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Long term durability test and post mortem for metal-supported solid oxide electrolysis cells

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Abstract

Hydrogen is a renewable energy carrier, and electrolysis to split water is the most environmentally friendly method to produce hydrogen. This work reports long-term durability and degradation mode analysis for metal-supported solid oxide electrolysis cells (MS-SOECs). Catalyst screening showed that MS-SOECs with composite electrode catalysts (samarium-doped ceria-nickel [SDC-Ni] serving as a fuel electrode catalyst, and praseodymium oxide [PrO_x]-SDC or La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O₃ [LSCF]-SDC serving as an air electrode catalyst) exhibit the highest electrochemical performance at 700 °C. The degradation rate of cells with LSCF-SDC as the air electrode catalyst was as low as 1.3%/100 h in long term durability tests at a current density of 0.33 A cm⁻², in contrast to rapid degradation observed for a cell with a PrO_x-SDC air electrode. Post-mortem analysis reveals the degradation is dependent on the primary modes of fuel electrode catalyst coarsening and Cr poisoning on the air electrode catalyst, as well as secondary modes of oxidation of the metal support and local elemental accumulation of Ni. Other degradation modes reported in conventional anode-supported SOECs, such as Ni migration, foreign element contamination, delamination of the cell, and nano-voids on the electrolyte, are not observed in the present MS-SOECs.

Keyword: Solid oxide electrolysis cell; Metal support; Infiltration; Long term; Durability

1. Introduction

Hydrogen fuel not only has the highest gravimetric energy density among all chemical fuels (143 kJ kg^{-1}), [1, 2] it also produces zero criteria or carbon dioxide (CO_2) emissions when it is converted from chemical energy to electrical or thermal energy. However, hydrogen does not exist naturally on the Earth, and most hydrogen producing processes are not environmentally friendly. More than 90% of hydrogen is produced from fossil fuels such as natural gas, oil, and coal, with accompanying by-products of carbon monoxide (CO), CO_2 and other greenhouse gases. [3-5] These emissions strengthen global warming via the greenhouse effect.

In contrast, electrolysis of water, which currently contributes to only a small amount of hydrogen production, is a green solution. Among the various water electrolysis methods, high-temperature electrolysis (HTE) using solid oxide electrolysis cells (SOECs) is the most viable approach, due to the SOECs' high conversion efficiency and low energy consumption, and because they do not require the use of noble metal-based catalysts. Unlike low-temperature cells, SOECs can achieve high efficiency at a high production rate because they can split water with both thermodynamic and kinetic benefits. [6] Recent SOECs have demonstrated high current density of around 1 A cm^{-2} with close to 100% efficiency. [7, 8] Despite these advantages, insufficient long term durability has prevented the commercialization of SOECs, although extensive efforts have been devoted to addressing SOEC durability. Graves et al. reported a degradation rate of 0.95 V kh^{-1} in a 420 h test at 1 A cm^{-2} . [9] Tong et al. reported a degradation rate of 0.024 V kh^{-1} in a 900 h test at 1 A cm^{-2} .

with nano-engineered electrodes, which was reported to be superior to the degradation rate of most previously studied SOECs.[10]

Extensive studies have been devoted to the degradation modes of all-ceramic SOECs. Electrolyte reduction,[11, 12] delamination,[13, 14] intergranular fracture and void formation along the grain boundaries of the electrolyte,[15] structure damage in thick yttria-stabilized zirconia (YSZ) electrolyte,[16] and formation of an insulating layer between the buffer layer and the electrolyte[17] all have been reported to degrade the electrolyte. Microstructure changes and cation interdiffusion,[18, 19] formation of nanoparticle clusters,[20] phase change,[17] SrO segregation on the surface,[21] and contaminants from iron-chromium (Fe-Cr) stainless steel[22, 23] have been reported to degrade perovskite air electrodes. Microstructure instability,[24, 25] agglomeration,[26] nickel (Ni) coarsening,[26] and contaminants from glass sealant and raw materials[15, 27] have been reported to degrade Ni-based hydrogen electrodes. As for metal-supported SOECs (MS-SOECs) with symmetric backbones, the durability is not yet reported, and their degradation modes are still unknown.

