Evaluation of the relationship between cathode microstructure and electrochemical behavior for SOFCs


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1. Introduction

In recent years, a drive toward high efficiency, low emissions, power sources has created a great deal of interest in fuel cells. Solid oxide fuel cells (SOFCs) have the potential to meet these requirements and run on a readily available fuel supply [1]. A lanthanum strontium manganite (La$_{1-x}$Sr$_x$MnO$_3$, LSM) cathode on yttria-stabilized zirconia (ZrO$_2$–Y$_2$O$_3$, YSZ) electrolyte system is currently the state of the art for high-temperature materials systems; however, the electrochemical performance of such devices is not well understood [2,3]. Several reaction pathways are under consideration and the identity of the rate-limiting step is not known conclusively. During fabrication or long term high-temperature operation, microstructural changes occur which affect performance of LSM on YSZ devices [4]. Because high temperatures are required for fabrication, these changes can not be avoided. Additionally, LSM on YSZ has been shown to react, forming insulating zirconate phases at the interface [5]. The overall result is that the cathodic reaction, which is dependent on oxygen gas flowing to the surface, diffusing toward the reacting site, and being transferred to the electrolyte is affected by the altered microstructure. The impact of microstructural and interfacial changes on the electrochemical steps contributing to the overall cathodic reaction is investigated herein.

One of the first authors to utilize knowledge of a relationship between polarization resistance and $L_{TPB}$ was Ostergard et al. who decreased polarization resistance by forming composite cathodes which have increased $L_{TPB}$ [6]. It has been reported that the dependence of polarization resistance on composite cathode thickness depends on the measurement temperature and that as composite cathode thickness increases, polarization resistance decreases until gas diffusion effects become important [7,8].

Several works have been performed with the goal of establishing a relationship between the triple phase boundary length ($L_{TPB}$) and electrochemical performance, the DC resistance from SOFC $I$–$V$ data, or the entire cathodic resistance determined from impedance spectroscopy. One of the most frequently cited works in the area was performed by Mizusaki et al. who used impedance spectroscopy to show that total cathode conductivity, measured at 1000 °C, divided by $L_{TPB}$ is essentially equal to a constant, indicating that resistance is proportional to $(L_{TPB})^{-1}$ for drip pyrolosis prepared La$_{0.6}$Ca$_{0.4}$MnO$_3$ LCM/YSZ/platinum cells sintered between 1100 and 1200 °C [9]. It should be pointed out that only two data points are plotted to give the observed dependence and more work is needed. Additionally, when a different fabrication technique was used, a non-linear power dependence of total cathodic polarization resistance on $L_{TPB}$ was reported.

Another frequently cited work was performed by Kuznecov et al. [10], who derived a relationship successfully explaining the linear dependence reported by Mizusaki i.e. $R_{cathode} \propto (L_{TPB})^{-1}$. In the model, the author assumes that surface diffusion of adsorbed species towards the TPB dominates $R_F$ and that the DC resistance can be modeled by...
considering this flow of adsorbed species to the TPB. The model basically relates the cathodic resistance to the flux of adsorbed species on the surface of the cathode. As reported by Macdonald a surface diffusion limitation is often manifested by Warburg behavior in the impedance profile [11]; however, we did not see Warburg behavior in the lower range of sintering temperatures studied and so the development described in the work may not be appropriate for our data.

In a later work by Kuznecov et al. it is reported that for kinetics controlled by bulk diffusion through the cathode, \( R_{\text{cathode}} \propto (\text{MIC/YSZ contact area})^{-0.5} \) [12]. This development is based on the work of Adler [13]. However, the model of Adler was intended to describe cathodes with significant ionic conductivity and is inconsistent with the primarily electronic conductivity of LSM. This model considers flow of ionic species through the cathode bulk to be the limiting factor and calculates the conductivity from this flow. From the data of Kuznecov et al., a power dependence of \(-0.39\) can be calculated (from only two data points) when relating total \( R_{\text{cathode}} \) to \( L_{\text{TPB}} \) for LSM measured at \( 12^\circ\)C [12].

