Porous Transport Layers Made of Niobium/Steel Composites for Water Electrolysis

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Abstract

In future energy concepts, water splitting by polymer electrolyte membrane (PEM) electrolysis is a key technology for converting regenerative energy from wind or sun into hydrogen. In this study, a novel porous transport layer for PEM electrolysis units was developed, which is based on a stainless steel substrate coated with a porous Nb layer. Nb layer is expected to improve the electrochemical performance and lifetime of electrolysis cells due to formation of a stable passivation layer with good electrical conductivity. Scalable powder metallurgical techniques like tape casting, screen printing and field assisted sintering/spark plasma sintering FAST/SPS were used for manufacturing this composite structure. The porous transport layer was characterized with respect to microstructure. FAST/SPS was found to be promising to decrease interdiffusion at the interface. Finally, first electrochemical tests were conducted on laboratory scale demonstrating the potential of the composite to replace state-of-the-art titanium-based transport layers.

1. Introduction

Power-to-gas is referred in the literature [1] as key process to store energy through converting regenerative energy from wind or sun into gas such as hydrogen. Electrochemical devices can be used for hydrogen production from water electrolysis. Among the technologies available for water electrolysis, Polymer Electrolyte Membranes (PEM) electrolyzers have attracted huge attention due their outstanding efficiencies and high power density. Moreover, they have the advantage of operating at low temperatures and producing hydrogen with high purity at high pressures. However, the high materials costs and limited long-term performance and durability of PEM electrolyzers are still the main challenges to widespread this technology [2].

A specific component of PEM electrolyzer that needs development is the porous transport layer (PTL) used on the anode side. PTLs have the function of controlling the transport of electrons, water and gas molecules, therefore they should have high and interconnected porosity as well as a homogeneous distribution of pores to enable gas to be expelled and water molecules to reach the catalytic active area [2,3]. Furthermore, PTLs require materials with sufficient corrosion resistance to withstand the high electrochemical over potential, acid environment and presence of oxygen in status nascendi. In addition, high electrical conductivity and suitable mechanical strength to resist differential pressures up to 50 bar in the case of operating the system in high pressure mode are prerequisite.

Passivated titanium has very high corrosion resistance and high mechanical strength. Thereby, porous titanium has been acknowledged in the literature as suitable material for PTL application and the commercially used PTL are made of titanium meshes, perforated titanium sheets or sintered titanium [3,4]. Nevertheless, the use of high amount of titanium components is one of the main reason for the high materials costs of PEM electrolyzers. Furthermore, proceeding growth of passivation layer during PEM electrolyzer operation significantly decreases electrical contact of the PTLs, and therefore the electrolyzer performance [5]. The current strategy to improve electrical conductivity for long-term operation is to cover PTLs with a platinum or gold layer, which further increases materials costs.

One of the first studies aiming to investigate the role of PTLs microstructure on PEM electrolyzers performance was reported by Griogriev et al. [3]. After that, efforts have been focused on optimization of PTLs microstructure and manufacturing process. For instance, Ojong et al. [6] evaluated the effect of pore size, pore amount and PTLs thickness. Majasan et al. [7] studied the effect of microstructure of commercial PTLs on their electrochemical performance. Kang et al. [8] evaluated PTLs manufacture by lithography of titanium foils and Hackemüller et al. [4] investigated the production of Ti-based PTLs by tape casting. More recently, some works have focused on strategies to avoid titanium passivation. For instance Bystron et al. [5] avoid excessive titanium passivation by applying an etch treatment while Liu et al. [9] increased the electrical contact of Ti-based PTLs by coating them with a thin iridium film. Nevertheless, the literature does not discuss high costs of PTLs related in the case of using high amounts of titanium. In this context, we have focused on developing stainless steel-based PTLs.

In this study, we investigate the potential of PTLs made of niobium/stainless steel composites. The use of stainless steel aims on lowering material and manufacturing costs. However, as stainless steel has limited corrosion resistance in harsh environments such as the anode of PEM electrolyzer, a niobium coating is proposed as proactive layer. Even that a niobium oxidation may occur during electrolyzer operation, niobium oxide has higher conductivity than the titanium oxide formed on the titanium surface during passivation (the electrical conductivity of Nb_2O_5 is around 10^{-4} $S\cdot cm^{-1}$ and of TiO_2 around 10^{-6} $S\cdot cm^{-1}$). A detailed investigation of manufacturing Niobium/stainless steel (SS316L) composites manufacturing by scalable powder metallurgical techniques like tape casting, screen printing and assisted sintering/spark plasma sintering FAST/SPS was undertaken. First electrochemical tests in a single PEM cell were performed to evaluate the viability of Nb/SS316L composites based PTLs.