A conventional all-ceramic electrolysis cell structure may not be ideal for intermittent operation due to low tolerance for redox cycling and thermal cycling. Instead, MS-SOECs that incorporate a porous ferritic steel as a substrate could be a potential solution, primarily due to their unique advantages of good redox stability and excellent thermal cycling resistance.[28, 29] Compared with conventional all-ceramic electrolysis cells, the material cost of MS-SOECs is lower, as 90 vol.% of the cell is metal support (stainless steel). Moreover, MS-SOECs possess high mechanical ruggedness, which is convenient during cell manufacture and good for mobile/intermittent applications. In recent years, substantial development of metal-supported fuel cells (MS-SOFCs)

has resulted in excellent performance and durability, and they have demonstrated the unique advantages discussed above.[30-34] In addition to our group, Nielsen et al. from Technical University of Denmark adopted a relatively thin metal support with a thickness of 175 μm and demonstrated high cell performance.[35] A long term stack operation of MS-SOFCs has been demonstrated by Topsoe Fuel Cell[36] and Ceres Power.[37] However, several challenges with MS-SOFCs have also been identified, and these are likewise expected to be relevant for electrolysis operation. These challenges include oxidation of the metal support, Cr contamination of the active materials from the metal support, and long term mechanical evolution of thin ceramic layers.

In this work, MS-SOECs, with Pr_6O_{11} (PrO_x)-samarium-doped ceria (SDC) or $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ (LSCF)-SDC as the air electrode catalyst and SDC-Ni as the fuel electrode catalyst, were tested at 0.33 A cm^{-2} and 700°C with 50 vol% H_2O -50 vol% H_2 and ambient air. The degradation rate was found to be as low as 1.3%/100 h when LSCF-SDC was used as the air electrode catalyst. This is the first time a study has reported long term durability of MS-SOECs with symmetric backbones, as well as exploration of degradation modes. Post-mortem analysis elucidates that the degradation is ascribed to fuel electrode catalyst coarsening, Cr poisoning on the air electrode catalyst, oxidation of the metal support, and local elemental accumulation of Ni.

2. Experimental

2.1. Metal-supported solid oxide electrolysis cell fabrication

The symmetric architecture of the MS-SOEC design is unique; it includes a thin ceramic electrolyte, scaffold backbone layers, and low-cost ferritic stainless steel supports, as shown in Figure 1. The dense electrolyte is $\sim 10\ \mu\text{m}$, and the ceramic backbone layer is $20\text{--}30\ \mu\text{m}$. The backbone is composed of micron-scale large pores and submicron-scale small pores, which can serve as triple phase boundaries. The metal support is the thickest component in the cell, $200\text{--}300\ \mu\text{m}$, providing mechanical support and current collection. The porosities of the metal support and backbone are approximately 30% and 43%, respectively.[38] The adequate porosity of the metal and ceramic layers enables catalyst infiltration throughout the cell structure without catalyst clogging, and without sacrificing the cell's mechanical ruggedness.

To tape cast a dense electrolyte, and porous backbone with polymethyl methacrylate (PMMA) pore-former beads (Esprit Technologies, USA), a 10% Sc and 1% Ce-stabilized zirconium oxide powder (ScSZ, DKKK, Japan) was used. Metal-support layers were prepared by tape casting P434L alloy powder (Ametek Specialty Metal Products, USA) and PMMA pore-former. These layers were then laminated to form a symmetric cell architecture after drying. Button cells were laser cut into circular shapes from laminated green tapes. The cut cells were debinded at $525\ ^\circ\text{C}$ for 1 h in air and then sintered at $1350\ ^\circ\text{C}$ for 2 h in a tube furnace with 2% $\text{H}_2\text{-Ar}$ atmosphere. Cells were pre-oxidized at $850\ ^\circ\text{C}$ for 10 h after co-sintering, as our previous study demonstrated that the pre-oxidization of cells at $850\ ^\circ\text{C}$ can enhance the durability of metal-supported solid oxide fuel cells.[30]