In another work, Fleig showed that for well defined, dense patterned LSM microelectrodes of circular geometry, the total cathodic resistance is proportional to electrode diameter (D) to the \(-2.1\) power when measured at \( 800^\circ\)C. In this geometry, \( L_{\text{TPB}} \) is equal to the circumference (C) where \( C_D^2 \) and therefore, \( R_{\text{cathode}} \propto (L_{\text{TPB}})^{-2.1} \). Additionally, Fleig reported that the resistance scales almost linearly with thickness and that application of a bias can change the exponential dependence observed [14,15]. Fleig concluded that since total cathodic resistance scales inversely with electrode contact area (area \(=0.25\pi D^2 \)) and linearly with thickness, a bulk path through the electrode determines the oxygen reduction rate, with transport of oxide ions in LSM being the rate-determining step. It should be pointed out that the dense circular electrodes used by Fleig had thicknesses of only 0.1 to 0.25 \( \mu m \) and diameter on the order of 60 \( \mu m \), so ionic transport through the electrode could be appreciable. In contrast, in the present work we used porous electrodes with thickness on the order of 20 \( \mu m \) and individual particle sizes of about 1 \( \mu m \). Therefore, different reaction pathways are likely. For example, if an oxygen molecule is adsorbed at the center of one of the circular disks, the adsorbed species must travel over 30 \( \mu m \) to reach the electrolyte via a surface path, but only 0.1 \( \mu m \) to reach the electrolyte through the cathode bulk. On the other hand, for relatively spherical particles, the path to the electrolyte via the surface will be around the same distance for both surface and bulk diffusion. Obviously, both the shape of the cathode and the relative ease of transport through the bulk versus on the surface will determine which path is favorable for an adsorbed species. Additionally, surface area (not volume normalized surface area) also scales linearly with cathode thickness and so additional evidence is needed to support the bulk transport conclusion.

Because the electrolyte is sintered to a dense state at temperatures higher than the operation temperature or any other fabrication steps, its microstructure is generally considered to be stable. However, the porous microstructure required for the cathode is sensitive to the sintering of the cathode and possibly operating conditions as well. A great deal of microstructural analysis has been performed, however most of the previous work is either a surface technique such as BET (Brunauer, Emmett, Teller adsorption technique), which is usually used for powder samples or a two-dimensional microscopy technique such as conventional SEM [16]. In contrast, this work makes use of a dual beam FIB/SEM (Focused ion beam/scanning electron microscope) for microstructural characterization that allows 3-D reconstruction. Of the microstructural parameters commonly studied, four are considered to be the most critical to electrochemical efficiency. These include pore surface area, triple phase boundary length \( L_{\text{TPB}} \), porosity, and tortuosity.

An oxygen molecule, which has diffused through the gas phase to the cathode, must first be adsorbed before it can participate in the reduction reaction. This adsorption can occur very close to the TPB or further away, depending on the diffusivity of the adsorbed species. It has been proposed in fact, that oxygen reduction in an electronic conductor can be co-limited by both adsorption and surface diffusion [17]. Both adsorption and surface diffusion are dependent on the pore surface area; therefore, pore surface area is one of the key microstructural parameters for our investigation.

As coarsening occurs, small cathode particles at the interface coalesce into larger ones, thus reducing the total \( L_{\text{TPB}} \) per surface area. Other authors have shown that increasing \( L_{\text{TPB}} \) results in reduced electrode resistance for LSM/YSZ systems [18,6]. This reduction is a direct consequence of the fact that in pure electronic conducting electrodes, the electrochemical reaction driving fuel cell operation is restricted to the TPB [19] due to the exclusion of ions from the bulk of the electronically conducting cathode and of electrons from the bulk of the electrolyte. We therefore can anticipate an increase in charge transfer resistance as sintering temperature is increased.

