

Performance and Degradation of Electrolyte Supported SOECs with Advanced GDC Thin-film Layers in Long-term Stack Test

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Electrolyte supported Solid Oxide Cells (ESCs) with advanced thin-film Gd-doped ceria layers deposited via EB-PVD method at 600 °C were assembled and electrochemically investigated in a so-called “rainbow” stack with 30 repeat units (RUs). At the initial stage of the SOEC operation, the stack reached a high performance with an electrical efficiency of 99.65 % at 75 % steam conversion and a total power input of 1.98 kW. A long-term stack test was performed in SOEC mode for over 5000 h and demonstrated a low voltage degradation of approx. +10.9 mV·kh⁻¹ per RU (+0.9% kh⁻¹). The RUs with EB-PVD GDC thin-films demonstrated similar initial performance and degradation rate to the state-of-the-art cells. In this paper, the investigation mainly focuses on the electrochemical characteristics of RUs containing the EB-PVD thin-film GDC layers.

Introduction

Solid oxide electrolyzer cell (SOEC) based on electrolyte-supported cell (ESC) architecture is proven to be highly efficient and reliable technology for green hydrogen production through high temperature electrolysis (1, 2). The performance, lifetime and robustness of the cells and stacks belong to the most important factors for a successful penetration of the SOEC technology into energy and chemistry sectors. A typical ESC consists of scandia- or yttria-stabilized zirconia electrolyte, Ni-cermet fuel electrode, lanthanum strontium cobalt ferrite (LSCF) oxygen electrode and Gd-doped ceria (GDC) layers with a thickness of 3-7 μm between electrolyte and electrodes. At the oxygen electrode side, the GDC layer mainly prevents Sr diffusion from LSCF electrode towards the zirconia-based electrolyte, while at the fuel electrode side, it is helpful to improve the electrode adherence to electrolyte support and to reduce the interfacial resistance. State-of-the-art GDC layers are fabricated by screen-printing methods and followed by a sinter process at high temperature between 1200 °C to 1300 °C. This fabrication route usually results in a partial porous structure in the GDC layers and residual stresses which reduce the mechanical strength of the cells. Aiming to improve the mechanical stability of ESCs and the properties (e.g. porosity and electrical conductivity) of GDC layers, the conventional screen-printed GDC layers either only at the oxygen electrode or at both electrodes were replaced by 0.5 μm thick thin-film GDC layers fabricated by electron-beam physical evaporation deposition (EB-PVD) method at 600 °C and demonstrated promising results on single cells with an active area of 16 cm² in electrochemical testing (3, 4).

In this work, ESCs with EB-PVD GDC thin-films and an active area of 128 cm² were assembled and electrochemically investigated in a so-called “rainbow” stack with 30 repeat units (RUs). The performance and degradation behaviour of the stack and representative RUs were investigated by means of current-voltage curves (j-V-curves) and electrochemical impedance spectroscopy (EIS). The initial performance and the degradation of the stack and the RUs with EB-PVD GDC thin-film layers were determined and discussed in order to evaluate the effectiveness of the modifications in the scenario of long-term SOEC stack testing.

Experimental

Cells and Stack

The cells used in this work are mechanically supported by 80 µm thick dense YSZ electrolyte (3YSZ) substrates. Before the deposition of oxygen electrodes and fuel electrodes, GDC layers were fabricated on both side of the electrolyte. In the state-of-the-art (SoA) cells, GDC was screen-printed on both sides of the electrolyte, followed by sintering at high temperature. In cells with modifications, the screen-printed GDC layers were replaced with GDC thin-films fabricated by EB-PVD at 600 °C, either only on the oxygen electrode side or on both sides of the electrolyte. In this paper, these cells with EB PVD thin-film modifications are noted as GDC cells and GDCx2 cells, respectively. The fuel electrode consists of a porous cermet of Ni and GDC. The porous oxygen electrode consists of LSCF-GDC composite. More details about the fabrication of the cells has been published elsewhere (3,4).

