MICRO-ENGINEERED CATHODE INTERFACE STUDIES

by

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MICRO-ENGINEERED CATHODE INTERFACE STUDIES

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INTRODUCTION

The aim of this work is to increase the performance of the cathode in solid oxide fuel cells (SOFCs) operating at 1000°C by decreasing the polarization resistance from 0.2 Ω-cm^2 at 300 mA/cm^2. Decreased polarization resistance will allow operation at higher current densities. This work is in support of the Westinghouse tubular SOFC technology using YSZ electrolyte and strontium doped lanthanum manganite (LSM) cathode.

THE PROBLEM

As a result of work performed last year at Argonne National Laboratory and information derived from the literature, the limitations at the cathode/electrolyte interface can be classified into two main areas. First, the ionic conductivity of the LSM cathode material is low which limits the reaction zone to an area very close to the interface, while the rest of the cathode thickness acts essentially as current collector with channels for gas access. Second, the electronic conductivity in YSZ is very low which limits the reaction zone to areas that are the boundaries between LSM and YSZ rather than the YSZ surface away from LSM at the interface.

APPROACH

Possible solutions to this problem being pursued are: 1) introducing an ionic conducting YSZ phase in LSM to form a porous two-phase mixture of LSM and YSZ; 2) applying a thin interlayer between the electrolyte and the cathode where the interlayer has high ionic and electronic conductivity and high catalytic activity for reduction of O_2; 3) increasing the ionic conductivity in the LSM by suitable doping; and 4) increasing the electronic conductivity in the electrolyte by doping or by depositing an appropriate mixed conducting layer on the YSZ before applying the cathode.

PROCEDURE

We obtained YSZ electrolyte discs of 200 μm from Marketech International. The appropriate microstructure of the electrode to be studied was then created on top of the YSZ

membrane so as to form the working electrode. A reference electrode was also made the same way on the same side of the disk as the working electrode but separated from the working electrode by about 5 mm. Similarly, a counter electrode and another reference electrode were deposited on the other side of the YSZ disc. The experimental arrangement is shown in Fig. 1.
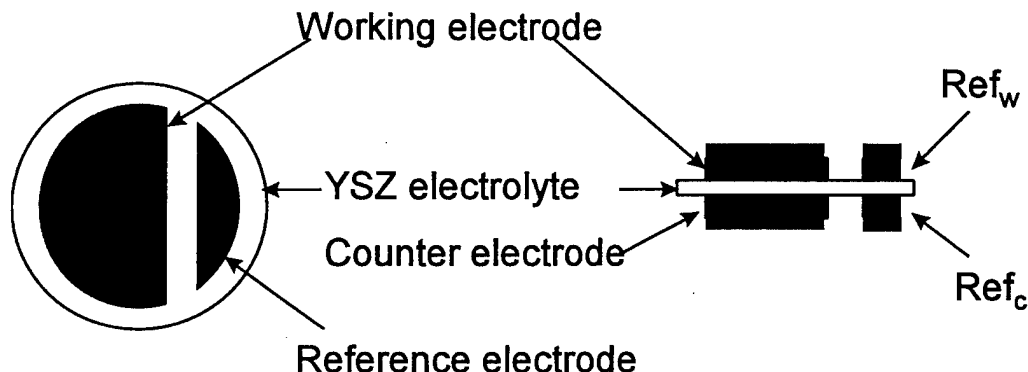

Fig. 1. Electrode setup for polarization tests.

Polarization resistance of each electrode was measured against the corresponding reference electrode using impedance spectroscopy. Overpotential measurements were performed as a function of current density using a galvanostat, and the potential of the working and counter electrodes were measured against each other and against the corresponding reference electrodes.

RESULTS

The effect of low ionic conductivity in LSM on the cathode polarization resistance (R_c) is evident from Fig. 2, which shows a dense LSM disc bonded to a YSZ disc with a thin layer of LSM applied between the two. These edges were sealed as shown with a glass-plus cement seal so that gas access to any LSM/YSZ interface is blocked off. In this way, all the oxygen from the air is forced to diffuse through the dense LSM. The R_c from impedance spectroscopy in such a case was high, 11 kΩ-cm^2. A cathode with high oxide ion conductivity should decrease the polarization resistance.

dense $La_{0.9}Sr_{0.1}MnO_3$ (~200μm)
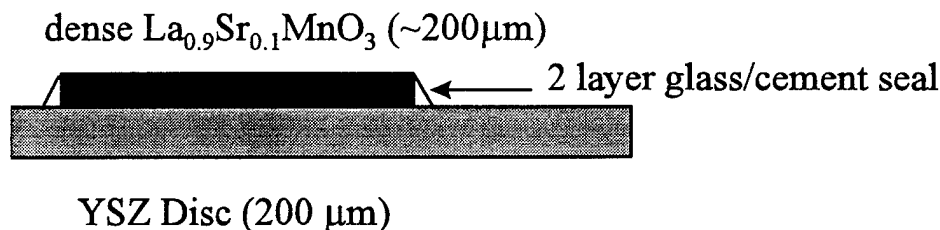

2 layer glass/cement seal

YSZ Disc (200 μm)

Fig. 2. Configuration of dense LSM on YSZ with sealed edges.

