Experimental investigation of segmented SOECs:

Locally-resolved impedance and degradation

characteristics

Benjamin Königshofera,∗, Michael Höbera, Norbert H. Menzlerb, Hartmuth

Schröttnerc, Christoph Hochenauera, Vanja Subotića

aInstitute of Thermal Engineering, Graz University of Technology,

Inffeldgasse 25/B, 8010 Graz,

Austria

bForschungzentrum Jülich GmbH, Institute of Energy and Climate Research

(IEK-1: Materials

Synthesis and Processing), 52425 Jülich, Germany

cAustrian Centre for Electron Microscopy and Nanoanalysis, Steyrergasse

17, 8010 Graz,

Austria

Abstract

High temperature solid oxide electrolysis cells (SOEC) provide an

innovative

solution for direct conversion of steam and electricity to hydrogen with

the addi-

tional capability of adding CO2 to produce syngas. However, specific

operating

conditions can have a negative impact on the performance and lifetime of

SOECs.

In this context, the distributions of operational parameters such as gas

species,

temperature and current density within the cell structure influence local

transport

processes and reaction kinetics and can lead to locally different

electrochemical

potentials and thus degradation phenomena. This study focuses on

experimental

investigations of steam-electrode supported SOECs with segmented air

electrodes

with the main objective to measure EIS and thus identify locally-resolved

impedance

and degradation characteristics caused by different operating conditions

in steam

and co-electrolysis mode. Thereby, significant correlations between

operating condi-

tions, local effects, electrode processes and degradation mechanisms were

observed and analyzed in detail using EIS,DRT and SEM.

Keywords:

Solid Oxide Electrolysis Cell (SOEC), Segmented, Locally-resolved, Electrochemical Analayis, Distribution of Relaxation Times (DRT)

1. Introduction

In order to mitigate the threatening effects of the advancing climate

change,

greenhouse gas emissions must be drastically reduced and the further

expansion of

renewable energy sources is indispensable [1]. With the associated future

increase

in intermittent electricity generation, energy storage in the form of

hydrogen and

emerging hydrogen production technologies have recently attracted

increasing

interest [2, 3]. High-temperature solid oxide electrolysis cells (SOECs)

provide a

practical solution for the direct conversion of steam and electricity to

hydrogen [4],

with the additional ability of adding CO2 to the process to produce

syngas [5, 6],

which can then be further processed into valuable liquid fuels [6, 7].

With recent

major improvements at cell, stack and system level, the SOEC technology

is well

on its way to achieving greater technological maturity [8, 9].

However, different operating conditions are known to have a negative

impact

on the performance and lifetime of SOECs [10--12]. It is also known that

the

distribution of current, gas species, potential and temperature varies

across the

area of industrial-sized solid oxide cells [13, 14]. In general, these

distributions

depend on transport phenomena such as mass, heat and charge transfer

[

15], which

affect all chemical and electrochemical reactions across the cell [16,

7]. In [18--20],

1

the authors also discuss the negative effect of such local

inhomogeneities on the

long-term stability of SOECs. In order to gain a deeper insight into

these local

processes locally resolved current density, species and temperature

distributions can

be investigated using different simulation approaches. In this context,

simulation

2

studies focus on a wide range of areas such as the investigation of heat

and

mass transfer and electrochemical reactions [21], carbon capture and

gasification

mechanisms [22, 23], flow configurations and electrical contact positions

20] and

[

mechanical reliability and durability [24, 25].

There are also a few studies that focus on the experimental investigation

of

the influence of various design-related parameters on local effects

during solid

oxide fuel cell (SOFC) operation. For example, the authors in [26]

experimentally

investigated the influence of different flow channel designs on the

temperature

distribution of SOFCs. In doing so, they proposed an alternative flow

field design

that offers a very homogeneous gas distribution as well as improved

current

collection at significantly lower manufacturing costs. Differently, the

authors in

[27] experimentally investigated the influence of different contacting

methods on

the long-term and thermal cycling stability of SOFCs. They found that

current

collection conditions significantly affect cell stability during thermal

cycling and

proposed an alternative in situ voltage measurement technique in order to

assess

the influence of different current collection types.

As these studies focus mainly on current, gas species and temperature

distribu-

tions, it can be considered as crucial for the further development of the

technology

to extend the knowledge in this area to include the aspect of locally

resolved

impedance characteristics. However, the experimental studies required for

this

purpose require sophisticated cell and housing design as well as the

proficient appli-

cation of appropriate in situ characterization methods. Electrochemical

impedance

spectroscopy (EIS) has emerged as one such promising in situ

characterization

and online monitoring technique that can reliably determine performance

changes

[

28--31] and degradation rates [32--34]. Further analysis of the

impedance data

using the distribution of relaxation times (DRT) allows the extraction of

the most

important time constants, which, if used appropriately, makes it even

easier to

3

track changes of different single or coupled processes within the SOEC.

[

13, 35, 36].

This can be particularly useful for monitoring and interpreting small

changes across

the surface of a single cell. However, analyzing DRT spectra and

assigning peaks

to specific processes can be challenging.

Generally, the DRT peaks in the frequency range between 1 and 10 Hz are

associated with gas diffusion overlapped with gas conversion impedance of

the

steam electrode [37--40]. The respective weighting of the influence of

these processes

on the peaks depends on the positioning of the peak, with conversion

processes

generally occurring at lower frequencies and diffusion processes at

higher frequencies

[

1

41--45]. In addition, DRT peaks in the frequency range between 10 and

00 Hz

can also be associated with gas diffusion in the steam electrode but

overlapped

with oxygen surface exchange and ion diffusion in the air electrode. [39,

4

0, 46--49].

Thereby, the air electrode processes typically cover a wider frequency

range between

1

0

0 - 500 Hz [37--39, 42, 43, 45, 50--52]. Furthermore, DRT peaks between

.1 - 50

kHz can be associated with steam electrode processes such as gas

diffusion, charge

transfer reaction and ionic transport in the functional layer [37--39,

4

1, 43, 53, 54].

The higher frequency gas diffusion processes can mainly be linked to the

lower part

of this wide frequency range partly overlapping with the air electrode

transport

processes [47, 48, 53, 54]. The charge transfer processes occur

predominantly at

higher frequencies between approximately 1 and 10 kHz overlapped with

higher

frequency gas diffusion processes. [42, 43, 45--47, 51, 53, 54]. The

processes related

to ionic transport in the functional layer are located at even higher

frequencies

between 10 - 50 kHz [42, 43, 51, 53, 55].

With proper application of this knowledge, it is feasible to correctly

identify and

interpret small differences in the EIS and DRT spectra, relate them to

the specific

processes and derive valuable information about the locally-resolved

impedance

and degradation behavior of SOEC.

4

1

.1. Scope of this study

This study focuses on experimental investigations of steam-electrode

supported

SOECs with segmented air electrodes in stack-relevant size. The main

objective is

to identify locally-resolved impedance and degradation characteristics

caused by

different operating conditions during operation in steam and co-

electrolysis mode.

In this way, extensive electrochemical analyses using EIS and DRT were

performed

throughout the experiments, identifying significant correlations between

local

effects, operating conditions, electrode processes and degradation

mechanisms.

2

2

. Experimental setup

.1. Cell design and housing

The experiments within this study were performed on steam-electrode

supported

SOEC single cells composed of a Ni-YSZ steam electrode support and a

similar

composed finder thin electrode, an YSZ electrolyte, a barrier layer made

of Gd-

doped ceria (GDC) and a segmented La0.58Sr0.4Co0.2Fe0.8O3−δ (LSFC) air

electrode.

More details on the composition and thickness of the cell layers are

described in [56].

Fig.1a/1b show a schematic representation of the cell and flow

configurations. The

cells are 10 x 10 cm2 in size, with the air electrode divided into four

equal sections,

each with an active area of 4.25 x 4.25 cm2. The labels L-1/2 and R-1/2

refer to

the four different segments of the cell. The entire air electrode area is

contacted

with a platinum mesh placed over all four segments and the inactive

cross-shaped

area between them. Separate sensing leads are attached to the outer

corners of the

mesh for each of the four segments. Eight platinum cables were mounted

evenly

along the outer rim of the mesh minimizing the influence of the current

collection

positions on the current distribution according to [20]. The cells were

installed in

a ceramic housing within the furnace of the test rig, which allows

operation in co-,

counter- and cross-flow by changing the direction of the air flow as

presented in

5

Fig.1b. Within the ceramic cell housing, gases are distributed to both

electrodes via

gas flow channels. Multiple thermocouples (Type N) were positioned at the

in- and

outlets of the gas flows and within the ceramic plates. It should be

mentioned that

due to this positioning of the thermocouples within the ceramic plates,

the relative

changes in temperatures over time are more relevant than the absolute

values.