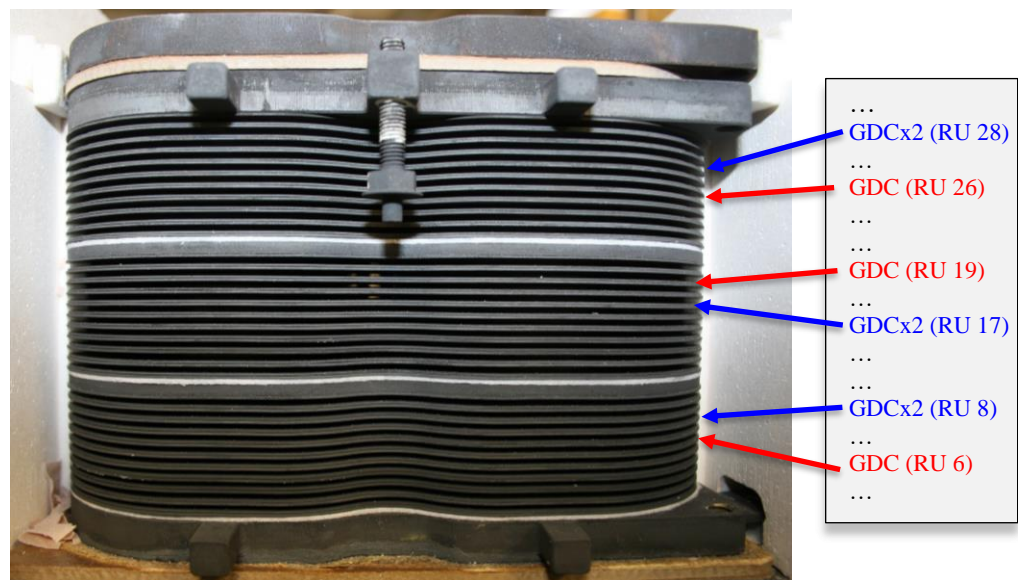


Figure 1. SOEC stack of Sunfire GmbH with 30 repeat units (RUs)

In total, 30 electrolyte supported cells with an active area of 128 cm² were sealed with glass sealings on bipolar plates made of stamped ferritic steel to form single repeat units (RUs). Figure 1 shows the SOEC stack assembled by Sunfire GmbH (Dresden, Germany). The stack has an open oxygen electrode and parallel co-flow design. The RUs from the

bottom of the stack to the top were numbered as RU 1 to RU 30, including RU 6, RU 19 and RU 26 with EB-PVD GDC layers at the oxygen electrode and screen-printed GDC at fuel electrode, RU 8, RU 17 and RU 28 with EB-PVD GDC layers at both electrodes and rest 24 RUs with screen-printed SoA GDC layers at both electrodes. In order to enhance the mechanical stability, the stack was subdivided into 3 sub-stacks by intermediate plates and each sub-stack contained 10 RUs.

Electrochemical Stack Test in SOEC Mode

The electrical current probes were connected to the top and bottom plates, while the voltage probes were welded to the edge of each RU in the stack. The mechanical load on the stack was 1,200 N. The stack temperatures were measured with four thermocouples inserted into different positions in the stack, i.e. in RU 1, 13, 17 and 30, which enable the analysis of temperature gradients inside the stack. The stack was firstly operated in SOFC mode for approx. 5200 h before switching to the long-term SOEC operation. This work will only focus on results obtained from the SOEC operation in the test period from 5200 h to 12000 h.

After the initial SOEC performance test, the stack was operated for over 5000 h in SOEC operation mode. For SOEC test, gas supply flow rate of $0.4872 \text{ H}_2\text{O} + 0.061 \text{ H}_2 + 0.061 \text{ N}_2$ SLPM/RU ($80\% \text{ H}_2\text{O} + 10\% \text{ H}_2 + 10\% \text{ N}_2$) on fuel electrode and air supply of 2 SLPM/RU on oxygen electrode were applied. The addition of $10\% \text{ N}_2$ in SOEC mode is helpful to stabilize the steam supply and minimize the electrolysis voltage fluctuations. The stack temperature in this paper is defined by the thermocouple placed in the middle of the stack (in RU 13) at OCV. The maximum stack temperature limit was set at $860 \text{ }^\circ\text{C}$. The degradation of the area specific resistance (ASR) was calculated by dividing the voltage increase by the applied electrical current density. Current-voltage (j-V) characteristics and electrochemical impedance spectra were recorded every 2000 h to 2500 h. For the j-V-characteristics the electrical current was increased and decreased at a very slow rate of $7 \text{ mA}\cdot\text{s}^{-1}$, in order to maintain the stack temperature close to thermal equilibrium.

