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by

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Introduction

The advantages of lowering the operating temperature of solid oxide fuel cells have led to efforts to develop fuel cells based on electrolytes like ceria which have a higher conductivity than zirconia. Lowering the operating temperature, however, causes increased electrode polarization. The currently used cathode material for higher temperature operation, lanthanum manganite, is inadequate for operation below 650-700°C. Therefore, to develop fuel cells for operation at 500°C, new electrode materials need to be developed. It is recognized that the cathode performance requires the most improvement due to significantly slower oxygen reduction kinetics and/or oxygen diffusion kinetics through the electrode. In fact, for fuel cells made with thin electrolytes, the cathode accounts for up to 90% of the total voltage loss under load. Results on fuel cell tests in methanol and hydrogen and on new cathode materials are reported here. The results on new cathode materials are compared with known material properties, like nonstoichiometry and oxygen diffusion coefficients.

Electrolyte Properties

The conductivity of the ceria-based electrolyte $Ce_{0.8}Gd_{0.2}O_{1.95}$ in air and in hydrogen environments is shown in Fig. 1 [1]. The two curves converge to the same value at about 450°C. Above this, the electrolyte exhibits mixed conductivity in fuel cell anodic conditions. The initial fuel cell tests were conducted on a 1.3-mm-thick pressed electrolyte and gave a maximum open-circuit voltage (OCV) of 0.98 V at 500°C. Subsequent tests, conducted with a thinner (0.5-mm) electrolyte resulted in OCV values of about 0.84 V. This lower voltage is believed to be due to (1)increased oxygen flux resulting from mixed conductivity in the thinner electrolyte and (2) undesirable characteristics of the starting electrolyte powder used for fabricating the electrolyte. For the thinner electrolyte, the starting powder was milled in alcohol with additions of binder and dispersant and then dried. The firing schedule was, therefore, altered and is believed to be the cause of some interconnected porosity which contributed to the lower OCV.

Fuel Cell Tests

Tests were conducted with solid oxide fuel cells having pressed and sintered electrolyte discs with screen-printed electrodes. The fuel cells were made up of $Ce_{0.8}Gd_{0.2}O_{1.95}$ electrolyte, nickel-cermet anode, and the cathode material was varied. A reference electrode was used on each side of the electrolyte to perform four-electrode ac and dc measurements. The electrode arrangement is shown in fig. 2. The fuel cell testing apparatus was described earlier [2]. Figure 3 shows the performance of such a fuel cell using a nickel-cermet anode and a single phase porous Co-Fe-based cathode in H_2/air at different temperatures. The high polarization resistance at the cathode gave low performance at 500°C. Among the cell components, the cathode performance accounted for most of the voltage drop (about 90%). At higher temperatures the cathode performance improved, along with a reduction in iR drop, to give respectable overall cell performance even when the electrolyte thickness was as high as 480 µm.

Cathode Development

Three possible cathode structures are being considered, as shown in fig. 4. All the results presented here are for the porous single-phase cathode structure (fig. 4b) unless specified otherwise.

Among the lanthanum-based perovskites, the cobaltites ($La_{1-x}Sr_xCoO_{3-\delta}$) and cobalt ferrites ($La_{1-x}Sr_xCo_yFe_{1-y}O_{3-\delta}$) are known to be more active electrodes for oxygen reduction. It is believed that the well-known ability of the cobalt-containing perovskites to lose oxygen easily leads to better reaction kinetics, and the higher diffusion coefficients measured in the same materials allow more of the bulk electrode material to participate in the oxygen transport. While these materials are more reactive with zirconia than the manganites, leading to the formation of insulating phases, no such insulating phases are formed with ceria. Figure 5 shows the voltage losses from four-electrode dc polarization measurements of various perovskites at 500°C. For comparison, a typical polarization curve for an optimized two-phase (LSM+YSZ) cathode on YSZ at 1000°C is shown. The cathodes with Co, Co+Fe, or Co+Mn cations on the B site of the perovskites showed lower polarization losses than the manganite ($La_{0.9}Sr_{0.1}MnO_{3-\delta}$) at 500°C on ceria. Cathode C is a new experimental material with significant nonstoichiometry and the ability to lose oxygen quickly. This material showed significantly better performance than the other compositions at 500°C.

