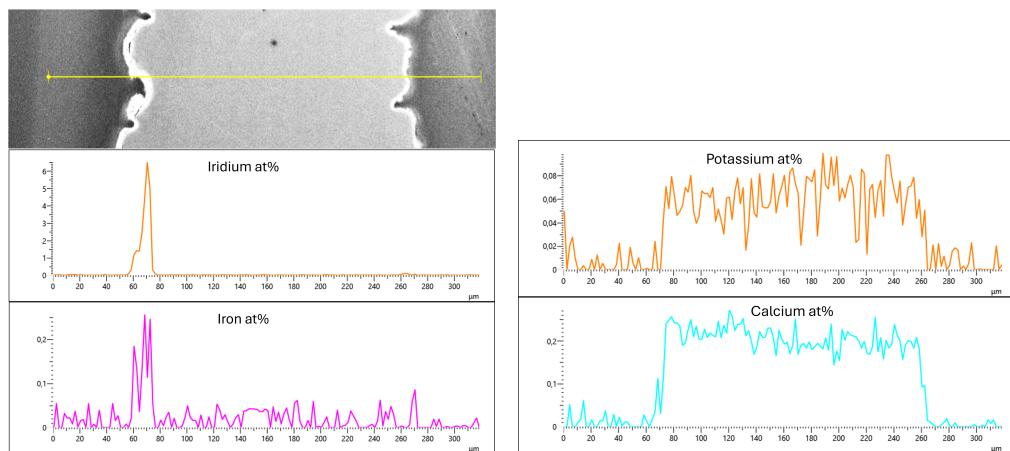


Figure A.32. Post mortem MEA cross section (SEM linescan 3) after 525 h at 2.0 V PEMWE single cell testing with SMF8_Pt_1 anode PTL with analysis of the distribution of Ir, Fe, K and Ca by means of EDX. Counts are given in atomic percent.

A. Appendix

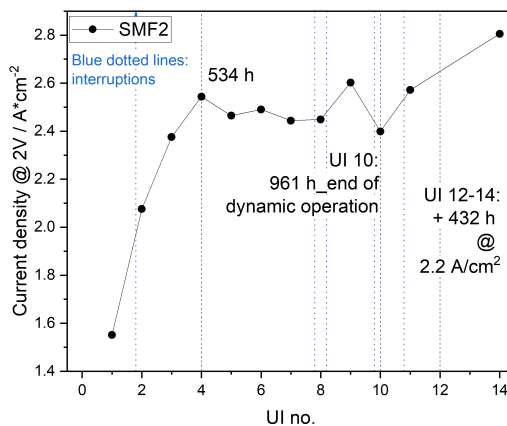


Figure A.33. Current density at 2.0 V from I-V curves between dynamic wind profile testing with PEMWE single cell with SMF8_Pt_2 anode PTL with indication of I-V curve number 4 and 10 which were recorded after 543 h and 961 h of dynamic wind profile operation. After I-V curve 11 and the cell was operated at a constant current density of $2.2 \text{ A} \cdot \text{cm}^{-2}$ for 432 h. Interruptions of the measurement are indicated by blue dotted lines.

Three linescans from MEAs that have been operated with SMF8_Pt_2 have been recorded. Two are shown in the following.

A. Appendix

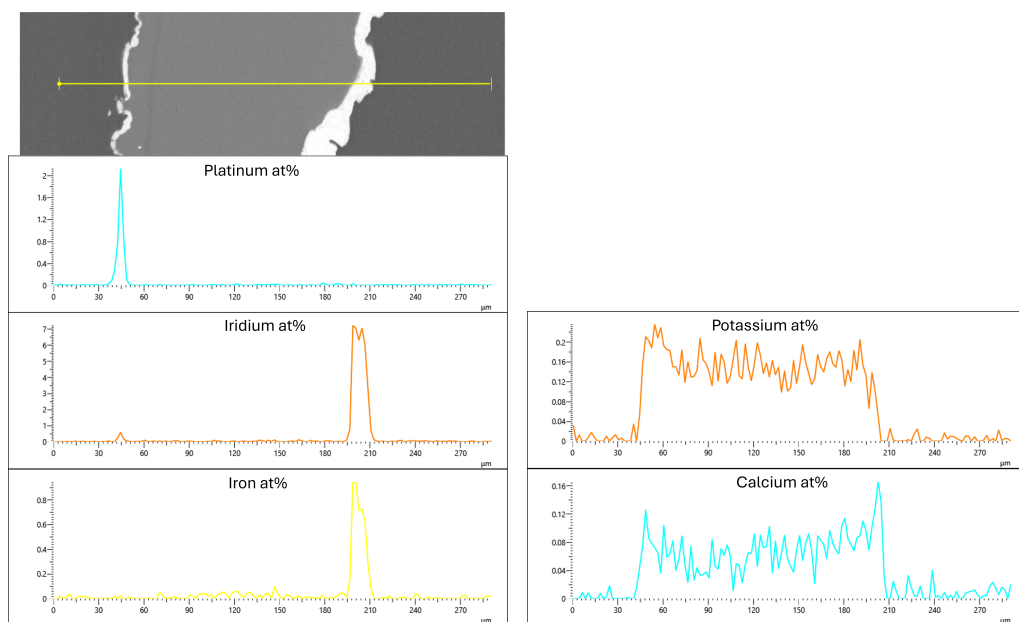


Figure A.34. Post mortem MEA cross section (SEM linescan 1) after 1452 h dynamic wind profile and galvanostatic PEMWE single cell operation with SMF8_Pt_2 anode PTL (316L felt on expanded mesh with Pt coating) with analysis of the distribution of Pt, Ir, Fe, K and Ca by means of EDX. Counts are given in atomic percent.

A. Appendix

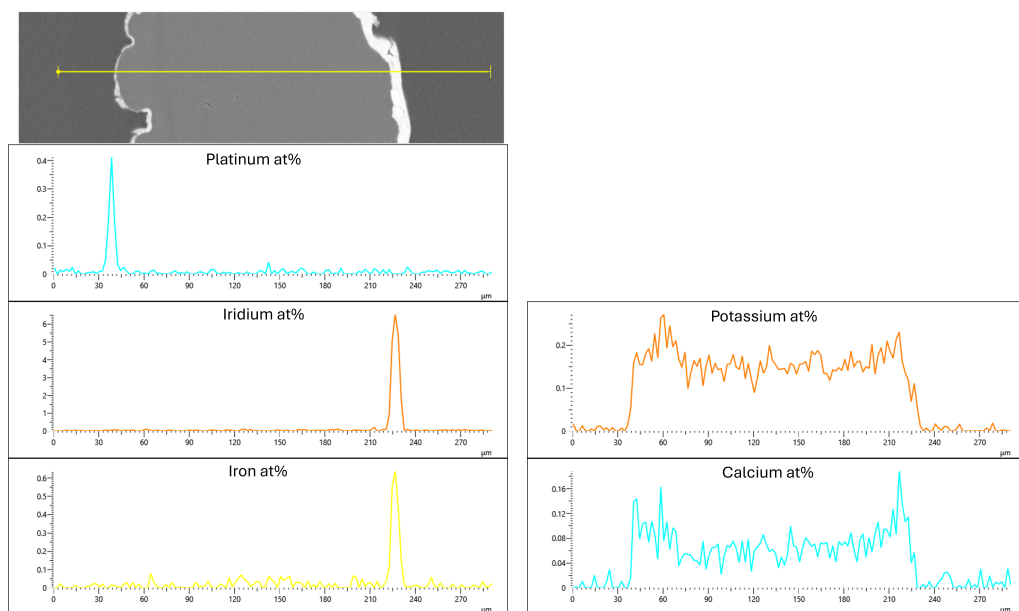


Figure A.35. Post mortem MEA cross section (SEM linescan 3) after 1452 h dynamic wind profile and galvanostatic PEMWE single cell operation with SMF8_Pt_2 anode PTL (316L felt on expanded mesh with Pt coating) with analysis of the distribution of Pt, Ir, Fe, K and Ca by means of EDX. Counts are given in atomic percent.