More details on the ceramic cell housing and the positioning of

thermocouples are

described in [57]. Additionally, the heat-up and reduction processes of

the cells are

described in [17].

2.2. Test rig

The scheme of the test rig used for the experiments is presented in

Fig.1c. A

gas control system with mass flow controllers regulates the mixing of the

inlet gas

compositions, with a separate steam generator used for the production of

steam.

The inlet gas mixtures are then pre-heated up to temperatures > 750 °C

before

entering the cell housing. The outlet gases pass through a water-cooled

condenser

to the exhaust. The test rig is further equipped with an electronic load,

impedance

analyzers and gas analyzers. More detailed information about the test rig

can be

found in [57].

6

Air, Cross-Flow

Air, Co-Flow

L-1 L-2

Fuel

Flow R-1 R-2 Air, Counter-Flow

(a) Exemplary representation of the cell (b) Cell segments and flow

configurations.

during installation in the cell housing.

Furnace,

Ceramic Cell Housing,

Cell

(c) Test rig. [28]

Figure 1: Experimental setup.

2.3. Operating parameters

In this study different operating conditions were applied to single cells

with

segmented air electrodes in electrolysis mode. In order to investigate

their influence

on the cell’s performance, the following parameters were varied during

the experi-

ments: gas inlet composition, temperature and current density. More

details about

the operating parameters are summarized in Tab.1 and 2. In this work, the

labels

containing "EC" refer to gas inlet mixtures with only steam as reactant.

The labels

7

Table 1: Gas inlet mixtures.

Label Fuel flow H2 H2O CO CO2 Air flow

SLPM % % % % SLPM

EC-50 2.0 50 50 2.0

CO-25 2.0 25 25 25 25 2.0

EC-90 2.0 10 90 2.0

CO-45 2.0 10 45 45 2.0

CC-90 2.0 10 90 2.0

Table 2: Operating parameters.

Fig. Mixture Temp. Current Flow Segment

°

2

3

4

5

6

7

8

9

9

1

1

C mA/cm2

EC-50 800 0-400/350 Co all

EC-90 750 150/300 Cross L-1/R-2

CC-90 750 150/300 Cross L-1/R-2

EC-50/EC-90 800 300 Cross L-1/R-2

EC-90/CO-45 750 300 Cross L-1/R-2

EC-50 750/800 300 Co L-1/R-2

CO-25 750/800 300 Co L-1/R-2

CC-90 750 250 Cross L-1

e EC-90 750 250 Cross L-1

0 CC-90 700 150 Cross L-1

0e EC-90 700 250 Cross L-1

containing "CO" describe gas inlet mixtures with steam and CO2 as

reactants and

the labels containing "CC" refer to gas inlet mixtures with only CO2 as

an initial

reactant. All labels also include a number indicating the relative amount

of the

specific reactant in the gas mixture.

2.4. Measurements and analysis methods

During the experiments the polarization curves were recorded with a

current

ramp of 10 A/min, whereby a moderate current ramp of 4 A/min was chosen

for

all other power supply changes. All operating temperature changes were

conducted

slowly with 1 K/min. After all experiments, a detailed post-mortem

analysis was

performed using a scanning electron microscope (SEM) and energy

dispersive X-ray

(EDS) analysis of the regions of interest.

In order to monitor the performance and state of health of the cell

electrochemical

8

impedance measurements (EIS) were performed throughout all experiments.

The

EIS measurements were performed in galvanostatic mode. Therefore, an

alternating

current with an amplitude of 4% of the applied direct current was

superimposed on

the direct current. The validity of the experimental data was checked by

applying

the Kramers-Kronig (KK) test and the Z-hit method, and further analysis

of the

data was performed only with data points that had a relative error of

less than 4%

between the original impedance and the impedance determined from the KK

test.

More detailed information is available in [58, 59]. In this study, the

impedance

data are represented in Nyquist diagrams and by the distribution of

relaxation

times (DRT). More information about the method used for calculation of

DRT

used within this study can be found in [60].

3. Results and discussion

This section summarizes the main results of the experimental campaign and

presents and analyzes the impedance data in the form of Nyquist and DRT

diagrams.

In addition, the data are presented in the form of distribution plots,

which were

chosen as a descriptive representation to easily present local changes in

ohmic

and polarization resistance (4Ro and 4Rp) based on interpolation between

the

four measurements taken at the corners of the cell (Fig.1b). Thereby, the

ohmic

resistance values were determined at Z’(Z" = 0) and the polarization

resistance

distribution was calculated between Z’(Z" = 0) and Z’(f = 0.5 Hz). The

colorbars of

the distribution plots are scaled equally within each subsection in order

to highlight

the differences in changes between steam and co-electrolysis mode.

Fig.2a and Fig.2b show initial polarization curves and EIS curves

recorded for

the four segments during co-flow operation at EC-50 (1) and 800°C. The

OCV was

912.6 ± 0.9 mV, thus being largely uniform between the segments. These

very small

variations in OCV values indicate that only a minor influence can be

attributed to

9

differences in manufacturing, contacting, gas and temperature

distribution. The

performance of the fuel inlet segments (Fig.1b, L-1/R-1) was slightly

lower than

that of the fuel outlet segments (Fig.1b, L-2/R-2) with voltages of

1

163.2 ± 1.82

mV for L-1/R-1 and 1151.2 ± 0.3 mV for L-2/R-2 at 400 mA/cm2. The

measured

ohmic resistances for the fuel inlet segments ranged from 334 to 337 mΩ

and from

285 to 286 for the fuel outlet segments, respectively. Differently, the

size of the

low- and high-frequency arc was minimally larger for the fuel outlet

segments. The

difference in ohmic resistance was attributed to the temperature gradient

along

the length of the cell during electrolysis operation. The minimally

larger low- and

high-frequency arcs were mostly linked to the different local partial

pressures of H2

and H2O in the steam electrode and O2 in the air electrode.

(a) Intial polarization curves (Co-Flow). (b) Intial EIS curves (Co-Flow)

at 350

mA/cm2.

Figure 2: Intial polarization curves and EIS curves. Labels L-1/2 and R-

1/2 refer to the four

segments (Fig.1b).

3.1. Influence of current density

Fig. 3 presents the results from steam electrolysis operation with EC-90

at

750°C and different current densities. Increasing the current density

from 150 to

1

3

0

00 mA/cm2 resulted in an increase of the size of the low-frequency arc

and a

slight decrease of the size of the high-frequency arc as shown in Fig.3c.

The ohmic

resistance remained mostly unchanged between 545 mΩ.cm2 (L-1) and 512

mΩ.cm2

(R-2), whereby a slight decrease of -1.5% was observed for the gas outlet

segments

L-2/R-2 with increasing current density (Fig.3a). The polarization

resistance

distribution (Fig.3b) was calculated between Z’(Z" = 0) and Z’(f = 0.5

Hz), with

the gas outlet segments L-2/R-2 presenting higher values of 13.0%

compared to

10.5% for the inlet segments L-1/R-1. The decreasing ohmic resistance of

the

gas outlet segments L-2/R-2 was mainly attributed to the increasing

temperature

gradient along the cell length with increasing current density. The

slightly higher

increase in polarization resistance of the gas outlet segments is

analyzed in detail

with DRT data of segments L-1 (blue) and R-2 (orange) in Fig.3d.

Increasing the current density from 150 to 300 mA/cm2 resulted in a

slight

shift of the low-frequency (LF) peak from 16 - 19 Hz (L-1) and from 14 -

1

7 Hz

(R-2). An additional small peak at 1 Hz was observed for the inlet

segment (L-1) at

150 mA/cm2, the occurrence of which was associated with inhibited

diffusion and

conversion processes due to minor inhomogeneities in the gas stream and

mixture

at the gas channel entry areas according to [23]. The shift of the LF

peak towards

higher frequencies as well as the disappearance of the small additional

peak at

L-1 and a small decrease of the amplitude at R-2 was interpreted to be

linked

to enhanced diffusion processes at higher current densities and higher

hydrogen

partial pressures according to [29, 44, 53]. Whereas peaks in this

frequency range

generally shift to higher frequency ranges when working with relatively

high gas

flow rates per cell area, according to [13, 47, 61]. The relatively small

changes of

this peak with increasing current density were further interpreted to

result from the

low conversion rates if compared to [29, 61]. The amplitude of the mid-

frequency

(MF) DRT peak of segment L-1 slightly decreased from 0.91 to 0.74 mΩ with

the

1

1

peak shifting from 88 to 178 Hz. Similarly, the amplitude of MF peak of

segment

R-2 decreased from 0.95 to 0.84 mΩ with the peak shifting from 89 to 192

Hz.