The polarization resistance of $AFe_{0.8}Co_{0.2}O_{3-\delta}$, $BMn_{0.8}Co_{0.2}O_{3-\delta}$, and cathode C was also measured by impedance spectroscopy, using the same four-electrode arrangement. In the case of $AFe_{0.8}Co_{0.2}O_{3-\delta}$, there is a very slow process at low frequencies which could not be resolved well, as a result, the data shown for this material are calculated from dc polarization results by using the measured iR drop from the complete cell. The results for all the tested cathode materials are shown in fig. 6 as a function of current density. Increasing polarization is equivalent to decreasing oxygen partial pressure (pO_2). In all cases, the resistance decreased with increasing current density. It is believed that this behavior is due to an increase in nonstoichiometry, δ. Cathode C exhibited the least resistance, about 0.6 Ω-cm^2, at the high current densities. For comparison the polarization resistance of an optimized LSM+YS cathode at 1000°C is shown.

While nonstoichiometry data are not available at 500°C due to the long equilibration times required, the change in δ as a function of cathode polarization (calculated from pO_2) is plotted in fig. 7 for 900°C. These data are taken from the literature. Both the cobaltite [8] and the ferrite [9] become significantly substoichiometric upon reaching a polarization value of above 100 mV. In contrast, the manganite [10] becomes stoichiometric quickly but then is stable in terms of δ until it is close to its decomposition voltage. While the ability of the cobalt and iron-containing perovskites to become substoichiometric may lead to higher performance, repeated cycling could cause stresses and cracking in the electrode. Therefore, the desired ideal electrode material will have a high and constant substoichiometry within the operating range of current densities or polarization (equivalent to change in pO_2 across the cathode).

Oxygen diffusion coefficient is another important property for an electrode material. Figure 8 gives the diffusion coefficients for some of the perovskite materials compared with values of the diffusion coefficient for lanthanum manganite from the literature [3]. Also included is the requirement for a dense electrode with a high activity for oxygen reduction on a ceria electrolyte. This curve was calculated from the ionic conductivity data reported earlier [1]. Lanthanum manganite shows very low oxygen diffusion coefficients compared to the cobalt and iron-containing perovskites. In comparison, the Co-Fe-containing perovskites exhibit more than seven orders of improvement over the manganite. These are still lower than the requirement for a dense cathode by about five orders of magnitude. Further improvements in diffusion coefficient are being made.

Encouraging fuel cell results were obtained with cathode C. Upon starting the cell and conditioning, the fuel cell performance is shown in fig. 9. Post-test examination revealed some penetration of the cathode material into the electrolyte through the interconnected porosity. We are working on improving the electrolyte processing to eliminate all porosity and on higher performance cathode materials to reduce the cathodic polarization.

In addition to the above considerations, the thermal expansion coefficients of the electrode material need to be better matched to those of ceria electrolyte (12.5-13 x 10^{-6} mm./mm./°C [4]) to maintain integrity through cycling from ambient to operating temperatures and through the processing temperature. In comparison to ceria, the thermal expansion of the manganites ranges from 11 to 12 x 10^{-6} mm./mm./°C, the cobaltites from 20 to 23 x 10^{-6} mm./mm./°C [5], and some of the cobalt ferrites from 14.5 to 15.5 x 10^{-6} mm./mm./°C [5,6,7]. Additions of the electrolyte secondary phase to the cathode should result in closer matching, as is the case with the anode in zirconia-based fuel cells.

Conclusions

The cathode accounts for the majority of the polarization loss between the cathode and anode. New cathode materials show promise in reducing this disparity. Materials with a high nonstoichiometry and high diffusion coefficient show better performance. Work is ongoing to develop cathode materials that meet these requirements and are stable throughout the operating range of pO_2 and current density.

