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# Analysis of Electrochemical Degradation Phenomena of SOC Stacks Operated in Reversible SOFC/SOEC Cycling Mode

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In recent years the degradation rates of high temperature stacks with solid oxide cells (SOC) during steady-state long-term operation in fuel cell (SOFC) and electrolysis (SOEC) mode have been steadily decreased. In contrast, the quantification and understanding of degradation mechanisms of SOC stacks during reversible SOFC/SOEC cycling operation still remains a challenging issue. Therefore, the present paper focusses on the detailed analysis and discussion of degradation phenomena of two SOC stacks during galvanostatic steady-state SOFC and reversible SOFC/SOEC cycling operation. The stacks with fuel electrode supported cells of Elcogen (Estonia) were fabricated by the industrial project partner E&KOA (Daejeon, Korea) within the Korean-German project "Solid Oxide Reversible Fuel Cell/Electrolysis Stack" (SORFES). The first 10-cell stack was tested at DLR during 1400 h and the results were used to improve the second 6-cell stack, which was operated at E&KOA during 2800 h. For electrochemical characterization jV-curves and electrochemical impedance spectroscopy were measured. The results between galvanostatic steady-state SOFC operation and reversible SOFC/SOEC cycling are compared. The degradation of the open circuit voltages, the performances and the resistances of the individual repeat units are presented and discussed. Moreover, possible degradation mechanisms are outlined.

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In order to increase the renewable electrical power produced by intermittent energy sources, such as wind, photovoltaic and solar thermal power, a significant expansion of the electrical grid, of the gas infrastructure and of the corresponding storage capacities is required.<sup>1</sup> A very promising option is the so-called "Power-to-Gas" (PtG or P2G) technology, according to which a fuel gas is produced by water electrolysis. This fuel gas (mainly hydrogen or methane) can either be stored temporarily for later reconversion into heat or electricity, used for processing of so-called synthetic fuels in the transport sector ("Power-to-Liquid") or serve as a chemical raw material (commonly referred to "Power-to-Chemicals").

The water electrolysis technology can be divided into low temperature (LTE) and high temperature electrolysis (HTE). In the low temperature range of ca. 100 °C alkaline electrolysis and more recently proton exchange membrane (PEM) electrolysis are proven technologies with increasing market penetration. In the high temperature regime of 700 °C-800 °C the solid oxide electrolysis (SOE) is being developed within the last decade as a promising new technology which offers several advantages compared to low temperature electrolysis. Firstly, the higher operating temperature of solid oxide cells (SOC) results in faster reaction kinetics and lower thermodynamic enthalpy for the splitting of the steam compared to liquid water.<sup>2</sup> This results in potentially lower electrical energy consumption and higher energy efficiencies.<sup>3</sup> Secondly, the cells can be operated reversely as solid oxide electrolysis cell (SOEC) and solid oxide fuel cell (SOFC), which is very advantageous for power-to-gas applications. In this context, power plants concepts based on reversible fuel cells promise very high overall electricity-to-electricity round-trip efficiencies of up to 70% with low H<sub>2</sub> production costs.<sup>4</sup> Thirdly, high temperature electrolysis/fuel cell technology can be applied for both the H2O/H2 and CO2/CO redox systems. On the one hand, this allows in electrolysis to not only split water steam but also carbon dioxide or a mixture of both, in order to produce synthesis gas or other energy carriers such as methane or methanol by subsequent catalytic conversion.<sup>5-8</sup> On the other hand, in fuel cell operation so-called "reformate" gases

containing  $\mathrm{H}_2$  and CO can be converted electrochemically into electrical energy.

#### SOFC/SOEC Technology

A solid oxide cell consists of three main components, a zirconium dioxide-based electrolyte and two electrodes. The solid oxide electrolyte is placed between the two electrodes and ensures at the high operating temperatures the conduction of the oxygen ions between the two electrodes. Figure 1 shows an example of a SOC, with the corresponding electrochemical redox reactions of the  $H_2/H_2O$  redox system:

$$H_2 O \leftrightarrow H_2 + \frac{1}{2}O_2 \tag{1}$$

In general, SOCs can be classified according to their mechanically support element, e.g. electrolyte supported cells (ESC), porous fuel electrode-, porous air electrode- or porous metal substrate supported cells. State-of-the-art SOCs usually consist of dense yttrium stabilized zirconium dioxide (YSZ) electrolytes, porous Ni+YSZ or Ni +GDC (gadolinium doped cerium dioxide) fuel electrodes and porous air electrodes made of lanthanum-strontium-cobalt ferrite (LSCF) or lanthanum-strontium-cobaltit (LSC), which are sometimes mixed with GDC. Current collector layers are usually applied on top of the air electrode in order to enhance the in-plane conductivity. Usually, several cells are assembled in series with metallic interconnector plates to a stack. Hence a stack consists of several cell-interconnect assembly units, which are called "repeat units" (RU).

