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DEGRADATION ISSUES IN SOLID OXIDE CELLS DURING HIGH TEMPERATURE ELECTROLYSIS

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ABSTRACT

Idaho National Laboratory (INL) is performing high-temperature electrolysis (HTE) research to generate hydrogen using solid oxide electrolysis cells (SOECs). The project goals are to address the technical and degradation issues associated with the SOECs. This paper provides a summary of ongoing INL and INL-sponsored activities aimed at addressing SOEC degradation. These activities include stack testing, post-test examination, degradation modeling, and issues that need to be addressed in the future.

Major degradation issues relating to solid oxide fuel cells (SOFC) are relatively better understood than those for SOECs. Some of the degradation mechanisms in SOFCs include contact problems between adjacent cell components, microstructural deterioration (coarsening) of the porous electrodes, and blocking of the reaction sites within the electrodes. Contact problems include delamination of an electrode from the electrolyte, growth of a poorly (electronically) conducting oxide layer between the metallic interconnect plates and the electrodes, and lack of contact between the interconnect and the electrode.

INL's test results on HTE using solid oxide cells do not provide clear evidence as to whether different events lead to similar or drastically different electrochemical degradation mechanisms. Post-test examination of the SOECs showed that the hydrogen electrode and interconnect get partially oxidized and become nonconductive. This is most likely caused by the hydrogen stream composition and flow rate during cooldown. The oxygen electrode side of the stacks seemed to be responsible for the observed degradation because of large areas of electrode delamination. Based on the oxygen electrode appearance, the degradation of these stacks was largely controlled by the oxygen electrode delamination rate.

Virkar et al. [19–22] have developed a SOEC model based on concepts in local thermodynamic equilibrium in systems otherwise in global thermodynamic nonequilibrium. This model is under continued development. It shows that electronic conduction through the electrolyte, however small, must be taken into account for determining local oxygen chemical potential within the electrolyte. The chemical potential within the electrolyte may lie out of bounds in relation to values at the electrodes in the electrolyzer mode. Under certain conditions, high pressures can develop in the electrolyte just under the oxygen electrode (anode)/electrolyte interface, leading to electrode delamination. This theory is being further refined and tested by introducing some electronic conduction in the electrolyte.

INTRODUCTION

Production of hydrogen as a secondary energy carrier has received considerable attention because of its potential to be a transportable and environmentally benign fuel with potential broad application for heating, electrical production (via fuel cells), and automobile transportation. It is also used as a raw material for many chemical processes, such as ammonia and methanol synthesis, iron ore processing, and petroleum processing. Consequently, there is a high level of interest in production of hydrogen from water splitting via high-temperature steam electrolysis using solid oxide cells.

SOFCs have been studied extensively for their application to power generation systems [1,2] at high temperatures. Same solid oxide cells are also operated in the electrolysis mode, consuming electrical power and process heat while producing hydrogen. The most common materials currently used for the solid oxide cells are listed in Table 1.[3] The ionic conductivity of ceramics is highly dependent on the ceramic temperature. Thus, high operating temperatures (800–1,000ºC) are required to obtain sufficient overall conductivity in the solid oxide cell. The most common electrolyte material for SOFCs is yttria-stabilized zirconia (YSZ). However, other electrolyte materials with higher ionic conductivity, such as scandia-stabilized zirconia (SSZ) and LaSrGaMgO (LSGM) are also receiving significant attention. If SOFCs using YSZ electrolyte, operate in lower temperature range, their ionic conductivity drops off significantly with temperature. Therefore, to achieve good performance at lower temperatures, electrolytes made from advanced materials have to be developed.

Table 1. Commonly used materials in SOFC/SOEC [3].

Component	Material	Acronym
Steam/H_2 - electrode	Ni - $Y_x\ Zr_{1-x}\ O_{2-x/2}$ (nickel-yttria stabilized zirconia)	Ni-YSZ
Electrolyte	$Y_x\ Zr_{1-x}\ O_{2-x/2}$ (yttria stabilized zirconia)	YSZ
Air/O_2 - electrode	$Sr_xLa_{1-x}\ MnO_{3-\delta} + Y_x\ Zr_{1-x}\ O_{2-x/2}$ (doped lanthanum manganite)	LSM-YSZ
Interconnect	Chromium based alloys/ceramics or stainless steel	SS

In comparison to SOFCs, SOECs have received relatively little attention in the literature. Polarization losses (degradation) have been studied mainly for a SOFC. The total polarization loss of an operating cell consists of three dominant parts: activation (or charge transfer) polarization (η_{act}), concentration (or diffusion) polarization which includes chemical reaction polarization (η_{conc}), and ohmic resistance polarization (η_{ohm}). Under the same operating conditions of temperature and current density, a SOFC and a SOEC are likely to have the same ohmic and activation overpotentials. However, the concentration overpotential values are different for the SOEC and SOFC because the gas transport mechanisms through the electrodes are different in two cases. Therefore, due caution should be applied when using the SOFC definitions/correlations for a SOEC case. The objective of this study is to discuss the problem of degradation in the SOECs.

An important performance parameter that quantifies the ohmic losses associated with the operation of SOECs is the area-specific resistance (ASR). This quantity is defined as:

$$ASR = \frac{E - E_{ref}}{i} \quad \text{where} \quad i = \frac{I}{A_{cell}} \qquad (1)$$

where E is the applied potential and E_{ref} is the reference or open-cell potential, I is the current, A_{cell} is the cell surface area, and i is the current density (A/cm^2). In calculating area-specific resistance, the reference voltage measured using the reference electrode on the button cell at each operating condition was used. Although it always represents an open-cell potential, this reference voltage varies slightly from the zero-current value as the current through the active cell is varied. This variation is caused by the change in local gas compositions at the electrode surfaces during cell operation.