Acknowledgments

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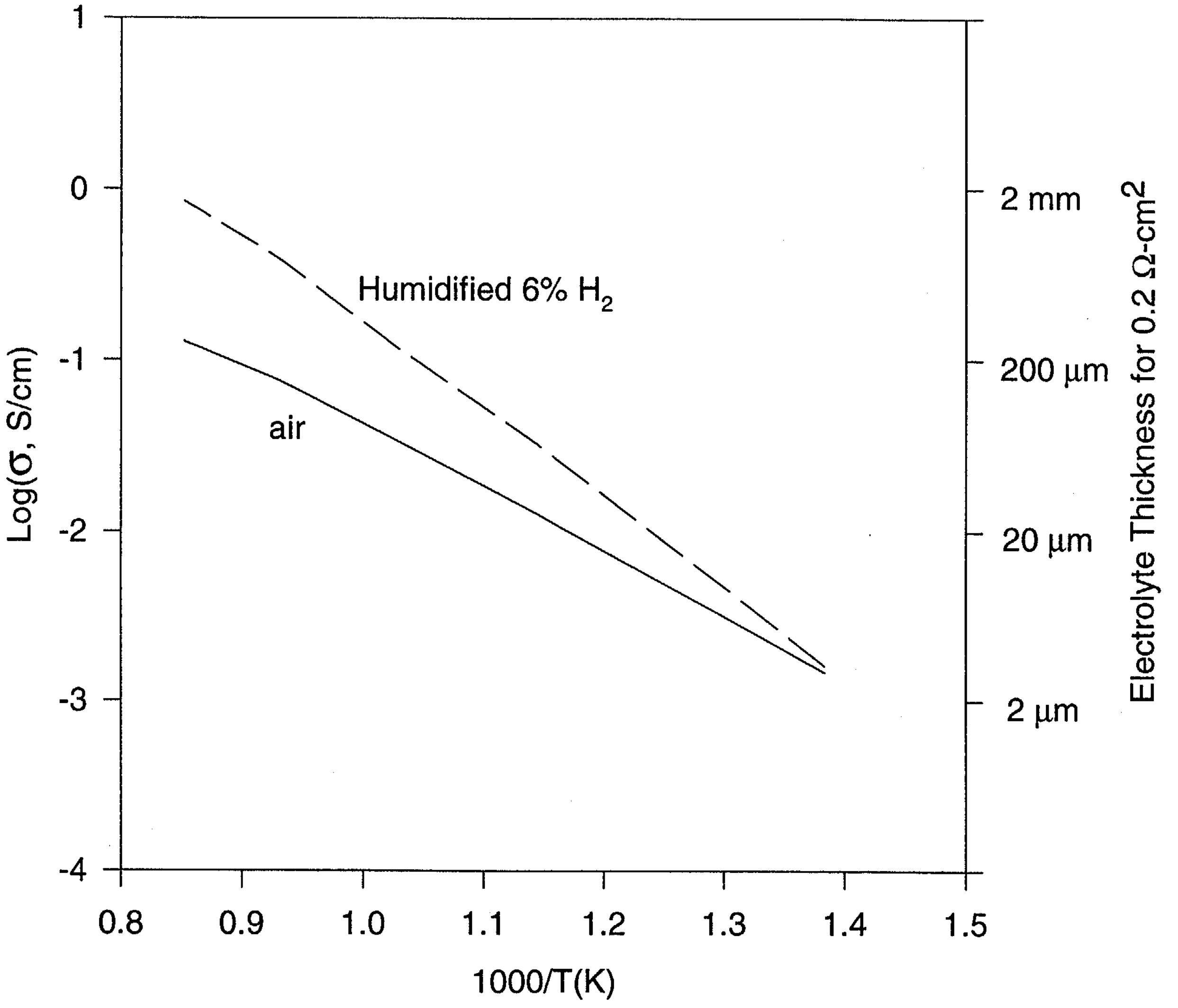

Fig. 1. Conductivity (σ) of ceria electrolyte from ref. [1]