These changes were interpreted to be linked to enhanced air electrode

transport

processes as a result of the higher electrochemical reaction rate and

higher oxygen

partial pressures at the LSCF air electrode at higher current densities

similar to

the results in [62]. The first high-frequency (HF-1) DRT peak shifted

from 503

to 623 Hz (L-1) and from 503 to 1023 Hz (R-2). The amplitudes of the

peaks

slightly decreased for both segments. The second high-frequency (HF-2)

DRT peak

shifted from 7.2 to 6.5 kHz (L-1) and from 7.8 to 7.6 Hz (R-2). The

amplitudes of

the peaks increased from 2.10 to 2.94 mΩ (L-1) and from 2.51 to 3.09 mΩ

(R-2).

Thereby, the larger shift of the HF-1 peak of the outlet segment (R-2)

was mainly

linked to enhanced gas diffusion processes due to locally higher hydrogen

partial

pressures if compared to the inlet segment (L-1).

1

2

(a) Local changes of ohmic resistance (4Ro). (b) Local changes of

polarization resistance

(4Rp).

(c) EIS at different current densities (L-1: (d) DRT at different current

densities (L-1:

top/blue, R-2: bottom/orange). top/blue, R-2: bottom/orange).

Figure 3: Influence of increasing current density at EC-90 and 750°C.

Fig. 4 presents the results from co-electrolysis operation with CC-90 at

7

50°C

and different current densities. Thereby, the ohmic resistance remained

mostly

constant at 555 mΩ.cm2 (Fig.4c) when increasing current density from 150

to

300 mA/cm2. Here, only a slight decrease was observed for the inlet

segments

(L-1/R-1) and slight increase was observed for the outlet segments (L-

2

/R-2) with

increasing current density as presented in Fig.4a. The polarization

resistance

1

3

significantly increased by more than 35% (Fig.4b) with increasing current

density,

whereby a significant increase of the high-frequency arc and a slight

decrease of

the low-frequency arc were observed at presented in Fig.4c. The higher

increase in

polarization resistance of the gas inlet segments is analyzed in detail

with DRT

data of segments L-1 (blue) and R-2 (orange) in Fig.4d.

The LF peaks cover a significantly wider frequency range between 2.5 - 50

Hz if

compared to the previous results. Here two major peaks were observed at

22 and 19

Hz for the segments L-1 and R-2, respectively. Increasing the current

density from

150 to 300 mA/cm2 resulted in a clearer formation of an additional low-

frequency

peak at approximately 5 Hz. The amplitude of MF peak of segment L-1

decreased

from 0.97 to 0.47 mΩ with the peak shifting from 198 to 169 Hz.

Similarly, the

amplitude of MF peak of segment R-2 decreased from 0.93 to 0.54 mΩ with

the

frequency remaining unchanged. The HF peaks range cover a wide frequency

range

between 0.5 - 10 kHz with no clear separation of the peaks at 150 mA/cm2.

At

3

1

00 mA/cm2 two separated HF peaks at 1200 and 6600 Hz (L-1) as well as

250

and 8000 Hz (R-2) with slightly higher amplitudes at the outlet segments

can be

observed.

Generally, the mass transfer and diffusion losses for CO2-electrolysis

are con-

sidered to be higher than for steam electrolysis [21, 63]. Therefore,

more heat

is generated by irreversible overvoltage losses in CO2-electrolysis than

in steam

electrolysis for the same current density [21]. This was considered to be

the main

influence on the opposite trend of local changes in ohmic resistance

(Fig.4a) for

steam and co-electrolysis. The relatively higher increase of the

polarization re-

sistance when increasing current density was also interpreted to be

linked to the

higher mass transfer and diffusion losses for co-electrolysis. These

changes are also

visible in Fig.4d with the formation of the dominant HF peak at

approximately 1

kHz suggesting inhibited gas diffusion and charge transfer reaction [39,

4

1

3, 64, 65].

4

Also, the development of the low-frequency peak at 5 Hz could be linked

to in-

hibited conversion processes in the steam electrode [42--44]. As a result

of the

comparatively slower mass transfer from CO2 to the TPB and the slower

diffusion

of CO [21], an increase in current density was interpreted as having a

negative

effect on local conversion rates, especially for the inlet regions of the

cell (Fig.4b).

This effect is weakened when the CO2/CO ratio decreases along the cell

length and

thus the diffusivity of the gas mixture increases.

(a) Local changes of ohmic resistance (4Ro). (b) Local changes of

polarization resistance

(4Rp).

(c) EIS at different current densities (L-1: (d) DRT at different current

densities (L-1:

top/blue, R-2: bottom/orange). top/blue, R-2: bottom/orange).

Figure 4: Influence of increasing current density at CC-90 and 750°C.

1

3

5

.2. Influence of inlet gas composition

Fig.5 presents the results from steam electrolysis operation at 300

mA/cm2

and 800°C with different H2O/H2-ratios. Thereby, the H2O/H2-ratio was

changed

from 50/50 (EC-50) to 90/10 (EC-90). Increasing the H2O/H2-ratio resulted

in an

increase of the ohmic resistance with higher value for the outlet

segments (Fig.5a)

and a locally uniform decrease of the polarization resistance (Fig.5b).

Analysis

of the impedance data further showed a decrease of the size of the low-

frequency

arc as well as an increase of the size of the high-frequency arc

(Fig.5c). The LF

peaks of both segments stayed at approximately 15 Hz with a minor

increase of the

amplitudes with increasing H2O/H2-ratio. An additional small peak

occurred at 1

Hz for operation at EC-90. Generally, higher absolute values were

observed for the

outlet segment. The MF peak of the inlet segment (L-1) shifted from 591

to 364

Hz and from 0.37 to 0.41 mΩ. Differently the MF peak of the outlet

segment (R-1)

split from 817 Hz and 0.53 mΩ into two new peaks at 264 and 641 Hz and

0

.22 to

0.33 mΩ. The HF peaks of both segments shifted towards higher frequencies

and

low amplitudes, whereby again higher frequencies and amplitudes were

observed

for the outlet segment.

The increase of ohmic resistance can mainly be linked to significantly

lower cell

temperatures at EC-90 with the thermal equilibrium dominated by the

endothermic

electrolysis reaction with less influence of the overvoltage losses

compared to

operation at EC-50. The relatively higher increase of the ohmic

resistance for

the outlet segment could also be interpreted to be the result of a non-

uniform

temperature distribution resulting from significantly different species

gradients

along the cell length during operation at EC-90. The shift of the LF peak

towards

slightly higher amplitudes as well as the occurrence of the additional

small peak

at 1 Hz was interpreted to be linked to changes in effective diffusivity

of the inlet

gas composition according to [37, 53]. The changes of the MF peaks could

indicate

1

6

a clearer separation of the high frequency gas diffusion processes from

the air

electrode transport processes which are dominant in this frequency area

according

to [47, 48, 53, 54]. The high frequency charge transfer processes present

a strong

dependency on the temperature which was 10-15°C higher at the L-1 segment

during operation at EC-50 compared to EC-90. These processes also present

a

minor dependency on steam partial pressure which shifts the HF peak

towards

higher frequencies and lower amplitudes during operation at EC-90

according to

[

1

47].

7

(a) Local changes of ohmic resistance (4Ro). (b) Local changes of

polarization resistance

(4Rp).

(c) EIS at different steam contents (L-1: (d) DRT at different steam

contents (L-1:

top/blue, R-2: bottom/orange). top/blue, R-2: bottom/orange).

Figure 5: Influence of increasing steam content at 300 mA/cm2 and 800°C

(EC-50/EC-90).

Fig.6 presents the results from steam and co-electrolysis operation at

3

00

mA/cm2 and 750°C with different inlet gas compositions. Thereby, the

H2O/CO2/H2-

ratio was changed from 90/0/10 (EC-90) to 45/45/10 (CO-45). Thereby, a

small

increase of the ohmic resistance which was uniform over the cell area was

observed

when switching from steam to co-electrolysis operation (Fig.6a).

Differently, a large

increase of the polarization resistance was observed with slightly higher

values for

1

8

the gas inlet segments (Fig.6b). Fig.6c shows an increase of both, the

low and high

frequency arcs.