The electrochemical impedance spectra were recorded with a Zahner IM6 impedance analyzer connected to an EL1000 electronic load. A voltage supply was integrated in the current circuit. In order to minimize high frequency artifacts, the electrical current and voltage probes were twisted separately (5). An AC amplitude of $15 \text{ mA}\cdot\text{cm}^{-2}$ with a frequency range of 25 mHz to 2 kHz was applied to the stack. The electrochemical impedance spectra of each RU were recorded at 75% steam conversion and a current density of $-410 \text{ mA}\cdot\text{cm}^{-2}$, and additionally near OCV conditions to avoid electrical current induced temperature effects.

Results and Discussion

Initial SOEC Stack Performance

Figure 2 shows the initial j-V-curve and the measured stack temperature (T 13) in the middle of the SOEC stack via thermal couples placed in the RU 13 with increasing current density. An OCV of 24.83 V was measured at $846 \text{ }^\circ\text{C}$ (T 13). The stack temperature (T 13) decreased with increasing current density in the endothermic reaction region of the steam

electrolysis. In this region, the electrolysis voltage increased almost linearly against current density range from 0 to $-170 \text{ mA}\cdot\text{cm}^{-2}$. The stack temperature started to increase after reaching the minimum temperature at a current density. This resulted in a decrease of the electrolysis overvoltages and a flattening of the j - V -curve at higher current density range from $-170 \text{ mA}\cdot\text{cm}^{-2}$ to $-430 \text{ mA}\cdot\text{cm}^{-2}$ (1).

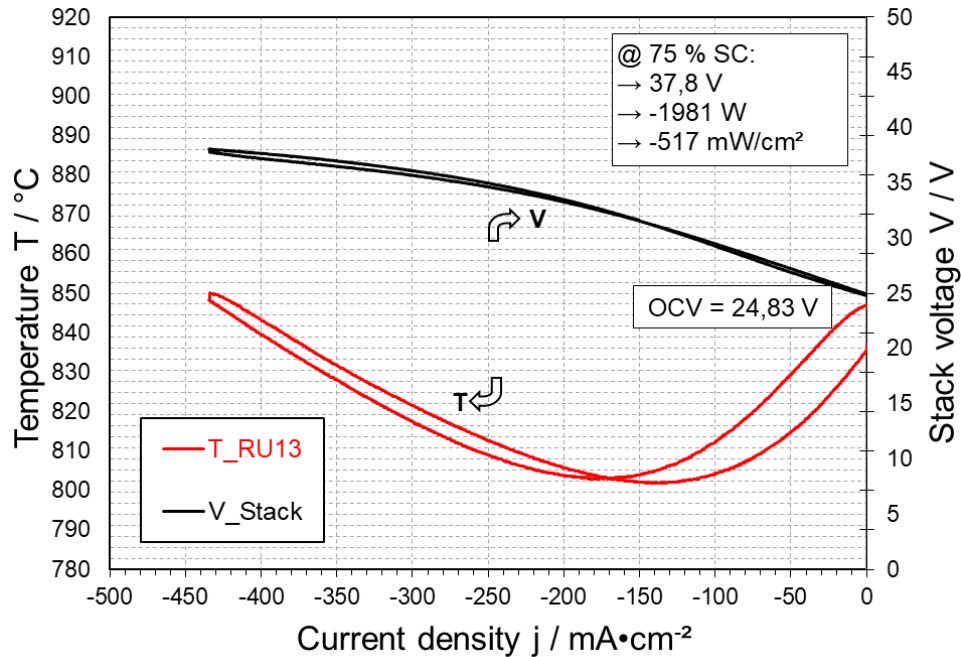


Figure 2. j - V -curve of 30-cell SOEC stack at $846 \text{ }^\circ\text{C}$ with fuel gas supply of $0.4872 \text{ H}_2\text{O} + 0.061 \text{ H}_2 + 0.061 \text{ N}_2$ SLPM/RU ($80\% \text{ H}_2\text{O} + 10\% \text{ H}_2 + 10\% \text{ N}_2$) on fuel electrode and air supply of 2 SLPM/RU on oxygen electrode

The stack temperature reached $846 \text{ }^\circ\text{C}$ again at current density of $-410 \text{ mA}\cdot\text{cm}^{-2}$. The stack voltage was measured as 37.8 V . The corresponding average RU voltage was 1.26 V , which was very close to the theoretical thermo-neutral voltage of 1.29 V . In the case of thermal-neutral electrolysis operation, the heat generated by the overvoltages equals the required entropic heat for the electrolysis. The measured value is lower compared to the theoretical one, possibly because the stack has not fully reached thermal equilibrium during the j - V -curve measurement (1).