SOCs are able to convert both  $H_2O$  and/or  $CO_2$ , however the present paper only addresses the  $H_2/H_2O$  redox system. In electrolysis mode electrons from a voltage source are supplied to the fuel electrode where the supplied steam is reduced to  $H_2$  (Eq. 2). The resulting  $O^{2-}$ -ions migrate through the solid ceramic electrolyte, which is ionically conductive at the high temperatures of ca. 700 °C. At the air electrode the oxygen ions are oxidized to  $O_2$  molecules (Eq. 3). The overall electrolysis water splitting reaction according to (Eq. 1) is endothermic. In fuel cell mode, the exothermic reactions are vice-versa. In this case, the  $O_2$  from the supplied air is reduced to  $O^{2-}$ -ions (Eq. 3), which are conducted through the electrolyte. At





Figure 1. Cross section of a high temperature solid oxide cell with  $H_2/H_2O$  redox reactions at the electrodes.

the fuel electrode the supplied  $H_2$  is oxidized to steam, thus generating electrical energy.

Fuel electrode: 
$$H_2O + 2e^- \leftrightarrow H_2 + O^{2-}$$
 [2]

Air electrode: 
$$O^{2-} \leftrightarrow \frac{1}{2}O_2 + 2e^-$$
 [3]

An entire survey of the formulary describing the electrochemical performance and characteristics of SOCs can be found in the documents of the European funded SOCTESQA ("Solid Oxide Cell and Stack Testing, Safety and Quality Assurance") project.<sup>9</sup> Moreover, in the technical specification document<sup>10</sup> of the International Electrotechnical Commission pre-normative standardized quality assurance guidelines are described in detail. The nomenclature of the symbols necessary for the understanding of this paper is given in Table I.

## Challenges of Reversible SOFC/SOEC Stack Operation

In recent years the degradation rates of SOC stacks during steady-state long-term operation in SOFC and SOEC single mode

Table I. List of Symbols.

have been steadily decreased.<sup>11</sup> Few documents can be found in the literature, which address the stack degradation in both SOFC and SOEC modes.<sup>12–14</sup> Moreover, the increasing need for energy storage via H<sub>2</sub> has fostered the research activities concerning SOC stack degradation in reversible SOFC/SOEC cycling operation mode.<sup>15</sup> However, the published stack degradation results during reversible cycling operation and the interpretations differ strongly from each other. The corresponding power degradation values in SOFC mode range from -0.5%/kh to -22%/kh and in SOEC mode from +0.1%/kh to +68%/kh. These discrepancies can mainly be explained by different stack designs and materials, different operating conditions in the two modes, different switching procedures between the two modes and different calculation methods for the degradation. Degradation values are often given as relative change mainly of the voltage or of the power density per time, which makes it nearly impossible to compare different stack results. It would be far better, especially for comparison, to give the change of resistances, e.g. area specific resistance (ASR), as the resistance increase is the physical origin of the degradation effects, irrespective of the underlying mechanism/reason. Hence, the understanding of degradation mechanisms during reversible SOFC/SOEC cycling operation remains an important and challenging issue.<sup>2</sup>

Therefore, the present paper focusses on the detailed analysis and discussion of degradation phenomena of two SOC stacks in the frame of the Korean-German project "Solid Oxide Reversible Fuel Cell/Electrolysis Stack" (SORFES). This project aims on the development of the core component technology for a 1 kW reversible SOC stack in order to enhance the hydrogen productivity and its utilization. The two stacks with fuel electrode supported cells of Elcogen (Estonia) were fabricated by the industrial project partner E&KOA (Daejeon, Korea). The stacks were first operated in galvanostatic steady-state SOFC mode and afterwards in reversible SOFC/SOEC cycling mode. The reversible cycles consist of day/ night switches between SOEC and SOFC, thus covering intermittent renewable electricity supply (e.g. of photovoltaics). The stacks were electrochemically characterized by jV-curves and electrochemical impedance spectroscopy (EIS). In order to better understand the stack degradation, the results between reversible SOFC/SOEC cycling and galvanostatic steady-state operation are compared. Moreover, the improvement of the components and the operating conditions between the two SOC stacks are outlined. The results

