ABSTRACT

Improved cathode materials are critical to reducing the operating temperature of SOFCs. State-of-the-art cathode materials require operating temperatures above 800°C to provide low interfacial resistance, and sintering temperatures >1000°C to achieve sufficient adherence to the electrolyte layer. Composite materials have been identified as a promising approach to improving electrode behavior through the increase of the three-phase-boundary (tpb) area. Electrocatalytic effects have also been proposed as a mechanism that may explain the reduction in interfacial resistance. To investigate the relationship between component composition, surface area, and processing routes, a series of low temperature anode and cathode materials have developed using a nanocomposite approach. It has been demonstrated nanocomposite materials allow significantly lower processing temperatures and better performance than conventional composite materials, but require careful processing to take full advantage of the synergistic effects.

INTRODUCTION

As SOFC systems approach commercialization, the emphasis of materials and system development has been placed on lowering the operating temperature and cost of SOFC systems. The motivation for reducing the operating temperature and system cost are related - lower operating temperatures allow system builders to consider lower-cost materials of construction; the lower operating temperatures minimize adverse chemical reactions between component materials, minimize adverse effects of thermal expansion mismatches between component materials, reduce cost by allowing less expensive metals to be used for interconnects and gas manifolds, and reduce the size and weight of the SOFC power generation system by lessening requirements on heat exchangers and thermal insulation. However, it has been difficult to achieve high SOFC power densities at low temperatures in solid oxide fuel cells because of increased electrolyte resistance and inefficiency of the electrode materials. Reducing the thickness of electrolyte membranes lowers electrolyte resistance. This has been achieved in SOFCs with planar geometries by using one of the porous electrodes (typically the anode) as the bulk structural support, depositing a dense, thin film (10-20 mm thick) of the electrolyte on the porous substrate, and subsequently depositing the opposite electrode (cathode) as a porous film (about fifty microns) on the electrolyte film surface. Very high SOFC power densities have been achieved at temperatures of 750 to 800°C with planar SOFCs.
produced with this type of configuration. However, even better SOFC performance and lower temperature operation will be achieved by using improved cathode materials.

Two approaches have been demonstrated for improving low-temperature performance of cathodes in solid oxide fuel cells. The first approach involves replacement of lanthanum strontium manganite (LSM), which conducts electricity solely via electron transport, with mixed conducting ceramic electrode materials; i.e. materials that conduct electricity via transport of both oxygen ions and electrons. Examples of mixed conducting electrode materials include (La, Sr)CoO$_3$ (LSC), (La, Sr)FeO$_3$ (LSF), and (La, Sr)(Co, Fe)O$_3$ (LSCF) (1-4). However, mixed-conducting electrode materials that provide optimum low-temperature cathode performance (e.g., LSCF) also exhibit very high thermal expansion, which leads to failures during thermal cycling of planar SOFC elements. The second approach to improving low-temperature cathode performance involves addition of electrolyte material to the electrode material (5-8). This improvement is due to increasing the volume of triple-point (air/electrode/electrolyte) regions where electrochemical reactions occur. This enhancement is most effective when ceria-based electrolytes (SDC or GDC) are added or when the particle size of the component (electrolyte and electrode) materials is reduced. This composite cathode approach has the advantage that thermal expansion mismatch problems are somewhat alleviated.

The development of a comprehensive understanding of composite cathodes has been slow to mature because of the complexity of the systems. It is generally accepted that composite approaches are capable of reducing the interfacial polarization effects at low operating temperatures, but there is little consensus as to processing routes, component ratios, or the mechanisms that control the electrochemical reaction at the interface. For the LSM-YSZ system, a 50:50 weight ratio of electrolyte to perovskite is considered optimum; the same is true for LSM-GDC in spite of a 20% difference in electrolyte density between the two systems (5,6). For LSCF-GDC, 30% GDC by weight is reported as being optimum for improved electrochemical performance (7). Comparisons of processing routes and precursors are equally frustrating—spray coating, painting, screen printing, and isostatic pressing of spray coated layers have all been reported as routes to cathode deposition (5,7,8). Given the sensitivity of the component materials’ properties to processing variations, powders from different groups and vendors are reported to have widely disparate particle sizes, surface areas and sintering behavior. Because of this variability in processing, it is not surprising that the behavior observed by different research groups varies and requires different interpretations.

