

CONF-961107--4
ANL/CMT/CP--89672

CHARACTERIZATION OF CERIA-BASED SOFCs

RECEIVED
APR 14 1997
OSTI

Rajiv Doshi,¹ Jules Roubort,² and Michael Krumpelt¹
¹Electrochemical Technology Program
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439

MASTER

The submitted manuscript has been authored by a contractor of the U. S. Government under contract No. W-31-109-ENG-38. Accordingly, the U. S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U. S. Government purposes.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

ph

Poster to be presented at the 1996 Fuel Cell Seminar to be held on November 17-20, 1996, Kissimmee, Florida.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

CHARACTERIZATION OF CERIA-BASED SOFCs

Rajiv Doshi¹, Jules Routbort², & Michael Krumpelt¹

¹Electrochemical Technology Program
Chemical Technology Division
²Energy Technology Division

Argonne National Laboratory
9700 S. Cass Avenue, Argonne, IL-60439

Solid Oxide Fuel Cells (SOFCs) operating at low temperatures (500-700°C) offer many advantages over the conventional zirconia-based fuel cells operating at higher temperatures. Reduced operating temperatures result in:

- Application of metallic interconnects with reduced oxidation problems
- Reduced time for start-up and lower energy consumption to reach operating temperatures
- Increased thermal cycle ability for the cell structure due to lower thermal stresses of expansion mismatches

While this type of fuel cell may be applied to stationary applications, mobile applications require the ability for rapid start-up and frequent thermal cycling.

Ceria-based fuel cells are currently being developed in the U.K. at Imperial College[1], Netherlands at ECN[2], and U.S.A. at Ceramatec[3]. The cells in each case are made from a doped ceria electrolyte and a $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_3$ cathode.

Electrolyte Properties

A reduced operating temperature requires using either of a very thin form (about 1 μm) of the conventional zirconia electrolyte or a different electrolyte with higher conductivity is. Using a 1- μm -thick electrolyte poses problems in fabrication and in integrity during cycling and operation. A cerium oxide electrolyte doped with a rare earth like gadolinium exhibits higher ionic conductivity in air than the zirconia (fig. 1).

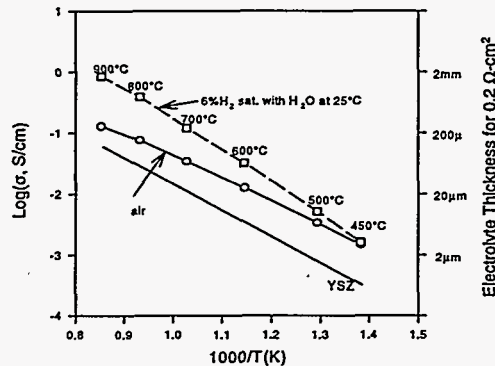


Fig. 1 Conductivity of electrolyte in air and H₂. Required thickness for 0.2 $\Omega\text{-cm}^2$ shown on right.

Unlike zirconia however, ceria exhibits significant electronic conductivity above 500°C in the fuel atmosphere because of the reduction of cerium oxide. The fraction of the Ce^{4+} ions reduced to Ce^{3+} as a function of temperature and oxygen partial pressure ($p\text{O}_2$) is shown in fig. 2. The partial reduction of cerium oxide generates mobile electrons and causes electronic conductivity in the

electrolyte at temperatures above 500°C. Below this temperature the electrolyte remains ionic and can be used as an electrolyte in a solid oxide fuel cell.

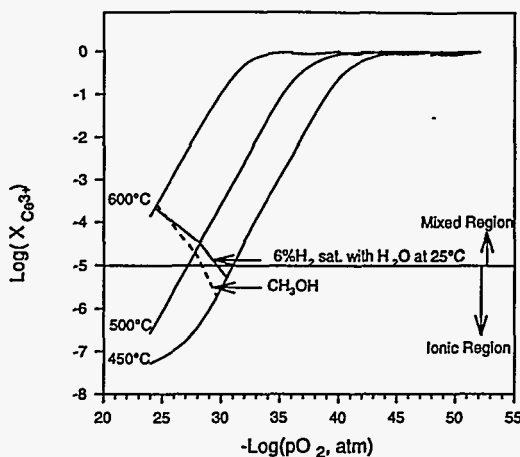


Fig. 2 Fraction of Ce⁴⁺ ions reduced to Ce³⁺ as a function of temperature and pO₂

Electronic conductivity in the electrolyte is evident from the measured values of the open circuit voltage (OCV) when compared to the Nernst potential as shown in the following table.