A. Appendix

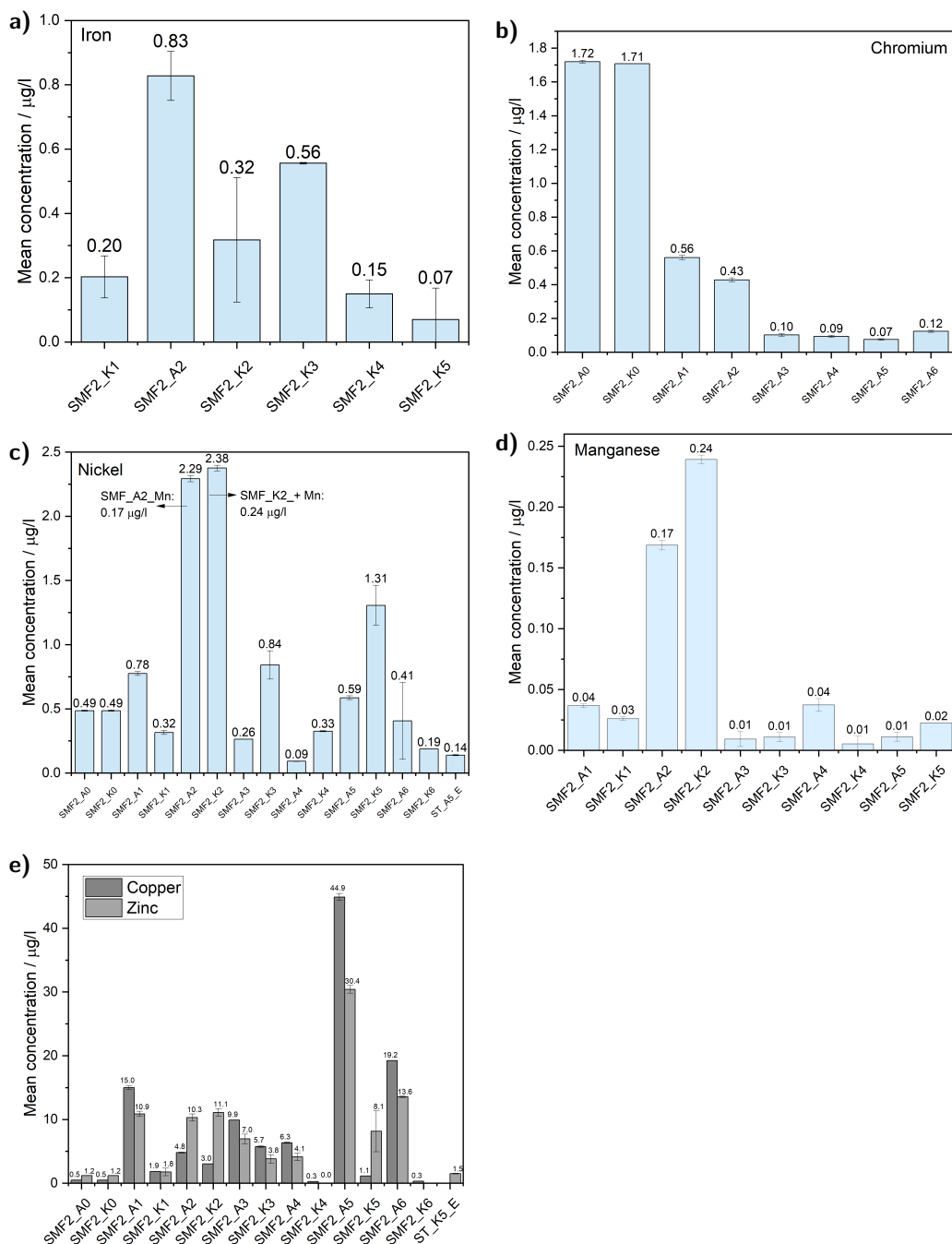


Figure A.36. ICP-MS analysis of Fe, Ni, Cr, Mn, Cu and Zn from effluent water from single cell operation with SMF8_Pt_2, A= anode side, K= cathode side, ST_A or K_E= storage tank anode or cathode at the end of test; Samples are sorted by the time of their collection. 0-samples were taken at the beginning of the test during the heat-up without electrolysis. c) In addition to Ni, Mn was found in samples A2 and K2.

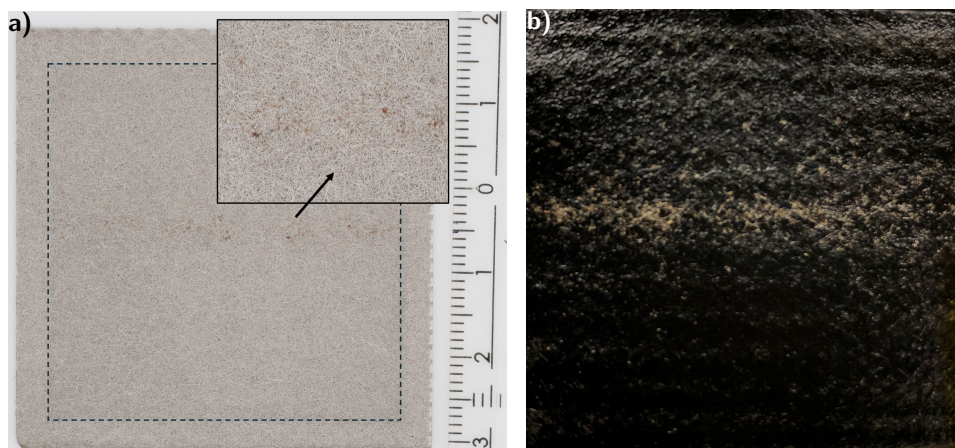


Figure A.37. Post mortem photographs of: a) 316L felt PTL (average fiber diameter of $22\text{ }\mu\text{m}$) coated with Pt, active area is marked with the dashed line, zoomed in picture at the upper right corner where corroded areas are visible, corroded spots were also visible on the back side, similar to Figure 7.7b; b) Corresponding anode catalyst layer with detached fibers from the PTL.

A.14. Appendix for 7.3 Results - Titanium-reduced and stainless steel-based anode PTLs: Ti PVD coating

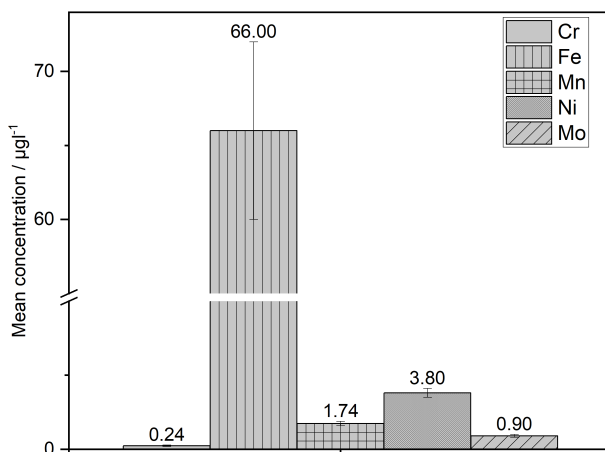


Figure A.38. ICP-MS analysis of water exposed to the 316L expanded mesh for about 90 h at 80.0 ± 1.0 °C and 80 h at room temperature, evaporated water was refilled.

A. Appendix

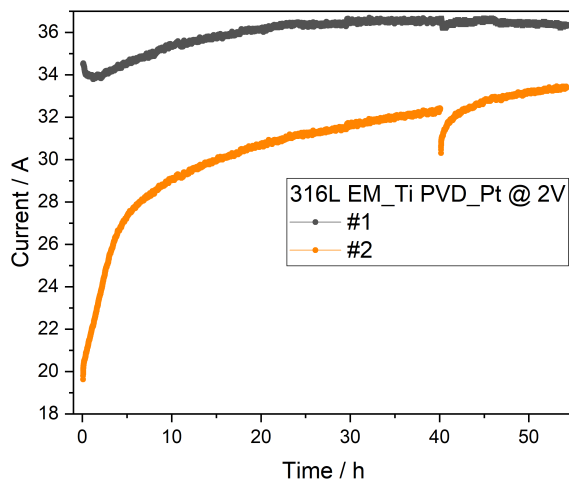


Figure A.39. Current from PEMWE single cells at 2.0V with Ti and Pt PVD coated 316LEM anode PTLs, sample number one and two.