Symbol	Description of quantity	Unit/Value
Α	Electrochemical active cell area	cm <sup>2</sup>
fi, in fi, out	Incoming/ Outcoming flow rate of component $i$ of the fuel gas	slpm, l/min
$\Delta^r G$ , $(\Delta^r G^0)$	Free enthalpy of reaction (at partial pressure 1)	kJ/mol
$\Delta^r H, (\Delta^r H^0)$	Enthalpy of reaction (at partial pressure 1)	kJ/mol
I, (j)	Electrical current (density)	A, $(A/cm^2)$
$LHV_i$	Lower heating value (LHV) of fuel gas component $i$	J/mol
Ν	Number of repeating units in the stack	
OCV	Open circuit voltage	V
$\eta_{el,LHV}$	Electrical efficiency based on LHV of fuels	%
$\eta_0$	Irreversible voltage losses	V
$P_{el,}(p_{el})$	Electrical power (density)	W, $(W/cm^2)$
$p_i$	Partial pressure of component <i>i</i> of the fuel gas	mbar, kPa
R	(Area specific) Resistance	$\Omega$ , ( $\Omega$ cm <sup>2</sup> )
Т	Temperature	K
$U_{gas}$	Gas utilization at the fuel electrode: fuel utilization (FU) in SOFC mode, steam conversion (SC) in SOEC mode	%
$V_{rev}$ , $(V^0_{rev})$	Theoretical thermodynamic reversible voltage (at partial pressure 1)	V
V(I)	Voltage at electrical current I	V
$V_{tn}$	Thermoneutral voltage	V
$\Delta V(I)$	Overvoltage losses at electrical current I	V
$V_{mol}$	Molar volume of gas	l/mol
z	Number of exchanged electrons	—

have been presented at the 18. International Conference on Solid Oxide Fuel Cells (SOFC XVIII) in  $2023.^{30}$ 

## Experimental

**Specifications of the SOC stacks.**—The two SOC stacks with cross-flow design and internal manifold for the fuel gas and the air were manufactured and supplied by E&KOA (Daejeon, Korea). Fuel electrode substrate supported cells (type "ASC-400B") from Elcogen (Tallinn, Estonia) with an active area of 100 cm<sup>2</sup> were integrated in the stacks. The cells consist of a porous support substrate and a fuel electrode, both made of Ni+YSZ, a  $(Y_{0.08},Zr_{0.92})O_2$  (8YSZ) electrolyte, a (Gd,Ce)O<sub>2</sub> (GDC) diffusion barrier layer and a two-layered (La,Sr)CoO<sub>3</sub> (LSC) air electrode. More details of these cells can be found in the specification documents of Elcogen.<sup>31,32</sup> The cells were sealed with glass sealings on machined metal interconnectors made of ferritic steel of type '460 FC'<sup>33</sup> from POSCO Int. Corp. (Pohang, South Korea).

The first stack with 10 cells was tested at DLR. Figure 2 shows the stack mounted in the test station. The fuel gas and the air were supplied to the stacks through gas tubes, which are connected at the bottom and the top of the stacks. The gases were preheated with two spiral coils located inside the two-zone furnace. The gas temperatures were measured with thermocouples, which were located near the gas in- and outlets. The electrical current probes were connected at the top and bottom plates, while the voltage probes were attached at each repeat unit of the stack. The mechanical load of  $18 \text{ N cm}^{-2}$  was applied onto the top plate of the stack via a pneumatic pressure unit.

The second improved SOC stack with 6 RUs was operated at E&KOA. The results of the 10-cell stack tested at DLR were used to improve the stack components, especially the contacting and sealing of the cells in the stack. In order to obtain high gas tightness and good electrical contact of the repeat units, the exposure of temperature and mechanical pressure during sealing of the stack have been adapted to the kind of glass sealing used. If the mechanical compression speed of the sealant is too fast, fine cracks may occur in cells with relatively weak mechanical strength. For the new stack the surface pressure procedure (a method of gradually increasing mechanical pressure) was optimized in terms of glass sealant viscosity, which strongly depends on temperature. With the new protocol good and uniform electrical contact of the entire cell area to the current collector and high gas tightness of the stack were achieved at the lowest required surface pressure. Moreover, the test protocol for the reversible SOFC/SOEC cycling operation was modified. In this context, the switching procedure between the two modes was optimized in terms of temperature gradients. An important factor was the reduction of the electrical current change rate during switching between the two modes.



Figure 2. Setup of the 10-cell SOC stack (E&KOA) inside the test station of DLR.

Test program of the SOC stacks.—Figure 3 shows the test program of the two SOC stacks. All tests were measured and evaluated according to pre-normative standardized test modules (TM) of the SOCTESQA project,<sup>34</sup> thus achieving high reproducibility and repeatability. After the start of operation (TM 02), the initial performance of the stacks was determined at 750 °C by jV-characteristics (TM 03) and electrochemical impedance spectra (TM 04). For the 10-cell stack tested at DLR a gas composition of 100% H<sub>2</sub>/air was used in SOFC. The setup of the 6-cell stack in the test station of E&KOA required to supply the fuel gas in SOFC through the steam generator. This configuration was associated in SOFC with a relatively high amount of residual adsorbed steam (from the SOEC operation) in the steam generator and in the pipes. In order to create reproducible fuel gas composition in SOFC, it was decided to add 5% of steam to the hydrogen. Hence, the 6-cell stack was operated in SOFC at E&KOA with 95% H<sub>2</sub>+5% H<sub>2</sub>O and air. In SOEC a mixture of 80% H<sub>2</sub>O+20%H<sub>2</sub>/air was used for both stacks. Please note that all gas compositions in this paper refer to vol%. The used air was pressurized, filtered and dried. In order to reach quasi-thermal equilibrium in the stack, the electrical current was changed very slowly ( $\pm 7 \text{ mA s}^{-1}$ ). A fast data sampling rate of 1 s was chosen in order to record possible voltage fluctuations. The EIS spectra were measured at 75% FU/SC with a "Zahner. Type IM 6" impedance analyzer connected to an electronic load "EL 1000." An AC amplitude of  $20 \text{ mA cm}^{-2}$  with a frequency range of 15 mHz to 50 kHz was applied to the stacks. The spectra were evaluated by complex nonlinear least square (CNLS) fitting with the software "Zahner SIM." More details of this method are described in Ref. 35 and Ref. 36 and the corresponding equivalent circuit model (ECM) can be found in Ref. 37 and Ref. 38. Moreover, the distribution of the relaxation times (DRT) of the different electrochemical processes were analyzed with the non-commercial software tool "ec-idea"39 developed by University of Bayreuth (Germany). For the analysis of the DRT spectra a regularization parameter of 0.2 was used.