With the given gas supply, the steam conversion rate is 75% at a stack voltage of 37.8 V and stack current of $-410 \text{ mA}\cdot\text{cm}^{-2}$. The stack power input is about -1.98 kW , corresponding to an average power density of $-517 \text{ mW}\cdot\text{cm}^{-2}$ on each RU level. At these operation conditions, 10.96 SLPM of H_2 were produced at an electrical stack efficiency of 99.65% . In comparison to the RUs in the middle of each 10-level sub-stack, lower operation voltages were observed on the RU 1, RU 2, RU 10, RU 11, RU 20, RU 21, RU 29 and RU 30 near the bottom, intermediate and top plates (Figure 3). Similar performance deviations at corresponding RUs are also observed and reported in former work (1). The measured values for these RUs were not considered for calculation of average degradation values in this paper. In general, the stack demonstrated a very good initial performance at the start of the SOEC operation. Operating at current density of $-410 \text{ mA}\cdot\text{cm}^{-2}$ with given

gas supply of 80% H₂O + 10% H₂ + 10% N₂ // air, the average voltage of GDC cells was approx. 1.265 V, which is slightly higher than the average voltage of 1.259 V obtained from SoA cells and GDCx2 cells.

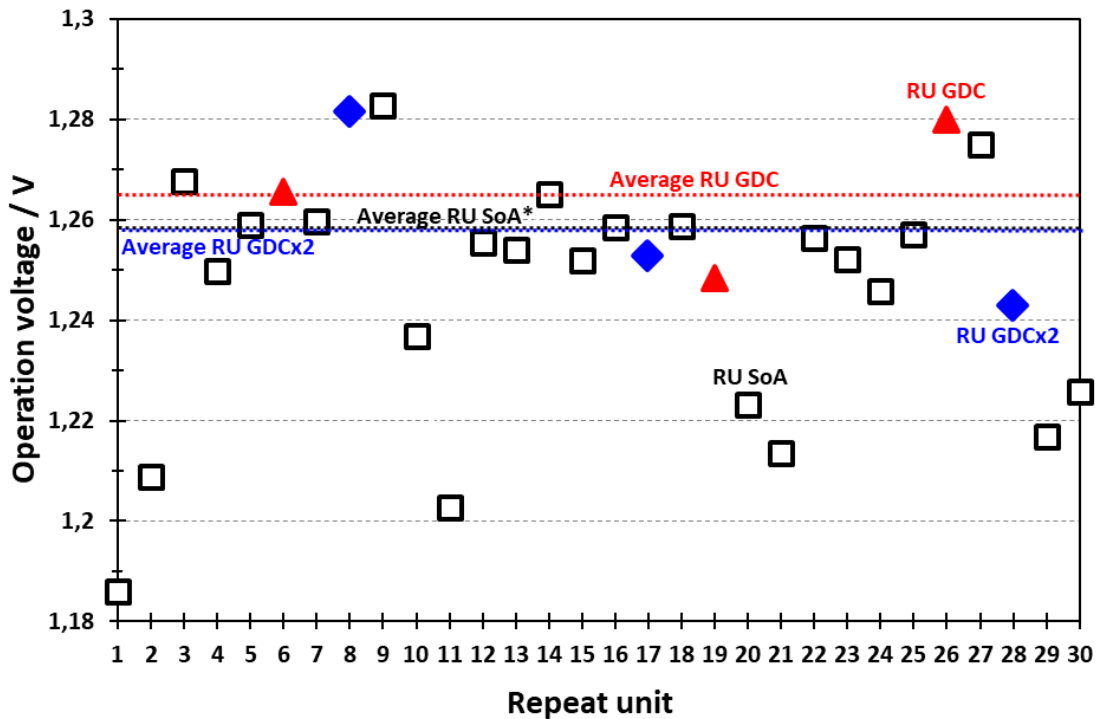


Figure 3. Initial operation voltage of RUs with SoA cells and cells with thin-film GDC layers at 846 °C (T 13) with fuel gas supply of 0.4872 H₂O + 0.061 H₂ + 0.061 N₂ SLPM/RU (80% H₂O + 10% H₂ + 10% N₂) on fuel electrode and air supply of 2 SLPM/RU on oxygen electrode (*The average operation voltage of RU SoA is calculated without RU 1, RU 2, RU 10, RU 11, RU 20, RU 21, RU 29 and RU 30.)

