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La0.6Sr0.4Co0.2Fe0.8O3 - Ce0.8Sm0.2O2-δ composite cathode for operation below 600 C

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$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ - $Ce_{0.8}Sm_{0.2}O_{2-\sigma}$ COMPOSITE CATHODE FOR OPERATION BELOW 600°C

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ABSTRACT

Composite cathodes of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ and $Ce_{0.8}Sm_{0.2}O_{2-\sigma}$ were evaluated by impedance analysis for assessing their potential for utilization in intermediate temperature solid oxide fuel cells operating at temperatures below 600°C. The composite cathodes were formed onto $Ce_{0.8}Sm_{0.2}O_{2-\sigma}$ electrolytes by spraying suspensions of submicron-scale composite cathode powders and then firing the coated electrolyte pellets in air. Impedance measurements showed that the electrode resistances of the composite cathodes have a dependence on their firing temperatures. The composite cathodes of 70 wt% $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ and 30 wt% $Ce_{0.8}Sm_{0.2}O_{2-\sigma}$ fired at 750 or 850°C were found to achieve area specific resistances of 0.3 Ωcm^2 at around 590°C, and 0.5 Ωcm^2 at 565°C, respectively, while the composite cathode fired at 950°C showed nearly one order of magnitude higher resistance values.

INTRODUCTION

For the operation of a solid oxide fuel cell (SOFC) at an intermediate temperature range of 500 to 600°C, the contribution of the cathode polarization to the total resistance becomes more significant than the anode polarization and the ohmic resistances from other cell components (1,2). In order to achieve an acceptable output performance of greater than 0.2 Wcm^{-2} during steady operation at intermediate temperatures, the cathode polarization resistance needs to be kept as low as possible, preferably with an area specific resistance (ASR) of less than 0.1 Ωcm^2. To achieve this, both the material and the structure of the cathode need to be optimized. Cobalt and iron based perovskite oxides such as $La_{1-x}Sr_xCoO_3$, $Pr_{1-x}Sr_xCoO_3$, $Sm_{1-x}Sr_xCoO_3$, $Gd_xSr_{1-x}CoO_3$ and $La_{1-x}Sr_xCo_{1-y}Fe_yO_3$ have been investigated and developed as cathode materials for intermediate temperature operation (3-7). Higher cobalt content gives higher conductivity, but higher cobalt content also leads to larger thermal expansion coefficients.

From a scale-up point of view, cathode materials having thermal expansion rates close to that of the electrolyte should be used in order to alleviate induced interfacial stresses which could cause structural damage during thermal cycles and decrease the electrochemical active area. Accordingly, the lower cobalt content perovskite, $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$, is thought to be a proper candidate for the cathode material.

It has been shown that the addition of $Ce_{0.9}Gd_{0.1}O_{2-\sigma}$ electrolyte material to the $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ cathode lowers the electrode resistance by extending the triple phase boundary (8). $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ based composite cathodes with gadolinium doped cerium oxide have been intensively investigated (9-11). In this study, $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF) composite cathodes with samarium doped cerium oxide $Ce_{0.8}Sm_{0.2}O_{2-\sigma}$ (SDC) were evaluated at temperatures below 600°C by impedance analysis on symmetrical cells composed of cathode | electrolyte | cathode.

EXPERIMENTAL

For the electrolyte pellets, 20 mol% samarium doped cerium oxide (SDC) powder was prepared by conventional solid state reaction using CeO_2 (Alfa Aesar, 99.99%) and Sm_2O_3 (Alfa Aesar, 99.99%). Calcined and milled SDC powder was compacted into the pellets by uniaxial pressing, and these pellets were finally sintered at 1500°C in air for 3 h to provide a relative density greater than 98%. After sintering, the SDC pellets were ground with #400 SiC paper and cleaned in an ultrasonic bath. Typical dimensions of ground sintered SDC pellets were about 14 mm in diameter and about 1 mm in thickness.