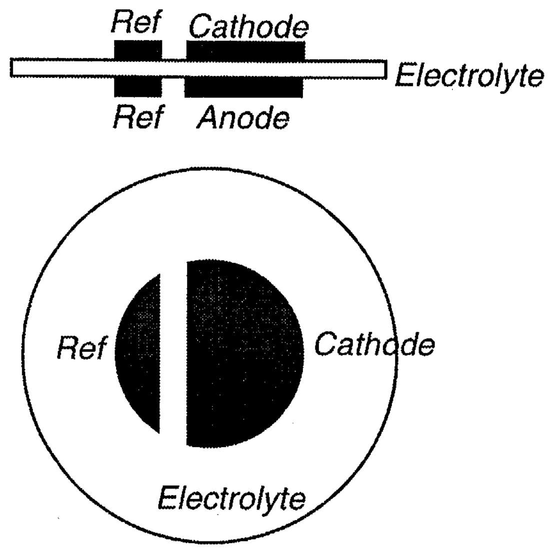

Fig. 2. Four-electrode arrangement for polarization measurements

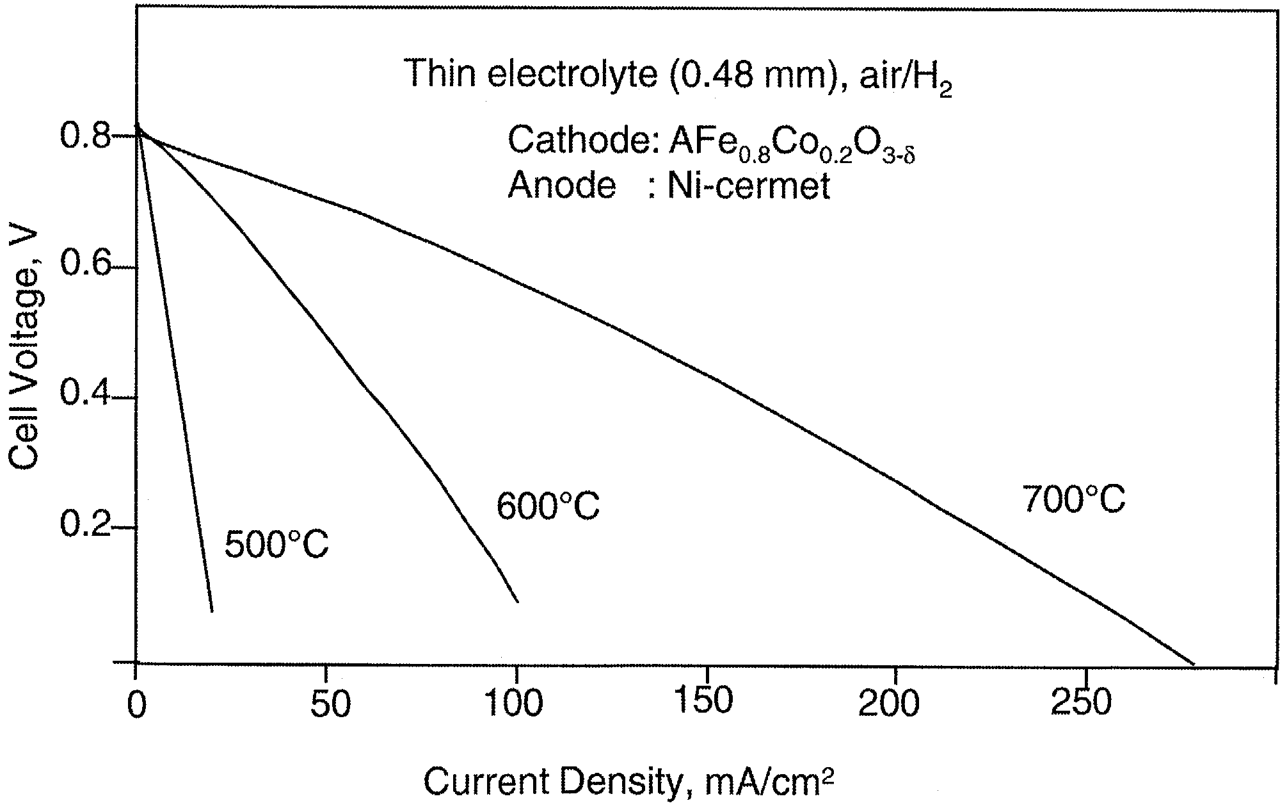

Fig. 3. Performance of a ceria fuel cell at different temperatures

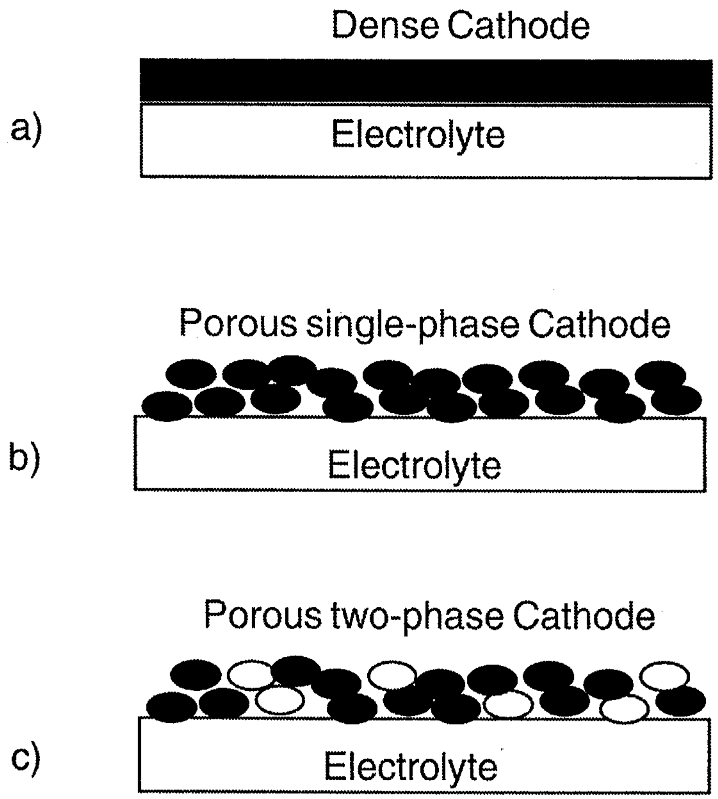