After the initial performance test, both stacks were operated for 500 h in galvanostatic steady-state SOFC mode (TM 12) at 200 mA cm<sup>-2</sup> at 75% FU. The first 10-cell stack was operated at 750 °C, whereas for the second improved 6-cell stack the temperature was lowered by 50 °C to 700 °C. In order to investigate the robustness of the stacks, a thermal cycle (TM 14) with cooling down to 300 °C was integrated after 250 h of operation. After that, 20 reversible SOFC/SOEC cycles with a duration of 12 h for each mode



Figure 3. Test program for the SOC stacks.

at 75% FU/SC were performed. The current densities during the reversible SOFC/SOEC cycling were rather low, specifically  $200 \text{ mA cm}^{-2}$  in SOFC and  $-300 \text{ mA cm}^{-2}$  in SOEC. The switching time for the gas and electrical current change between the two modes was 3 h. In order to investigate the influence of temperature on the stack behavior, the optimized 6-cell stack was tested once more at 750 °C with the test program as shown in Fig. 3 (see also Fig. 9). Moreover, as described above for this stack the surface pressure protocol onto the stack and the operating conditions during switching between SOFC and SOEC were optimized. After having finished the SOFC/SOEC cycling test, the final performance of the two stacks in SOFC and SOEC was analyzed by jV and EIS measurements and the stacks were cooled down (TM 16).

#### **Results and Discussion**

Initial performance of the SOC stacks.-Figure 4 shows the initial iV-curves of the two stacks in SOFC and SOEC mode with increasing current density. A comparison of the initial performance values of the two stacks is given in Table II. The stack open circuit voltages (OCV) in SOFC were 12.3 V and 6.5 V, which correspond to average OCVs of the RUs of 1.23 V. and 1.08 V, respectively. These values are in good agreement with the theoretical values calculated with the Nernst equation, which are based on estimated fuel gas compositions of 99.8%H<sub>2</sub>+0.2%H<sub>2</sub>O for the 10-cell stack and 95.0%H<sub>2</sub>+5.0%H<sub>2</sub>O for the 6-cell stack. Hence, at the beginning of operation a good sealing and a high gas tightness of the stacks is proven. The nonlinear progression of the jV-curve is similar to the previously tested stacks at DLR with fuel electrode supported cells and has been described in Ref. 40. Due to the exothermic oxidation reaction of H<sub>2</sub> to steam in SOFC, the gas outlet temperatures increased by ca. 10 °C at the maximum current density of  $200 \text{ mA cm}^{-2}$ .

At 75% FU, which corresponds to  $200 \text{ mA cm}^{-2}$ , both stacks achieved a power density of  $180 \text{ mW cm}^{-2}$  and an electrical efficiency of ca. 54%. These values are based on low ASR values of the repeat units, for which an average value of ca. 0.735  $\Omega$  cm<sup>2</sup> was calculated. Compared to literature data $^{12-14,41,42}$  the initial stack performances in SOFC are in the same range or even higher. One reason for the good initial performance might be the dual stack manifold arrangement, which is a special feature of the stack design of E&KOA compared to other stack manufacturers. If the fuel gas and the air are supplied at the bottom of the stack (so-called "single manifold"), the streamline length for the different cells increases along the height of the stack. Hence, cells which are located at the bottom of the stack have much shorter streamline length and larger pressure differences between inlet and outlet compared to cells which are located at the top of the stack. This effect was minimized/ eliminated in the current stack design of E&KOA by moving both the air inlet and the fuel gas outlet from the bottom to the top of the stack (so-called "dual manifold"). Numerical simulations have shown improved stack performance of the dual manifold compared to the single manifold.



Figure 4. jV-curves of the 10-cell and 6-cell stack at 750 °C in SOFC and SOEC at the beginning of operation.