Porosity is the ratio of the void space in the microstructure to total volume. Before the cathodic reaction can occur in an electronic conducting cathode such as LSM, oxygen molecules must first diffuse through open pores to the vicinity of the TPB, the area where the cathode, electrolyte, and oxidant meet. An ideal microstructure has ample void space for molecular gas diffusion, while a partially dense microstructure impedes the flow of molecules to the TPB, thus inhibiting the cathodic reaction.

Tortuosity is a property that quantifies the complexity of the path through which a diffusing particle must travel in order to reach a desired destination. In terms of SOFCs, tortuosity is a unitless parameter defined as the distance traveled by a molecule exiting an impinging gas flow as it travels through the porous cathode to reach the solid electrolyte, divided by the straight-line distance. A large tortuosity corresponds to a convoluted path for a given gas molecule to traverse in order to go from the gas stream to the TPB. Because data in three dimensions is necessary for a true tortuosity analysis, very little work is published for actual systems. The dual beam FIB gives us the three-dimensional data necessary for the mathematical evaluation. We expect that cathode microstructures with a large tortuosity will show an increase in gas diffusion polarization resistance and related electrochemical properties.

2. Experimental

Symmetrical cathode/electrolyte/cathode test samples were produced for the work. The electrolyte in this work, YSZ, was prepared by tapecasting (Marketech International, Inc.). The YSZ contained 8 mol% yttria and had dimensions of 10.0 \( \times \) 20.0 \( \times \) 0.1 mm. The cathode was made from LSM \([(La_{0.6}Sr_{0.4})_{0.98}MnO_3-d\] ink supplied by Nextech Materials, Ltd. YSZ was screen printed on both sides of the electrolyte in two layers with a square area of 64 mm\(^2\), resulting in the symmetric sample shown in Fig. 1. A drying step was performed after the screen-printing of each layer in a Fisher Isotemp drying oven at 120 \( ^\circ\)C for 1 h. After drying, sintering was performed in a Lindberg/Blue high-temperature box furnace. Samples were sintered at temperatures ranging from 1150 to 1325 \( ^\circ\)C for investigation of charge transfer and adsorption. The resulting symmetrical samples had a cathode thickness of about 20 \( \mu m \) and YSZ thickness of 100 \( \mu m \).

Impedance analysis was performed on these samples followed by extensive microstructural analysis. For impedance analysis, the samples were mounted in a quartz reaction tube inside a Barnstead/Thermolyne furnace with pressure contact leads to the frequency response analyzer. The quartz tube consisted of an inlet and outlet for gas flow, gold leads shielded by alumina rods with platinum paint, and a pressure contact sample holder. The gold leads were connected by platinum wires to a platinum mesh, which was used as the current collector. The pressure contact holder was designed in a way that exposes the platinum mesh and adjacent cathode to the ambient gas. Air was flowed over the samples at 40 sccm.

Electrochemical impedance spectroscopy (EIS) using a Solartron 1260 impedance gain analyzer was performed in order to measure the frequency response of the prepared samples. A 50 mV AC voltage was applied and the induced current was measured to produce the impedance spectra. Measurement was made via a Z-point connection
The inter-particular unions have become primarily of the face-to-face variety with face diameter almost equal to particle diameter; the connectivity has increased. By 1300 °C, the coarsening has progressed to the point that individual particles no longer exist; the material is now very connected. As the particles coalesce into large particles, the number of pores decrease and only a smaller number of large pores are left, effectively doubling the average pore diameter between 1200 and 1300 °C.