REVIEW OF PAST EXPERIMENTS ON SOEC DEGRADATION

Hardly any comprehensive studies currently on degradation of solid oxide electrolysis cells, although extensive research has been performed relating to SOFC. Yet SOFCs have not reached their complete commercial success because of problems relating to their degradation, longevity, and cost. Some of the degradation mechanisms include contact problems between adjacent cell components, microstructural deterioration (coarsening) of the porous electrodes, and blocking of the reaction sites within the electrodes. Contact problems include delamination of an electrode from the electrolyte, growth of a poorly (electronically) conducting oxide layer between the metallic interconnect plates and the electrodes, and lack of contact between the interconnect and the electrode. Examples of microstructural degradation are oxygen electrode sintering, carbon deposition, and sulfur or chromium poisoning. Delamination, caused by thermal cycling, increases ohmic resistance proportional to the delaminated area. The delaminated area also becomes inactive for electrochemical transport of ions across the electrode and the electrolyte. Chromium-based interconnect oxidation is another important mode that contributes to reducing electrical conductivity between the electrode and interconnect. Ceramic coatings are sometimes used to slow down the rate of oxidation and reduce the rate of chromia evaporation from the interconnects. It was also shown that the loss of performance resulting from interconnect detachment is less severe than that caused by electrode delamination because blocked transport of electrons can now easily move laterally in the electrodes as compared to ions being able to move within the electrolyte. The modeling exercise indicated that results of delamination are highly dependent on the inaccuracies in the knowledge of various cell parameters.

Guan et al.[4] tested reversible solid oxide cells for over 1,000 hours, which alternated between fuel cell and electrolysis modes. They selected YSZ (8 mol% Y_2O_3 doped zirconia) as electrolyte material. Selected O_2-electrodes were strontium-doped lanthanum manganite (LSM), strontium-doped lanthanum ferrite (LSF), and lanthanum strontium cobalt iron oxide (LSCF). They used a samaria-doped ceria (SDC) interlayer for LSF and LSCF. LSCFs have increased ionic conductivity and may reduce degradation rate in electrolysis mode. For H_2-electrode, Ni-YSZ was selected with varying volume fraction of Ni (40-80%). Figure 1 shows cell degradation in terms of area specific resistance (ASR) increase for three cells.

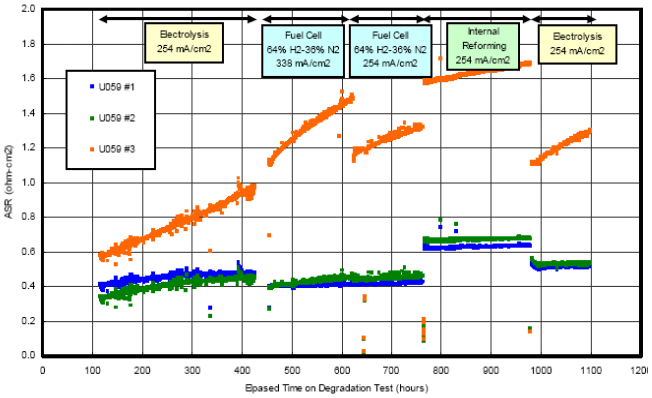

Figure 1. Individual cell performance in a three-cell stack operating at 800°C for >1,000 h [4].

The higher degradation shown for Cell 3 may be the result of increased contact resistance between electrodes and interconnects. The microstructure of another stack was examined after a test run with secondary electron microscopy; the results are shown in Figure 2. Delamination was observed between the electrolyte and SDC barrier layer, and the barrier layer and O_2-electrode, which can cause performance degradation. They also show that performance of various O_2-electrodes was in the order LSCF > LSF > LSM-YSZ, however, degradation of the LSCF electrode was probably more than other electrodes. Cell degradation was higher with stainless-steel interconnects than with gold interconnects. However, the degradation rate with coated stainless-steel interconnects was reduced in half, ~0.2–0.3 ohm-cm^2/1,000 h.

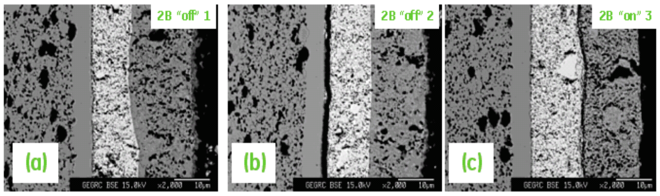

Figure 2. Microstructure of a typical cell stack (from left to right: fuel electrode, electrolyte, barrier layer, and oxygen electrode); (a) a typical cross-section, (b) cross-section showing delamination between electrolyte and barrier layer, and (c) cross-section showing delamination between barrier layer and O_2-electrode [4].

Hauch et al.[5–8] also tested solid oxide cells in the electrolysis mode at the Risø National Laboratory at temperatures from 650–950°C. The cells were made from 10–15 μm thick H_2-electrode of Ni/YSZ, supported by a ~300 μm Ni/YSZ layer, a 10–15 μm YSZ electrolyte, and a 15–20 μm thick LSM-YSZ composite O_2-electrode. The SOEC tests showed ASRs of 0.26 Ω-cm^2 at 850°C and 0.17 Ω-cm^2 at 950°C as obtained from the i-V curves and a current density of -3.6 A/cm^2 at 1.49 V and 950°C. Long-term degradation of 2%/1,000 hours was obtained at 850°C and current density of -0.5 A/cm^2, whereas the degradation rate increased to 6%/1,000 hours at 950°C and current density of -1.0 A/cm^2. These are significantly higher than those for similar cells tested in fuel cell mode (< 2%/1,000 hours at 950°C, and -1.7 A/cm^2).