While the experimental literature concerning cathode development is complicated by many different materials sets and experimental approaches, the theoretical literature is comparatively straightforward. There are two schools of thought proposed to describe the observed improvement in ASR values for composite cathode materials. The charge transfer models describe interfacial resistance as a function of the electronic and ionic transport within the two components and the morphology of these components (9,10). Other models have been used to describe the interfacial resistance primarily in terms of the internal porosity and the kinetics of oxygen diffusion and surface exchange in the composite material (11). Both models provide insights into the parameters that influence the performance of composite electrodes and, by taking cues from their conclusions, the path to improved electrode compositions can be predicted.
The charge transfer models of interfacial resistance in a composite electrodes calculates the resistance primarily from the microstructural characteristics of the materials (grain size L, porosity p) and the electrical properties of the components such as the ionic conductivity of the electrolyte phase $\sigma_{O_2^-}$, and the intrinsic charge transfer resistances $R_{ct}$ of the electrocatalyst/electrolyte pair. The $R_{ct}$ is a function of the electrochemical properties of the pair and the grain size of the electrocatalyst, and is treated as an empirical value. The resulting relationship derived is:

$$R_{ct} = \sqrt{\frac{R_a L}{\sigma_{O_2^-} (1 - p)}}.$$  \[1\]

From this treatment, several microstructural and performance trends are apparent—finer electrolyte material provides significant enhancements of performance (provided grain growth can be controlled during operation), higher electrolyte conductivity reduces the interfacial resistance, and lower pore volumes reduce the resistance of the electrode. More subtly, this performance is controlled by the factors that control $R_{ct}$, the grain size of the perovskite material and the charge transfer interaction of the material set.

The catalytic models takes a very different approach to interpreting the polarization reactions at the cathode (11,12). Assuming the composite material functions effectively as a MEIC (as the authors contend that the $R_{ct}$ of the previous model is actually quite small) the resistance is instead expressed as:

$$R_{chem} = \frac{RT}{2F^2 \sqrt{(1 - \varepsilon)a C_0^2 D^* k}}.$$  \[2\]

Where, $R_{chem}$ is the chemical reaction contribution to the interfacial resistance, $D^*$ is the oxygen self-diffusion coefficient, $k$ is the oxygen surface exchange coefficient, $\tau$ is the tortuosity of the cathode, $\varepsilon$ is the fractional porosity, $a$ is the internal surface area/unit volume. Based on this model, it has been suggested that composite performance can be most improved by increasing the oxygen surface exchange coefficient (k) of the material. In addition to the k coefficient, the diffusion coefficient of oxygen in the material (related to ionic conductivity), the grain size (inversely proportional to a), and the porosity of the cathode have similar influences on performance as in the charge transfer model.

**EXPERIMENTAL APPROACH**

The focus of this study is to develop an improved understanding of the effect of processing parameters on cathode interfacial resistance. As predicted by the above models, composite materials can be remarkably sensitive microstructural parameters which are, in turn, controlled by processing conditions. To provide the most objective comparison of cathode performance, a single electrode deposition route (screen-printing) was chosen. The materials reported here were all processed to optimize their particle size (1-2 µm average particle size) and surface area (5-10 m²/g) for this deposition technique. Materials with higher surface areas and finer particle sizes require high organic loading in screen printing inks and tend to crack during heat treatment. Materials with large particle sizes and low surface areas tend to require high processing temperatures, which have been noted to degrade electrical performance.
Samples for electrical testing were prepared using single-phase perovskite electrode powders and composite materials based on $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_3$ (LSF) and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ (LSCF). The pure LSF and LSCF powders were prepared from NexTech’s commercial powders. Composite cathode materials were prepared by mechanically mixing precursor electrode and electrolyte powders to achieve homogeneous phase distributions. As required, the surface area and particle size of the mixtures were modified by calcination or milling to make them amenable to screen-printing. Screen-printing inks were prepared by dispersing the cathode powder into a terpineol-based ink vehicle, using a three-roll mill. Circular patterns (1.27 cm diameter) were deposited by screen-printing onto opposite faces of 300-micron thick GDC discs. The electrode-coated GDC discs were then annealed at 950°C for 1 hour so that the electrodes adhered to the GDC discs. After annealing, thickness of the electrode coatings was about 50 microns for both sides.