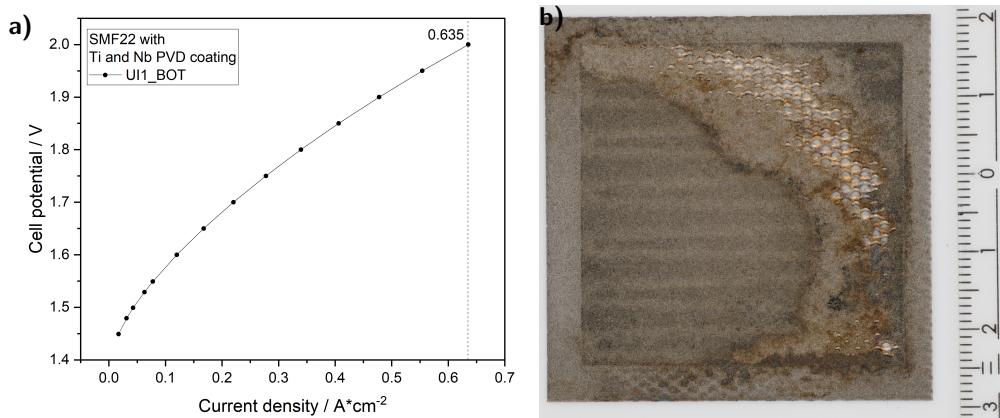


Figure A.40. a) I-V curve of a PEMWE single cell with 316L Ti and Nb PVD coated anode felt PTLs with a mean fibre diameter of 22 μ m (SMF22); b) Photograph of SMF22_Ti_Nb_PVD post mortem.

A. Appendix

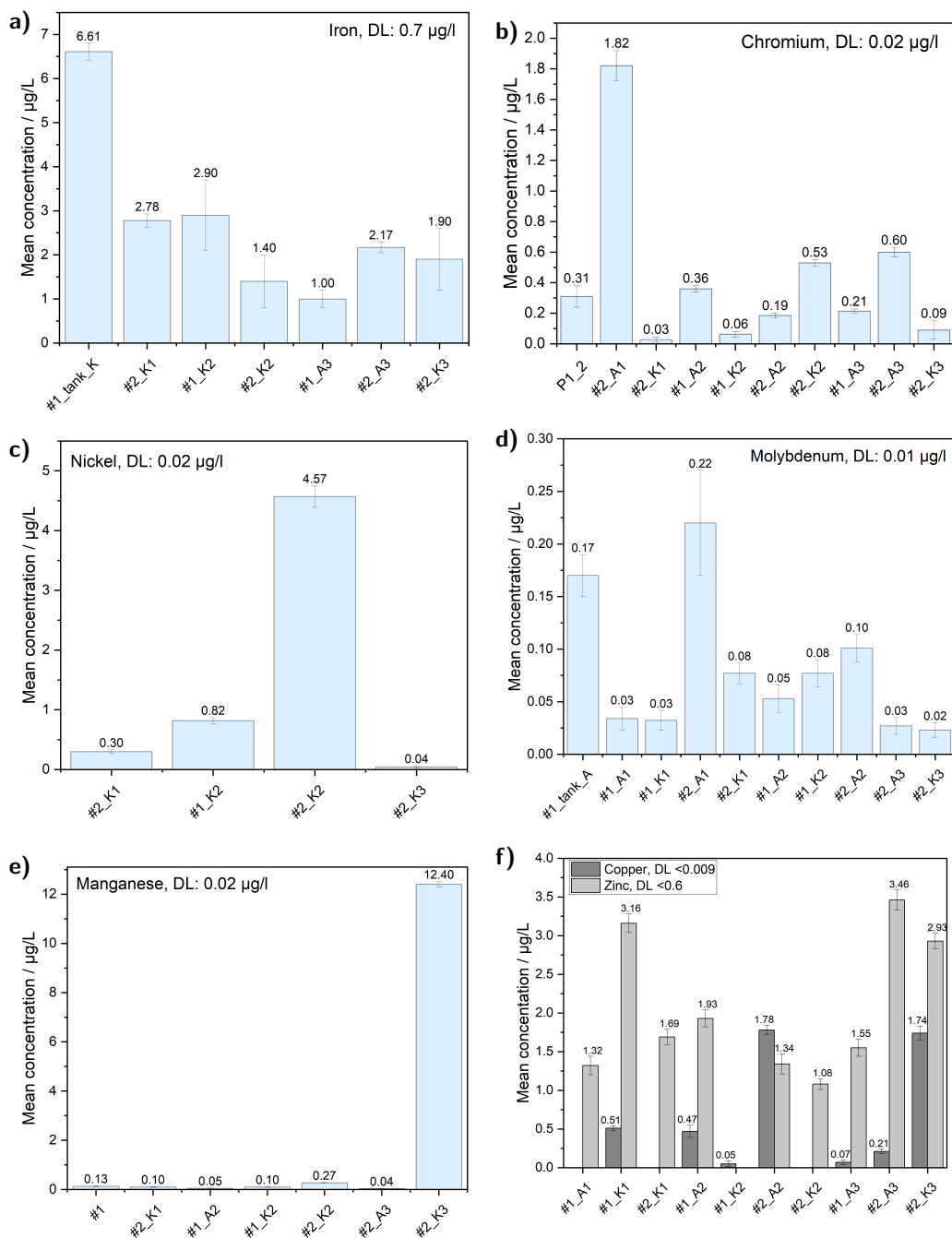


Figure A.41. Mean concentrations of Fe, Cr, Ni, Mn, Mo, Cu and Zn from single cell operation with 31LEM_Ti_PVD_Pt (two cells, see subsection 7.3.1) analyzed with ICP-MS, A= effluent samples from the anode side, K= effluent samples from the cathode side; The water samples are sorted by the time of their collection. All samples in which the corresponding analytes were below the detection limit are not shown.

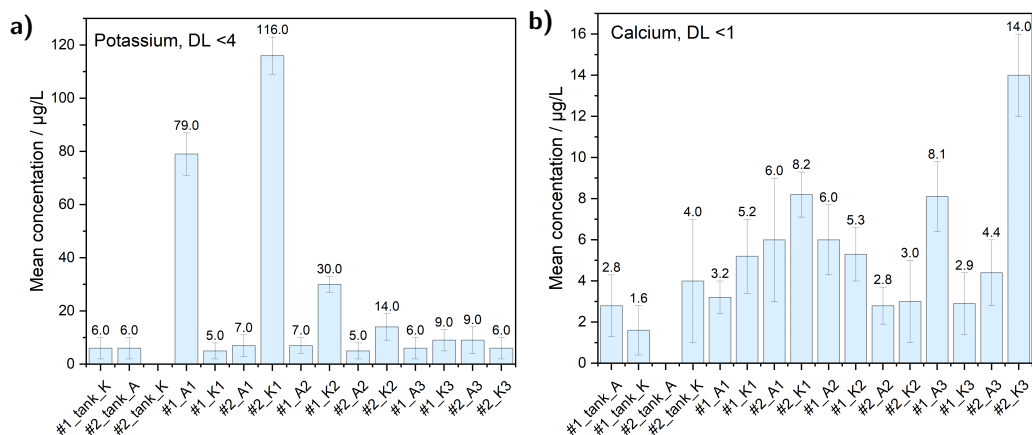


Figure A.42. Mean concentrations of Ka and Ca from single cell operation with 316LEM_Ti_PVD_Pt (two cells, see subsection 7.3.1) analyzed with ICP-MS, A= effluent samples from the anode side, K= effluent samples from the cathode side; The water samples are sorted by the time of their collection. All samples in which the corresponding analytes were below the detection limit are not shown.