2. Experimental

Spherical stainless steel 316L powder (D_{10} = 11.7 µm, D_{50} = 18.6 µm, D_{90} = 29.0 µm) manufactured by Sandvik Osprey Powder, UK and acicular shaped niobium powder (D_{10} = 23.8 µm, D_{50} = 40.6 µm, D_{90} = 58.2 µm) manufactured by HC Stark, Germany were used as starting powders.

First, stainless steel (SS316L) substrates of 140 x 140 mm^2 and ca. 260 µm thickness were produced by tape casting using an automated tape casting line (FGA500, SAMA, Germany). For tape casting an alcohol-based slurry developed in house [4] was used. For final shape, the tapes were cut into 70 x 70 mm^2. Then, the samples were heated up to 500ºC under argon flow to remove binder. After that sintering took place at 1100ºC under vacuum (10^{-3} Pa).

Nb/SS316L composites were produced by screen-printing a Nb layer on the surface of the tape casted SS316L substrates. For that, a Nb slurry – based on a Terpineol and ethylcellulose solution – was printed using a semi-automatic screen printer (EKRA, Germany). Screen-printing of Nb layer was investigated on green and pre-sintered SS316L tapes. Pre-sintering was done at 1100°C. After printing, the samples were placed in an oven at 50 ºC for 3 h to remove solvents and then they were co-sintered in a vacuum furnace (10^{-3} Pa) at a temperature varying between 1000 and 1150ºC for 3 h.

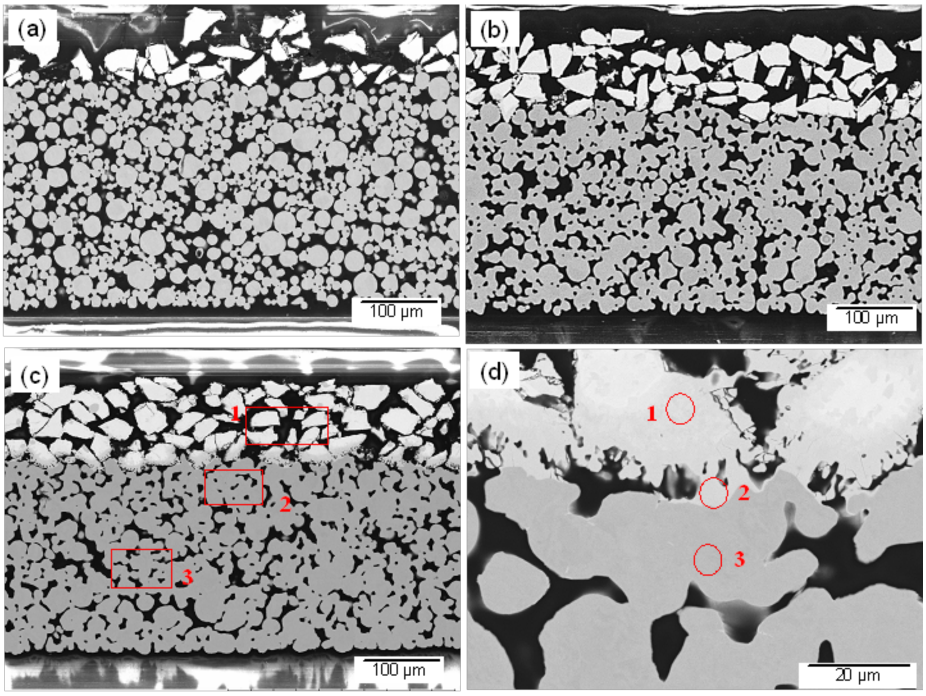
Field assisted sintering/spark plasma sintering FAST/SPS of Nb/SS316L composited was also investigated. FAST/SPS aims to decrease the interdiffusion at the interface between Niobium and SS316L layer. At this stage of development, only dense layers were produced, since dense layers enabled to achieve a more defined Nb/SS316L interface. FAST/SPS experiments were carried out in a lab-scale device (FCY-HPD5, FCT Systeme GmbH, Germany) with standard graphite tool of 20 mm inner diameter. A detailed description can be found in our recent publication [10]. First, Nb was poured in the pressing die and pre-compacted by uniaxial pressure, than Nb layer was sintered by FAST/SPS under vacuum (ca. 3 Pa) at 1500 ºC using a uniaxial pressure of 50 MPa with a dwell time of 30 s at sintering temperature. After sintering, the carbide layer was removed by grinding and polishing the Nb part. Afterwards, the Nb part was put back into the graphite die, the SS316L powder was added and the mixture was pre-compacted using uniaxial pressure of 50 MPa for 60 s. After that, Nb/SS316L composites were sintered by FAST/SPS under vacuum (ca. 3 Pa) at 1000 ºC with axial pressure of 50 MPa, the sintering temperature was held for 20 s.

