COMPARISON BETWEEN LSCF-CGO AND GSC-CGO COMPOSITE CATHODES ON A CGO ELECTROLYTE FOR IT-SOFC

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ABSTRACT

High temperature operation causes many materials problems; such as degradation of key components, a limited choice of materials, etc. With the drive to lower operating temperatures for solid oxide fuel cells (SOFCs), several critical components within each cell require further improvement. Arguably, the cathode is the component that requires the greatest improvement. Composite cathodes offer the possibility of developing a high performance electrode for intermediate temperature (500°C) SOFC operation. To this end the electrochemical properties of Lao.6Sr0.4CoO.2Fe0.8O3-8 (LSCF)/Ceo.8Gdo.202-s (CGO 20-80) composite cathodes and Gdo.6Sr0.4CoOxide (GSC)/Ceo.8Gdo.2O2-8 (CGO 20-80) on Ceo.9Gdo.102-8 (CGO 10-90) have been investigated for use in intermediate temperature (500-700°C) SOFCs, using ac impedance spectroscopy. Both these composite cathodes were sintered at 1000°C onto the electrolyte; however, LSCF/CGO is very dense at 1000°C, hence a pore former (carbon) was used to promote porosity in this cathode. A CGO/LSCF/carbon composite cathode had an ASR value of 5 Ωcm² at 500°C and around 1 Ωcm² at 600°C. In contrast, GSC/CGO composite cathode had an ASR value of 3 Ωcm² at 500°C and around 0.4 Ωcm² at 600°C.

INTRODUCTION

Conventional solid oxide fuel cells (SOFCs) are operated at 1000°C or higher in order to attain reasonable power density. The electrode sintering, degradation of SOFC components, limited choice of materials, mechanical stress due to different thermal expansion coefficients, and interfacial diffusion between electrolyte and electrode are some of the materials problems associated with a high SOFC operating temperature (1000°C). The commercial development of SOFCs has been limited by these problems. Therefore, it is desirable to operate a fuel cell at reduced temperatures, while still maintaining the power densities achieved at high temperatures. One of the main limitations of lower temperature operations is the selection of a suitable cathode that will display sufficient catalytic activity for oxygen.

The main function of the cathode is to provide reaction sites for the electrochemical reduction of the oxidant. Therefore a cathode material for solid oxide fuel cells should meet several requirements in respect to preparation and operating conditions (1):

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• High electronic conductivity. Mixed ionic-and-electronic conductivity
• Porosity: the cathode must have sufficient porosity to allow gas transport to the reaction sites.
• High catalytic activity
• Thermal expansion coefficient compatible (from room temperature to operation and fabrication temperature) with other cell components
• Chemical compatibility with the electrolyte and the interconnect
• Stability (chemically, morphologically and dimensionally) in oxidant environment at high temperatures
• Ability to be formed into films

Adler et al (2) have provided both theoretical and experimental evidence for understanding the linear AC polarisation values for single phase mixed conducting cathodes (3). This model indicates that for mixed conductors with fast ion transport (e.g. LSCF), the impedance can be dominated by O₂ surface exchange and diffusion processes. A schematic representation of the ALS model is provided in Figure 1. The electronic charge transfer impedance at the interface between the current collector and mixed conducting oxide cathode can usually be neglected. The second arc can be attributed to the ionic charge transfer across the mixed conducting cathode/electrolyte interface. This charge transfer impedance only makes a minor contribution to the total electrode impedance provided that the interface is not contaminated by siliceous impurities. Zchem provides the major contribution, which is the convoluted contribution of non-charge transfer processes including oxygen surface exchange, solid-state diffusion, and gas-phase diffusion inside and outside the cathode (4). This model then enables the heterogeneous chemical reaction contribution (Rchem) to be calculated from the following expression (5):

\[
R_{\text{chem}} = \frac{RT}{2F^2} \sqrt{\frac{\tau}{(1 - \varepsilon) \mu C_0^2 D^* k}}
\]

Where:

- \( D^* \) is the Oxygen self-diffusion coefficient
- \( R \rightarrow \) Gas constant
- \( T \rightarrow \) Temperature
- \( F \rightarrow \) Faraday's constant
- \( k \rightarrow \) Oxygen surface exchange coefficient
- \( \varepsilon \rightarrow \) Fractional porosity
- \( a \rightarrow \) Internal surface area/unit volume
- \( \tau \rightarrow \) Tortuosity
- \( C_0 \rightarrow \) Molar concentration of oxygen ions

The area specific resistance (ASR) of the cathodes thus depends upon kinetic (oxygen self-diffusion coefficient, \( D^* \text{ cm}^2\text{s}^{-1} \), and oxygen surface exchange coefficient, \( k \text{ cm s}^{-1} \)) and microstructural (tortuosity, particle size and porosity) parameters. The kinetic parameters are fixed by the choice of materials, however the microstructural variables can, in principle be controlled by controlled processing.

The use of composite electrodes to improve the performance is beneficial for intermediate temperature (500-700°C) solid oxide fuel cells (IT-SOFC). The classical cathode material for intermediate temperature solid oxide fuel cell is lanthanum strontium...
cobalt iron oxide (LSCF). This has been found to possess mixed ionic-electronic conductivity at 700°C, however it becomes predominantly an electronic conductor at 500°C. Composite electrodes comprising a mixture of LSCF and the electrolyte material ceria gadolinia oxide (CGO) have better performance than electrodes consisting of LSCF only (6), due to the presence of active triple phase boundary (TPB) points between LSCF, CGO and gas phase in the bulk of the electrode.

The Adler model is not applicable to a composite material as such, however as a first approximation we can treat the material as a homogeneous mixed conducting medium and assume that the diffusion coefficient is determined by the electronically conducting perovskite phase. Using this assumption we can estimate the expected ASR of a composite material.

Data (7) for $D^*$ and $K$ at 500°C are $2.0 \times 10^{-8} \text{cm}^2\text{s}^{-1}$ (CGO) and $2.0 \times 10^{-8} \text{cm}\text{s}^{-1}$ (LSCF). The following typical values for the microstructural parameters were assumed and the fraction porosity was calculated from the Archimedes principle:

\[
\begin{align*}
\tau \text{ (tortuosity)} &= 1.5 \\
a \text{ (internal surface area/unit volume)} &= 20000 \text{ cm}^{-1} \\
Co &= 0.08 \text{ mol O cm}^{-1} \text{ in LSCF} \\
\varepsilon &= 0.6
\end{align*}
\]

These data were used to calculate the relevant $R_{chem}$ values at 498°C and 550°C and they were found to be around $2.87 \Omega \text{cm}^2$ and $1.55 \Omega \text{cm}^2$, respectively.

**EXPERIMENTAL PROCEDURE**

**Powder Preparation**

The composition of the optimised cathode material CGO/LSCF is 30 weight % $\text{Co}_0.8\text{Gd}_{0.2}\text{O}_{2-δ}$ addition to 70 weight % $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-δ}$. The CGO-LSCF powder was prepared by mixing the desired quantities of CGO and LSCF powders with ethanol and ball milled with zirconia balls for 24 hours to ensure even mixing. The paste was then dried and sieved through a 38μm stainless steel mesh. The same method was used when preparing CGO/GSC composite cathode. The composition of the optimised cathode material CGO/GSC is 28 weight % $\text{Co}_0.8\text{Gd}_{0.2}\text{O}_{2-δ}$ addition to 68 weight % GSC.

**Sample Preparation**

**For Dilatometry:** A relatively small 6mm die was selected to compact all powders covering all the composition range between 20CGO and LSCF, and 20CGO and GSC into green bodies. Cylindrical samples of 6 mm in diameter were uniaxially pressed at 1 ton and were approximately 4 mm in length.