Hauch [6] summarized the general observations of the SOEC tests as (1) a short-term passivation (reduction of the reactivity by electrochemical polarization) in the first few hundred hours, (2) an activation, and (3) a subsequent long-term degradation. The ohmic resistance remained nearly unaffected during the short term passivation period, but polarization resistance increased and decreased during the same period. Upon reduction of steam in the H_2 electrode, in the few microns closest to the electrolyte, the equilibrium between $Si(OH)_4$ and silica is shifted towards formation of silica leading to a contamination of the triple phase boundary (TPBs) of the electrode. Both the short-term passivation and the long-term degradation appear mainly to be related to processes in the H_2-electrode. Spectroscopy and microscopy observations after the test showed that Ni particle size change is not the main cause of SOEC degradation, but it is the accumulation of glassy phase impurities at the TPBs in the size range of 50–500 nm and as rims around Ni particles. The impurities are silicates, alumina silicates, and in some cases sodium alumina silicates. These impurities that diffused to and accumulated at the TPBs of the H_2-electrode were thought to be the main reason for the degradation of the SOECs. Also, impedance spectra showed that the main part of the irreversible degradation is caused by increased losses in the hydrogen electrode. Postmortem scanning electron microscopy (SEM) analysis showed that there was a significant microstructural change at the H_2-electrode-electrolyte interface. A 2–4 μm thick dense layer of Ni and YSZ was formed at the interface caused by relocation of Ni particles.

Hauch [6] suggested simple possible mechanisms leading to degradation at the steam/H_2-electrode based on several previous publications. The four possible reaction scenarios shown in Figure 3 are based on various possibilities proposed by other researchers and cited by Hauch [6], but several intermediate reactions, including adsorbed OH and vacancies, are not shown.

As shown in Figure 3(a), the inlet reactants at the steam/H_2-electrode reach near the TPB via the pores in the H_2-electrode and the reaction at the electrode proceeds via adsorption of H_2O on the YSZ surface in the vicinity of the TPB. Hydrogen either diffuses through the YSZ and Ni to a vacant Ni site, and $H_2(g)$ desorbs or hydrogen diffuses on the surface of the YSZ and Ni (dashed lines). Figure 3(b) shows another possible reaction assuming adsorption of H_2O on the YSZ surface, conduction of electrons in the YSZ and Ni, and release of $H_2(g)$. Figure 3(c) illustrates a mechanism with adsorption of H_2O on the Ni surface.

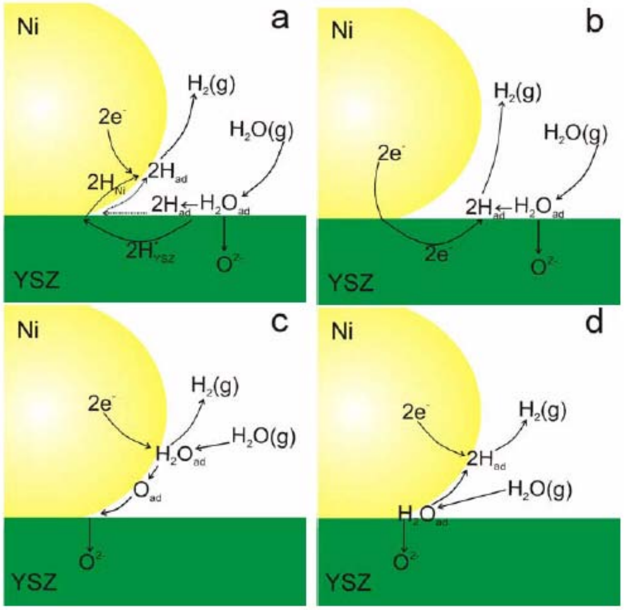

Figure 3. Possible reaction mechanisms at the steam/H_2-electrode in a SOEC [6]: (a) adsorption of H_2O on the YSZ surface and proton diffusion on the surface or in the bulk of YSZ, (b) adsorption of H_2O on the YSZ surface and electronic conduction in YSZ is assumed, (c) adsorption of H_2O on the Ni surface and diffusion of oxygen on the Ni surface, and (d) H_2O adsorbed at the TPB and hydrogen diffusion on the Ni surface.

This reaction mechanism has been questioned by some researchers because (a) in catalysis literature, adsorbed hydrogen is indeed very fast moving on Ni surfaces and it seems unlikely that diffusion of hydrogen adsorbed on the Ni surface should be rate determining, and (b) most researchers report more than one, typically three, arcs in the impedance spectra obtained on YSZ-Ni cermets and the mechanism suggested in Figure 3(c) does not seem to be able to account for that. An ideal reaction mechanism is shown in Figure 3(d). Here, H_2O is assumed to be adsorbed at the TPB and only hydrogen has to diffuse on the Ni surface and is desorbed as $H_2(g)$. In reality an unlimited number of TPBs are not available and the actual number of TPBs will set an upper limit for the reaction mechanism shown in Figure 3(d), especially at high current densities.

In the above reactions mechanisms, the presence of impurities at the grain boundaries is not included, which are always there. Levels of impurities in the raw materials and their chemical composition upon segregation to the grain boundaries may play an important role in the electrode reaction mechanisms and be part of the discrepancy in the results reported on the reaction mechanisms for the H_2-H_2O-Ni-YSZ system. A complete and well understood electrode reaction mechanism at anodic polarization for the H_2-H_2O reactants and YSZ-Ni electrode system does not exist, and even less is known about the reaction mechanism under cathodic polarization.

Electrochemical impedance spectroscopy (EIS) results showed that changes in impedance spectra resulting from gas variation experiments before and after electrolysis operation verifies that the main passivation of the SOECs is caused by loss of performance in the H_2 electrode. SEM investigations of the Ni particle size distribution showed that the Ni size distribution for SOEC changed compared to those for reference cells. However, these changed Ni distributions were similar to those obtained for fuel cells tested for the same time period. Hence, a change in Ni particle size distribution is not the main reason for the performance degradation of the SOECs. Silicon containing impurities were observed to segregate to the innermost few microns of the H_2-electrode closest to the electrolyte. These impurities were also found as rims around the Ni particles. These impurities that diffused to and accumulated at the TPBs of the H_2-electrode were thought to be the main reason for the degradation of the SOECs.