In another experiment a YSZ disc was ion implanted with manganese ions to 0.1 μm below the surface. Upon heating up to 900°C, the polarization resistance was found to be low, 0.38 Ω-cm^2. Over time, this value increased as manganese ions diffused away from the surface of the YSZ into the bulk. However, it showed that increasing the ionic conductivity of YSZ at the surface helps to spread out the reaction zone and decreases polarization.

Based on the above two observations, compositions were devised to increase the ionic conductivity of the cathode by doping an LSM composition with Co and by increasing the substitution of La by Sr. New materials like the cobalt-ferrite composition were also tried. The aim here is to either replace the LSM cathode or use the new materials as a thin interlayer between LSM and YSZ.

A cobalt-doped LSM composition, $(La_{0.6}Sr_{0.4})_{0.9}Mn_{0.95}Co_{0.05}O_3$ (designated LSCM-2) sintered at 1300°C and tested last month showed good performance (R_c around 0.1 Ω-cm^2) as a cathode on YSZ with no load. This was presumably due to increased ionic conductivity from the cobalt doping. Further testing at different loads (current densities) showed good performance as well. Figure 3 is a plot of overpotential versus current density after holding the sample at a 1000°C for a cumulative 48 hours with two temperature cycles where it was cooled to room temperature and heated back up to 1000°C. The overpotential at 300 mA/cm^2 was 39 mV, compared with a typical 60 mV overpotential for Westinghouse's cathode at the same current density.

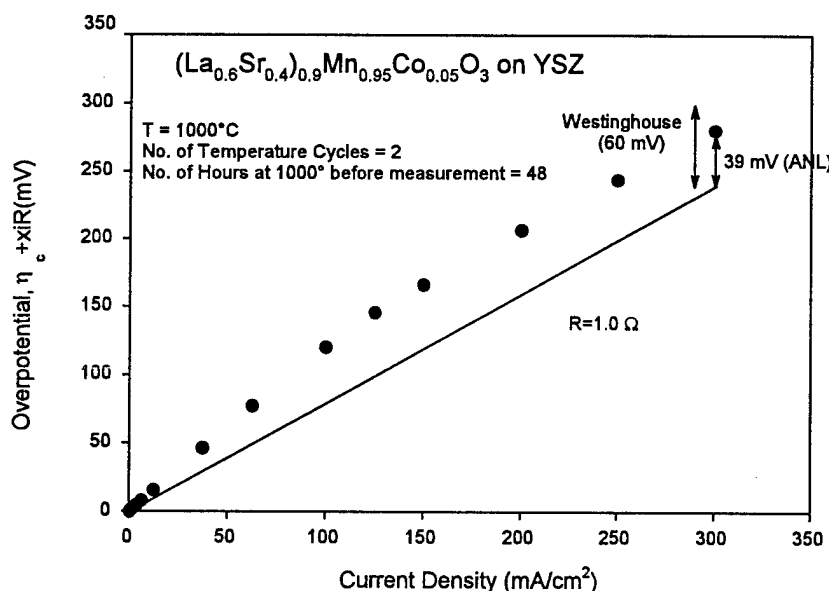**Fig. 3. Overpotential of LSCM-2 decreases with increasing I.**

Another cobalt-doped composition, $(La_{0.85}Sr_{0.15})_{0.9}Mn_{0.98}Co_{0.02}O_3$ (LSCM-1), was tested both with sintering at 1300°C and sintered in situ at the operating temperature of 1000°C, (see Fig. 4). The sintered composition exhibited a higher R_c of about 0.34 Ω-cm^2, while the in situ sintered sample had an initial R_c of 0.03 Ω-cm^2 without any load. This compares very well to a value of 0.2 Ω-cm^2 for Westinghouse's cathode at 300 mA/cm^2. The in situ composition started