Long-Term Stability of SOEC Operation

The stack voltage, current and the stack temperature during the long-term SOEC operation are presented in Figure 4. The first 400 h were dedicated for initial characterization in SOFC and SOEC mode followed by 4000 h of SOEC operation at 846 °C (at OCV) under constant current density of $-410 \text{ mA}\cdot\text{cm}^{-2}$, which corresponds to 75% steam conversion. The spikes in Figure 4 represent the recordings of j-V-curves and EIS spectra. At 9363 h of operation, a voltage drop of the stack was observed, which was later attributed to a failure in RU 1. The stack was cooled down/heated up twice in the elapsed time period of 9578 h to 10053 h in order to figure out the cause of the voltage drop in RU 1. After confirming the failure of RU 1 is not fixable, the stack was heated up again for further long-term SOEC test in an isothermal operation by maintaining the temperature of the T 13 unchanged for over 1800 h during elapsed time period of 10105 h to 11932 h.

During the first 4000 h of SOEC operation, the OCV of the stack remained almost constant, which proved the reliable quality and long-term stability of the cells and glass sealings in the stack. In electrolysis operation at 75% SC, the voltage degradation was

approx. $+10.9 \text{ mV}\cdot\text{kh}^{-1}$ per RU which corresponds to $+0.9\% \text{ kh}^{-1}$. From the elapsed time period of 6615 h to 9391 h, the stack temperature increased in total by $3.8 \text{ }^\circ\text{C}$ with a very low increase rate of $1.37 \text{ K}\cdot\text{kh}^{-1}$, which resulted from small resistance increase.

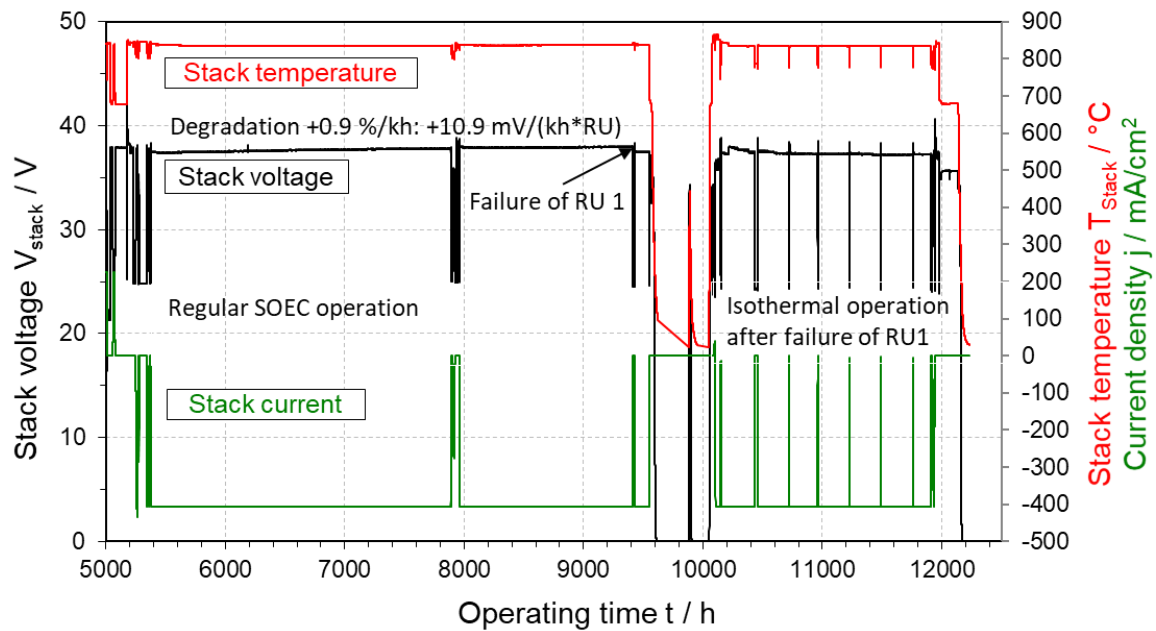


Figure 4. Long-term behaviour of the stack during the SOEC operation at $846 \text{ }^\circ\text{C}$, a current density of $-410 \text{ mA}\cdot\text{cm}^{-2}$ (75% SC) with fuel gas supply of $0.4872 \text{ H}_2\text{O} + 0.061 \text{ H}_2 + 0.061 \text{ N}_2$ SLPM/RU ($80\% \text{ H}_2\text{O} + 10\% \text{ H}_2 + 10\% \text{ N}_2$) on fuel electrode and air supply of 2 SLPM/RU on oxygen electrode

