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CATHODES FOR CERIA-BASED FUEL CELLS

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by

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ABSTRACT

Work is underway to develop a solid oxide fuel cell that has a ceria-based electrolyte and operates at lower temperatures (500-600°C) than conventional zirconia-based cells. At present the performance of this ceria-based solid oxide fuel cell is limited by the polarization of conventional cathode materials. The performance of alternative cathodes was measured by impedance spectroscopy and dc polarization. The performance was found to improve by using a thin dense interface layer and by using two-phase cathodes with an electrolyte and an electronic phase. The cathode performance was also found to increase with increasing ionic conductivity for single phase cathodes.

INTRODUCTION

Solid oxide fuel cells (SOFCs) operating at lower temperatures (500-600°C) than conventional zirconia-based systems (800-1000°C) offer several advantages. At these operating temperatures, transportation applications can be considered along with small systems for backup generators for the home. At present, however, the cost of the interconnect material (strontium or calcium doped lanthanum chromite) and its fabrication is a major factor in the high total cost of fuel cell systems. Therefore, the other major advantage of lower temperature operation is that metallic interconnects made from the much cheaper commercially available stainless steels would be feasible.

The conductivity of the doped ceria electrolyte, $Ce_{1-x}Gd_xO_{2-\delta}$ (CGO) was presented earlier [1]. It was also shown that the electrolyte exhibits ionic behavior in the fuel atmosphere at temperatures below 500°C [1]. Initial fuel cell tests were conducted with a nickel-ceria anode and a $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF) cathode in a four-electrode arrangement. Two reference electrodes were used to assess the voltage losses of each component of the fuel cell. It was immediately evident that the two major losses were the iR drop across the 1.1 mm thick electrolyte and polarization across the cathode. While the iR drop can be minimized by decreasing the electrolyte thickness, the cathode polarization needs to be minimized by developing improved cathode materials or altering the morphology of the cathode microstructure.

The reduction in operation temperature increases the cathode polarization with nearly the same activation energy as a decrease in the ionic conductivity of the electrolyte. This is because the oxygen ion conductivity of the cathode becomes very important for achieving high performance at the cathode. As a result, materials with a low or negligible oxygen ion conductivity only work as two-phase materials with an electrolyte phase mixed in. The standard cathode material for high-temperature SOFCs, lanthanum manganite (LSM), has been reported to perform quite well even at temperatures of about 700°C when it is employed as a two-phase mixture with the zirconia electrolyte as the second phase [2]. To reduce this temperature further, new materials with higher oxygen ion conductivity and high activity for the oxygen reduction reaction at the cathode are required. One such material, LSCF, has been studied and reported by Anderson [3] and Steele [4]. In addition to LSCF, there are other compositions, like the pure cobaltite $La_{0.6}Sr_{0.4}CoO_3$ (LSC), which have the requisite properties but could not be used with zirconia based fuel cells owing to their high reactivity with zirconia at high temperatures and their much higher thermal expansion coefficients than any of the currently used electrolytes. This article presents the impedance and polarization measurements of ceria-based electrolyte with variuos alternative cathodes in a four-electrode arrangement.

EXPERIMENTAL

Electrolyte discs of about 2.5 cm diameter were made from commercial $Ce_{0.9}Gd_{0.1}O_{1.95}$ powder manufactured by Rhone-Poulenc. The powder was pressed and sintered at 1450°C for 1 h to form a thick, dense electrolyte. The LSCF cathode powder was made by the Pechini [5] method and calcined at 800°C for 4 h. The other cathode powders were made by solid state synthesis, except for Cathode A, which was made by a coprecipitation method. The powders were analyzed and found to form the desired phase after three cycles of milling, pressing, and sintering for the solid-state synthesized powders and a single-step calcination for the other powders.

The electrode powders were applied by screen printing the electrolyte disc with two electrodes on each side, a working and a reference electrode. The four electrode arrangement allowed the measurement of the polarization of each electrode separately. Electrode characteristics were measured using a dc polarization method with a PAR 273 galvanostat and ac impedance spectroscopy with an impedance analyzer across the working and reference electrodes.

RESULTS & DISCUSSION

The performance of the ceria-based SOFC can be increased by three routes: (1) improving the single-phase cathode material properties such as ionic and electronic conductivities and the catalytic activity for oxygen reduction, (2) using a two-phase material, where each phase is used to improve one or more of the desired electrochemical properties, and then optimizing the distribution of each phase, and (3) improving the morphological structure of the cathode/electrolyte interface and the cathode itself. Here we report results on all of the above cathode types.