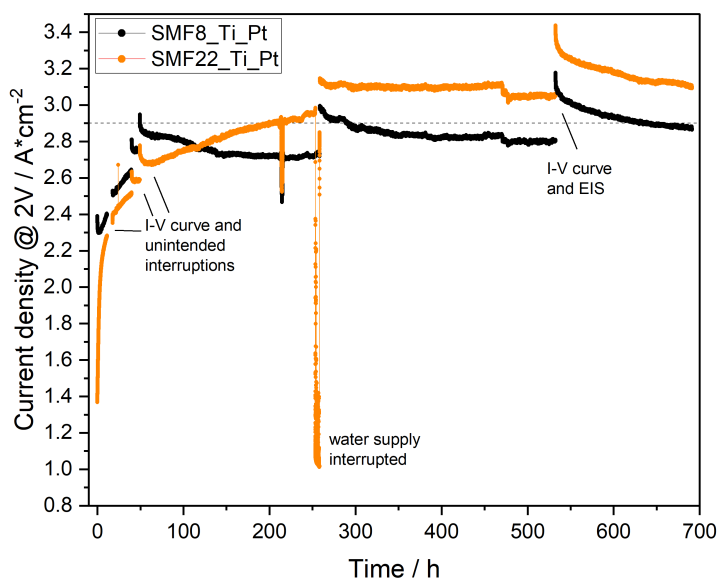


Figure A.43. Current density at 2.0 V of two PEMWE single cells with 316L Pt coated anode felt PTLs with a mean fiber diameter of 8 µm (SMF8) and 22 µm (SMF22) with titanium and platinum PVD coating (see subsection 7.3.2). The dashed line marks 2.9 A cm⁻² corresponding to the average current density measured with benchmark cells at 2.0 V.

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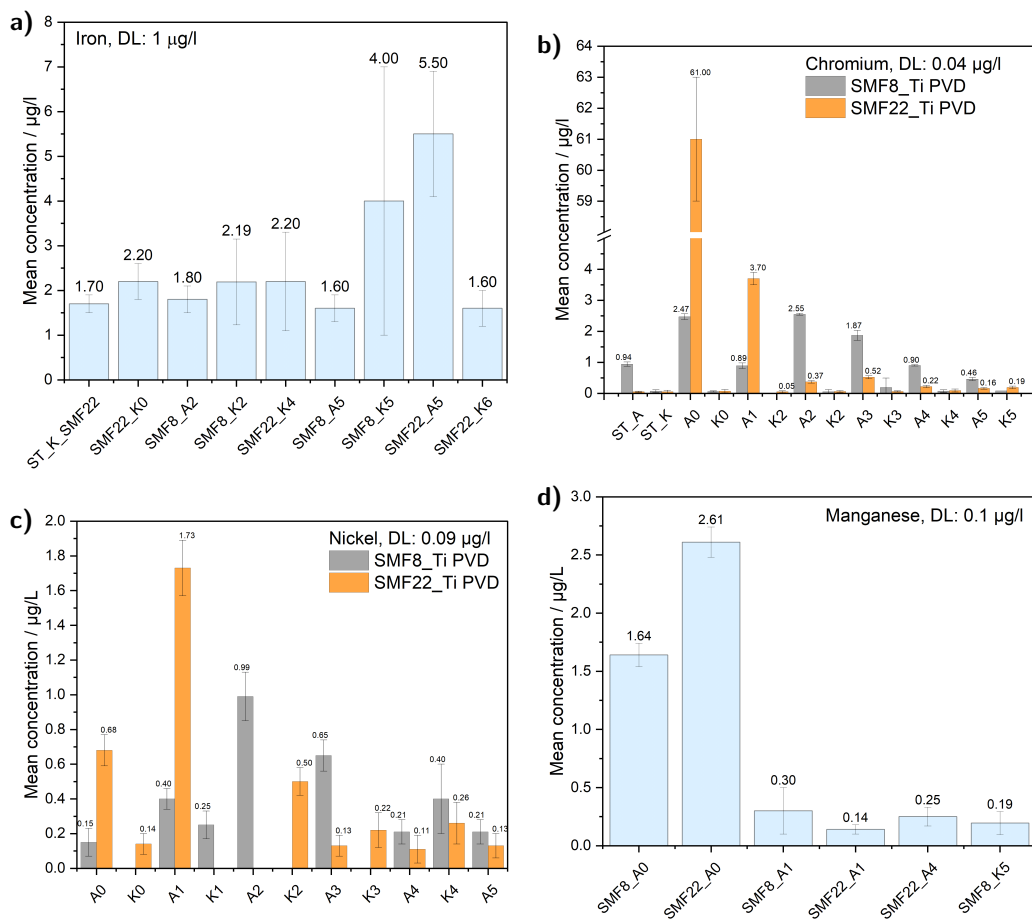


Figure A.44. Mean concentrations from single cell operation with SMF_Ti_PVD_Pt (two cells, see subsection 7.3.2) analyzed with ICP-MS, ST_A= storage tank anode, ST_K= storage tank cathode, A= effluent samples from the anode side, K= effluent samples from the cathode side; The water samples are sorted by the time of their collection. All samples in which the corresponding analytes were below the detection limit are not shown.

A. Appendix

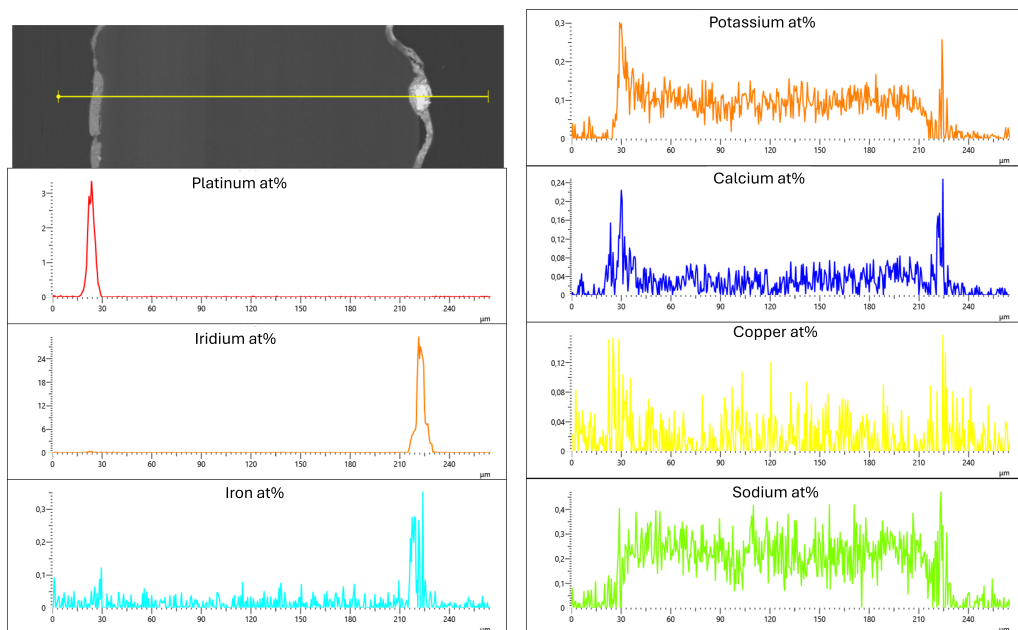


Figure A.45. Post mortem MEA cross section (SEM linescan 1) after 691 h at 2.0 V PEMWE single cell testing with SMF8_Ti-PVD_Pt anode PTL with analysis of the distribution of Pt, Ir, Fe, K, Ca, Cu and Na by means of EDX. Pt detected in the membrane originates from sputtering the cross-section with Pt to prevent the membrane from becoming charged.

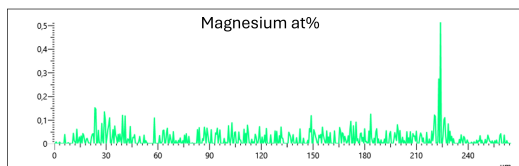


Figure A.46. Post mortem MEA cross section (SEM linescan 1) corresponding to Figure A.45 with analysis of the distribution of Mg by means of EDX. Pt detected in the membrane originates from sputtering the cross-section with Pt to prevent the membrane from becoming charged.