Moreover, the SOFC performance values of both stacks are almost identical, which proves a high reproducibility of stack testing among the project partner E&KOA and DLR. However, the abovementioned optimizations of the 6-cell stack did not result in higher initial performance but only in lower degradation, which will be discussed below. At 75% fuel utilization no severe gas diffusion overvoltage increase can be observed. Concerning the homogeneity across the height of the stacks, the OCVs, the ASRs and the power densities of the different RUs were quite uniform. In this context, very low standard deviations of the power density of the RUs of about 2–3 mW cm<sup>-2</sup> (Table II) were calculated. Moreover, electrochemical impedance spectra have shown homogeneous ohmic resistances of the RUs along the stack height, which indicates uniform electrical contacts of the cells in the stack, thus reflecting a high and reproducible stack manufacturing quality at E&KOA.

In SOEC operation the OCVs were much lower (8.9 V and 5.5 V, respectively) compared to SOFC due to 80% steam content in the fuel gas. Moreover, the voltage in SOEC increased almost linearly. This can be explained by the lower fuel electrode polarization and gas concentration resistances at the high steam content in the fuel gas<sup>21,26</sup> and the corresponding lower sensitivity on the electrical current. In SOEC voltage instabilities can be observed which were caused by small fluctuation of the steam partial pressure due to instable vaporization of water in the steam generator. This is a well-known issue in SOEC operation. The voltage fluctuations increased with increasing current density. Due to the endothermic reaction of water electrolysis the stack temperature decreased with increasing current density until reaching a minimum at  $-300 \text{ mA cm}^{-2}$ . The

Table II. Comparison of initial performan	es of the two	SOC stacks in	SOFC and	SOEC
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Quantity in SOFC mode at 75% FU	10-cell stack	6-cell stack
Power density $p_{el}$ Electrical efficiency $\eta_{el}$ Area specific resistance (average of RUs) Standard deviation of RUs (power density)	$180 \text{ mW cm}^{-2} \\ 54.0\% \\ 0.735 \ \Omega \text{ cm}^{2} \\ 2.13 \text{ mW cm}^{-2}$	$180 \text{ mW cm}^{-2} \\ 53.4\% \\ 0.725 \ \Omega \text{ cm}^{2} \\ 3.31 \text{ mW cm}^{-2}$
Quantity in SOEC mode at 75% SC	10-cell stack	6-cell stack
Power density $p_{el}$ Electrical efficiency $\eta_{el}$ Area specific resistance (average of RUs) Standard deviation of RUs (power density)	$-312 \text{ mW cm}^{-2}$ $132.0\%$ $0.645 \ \Omega \text{ cm}^{2}$ $3.65 \text{ mW cm}^{-2}$	$\begin{array}{c} -320 \text{ mW cm}^{-2} \\ 118.4\% \\ 0.690 \ \Omega \ \text{cm}^2 \\ 4.73 \ \text{mW cm}^{-2} \end{array}$

average electrolysis voltage of the RUs at this current density amounts to ca. 1.05 V. The corresponding thermo-neutral voltage at 750 °C, which is based on the standard molar enthalpy of reaction  $\Delta^{r}$ H<sup>0</sup>(750 °C) for steam electrolysis of about 248 kJmol<sup>-1</sup>,<sup>44</sup> can be calculated to 1.285 V. Hence the thermo-neutral point was not reached. In order to split 75% of the supplied steam at  $-300 \text{ mA cm}^{-2}$ for both stacks a power density of ca. -300 mA cm, for both stacks a power density of ca. -320 mW cm<sup>-2</sup> was required. At these operating conditions 2.3 SLPM (10-cell stack) and 1.4 SLPM (6-cell stack) of H<sub>2</sub> were produced with high electrical stack efficiencies of 132% and 118%, respectively. The electrical efficiency above 100% can be explained with the heat transfer from the furnace to the stack during the endothermal electrolysis operation. Similar to SOFC, the initial SOEC performance of both stacks was homogeneous across the stack height with low standard deviations of the power density in the range of 3.7-4.7 mW cm<sup>-</sup> (Table II). Moreover, the SOEC stack performances were similar high compared to literature data.<sup>18,21,24,28,41,42,45–47</sup>