Because the TPB is of particular importance to the cathodic reaction, we closely examined the cathode/electrolyte interface. On initial inspection, it appears that the cathode to electrolyte contact surface is larger for the 1200 °C sintered sample than the 1100 °C sintered sample. Several of the particles close to the electrolyte for the 1100 °C sintered sample do not appear to contact the electrolyte. In contrast, for the 1200 °C sintered sample face-to-face contacts have been formed between the cathode and the electrolyte. The nature of interfacial voids also changes significantly between 1200 and 1300 °C. Fig. 3(c) shows the formation of large interfacial voids at the cathode/electrolyte interface. These large interfacial voids form as smaller voids coalesce while being restricted from the dense electrolyte. Formation of these interfacial voids will greatly reduce the measurable $L_{\text{TPB}}$.

FIB/SEM was performed on samples sintered at the various temperatures and microstructural features were quantified as described in the following. Porosity ($p$), volume normalized pore surface area ($S_V$), and $L_{\text{TPB}}$ values were calculated at each temperature, while tortuosity ($\tau$) values were calculated from the 3-D data attained at selected temperatures. Porosity was calculated from the pore area/total area in each SEM image. The calculation was repeated for all slices in the sample and an average porosity was attained. These results are plotted in Figs. 4 and 5.
The pore surface area reported is normalized per unit volume. From [22,23], the pore surface area \( S_V \) per unit volume can be calculated according to Eq. (1).

\[
S_V = \frac{1}{L^3} \int \int dS = 2P_L.
\]  

(1)

In Eq. (1), \( dS \) is the surface area element, \( L^3 \) is the unit volume, and \( P_L \) is the number of phase changes (gas to solid) per unit length and was counted manually from each of the SEM images through the bulk of the cathode.

The triple phase boundary length \( L_{TPB} \) was calculated by application of the following equation [22,23].

\[
L_{TPB} = \frac{\pi}{2} P_L.
\]  

(2)

For \( L_{TPB} \), \( P_L \) was counted from the pore/LSM phase changes per unit length in the SEM images at the LSM/YSZ interface. The units for the calculation of \( L_{TPB} \) and \( S_V \) are \( \mu \text{m}^{-1} \), which is dimensionally accurate for a length normalized per unit surface area and an area normalized per unit volume.

The tortuosity was the only microstructural parameter that was not attained for each SEM and averaged making use of the uniformly spaced FIB slices. Tortuosity was calculated by estimating the length a gas particle must travel as it departs the impinging gas flow and travels to the electrolyte divided by the straight-line thickness. The method used for the tortuosity calculation was based on the definition of tortuosity. The length traveled by a gas particle was calculated by first determining \( x, y, \) and \( z \) coordinates of the center of pores in adjacent slices and then tracking the changes in pore center location from slice to slice. Eq. (3) can be used to estimate the total distance traveled by a particle \( L_T \) using the Pythagorean Theorem.

\[
L_T = \sum_{n=1}^{N} \sqrt{(x_{n+1} - x_n)^2 + (y_{n+1} - y_n)^2 + (Z_{n+1} - Z_n)^2}.
\]  

(3)

In Eq. (3) \( (x_n, y_n, z_n) \) are the coordinates of the \( n \)th point used and there are \( N \) total points determined. Once attained, \( L_T \) can be divided by the straight-line distance to give the tortuosity.

The volume normalized pore surface area was calculated as described in Eq. (1) using three SEM images for each sintering temperature. For each image a line was taken in three directions for a total of nine measurements per sintering temperature. The temperature dependence of the average pore surface area and corresponding standard deviation as a function of temperature is plotted in Fig. 4(a).

For the area normalized triple phase boundary length, a single line near...
the interface was taken from each of three SEM images per sintering temperature. The results were averaged and plotted in Fig. 4(b).

From Fig. 3, we can see that as the sintering temperature increases from 1100 to 1300 °C, the microstructure changes from one with small pores to a microstructure with large pores. From elementary geometry, we would expect a microstructure with many small pores to have a larger surface area than one with large pores. Fig. 4(a) confirms this finding and shows that the volume normalized pore surface area decreases as sintering temperature increases from 1150 to 1325 °C.