Fig. 4. Three possible cathode structures

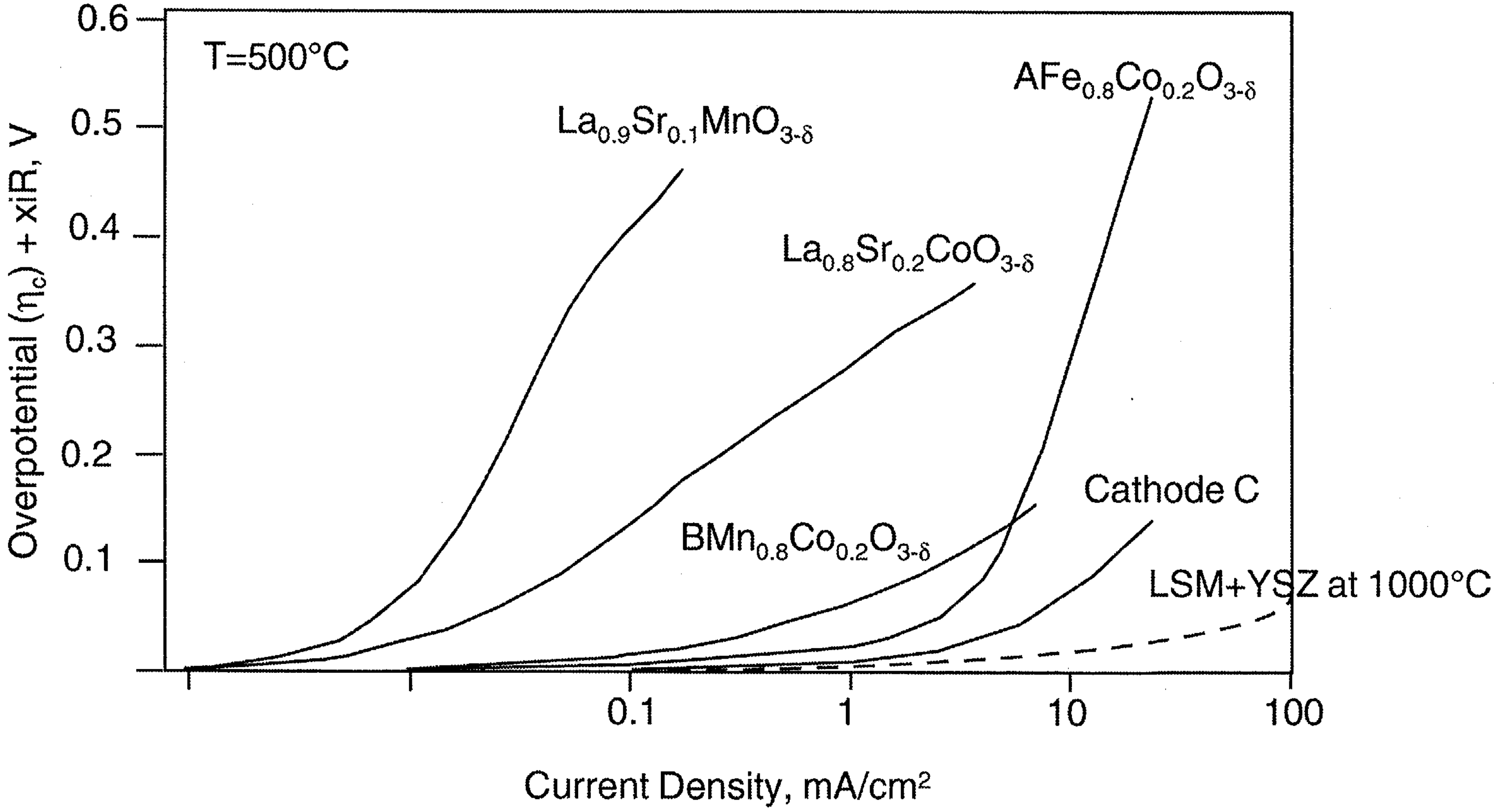

Fig. 5. dc polarization measurements for different cathode materials..
All measurements onc eria electrolyte except for LSM+YSZ on YSZ electrolyte