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sintering with time at 1000°C, which caused an increase of the R_c from an initial value of 0.03 Ω-cm^2 to 0.1 Ω-cm^2 after 67 hr. Sintering this composition caused a decrease in the actual area of contact between YSZ and LSCM while increasing the area of contact between LSCM particles. This indicated that cobalt-doped LSM (LSCM) shows promise as an interlayer if it is made with a large contact area between LSCM and YSZ that does not decrease with time under operating conditions.
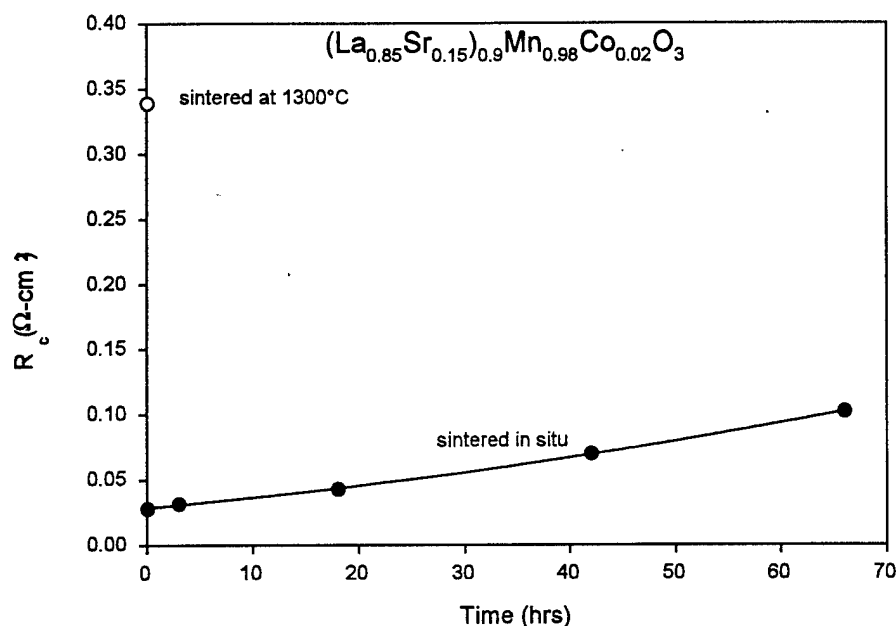

Fig. 4. LSCM-1 shows good performance initially when sintered in situ.

It has been reported in the literature that manganites of praseodymium (PrMnO$_3$) showed higher performance than LaMnO$_3$. To utilize this fact, we synthesized praseodymium counterparts of LSCM-1 and LSCM-2, by the Pechini method, (Pr$_{0.85}$Sr$_{0.15}$)$_{0.9}$Mn$_{0.98}$Co$_{0.02}$O$_3$ (PSCM-1) and (Pr$_{0.6}$Sr$_{0.4}$)$_{0.9}$Mn$_{0.95}$Co$_{0.05}$O$_3$ (PSCM-2). It is expected that the cobalt-doping in PSM also increases ionic conductivity.

Figure 5 gives the performance of PSCM-1 for one electrode sintered at 1300°C and another in situ. In this case the 1300°C sintered composition exhibited better performance than the one sintered in situ, and both cathodes showed a deterioration in performance with time at 1000°C. The PSCM-2 also showed the same trend, but with a much steeper increase in R_c with time. Since both compositions show the same trend, the deterioration is probably due to change in cathode composition with time, possibly by Co or Mn diffusion from PSCM to YSZ.
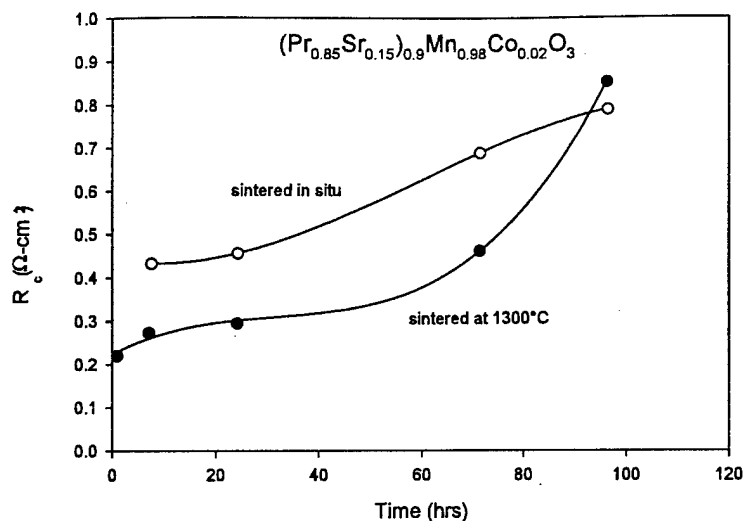
Fig. 5. R_c for PSCM-1 sharply increases with time after 40 hrs.