**For AC Impedance:** Uniaxially pressed pellets of 13mm in diameter of 10CGO ($\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2-δ}$) powder were sintered at 1400°C at a rate of 10°C/min for 5 hours in air to produce a dense electrolyte sample. Several composite powders covering the 30
weight% 20CGO and 70 weight% LSCF were obtained by weighing appropriate amounts of materials. The addition of pore former to the composite CGO/LSCF was at a ratio of 30 volume % to 70 volume %. After ball milling in acetone and 5g of binder ("blyth") using the zirconia balls, the ink was sprayed to the dense 10CGO electrolyte pellet with a pressurized sprayer. Then these were calcined at 1050°C for 2 hours before studying the electrical properties. The same applied to the CGO/GSC composite cathode, but in contrast this composite cathode was very porous at 1000°C, hence no pore former was added to this composite.

RESULTS AND DISCUSSION

Dilatometry

![Figure 1: Dilatometry graph of CGO/LSCF.](image1)

![Figure 2: Dilatometry graph of CGO/LSCF/carbon.](image2)
Figures 1 to 3 show the change in length versus temperature data obtained from dilatometer during the sintering of green powder compacts of composite CGO/LSCF, CGO/LSCF/Carbon and CGO/GSC. The onset of shrinkage for both the CGO/LSCF composite materials commences around 800°C. The small increase in length from room temperature to 800°C is due to thermal expansion. There is a large expansion shown in figure 2 between 400°C and 600°C. This is possibly due to the oxidation of carbon, which occurs at these temperatures. The reaction of carbon in an air atmosphere gives rise to carbon monoxide according to the following reaction (8):

\[
2\text{(C)} + \{\text{O}_2\} \rightarrow 2\{\text{CO}\}
\]

followed by carbon monoxide (CO) further oxidizing to carbon dioxide (CO\(_2\)).

\[
\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2
\]

It is thus likely that within the body of the pellet, where the oxygen in flux is limited by diffusion down pores the ambient is predominantly carbon monoxide (CO) with a consequent low resultant PO\(_2\). Thus between 400°C and 600°C a substantial portion of the CGO/LSCF material is exposed to a reducing atmosphere due to the presence of carbon monoxide. Hence the large increase in the change in length between 400°C and 600°C shown in figure 2 is due to the chemical expansion of the perovskite material as it loses oxygen. After 600°C, the linear portion signifies either the complete reduction of the perovskite phase or the completion of carbon burnout. At around 800°C shrinkage begins and the material starts to sinter. In figure 3, the onset of sintering for the CGO/GSC commences at around 950°C, which is about 150°C higher than that which occurs in the CGO/LSCF composite cathodes. This reflects in the higher percentage of
porosity seen with the CGO/GSC cathode when sintered at 1050°C, and hence there was no need for the addition of pore former.

**SEM**

![SEM images of CGO/LSCF](image)

**Figure 4. CGO/LSCF calcined at 1050°C.**

**Figure 5: CGO/GSC calcined at 1050°C.**

Figure 4 shows the SEM images (x 1000) of an uniaxially pressed CGO/LSCF (70 weight % LSCF) composite materials sintered at 1050°C without (a) and with (b and c) the addition of the pore former, respectively. Figure 4a shows a highly dense electrode (> 71.1% theoretical density). The two oxides in this composite seem well mixed. Traditional method of developing porosity is by burning out the inclusions added to the composites during sintering in air. Two of those inclusions are polymethylmethacrylate (PMMA) and carbon, which will burn out around 400-500°C. Figure 4b shows the SEM image of CGO/LSCF composite mixed with PMMA of 40 μm in particle size and sintered in air at 1050°C. Uniform pores were apparent because of the voids left by the PMMA, while the matrix around these pores appears very dense. The percentage of porosity presented in this composite is calculated to be around 45%. Although high percentages of pores with diameter in the range 30-40 μm were found in this sample, however these pores are not interconnected which will result in no oxygen penetration through this composite when the fuel cell is in operation. Figures 4c show the SEM micrographs of the cross sections of the CGO/LSCF/carbon (30 volume % carbon) cathode layers sintered at 1050°C for 2 hours. The carbon oxidised at around 400-500°C, leaving voids in the structure, hence a highly interconnecting porous electrode is...
distinguishable with pore diameters around 1-10 μm. The percentage of porosity in this composite is calculated to be around 40.9%.