Fig. 4(b) shows that \( L_{TPB} \) decreases linearly as sintering temperature is increased in the temperature range displayed. There are minor outliers at 1225 and 1250 °C. These deviations could be caused by localized interfacial voids, an unusually fine interfacial microstructure, or a lower than anticipated sinter. A determination as to whether the cause of the outlying points is a local anomaly or a characteristic of the bulk sample can be made by studying the electrochemical behavior of the samples in question, which is performed later.

Fig. 5(a) shows that the porosity starts at about 30% for a 950 °C sintered sample and increases slightly with increasing sintering temperature to 1200 °C and then begins to drop off. By 1400 °C (not shown), the porosity has dropped to less than 5% indicating an almost dense cathode layer. This trend is supported by our qualitative analysis of Fig. 3 and the fact that the melting temperature of LSM on YSZ is on the order of 1450 °C [24].

The tortuosity was calculated for select temperatures. Tortuosity values of 3.23, 2.18, and 4.27 were calculated for the 1100, 1200, and 1300 °C annealed samples, respectively. The minimum tortuosity occurs at about 1200 °C indicating that the gas molecules have the most direct path to the interface. Opposing trends accounts for the minimum that is observed. At low sintering temperatures, particle size remains small, and gas molecules are redirected many times as they traverse the path to the LSM/YSZ interface. At higher sintering temperatures the pores are large; however, some of the paths may become closed off, limiting the number of available pathways.

### 3.2. Effect of sintering on impedance

#### 3.2.1. General observed trends

Figs. 6 and 7 show 800 °C impedance measurements of LSM on YSZ sintered at various temperatures in air. Fig. 6(a) and (b) shows the Nyquist plots covering the entire frequency range and high-frequencies only, respectively. The profiles shown in Fig. 6(a) are generally asymmetrical in the high-frequency regime. The effect is more pronounced in Fig. 6(b), which only shows the highest frequency portion of the data. The cause of this asymmetry is the presence of multiple processes occurring over the frequency range examined. As sintering temperature is increased, the presence of the high-frequency process becomes more pronounced as seen in Fig. 6(b). Fig. 7 displays the frequency dependence of the imaginary impedance. Displaying the data in this format makes apparent the decrease in peak frequency of the overall reaction as sintering temperature is increased. The 1325 °C sintered sample shows a change in slope at about 1 kHz. An inflection is only observed when two or more electrochemical processes are significant.

Impedance spectroscopy of LSM cathodes on YSZ substrates has been the subject of a multitude of works [25,26]. Most authors agree that two noticeable processes occur in optimally sintered LSM on YSZ at high measurement temperatures in oxygen rich atmospheres. At low oxygen partial pressures a third process related to the diffusion of oxygen gas molecules through the open pores of the cathode to the active region is observed.

Unfortunately, agreement on the isolation and identification of the high and intermediate-frequency processes has not been as complete.
Reasons for disagreement include 1) the mechanism of reaction is dependent on measurement conditions, 2) the mechanism of reaction is dependent on the sample preparation and sample history, and 3) no consensus is reached for evaluation of impedance data. To overcome the first two problems it is important for authors to specify as completely as possible all experimental details, particularly when microstructure is not analyzed. In this work, we have characterized the microstructure and will relate electrochemical properties directly to the microstructure of each sample. The third problem is not easily solved.