The symmetric cathode coated samples were subjected to electrical testing to verify the beneficial effects obtained by using the nano-composite electrodes and methods for preparing these nano-composite electrodes. The same measurement protocol was used for all samples. Silver paste was applied to the electrode surfaces, and two silver lead wires were attached to each electrode face. A digital voltmeter was used to measure the resistance of the electrode GDC discs at temperatures between 400 and 800°C. Two resistance measurements were made at each temperature (with opposite polarities), the average of the two resistance measurements was determined and recorded. This resistance corresponds to the total of the ohmic resistance of the GDC electrolyte, the resistance associated with the interfaces between the electrolyte and electrodes (where electrochemical reactions take place), and the ohmic resistance of the electrodes themselves (which is negligible). The resistance associated with the GDC electrolyte was calculated from the specimen geometry using ionic conductivity data obtained on GDC ceramics. After subtracting the electrolyte component, the resulting resistance value was assumed to be the resistance associated with the electrodes, which was primarily due to interfacial resistance. The specific electrode resistance (or normalized to the electrode area) value was calculated by multiplying by the electrode area ($1.267 \text{ cm}^2$) and dividing by two (the number of electrodes per sample).

RESULTS

A number of processing parameters were investigated, including the chemical composition, content, and morphology of the two component phases. To demonstrate the importance of the electrolyte content on the composite material, cathode inks were prepared with varying GDC content. As shown in Figure 1, the effect on interfacial resistance is significant. The addition of GDC has a noticeable effect on interfacial resistance for all three samples. At 30 volume percent, a perceptible drop in electrode resistance is observed, which decreases further as the GDC content is increased to 40 volume percent. The resistance of the 50 volume percent samples shows higher resistivity than either of the other composites, and higher resistance than pure LSCF at high temperatures. This change in performance may represent the level at which the lower conductivity of the electrolyte material outweighs the effect of increased three-phase boundary area and/or improved catalytic performance in the composite.
Composite cathodes have characteristic levels of performance that is dictated by the composition of the perovskite phase, as shown in Figure 2. The electrical resistance of four cathode materials are shown; two pure perovskite materials and two composite materials. The processing of the composites has been optimized to achieve good homogeneity, adherence, and high three-phase boundary area. While both the LSF and LSCF materials can be improved by composite approaches, it is also apparent that the pure and composite materials demonstrate performance of the same magnitude and show similar slopes with respect to 1/T. This result demonstrates that, while cathode electrochemical performance can be enhanced by tailored processing, the enhancements that can be achieved is limited by component selection.
Finally, while materials selection may set the limits for obtainable levels of performance, processing remains a critical consideration. In Figures 3 and 4, the importance of proper processing is demonstrated. Cathode materials with nominally the same composition were produced by two different routes; conventional composite samples were prepared by mixing commercial LSF and LSCF powders mixed with a GDC material with a surface area of 15 m$^2$/g and processing the material as described previously. The optimized materials were produced using processing routes to achieve nanoscale mixing.

![Figure 3. Comparison of conventional and optimized electrode resistance in symmetric LSF-based cathode cells.](image)

The performance of the cathodes is shown in comparison to the pure perovskite powder. In both cases, the electrode materials produced by the optimized route give lower electrode resistance values than the coarser conventional materials. In Figure 3, the conventional powder exhibits higher resistance than even the pure perovskite, demonstrating that, while materials selection may set the limits of achievable performance, poor processing can create more problems than it solves. The difference in performance can be attributed to the higher three-phase-boundary area of the nanoscale composite and better adherence expected from the finer scale material.

**CONCLUSIONS**

The current study demonstrates that composite cathode materials provide a promising path to low temperature cathodes in SOFCs. The performance of such composites is controlled by materials selection, the phase distribution, and the processing of the component materials. While optimized processing can improve the performance of a materials set, poorly controlled processing can result in significant departures from expected performance. Further research is underway to tailor the performance of component phases for operation in composite cathodes, based on the observations and processes developed in this work.
Figure 4. Comparison of conventional and optimized electrode resistance in symmetric LSCF-based cathode cells.

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