Sintering of CGO/GSC at 1050°C for 2 hours (Fig. 5) resulted in a structure with reasonable porosity that was connected with by narrow bottleneck-type bridges.

**AC Impedance**

Figure 6 to 8 show typical AC impedance spectra of CGO/LSCF, CGO/LSCF/carbon and CGO/GSC composite coated onto a dense electrolyte pellet and sintered in air at 1050°C. The pellets were tested with excitation potentials of 50 mV over a frequency range from 1MHz to 0.01 Hz at 500°C and 550°C in air. The electrode resistances were calculated from the differences between the low and high frequency intercepts of the electrode polarisation arc and divided by two due to the symmetrical electrode layers. Area specific resistances (ASR) of the CGO/LSCF and CGO/LSCF/carbon electrodes are shown as Arrhenius plot in figure 8. The activation energy for CGO/LSCF composite cathode is found to be 0.84 ev and for CGO/LSCF/carbon was around 1.22 ev. We observed that the ASR value for the CGO/LSCF cathode was found to be 30.43 Ω.cm² at 502.5°C (± 1°C), 15.72 Ω.cm² at around 549°C and around 8 Ω.cm² at 599°C. This was greater by a factor of 15 when compared to the previous work conducted by Kilner and Dusastre (2). The differences in the above ASR values are associated with the electrode processing quality, governed by parameters such as porosity, sintering temperature and the extent of particle agglomeration. However for CGO/LSCF/carbon the ASR value was found to be 6.51
Ω cm² at around 498°C (± 1°C), 2.63 Ω cm² at around 548°C and around 1 Ω cm² at 600°C. This agrees well with the previous work conducted by Kilner and Dusastre (6). However when compared to the theoretical values calculated from the Adler model, the experimental ASR values are two times higher. The differences between the theoretical and experimental ASR values is maybe associated with the electrode processing quality (poor contact between the cathode and the electrolyte), governed by parameters such as particle size, sintering temperature and the extent of particle agglomeration. Although we have improved the performance of the CGO/LSCF cathode by promoting porosity into the electrode structure, however the values are still slightly higher when compared to the CGO/GSC electrode. In contrast, GSC/CGO composite cathode had an ASR value of 3 Ω cm² at 500°C, 1 Ω cm² at 553°C and around 0.4 Ω cm² at 600°C. The activation energy for CGO/GSC composite cathode is found to be 1.28 ev.

![Graph showing area specific resistance of composite cathodes calcined at 1050°C.](image)

**CONCLUSIONS**

The correlation between performance and microstructure of SOFC cathodes consisting of a composite CGO/LSCF on a dense CGO electrolyte has been studied using an AC impedance spectroscopy. The area specific resistivities of this composite cathode were measured and it was found to exhibit poor performance at low temperature when compared to other results in the literature with the same operating conditions. This was due to only 29.9% of porosity present in the cathode structure.

Several methods were undertaken to improve the microstructure (porosity) of the cathode. One method was to add inclusions to the composites and burn them out during sintering. Hence the voids left by these inclusions will lead to pores in the composites. This was performed using polymethylmethacrylate (PMMA) and Carbon. The addition of PMMA produced pores in 30-40 μm in diameter. The percentage of porosity presented in this composite is calculated to be around 45%. However the pores are not interconnected which will result in no oxygen penetration through this composite when the fuel cell is in operation. The addition of carbon seemed to produce more (40-45%) porosity and there are sufficient connections among the grains leading to a long three-phase boundary. The performance of the CGO/LSCF/Carbon composite cathode was much better than CGO/LSCF. However when compared to the CGO/GSC electrode (without the addition...
of pore former) the values are still slightly higher. The area specific resistance of the CGO/GSC electrode is found to be better by factor of 2.

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