The composite cathodes were formed on the SDC electrolyte pellets by spraying a suspension of the composite cathode powders and then firing in air. The composite cathode materials used for suspension were commercially available $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ powder (Praxair, Lot#03-P2447AM, 99.9% d_{50}=0.6 μm, SSA=6 m^2g^{-1}) and $Ce_{0.8}Sm_{0.2}O_{2-\sigma}$ powder (Praxair, Lot#03-P3995DM, 99.9%, d_{50}=0.7 μm, SSA=32 m^2g^{-1}). The desired quantities of these powers were mixed and milled in ethanol with zirconia balls (Tosoh, YTZ ball) using a ball milling apparatus (conventional: U.S. Stoneware, Model 755RMV, high-energy mill: SPEX, Model 8000M) to prepare the suspensions for spraying. The particle size distributions of the suspensions were checked with a particle size analyzer (Malvern, Model Zetasizer 2000). The composite cathode-ethanol suspension was sprayed onto both sides of the SDC electrolyte pellets at room temperature with an air-spray gun. Sprayed cathode layers were less than 2 $mg{\cdot}cm^{-2}$ in mass loading. The resulting symmetrical cells were then fired at 750, 850 or 950°C in air for 1 h to develop adhesion of the composite cathodes to the SDC electrolyte pellets.

Impedance measurements were made on the symmetrical cells (composite cathode | SDC electrolyte | composite cathode) at temperatures ranging from 400 to 600°C in air using a frequency response analyzer (Solartron, Model 1260) equipped with an electrochemical interface (Solartron, Model 1287). Gold mesh (82 mesh size, 0.06 mm diameter wire) was used for current collecting and was attached onto the electrodes without conductive pastes using a specially designed spring-loaded fixture. Typical measurement settings for the impedance measurements were 100 kHz to 10 mHz for the frequency range and 10 mV for the AC amplitude.

RESULTS AND DISCUSSION

Suspensions prepared with a conventional ball mill (rotational speed of about 60 rpm), milled for as long as 10 h, began settling in several minutes after milling. Consequently, composite cathodes could not be sprayed evenly without continuous agitation of the suspension during the spraying procedure. On the other hand, suspensions prepared with a high-energy ball mill (amplitude of about 25 mm at less than 1700 rpm) for as short as

1 min were found to be stable over several tens of minutes without any significant settling of the suspended powders. The nominal d_{50} values of as-received powders were 0.7 μm for SDC and 0.6 μm for LSCF. However, these particles were thought to be highly agglomerated as the conventional ball milling did not produce stable suspensions.

The composite cathodes of 70 wt% LSCF and 30 wt% SDC were milled under various conditions using a high-energy ball mill. It was found that high-energy milling in ethanol for 5 min allowed agglomerated particles to be milled to finer particles with a mean particle size of around 0.4 μm (Figure 1), and that these milled suspensions were very stable. Accordingly, for the preparation of composite cathode suspensions, high-energy ball milling was employed.

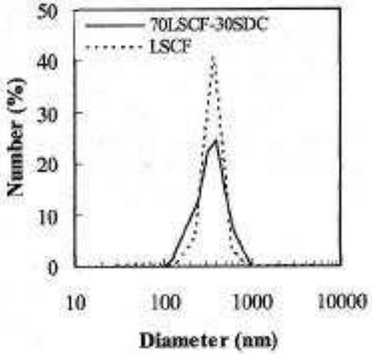

Figure 1. Particle size distribution of 70 wt% LSCF – 30 wt% SDC and 100 wt% LSCF.

For spraying, suspensions were adjusted for solid-loadings to be about 2 wt%. After firing of the composite cathodes at various temperatures, a simple adhesion test of fired composite cathodes using scotch tape was conducted. Figure 2 shows a photograph of the composite cathodes remaining on the adhesive coated side of the scotch tape after sticking it on and taking it off from the fired composite cathode surfaces. Hardly any material was removed from the composite cathode fired at 950°C, while a substantial amount of the composite cathode fired at 750°C was easily peeled off. However even in the case of the composite cathode fired at 750°C, most of the composite cathode layer remained on the SDC electrolyte surface. It is thought that some extent of elemental diffusion occurred even at 750°C which provided a sufficient level of mechanical bonding between the composite cathode and the SDC electrolyte.

