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MICROENGINEERED CATHODE INTERFACE STUDIES

by

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## **Microengineered Cathode Interface Studies**

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### **OBJECTIVES**

The overpotential at the cathode/electrolyte interface has been recognized as an important limitation on the performance of solid oxide fuel cells (SOFCs). This project is an effort to gain a scientific understanding of which interface features and conditions contribute to cathode polarization in SOFCs.

### **BACKGROUND INFORMATION**

The Westinghouse tubular SOFC program has identified the cathode overpotential as an important limitation on SOFC performance. The source of this overpotential has been debated extensively in the literature, and a number of reactions have been proposed to be rate-limiting [1,2]. The site of the proposed limiting reaction will determine which characteristics of the cathode/electrolyte interface need to be improved.

It is generally agreed that the total length of the air/electrode/electrolyte triple interface should be maximized, but that the cathode reaction is not necessarily limited to this triple interface. Mixed conductivity in either the electrode or electrolyte near the interface could allow reactions to take place on the surface of the mixed conducting material. In these cases, the degree of mixed conductivity or the surface properties of either material could determine the reaction rate. Thus, in addition to the geometry of the triple interface, properties of the materials that may be rate limiting include the electronic conductivity of the electrolyte, the ionic conductivity of the cathode, and the catalytic properties of the surfaces.

Significant electronic conductivity in the zirconia electrolyte could arise in several ways. Cations from the cathode are expected to diffuse into zirconia to some extent during normal fuel cell fabrication, possibly increasing the electronic conductivity. Dopants can also be introduced intentionally at the electrolyte surface. While such intentional doping has improved cathode performance, it is unclear whether this improvement is due to electronic conductivity or to some other effect, such as chemical stabilization of the interface [3,4].

Cathode materials vary widely in their ionic conductivity, and when mixed-conducting materials are used the performance is usually superior. It is thus likely that the cathode reaction takes place on the electrode surface. However, good performance is also seen when strontium-doped lanthanum manganite (LSM), normally a poor ionic conductor, is used. An important factor may be the changes created in the oxygen content of the cathode material when current is flowing;

ionic conductivity in the cathode is undoubtedly a function of potential in the cathode near the interface.

Extension of the reaction area away from the triple interface by the mixed-conduction mechanisms discussed above is probably necessary to some extent for good cathode performance. However, the more important characteristic may in fact be the geometry of the electrode near the interface. Even if the reaction can occur over a large surface area, performance is still dependent on transport of the reactants and electrons through the porous electrode. The density and tortuosity of the sintered cathode particles, as well as the interfacial area with the electrolyte, may be the factors most in need of optimization to improve cathode performance. Recent research by many groups has shown that cathode/electrolyte interface characteristics such as the pore structure and cathode density at the interface must be carefully controlled to reduce the cathode overpotential [2,5].

### PROJECT DESCRIPTION

Our approach has been to fabricate and test highly controlled interface structures that are designed to affect the three possible rate-limiting factors in the cathode reaction discussed above. The electrochemical performance of these interfaces has been correlated with the observed microstructure.

Commercially available 300- $\mu\text{m}$  thick zirconia wafers were used as substrates for these tests, for the sake of reproducibility. The only designed variability in the electrolyte is in the immediate vicinity of the cathode, as discussed below.

The electronic conductivity of the electrolyte has been altered by using ion implantation to dope the surface with manganese. Ion implantation adds a controlled amount of dopant directly into the bulk zirconia in a thin layer near the surface. Manganese is implanted uniformly over a 1  $\text{cm}^2$  sample area using a 50-60 keV machine, which results in a peak concentration of dopant about 0.1  $\mu\text{m}$  below the electrolyte surface. Saturation typically is reached at about 10 wt % dopant after a few minutes. Ion-implanted electrolytes are then used as substrates for porous cathode deposition.

The role of ionic conductivity in the electrode has been examined primarily through the study of dense  $\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_3$  layers. When nonporous electrodes are used, the triple interface is effectively eliminated, and the cathode reaction must take place at the cathode surface, with oxygen ion transport taking place through the cathode. There exist significant experimental difficulties in performing such tests. The presence of any porosity or incomplete coverage of the electrolyte (including edge effects) adds triple-interface areas that may render the oxygen ion transport unimportant. We have looked at films formed by a number of methods.