INL TESTS ON SOEC DEGRADATION

O'Brien et al.[9] recently summarized INL's test results on HTE tests using solid oxide cells, including observations of long-term performance degradation of SOECs. Note that INL cells and stacks utilize scandia-stablized zirconia (ScSZ) electrolyte-supported cells, which do not necessarily represent the state-of-the-art in cell design. The Scandia dopant level in these cells was only about 6 mol%, which is not high enough to be considered fully stabilized. In addition, ScSZ with dopant levels less than 10% have been shown to exhibit an aging effect with annealing at 1,000°C.[10]

Performance degradation results with a 25-cell SOEC stack tested for 1,000 hours at INL were presented by O'Brien et al.[11] and are shown in Figures 4 and 5. Figure 4 plots the stack ASR as a function of time for the 1,000 hours. The furnace temperature was increased from 800 to 830°C over an elapsed time of 118 hours, resulting in a sudden drop in ASR. The increase in ASR with time represents degradation in stack performance. The degradation rate decreases with time and is relatively low for the last 200 hours of the test. However, from the 118-hour mark to the end of the test, the ASR increased more than 40% over approximately 900 hours. Reduction of this performance degradation is an objective of ongoing research. Figure 5 shows the corresponding generation of hydrogen.

Performance degradation of the Integrated Laboratory System (ILS) system is documented in Figure 6. Over a test period of 700 hours, module-average ASR value increased by about a factor of 5, from an initial value near 1.5 Ohm-cm^2. Some of the observed degradation was caused by balance-of-plant issues. For example, prior to about 480 hours of testing, unanticipated condensation

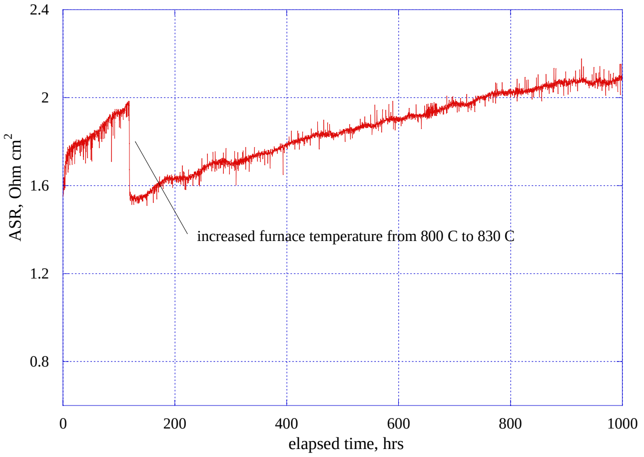

Figure 4. Area-specific resistance of a 25-cell stack as a function of time for a 1,000-hour test; O’Brien et al [11].

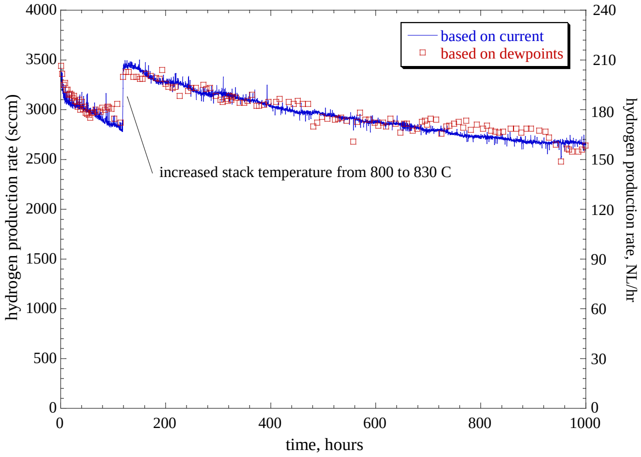

Figure 5. Hydrogen production rates during 1,000-hour long-term test; O’Brien et al [11].

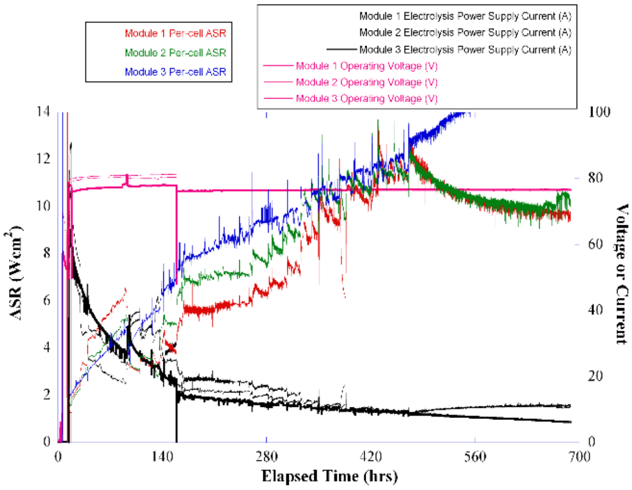

Figure 6. Time history of ILS module ASR values, voltages, and current over 700 hours of operation [9].

occurred in the hydrogen recycle system which led to erratic control of the hydrogen flow rate because of the intermittent presence of liquid water in the mass flow controllers. This problem led to time periods during which there may have been no hydrogen flow to the ILS stacks, in turn leading to accelerated performance degradation associated with oxidation of the nickel cermet electrodes. Figure 7 shows ILS hydrogen production with peak electrolysis power consumption where the hydrogen production rates were 18 kW and 5.7 Nm^3/hr, respectively.

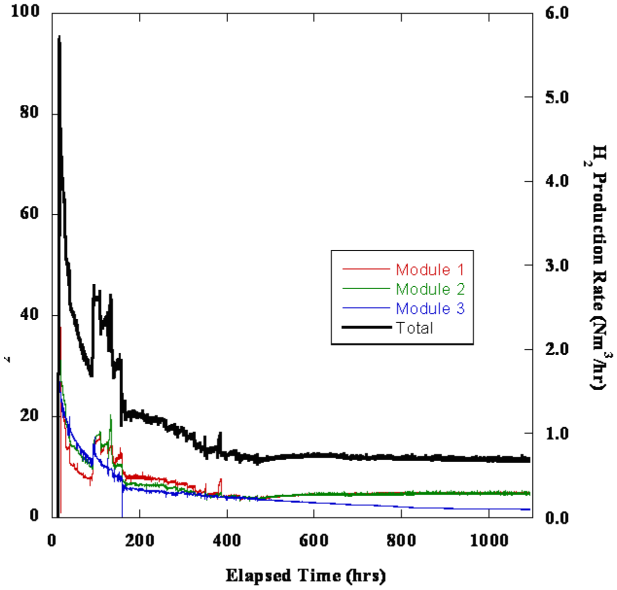

Figure 7. Time history of H_2 production rate in the ILS [9].