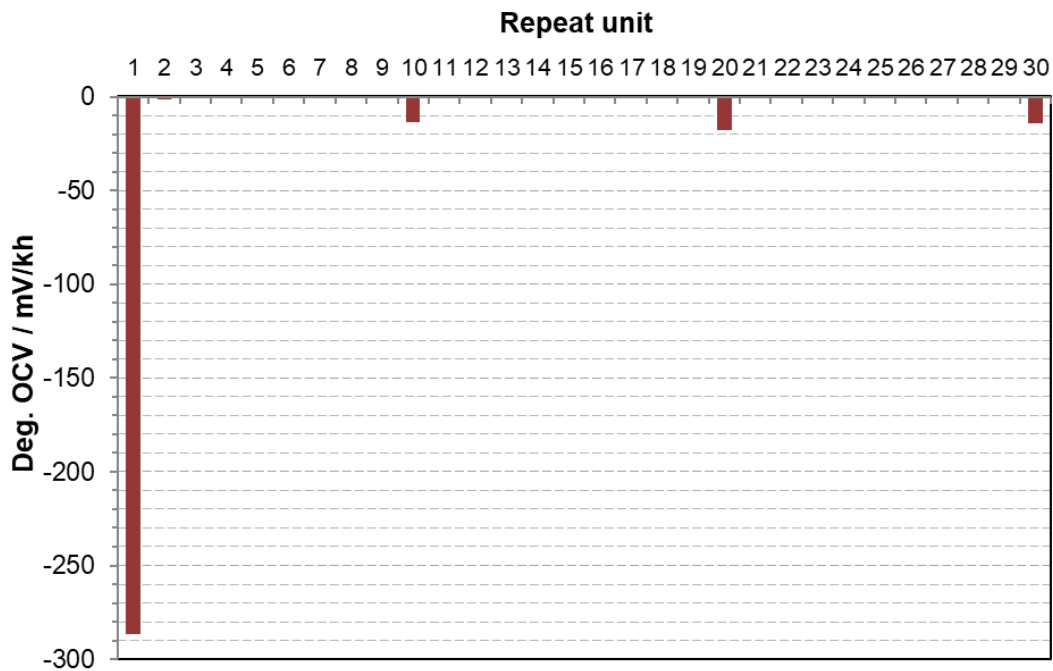


Figure 5. OCV degradation of RUs during the test period from 5000 h to 12000 h

Figure 5 shows the OCV degradation of each RU during the test period from 5000 h to 12000 h. Significant OCV drop on RU 1 is observed. It should be related to its sudden failure at the operation time of 9363 h. Near the intermediate plates and top plate, RU 10, RU 20 and RU 30 also present visible OCV degradation. All the other 26 RUs show almost no OCV change. During the SOEC operation at constant current density of $-410 \text{ mA}\cdot\text{cm}^{-2}$ and 75% steam conversion, the average electrolysis operation voltage degradation differs, i.e. $+10.1 \text{ mV}\cdot\text{kh}^{-1}$ for RUs with SoA cells, $+9.4 \text{ mV}\cdot\text{kh}^{-1}$ for RUs with thin-film GDC on the oxygen electrode side, and $+12.0 \text{ mV}\cdot\text{kh}^{-1}$ for RUs with thin-film GDC on both sides. The corresponding ASR degradations for the different RUs are $+24.7 \text{ m}\Omega\cdot\text{cm}^2\cdot\text{kh}^{-1}$, $+22.9 \text{ m}\Omega\cdot\text{cm}^2\cdot\text{kh}^{-1}$, and $+29.2 \text{ m}\Omega\cdot\text{cm}^2\cdot\text{kh}^{-1}$, respectively. The operation and ASR degradation rates of the cells with EB-PVD GDC thin-films are quite comparable to that of SoA cells, as seen in Figure 6.