The LF peaks of both segments slightly shifted from 15 to 18 Hz with

increasing

amplitudes with substitution of H2O with CO2. Higher absolute amplitude

values

were observed for the outlet segment but higher changes at inlet segment.

Again

the occurrence of an additional peak at 1 Hz was observed whereby the

amplitude

was significantly higher compared to the previous experiment with

increasing

H2O/H2-ratio. The MF peaks stayed mostly unchanged. The first HF peak for

EC-90 was located at 724 Hz for the inlet segment L-1 and at 1084 Hz for

the

outlet segment R-2. the first HF peak for CO-45 was located at 1084 Hz

for L-1

and at 1418 Hz for R-2. Similar to the trend of LF peaks, higher

amplitudes and

frequencies were observed for the outlet segment, with uniform rates of

change.

The second HF peak for EC-90 was located at 6.1 kHz for L-1 and at 6.3

kHz for

R-2. The second HF peak for CO-45 shifted to 7.5 kHz for L-1 and 8.0 kHz

for R-2.

Similar to the trend of the LF peaks, a more pronounced change of the

amplitude

was observed for the inlet segment with changing gas composition.

The uniform change in ohmic resistance could most likely be related to

the

locally canceling interactions between the different potentials of the

endothermic

electrolysis of H2O and CO2, different heat-generating irreversible

overvoltage

losses, and the reaction rate of the water-gas shift reaction (WGSR)

along the cell

length [21]. The high absolute increase of the polarization resistance

compared

to the previous experiment and the relatively higher change of the

polarization

resistance at the inlet segments with the changes of the process specific

DRT peaks

can be linked to different phenomena. Generally, the concentration

overpotential,

which summarized transport losses between the gas channel and the TPB

[

66],

is considered lower for steam electrolysis than for CO2-electrolysis [21,

3]. The

6

resulting steeper hydrogen gradient along the cell length (compared to

CO) and

1

9

the lower diffusivity of CO also lead to a positive reaction rate of the

WGSR

[67, 68]. At these operating temperatures a relatively higher reaction

rate can

be expected for in the inlet regions of the cell [21]. Comparably changes

of the

steam electrode specific DRT peaks were observed during electrolysis

operation

with different H2O/CO2-ratios and were linked to increasing conversion,

diffusion

and charge transfer losses [48, 65]. The dominant changes in these DRT

peaks

at approx. 1 kHz, 20 Hz and the newly formed peak at 1 Hz were

interpreted as

the result of a combination of higher mass transfer, diffusion and

conversion losses

during co-electrolysis operation as well as effects of the WGSR. In the

inlet areas

of the cell, where CO is practically absent, the CO2 electrolysis

reaction is less

favored, with a competing temperature-depended WGSR [21] and a higher

change

for adsorption of carbonaceous species [23]. This likely resulted in an

unstable

equilibrium which is one of the determining factors for the higher local

changes in

polarization resistance. At overall conversion of the inlet gas mixture

and the local

less dominant effect of the WGSR towards the outlet segments of the cell

result in

a more stable local equilibrium with lower local losses.

2

0

(a) Local changes of ohmic resistance (4Ro). (b) Local changes of

polarization resistance

(4Rp).

(c) EIS at different CO2 contents (L-1: (d) DRT at different CO2 contents

(L-1:

top/blue, R-2: bottom/orange). top/blue, R-2: bottom/orange).

Figure 6: Influence of increasing CO2 content at 300 mA/cm2 and 750°C

(EC-90/CO-45).

3.3. Influence of temperature

Fig.7 presents the results from steam electrolysis operation at 300

mA/cm2 and

different operating temperatures. Decreasing the operating temperature

from 800 to

750°C resulted in a significant increase of the ohmic resistance with

relatively higher

changes measured at the outlet segments (Fig.7a). Differently the

polarization

resistance only presented a small increase with no significant gradient

over the cell

2

1

area (Fig.7b).

The LF peaks of both segments remained mostly unchanged. The MF and HF

peaks between 0.1 and 10 kHz also only present small changes with the MF

peaks

of both segments shifted towards slightly higher frequencies and higher

amplitudes.

The HF peaks of both segments no longer show a clear separation when

decreasing

the temperature, with the observed changes being basically identical for

both

segments. The shift of the MF peak towards higher frequencies was

interpreted to

possibly indicate the increasing influence of the ionic exchange

processes over O2

diffusivity processes with the increasing amplitude being the result of

decreasing

ionic conductivity of LSCF [47, 61]. However, because of the very small

changes

in these frequency ranges, which can cover both air-electrode and fuel-

electrode

processes [48], the changes cannot be completely attributed to just one

of these

processes. The shift of the HF peaks to the intervening frequency range

was

associated with a slightly stronger influence of the gas diffusion

processes compared

to the other TPB processes characteristic of this frequency range.

Decreasing

temperature in steam electrolysis mode mainly increased the ohmic

resistance as a

result of decreasing electronic conductivity and decreasing ionic

conductivity of

YSZ and LSCF with the DRT peaks between 0.1 - 10 kHz presenting a certain

dependency on the operation temperature as well as similar to the results

presented

in [47]. The relatively higher increase in ohmic resistance at the outlet

segments

was mainly associated with the approximately 5 °C steeper temperature

gradient

across the cell length during operation at 800 °C.

2

2

(a) Local changes of ohmic resistance (4Ro). (b) Local changes of

polarization resistance

(4Rp).

(c) EIS at different temperatures (L-1: (d) DRT at different temperatures

(L-1:

top/blue, R-2: bottom/orange). top/blue, R-2: bottom/orange).

Figure 7: Influence of decreasing temperature at EC-50 and 300 mA/cm2.

Fig.8 presents the results from co-electrolysis operation at 300 mA/cm2

and

different operating temperatures. Similar to steam electrolysis

operation, the ohmic

resistance increased with relatively higher changes measured at the

outlet segments

when decreasing the operating temperature from 800 to 750°C (Fig.8a).

Differently

to steam electrolysis operation, the polarization resistance presented a

significant

increase whereby relatively higher changes were observed for the inlet

segments

2

3

(Fig.8b). The LF peak of the inlet segment (L-1) shifts from 5 Hz and

1.27 mΩ

towards a wider frequency range between 3-12 Hz with two main peaks at

0

.8 and

4 Hz. Differently, the LF peak of the outlet segment (R-2) shifts from 5

Hz and

1.66 mΩ to 7 Hz and 1.24 mΩ when decreasing operating temperature from

8

00

to 750°C. The MF peaks presented a comparable increase of amplitude for

both

segments but a significantly more pronounced shift towards lower

frequencies for

the L-1 segment. The HF peaks at 545 Hz merges with the other HF peaks at

4

.5

kHz over a wide frequency range between 0.5 and 10 kHz, with a slightly

wider

frequency window for the outlet segment.

It can be seen that decreasing operating temperature significantly

affects the

polarization resistance in co-electrolysis operation compared to steam

electrolysis

operation, although the effect of temperature on ohmic resistance is

comparable.

The increase of the impedance with decreasing temperature can be mainly

linked

to decreasing electronic and ionic conductivity with inhibited steam

electrode

TPB processes [47]. The very high absolute increase of the polarization

resistance

compared to steam electrolysis can be further linked to an increase in

mass transfer,

diffusion and conversion losses in the steam electrode for co-

electrolysis of H2O and

CO2 [48, 65]. Generally, the difference in potentials for electrolysis of

H2O and CO2

is reduced at lower temperatures as a result of the lower equilibrium

potential under

standard conditions of CO2-electrolysis compared to steam electrolysis

[21, 69].

The authors in [21] also describe that the WGSR reaction rates are

significantly

higher at higher temperatures and locally at the inlet areas of a cell.

According

to their research, the gradient of the WGSR reaction rates along the cell

length

is also higher, even leading to a strongly reversed WGSR at temperatures

of 800

°C at the outlet areas of the cell. Therefore, the effect of decreasing

temperature

during co-electrolysis operation was assumed to be influenced not only by

lower

electronic and ionic conductivity [47] and lower electrolysis reaction

rates, but also

2

4

by the strongly locally dependent WGSR [21].

(a) Local changes of ohmic resistance (4Ro). (b) Local changes of

polarization resistance

(4Rp).

(c) EIS at different temperatures (L-1: (d) DRT at different temperatures

(L-1:

top/blue, R-2: bottom/orange). top/blue, R-2: bottom/orange).

Figure 8: Influence of decreasing temperature at CO-25 and 300 mA/cm2.