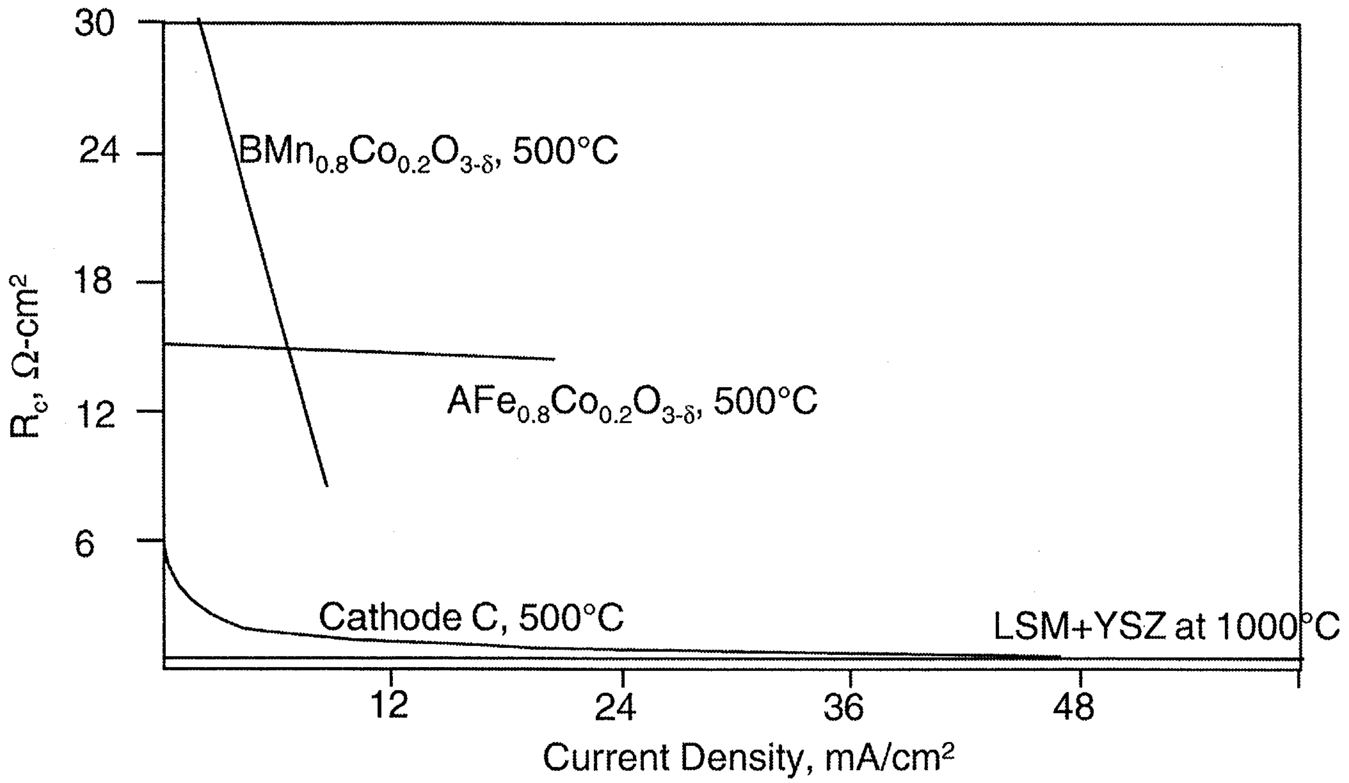

Fig. 6. ac impedance measurements except for various cathode materials (for $AFe_{0.8}Co_{0.2}O_{3-\delta}$ data calculated from dc measurements and iR drop)