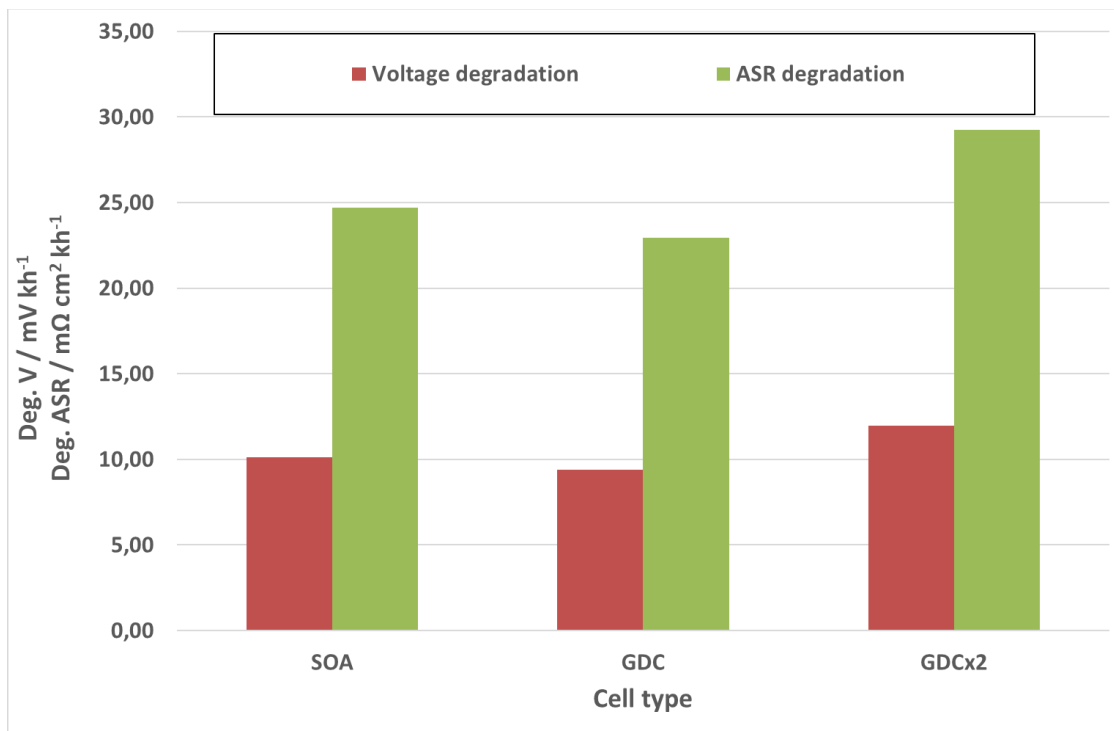


Figure 6. Average operation voltage and ASR degradation of different cell types during the long-term SOEC test at constant current density of $-410 \text{ mA}\cdot\text{cm}^{-2}$. (The average degradation of RU SoA is calculated without RU 1, RU 2, RU 10, RU 11, RU 20, RU 21, RU 29 and RU 30.)

During the long-term operation, electrochemical impedance spectra of the different types of cells degraded in a similar way. As an example, impedance spectra of representative RU 17 with a GDCx2 cell are shown in Figure 7. During the regular SOEC operation from time point of 5180 h to 7935 h, the R_{total} increased from $991 \text{ m}\Omega\cdot\text{cm}^2$ to $1081 \text{ m}\Omega\cdot\text{cm}^2$, i.e. $+32.7 \text{ m}\Omega\cdot\text{cm}^2\cdot\text{kh}^{-1}$. The R_{ohm} increased from $721 \text{ m}\Omega\cdot\text{cm}^2$ to $730 \text{ m}\Omega\cdot\text{cm}^2$ in the same SOEC testing period, corresponding to degradation of $+3.3 \text{ m}\Omega\cdot\text{cm}^2\cdot\text{kh}^{-1}$. A significant R_{ohm} increase was observed at the end of the SOEC test on the impedance spectra. This

may be attributed to the thermal cycles imposed to the stack after the failure of RU 1, which may cause interfacial and structural changes in the stack and RUs.