POSTMORTEM OF INL SOEC BY ARGONNE NATIONAL LABORATORY

In an effort to understand degradation in SOEC and its distinction from degradation in SOFC, a postmortem of INL electrolysis cells was performed by Argonne National Laboratory (ANL) [12]. Mawsdley et al.[13,14] presented results of post-test evaluation of the Ceramatec SOECs after a 1,000-hour test at ~830°C (O’Brien et al.[9]). ANL employed x-ray fluorescence, x-ray absorption near edge structure, four-point resistivity, SEM, energy dispersive spectroscopy, x-ray diffraction, and Raman micro-spectroscopy to determine possible causes for the degradation. The surface characteristics of cells and the bipolar plates were examined for potential causes of long-term degradation. The x-ray fluorescence measurements revealed that during the test, Mn and Co from the O_2-electrode and bond layer showed no macroscale interdiffusion. On the other hand, Cr had diffused from the ferritic stainless steel bipolar plate toward the electrode-electrolyte interface, preferentially through the active electrode area. Raman spectroscopy identified a monoclinic phase in the exposed regions of the zirconia plate near the edge of the plates, which gives evidence of instability of the zirconia cubic phase. Also, Cr-doped Al_2O_3 was identified in areas near the seal. SEM images showed delamination and cracking on the edges of the electrodes, where most of the cell degradation occurred. For example, the image in Figure 8 shows that the O_2-electrode had begun to delaminate from the electrolyte near the edge where the four-point measurements had shown a large increase in resistivity. Cracks can also be seen within the O_2-electrode, which would increase resistivity. Towards the center of the cell (right), adherence to the electrolyte improves and the cracks begin to disappear. This delamination would become a source of cell degradation.

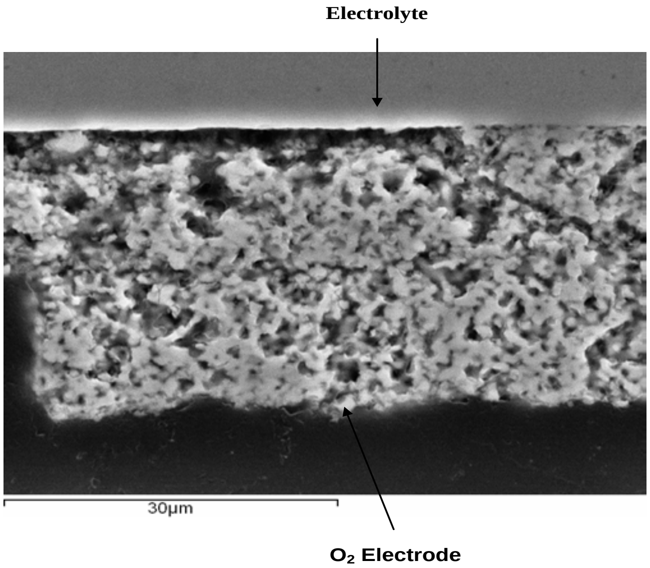

Figure 8. SEM view of the electrolyte and O_2-electrode. [13]

The outcome of these investigations reinforced the need for a comprehensive investigation of the degradation phenomena to advance SOEC technology. They determined that Cr movement (contamination) in SOECs is different than it is in SOFCs. In SOECs, because oxygen flows away from O_2-electrode-electrolyte interface, chromium uniformly diffuses into the cell as seen in the left side of Figure 9. In SOFCs, the direction of oxygen flow is reversed and chromium diffuses discretely in various regions of the cell as shown in the right side of Figure 9. However, the severity of chromium contamination is not well understood because of conflicting opinions about it.

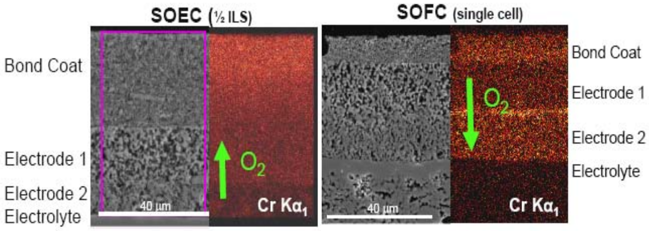

Figure 9. Chromium deposition in SOEC and SOFC. [12]

At the O_2-electrode inlet, ANL found delamination of the electrode from the electrolyte as determined by x-ray fluorescence mapping and SEM imaging. One possible reason of this delamination is excessive pressure build-up with high O_2 flow in the over-sintered (larger grain size and smaller pores formed at higher temperature) region. Delamination between O_2-electrode and electrolyte is shown in Figure 10 [12].

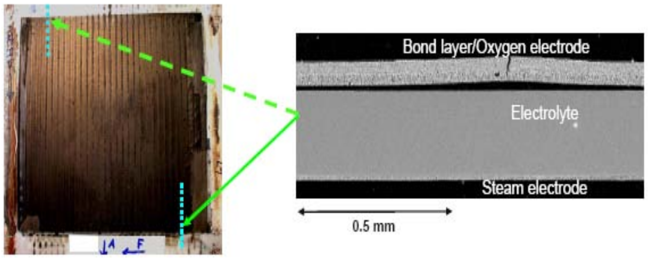

Figure 10. Electrode delamination after 1,500 hr of operation. [12]

Steam at the steam/H_2-electrode inlet can also carry Si from the seal and deposit it on the H_2-electrode as shown in Figure 11. [12] SiO_x can also come from interconnects, but the bond layer on the H_2-electrode does not show the same kind of degradation/delamination as is seen on O_2-electrode in Figure 10. Evidence of Mn, Si, and Ti deposition on the interconnect surface and interconnect-passivation layer interface was also found.