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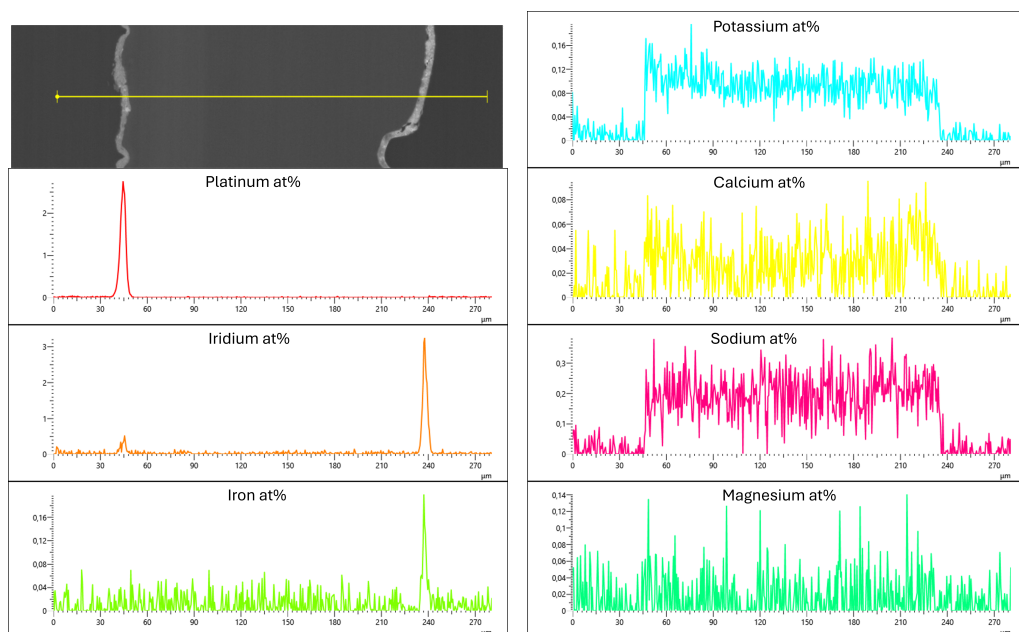


Figure A.47. Post mortem MEA cross section (SEM linescan 2) after 691 h at 2.0 V PEMWE single cell testing with SMF8_Ti-PVD_Pt anode PTL with analysis of the distribution of Pt, Ir, Fe, K, Ca, Na and Mg by means of EDX. Pt detected in the membrane originates from sputtering the cross-section with Pt to prevent the membrane from becoming charged.

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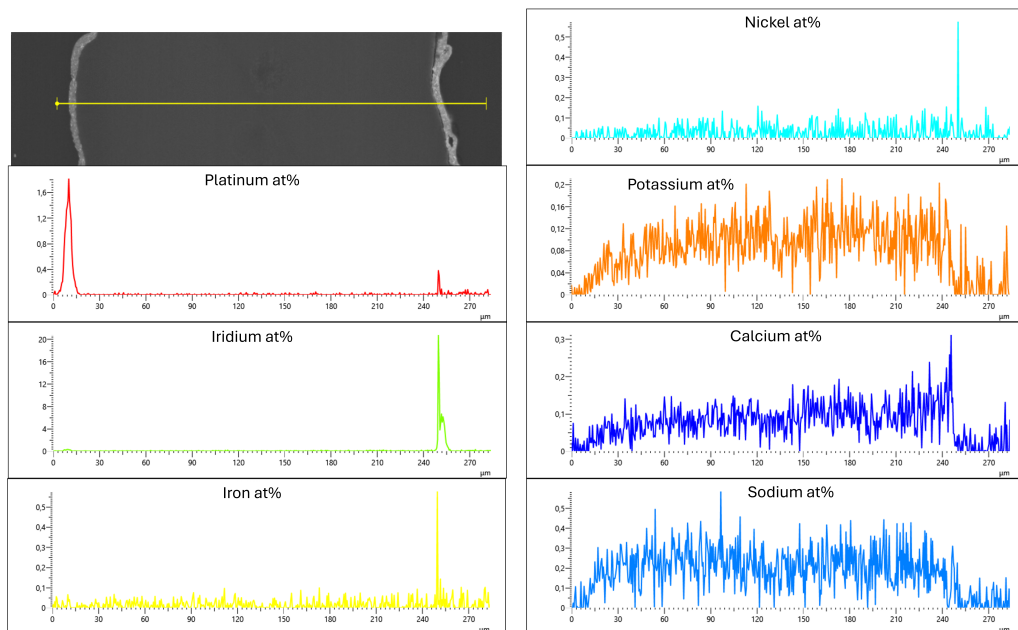


Figure A.48. Post mortem MEA cross section (SEM linescan 1) after 691 h at 2.0 V PEMWE single cell testing with SMF22_Ti-PVD_Pt anode PTL with analysis of the distribution of Pt, Ir, Fe, Ni, K, Ca and Na by means of EDX. Pt detected in the membrane originates from sputtering the cross-section with Pt to prevent the membrane from becoming charged.

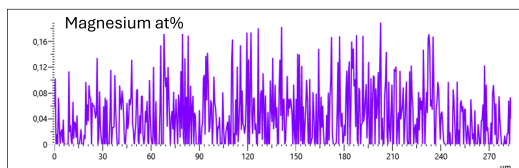


Figure A.49. Post mortem MEA cross section (SEM linescan 1) corresponding to Figure A.48 with analysis of the distribution of Mg by means of EDX. Pt detected in the membrane originates from sputtering the cross-section with Pt to prevent the membrane from becoming charged.

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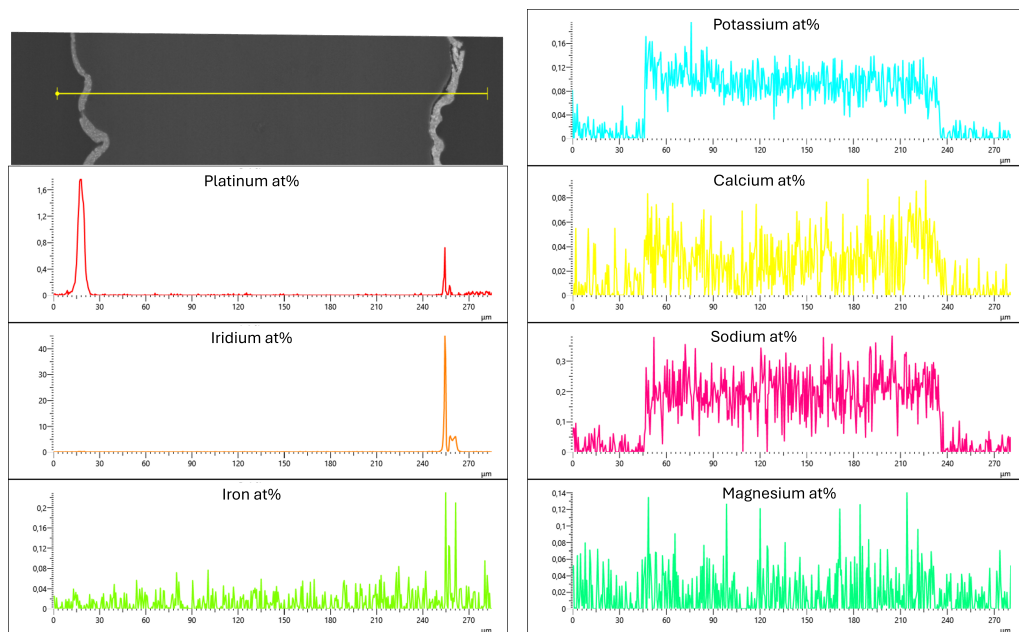


Figure A.50. Post mortem MEA cross section (SEM linescan 2) after 691 h at 2.0 V PEMWE single cell testing with SMF22_Ti-PVD_Pt anode PTL with analysis of the distribution of Pt, Ir, Fe, Ni, K, Ca and Na by means of EDX. Pt detected in the membrane originates from sputtering the cross-section with Pt to prevent the membrane from becoming charged.

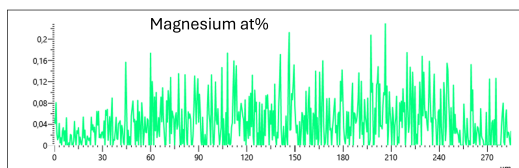


Figure A.51. Post mortem MEA cross section (SEM linescan 2) corresponding to Figure A.50 with analysis of the distribution of Mg by means of EDX. Pt detected in the membrane originates from sputtering the cross-section with Pt to prevent the membrane from becoming charged.