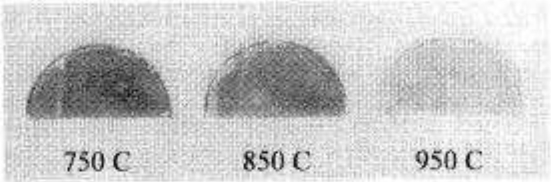

Figure 2. Photograph of composite cathodes fired at various temperatures remaining on scotch tape.

Figure 3 shows typical impedance spectra in Ωcm for the composite cathode of 70 wt% LSCF – 30 wt% SDC fired at 850°C at applied AC amplitudes of 10 and 1000 mV. The impedance measurement was made at 394°C in air. There seems to be two arcs; one is a large clear arc at a frequency range of 100 kHz to 100 Hz and the other is a distorted small arc from 100 Hz to 10 mHz. The AC amplitude of 1000 mV appears to have an influence on the small arc at a frequency range of 100 Hz to 10 mHz, while there is no AC amplitude dependence on the large arc. The resistivities of bulk and grain boundary for both SDC and LSCF are expected to be ohmic, while the electrode resistance is not always ohmic especially for the symmetrical cell configuration. When polarization due to the electrode reaction becomes not to be negligible at lower frequency ranges, one electrode interface on the symmetrical cell is exposed to cathodic current, while the other to anodic current coincidently, so different electrode reactions with different electrode resistances could happen on two electrode interfaces, and this becomes more significant as the current increases. Accordingly, it was considered that the distorted small arc was a reflection of the interfacial resistances of the electrodes on the symmetrical cell, and that the large arc was attributed to the grain boundary contributions. Since there was a difficulty to fit an adequate equivalent circuit to the distorted small arc, the resistance between the intercept of the distorted small arc at low frequency, at the AC amplitude of 10 mV, and the higher intercept of a fitted semi-circle to the large arc was used as electrode resistance.

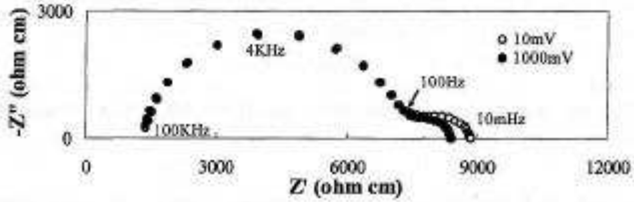

Figure 3. Typical impedance spectra for a symmetrical cell of 70 wt% LSCF-30 wt% SDC | SDC | 70 wt% LSCF-30 wt% SDC in air at 394°C at applied AC amplitudes of 10 and 1000 mV.

The area specific resistance (in Ωcm^2) for 70 wt% LSCF – 30 wt% SDC composite cathodes fired at various temperatures is plotted as a function of reciprocal temperature in Figure 4 along with reference data for 70 wt% $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ – 30 wt% $Ce_{0.9}Gd_{0.1}O_{2-\sigma}$ on $Ce_{0.9}Gd_{0.1}O_{2-\sigma}$ electrolyte as reported by V. Dusastre et al (8). The composite cathodes fired at 750 and 850°C show a similar ASR value at each temperature, and it is estimated that the 70 wt% LSCF – 30 wt% SDC composite cathode can achieve 0.3 Ωcm^2 at around 590°C and 0.5 Ωcm^2 at around 565 °C, respectively. On the other hand, the 950°C firing is found to increase the ASR by up to one order of magnitude in comparison to the data for the 750 and 850°C firings.

In Figure 5, the difference observed in impedance spectra for the composite cathodes fired at 850 and 950°C is shown. For the 950°C firing, the arc at the frequency range below 100 Hz, which is thought to be due to electrode reaction, is distinct in comparison with that of the specimen fired at 850°C.

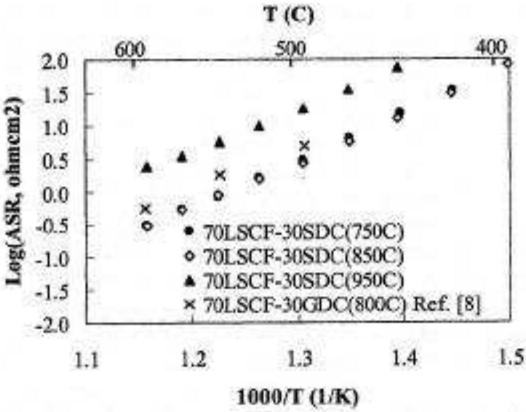

Figure 4. Log ASR as a function of reciprocal temperature for composite cathodes fired at various temperatures.

