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Towards a Fundamental Understanding of the Cathode Degradation Mechanisms

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While impressive solid oxide fuel cell (SOFC) performance has been achieved, durability under "real world" conditions is still an issue for commercial deployment. In particular cathode exposure to H₂O and CO₂ can result in long-term performance degradation issues. Therefore, we have embarked on a multi-faceted fundamental investigation of the effect of these contaminants on cathode degradation mechanisms in order to establish cathode composition/structures and operational conditions to enhance cathode durability. Using a Focused Ion Beam (FIB)/SEM we are quantifying in 3-D the microstructural changes of the cathode before and after the onset of cathode performance degradation. This includes changes in TPB density, phase-connectivity, and tortuosity, as well as tertiary phase formation. This is then linked to heterogeneous catalysis methods to elucidate the cathode oxygen reduction reaction (ORR) mechanism to determine how H₂O and CO₂ affect the ORR as a function of temperature, time, and composition. By use of *in-situ* ¹⁸O-isotope exchange of labeled contaminants we are investigating whether oxygen incorporated in the lattice of LSM and LSCF, and their composites with YSZ and GDC, respectively, originated from ambient O_2 or the contaminant, as well as intermediate adsorbed species and mechanisms that lead to degradation. The results will be used to develop a cohesive and overarching theory that explains the microstructural and compositional cathode performance degradation mechanisms.

Introduction

Fuel cells offer great promise as a clean and efficient process for directly converting chemical energy to electricity while providing significant environmental benefits. Among the different fuel cell technologies, solid oxide fuel cells (SOFCs) are unique in their ability to operate within the current hydrocarbon based fueling infrastructure. Unfortunately, the degradation of cathode materials under "real world" working conditions is a factor that limits SOFC applications.¹⁻⁵

In order to improve the stability of cathodes at elevated temperatures in the presence of water, and CO_2 , common cathode gas contaminants, we need to understand the fundamentals that govern the oxygen reduction reaction (ORR) occurring at the cathode surface. We employ a multi-faceted approach to identify the effects of contaminants on the different contributions to cathode polarization resistance (R), which can be broken down into the following:

 $R_{Cathode} = R_{Gas \ Diffussion} + R_{Surface \ Adsorbtion/Diffusion} + R_{Charge \ Transfer} + R_{Ohmic}$

Each of these is a subsequent product of microstructure and material kinetic properties:

 $R_{Gas \ Diffussion}$ and R_{Ohmic} are functions of:

- Microstructure (porosity & phase fraction, tortuosity, connectivity)
- Conductance (solid phase conductivity or gas phase diffusivity)

*R*_{Surface Adsorbtion/Diffusion} are functions of:

- Microstructure (surface area/volume)
- Kinetics (surface coverage, surface diffusivity)

*R*_{Charge Transfer} is function of:

- Microstructure (L_{TPB}, surface area/volume)
- Kinetics (Oxygen reduction rate)

As cathode materials are exposed to contaminants there are changes in the conductivity, microstructure and kinetics of the material. The experiments described throughout provide information on how these materials properties change, and further, how they alter cathode polarization.

FIB/SEM 3D Reconstruction and Quantification of Microstructure

We pioneered the use Focused Ion Beam & Scanning Electron Microscope (FIB/SEM) to quantify SOFC cathode microstructures and reconstruct them in threedimensions (3D).⁷⁻⁹ An example of the 3D reconstruction capability is shown in Figure 1. This reconstruction is then used to quantify microstructural properties of the porous cathode such as average particle size, average pore size, closed porosity, open porosity, tortuosity, pore surface area, porosity grading, and Triple Phase Boundary Length (L_{TPB}).

We have extended this to phase connectivity, which is critical to quantifying R_{Gas} _{Difussion} and R_{Ohmic} .¹⁰ Figure 1 shows an example of this technique for an LSM/YSZ cathode. The centroid 3D skeleton provides the connectivity of each phase.



Figure 1. Schematic showing the transition from scanning electron image stack (a), which is used to generate a 3D reconstruction (b), which is then reduced to a mass centroid 3D skeleton (c) of each phase: LSM(red), YSZ(yellow), and continuous pore network (gray).

Comparison of Microstructure Degradation with Electrochemical Performance

In previous research, symmetrical cells of LSM on YSZ were fabricated to study the relationship between electrochemical impedance and the microstructural features of the cathode. These microstructural features, analyzed using 3D reconstruction of FIB-SEM images, include the TPB, porosity and tortuosity of the various networks. Variations in sintering temperature were used to induce variations in cathode microstructure. Electrochemical impedance spectroscopy was performed on each of the samples to obtain impedance measurements. From the obtained impedance profiles charge transfer, dissociative adsorption, and gas diffusion related processes were identified.



Figure 2. Effect of LSM microstructure on cathode polarization; dissociative adsorption as a function of pore surface area, and charge transfer polarization as a function of triple phase boundary length; at 800°C in air.



Air (Synthetic) + Contaminant

Figure 3. Sketch of top view (a) and center-cut (b) of symmetrical button cell. The cathode material (gray) is screen printed onto an electrolyte support (white). WE, CE, RE and Alt. RE, denote the working, counter, reference, and alternate reference electrodes, respectively.