Single Phase Cathodes

The overpotential results of four electrode experiments at 500°C are given in Fig. 1 along with the results for the conventional cathode (LSM + YSZ) at 1000°C. The polarization on a cathode of single-phase $La_{0.9}Sr_{0.1}MnO_3$ (LSM) is extremely high at 500°C owing to a low oxide ion diffusion coefficient (D*) compared to the CGO electrolyte as shown in Fig. 2. Some of the other materials with a higher D*, like LSCF (Fig. 2) showed improved performance in the form of lower overpotential (Fig. 1) at 500°C. The LSCF and related materials such as LSC have the ability to lose oxygen easier than LSM with decreasing oxygen partial pressure. This causes the polarization resistance of the electrode to decrease with increasing current density, as shown in Fig. 3 for LSCF and for cathode A (proprietary composition). An example of another such material is $Pr_{0.5}Gd_{0.1}Sr_{0.4}Mn_{0.8}Co_{0.2}O_3$ (PGSMC) also shown in Fig. 3. The polarization resistance measured by impedance spectroscopy for PGSMC decreased from more than 100 Ω-cm^2 to about 7 Ω-cm^2 under load. Cathode A is a new cathode material that has the ability to lose oxygen easier than LSCF, and its polarization resistance decreased from 6 Ω-cm^2 at open circuit to 0.6 Ω-cm^2 under a load of 30 mA/cm^2 at 500°C. While the low polarization resistance under load looks very promising, such a large change in polarization resistance is accompanied by a large change in oxygen stoichiometry. Iin turn, this causes a large change in thermal expansion, which is detrimental for long-term cathode performance.

Two-Phase Cathodes

Cathode B, a two-phase cathode, gave both low cathode overpotential (Fig. 1) and low polarization. Unlike the single-phase cathode, the polarization resistance remained constant (at 1.78 Ω-cm^2) under load (Fig. 3). This is because the cathode material does not undergo significant changes in stoichiometry under load. This cathode material is the most promising material we have developed, and efforts are underway to improve it even further.

Interface Additions

Microscopic examination of cathode/electrolyte interfaces on cells using an LSCF cathode on a CGO electrolyte indicated that the actual area of contact at the interface was significantly less than the apparent area of the cathode. This is probably due to the high sinterability of the LSCF cathode and the higher thermal expansion of the LSCF (13.5-14.0 x 10^{-6} cm/cm/°C), causing shrinking, as compared to doped ceria (12.5-13.0 x 10^{-6} cm/cm/°C). Therefore attempts were made to first deposit a 0.25-0.5 μm thin film of high density (>70%) of the same material as the porous cathode structure on top. The improved area of contact for such a thin-film interface cathode, LSCF(TF), reducted the polarization resistance from 14 to 7 Ω-cm^2 (Fig. 3).

CONCLUSIONS

Cathode materials with improved performance have been developed for SOFC operation at 500°C with doped-ceria electrolytes. This improvement was accomplished with single-phase and two-phase cathodes and with morphologically tailored cathode microstructures. The increased performance resulted from improvements in the ionic and electronic conductivities of the cathode material and on the interface between the cathode and the electrolyte.

ACKNOWLEDGMENTS

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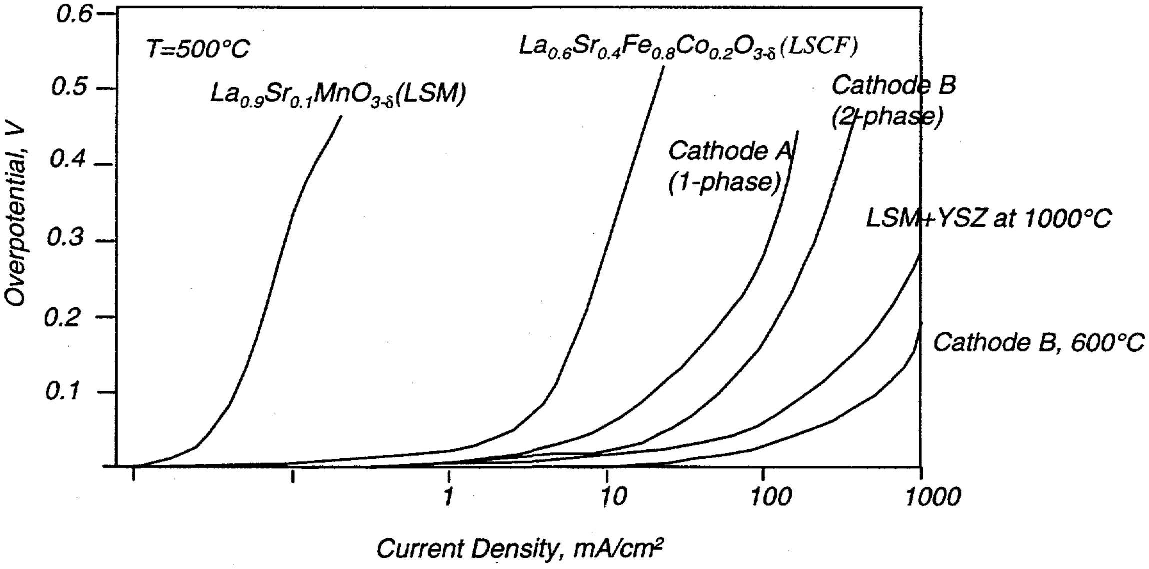

Fig.1. Overpotential of new cathode materials at 500°C compared with conventional cathodes.