2.2. Catalyst infiltration

Electrode catalysts were introduced by infiltration into the porous ScSZ backbones on both the fuel and air electrode sides.[32, 39] The active area of a cell is $\sim 3 \text{ cm}^2$. Stoichiometric nitrate salts, as the precursors of cations, were dissolved in water with surfactant (Triton-X 100, Sigma-Aldrich) at $\sim 50^\circ \text{C}$ with magnetic stirring. Typically, 4.22 g $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 1.38 g $\text{Sr}(\text{NO}_3)_2$, 1.00 g $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and 5.53 g $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved in a 3.1 g mixture of water and Triton-X 100 to prepare the LSCF. Then 1.52 g $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and 5.94 g $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were dissolved in a 5.6 g mixture of water and Triton X100 to prepare the $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_3$ (SDC). The precursor solutions were pre-heated to $\sim 90^\circ \text{C}$ in an oil bath, before submerging the cells. The aforementioned two solutions were alternately infiltrated under a vacuum at the air electrode side for three and two times, respectively. The first cycle of both the LSCF and the SDC was fired at 850°C for 30 min and the rest were fired at 600°C for 30 min. Any loose catalysts on the surface of the cells were removed by compressed air. The particle size of the air electrode catalyst was $\sim 30 \text{ nm}$, as shown in Figure 1.

To infiltrate the catalyst on the fuel side of the cells, 1.52 g $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 5.94 g $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, and 11.12 g $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in a 5.6 g mixture of water and Triton-X 100 to prepare the SDC and nickel oxide (NiO). The volume ratio of SDC to Ni was 60:40 (denoted as SDCN40). The same infiltration and firing procedure used for the air electrode was employed for the fuel electrode catalyst and other air electrode catalysts. The particle size of the fuel electrode catalyst after reducing it at 700°C with flowing hydrogen was $\sim 40 \text{ nm}$, as shown in Figure 1(d).

2.3. Cell assembly and electrochemical test

After a full cell was fabricated, platinum mesh was spot-welded on the fuel electrode side of the cell and two nickel-chromium alloy wires were spot-welded on each platinum mesh for the electrical connection. The cell was then mounted on a 410 stainless steel test rig using glass paste. Glass paste was prepared with 80 wt.% glass powder (GM31107, Schott) and 20 wt.% glass ink vehicle (Fuel Cell Materials, USA). The cell was then heated at $2\text{ }^{\circ}\text{C min}^{-1}$ to $200\text{ }^{\circ}\text{C}$ to remove solvent and then at $10\text{ }^{\circ}\text{C min}^{-1}$ to $700\text{ }^{\circ}\text{C}$ for 1 h to cure the glass sealant in ambient air. A second round of glass paste loading was conducted after platinum mesh and nickel-chromium alloy wires were spot-welded onto the air electrode side. After curing the glass paste, the chamber of the test rig was flushed with nitrogen, and hydrogen was then bubbled through a water bath at a flow rate of $75\text{ cm}^3\text{ min}^{-1}$. Open-circuit voltage (OCV) was monitored to confirm the leak tightness of the cell and the test rig, as shown in Figure S1. The NiO on the fuel electrode side was completely reduced to Ni metal when the OCV of the cell was stabilized at $\sim 1.12\text{ V}$. Hydrogen was used as the carrier gas in the fuel electrode, and the steam content was controlled by the temperature of the water bath. The steam content is 50 vol.% when the temperature of the water bath is $\sim 82\text{ }^{\circ}\text{C}$. The fuel pipe was wrapped by heating tape. During cell testing, the oxygen electrode was always exposed to static ambient air. The cells were tested at $700\text{ }^{\circ}\text{C}$ under electrolysis mode. For the I-V curve measurement, potentiodynamic scans starting from the OCV to the electrolysis (positive) direction were performed, at a voltage scan rate of 10 mV s^{-1} . Electrochemical impedance spectroscopy (EIS) measurements were performed in the frequency range from 200 kHz to 100 mHz with a sinus amplitude of 5 mV, at OCV. All electrochemical

measurements were conducted with a multichannel potentio/galvanostat (Biologic VMP3, France) equipped with power boosters (Biologic VMP3B-5, France).

2.4. Characterization

The micron-scale cell structures were observed on a polished cross-section mounted in epoxy using a tabletop scanning electron microscope (SEM, Hitachi TM-1000, Japan). The nanostructured catalysts in the fractured cell cross section were imaged using the secondary electron detector of a field-emission scanning electron microscope (FESEM, Zeiss Gemini Ultra-55). An energy dispersive X-ray analysis (EDAX) detector was used for energy dispersive X-ray spectroscopy (EDS) analysis, with a beam energy of 20 kV. Crystal structures of catalysts were characterized by x-ray diffraction (XRD, Bruker D2 Phaser), with the scanning speed of $10^\circ \text{ min}^{-1}$ at a step of 0.02° . Micro-tomography was conducted at the Advanced Light Source (ALS) Beamline 8.3.2 at Lawrence Berkeley National Laboratory with whitebeam x-ray illumination, whose resolution is $\sim 1 \mu\text{m}$.