Microstructural characterization was performed in the cross section of polished samples using a tabletop scanning electron microscope a (TM3030, Hitachi High Technology, Japan). Chemical composition was analyzed by Energy Dispersive Spectroscopy (EDS) performed using a Quantax 75 (Bruker Nano GmbH, Germnay). The X-Ray diffraction analyses were taken on SS316L substrate side, top surface (Nb layer) and Nb/SS316L interface using Bragg-Brentano geometry (θ-2 θ) in a Bruker D4 X-Ray Diffractometer (Bruker GmbH, Germany). Sample topography was investigated by optical profilometry (Cyber Scan CT300, Cyber Technologies, Germany). The electrochemical measurements were taken using the standard membrane electrode assembly MEA for PEM electrolysis at the Forschungszentrum Jülich. More details on the experimental setup can be found in the literature [4, 10]. The Nb/SS316L composites were cut into 42 x 42 mm^2 pieces and mounted on the anode side in a single test ring. The anode side was fed with water with a volume of 25 $ml\cdot min^{-1}$. The polarization curves were taken at 80 ºC with steps of 2 $A\cdot cm^{-2}$ and 5 min dwell time per measuring point, up to a voltage of 2.2 V. PTLs made of sintered titanium tapes were used as reference samples [4].

3. Results and discussion

3.1. Physical Properties

Nb/SS316L composites produced by screen-printing a Nb layer on green SS316L tapes and co-sintering at 1000, 1100 and 1150 ºC are shown in **Figure 1**. Due to weak sintering of Nb at 1000°C, Nb particles tend to partly flake off resulting in a slightly reduced layer thickness. With increasing sintering temperature, a higher interdiffusion of Nb, Fe, Cr, Mn and Ni atoms was found at the interface (**Figure 1**) resulting in the formation of intermetallic compounds as confirmed by XRD (results not shown here). The formation of intermetallic compounds was mainly restricted to the interface region, nonetheless intermetallic compounds can decrease the corrosion resistance and lead to embrittlement. Furthermore, the difference of sintering activity and shrinkage between the niobium and SS316L layers resulted in a convex sample bending at sintering temperatures above 1100ºC.



(e)

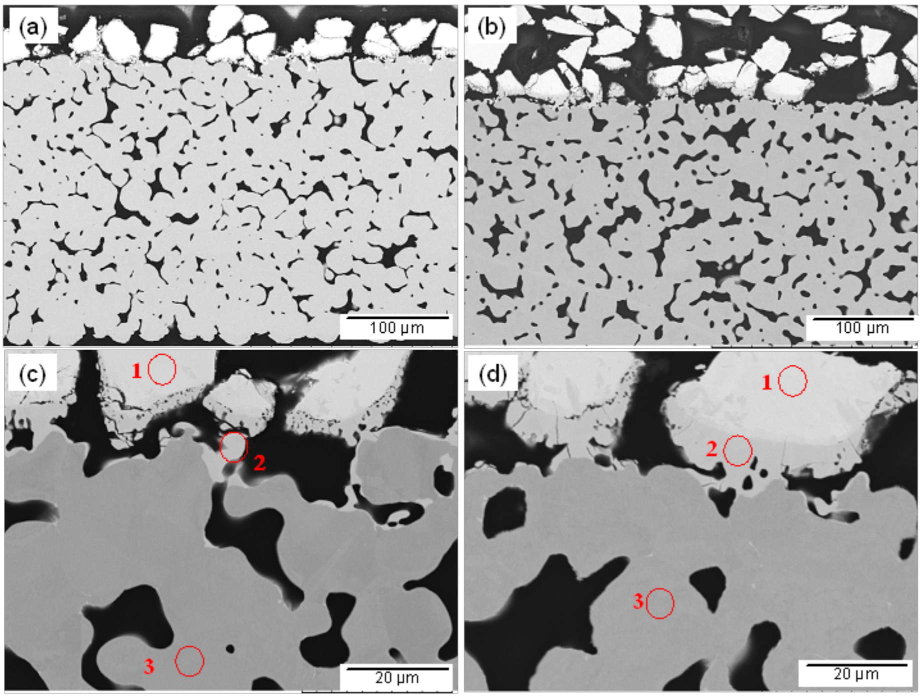
Point	Nb (wt.%)	Fe (wt.%)	Cr (wt.%)	Ni (wt.%)	Mo (wt.%)	Mn (wt.%)
1	97	0.6	0.2	0.1	1.9	0.1
2	0.8	69.2	16.0	10.8	2.9	0.3
3	0.2	69.3	16.5	10.7	2.5	0.8