Degradation of first 10-cell stack .- In Fig. 5 the voltage, the electrical current and the temperature (fuel gas inlet) of the first 10cell stack during 1400 h of total operation are shown. The stack has been operated previously at E&KOA for about 250 h, which is considered at the time axis of Fig. 5. During the steady-state operation in SOFC at constant current (75% FU) from 300 h to 900 h (with a thermal cycle in between) the stack showed a rather stable behavior with a voltage degradation rate of  $-108 \text{ mV kh}^{-1}$ (-1.2%/kh). This degradation rate is slightly higher compared to published literature results, which are below 1%/kh.48,49 During steady-state SOFC operation the OCV of the RUs remained almost stable ( $-9.6 \text{ mV kh}^{-1}$  or -0.77%/kh). Hence, sufficient gas tightness of the stack is proven. In contrast, during the following reversible SOFC/SOEC cycling (900 h to 1400 h) at 75% FU/SC far higher stack degradation rates of  $-410 \text{ mV kh}^{-1}$  (-4.6%/kh) in SOFC mode and +806 mV kh<sup>-1</sup> (+7.5%/kh) in SOEC mode are observed. These degradation rates during reversible cycling were connected with OCV decrease rates, which are about 4-5 times higher compared to galvanostatic steady-state SOFC operation. Disassembling of the stack after operation has shown, that this effect was caused by decreasing gas tightness of the cell glass sealings whereas no damage of the cells was observed. In this context, it is very likely that strong temperature gradients and thermo-mechanical stresses along the height of the stack occurred,<sup>21</sup> which even change their direction during reversible exothermic (SOFC) and endothermic (SOEC) cycling operation.<sup>26</sup> At this point it has to be mentioned that the higher stack degradation in reversible cycling operation compared to steady-state degradation is in good agreement with literature results at cell level.<sup>50–52</sup> However, the reported degradation mechanisms for cells strongly differ from the observed degradation mechanisms of the tested stack. This issue will be discussed more detailed below with the EIS spectra.

In order to investigate the degradation homogeneity over the stack height, Fig. 6 shows the modulus values of the voltage degradations of the repeat units at 75% FU (SOFC) and 75% SC (SOEC) during steady-state and reversible cycling operation. The stack shows an inhomogeneous degradation behavior across the RUs, which is consistent with other research groups.<sup>53–56</sup> Especially during reversible cycling, with exception of RU 1 (top), the degradation tended to be higher in the middle of the stack compared to the bottom and top. This behavior will be discussed more detailed with the EIS spectra in the next section (Fig. 9). In general, the voltage degradation in SOEC were higher compared to SOFC, which is due to the higher current density.

In order to analyze the different degradations of the RUs, impedance spectra were measured at the same conditions as for the reversible SOFC/SOEC cycling operation. In Fig. 7 the EIS spectra (Nyquist plot) of RU 10 (bottom) under SOFC and SOEC conditions at 750 °C and 75% fuel utilization/steam conversion are displayed at the beginning and end of operation. Figure 8 shows the corresponding distribution of relaxation times (DRT) spectra in both



Figure 5. Behavior of first 10-cell stack during steady-state SOFC and reversible SOFC/SOEC operations.

modes at the beginning and end of operation. The EIS spectra of RU 10 reveal rather low increase of the impedances, which is consistent with the lowest degradation of this RU (Fig. 6). The high frequency impedances at about 10 kHz represent the ohmic resistances R(ohm) of the RU. In this paper, the intersection with the *x*-axis was taken as representative value for R(ohm). The ohmic resistances in SOEC were higher compared to SOFC which is due to the lower temperature (endothermic reaction). In SOFC and SOEC the ohmic resistances increased from about 0.13  $\Omega$ cm<sup>2</sup> to 0.19  $\Omega$ cm<sup>2</sup> and from 0.16  $\Omega$ cm<sup>2</sup> to 0.2  $\Omega$ cm<sup>2</sup>, respectively.

Two distinct semi-circles can be identified in the Nyquist plots (Fig. 7): a small semicircle in the high/middle frequency range and a larger semicircle at low frequencies. In the DRT spectrum in Fig. 8 the small semicircle in the frequency range 60 Hz–1 kHz can be separated into two different processes, namely the fuel electrode and the air electrode processes. Previous stack tests at DLR<sup>37,38,41</sup> and EIS/DRT results of other research groups<sup>45,50,57–59</sup> have shown, that these two processes represent the electrochemical H<sub>2</sub>/H<sup>+</sup> redox-reaction at the fuel electrode P3 (FE) at high frequencies (ca. 1 kHz) and the electrochemical  $O_2/O^{2-}$  redox-reaction at the air electrode P2 (AE) in the middle frequency range (ca. 100 Hz). In the EIS spectra in Fig. 7 in both operating modes small increases of the electrode polarization impedance arcs can be observed during operation of the stack.

The dominating impedances at low frequencies of ca. 0.1-5 Hz represents a gas concentration/diffusion process P1 (GC) in the pores of the fuel electrode support substrate and in the gas channels of the



Figure 6. Voltage degradation values (modulus) of the RUs of the first 10cell stack during steady-state SOFC and reversible SOFC/SOEC operations.



Figure 7. Impedance spectra of RU 10 (bottom) measured under SOFC and SOEC conditions (750  $^{\circ}$ C, 75% FU/SC) before and after operation.

interconnect plates.<sup>60–62</sup> The spectra measured under SOEC conditions revealed smaller gas concentration impedances compared to SOFC, which can be explained by the higher steam content in the fuel gas. Moreover, in Fig. 8 the low frequency gas concentration DRT signal in SOFC consists of two separated peaks, whereas in SOEC the relaxation times are closer together. In SOFC the different RUs revealed inhomogeneous gas concentration behavior with increasing (degradation) and decreasing (improvement) values during operation. Except this difference, the spectra in SOEC and SOFC represented nearly the same evolution with proceeding operation time.