A.15. Appendix for 7.4.1 Results - Titanium-reduced and stainless steel-based anode PTLs: 60 μm titanium CGS

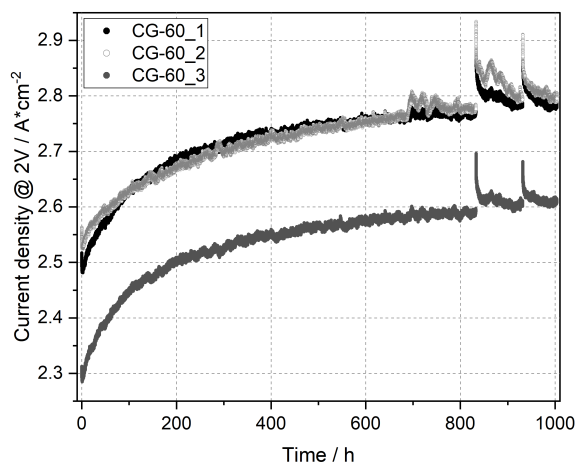


Figure A.52. Current density at 2.0 V with CG-60 PTLs, corresponding to section 7.4.

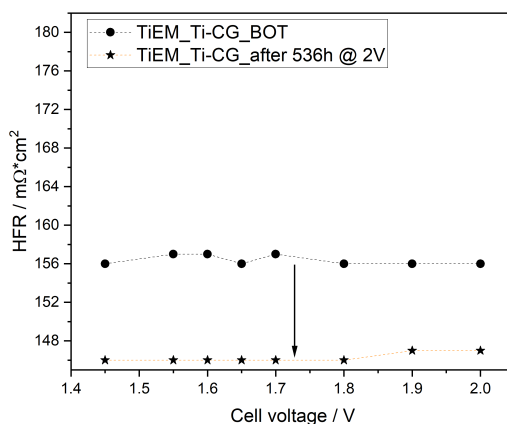


Figure A.53. High frequency resistances from impedance spectra in dependence of the cell voltage with TiEM_Ti-CG.

A. Appendix

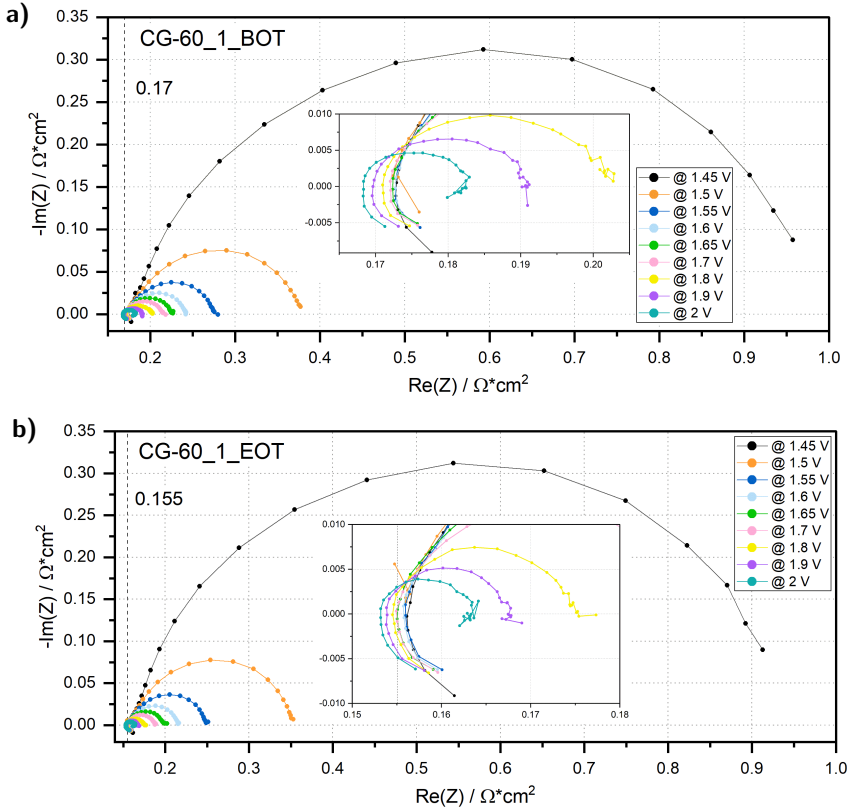


Figure A.54. Impedance spectra between 100 mHz and 10 kHz of a PEMWE single cell with CG-60_1 anode PTL. a) after conditioning and three I-V curves; b) EOT after 1006 h of operation at 2.0 V.

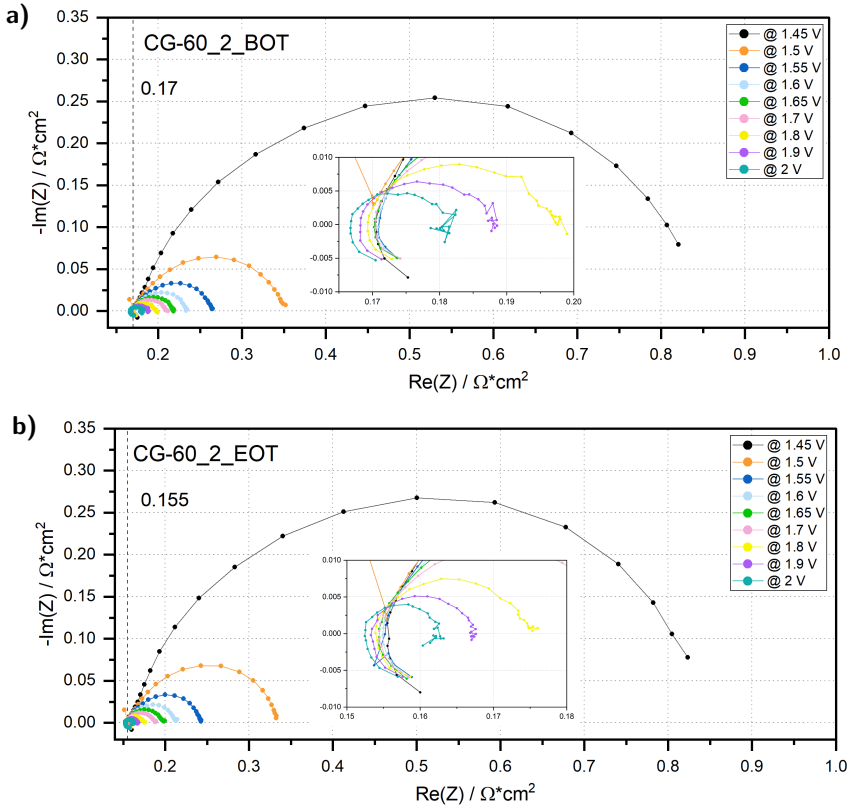


Figure A.55. Impedance spectra between 100 mHz and 10 kHz of a PEMWE single cell with CG-60_2 anode PTL. a) after conditioning and three I-V curves; b) EOT after 1006 h of operation at 2.0 V.