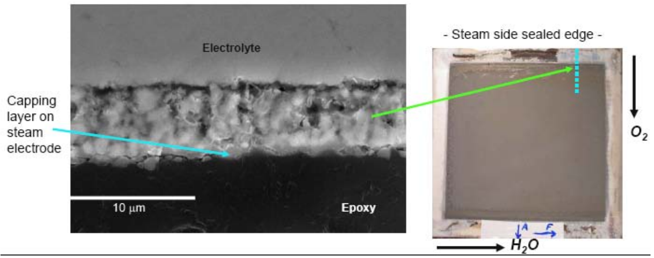

Figure 11. Si capping layer on H_2-electrode. [12]

ANL tested two cells in both (reversible) electrolysis and fuel cell modes.[12] A cell was operated in electrolysis mode for ~310 hours, then reversed to be operated in fuel cell mode for ~100 hours, and finally operated again in the electrolysis mode for ~100 hours. The only difference between the two cells was in the shape of the flow channels (corrugated and square) as shown in Figure 12. A similar cell operated in the fuel cell mode showed stable or even some improvement in performance. The flow channels do not show any signs of degradation. In all the investigations, it was noted that the bond layer on the O_2-electrode degraded.

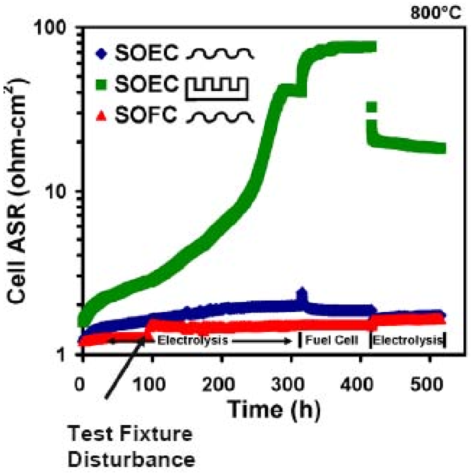

Figure 12. Partial recovery of SOEC degradation [12].

ANL concluded [14] that two phenomena were likely the cause of increasingly poor O_2-electrode performance over time. The first source of degradation was chromium substitution into the O_2-electrode bond layer, which bonds the cell to the flow field and interconnect. This is caused by migration of a chromium species from the bipolar plate. The effect of this is a significant increase in the electrical resistance of the bond layer material. The other source of degradation identified was O_2-electrode delamination. The cause of O_2-electrode delamination is unclear.

SOEC POSTMORTEM BY THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY

Sharma and Yildiz [15,16] investigated the interaction of different constituents of SOECs. The SOEC was provided by Ceramatec after an electrolysis test. The H_2-electrode of the SOEC consists of a Ni–scandia stabilized zirconia (ScSZ) cermet. The electrolyte consists of ScSZ (10% Sc_2O_3–ZrO_2). The O_2-electrode is made of a perovskite oxide, $A_{0.8}Sr_{0.2}MnO_3$ (where A is a proprietary material of Ceramatec). The contact layer between the O_2-electrode and the stainless-steel interconnects consists of a perovskite oxide, $La_{0.8}Sr_{0.2}CoO_3$ (LSC). In order to investigate the SOEC degradation processes and their reasons in the LSC bond layer, Massachusetts Institute of Technology (MIT) researchers employed a range of spectroscopy and microscopy techniques to perform a high-resolution postmortem analysis.

As a general rule, it is assumed that, at a high level, SOEC degradation is likely to be controlled by the same processes as those in SOFC degradation. These being transport of Cr-containing species from steel interconnects into O_2-electrode and bond layer in SOECs, cation segregation and phase separation in the bond layer, and interdiffusion of cations between the electrolyte and O_2-electrode grains. However, the exact mechanisms and the consequent secondary phases could be different from those in an SOFC operation because of the different thermodynamic and electrochemical conditions and the reverse path of ionic and electronic transport in SOECs as compared to that in SOFCs.

Sharma and Yildiz [16] summarized three main hypotheses based on related published literature to explain the Cr-poisoning mechanisms. The first hypothesis implies that Cr-poisoning is initiated through the formation of gaseous species containing Cr^{6+}, such as CrO_3 or $CrO_2(OH)_2$, from the oxidation of chromium oxide on the interconnect. The volatile Cr species are then reduced at the triple-phase boundaries of electrode-electrolyte-air to form solid Cr_2O_3 and other Cr-rich phases, which impede the desired electrochemical process at the electrode and increase polarization losses.

The second hypothesis suggests that reduction of the Cr containing species and solid-state diffusion of the Cr-containing species into the O_2-electrode and chemical dissociation of the electrode material are underlining mechanisms in the deposition of Cr.

The third hypothesis suggests that the Cr deposition on the O_2-electrode takes place because of thermodynamic characteristics and the process is kinetically limited by a reaction between the Cr species being transported and a "nucleation agent" on the electrode. It has also been suggested that an electrically insulating oxide layer forms between the contact layer and the interconnect, which creates barriers in the electronic path from the interconnect to the O_2-electrode. These hypotheses show that there is no consensus about the exact mechanism of how Cr degrades the performance of the electrodes.

Sharma and Yildiz [15,16] used Raman spectroscopy to identify secondary phases formed on the surface of the bond layer. Nanoprobe Auger electron spectroscopy was used to determine the electrode surface microstructure and its variation across the surface at a nanometer to micron scale. Energy dispersive x-ray spectroscopy and transmission electron microscopy were used for high resolution identification of the primary composition and secondary compounds formed on the electrode surface.

Sharma and Yildiz [16] showed that the LSC contact layer had partially dissociated into secondary phases of Co_3O_4, Cr_2O_3, $LaCrO_3$, and La_2CrO_6 having a lower electrical conductivity than that of the original composition. It indicated that Cr transported from the stainless-steel interconnects into the LSC layer, leading to electronic deactivation of the contact layer.