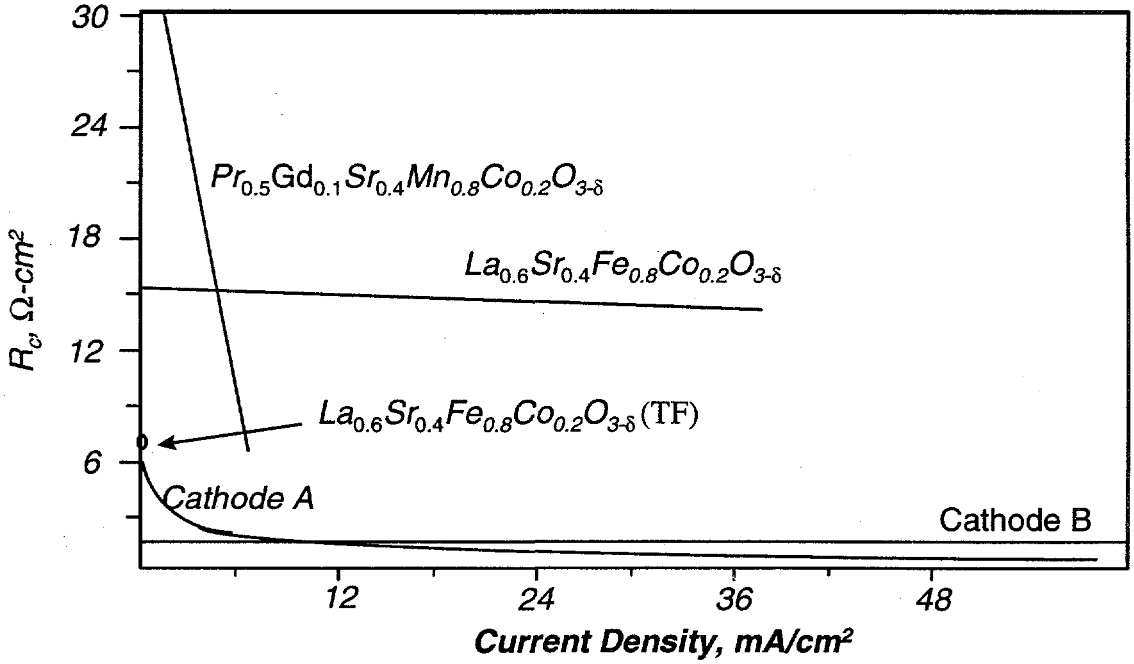

Fig. 2. Polarization resistance of cathode materials as a function of load.

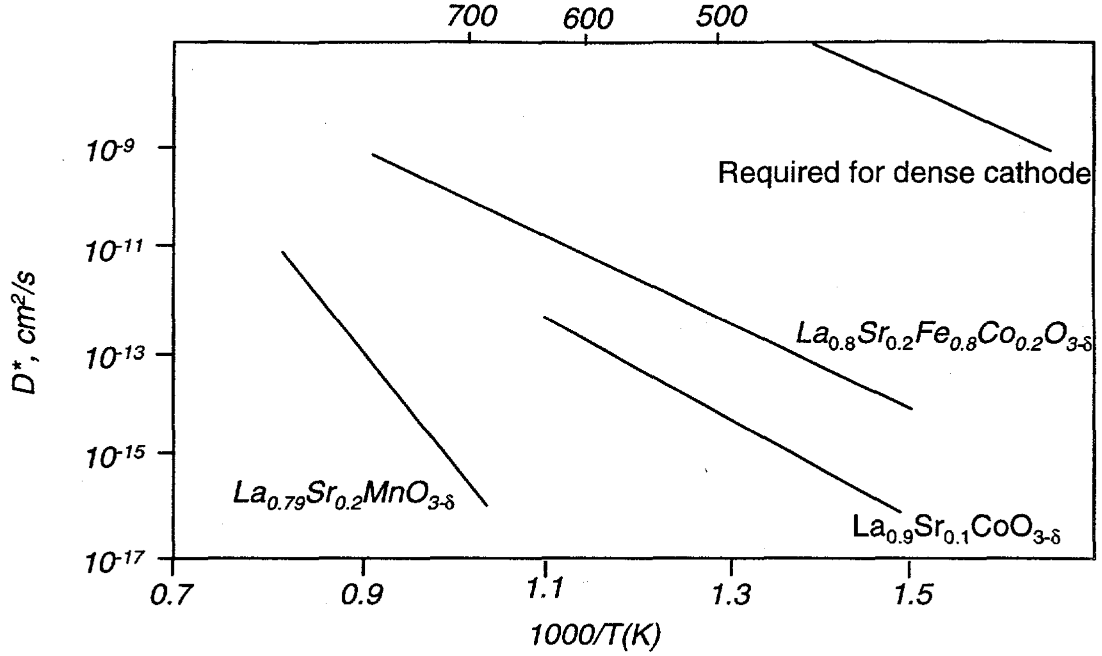

Fig.3. Oxide ion diffusion coefficients of cathode materials compared to that required for a dense cathode (equals that for electrolyte calculated from ionic conductivity).