### 3.2.2. Impedance data analysis

Typically, impedance data is analyzed by fitting the data to an equivalent circuit. One school of thought proposes developing a model which is based on a priori knowledge of the system. Several authors have analyzed LSM on YSZ using this method. The most often used circuit contains a double layer capacitance in parallel with a series connection of a charge transfer resistance and a mass transfer related element. For electronic conductors, the mass transfer interpretation is replaced by adsorption and/or surface diffusion. The mass transfer related element is either a Voigt element, a finite-length Warburg element, or some general diffusion element that is not easily defined in terms of circuit elements. Additionally, all capacitors may be replaced by constant phase elements to account for inhomogeneities in the system. This type of circuit with slight variations has been used by several authors for SOFC impedance modeling, often specifically for LSM on YSZ, and is depicted in Fig. 8[27–31]. The major drawback of this model is that each author typically has their own variation of the model making comparison of parameters attained between groups difficult. The commonly used nested circuit shown in Fig. 8 (with capacitors instead of constant phase elements) was produced from a more general model in a work by Jamnik and Maier [32]. In the model, CPE$_{dl}$ represents the double layer capacitance, $R_c$ represents the charge transfer resistance, and $R_{ads}$ and CPE$_{ads}$ represent a mass transfer phenomenon. Henceforth, we will treat LSM as an electronic conductor and therefore replace the mass transfer process by adsorption and/or surface diffusion. MacDonald explains that when surface diffusion is significant the Randles equivalent circuit is expected; however, if no significantly diffusing intermediates are present the diffusional impedance is replaced by a resistor and capacitor in parallel [11]. In this work, a Warburg type slope was not seen for most sintering temperatures; therefore, it is likely that adsorption is more significant than surface diffusion.

An alternative equivalent circuit based on a series connection of Voigt elements is also used by many authors and displayed in Fig. 9[33–36]. In this type of model, assignment of identities to the individual processes is accomplished by identification of activation energies, $pO_2$ dependences, bias voltage dependences, and other circumstantial evidence. The major advantage of modeling in this fashion is that comparison of efforts between different groups is facilitated; however, because the model is not derived specifically for the system, confidence is diminished. Jiang et al. has used error structure analysis to show that both of these models can accurately produce the desired response [37]. In both models, $Z_{ds}$ represents the total impedance of all processes occurring at too high a frequency to be represented in the frequency response. These processes include electrolyte resistance, residual inductive artifacts and any ohmic resistances.

An analysis was performed to determine the likeliest identities for the resistances $R_1$, $R_2$, and $R_3$ of the series model. Impedance spectroscopy was performed on an LSM/YSZ/LSM sample sintered at 1100 °C at various measurement temperatures and oxygen partial pressures. Activation energies, oxygen partial pressure dependencies, and time constants were calculated for the various cathodic resistances of the model. The results indicated that three cathodic processes, $R_1$, $R_2$, and $R_3$, were active. Of these three processes, only $R_1$ and $R_2$ were significant at higher partial pressures of oxygen. $R_1$ was shown to be independent of oxygen partial pressure, had an activation energy 0.97 eV and a time constant of $8.5 \times 10^{-5}$ s at 800 °C.

![Fig. 7. Imaginary impedance versus frequency plot measured at 800 °C for LSM sintered at various temperatures (given in °C) in air.](image)

![Fig. 8. Nested element equivalent circuit used for fitting. $Z_{hf}$ represents features occurring at too high a frequency to be analyzed. CPE$_{dl}$ is associated with the double layer capacitance, $R_c$ is the charge transfer resistance, and $R_{ads}$ and CPE$_{ads}$ are related to adsorption.](image)

![Fig. 9. Series Voigt element equivalent circuit used for fitting. $Z_{ds}$ represents features occurring at too high a frequency to be analyzed. Each Voigt element is composed of a resistor and a constant phase element.](image)

![Fig. 10. Deconvolution of impedance profile from 1200 °C sintered sample, measured at 800 °C in air, using both equivalent circuit models. a) Nested model. b) Series model.](image)
R2 was dependent on $pO_2$ to the $-0.16$ power, had an activation energy of 1.2 eV, and had a time constant of $1.8 \times 10^{-1}$ s at 800 °C. Upon comparing these results with the work of others [25,26,38], it was determined that charge transfer is the most likely identity of R1, while dissociative adsorption is the most likely identity of R2. R3, which is only significant at low oxygen $pO_2$s is attributed to bulk gas diffusion.