Figure 1. Cell structure. (a) Schematic and (b-c) cross sectional SEM images of the symmetric MS-SOFC structure: metal support/SCSZ backbone/SCSZ electrolyte/SCSZ backbone/metal-support. (d) Reduced SDCN40 fuel electrode catalyst. (e) Fresh LSCF-SDC air electrode catalyst.

3. Results and discussion

3.1. Electrochemical performance

The study here focuses on PrO_x and LSCF-based oxygen electrocatalysts, selected on the basis of initial performance reported in our previous work.[38] Various catalyst materials, including air electrodes $\text{La}_{0.15}\text{Sr}_{0.85}\text{MnO}_{3-\delta}$ (LSM), LSCF, PrO_x , $\text{SrTi}_{0.3}\text{Fe}_{0.7}\text{O}_{3-\delta}$ (STF), $\text{SrTi}_{0.3}\text{Fe}_{0.63}\text{Co}_{0.07}\text{O}_{3-\delta}$ (STFC), PrO_x -SDC, LSCF-SDC, and hydrogen electrode SDCN40 were successfully infiltrated into MS-SOECs, with their phases confirmed by XRD (Figure S2(a)). The thermal durability of these catalysts under OCV condition were investigated using impedance of symmetric cells (Figure S2(b)). The magnitude of the initial electrode polarization impedances was: $\text{SDCN40} < \text{PrO}_x\text{-SDC} < \text{LSCF-SDC} < \text{PrO}_x < \text{STFC} < \text{STF} < \text{LSM}$. When annealing the catalysts at 700 °C, it appears that fuel electrode SDCN40 and composite air electrodes PrO_x -SDC and LSCF-SDC have better durability; whereas, impedances of air electrodes with single catalysts such as PrO_x , LSM, STF, and STFC-07 increase rapidly with elapsed time. Therefore, the fuel electrode catalyst SDCN40 and the air electrode catalysts PrO_x -SDC and LSCF-SDC were downselected for a durability study in the full cell test.

The durability of cells with air electrode catalysts PrO_x -SDC and LSCF-SDC were compared, and LSCF-SDC was found to be more durable (Figure 2). The initial electrolysis performance of the PrO_x -SDC cell was higher than that of the LSCF-SDC cell at 700 °C with 50 vol% H_2 -50 vol% H_2O on

the fuel side (Figure 2(b)), which is consistent with our previous work.[38] The OCV was ~ 0.98 V for all the cells, which is consistent with the theoretical OCV for 50 vol% H₂-50 vol% H₂O. At a 1.3 V cell voltage, the current densities for PrO_x-SDC and LSCF-SDC were -0.54 and -0.41 A cm⁻², respectively. This is consistent with the symmetric cell performance in Figure S2(b). All the cells were pre-coarsened *in-situ* at 750 °C for 4 h at OCV with 50 vol% H₂-50 vol% H₂O on the fuel side before the durability test. Based on our previous study of SOFC mode operation, pre-coarsening can enhance durability, but at the expense of sacrificing initial performance.[30] After pre-coarsening, the cell with PrO_x-SDC as the air electrode catalyst was operated for ~ 146 h at constant current mode (0.33 A cm⁻²) at 700 °C. The voltage increased from 1.18 V to 1.97 V, and the average degradation rate was calculated to be 54.1%/100 h on a voltage basis. This could be due to the fast Cr accumulation on PrO_x catalyst, generating PrCrO₄. The ratio of Cr:Pr is 1.10 ± 0.06 after 300 h test. The long term durability of the LSCF-SDC cell (Cell 1) was dramatically improved at the same operational conditions. Its voltage increased from 1.30 V to 1.51 V in 1000 h, with an average degradation rate of 1.6%/100 h. To reproduce the test, another LSCF-SDC cell (Cell 2) was tested for 860 h, and its degradation rate was 1.3%/100 h. The degradation rate of the LSCF-SDC cell was only 2.4% of the PrO_x-SDC cell degradation rate. The noise in the voltage signal was due to formation of water droplets at the outlet of the test rig. The EIS of the LSCF-SDC cell was measured before pre-coarsening, after pre-coarsening, and after the 1000 h test, as shown in Figure 2(c). The ohmic and polarization impedances increased after pre-coarsening, and after the 1000 h test. The ohmic impedance increased from 0.27 to 0.33, then to $0.42 \Omega \text{ cm}^2$ at 50 vol% steam on the fuel electrode side. Polarization impedance increased from 0.48 to 0.69, then to

1.51 $\Omega \text{ cm}^2$. The impedance increases during test, and degradation modes will be discussed in the following sections.