Relating the microstructural and electrochemical results revealed that charge transfer polarization resistance $(R_{\rm CT})$ decreased as $L_{\rm TPB}$ increased and polarization due to dissociative decreased adsorption $(R_{\rm DA})$ as S_V increased. Excellent power law fits were obtained for both microstructural polarization relationships (Fig. 2).

These, first ever reported, direct relationships between microstructure and electrochemical performance of "real" porous cathode structures can now be used for the development of cathode degradation models. More detail on these experiments can be found in the reference material.⁹

The relationship between cell impedance and microstructure can be extended to analyze cathode degradation in the presence of contaminants. To quantify the effects of degradation on microstructure and composition symmetrical button cells (cathode/electrolyte/cathode) have been fabricated. Electrolyte supports are created using tape casting methods and cathode materials are subsequently screen-printed onto the sintered electrolyte supports in a symmetric fashion, such as that shown in Fig. 3. These cells are then tested in a button cell reactor that has the ability to feed gases to both sides of the cell, much the same as a typical fuel cell test setup. The control side (counter electrode) of the cell is exposed to synthetic air, while the opposite side of the cell, the working electrode, is subjected to air plus a contaminant (H₂O or CO₂ or a combination). Electrochemical impedance spectroscopy (EIS) is used to measure cell impedance as a function of gas composition, temperature, and time. The impedance is then de-convoluted into the various contributions to the overall cathode degradation. By using a symmetric cell, we can subtract out the polarization effects due to thermal cycling and time, and look only at the effects of contaminants present in the gas stream.

Determination of Fundamental Cathode Degradation Mechanisms

The application of heterogeneous catalysis techniques to test the kinetics of our cathode powders is the next step in understanding degradation due to gas contaminants. We have shown previously that experiments such as Temperature Programmed Desorption (TPD), Temperature Programmed Exchange (TPX) and others, are quite useful in determining the mechanistic steps comprising the ORR.¹¹⁻¹⁵ These previous investigations indicate that SOFC cathodes operate with a two step ORR mechanism:

1. Dissociative Adsorption $O_2(g) + 2S \stackrel{k_1}{\underset{k_2}{\longleftrightarrow}} 2O_{ads}$ 2. Incorporation $O_{ads} + V_o \stackrel{k_2}{\underset{k_2}{\longleftrightarrow}} O_o + S$

Where O_{ads} is a surface adsorbed oxygen (blue), O_o a lattice oxygen in the surface layer (green), V_o a surface oxygen vacancy (empty), and S a surface site. This is shown schematically below, where the incorporation step (2 vs. 2') is influenced by the different cations (orange vs. black).



Figure 4. Two step ORR mechanism.

Due to the high catalytic activity of perovskites, contaminants such as CO_2 and H_2O that are present in the system can interact with cathode surface. To look at how these contaminants interact with the cathode surface at different temperatures, we use TPX. In TPX, isotopically labeled oxygen ($^{18}O_2$) is flowed over cathode powders during a temperature ramp while the effluent gas is analyzed with a mass spectrometer. Details and schematics of the experimental setup were given previously.¹⁴⁻¹⁵ Samples were normalized by surface area to 0.1 m² for direct comparison. The benefit of testing a powder is that the sample thickness is the particle

size (~80-300 nm for this study), which is much smaller than characteristic thickness (L_c), allowing for kinetic measurement in a surface exchange controlled regime. Each sample was placed in the center of a continuous flow quartz reactor and heated from 50°C to 800°C at a constant ramp rate of 30°C/min. A flow rate of 20 SCCM was established and the sample was heated under different concentrations of ¹⁸O₂ balanced with He. The rise and fall of different mass/charge (m/z) signals of oxygen species and contaminant species 18 (H₂¹⁶O), 20 (H₂¹⁸O), 32 (¹⁶O₂), 34 (¹⁶O¹⁸O), 36 (¹⁸O₂), 44 (C¹⁶O₂), 46 (C¹⁶O¹⁸O), and 48 (C¹⁸O₂) are monitored using the quadrupole mass spectrometer. From these profiles, the rate of ¹⁸O exchange with the lattice ¹⁶O or contaminants as a function of temperature was determined. We can then trace the movement of ¹⁸O to directly probe the interaction of contaminants in the ORR at different temperatures. Therefore, the influence of H₂O and CO₂ on ORR can be observed from the presence of ¹⁸O in the effluent gas molecules (H₂¹⁸O, C¹⁸O₂, C¹⁶O¹⁸O).

An example of TPX of LSM with and without the presence of 0.3% H₂O is shown in Figure 5(a) and (b). The formation of ¹⁶O¹⁸O begins at 300°C, revealing that oxygen molecules are dissociated on the LSM surface at this temperature. At 400°C ¹⁸O atoms on the surface begin to exchange with the oxygen in H₂O. However, as the temperature increases, the exchange of ¹⁸O₂ gas with LSM surface oxygen becomes dominant. The difference between TPX with and without H₂O is shown in Figure 5 (c). The

consumption of $^{18}O^{18}O$ and formation of $^{16}O^{18}O$ between 400-700°C indicates the dominance of H₂O in surface exchange.