The density and tortuosity of the sintered cathode particles, as well as the interfacial area with the electrolyte, have been controlled primarily through densification of the cathode in reducing conditions. Cathodic current conditioning has been shown to create significant microstructural changes, and this method has been used to demonstrate the importance of the cathode geometry near the interface.

We have also examined the role of the cathode surface area by fabricating a porous zirconia "electrolyte" layer on a dense cathode substrate; oxygen has access to the interface through the porous zirconia in single-atmosphere testing, allowing the normal cathode reaction to take place, but in this case the surface area of the zirconia is much greater than that of the cathode.

The microengineered interfaces were characterized in single-atmosphere electrochemical testing at 700-900°C. Platinum counter electrodes with a much larger area than the cathode and were fabricated in the same way for each test. Platinum current collectors were used on each electrode; in some cases, the current collector consisted of a single platinum wire tip held against the electrode. AC impedance spectroscopy was performed at open circuit as well as superimposed on DC cathodic currents. Polarization curves were also taken. Steady applied cathodic voltages were used to study changes caused by conditioning of the electrode structures. Microstructural examination using scanning electron microscopy (SEM) and X-ray analysis was performed on samples before and after conditioning.

## RESULTS

### Electronic Conductivity in the Electrolyte

Ion implantation was successfully used to dope zirconia substrates with 4-6% manganese. Porous LSM cathodes were slurry-coated on the doped surface. Results from both impedance spectroscopy and polarization testing indicate that the doping failed to significantly change the cathode polarization. Both doped and undoped electrolytes gave similar improvements in performance with cathodic potential conditioning (as discussed below). The unchanged behavior of the electrodes with doping indicates that electronic conduction within the electrolyte, if it is involved in the cathode reaction, is adequately provided by manganese diffusion from standard cathode fabrication methods.

Significant changes in the distribution of manganese were observed after the electrochemical testing. Diffusion away from the interface causes the manganese-implanted areas of the electrolyte to lose most of the dopant after 48 hours at 800°C. Examination of the fracture surfaces of cathodes that had been broken away from the electrolyte after testing revealed a difference when implanted electrolytes were used: undoped electrolytes typically caused a small percentage of the cathode surface to be low in manganese, possibly indicating the presence of lanthanum zirconates. However, when manganese-doped electrolytes were used, the cathode fracture surfaces tended to have uniform Mn contents. Cathodes on the doped substrates also tended to have lower wetting/adhesion to the electrolytes (they were easier to separate after testing). Thus, the absence of a reaction layer is suggested for doped electrolytes (although no corresponding change in electrochemical behavior was observed).

### Ionic Conductivity in the Cathode

Our study of dense blocking cathode layers has shown poor ionic conductivity in thick layers and inconclusive results in thinner layers. We have prepared thick, dense LSM layers by uniaxially pressing 200- $\mu$ m-thick LSM pellets, firing to near full density, and joining these to

electrolyte substrates with a thin, slurry-coated LSM layer. Glass sealing material is then used to insure that the edges of the dense cathodes do not permit air exchange. This process should insure that ionic conduction through the cathode is necessary for steady-state current flow. We found resistances of  $200 \Omega\text{-cm}^2$  when testing such samples with a steady-state cathodic current. Thin-film deposition methods may be more appropriate for these tests, as reduction of a thin, dense cathode layer may improve ionic conductivity, and our attention is currently focused there. We used a nitrate deposition method for producing thin dense LSM layers but were not able to obtain sufficiently dense films. When these films were sintered in reducing atmosphere, the density greatly improved, but we have not yet been able to get a completely defect-free film. Electrochemical testing on these films shows that these cathodes have good performance, but it is unclear whether this performance reflects ionic conductivity or is instead dependent on the small amount of porosity that is still present.

### **Cathode Geometry Near the Interface**

Our results indicate that the density of the LSM cathodes near the electrolyte interface plays an important role in determining the cathode overpotential. Large improvements in cathode performance with conditioning treatments correlated well with observed densification of the microstructure at the interface during these treatments.