Both equivalent circuit models were used to fit impedance profiles such as the ones shown in Fig. 6. Fig. 10 is included as an example illustrating the deconvolution of the data. The impedance profile shown is for the 1200 °C sintered sample measured at 800 °C air. Fig. 10(a) shows the data and the fitting obtained using the nested model, while Fig. 10(b) shows the data along with the fitting (solid line) from the series model. Additionally, Fig. 10(b) shows the individual components which are summed to produce the series model fitting. Because both models accurately fit the data, more analysis is necessary to determine which of the two is more appropriate.

### 3.2.3. Analysis of the present data

Looking back at Figs. 6 and 7 we see that the intermediate frequency process has a larger polarization resistance magnitude but that the high frequency process increases in relative magnitude as sintering temperature is increased. An increase in charge transfer resistance is evidence of a decrease in the quality of the cathode/electrolyte interface, where charge transfer occurs. Charge transfer polarization resistance becomes more significant at higher sintering temperatures due to the deterioration of the triple phase boundary. As sintering temperature is decreased, this high-frequency process becomes less pronounced and inductive artifacts become significant in the high-frequency portion of the data.

Since the measurement was done in air, the polarization resistance due to bulk gas diffusion is negligible and only two Voigt elements are necessary in the series fitting, one for R1, attributed to charge transfer, and one for R2, attributed to dissociative adsorption. As can be seen in Fig. 10(b), a single process with relatively large magnitude (R2) provides the major contribution to the profile. Above $10^4$ Hz, charge transfer becomes significant and causes the overall profile to deviate from the symmetric contribution due to adsorption. From each of the Voigt elements used, polarization resistance ($R_p$) values and constant phase element parameters were attained for charge transfer and adsorption. From the fitting using the nested equivalent circuit, double-layer capacitance, charge transfer resistance, and parameters associated with adsorption were attained.

The process was repeated at various sintering temperatures ranging between 1150 and 1325 °C. The sintering temperature range was chosen to begin above temperatures where sintering is incomplete and end below the melting temperature of LSM on YSZ, which is around 1450 °C [24]. Previous research shows that by 1400 °C, the charge transfer resistance has increased dramatically because the LSM layer is fully dense, effectively destroying any triple phase boundaries [4]. The impedance was performed at 800 °C in air. In future work, we will examine the cathodic reaction in low oxygen partial pressure regime and relate the bulk gas diffusion polarization resistance to porosity and tortuosity. Fig. 11(a) shows the sintering temperature dependence of charge transfer $R_p$ determined from both models. For both models, the charge transfer polarization resistance increases exponentially as
sintering temperature is increased. The individual nature of the Voigt elements in the series model may contribute to the improved fit for the series model as compared to the nested model for charge transfer resistance. The relatively large scatter in the charge transfer data for the nested model is related to the fact that charge transfer $R_P$ is an order of magnitude smaller than the adsorption $R_{ads}$ and the two processes are solved for simultaneously. In contrast, a subtraction technique which removed processes individually was used in the deconvolution for the series model. Fig. 11(b) shows the dependence of adsorption $R_{ads}$ on sintering temperature.

3.3. Effect of microstructure on impedance

Fig. 12 relates the change in electrochemical performance caused by varying sintering temperature to the corresponding microstructural changes by showing the influence of $L_{TPB}$ on $R_c$ and adsorption $R_{ads}$. Eqs. (4) and (5) are calculated by fitting the data in Fig. 12(a) which uses the nested equivalent circuit.

$$R_c = 7.43 (L_{TPB})^{-1.6}$$  \hspace{1cm} (4)

$$R_{ads} = 86.1 (L_{TPB})^{-2.1}.$$  \hspace{1cm} (5)