(f)

Point	Nb (wt.%)	Fe (wt.%)	Cr (wt.%)	Ni (wt.%)	Mo (wt.%)	Mn (wt.%)
1	95.2	1.4	0.2	0.5	2.7	0.0
2	25.6	50.0	11.3	6.1	6.4	1.6
3	0.9	70.5	18.1	9.0	1.5	0.05

Figure 1. SEM images of Nb/SS316L composites produced by printing Nb powders on green SS316L tapes and co-sintering at: (a) 1000°C, (b) 1100°C, (c,d) 1150°C, (e) EDS of points indicated in (Fig c) and (f) EDS of points indicated in (Fig d).

In order to decrease the bending during co-sintering, Nb/SS316L composites were produced from screen-printing Nb powders on pre-sintered SS316L tapes followed by co-sintering at 1100 and 1150 ºC (**Figure 2**). The resulting microstructures and interdiffusion at the interface were found to be similar on green and pre-sintered tapes. Nevertheless, screen-printing and sintering of Nb powders on pre-sintered tapes reduced shrinkage and bending of SS316L layer. Again, weak sintering of Nb at 1100°C lead to partial flaking of Nb particles, therefore a reduced layer thickness resulted at this temperature. However, the bending of samples increased with sintering temperature (**Figure 3**). Some strategies like controlled plastic deformation could be applied to decrease sample bending and will be part of our ongoing studies.



(e)

Point	Nb (wt.%)	Fe (wt.%)	Cr (wt.%)	Ni (wt.%)	Mo (wt.%)	Mn (wt.%)
1	96.6	0.64	0	0.52	2.21	0
2	60.3	29.2	4.06	4.47	1.7	0.35
3	0.88	72.5	13.4	10.1	2.45	0.16

(f)

Point	Nb (wt.%)	Fe (wt.%)	Cr (wt.%)	Ni (wt.%)	Mo (wt.%)	Mn (wt.%)
1	96.7	1.02	0.48	0	1.82	0
2	47.8	31.6	7.3	6.0	7.31	0
3	0.68	70.99	14.2	14.2	3.49	1.0

Figure 2. SEM images of Nb/SS316L composites produced by printing Nb powders on pre-sintered SS316L tapes and co-sintering at: (a,c) 1100°C, (b, d) 1150°C. (e) EDS of points showed in (Fig c) and (f) EDS of points showed in (Fig d).

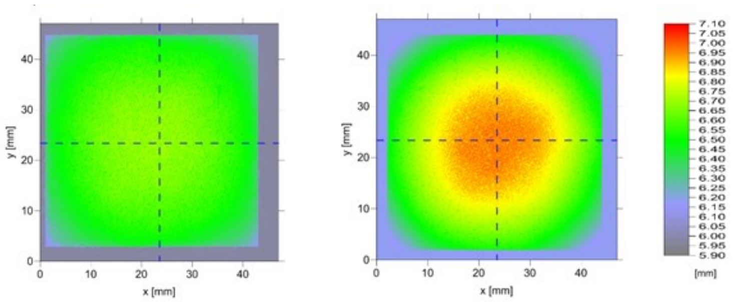


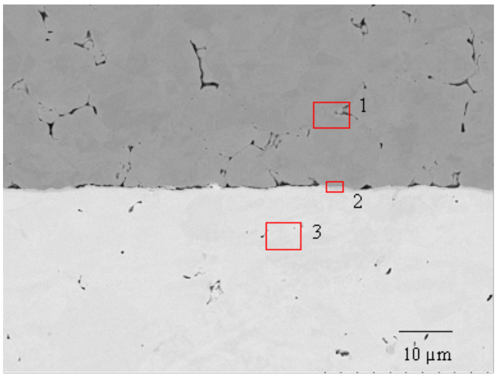
Figure 3. Optical profilometer analysis of Nb/SS316L composites produced by screen-printing Nb powders on pre-sintered SS316L tapes. Sintering of Nb layer was done at (a) 1100ºC and (b) 1150ºC.

Preliminary experiments were also conducted to evaluate the potential of FAST/SPS to produce Nb/SS316L composites. FAST/SPS enabled sintering with very short dwell times, which considerable decreased the interdiffusion (**Figure 4**). The low interdiffusion contributed to avoid the formation of secondary phases and carbides; only a thin interdiffusion layer was formed. The results obtained so far indicated that FAST/SPS is promising route for production of Nb/SS316L composites for PTLs application, and therefore our ongoing work will focus on applying this sintering technique.