Testing of porous LSM cathodes with platinum wire-tip contacts clearly showed that the cathode performance improves dramatically with cathodic potential conditioning. The cathode polarization at  $800^\circ\text{C}$  drops from an initial value of  $2.8 \Omega\text{-cm}^2$  to less than  $0.03 \Omega\text{-cm}^2$  after a conditioning period of 60 h at 750 mV. This improvement is more dramatic than the effects seen on cathodes with larger area and may be partially due an increase in the effective electrode area due to diffusion. More typical cathode performance improvements with large-area cathodes were  $0.9 \Omega\text{-cm}^2$  to  $0.68 \Omega\text{-cm}^2$  after conditioning. The most dramatic improvements were found when previously unsintered porous cathodes were conditioned; in this case, cathode resistances decreased from  $100 \Omega\text{-cm}^2$  to  $6 \Omega\text{-cm}^2$  after conditioning. From these results, the improvement during conditioning appears related to a sintering effect.

Clear microstructural changes in the cathode were found to accompany the cathodic potential conditioning. In post-test SEM analysis, a local sintering effect was observed near the current collector contact points, but it was unclear to what extent the current was concentrated in these regions. Wire-tip contact experiments were then used to provide a well-defined current flow through a given region of the electrode. For such samples, an obvious sintering effect was seen that extended outward from the contact to form a sintered disc with a diameter of  $30\text{--}40 \mu\text{m}$ ; outside this area the porous structure of the LSM appears unchanged. The examined contact had been conditioned at 750 mV for 60 hours, which led to a peak current density of  $1.8 \text{ A/cm}^2$ .

We studied the sintering behavior of LSM in reducing atmosphere to check whether the reducing potential could be the cause of the local densification. We found that densification of slurry-coated LSM powders at  $1100^\circ\text{C}$  significantly increased when 6% hydrogen (balance helium) atmosphere was used as opposed to sintering in air. The reducing atmosphere resulted in a 85% dense structure, compared with a 60% dense structure after the same heat treatment in air. With this information, it appears likely that the reducing potential during conditioning is

responsible for the microstructural evolution seen in our cathodes. Enhanced cation transport in reducing conditions is also indicated by results from the low-surface-area cathode samples (discussed below).

The remaining porosity in the cathode has a slightly different structure for the two types of reduction-aided sintering, with what would appear to be a more optimized structure for cathodic-potential-conditioned layers. Such conditioned cathodes tend to consist of a dense layer sintered intimately onto the electrolyte, with very little porosity near the electrolyte interface. The cathodes sintered in reducing atmosphere, on the other hand, had enhanced densification primarily in the part of the electrode layer furthest away from the electrolyte, with some porosity remaining near the electrolyte interface. Thus, cathodic conditioning may be necessary to provide the optimum structure, with a high cathode/electrolyte interfacial area and direct current paths through the cathode structure.

### **Cathode Surface Area**

The low-surface-area cathode sample (created by applying a porous electrolyte onto a dense LSM pellet) gave slightly higher cathode polarization than normal samples ( $1.38 \Omega\text{-cm}^2$ ). The porous electrolyte used in this test also resulted in transport of manganese oxide from the cathode into the electrolyte during cathodic potential conditioning, presumably in the vapor phase. This observation further supports the view that cation mobility in the cathode is enhanced during cathodic polarization.

The fact that the performance of this interface before polarization suffered only slightly as a result of the low cathode surface area indicates that (1) reactions on the cathode surface are not wholly responsible for performance limitations, and (2) increased electrolyte surface area may be electrochemically active, especially with mobile manganese oxide deposited on the electrolyte particles.

### **FUTURE WORK**

Continuing research at Argonne will focus on novel processing techniques that lead to highly controlled cathode/electrolyte interfaces, as well as the study of multilayered cathode structures. Different spatial arrangements of thin, dense layers of cathode materials will be used to study the effects of geometry on cathode electrochemical performance. A range of cathode materials including good ionic conductors and poor ionic conductors, as well as different thicknesses of the dense cathode films, will be used to determine the role of ionic conductivity in the spatial expansion of the cathode reaction. Ion implantation will also be used to study the effect of changes in the surface composition for both the electrolyte and the cathode surface; atoms with redox chemistry will be implanted in these surfaces.

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