Calculation of theoretical titanium savings of a CG-60 coating on 316L mesh over a full TiF PTL

The specific weight of the commercially available TiF from Bekaert with an area of 17.64 cm^2 and a thickness of $360 \mu\text{m}$ can be calculated as follows:

Total volume of the felt:

$$V_{TiF} = 17.64 \text{ cm}^2 \cdot 0.036 \text{ cm} = 0.635 \text{ cm}^3 \quad (\text{A.3})$$

Volume of titanium in the PTL, taking porosity into account:

$$V_{Ti} = 0.635 \text{ cm}^3 \cdot (1 - 0.68) = 0.2032 \text{ cm}^3 \quad (\text{A.4})$$

Total mass of the titanium felt, with a titanium density of 4.5 g cm^{-3} :

$$m_{TiF} = 0.2032 \text{ cm}^3 \cdot 4.5 \text{ g cm}^{-3} = 0.9144 \text{ g} \quad (\text{A.5})$$

Area-specific weight of the titanium felt:

$$m_{TiF_area-specific} = \frac{0.9144 \text{ g}}{17.64 \text{ cm}^2} = 0.0518 \text{ g cm}^{-2} \quad (\text{A.6})$$

With an area-specific weight of the CG-60 coating of 21.6 mg cm^{-2} and deposition efficiency of 55 % of the CGS process, the amount of Ti used for the coating amounts for:

$$m_{Ti-CGS_area-specific} = 21.6 \text{ mg cm}^{-2} \cdot \frac{100}{55} \quad (\text{A.7})$$

$$= 39.3 \text{ mg cm}^{-2} \quad (\text{A.8})$$

Thereby, the deposition efficiency only takes into account the proportion of powder that passes through the openings of the expanded metal. Powder that is deposited on the walls of the spray chamber outside the expanded metal in the edge areas is disregarded, as this proportion varies depending on the size of the substrate. The theoretical titanium savings results as follows:

$$Titanium \text{ saving} = \frac{52 \text{ mg cm}^{-2} - 39 \text{ mg cm}^{-2}}{52 \text{ mg cm}^{-2}} \cdot 100 = 25\% \quad (\text{A.9})$$

A.16. Appendix for 7.4.2 Results - Titanium-reduced and stainless steel-based anode PTLs: 48 μm and 33 μm titanium CGS

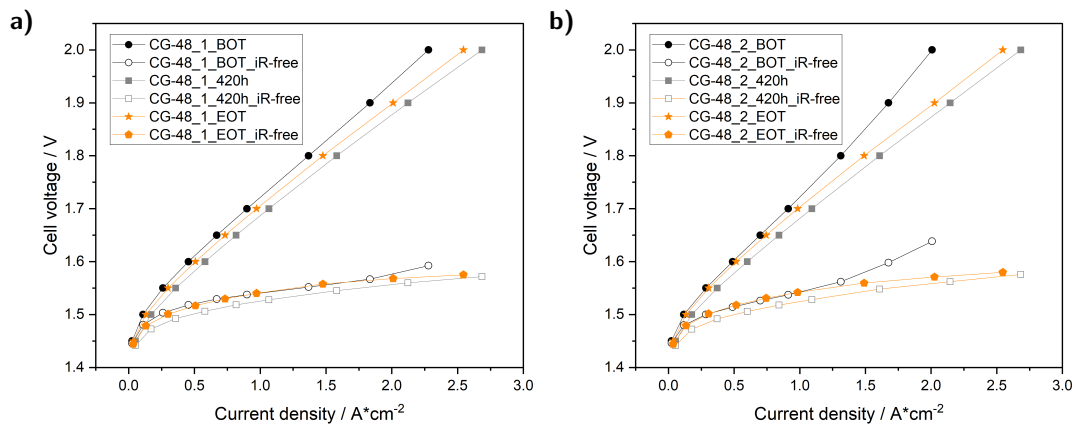


Figure A.56. I-V curves and iR-free I-V curves of two PEMWE single cells BOT, after 420 h and after operation at 2.0 V for 1004 h; a) CG-48_1; b) CG-48_2.

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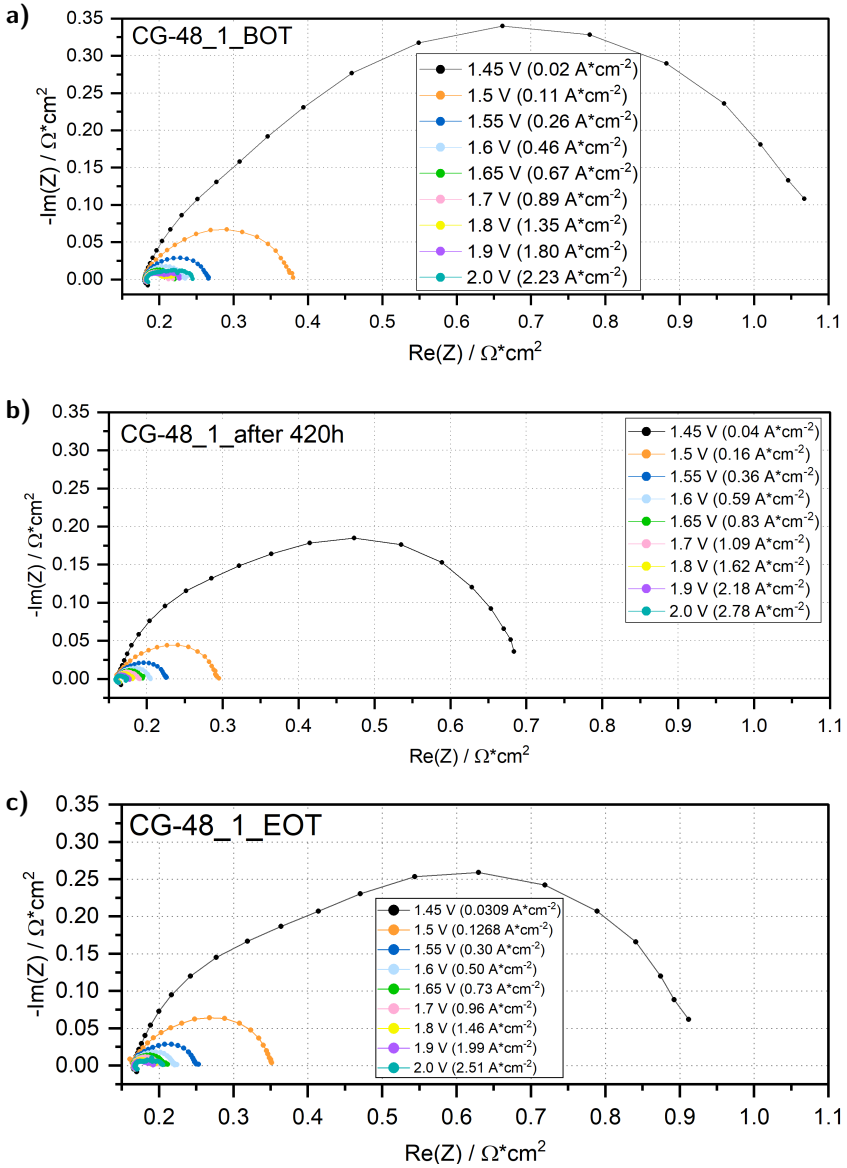


Figure A.57. Impedance spectra between 100 mHz and 10 kHz of a PEMWE single cell with CG-48_1; EOT= 1004 h.