3.4. Short-term degradation

Fig.9 presents the results of 66 hours of operation at CC-90, 250 mA/cm2

and

750°C. The mean cell voltage increased by 14.0% from 1.172 to 1.336 V and

the

measured cell temperatures for the four segments increased by about 1 °C.

The

ohmic resistance RO stay mostly unchanged with a minimal gradient along

the

2

5

diagonal of the cell surface. Differently, the polarization resistance RP

increased

drastically, with increasing intensity at the fuel inlet areas (L-1/R-1)

as presented in

Fig.9c. The changes visible in Fig.9d could be interpreted to be linked

to inhibited

TPB processes within the steam electrode according to [64, 65]. The

authors in [23]

state that the build-up of a solid phase such as carbon can negatively

affect the

catalytically active sites, porosity and tortuosity. The deposition of

carbon is also

reported to block gas pores which leads to inhibited electrochemical

reactions and

gas distribution within the steam electrode [30]. The authors in [10, 70]

discuss

similar changes of the high frequency processes to be caused by

deposition of

impurities within the steam electrode. Nevertheless, the observed changes

were not

irreversible since the cell could also be reactivated within 24 hours by

regenerative

operation with an H2O/H2 ratio of 4 at OCV. The authors in [57] also

report

that carbon formation within the steam electrode affects cell performance

but may

not lead to irreversible degradation, whereas complete removal of solid

carbon

may take several hours if the carbon was identified at an reversible

stage. The

relatively stable ohmic resistance during operation at CC-90 indicates no

significant

structural damage to electrode/electrolyte interface as a consequence of

potential

coke formation according to [70].

2

6

(a) Mean cell voltage and local temperature changes.

(b) Local changes of ohmic resistance (4Ro). (c) Local changes of

polarization resistance

(4Rp).

(d) Evolution of EIS curves (L-1). (e) Regeneration of performance at EC-

9

2

0 and

50 mA/cm2.

Figure 9: Short-term experiment at CC-90, 250 mA/cm2 and 750°C.

Fig.10 presents the results of 66 hours of operation at CC-90, 150 mA/cm2

and

lower temperatures of 700°C. Thereby, the mean cell voltage increased by

12.6%

from 1.234 to 1.390 V and the measured cell temperatures for the four

segments

2

7

increased again by less than 1 °C. The ohmic resistance RO slightly

increased by

0.6 - 1.0% with a steeper gradient along the diagonal of the cell surface

compared

to the previous experiment at 750°C. Also, the polarization resistance RP

increased

less dramatically and uniformly over the whole cell area. After this

experiment the

cell could not be fully reactivated within 48 hours by regenerative

operation with

an H2O/H2 ratio of 4 at OCV as visible in Fig.10e. After 120 hours of

regeneration

operation, the cell appeared to have nearly recovered, although a slight

deviation

from the initial condition was still apparent for the fuel outlet

segments (L-2/R-2).

The authors in [23] also point out that the regeneration time for carbon

gasification

increases nonlinearly with a decrease in temperature, with an increasing

amount

of steam slightly accelerating the process in the case of reversible

degradation,

although 100% regeneration is not always possible. Most of the carbon

deposits

visible in Figs.11b/11e could possibly be related to residues from

operation at

these operating conditions. A significantly higher density of carbon

deposits was

observed at the fuel outlet segments, indicating lower re-regeneration

rates in these

areas.

2

8

(a) Mean cell voltage and local temperature changes.

(b) Local changes of ohmic resistance (4Ro). (c) Local changes of

polarization resistance

(4Rp).

(d) Evolution of EIS curves (L-1). (e) Regeneration of performance at EC-

9

2

0 and

50 mA/cm2.

Figure 10: Short-term experiment at CC-90, 150 mA/cm2 and 700°C.

3.5. SEM analysis

Fig.11 presents an excerpt of the results from the SEM analysis performed

with

the tested cells. Fig.11a/11c/11f present a reference for the health

state of the

2

9

cell. SEM analysis of all cells presented Ni redistribution and Ni

agglomeration

(Fig.11d), as they usually occur after electrolysis experiments [13, 28].

SEM and

EDS analysis of the cell operated in co- electrolysis mode for the short-

term

degradation experiments showed carbon deposits (Fig.11b/11e). Some

localized

cases of grain growth on the air electrode were also noted, which were

not linked

to any particular phenomenon due to the very low frequency thereof

(Fig.11g).

Although thermodynamics do not predict carbon formation, carbon formation

can

be a question of kinetics and local processes according to [71--74]. The

authors in

[71] further state that a low porosity of the steam electrode increases

the risk of

carbon formation. With decreasing porosity within the steam electrode as

a result

of Ni agglomeration and redistribution, it would be conceivable that

these local

carbon deposition occurred due to locally low CO2/CO-ratios during

operation at

7

3

1

00°C.

0

0 µm 10 µm 2 µm

(a) Reference I, Steam electrode. (b) Carbon deposition, Steam (c)

Reference II, Steam elec-

electrode. trode.

2 µm 2 µm 2 µm

(d) Redistribution and agglom- (e) Carbon deposition, Steam (f) Reference

III, Air electrode.

eration of Ni, Steam electrode. electrode.

2 µm

(g) Local grain growth, Air elec-

trode.

Figure 11: Overview SEM analysis.

4. Conclusion

In this study, locally resolved impedance and degradation characteristics

were

determined for SOECs operating in steam and co-electrolysis modes. For

this

case, steam-electrode SOECs with segmented air electrodes were tested

under

different operating conditions, whereby different types and degrees of

effects on

the performance of the cells were observed and analyzed in detail.

Significant

3

1

correlations between local effects, operating conditions, electrode

processes and

degradation mechanisms were identified through electrochemical impedance

spec-

troscopy (EIS), analysis via distribution of relaxation times (DRT) and

scanning

electron microscopy (SEM). The results presented quite different local

phenomena

for steam and co-electrolysis. The main influences on ohmic resistance

can be sum-

marized as changes due to temperature-related effects and thus inhibited

electronic

conductivity and decreasing ionic conductivity of the cell materials. In

addition, a

relatively higher increase in ohmic resistance at the outlet segments was

associated

with a steeper temperature gradient across the cell at higher

temperatures. In

general, polarization resistance showed a much stronger influence on

changes in

operating parameters such as current, input gas composition, and

temperature in

co-electrolysis operation compared to steam electrolysis operation. The

gas inlet

segments were significantly more affected. These changes were identified

to be

mainly linked to (i) a higher concentration overpotential for co-

electrolysis than

steam electrolysis and local CO2/CO-ratio dependent mass transfer and

diffusion

losses and (ii) species and temperature dependent local reaction rate of

the water-gas

shift reaction (WGSR). Short-term degradation experiments during co-

electrolysis

showed the formation of local carbon deposits, possibly due to

unfavorable reac-

tion kinetics and locally occurring reactions. In addition,

microstructural changes

which lead to a decrease in porosity of the steam electrode were

observed, which

could create favorable conditions for carbon deposition at locally low

CO2/CO

ratios and low temperatures. Therefore, it is recommended to adjust the

inlet gas

composition, current density and temperature for co-electrolysis mode in

a way

that the operational point is far from the theoretical carbon threshold.

In addition,

the application and further development of appropriate degradation

mitigation

strategies is recommended to extend the lifetime of the technology under

challeng-

ing operating conditions. Nevertheless, negative cumulative influences

due to the

3

2

succession of several experiments must be considered and additional

experiments

are suggested to further verify the presented conclusions under

additional operating

conditions.

Acknowledgement

The authors gratefully acknowledge the funding of the project

"

Degradation monitor-

ing and performance optimisation of SOECs" (project number I 3994) by

Austrian

Science Fund (FWF). The cell manufacturing team at IEK-1 of

Forschungszentrum

Jülich is acknowledged for the cell fabrication.

3

3

Glossary

Table 3: Glossary of Symbols.

Symbol Description

SOEC/EC Solid oxide electrolysis cell

SOFC/FC Solid oxide fuel cell

Ni− Y SZ Nickel

Y SZ Yttria-stabilized zirconia

LSCF Lanthanum strontium cobalt ferrite

H2 Hydrogen

H2O Water/Steam

CO Carbon monoxide

CO2 Carbon dioxide

O2 Oxygen

O2− Oxygen-ion

WGSR Water gas shift reaction

TPB Triple phase boundary

OCV Open circuit voltage

RO Ohmic resistance

RP Polarization resistance

SLPM Standard litres per minute

EIS Electrochemical impedance spectroscopy

DRT Distribution od relaxation times

KK Kramers-Kronig

SEM Scanning electron microscope

EDS Energy dispersive X-ray

3

4

References

[1] IPCC, Assessment Report 6 Climate Change 2021: The Physical Science

Basis

(2021). URL: https://www.ipcc.ch/report/ar6/wg1/.