Figure 2. MS-SOEC initial performance and durability. (a) Durability of the cells with PrO_x-SDC (baseline) and LSCF-SDC (improved) air electrode catalysts at 0.33 A cm⁻² constant current and 700 °C, with 50% H₂-50% H₂O. The fuel electrode catalyst was SDCN40. (b) Initial I-V curves of the three cells before pre-coarsening. (c) EIS of Cell 1 at OCV with 50% moisture; fresh, pre-coarsened, and after 1000 h test.

3.2. Degradation modes

As the degradation modes specific to MS-SOECs are not yet reported, post-mortem analysis was conducted after long term operation of the LSCF-SDC cell. The degradation modes considered include catalyst coarsening, Cr poisoning on the air electrode catalyst, Ni migration, oxidation of metal support, degradation or migration of glass sealant, foreign element contamination, delamination of the cell, and nano-voids in the electrolyte. These modes are discussed in detail below.

3.2.1. Catalyst coarsening

Coarsening of the fuel electrode catalyst, but not the air electrode catalyst, was found to be a primary degradation mode for infiltrated MS-SOECs. The catalyst microstructure of cells tested for 0 h, 210 h, and 1000 h was examined by SEM. Catalyst coarsening was observed on the fuel electrode (Figure 3(a)-(c)). The initial particle size of fuel electrode catalyst SDCN40 was about 40 nm. A relatively dense catalyst layer was deposited on the backbone, as well as a less dense bulk catalyst towards the interior of the pore. The bulk catalyst became denser after the 210 h test and densified further after the 1000 h test. The particle size was 80–100 nm after the 1000 h test, leading to the loss of triple phase boundaries. A minor secondary morphology of the SDCN40 catalyst reminiscent of frog eggs was observed in a few locations after the 1000 h test (Figure S3), and could be related to inhomogeneous distribution of the current.

Unlike the fuel electrode catalyst, the air electrode LSCF-SDC catalyst did not coarsen during the long term durability test. In contrast, SEM images showed that the air electrode catalyst LSCF-SDC was uniform, with a particle size of ~30 nm (Figure 3(d)-(f)). After the 1000 h durability test, the bulk catalyst was still porous, and the particle size remained approximately 30 nm. This is contrary to our previous study of SOFC mode operation, where significant coarsening occurred on the PrO_x cathode catalyst, even after only 100 h operation.[30]

Coarsening of the SDCN40 catalyst is promoted primarily by electrochemical reaction, not thermal exposure. Symmetrical cells with fuel electrode catalyst (SDCN40) and air electrode catalyst (LSCF-SDC) were thermally treated at 700 °C for 1000 h with 50% H_2 -50% H_2O and static air, respectively. After exposure, the particle sizes of the SDCN40 catalyst and LSCF-SDC were ~40

nm (Figure S4(a)) and ~ 30 nm (Figure S4(b)), respectively, both similar to the initial particle sizes. This means thermal treatment at 700 °C is not responsible for the fuel-side catalyst coarsening observed after long-term full cell operation.

Figure 3. Evolution of the catalyst microstructure. Fuel (a, b, c) and air (d, e, f) electrode catalysts after operation times of 0 h (a) (d), 210 h (b) (e), and 1000 h (c) (f). The scale bar is 100 nm for all the images.

3.2.2. Chromium poisoning

Chromium poisoning is found to be another primary degradation mode for MS-SOECs with metal support on the air side. Chromium poisoning has been reported to massively degrade the performance of anode-supported SOFCs (ASC) with chromium-containing stainless steel interconnects.[22, 23, 40] Due to the metal support, both fuel and air electrodes of MS-SOEC are exposed to chromium. On the fuel electrode, chromium poisoning is negligible during long term running due to the extremely low oxygen partial pressure, which prevents formation of volatile chromium-oxide or -oxyhydroxide species. Chromium poisoning on the air electrode is studied