AES results showed that the as-prepared surface chemistry of LSC showed a spatially uniform A-site (La and Sr) enrichment. In the tested SOEC stack cells, an average of 7% Cr on the cross-sectional surface of the LSC layer was found. The La/Co ratio showed a severe and nonuniform dissociation of the contact layer. Long-range transport of the Sr and Co cations to the top of the contact layer particularly prevailed with no detectable Sr remaining in the bulk of the layer. The top of the contact layer (LSC/interconnect interface) was decorated by Co-rich crystallites, possibly Co–Cr oxides, and a Sr-rich surface layer. This process could be associated with cation segregation and phase separation under the electrolytic potential and electronic and ionic current conditions and/or the presence of Cr species driving reactions to dissociate LSC.

Scanning transmission electron microscope (STEM) analysis confirmed the dissociation of the LSC contact layer because of the formation of secondary phases separated at the nanoscale. The bulk had a larger Cr content (10–33%) than the surface of the layer grains, indicating different composition profiles for Cr reactions in the bulk and at the surface. Cr and La coexisted in phase-separated regions, identified as either $LaCrO_3$ or La_2CrO_6 in the bulk of the layer. Consistent with the AES results from the surface, the Sr signal was absent from the bulk, indicating the complete separation of Sr from the bulk contact layer microstructure and microchemistry.

EIS and AES analysis of the referenced half-cells operated in controlled electrochemical environments in air showed that the cells degraded even in the absence of Cr in the system. However, the microstructure and surface composition of the LSC contact layer were stable and uniform throughout, although largely A-site enriched, with clear presence of Sr in the structure. These observations show that the LSC contact layer stayed stable under electrolytic (anodic) conditions when not subjected to Cr-containing species. We therefore conclude that the formation of poorly conducting secondary phases caused by the dissociation of the LSC contact layer leads to the deterioration of the electronic activation of the anode and thus contributes to the significant degradation of the SOEC performance. Our results indicate that the dominant cause for the LSC dissociation is the inward transport of the Cr-containing phases from the stainless-steel interconnects into the contact layer microstructure, which is driven by the thermodynamics governing (La and Sr) Cr–O phases under electrolytic polarization and oxygen partial pressure conditions. These results suggest a mechanism for Cr deposition, which can nucleate between the volatile Cr-containing species _CrO_3 or $CrO_2(OH)$ and the La–O and Sr–O segregates on the initial LSC surface, initiating the formation of secondary phases. The exact mechanism by which Cr causes such long-range transport of Sr and Co cations and the consequent La–Cr–O phase formations and the relation of this process to the electrochemical potential and gas pressure conditions in SOEC anode should be further quantified in terms of the thermodynamics involved in these reactions.

MODELING OF SOEC DEGRADATION BY UNIVERSITY OF UTAH

Virkar [17,18] and Lim and Virkar [19] have been developing a solid oxide cell degradation model based on non-equilibrium thermodynamics. Currently, Virkar [20] is extending this modeling approach to SOEC also. In SOECs, the rate of degradation, as measured by the increase in cell resistance with operational time, is typically greater than if the same cells are operated as SOFC for power generation. As shown by postmortem examination (discussed in previous sections) of the electrolysis cells, one cause of the degradation is delamination of the O_2-electrode.

The objective of the modeling is to develop a fundamental and a generic mechanism of degradation of SOEC. It is known that all electrochemical devices represent systems that are usually not in global thermodynamic equilibrium. However, local thermodynamic equilibrium is almost always established. This modeling approach—the applicability of the local equilibrium criterion to solid electrolytes—leads to a very important conclusion: electronic current cannot be assumed as mathematically zero, even in a so-called ‘pure’ ionic conductor such as yttria-stabilized zirconia (YSZ). In oxygen ion conductors, the electronic current, however small, plays a central role in determining local oxygen chemical potential. It can be shown that the lower the electronic conductivity of the electrolyte, the higher the tendency for the generation of high internal oxygen chemical potential, which leads to high internal oxygen pressure and thus concomitant O_2-electrode delamination. It is well known that YSZ has high ionic conductivity and negligible electronic conductivity. At 800^oC, for example, the electronic conductivity of YSZ is almost immeasurable (~10^{-8} to 10^{-7} S/cm). As a result, the tendency for oxygen electrode delamination is as high with YSZ as it is with the electrolyte. The model demonstrates that a certain parameter comprised of electrode polarization resistances and the electrolyte resistances can be devised whose value in relation to the operating conditions (e.g., applied voltage) of a SOEC determines whether or not electrode delamination will occur. The cell parameter of interest is $\frac{r_e^a R_i}{r_i^a R_e}$,

where

r_i^a = specific charge transfer resistance at the electrolyte/O_2-electrode interface

r_e^a = specific electronic resistance at the electrolyte/ O_2-electrode interface

R_i = specific ionic resistance of the cell

R_e = specific electronic resistance of the cell.

The relevant parameter that describes these operating conditions is $\frac{E_A - E_N}{E_A}$. The model shows that if $\frac{E_A - E_N}{E_A} \le \frac{r_e^a R_i}{r_i^a R_e}$, O_2-electrode delamination should not occur, but if $\frac{E_A - E_N}{E_A} > \frac{r_e^a R_i}{r_i^a R_e}$, O_2-electrode delamination may occur. The model thus shows how SOEC materials and design should be selected to prevent (or minimize) degradation.

SUMMARY OF LEADING CAUSES OF SOEC DEGRADATION AND FUTURE RESEARCH NEEDS

Causes of Degradation

Main sources of degradation come from several cell components. Details about the following list of general observations and main sources of SOEC stack degradation have been discussed in earlier sections [21,22]:

- Microstructural changes in bond layer on the O_2-electrode
- Cr poisoning and dissociation of bond layer on O_2-electrode
- Resulting delamination of O_2-electrode
- Loss of electrical/ionic conductivity of electrolyte
- Generation of contaminants from the interconnect
- No degradation of bond layer on steam/H_2-electrode
- Air and steam/H_2-flow channels are not degrading.