High ionic and electronic conductivity is well known in $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF) and similar cobaltite or cobalt-ferrite compositions. We previously reported data on some LSCF compositions where the LSCF composition was slightly deficient on the A-site, $(La_{0.6}Sr_{0.4})_{0.99}Co_{0.2}Fe_{0.8}O_3$. While this yielded very low R values of 0.02 Ω-cm^2 or even less initially, the formation of an insulating $CoFe_2O_4$ caused the R_c to increase to almost 10 Ω-cm^2 in less than three days. This time we report results on stoichiometric LSCF with the composition $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$. The polarization resistance, R_c, for this LSCF still increases with time, (see Fig. 6), but at a slower rate than before. The ohmic resistance component through the electrolyte plus cathode, if any, also rises. This indicates that the increase in R_c is accompanied by an increase in resistance. The rate of increase in resistance indicates the formation of an insulating phase. Both $La_2Zr_2O_7$ and $SrZrO_3$ have been reported to form when LSCF electrode is used on a YSZ electrolyte at 1000°C.
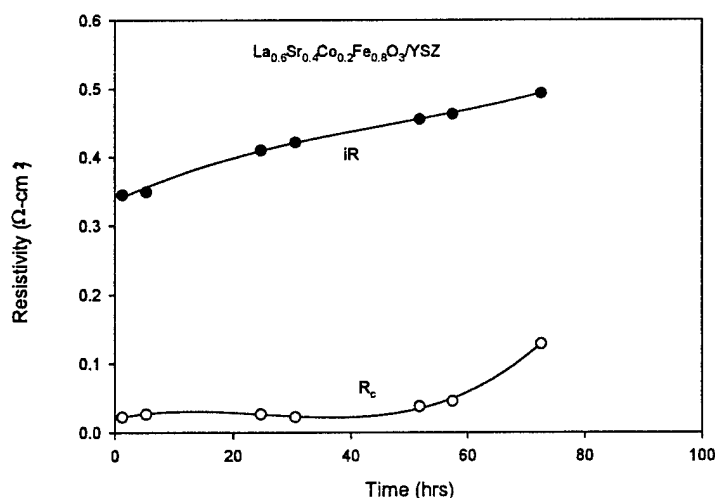

Fig. 6. Both the R_c and the resistance part of iR drop increase with time for LSCF.

5.

In order to decrease the interaction between YSZ and LSCF, an attempt was made to deposit a thin (< 1 μm) dense layer of $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ on YSZ, followed by the deposition of LSCF on top of the ceria layer. The ceria layer made by us turned out to be porous. Nevertheless, two such electrodes were tested with the following configurations: stoichiometric LSCF/porous CG1/YSZ and LSCM-2/porous CG1/YSZ.

Results of cathode tests of both configurations are shown in Fig. 7. The LSCF cathode showed a higher initial R_c (0.2 Ω-cm^2) than the previously tested LSCF/YSZ configurations and also showed an increase in R_c to 0.33 Ω-cm^2 over 115 hr. However, the plot shows that the R $_c$value stabilized and, after 115 hr, is less than the LSCF/YSZ polarization resistance of 1 Ω-cm^2 after 63 hr. Therefore, a ceria interlayer did prevent significant reaction between LSCF and YSZ. Similarly, for the LSCM-2 cathode with ceria interlayer, the value of $_c$ was initially 0.47 Ω-cm^2, which actually decreased and stabilized at 0.44 Ω-cm^2 after 115 hr. The reason for a decrease in R_c for LSCM-2 versus an increase for LSCF is not known at this time; however, it may be linked to differences in thermal expansion coefficient between the cathode and the interlayer.
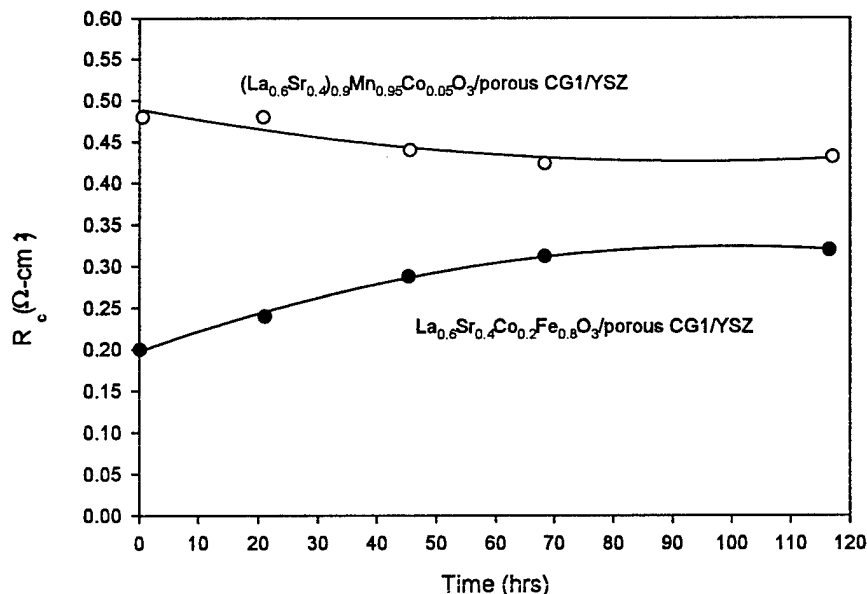
Fig. 7. Stable but higher polarization resistances obtained with an interlayer of porous ceria.