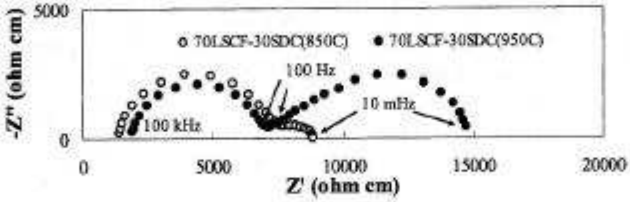

Figure 5. Impedance spectra at 394°C in air for composite cathodes fired at 850 and 950°C.

In contrast with the composite cathodes, for 100 wt% LSCF cathodes, there seems to be less dependence of the ASR on the firing temperature as can be seen in Figure 6.

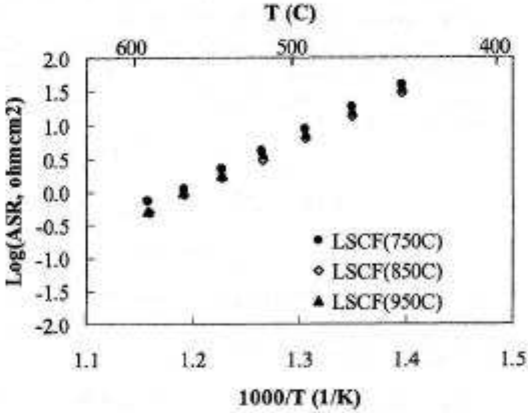

Figure 6. Log ASR as a function of reciprocal temperature for 100 wt% LSCF cathode fired at various temperatures.

For doped cerium oxide systems made of nano-scale particles, linear shrinkage rates of compacted bodies during sintering were reported to show highest values at around 900°C (12). Therefore, it is thought that the surfaces of nano-scale doped cerium oxide particles at around 900°C are active enough to facilitate particle rearrangement and elemental diffusion. As can be readily seen in Figure 2, the bonding of the LSCF – SDC composite cathode to the SDC electrolyte is very good when fired at 950°C. The observed difference in dependence of the ASR on firing-temperature between composite LSCF and pure LSCF cathodes could imply not only that the LSCF matrix starts the densification at temperatures greater than 900°C but also that there is a significant elemental diffusion between the matrix of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ and the added phase of $Ce_{0.8}Sm_{0.2}O_{2-\delta}$. With regards to processing of composite cathodes designed for intermediate temperature operation, the composite cathodes of this study should not be co-fired with other cell components at high temperatures in order to avoid the detrimental interfacial reaction between the LSCF and the SDC in composite.

Since the compaction of composite cathodes by iso-static pressing (8) and pore formation by burning incorporated organics (9) have been reported to have a large impact on the electrode resistance, it is thought to be conceivable that the ASR is susceptible to the processing history. In particular, processing history can control pore size distribution, pore orientation, matrix structure, phase distribution in composites, and chemical interaction between the matrix and the added phase. In this study, the composite cathodes were formed by spraying a suspension prepared by high-energy ball milling of submicron LSCF and SDC powders in ethanol. It must also be considered that the initial particle size and the distribution of composite powders can have a significant effect on the electrode resistance.

SUMMARY

This study has shown that high-energy ball milling could provide stable suspensions of submicron size particles of LSCF and SDC. Impedance measurements showed that there was a dependence of the electrode resistance on the firing temperature of the cathodes being after coated onto the electrolyte pellets, and that the composite cathodes of 70 wt% $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ and 30 wt% $Ce_{0.8}Sm_{0.2}O_{2-\sigma}$ fired at 750 and 850°C achieved area specific resistances of 0.3 Ωcm^2 at around 590°C, and 0.5 Ωcm^2 at 565°C, respectively. On the other hand, the composite cathode fired at 950°C showed nearly one order of magnitude higher resistance values.

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