[2] M. Laguna-Bercero, Recent advances in high temperature electrolysis

using

solid oxide fuel cells: A review, Journal of Power Sources 203 (2012) 4--

1

6.

doi:10.1016/j.jpowsour.2011.12.019.

[3] A. Kovac, M. Paranos, D. Marcius, Hydrogen in energy transition: A

review,

International Journal of Hydrogen Energy 46 (2021) 10016--10035. URL:

https://www.sciencedirect.com/science/article/pii/S0360319920345079.

doi:https://doi.org/10.1016/j.ijhydene.2020.11.256, hydrogen and Fuel

Cells.

[4] M. B. Mogensen, M. Chen, H. L. Frandsen, C. Graves, J. B. Hansen, K.

V.

Hansen, A. Hauch, T. Jacobsen, S. H. Jensen, T. L. Skafte, X. Sun,

Reversible

solid-oxide cells for clean and sustainable energy, Clean Energy 3 (2019)

1

[

75--201. doi:10.1093/ce/zkz023.

5] M. Lo Faro, S. Trocino, S. C. Zignani, V. Antonucci, A. S. Aricò,

Production

of syngas by solid oxide electrolysis: A case study, International

Journal of

Hydrogen Energy 42 (2017) 27859--27865.

doi:10.1016/j.ijhydene.2017.06.157.

[

6] O. Posdziech, K. Schwarze, J. Brabandt, Efficient hydrogen produc-

tion for industry and electricity storage via high-temperature electroly-

sis, International Journal of Hydrogen Energy 4 (2019) 19089--19101.

doi:10.1016/j.ijhydene.2018.05.169.

[

7] A. S. Nielsen, M. Ostadi, B. Austbø, M. Hillestad, G. del Alamo,

O. Burheim, Enhancing the efficiency of power- and biomass-to-liquid

fuel processes using fuel-assisted solid oxide electrolysis cells, Fuel

3

3

5

21 (2022) 123987. URL: https://doi.org/10.1016/j.fuel.2022.123987.

doi:10.1016/j.fuel.2022.123987.

[8] A. Hauch, R. Küngas, P. Blennow, A. B. Hansen, J. B. Hansen, B. V.

Math-

iesen, M. B. Mogensen, Recent advances in solid oxide cell technology for

electrolysis, Science 370 (2020). doi:10.1126/science.aba6118.

[9] V. Subotić, C. Hochenauer, Analysis of solid oxide fuel and

electrolysis cells

operated in a real-system environment: State-of-the-health diagnostic,

failure

modes, degradation mitigation and performance regeneration, Progress in

Energy and Combustion Science 93 (2022). doi:10.1016/j.pecs.2022.101011.

[10] C. Graves, S. D. Ebbesen, M. Mogensen, Co-electrolysis of CO2 and

H2O in

solid oxide cells: Performance and durability, in: Solid State Ionics,

volume

1

[

92, 2011, pp. 398--403. doi:10.1016/j.ssi.2010.06.014.

11] Q. Fang, L. Blum, N. H. Menzler, D. Stolten, Solid oxide

electrolyzer

stack with 20,000 h of operation, ECS Transactions 78 (2017) 2885--2893.

doi:10.1149/07801.2885ecst.

[12] V. Subotić, T. Thaller, B. Königshofer, N. H. Menzler, E. Bucher, A.

Eg-

ger, C. Hochenauer, Performance assessment of industrial-sized solid

oxide

cells operated in a reversible mode: Detailed numerical and experimental

study, International Journal of Hydrogen Energy 45 (2020) 29166--29185.

doi:10.1016/j.ijhydene.2020.07.165.

[13] V. Subotic, B. Königshofer, D. Juricic, M. Kusnezoff, H. Schröttner,

C. Hochenauer, P. Boskoski, Detailed insight into processes of reversible

solid oxide cells and stacks using drt analysis, Energy Conversion and

Man-

agement 226 (2020). doi:10.1016/j.enconman.2020.113509.

3

[

6

14] S. Song, X. Xiong, X. Wu, Z. Xue, Modeling the SOFC by BP neural

network algorithm, International Journal of Hydrogen Energy 46 (2021)

20065--20077. URL: https://doi.org/10.1016/j.ijhydene.2021.03.132.

doi:10.1016/j.ijhydene.2021.03.132.

[15] C. Schluckner, V. Subotić, V. Lawlor, C. Hochenauer, Three-

dimensional

numerical and experimental investigation of an industrial-sized SOFC

fueled by

diesel reformat - Part I: Creation of a base model for further carbon

deposition

modeling, International Journal of Hydrogen Energy 39 (2014) 19102--

1

9118.

doi:10.1016/j.ijhydene.2014.09.108.

[16] C. Schluckner, V. Subotić, V. Lawlor, C. Hochenauer, Numerical SOFC

Anode Catalyst Occupation Study: Internal Reforming of Carbonaceous Fuel

Mixtures, Journal of The Electrochemical Society 163 (2016) F761--F770.

doi:10.1149/2.0061608jes.

[17] B. Stoeckl, V. Subotić, M. Preininger, H. Schroettner, C.

Hochenauer,

SOFC operation with carbon oxides: Experimental analysis of per-

formance and degradation, Electrochimica Acta 275 (2018) 256--264.

doi:10.1016/j.electacta.2018.04.036.

[18] W. G. Bessler, S. Gewies, C. Willich, G. Schiller, K. A. Friedrich,

Spa-

tial distribution of electrochemical performance in a segmented SOFC: A

combined modeling and experimental study, Fuel Cells 10 (2010) 411--418.

doi:10.1002/fuce.200900083.

[19] L. Blum, U. Packbier, I. C. Vinke, L. G. De Haart, Long-term testing

of

SOFC stacks at forschungszentrum jülich, Fuel Cells 13 (2013) 646--653.

doi:10.1002/fuce.201200151.

3

7

[20] C. Schluckner, V. Subotić, S. Preißl, C. Hochenauer, Numerical

analysis of

flow configurations and electrical contact positions in SOFC single cells

and

their impact on local effects, International Journal of Hydrogen Energy

4

4

(2019) 1877--1895. doi:10.1016/j.ijhydene.2018.11.132.

[21] M. Ni, 2D thermal modeling of a solid oxide electrolyzer cell

(SOEC) for syngas production by H2O/CO2 co-electrolysis, In-

ternational Journal of Hydrogen Energy 37 (2012) 6389--6399.

URL: http://dx.doi.org/10.1016/j.ijhydene.2012.01.072.

doi:10.1016/j.ijhydene.2012.01.072.

[22] C. Schluckner, V. Subotić, V. Lawlor, C. Hochenauer, Three-

dimensional

numerical and experimental investigation of an industrial-sized SOFC

fueled by

diesel reformat - Part II: Detailed reforming chemistry and carbon

deposition

analysis, International Journal of Hydrogen Energy 40 (2015) 10943--

1

0959.

doi:10.1016/j.ijhydene.2015.06.024.

[23] C. Schluckner, V. Subotić, V. Lawlor, C. Hochenauer, CFD-simulation

of

effective carbon gasification strategies from high temperature SOFC Ni–

YSZ

cermet anodes, International Journal of Hydrogen Energy 42 (2017) 4434--

4

448.

doi:10.1016/j.ijhydene.2016.11.162.

[

24] A. Nakajo, F. Mueller, J. Brouwer, J. Van Herle, D. Favrat, Me-

chanical reliability and durability of SOFC stacks. Part I: Mod-

elling of the effect of operating conditions and design alternatives on

the reliability, International Journal of Hydrogen Energy 37 (2012)

9

249--9268. URL: http://dx.doi.org/10.1016/j.ijhydene.2012.03.043.

doi:10.1016/j.ijhydene.2012.03.043.

[25] A. Nakajo, F. Mueller, J. Brouwer, J. Van Herle, D. Favrat,

Mechanical relia-

3

8

bility and durability of SOFC stacks. Part II: Modelling of mechanical

failures

during ageing and cycling, International Journal of Hydrogen Energy 37

(2012)

9269--9286. URL: http://dx.doi.org/10.1016/j.ijhydene.2012.03.023.

doi:10.1016/j.ijhydene.2012.03.023.