In order to improve the overall Rc value for LSCF/CG1/YSZ cathodes, a thin 0.5 μm dense CG1 film was deposited by Prof. Harlan Anderson at the University of Missouri-Rolla on a YSZ disc supplied by us. We then applied the LSCF cathode and tested the cell as a function of time. The results of this test (Fig. 8) show a low initial R_c of 0.024 Ω-cm^2 which then decreases slightly and monotonously to less than 0.018 Ω-cm^2 over 72 hrs. This electrode again is a combination of steps 3 and 4 as outlined earlier.
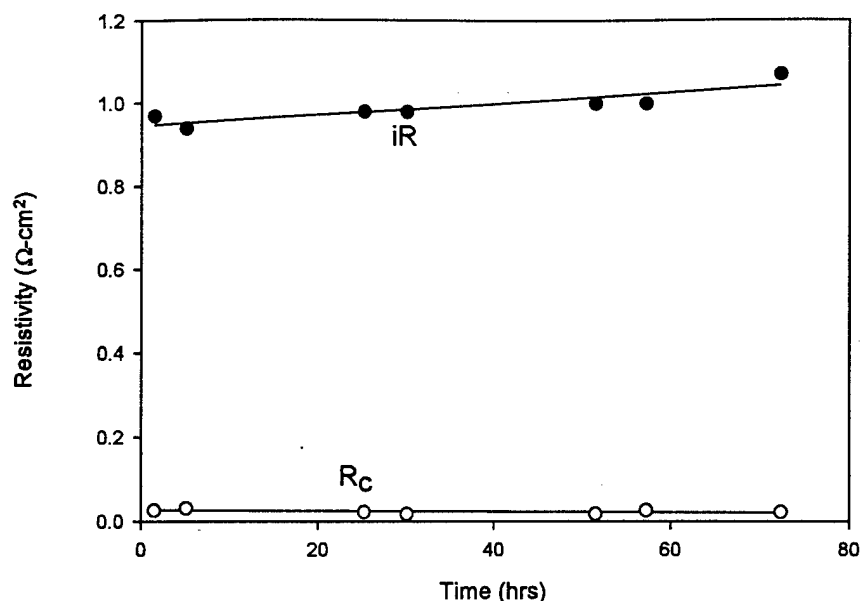
Fig. 8. Very low and stable R_c obtained with a thin dense interlayer of ceria.

We are also currently working on a composition that can be used directly as a cathode with no interlayers. The goal here is to increase the ionic conductivity without decreasing the electronic conductivity of LSM or its catalytic activity for oxygen reduction. In addition, the thermal expansion coefficient will be matched to the YSZ electrolyte and it will not be reactive with YSZ. Initial results show some promise with about a 112 mV polarization at 300 mA/cm^2. Further work is in progress to understand and improve this composition.

BENEFITS

Increased cathode performance or decreased cathode polarization resistance will help to operate at higher power density or with higher efficiency.

FUTURE WORK

1) Development of new compositions that can be used as cathodes without interlayers. These materials will be analyzed for performance over time and as a function of compositional changes. The aim here is to increase ionic conductivity substantially compared to LSM.

2) Continued development of Co or other transition metal-doped LSM. We will select a promising material and develop a cathode with an interlayer microstructure of a two-phase mixture of YSZ and doped LSM. It will be analyzed in terms of performance over time and its thermal expansion coefficient will be measured.

3) Analysis of previously tested cathode/electrolyte and cathode/interlayer/electrolyte samples. These samples will be analyzed for microstructural characteristics including porosity, interface bonding, and interdiffusion of cations across the interface.

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