Fig. 12(b) makes use of the series equivalent circuit and fitting gives Eqs. (6) and (7).

$$R_c = 2.93 (L_{TPB})^{-3.5}$$ \hspace{1cm} (6)

$$R_{ads} = 96.8 (L_{TPB})^{-2.8}.$$ \hspace{1cm} (7)

The power dependence of $R_c$ on $L_{TPB}$ from the nested model, $-1.6$, is significantly different from that determined from the series model, $-3.5$. The power dependence of $R_{ads}$ on $L_{TPB}$ ($-2.1$) from the nested model is lower than the power dependence observed for the series model, $(L_{TPB})^{-2.8}$, but is identical to the value reported by Fleig [14] for the dependence of total resistance at 800 °C. This agreement is not unexpected since $R_{ads}$ has the larger magnitude of the two processes and makes up the majority of the cathodic impedance.

Fig. 13 relates $R_{ads}$ to surface area per unit volume, $S_V$. The fitting gives Eq. (8) for the nested equivalent circuit and Eq. (9) for the series equivalent circuit.

$$R_{ads} = 497 (S_V)^{-1.3}$$ \hspace{1cm} (8)

$$R_{ads} = 1030 (S_V)^{-1.8}.$$ \hspace{1cm} (9)

If adsorption polarization resistance shows a dependence on $L_{TPB}$ to the $-2$ power (as observed for the nested model) then the same process would show a dependence on pore surface area to the $-1$ power if the particles are relatively uniform in size and spherical in shape. For spherical particles, the circumference, $2\pi r$, is equal to $L_{TPB}$ and the surface area is equal to $4\pi r^2$. In this light, the power dependence observed for $R_{ads}$ on $L_{TPB}$, $-2.1$, is consistent with the dependence observed for $R_{ads}$ on $S_V$, $-1.3$, for the nested model.

4. Conclusion

We have evaluated the effects of sintering temperature on both the electrochemical and microstructural characteristics of LSM on YSZ symmetric cells. A FIB/SEM system was used to analyze the microstructure. 3-D images were used to determine the tortuosity at select sintering temperatures, while evenly spaced 2-D images were used for the evaluation of triple phase boundary length, volume normalized pore surface area, and porosity. Impedance data from LSM on YSZ symmetric samples measured at 800 °C was fitted to two commonly used equivalent circuits, generating different results.

Of the two equivalent circuits, it was found that the results obtained using the nested equivalent circuit are self-consistent for $L_{TPB}$ and $S_V$. Additionally, these results were consistent with the work of others. This may be an indication that the development of an equivalent circuit based on theory rather than a generic series model is necessary for analysis such as that performed in the present work. Comparison of electrochemical parameters from the nested model to the microstructural data revealed a dependence of $-1.6$ and $-2.1$ for charge transfer and adsorption on $L_{TPB}$, respectively and a dependence of adsorption related polarization resistance on $S_V$ to the $-1.3$ power.

Since adsorption related polarization resistance makes up the majority of the total cathodic resistance, this individual process can be compared to the results of others who reported only total cathodic resistance or conductivity. Our results were consistent with those of Fleig [14] whose analysis was performed on the same material at the same measurement temperature. Fleig concluded that since total cathodic resistance is proportional to $(L_{TPB})^{-2}$, and scales linearly with cathode thickness, bulk conductivity through the LSM is significant. Other authors have used higher measurement temperatures and produced results inconsistent with ours, however, few data points were used to demonstrate a relationship between resistance and $L_{TPB}$. Additionally, it is reported that a change from Warburg behavior to non-Warburg behavior occurs at around 800 °C indicating that the rate-limiting step may undergo a transition in this temperature regime [30]. The works of Kuznecov et al. (LSM, 950 °C) and Mizusaki et al. (LCM, 1000 °C) were performed at higher temperatures where faster reaction kinetics at the TPB and higher ionic conductivity in LSM are expected [12].

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References