[26] M. Canavar, A. Mat, S. Celik, B. Timurkutluk, Y. Kaplan,

Investigation of tem-

perature distribution and performance of SOFC short stack with/without

ma-

chined gas channels, International Journal of Hydrogen Energy 41 (2016)

10030-

-

10036. URL: http://dx.doi.org/10.1016/j.ijhydene.2016.02.045.

doi:10.1016/j.ijhydene.2016.02.045.

[27] K. D. Seo, Y. J. Kim, J. young Park, H. T. Lim, Investigating the

effect of

current collecting conditions on solid oxide fuel cell (SOFC) performance

with

additional voltage probes, International Journal of Hydrogen Energy 43

(2018)

2349--2358. URL: https://doi.org/10.1016/j.ijhydene.2017.11.109.

doi:10.1016/j.ijhydene.2017.11.109.

[28] B. Königshofer, G. Pongratz, G. Nusev, P. Boškoski, M. Höber, D.

Juričić,

M. Kusnezoff, N. Trofimenko, H. Schröttner, C. Hochenauer, V. Subotić,

Development of test protocols for solid oxide electrolysis cells operated

under

accelerated degradation conditions, Journal of Power Sources 497 (2021).

doi:10.1016/j.jpowsour.2021.229875.

[29] B. Königshofer, P. Boškoski, G. Nusev, M. Koroschetz, M.

Hochfellner,

M. Schwaiger, D. Juričić, C. Hochenauer, V. Subotić, Performance as-

sessment and evaluation of SOC stacks designed for application in a re-

versible operated 150 kW rSOC power plant, Applied Energy 283 (2021).

doi:10.1016/j.apenergy.2020.116372.

[30] V. Subotić, C. Schluckner, J. Strasser, V. Lawlor, J. Mathe, J.

Rechberger,

3

9

H. Schroettner, C. Hochenauer, In-situ electrochemical characterization

meth-

ods for industrial-sized planar solid oxide fuel cells Part I:

Methodology,

qualification and detection of carbon deposition, Electrochimica Acta 207

(2016) 224--236. doi:10.1016/j.electacta.2016.05.025.

[

31] M. Höber, P. Wachter, B. Königshofer, F. Mütter, H. Schröttner,

C. Hochenauer, V. Subotić, In operando electrochemical impedance

spectroscopy monitoring of nickel catalysts for hydrogen production, Part

I:

Methodology and performance characterization, Fuel 324 (2022) 124256.

URL:

https://linkinghub.elsevier.com/retrieve/pii/S001623612201105X.

doi:10.1016/j.fuel.2022.124256.

[32] M. Lang, S. Raab, M. S. Lemcke, C. Bohn, M. Pysik, Long term

behavior of

solid oxide electrolyser (soec) stacks, ECS Transactions 91 (2019) 2713--

2

725.

doi:10.1149/09101.2713ecst.

[33] C. Comminges, Q. X. Fu, M. Zahid, N. Y. Steiner, O. Bucheli,

Monitoring

the degradation of a solid oxide fuel cell stack during 10,000 h via

electro-

chemical impedance spectroscopy, Electrochimica Acta 59 (2012) 367--375.

doi:10.1016/j.electacta.2011.10.080.

[34] B. Königshofer, M. Höber, G. Nusev, P. Boškoski, C. Hochenauer, V.

Subotić,

Accelerated degradation for solid oxide electrolysers : Analysis and

prediction of

performance for varying operating environments, Journal of Power Sources

5

23

(2022) 230982. URL: https://doi.org/10.1016/j.jpowsour.2022.230982.

doi:10.1016/j.jpowsour.2022.230982.

[35] V. Subotić, B. Stoeckl, V. Lawlor, J. Strasser, H. Schroettner, C.

Hochenauer,

Towards a practical tool for online monitoring of solid oxide fuel cell

operation:

4

0

An experimental study and application of advanced data analysis

approaches,

Applied Energy 222 (2018) 748--761. doi:10.1016/j.apenergy.2018.03.182.

[

36] N. Schlüter, S. Ernst, U. Schröder, Finding the Opti-

mal Regularization Parameter in Distribution of Relaxation

Times Analysis, ChemElectroChem 6 (2019) 6027--6037. URL:

https://onlinelibrary.wiley.com/doi/abs/10.1002/celc.201901863.

doi:10.1002/celc.201901863.

[37] Q. Fang, L. Blum, N. H. Menzler, Performance and degradation of

solid oxide

electrolysis cells in stack, Journal of The Electrochemical Society 162

(2015)

F907--F912. doi:10.1149/2.0941508jes.

[38] Y. Yan, Q. Fang, L. Blum, W. Lehnert, Performance and degradation of

an

soec stack with different cell components, Electrochimica Acta 258 (2017)

1

[

254--1261. doi:10.1016/j.electacta.2017.11.180.

39] S. Dierickx, A. Weber, E. Ivers-Tiffée, How the distribution of

relaxation

times enhances complex equivalent circuit models for fuel cells,

Electrochimica

Acta 355 (2020) 136764. doi:10.1016/j.electacta.2020.136764.

[40] T. Zhang, Y. Zhao, X. Zhang, H. Zhang, N. Yu, T. Liu, Y. Wang,

Thermal

Stability of an in Situ Exsolved Metallic Nanoparticle Structured

Perovskite

Type Hydrogen Electrode for Solid Oxide Cells, ACS Sustainable Chemistry

and Engineering 7 (2019) 17834--17844. doi:10.1021/acssuschemeng.9b04350.

[41] R. Knibbe, M. L. Traulsen, A. Hauch, S. D. Ebbesen, M. Mogensen,

Solid

oxide electrolysis cells: Degradation at high current densities, Journal

of The

Electrochemical Society 157 (2010) B1209. doi:10.1149/1.3447752.

[42] P. Hjalmarsson, X. Sun, Y. L. Liu, M. Chen, Durability of high per-

formance Ni-yttria stabilized zirconia supported solid oxide electrolysis

4

1

cells at high current density, Journal of Power Sources 262 (2014)

316--322. URL: http://dx.doi.org/10.1016/j.jpowsour.2014.03.133.

doi:10.1016/j.jpowsour.2014.03.133.

[43] C. Jia, M. Chen, M. Han, Performance and electrochemical analysis of

solid

oxide fuel cells based on LSCF-YSZ nano-electrode, International Journal

of

Applied Ceramic Technology 14 (2017) 1006--1012. doi:10.1111/ijac.12748.

[44] M. Rao, S. H. Jensen, X. Sun, A. Hagen, Unwinding Entangled Degra-

dation Mechanisms in Solid Oxide Electrolysis Cells Through Electrode

Modifications and Impedance Analysis, Fuel Cells 19 (2019) 445--457.

doi:10.1002/fuce.201800166.

[

45] Y. Yang, X. Tong, A. Hauch, X. Sun, Z. Yang, S. Peng, M. Chen, Study

of solid oxide electrolysis cells operated in potentiostatic mode: Effect

of

operating temperature on durability, Chemical Engineering Journal 417

(2021)

1

[

29260. doi:10.1016/j.cej.2021.129260.

46] A. Leonide, V. Sonn, A. Weber, E. Ivers-Tiffée, Evaluation and

modeling of

the cell resistance in anode-supported solid oxide fuel cells, Journal of

The

Electrochemical Society 155 (2008) B36. doi:10.1149/1.2801372.

[47] P. Caliandro, A. Nakajo, S. Diethelm, J. Van herle, Model-assisted

identifi-

cation of solid oxide cell elementary processes by electrochemical

impedance

spectroscopy measurements, Journal of Power Sources 436 (2019) 226838.

doi:10.1016/j.jpowsour.2019.226838.

[48] M. Rao, X. Sun, A. Hagen, Durability of solid oxide electrolysis

stack under

dynamic load cycling for syngas production, Journal of Power Sources 451

(2020) 227781. URL: https://doi.org/10.1016/j.jpowsour.2020.227781.

doi:10.1016/j.jpowsour.2020.227781.

4

[

2

49] X. Meng, Y. Wang, Y. Zhao, T. Zhang, N. Yu, X. Chen, M. Miao, T.

Liu,

In-situ exsolution of nanoparticles from Ni substituted Sr2Fe1.5Mo0.5O6

perovskite oxides with different Ni doping contents, Electrochimica Acta

3

48

(2020) 1--12. doi:10.1016/j.electacta.2020.136351.

[50] X. Sun, A. D. Bonaccorso, C. Graves, S. D. Ebbesen, S. H. Jensen, A.

Hagen,

P. Holtappels, P. V. Hendriksen, M. B. Mogensen, Performance

characteriza-

tion of solid oxide cells under high pressure, Fuel Cells 15 (2015) 697--

7

02.

doi:10.1002/fuce.201500020.