<u>Temperature (°C)</u>	<u>Theoretical OCV, mV</u>	<u>Measured OCV, mV</u>
500	1054	995
600	1025	941
700	997	869

Electrochemical Characterization

Figure 3 plots the performance from 500 to 700°C of a cell with the following configuration:

La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O₃ (LSCF) / Ce_{0.8}Gd_{0.2}O_{1.9} Electrolyte / Ni-Ce_{0.8}Gd_{0.2}O_{1.9}

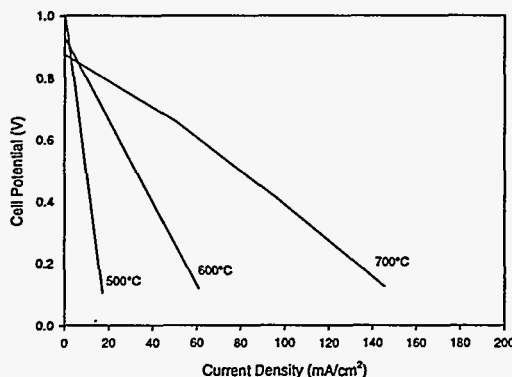


Fig. 3 Cell performance with a 1.2 mm thick electrolyte, LSCF cathode and Ni-cermet anode

It shows that the performance of the cell at 500°C is inadequate. We found that the majority of the voltage losses apart from the electrolyte resistance were at the cathode electrolyte interface. Figure 4 shows the proportion of the voltage loss from the cathode compared to the anode. The electrolyte loss can be reduced by using 10- and 20-µm-thick electrolytes as shown on the right

side of fig. 1. Cathode performance improvement requires either new microstructures or new materials that are more active while being compatible with the electrolyte.

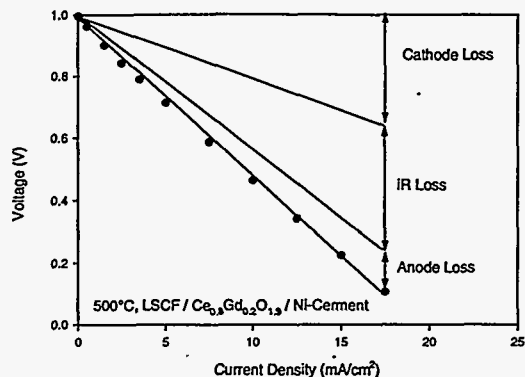


Fig. 4 Voltage losses in the fuel cell showing the large magnitude of the cathode loss

Cathode Properties

The interface resistances of several cathode materials measured by impedance spectroscopy using reference electrodes are shown in fig. 5. Single phase porous cathodes ($\text{La}_{0.6}\text{Sr}_{0.4}\text{Mn}_{0.8}\text{Co}_{0.2}\text{O}_{3.5}$ and LSCF) performed better for materials with an increasing ability to lose oxygen from its lattice when compared to the $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3.5}$ (not shown in figure) cathode used with zirconia-based fuel cells. This presumably stems from an increased ionic conductivity or diffusion while still maintaining electronic conductivity high enough for a cathode.

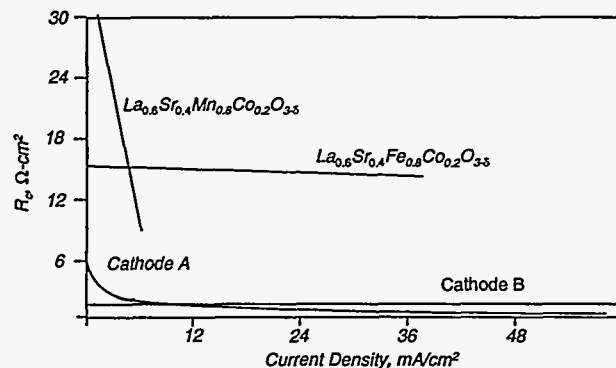


Fig. 5 Interface resistance of cathode electrolyte interface for different cathodes

This hypothesis is supported by the diffusion coefficients of some cathode materials measured on dense samples by isotope (O^{18}) exchange and SIMS which are given in figure 6.