A. Appendix

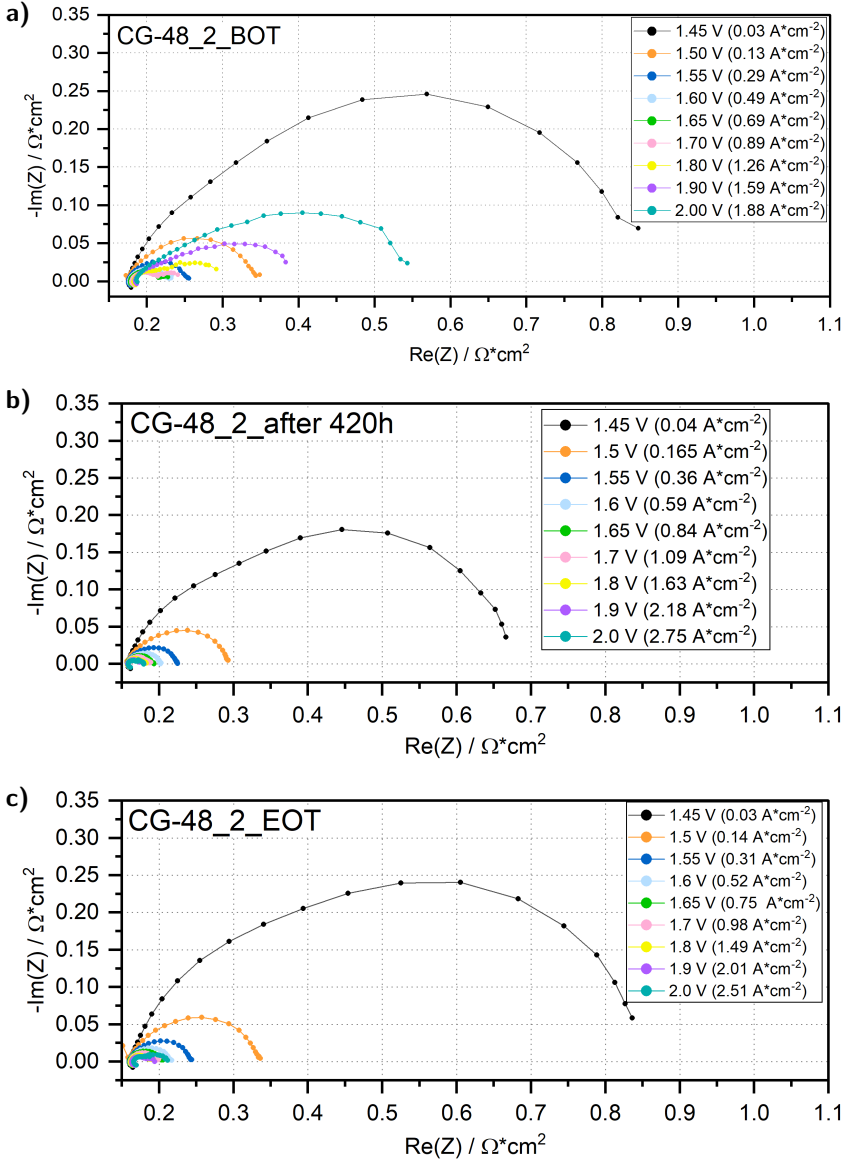


Figure A.58. Impedance spectra between 100 mHz and 10 kHz of a PEMWE single cell with CG-48_2; EOT= 1004 h.

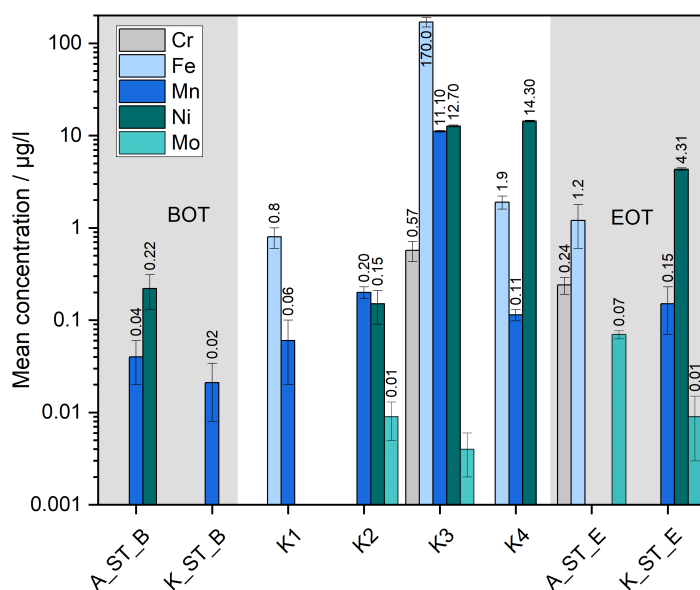


Figure A.59. ICP-MS analysis from single cell operation with Ti CGS coated 316LEM (CG-33, corresponding to subsection 7.4.2). Samples with a gray background were taken from the storage tanks (ST), left before starting electrolysis (BOT) and right after the experiment (EOT). K= effluent samples from the cathode side; The water samples are sorted by the time of their collection. All samples in which the corresponding analytes were below the detection limit are not shown.

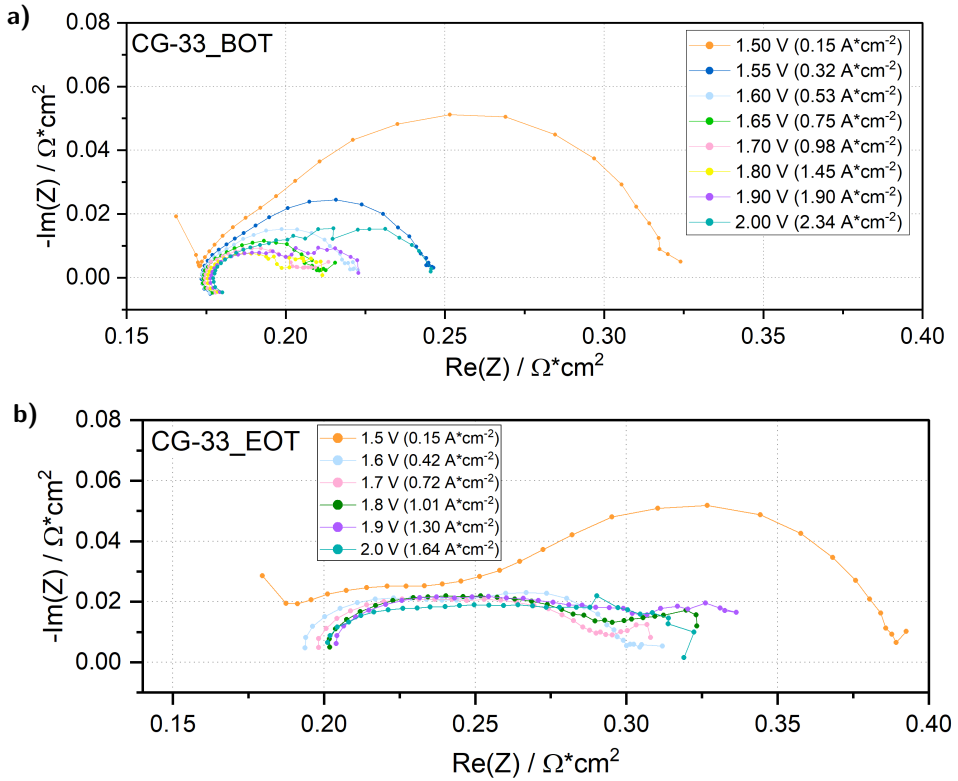


Figure A.60. Impedance spectra between 100 mHz and 10 kHz of a PEMWE single cell with CG-33; EOT= 362 h.

A.17. Appendix for 8 Results - Dynamic operation

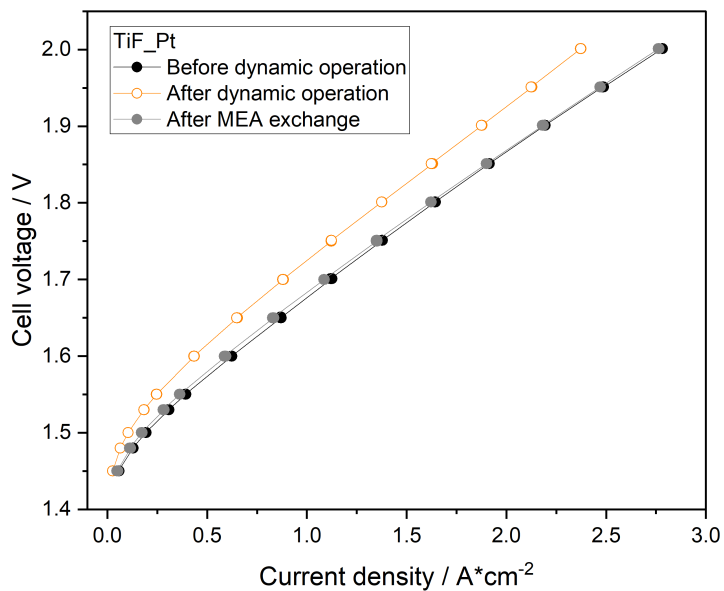


Figure A.61. I-V curves from cell 39 after experiments conducted in chapter 4, dynamic operation consisting of switching between 0 V and 2.0 V every 20 s and replacement of the MEA.

Dank

Mein erster und aufrichtiger Dank gilt Ulf-Peter Apfel, Ralf Peters und Werner Lehnert, Martin Müller und Andreas Glösen, die mir die Chance und Möglichkeit gegeben haben, mein Promotionsprojekt anzugehen sowie Bastian Mei für die Übernahme des dritten Gutachtens.

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Diese Liste könnte noch länger sein, denn alle am IET-4 und der AG-Apfel haben mir immer bei Fragen zur Verfügung gestanden, das weiss ich sehr zu schätzen!

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