Figure 5: Oxygen(a)(b) and water(d) signals from TPX of LSM without $H_2O(a)$ and in 0.3% $H_2O(b)$. The difference(c) of the oxygen signals show an increase of ${}^{16}O{}^{18}O$ (red) and a decrease of ${}^{18}O{}^{18}O$ (blue).

To probe the interaction between contaminants and lattice oxygen at different temperatures, a technique called Isotope Saturated Temperature Programmed Exchange (ISTPX) was developed (Figure 6). Contaminant gases are introduced into a reactor that contains a powder sample that was previously saturated with ¹⁸O. These contaminant gases then exchange with the isotopically labeled oxygen on the powder surface, creating isotopically labeled contaminant gases. Different surface exchange mechanisms dominate in different temperature regions.



Figure 6. Schematic of Isotope Saturated Temperature Programmed Exchange (ISTPX). ${}^{16}O_2$ and contaminants gas are introduced to the cathode powder (LSM or LSCF), whose surface was saturated with ${}^{18}O$. By tracing the exchange of labeled ${}^{18}O$ to different gases at different temperatures we can determine the dominant surface reaction mechanisms.

Figure 7(a) shows ISTPX of LSCF while flowing CO₂. Interestingly, the ¹⁶O in CO₂ starts to exchange with lattice ¹⁸O below 100°C. When the temperature is lower than 350°C, a single exchange of one oxygen in CO₂ with one lattice oxygen (C¹⁶O¹⁸O) dominates and has a peak near 250°C. When the temperature is higher than 350 °C, the double exchange of oxygen in CO₂ with lattice oxygen dominates and forms C¹⁸O₂. Almost all of the CO₂ participates in the surface exchange reaction. Figure 2(b) shows the exchange of 3000ppm H₂O with lattice ¹⁸O. The oxygen in H₂O begins to exchange with lattice ¹⁸O at 350°C, and almost all H₂¹⁶O is converted to H₂¹⁸O at 700°C.



Figure 7. ISTPX of LSCF with (a) 1250ppm CO₂ and (b) 3000ppm H₂O.

Figure 8 summarizes the results of TPX and ISTPX. The temperature ranges where ¹⁸O-isotope-exchange reaction rates of H₂O and CO₂ with LSM and LSCF powders are the highest and the lowest at PO_2 =0.025 atm. are plotted. Figure 8(a) shows the temperature ranges in which the various gases dominate surface exchange on LSM. It is shown that H₂O surface exchange dominates from 400-600°C, while at higher temperature, above 600°C, the exchange between O₂ and the LSM surface dominates. Also, it can be seen that CO₂ starts to exchange with lattice oxygen at 100°C and dominates surface exchange from 100-350°C. The mechanism of CO₂ exchange with LSM surface switches from single exchange of one oxygen of CO₂ to double exchange of both oxygen of CO₂ at around 200°C. At high temperature, the exchange of O₂ and CO₂, on LSM surface happens in parallel. Figure 8(b) shows how these same gases exchange with the surface of LSCF powder.



Figure 8. Diagram of Temperature Range of Reaction Dominations (a) LSM and (b) LSCF at $PO_2=0.025$ atm.

ISTPX of LSM and LSCF with fixed CO₂ concentration (2500ppm) in different oxygen partial pressure are shown in Figures 9. This technique allows the oxygen partial pressure to range up to 20% (without saturating mass spec signal) in order to account for "real world" operating conditions. LSCF, which is a mixed ionic and electronic conducting material, exhibited higher overall exchange activity than LSM, which is known as an electronic conducting material. Compared to LSM CO₂ and O₂ exchange with LSCF lattice ¹⁸O at lower temperatures. O₂ and CO₂ demonstrate characteristics of competitive adsorption/desorption. CO₂ exchange dominates in low *P*O₂ for both LSM and LSCF. For LSM, as the concentration of oxygen increases, we can see that CO₂ surface exchange is suppressed, as shown in Figure 9 (a) and (b). The oxygen partial pressure dependence of CO₂ surface exchange on LSCF is displayed in Figure 9 (c) and (d). For LSCF the surface exchange of CO₂ at higher *P*O₂ is not suppressed, as it is for LSM powder.



Figure 9. ISTPX of LSM (a)(b)(e)(f) at PO_2 = (a)(e) 2.5%, (b)(f) 20% and ISTPX of LSCF (c)(d)(g)(h) at PO_2 = (c)(g) 2.5%, (d)(h) 20% with 2500 ppm CO₂. Where oxygen and carbon dioxide related signals are in the left and right columns, respectively.

Conclusions

We have demonstrated all of the necessary techniques to de-convolute SOFC cathode degradation and are linking the effects of contaminant degradation to the fundamental ORR mechanism rates and rate constants. The competitive adsorption/desorption process between O_2 , CO_2 and H_2O on cathode surfaces is observed, as well as the dominance of each gas at different temperatures and concentrations. The kinetic results point the way to elucidate the degradation mechanisms. Ultimately we will be able to integrate these results and rationally design stable low polarization cathodes.

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