This list is not all inclusive, but represents a majority opinion expressed at the workshop. Main sources of degradation come from several cell components.

FUTURE RESEARCH NEEDS

This section summarizes various goals for future research, which are a collective opinion of several researchers who participated in a workshop on Degradation in Solid Oxide Electrolysis Cells and Strategies for its Mitigation, October 27, 2008, *Fuel Cell Seminar & Exposition, Phoenix, AZ* [21]. It may also be desirable to establish some SOEC performance targets in terms of current density, tolerable degradation rate, and desired lifetime of the SOEC stacks; for example, a lifetime of 20,000 hours may be desirable.

Electrochemical Phenomena in SOEC Cells and Stacks

Addressing the problem of degradation in a SOEC stack will require an understanding of all the electrochemical phenomena at a single cell level. The same phenomena should then be scaled-up to a stack level. However, it is generally accepted that a single cell's performance cannot predict the performance of a stack made from the same cell. Therefore, the differences between the electrochemical behavior of a single cell and a stack should be clearly identified. Electrochemical similarities and differences between operations of SOEC and SOFC stack operations should also be clearly identified. It is hoped that understanding the electrochemical phenomena during normal operation of a SOEC stack will lead to an understanding of off-normal operation resulting from a degraded stack. Many of the phenomena require the cells to behave in a nonequilibrium thermodynamic manner. This approach is being promoted by Virkar [18]. Such fundamental understanding can benefit in identifying the causes of degradation and resolving the same.

Electrochemical Phenomena in SOEC Stacks and Cell Material Composition

The electrochemical behavior of a SOEC stack in relation to the material composition of all cell components needs to be understood. Many electrochemical events responsible for normal and off-normal cell operation occur at the interface between various components, for example O_2-electrode-bond layer, TPB. Different material compositions of various components impact a cell's electrochemical behavior differently. Thus, the relationship between various materials and their corresponding degradation in a SOEC stack needs to be established. If successful, this could lead to cell composition that result in lower degradation rates. This knowledge can be very useful for a SOEC cell manufacturer.

Modeling Electrochemical Phenomena and Stack Degradation

Understanding electrochemical phenomena is essential for developing a model of a SOEC stack. With a suitable model, various stack characteristics and operating parameters, such as, materials of composition, operational transients, thermal cycling, redox cycling, etc., can be modeled to understand the impact of a single or several parameters on stack degradation. It can also help to understand the relative importance of various cell/stack parameters. A functioning model could thus be used to improve the material composition of cell components. As a general rule, any process model is used to plan for experimental testing and improve operation. If the coupling of various electrochemical phenomena are too complex, as a minimum, single phenomenon models should be developed that can also be verified by experimentation

Delamination of O_2-Electrode and Bond-Layer

The delamination of an O_2-electrode and its role in causing cell degradation is a major problem that needs to be addressed. Therefore, understanding the causes of O_2-electrode delamination and its mitigation should be considered a high priority.

Contaminant Transport and Deposition

Almost everyone actively involved in SOFC research emphasizes that the deposition of contaminants (chromium, nickel, silica, etc.) at reaction sites (for example triple phase boundary) leads to degradation of SOFC performance. However, their relative contribution to degradation in SOEC is not well known. Some groups (for example, Risø National Laboratory, Denmark) strongly believe that even in SOEC, contaminants have significant impact on degradation. Others such as Virkar [18] believe that other phenomena are the primary causes of cell degradation/failure. The source of these contaminants could be balance-of-plant, interconnects, seals, and external sources. In view of these differing opinions, the source of contaminants and their transport mechanism poisoning and deactivating reaction sites, and the build-up of scales and layers and their relative impact on degradation should be resolved.

Redox Cycling and its Impact on Degradation

Reduction and oxidation (Redox) cycling is a common issue in H_2-electrode (anode in SOFC) supported cells. Redox cycling leads to electrode instability. H_2-electrodes must possess a high performance in terms of high electrochemical activity and high redox stability. Ni-YSZ H_2-electrodes are often above 80°C, thus normally not redox stable. Volume changes in Ni-YSZ electrodes caused by the reduction and oxidation of Ni results in mechanical stresses in the electrode material that degrades cell performance. For SOFCs, researchers are looking for an electrode material (usually ceramic based) that will have a minimal impact on the redox problem. The relative impact of redox on SOEC cell degradation is not well understood.

Interconnects and Seals Related Problems

Chromium evaporation and/or condensation from interconnects, seal leaks, and the origin of contaminants from interconnects and seals also contribute to the degradation of SOEC performance. Seal leaks, SiO_X, Mn poisoning, etc., are considered second order effects. Hence, their relative impact on degradation needs to be quantified and acceptable solutions need to be developed.

Other Related Issues

Several researchers, especially with SOFC experience, have pointed out other issues, some of which have not been examined in the SOEC scenario. Hence, they may not have the same degree of impact in a SOEC as they do in a SOFC. Corrosion is a common issue and can increase resistivity and change dimensions because of cell component swelling. SOEC electrode material may need to be improved to improve gaseous transport, improve reaction sites, increase mechanical strength, and improve conductivity. Overall, these improvements should decrease the degradation rate.

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NOMENCLATURE

A_{cell}	active cell area, cm^2
ASR	area-specific resistance, $\Omega \cdot cm^2$
E	cell potential, V
E_A	applied voltage, V
E_N	Nernst potential, V
F	Faraday number, J/V mol
i	current density, A/cm^2
I	electrical current, A
j	moles of electrons per mole of fuel
$\dot{N}$	molar flow rate, mol/s
r_i^a	specific charge transfer resistance at the electrolyte/O_2-electrode interface,
r_e^a	specific electronic resistance at the electrolyte/ O_2-electrode interface,
R_i	specific ionic resistance of the cell
R_e	specific electronic resistance of the cell.
R_u	universal gas constant, J/mol K
T	temperature
y	mole fraction

Subscripts

i	inlet
ref	reference
sat	saturation
std	standard-state

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