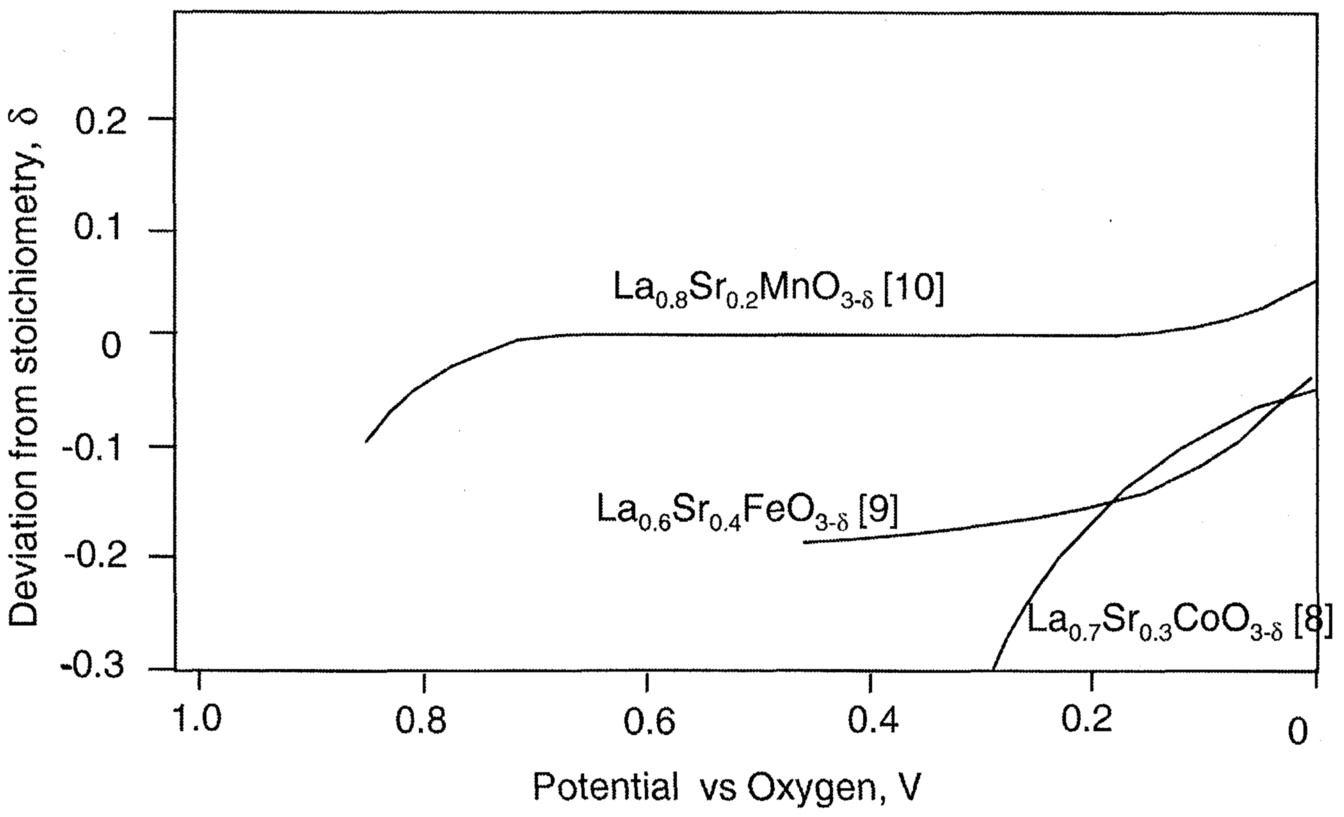

Fig. 7. Nonstoichiometry of some perovskites at 900°C from literature

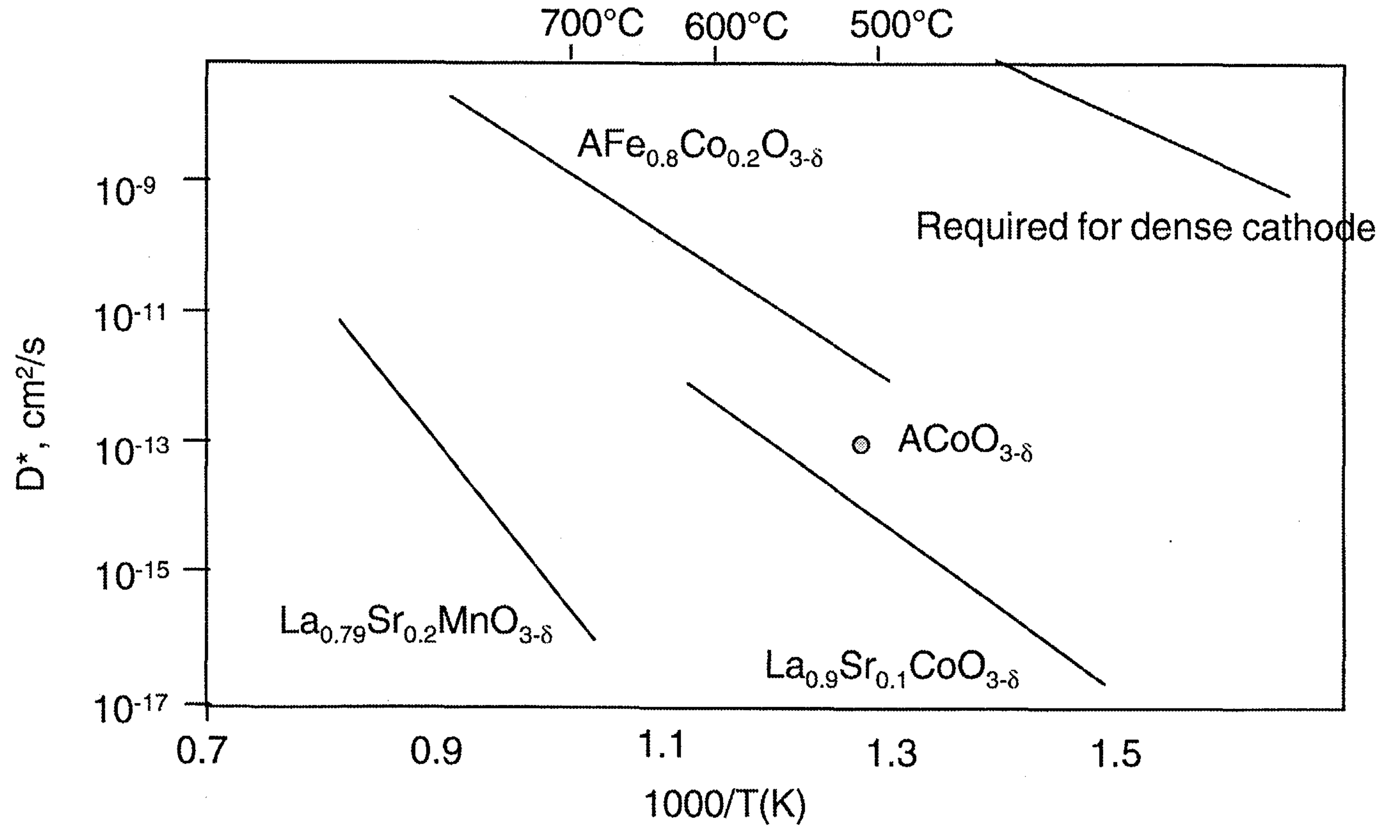

Fig. 8. Oxygen self-diffusion coefficients of some perovskites. Data on the manganite from ref. [3]. Values