by EDS mapping (Figure 4(a)). The distribution of Cr completely overlaps with the LSCF-SDC catalyst. Additionally, the uniform distribution of Ce and La demonstrates the uniform deposition of LSCF and SDC during catalyst infiltration, and the absence of significant LSCF and SDC segregation during operation as the Sr distribution is essentially overlapped with La and Sr accumulation is not observed. As shown in Figure 4(b), a small amount of Cr is detected on the air electrode even for 0 h operation. That is because the catalyst was fired in air at 850°C during cell assembly and at 750°C during pre-coarsening, and Cr migration is accelerated at elevated temperatures. The ratio of Cr to La increases rapidly from 0.17 at 0 h to 0.53 at 210 h, then gradually increases to 0.61 at 1000 h. Adding a protective coating on the metal support could help to inhibit the Cr poisoning of the air electrode catalyst. For example, a thin Co coating has been demonstrated to be effective in the SOFC mode in our previous study.[30] Selection and validation of coatings for SOEC mode is the subject of upcoming work.

Figure 4. Elemental distribution on the LSCF-SDC air electrode catalyst near the electrode/metal support interface. (a) EDS mapping of La, Sr, Ce, and Cr after 1000 h operation. (b) The atomic ratio of Cr/La as a function of operation time on the air electrode catalyst.

3.2.3. Ni migration

No Ni migration was detected in the MS-SOEC fuel electrode after 1000 h operation. Ni particles migrating away from the electrolyte in anode-supported SOEC (AS-SOEC), leading to loss of contact between Ni and ceramic particles and between adjacent Ni particles, has been reported.[41, 42] EDS mapping was used to observe if a Ni gradient exists between the metal support and electrolyte after 1000 h operation (Figure 5). Generally, the distribution of Ni and Ce overlapped, and no Ni depletion region was identified. The lack of Ni migration is likely due to the high tortuosity of the porous backbone, nano-scale of the Ni catalyst, presence of SDC, or moderate current density. Minor local Ni accumulation in pores was observed, and is thought to be due to local coarsening/agglomeration of the nanoscale Ni catalyst.[43]

Figure 5. Ni and Ce distribution at the fuel electrode after 1000 h operation, showing an absence of Ni migration.

3.2.4. Oxidation of the metal support

Oxidation of the metal support is found to be a secondary degradation mode for MS-SOEC. Our cell structure contains metal supports on both air and fuel sides, and the metal support is Cr-containing stainless steel. During long term operation, oxidation of the steel occurs, and Cr diffuses and accumulates at the surface of the metal as Cr_2O_3 . The chromia thickness at both electrodes was very similar ($\sim 0.8 \mu\text{m}$) after cell fabrication, and is ascribed to the elevated temperature during pre-oxidization and catalyst firing. Obvious chromium accumulation was observed at the interface between the metal support and the pore (Figure 6(a)(b)). Red color is used to represent Cr distribution, and the Cr-rich layer is thicker after 1000 h operation. The thickness of chromia increased to $\sim 2 \mu\text{m}$ on the air electrode side after the 1000 h test, measured from ~ 10 representative pores, and it's $< 1 \mu\text{m}$ on the fuel electrode side after the operation. This is consistent with the calculation of chromia thickness based on the parabolic growth rate law.[28] The growth of the chromia layer at the metal support/electrode interface will increase electronic resistance, though this is expected to be a minor contribution to total cell area specific resistance (ASR). In addition, a chromia layer with thickness of $\sim 2 \mu\text{m}$ between the backbone and the metal support on the air electrode side was present after the 1000 h operation due to the oxidation of metal support (Figure 6(d)), which lowers electrical conduction.

Figure 6. The chromia scale grows primarily on the air electrode side. Chromia accumulation on the metal support of the air electrode side (a) after reducing and (b) after 1000 h operation. (c) Chromia thickness statistic from 10 pores for each condition. (d) Cr accumulation between the backbone and the metal support on the air electrode side after 1000 h operation.

3.2.5. Glass sealant

The glass sealant is found to be compatible with the other components of the MS-SOEC, and survives the operating conditions. The microstructure and compositional evolution of the glass sealant is crucial to long term stability, as catalyst poisoning arising from the glass sealant limited previous long term operation of AS-SOECs.[44, 45] Moreover, cracked glass sealant would lead to an OCV issue and even safety concerns. The SEM image shows the sealant used here was dense and uniform (Figure 7(a)). After reduction (sealant heated to 700 °C and cured for 1 h with the