[51] D. Papurello, D. Menichini, A. Lanzini, Distributed relaxation times

technique

for the determination of fuel cell losses with an equivalent circuit

model to iden-

tify physicochemical processes, Electrochimica Acta 258 (2017) 98--109.

URL:

https://linkinghub.elsevier.com/retrieve/pii/S0013468617321503.

doi:10.1016/j.electacta.2017.10.052.

[52] H. Sumi, H. Shimada, Y. Yamaguchi, T. Yamaguchi, Y. Fujishiro,

Degra-

dation evaluation by distribution of relaxation times analysis for micro-

tubular solid oxide fuel cells, Electrochimica Acta 339 (2020) 135913.

doi:10.1016/j.electacta.2020.135913.

[53] V. Sonn, A. Leonide, E. Ivers-Tiffée, Combined deconvolution and

cnls

fitting approach applied on the impedance response of technical ni/8ysz

cermet electrodes, Journal of The Electrochemical Society 155 (2008)

B675.

doi:10.1149/1.2908860.

[54] A. Leonide, B. Rüger, A. Weber, W. A. Meulenberg, E. Ivers-Tiffée,

Impedance

Study of Alternative (La,Sr)FeO[sub 3−δ] and (La,Sr)(Co,Fe)O[sub 3−δ]

MIEC Cathode Compositions, Journal of The Electrochemical Society 157

(2010) B234. doi:10.1149/1.3265473.

4

[

3

55] M. Rao, X. Sun, A. Hagen, A Comparative Study of Durability of Solid

Oxide Electrolysis Cells Tested for Co-Electrolysis under Galvanostatic

and

Potentiostatic Conditions, Journal of The Electrochemical Society 165

(2018)

F748--F755. doi:10.1149/2.0151810jes.

[56] V. Subotić, C. Schluckner, B. Stöckl, V. Lawlor, H. Schroettner, C.

Hochenauer,

Strategy for Carbon Gasification from Porous Ni-YSZ Anodes of Industrial-

Sized ASC-SOFCs and Effects of Carbon Growth, Journal of The Electro-

chemical Society 163 (2016) F1515--F1522. doi:10.1149/2.0521614jes.

[

57] V. Subotic, C. Schluckner, J. Mathe, J. Rechberger, H. Schroettner,

C. Hochenauer, Anode regeneration following carbon depositions in an

industrial-sized anode supported solid oxide fuel cell operating on syn-

thetic diesel reformate, Journal of Power Sources 295 (2015) 55--66.

doi:10.1016/j.jpowsour.2015.06.133.

[58] P. Agarwal, M. E. Orazem, L. H. Garcia-Rubio, Application of

measurement

models to impedance spectroscopy iii. evaluation of consistency with the

kramers-kronig relations, Journal of the Electrochemical Society 142

(1995)

4

[

159--4168.

59] W. Ehm, R. Kaus, C.-A. S. W. Strunz, Z-hit : A simple relation

between

impedance modulus and phase angle. providing a new way to the validation

of

electrochemical impedance spectra, in: F. Mansfeld, F. Huet, O. Mattos

(Eds.),

New Trends in Electrochemical Impedance Spectroscopy and Electrochemical

Noise Analysis, Electrochemical Society Inc (2001) 1--10.

[60] F. Ciucci, C. Chen, Analysis of electrochemical impedance

spectroscopy data

using the distribution of relaxation times: A bayesian and hierarchical

bayesian

approach, Electrochimica Acta (2015).

doi:10.1016/j.electacta.2015.03.123.

4

[

4

61] B. Königshofer, M. Höber, P. Boškoski, G. Nusev, D. Juričić, C.

Hochenauer,

V. Subotic, Performance investigation and optimization of a SOEC stack

operated under industrially relevant conditions, ECS Transactions 103

(2021)

5

[

19--528. doi:10.1149/10301.0519ecst.

62] V. Subotić, S. Futamura, G. F. Harrington, J. Matsuda, K. Nat-

sukoshi, K. Sasaki, Towards understanding of oxygen electrode pro-

cesses during solid oxide electrolysis operation to improve simultaneous

fuel and oxygen generation, Journal of Power Sources 492 (2021) 229600.

doi:10.1016/j.jpowsour.2021.229600.

[63] Y. Wang, T. Liu, L. Lei, F. Chen, High temperature solid oxide

h2o/co2

co-electrolysis for syngas production, Fuel Processing Technology 161

(2017)

2

[

48--258. doi:10.1016/j.fuproc.2016.08.009.

64] A. Hauch, M. Marchese, A. Lanzini, C. Graves, Re-activation of

degraded nickel cermet anodes - Nano-particle formation via re-

verse current pulses, Journal of Power Sources 377 (2018) 110-

-

120. URL: https://doi.org/10.1016/j.jpowsour.2017.11.088.

doi:10.1016/j.jpowsour.2017.11.088.

[

65] X. Sun, Y. Liu, P. V. Hendriksen, M. Chen, An opera-

tion strategy for mitigating the degradation of solid oxide electrol-

ysis cells for syngas production, Journal of Power Sources 506

(2021) 230136. URL: https://doi.org/10.1016/j.jpowsour.2021.230136.

doi:10.1016/j.jpowsour.2021.230136.

[66] I. Dincer, Y. Bicer, 2.1 ammonia, in: I. Dincer (Ed.), Compre-

hensive Energy Systems, Elsevier, Oxford, 2018, pp. 1--39. URL:

4

5

https://www.sciencedirect.com/science/article/pii/B9780128095973002017.

doi:https://doi.org/10.1016/B978-0-12-809597-3.00201-7.

[67] M. Ni, Computational fluid dynamics modeling of a solid oxide

electrolyzer cell

for hydrogen production, International Journal of Hydrogen Energy 34

(2009)

7

795--7806. URL: http://dx.doi.org/10.1016/j.ijhydene.2009.07.080.

doi:10.1016/j.ijhydene.2009.07.080.

[

68] M. Ni, Modeling of a solid oxide electrolysis cell for carbon

dioxide electrolysis, Chemical Engineering Journal 164 (2010)

46--254. URL: http://dx.doi.org/10.1016/j.cej.2010.08.032.

2

doi:10.1016/j.cej.2010.08.032.

[

69] M. Ni, An electrochemical model for syngas production by co-

electrolysis of H 2O and CO 2, Journal of Power Sources 202 (2012)

09--216. URL: http://dx.doi.org/10.1016/j.jpowsour.2011.11.080.

2

doi:10.1016/j.jpowsour.2011.11.080.

[70] S. D. Ebbesen, M. Mogensen, Electrolysis of carbon dioxide in Solid

Oxide Electrolysis Cells, Journal of Power Sources 193 (2009) 349--358.

doi:10.1016/j.jpowsour.2009.02.093.

[

71] T. L. Skafte, P. Blennow, J. Hjelm, C. Graves, Carbon de-

position and sulfur poisoning during CO2 electrolysis in nickel-

based solid oxide cell electrodes, Journal of Power Sources 373

(2018) 54--60. URL: https://doi.org/10.1016/j.jpowsour.2017.10.097.

doi:10.1016/j.jpowsour.2017.10.097.

[72] Y. Tao, S. D. Ebbesen, M. B. Mogensen, Carbon Deposition in Solid

Oxide

Cells during Co-Electrolysis of H 2 O and CO 2 , Journal of The

Electrochemical

Society 161 (2014) F337--F343. doi:10.1149/2.079403jes.

4

[

6

73] Z. Han, Z. Yang, M. Han, Comprehensive investigation of methane con-

version over Ni(111) surface under a consistent DFT framework: Impli-

cations for anti-coking of SOFC anodes, Applied Surface Science 480

(2019) 243--255. URL: https://doi.org/10.1016/j.apsusc.2019.02.084.

doi:10.1016/j.apsusc.2019.02.084.

[

74] V. Duboviks, M. Lomberg, R. C. Maher, L. F. Cohen, N. P. Bran-

don, G. J. Offer, Carbon deposition behaviour in metal-infiltrated

gadolinia doped ceria electrodes for simulated biogas upgrading in

solid oxide electrolysis cells, Journal of Power Sources 293 (2015)

9

12--921. URL: http://dx.doi.org/10.1016/j.jpowsour.2015.06.003.

doi:10.1016/j.jpowsour.2015.06.003.

4

7

Highlights

-

-

Locally resolved impedance and degradation characteristics of SOECs.

Experimental results of SOECs performance under different operating

conditions.

-

Detailed insight into electrode processes and mechanisms via DRT and

SEM

analysis.