required for dense cathode calculated from ionic conductivity of ceria electrolyte [1].

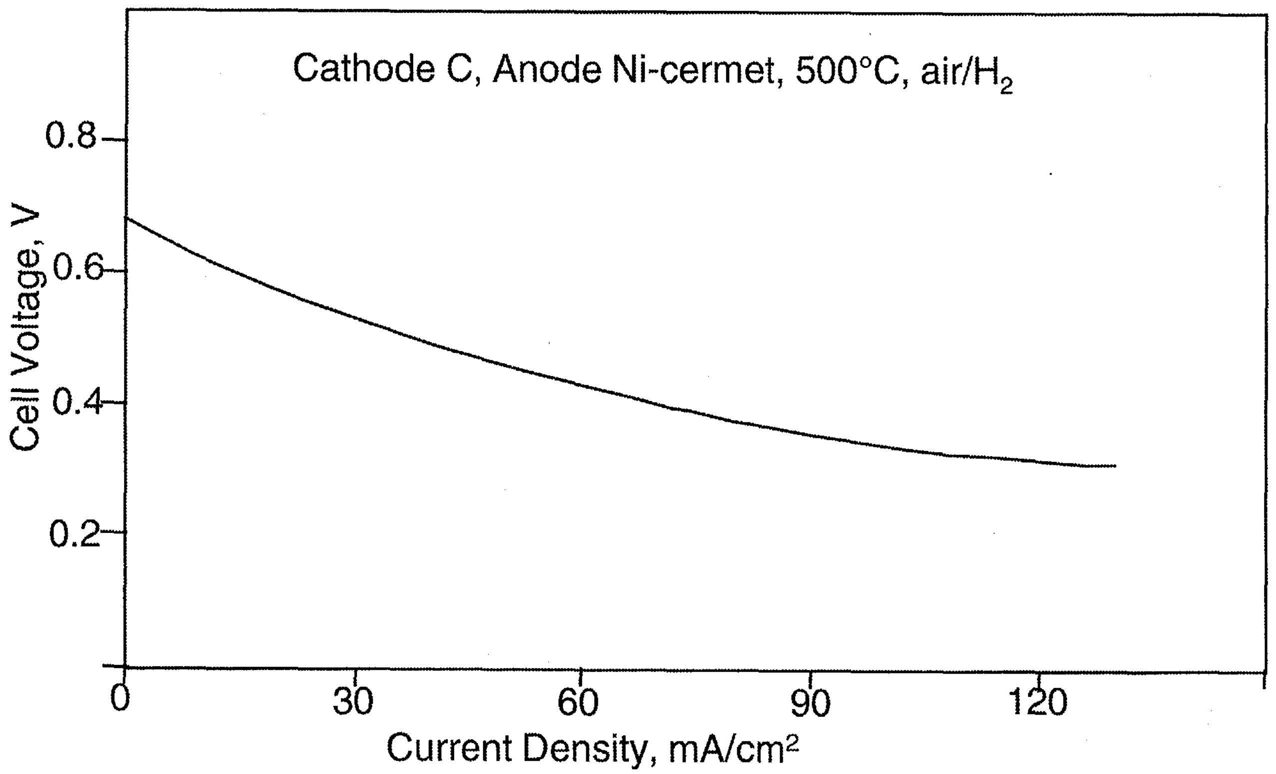

Fig. 9. Fuel cell performance with cathode C at 500°C. Some penetration of cathode material into interconnected porosity observed.