3.2. Electrochemical Performance

Figure 5 compares the polarization curves of Nb/SS316L composites with the Jülich standard Ti-based PTLs measured in PEM single cell testing setup. At current densities below 1 A·cm^{-2}, Nb/SS316L composites and Ti-based PTL delivered similar voltages. However, at higher current densities, Nb/SS316L composites showed an increased overpotential. We believe that the high overpotential of Nb/SS316L composites in comparison with Ti-based PTLs was caused by the relatively low porosity of the SS316L layer and the partial flaking of Nb particles – such particles can enter the surface pores and hinder the water transport. Therefore, we expect that by optimizing the porosity and sintering of the Nb layer the adherence of Nb particles and the contact between the catalytic layer and the PTL will be improved and consequently the cell performance will be enhanced.

These preliminary results indicate that Nb/SS316L composites are promising candidates for application as PTLs of PEM electrolyzers. However, further studies are required to improve microstructure and to investigate durability and long-term performance of Nb/SS316L based PTLs.



Point	Nb (wt.%)	Fe (wt.%)	Cr (wt.%)	Ni (wt.%)	Mo (wt.%)	Mn (wt.%)
1	97.7	0.1	0.01	0.03	1.9	0.15
2	71.0	17.9	4.2	2.2	4.6	0
3	0.2	70.9	17.2	8.5	2.2	1.0

Figure 4. SEM image and EDS composition of the cross section of SS316L/Nb composites produced by FAST/SPS. Nb Layer was consolidated at 1500ºC and SS316L layer at 1100ºC.

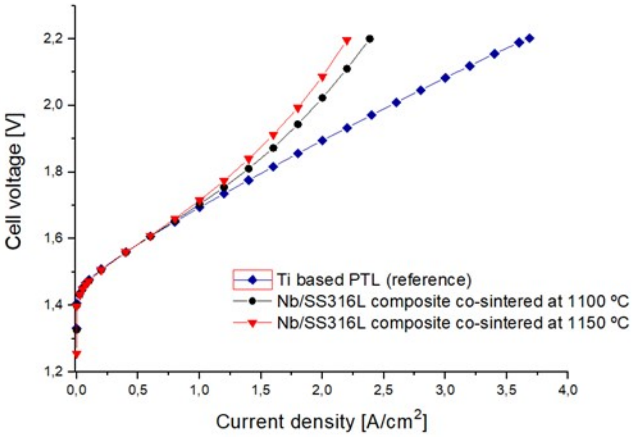


Figure 5. Polarization curves of Ti-based PTL and PTLs made of Nb/SS316L composites recorded in PEM single cell.

4. Conclusions

Nb/SS316L composites were successfully produced by screen-printing Nb powders on green and pre-sintered SS316L tapes. As expected, co-sintering temperature had a significant effect on the microstructure of the composites. Higher sintering temperatures improved sintering of Nb particles and reduced flaking of weakly sintered Nb particles. Consequently, a thicker Nb layer was achieved. On the other hand, higher sintering temperatures increased sample bending and decreased overall porosity. Screen-printing Nb powders on pre-sintered SS316L substrate reduced samples bending to some extent, however it adds an additional sintering step to the manufacturing process. A final overall thickness of 330 µm and an average porosity of 21.4 vol. % was achieved in the samples produced by screen-printing Nb powders on pre-sintered SS 316L tapes and subsequent co-sintering at 1100 ºC, which is in the range reported in the literature as suitable for PTL application. Up to now, samples produced with these parameters tend to be the best compromise, but more experimental work is still required to draw final conclusions.

The first electrochemical tests of the composite PTL in a PEM single cell test showed that Nb/SS316L composites behave similarly to Ti-based PTLs at current densities bellow 1 A·cm^{-2}. However, a mass transport limitation was indicated at higher current densities. Anyway, the results achieved so far demonstrate that Nb/SS316L composites are candidates for PTLs application. It is expected that by optimizing the microstructure of Nb/SS316L composites mass transport will be further improved. Related investigations are on the way.

FAST/SPS is another suitable manufacturing route for manufacturing of Nb/SS316L composites. The advantages of FAST/SPS are improved sintering of Nb particles and decreased interdiffusion between Nb and SS 316 L layer, which may result in an improved corrosion resistance. However, more efforts are required to enable the production of porous components by FAST/SPS being suitable for single cell testing and avoiding the formation of carbide layer at sample surface due to the contact with the graphite tool.

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