In Fig. 9 the degradation of the ohmic and overall polarization ASRs of the different RUs under SOFC and SOEC conditions (750 °C, 75% FU/SC) at the beginning and end of operation are shown. The data were obtained by fitting of the corresponding EIS spectra with an equivalent circuit model. In this context, the abovementioned increase of gas leakage of the different RUs results in different changes of the gas environments of both electrodes and of the local temperature. Hence, the quantification of the individual impedance contributions is quite difficult and the impedance analysis method can only supply qualitative interpretation results.

However, the increase of the ohmic resistances follows the same trend of the voltage degradations in Fig. 6. According to the theory, the ohmic degradations in SOFC and SOEC were in the same range. The small variations can be explained by temperature differences during operation in the two modes. With exception of RU 1 (top), the RUs in the middle of the stack showed higher ohmic degradations compared to the bottom and top. For RU 1 a very high and progressive ohmic resistance enhancement can be observed in both modes. The increase in ohmic resistances might be explained by deterioration of the electrical contact of the cells in the stack, which has also been assumed by other research groups.<sup>54,55</sup> This assumption was confirmed during disassembling of the stack after operation, where for some cells the air electrode areas were partially detached geometrically from the air electrode contact element. This degradation effect can be explained by thermo-mechanical stresses, which were caused by temperature gradients and changes during reversible SOFC/SOEC cycling. Previous stack tests at DLR have shown, that the temperature gradients and changes in the center of the stack during reversible SOFC/SOEC cycling are higher compared to the bottom and top.<sup>26</sup> At this point it has to be mentioned, that the degradation mechanisms of SOC stacks can strongly differ from those of SOC single cells. Sun et al.<sup>50</sup> have analyzed the reversible SOFC/SOEC cycling behavior of different SOC single cells. According to their study, the dominating degradation mechanism is caused by electrode polarization increase whereas the ohmic resistance remains almost constant. This strengthens the assumption, that the observed ohmic resistance increase of the tested stack of this work is not based on the cells itself but on deterioration of their geometrical contact area to the interconnect plates.



Figure 8. DRT spectra of RU 10 (bottom) measured under SOFC and SOEC conditions (750  $^{\circ}$ C, 75% FU/SC) before and after operation.

The changes in the overall polarization resistances across the height of the stack (Fig. 9) were quite inhomogeneous. Moreover, in SOFC even negative (improvement) and positive (degradation) values can be observed. The overall polarization resistance is composed of the polarization resistances of the fuel gas and air electrode and of the gas concentration resistance. In the spectra of all RUs increasing electrode polarization impedances were observed. In contrast, the repeat units located in the middle of the stack (RU 4 to RU 8) revealed decreasing gas concentration resistances which might be explained by changing gas composition mainly at the fuel electrodes and/or temperature changes. The decrease in gas concentration resistances, which strongly depend on the amount of steam in the fuel gas, 60-62 only occurred in SOFC mode and can be explained by the above-mentioned gas tightness deterioration.

Concerning the electrode degradation mechanisms, the increase of the DRT peaks P3 (FE) and P2 (AE) in the high and middle frequency range in Fig. 8 indicates degradation of the electrochemical activity of the fuel and air electrodes. In this context it is very likely that the well-known material and structural electrode degradation mechanisms, e.g. coarsening, migration and depletion of Ni of the fuel electrode, ion segregation and Cr-poisoning of the air electrode and interdiffusion at the electrode-electrolyte interfaces, play an important role.<sup>63–67</sup> These degradation effects have very different time scales. e.g. Ni coarsening may happen very early during the first less hundreds of operation hours while Ni migration will happen on the long-time scale in SOEC mode. Moreover, Ni migration strongly depends on the level of current density, which was rather low for this stack. Furthermore, Cr-poisoning is a very complex interaction of Cr species with air electrodes leading to



Figure 9. Degradation of the resistances of the RUs under SOFC and SOEC conditions (750 °C, 75% FU/SC) before and after operation.

different effects on different time scales. The complexity of the different degradation mechanisms requires detailed post-test analysis of the microstructure and material of the individual stack components. Therefore, ongoing activities concentrate on the post-test analysis of the stack mainly by scanning electron microscopy (SEM) and energy dispersive X-ray microanalysis (EDX).