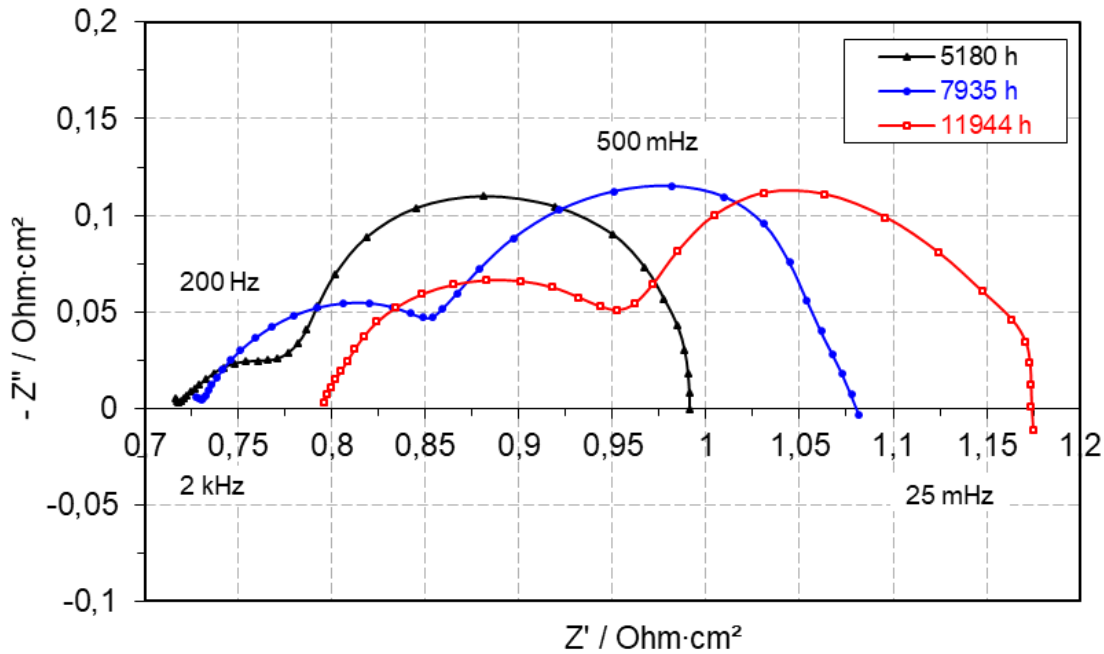


Figure 7. Impedance spectra of RU 17 measured at SOEC conditions at 846 °C and 75% SC ($-410 \text{ mA}\cdot\text{cm}^{-2}$) with fuel gas supply of $0.4872 \text{ H}_2\text{O} + 0.061 \text{ H}_2 + 0.061 \text{ N}_2$ SLPM/RU (80% $\text{H}_2\text{O} + 10\% \text{ H}_2 + 10\% \text{ N}_2$) on fuel electrode and air supply of 2 SLPM/RU on oxygen electrode at different operating times

Conclusions

Electrolyte supported solid oxide cells (ESCs) with EB-PVD-fabricated thin-film GDC layers were electrochemically characterized in a so-called “rainbow” stack with 30 repeat units (RUs). The stack was operated for over 5000 h in SOEC mode under a current density of $-410 \text{ mA}\cdot\text{cm}^{-2}$ and 75 % steam conversion. The initial performance of the cells with the EB-PVD GDC thin-films are comparable to the state-of-the-art cells. During the first 4000 h of regular SOEC operation, the stack demonstrated a low voltage degradation rate of approx. $+10.9 \text{ mV}\cdot\text{kh}^{-1}$ per RU, corresponding to $+0.9\% \text{ kh}^{-1}$. The average OCV of all RU types in each 10-level sub-stack remained unchanged, proving good reliability and durability of the glass sealings, and the reproducibility of the stack and individual RUs. The average electrolysis operation voltage degradations of RUs with variant cell types are slightly deferent, i.e. $+10.1 \text{ mV}\cdot\text{kh}^{-1}$ for RUs with SoA cells, $+9.4 \text{ mV}\cdot\text{kh}^{-1}$ for RUs with thin-film GDC on the oxygen electrode side, and $+12.0 \text{ mV}\cdot\text{kh}^{-1}$ for RUs with thin-film GDC on both sides. At the given operation conditions, the calculated ASR degradations for RUs with SoA cells, GDC cells and GDCx2 cells are $+24.7 \text{ m}\Omega\cdot\text{cm}^2\cdot\text{kh}^{-1}$, $+22.9 \text{ m}\Omega\cdot\text{cm}^2\cdot\text{kh}^{-1}$, and $+29.2 \text{ m}\Omega\cdot\text{cm}^2\cdot\text{kh}^{-1}$, respectively. According to the measured impedance spectra, the R_{total} and R_{ohm} degradation during the regular operation were $+32.7 \text{ m}\Omega\cdot\text{cm}^2\cdot\text{kh}^{-1}$ and $+3.3 \text{ m}\Omega\cdot\text{cm}^2\cdot\text{kh}^{-1}$, respectively. In order to explain more details about the degradations, a subsequent post-mortem analysis will be performed in the near future.

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