Two phase cathodes performed better still as shown by cathodes A and B in fig. 5. In addition cathode A has the ability to lose oxygen more easily than all other cathodes. This caused an increase in performance with increasing current density.

While the ability of the cathode material to lose oxygen increases the electrode performance for the materials considered, it is also known that this can cause an expansion mismatch with other fuel cell components. It is desirable then to work with materials that exhibit a constant performance at

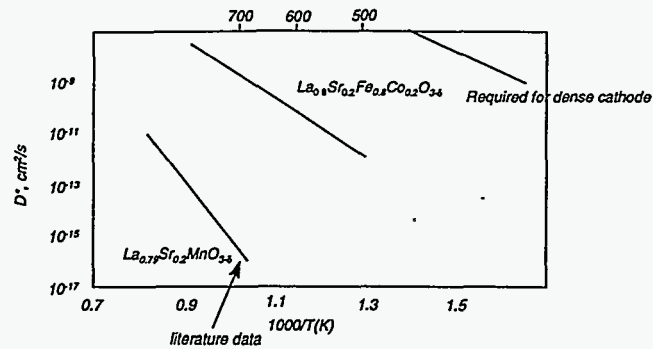


Fig. 6 Oxygen self-diffusion for selected cathode materials

different current densities. Cathode B is such a material with good performance ($2.4 \Omega\text{-cm}^2$ at 500°C) however some improvement is still required to achieve values of less than $1 \Omega\text{-cm}^2$.

The performance of a cell with cathode A is shown in figure 7. The OCV was considerably lower owing to significant porosity when the electrolyte was thinner ($200 \mu\text{m}$). The thinner electrolyte had a reduced resistance, which raised overall performance. Also shown in the figure is a calculated performance curve for a dense electrolyte with negligible thickness.

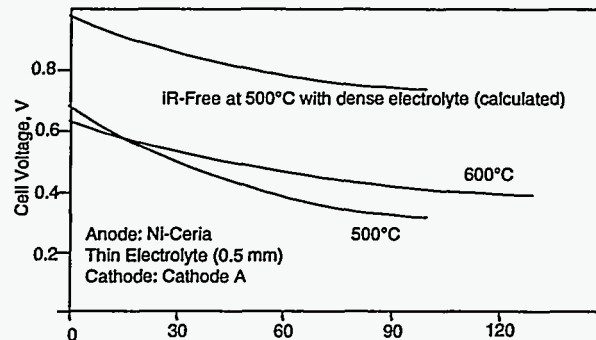


Fig. 7 Cell performance with cathode A. Measured OCV lower due to interconnected porosity.

Cathode performance is also being increased by using improved microstructures. Steele[4] has recently been demonstrated that a thin $1\text{-}\mu\text{m}$ LSCF layer between the electrolyte and a coarser porous thick LSCF electrode exhibited only $0.4 \Omega\text{-cm}^2$ interface resistance.

Conclusions

Cathode performance is being improved by using better materials and/or microstructures. Fabrication of thin dense electrolytes is also necessary to achieve high cell performances.

Acknowledgements

This work is supported by the OTT-DOE under Contract No.W-31-109-ENG-38.

References

- [1] M. Sahibzada et al., Proc. of 2nd European SOFC Forum, Oslo, Norway, May 1996, p687-696
- [2] B.C.H. Steele et al., Proc. of the Fuel Cell Seminar, San Diego, CA, Nov. 1994, p479-482
- [3] C. Milliken et al., EPRI/GRI Fuel Cell Workshop, Tempe, AZ, Apr. 2-3, 1996
- [4] B.C.H. Steele, private communication, July 1996.