Degradation of second improved 6-cell stack.—Figure 10 shows the steady-state SOFC and reversible SOFC/SOEC cycling operations of the second improved 6-cell stack during 2800 h of test at E&KOA. In Table III the degradation values of the first 10-cell stack and the improved 6-cell stack are compared to each other. This stack revealed very low degradation rates throughout the entire durability test. During the two steady-state operations in SOFC (75% FU) at 700 °C and 750 °C very stable behavior can be observed. The corresponding voltage improvement at 700 °C was +25 mV kh<sup>-</sup> (+0.5%/kh) and the degradation at 750 °C was -29 mV kh<sup>-1</sup> (-0.5%/kh). Hence, compared to literature degradation values<sup>11</sup> improved steady-state SOFC stack stability is confirmed. In contrast to the first 10-cell stack, during the two reversible SOFC/SOEC cycling operations very low voltage degradation rates of -1.4%/kh and -0.8%/kh in SOFC mode and +1.7%/kh and +2.1%/kh in SOEC mode were measured. These values are in the same range or even lower compared to literature data.<sup>17,18,21-28</sup>

In Fig. 11 the voltage degradations of the RUs at 75% FU (SOFC) and 75% SC (SOEC) during the different mid-term operations are displayed. The improved 6-cell stack shows a quite homogeneous degradation behavior across the RUs with very low degradation values. Especially during galvanostatic SOFC operation at constant current all RUs revealed very high mid-term stability. During reversible cycling the voltage degradations in SOEC were higher compared to SOFC which is caused by the higher current density. Compared to the first 10-cell stack (Fig. 6, in both operation modes the degradation of the improved 6-cell stack could be minimized significantly by a factor of 3–5. The OCV of the RUs remained almost constant during the entire operation of the stack,



Figure 10. Behavior of the second improved 6-cell stack during 2800 h of steady-state SOFC and reversible SOFC/SOEC operations.



Figure 11. Voltage degradation values of the RUs of the improved 6-cell stack during steady-state SOFC and reversible SOFC/SOEC operations.

which confirms robustness of the cell glass sealings upon reversible cycling. Moreover, the measured low degradation rates prove high stability of the electrical contact of the cells in the stack during reversible cycling. Hence, the above-mentioned optimizations in stack hardware and operating conditions have been very effective in reducing the degradation during reversible SOFC/SOEC cycling.

#### Conclusions

In the frame of the Korean-German project "Solid Oxide Reversible Fuel Cell/Electrolysis Stack" (SORFES) two SOC stacks from E&KOA (Korea) with fuel electrode supported cells from Elcogen (Estonia) were operated first in galvanostatic steady-state SOFC mode and afterwards in reversible SOFC/SOEC cycling mode. The first 10-cell stack was tested at DLR and the corresponding results were used to improve the second 6-cell stack, which was tested at E&KOA. At the beginning of operation both stacks achieved high and reproducible performances. In SOFC and SOEC electrical efficiencies higher than 50% and 100% at 75% fuel utilization/steam conversion were measured, respectively. Moreover, during galvanostatic steady-state operation in SOFC both stacks revealed very good stability with degradation rates lower than -1.2%/kh.

During reversible SOFC/SOEC cycling the first 10-cell stack showed high voltage degradation rates of -5%/kh (SOFC) and +7%/ kh (SOEC). These degradation rates were mainly caused by OCV decrease and ohmic resistance increase of the RUs which can be attributed to decreasing gas tightness of the cell glass sealings and deterioration of the geometrical contact area of the cells in the stack. Moreover, the degradation tends to be higher in the middle of the stack compared to the bottom and top. The observed degradation behavior might be explained by thermo-mechanical stresses which are caused by strong temperature gradients and changes inside the stack during reversible exothermic (SOFC) and endothermic (SOEC) cycling.

Table III. Comparison of degradation values of the two SOC stacks.

On employee and a	Deg. 10-cell stack (per RU)		Deg. 6-cell stack (per RU)	
Operating mode	Absolute	Relative	Absolute	Relative
Steady-state SOFC Rev. cycling (@ SOFC)	$-10.8 \text{ mV } \text{kh}^{-1}$ -41.0 mV kh^{-1}	−1.2%/kh −4.6%/kh	$-0.7 \text{ mV } \text{kh}^{-1}$ -9.7 mV/	-0.04%/kh -1.1%/kh
Rev. cycling (@ SOEC)	$+80.6 \text{ mV } \text{kh}^{-1}$	+7.5%/kh	$+21.0 \text{ mV } \text{kh}^{-1}$	+1.9%/kh

In order to reduce the degradation, the contacting and sealing of the cells in the stack and the switching conditions between SOFC and SOEC were optimized for the second 6-cell stack. During reversible SOFC/SOEC cycling the improved 6-cell stack revealed very low voltage degradation rates, which were in the range of -1%/kh in SOFC and +2%/kh in SOEC. Moreover, the degradation of the different RUs was quite homogeneous and the OCVs remained almost constant during operation. Hence, the optimizations in stack hardware and operating conditions have been very effective in improving the degradation. In order to minimize the thermo-mechanical stresses during reversible cycling it is therefore recommended to slowly change the operating parameters during switching between the two mode.

Ongoing activities focus on the disassembling and the post-test analysis of the stack components by SEM and EDX in order to analyse the degradation mechanisms. The results of the present paper help to understand and reduce the degradation of SOC stacks during reversible SOFC/SOEC cycling, thus promoting the SOC technology for efficient and cost-effective hydrogen applications.

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