fuel electrode exposed to 3 vol% H₂O-H₂), the distribution of Ca and other elements was uniform (Figure 7(b)). After pre-coarsening at 750 °C for 4 h, the microstructure looks crystallized and Ca accumulated locally (Figure 7(c)(d)). After the 1000 h test at 700 °C, further microstructure change was not obvious, but the element distribution was more non-uniform (Figure 7(b)). This was confirmed by EDS spot analysis, with three different locations analyzed to obtain the average concentration and deviation for Al, Si, Ca, and Ba elements (Figure 7(c)). Although the concentration of each element was still in the range of deviation, the deviation increased with operation time. Surprisingly, no element migration from the metal support or test rig to the glass (Figure S5), or from the glass to the catalysts (Section 3.2.6) was detected after 1000 h operation. The OCVs of the two LSCF-SDC cells stabilized at about 0.98 V during the long term test (Figure 7(d)), indicating adequate sealing throughout operation.

Figure 7. The glass sealant was stable during long term operation. The (a) microstructure and (b) Ca element distribution of the fracture section of glass sealants from the Reduced, 0 h, and 1000 h cells; (c) Al, Si, Ca and Ba element composition evolution over the cell operation time; and (d) OCV monitoring during operation.

3.2.6. Other degradation modes

Delamination between layers, nano-void growth on the ScSZ electrolyte, and foreign element poisoning were not detected on the MS-SOEC after 1000 h operation. As green tapes were laminated by isostatic pressing, individual layers could delaminate after a long term durability test, potentially weakening the electrical or ionic percolation. For AS-SOECs in some cases, void formation at the interface between the electrolyte and air electrode causes delamination.[46] Global SEM images (Figure 8(a)) and micro-tomography at the middle of the cell (Figure 8(b)) demonstrate the cell structure was intact, and the layers did not delaminate after 1000 h operation. Delamination was not observed throughout the volume probed with tomography, and other representative cross-section images are shown in Figure S6. The ScSZ electrolyte remained dense, and no pinholes or nano-voids were found (Figure 8(c)), even with a high magnification SEM image (Figure 8(d)). Similar to a fresh ScSZ electrolyte, grain boundaries remained thin after 1000 h operation.

Figure 8. Cell structure after 1000 h operation. (a) Cross sectional SEM image of the cell and (b) a corresponding micro-tomography image at the middle of the cell, showing no delamination in the cell. (c) SEM overview and (d) high magnification images of the SCSZ electrolyte, showing no nano-voids between the grains.

An EDS survey was conducted on both fuel electrode (Figure S7(a) and (b)) and air electrode catalysts (Figure S7(c)-(e)). The results showed no foreign elements diffused to the catalysts after 1000 h operation, except Cr poisoning discussed above in Section 3.2.2. Notably, the glass seal components did not migrate to the electrodes. Only the expected Ce, Sm, and Ni were detected on the fuel electrode catalyst and La, Sr, Co, Fe, Ce, Sm, and Cr were detected on the air electrode catalyst.

4. Conclusions

A low degradation rate during 1000 h of MS-SOEC operation was achieved and post-mortem analysis was conducted to determine MS-SOEC degradation modes. Air electrode catalyst screening demonstrated that PrO_x and LSCF are the top two candidates, and that composite catalyst with SDC is more stable than the pure catalysts. MS-SOECs with an LSCF-SDC air electrode catalyst were more stable than a cell with PrO_x -SDC catalyst, and achieved a degradation rate as low as 1.3%/100 h at 700 °C with 50 vol% H_2 -50 vol% H_2O on the fuel electrode side, which is a new record for MS-SOECs in a long term durability test. Nevertheless, the degradation rate must be further improved for commercialization. Post-mortem analysis demonstrated that a primary degradation mode is fuel electrode catalyst coarsening. In contrast, the air electrode catalyst

does not coarsen, which is contrary to previous results for long-term fuel cell mode operation of infiltrated MS-SOFCs. An additional primary degradation mode is Cr poisoning on the air electrode catalyst. Oxidation of metal support and local elemental accumulation of Ni are found to be secondary degradation modes. Other potential degradation modes reported previously for AS-SOFCs/SOECs, such as Ni migration, delamination of the cell, nano-voids in the electrolyte, and foreign elements contamination, were not found. Improving the pre-coarsening temperature to coarsen the initial particle size of catalysts is promising to overcome the fuel electrode catalyst coarsening. Protective coating on metal support, such as Co_3O_4 , has been demonstrated effectiveness on inhibiting Cr diffusion toward catalysts with the same cell structure, which will be applied to MS-SOECs too.

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