

SIMPLE INFILTRATED MICROSTRUCTURE POLARIZATION LOSS ESTIMATION
(SIMPLE) MODEL VALIDATION AND ITS USE IN PREDICTING SOLID OXIDE FUEL
CELL CATHODE PERFORMANCE

By

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ABSTRACT

SIMPLE INFILTRATION MICROSTRUCTURE POLARIZATION LOSS ESTIMATION (SIMPLE) MODEL VALIDATION AND ITS PREDICTION IN SOLID OXIDE FUEL CELL CATHODES OPTIMIZATION

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In this work, $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ – $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (LSCF-GDC) nano-composite cathodes (NCCs) with different LSCF loading levels have been made by the infiltration method. The polarization resistance R_p has been characterized by Electrochemical Impedance Spectroscopy, which decreases with the LSCF loading level. The Simple Infiltration Microstructure Polarization Loss Estimation (SIMPLE) model has been used to predict the LSCF-GDC cathodes behavior. The model fits agree within 73% at all temperatures as R_p ranges over five orders of magnitude without using fitting parameter. The SIMPLE model has also been validated by fitting the literature existing NCCs produced in the literature, and the SIMPLE model calculated R_p agree to within 137% at all tested temperatures and compositions without the use of fitting parameters as the R_p varies over four orders of magnitude. The SIMPLE model has also been used to predict the R_p change with materials' properties and cathode microstructure. Artificially lowering the oxygen surface exchange resistance of the to one order of magnitude less than $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ and artificially increasing the ionic conductor ionic conductivity to one order of magnitude greater than $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ results in a decrease of the solid oxide fuel cell's operation temperature by $\sim 100^\circ\text{C}$.

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LIST OF ABBREVIATIONS

EC	Electronic conductor
GDC	Gadolinium doped ceria. The specific composition in this thesis is $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$
IC	Ionic conductor
LSCF	$(\text{La},\text{Sr})(\text{Co},\text{Fe})\text{O}_{3-\delta}$. The specific composition in this thesis is $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$.
LSM	$(\text{La},\text{Sr})\text{MnO}_{3-\delta}$. The specific composition in this thesis is $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.98}\text{MnO}_{3-\delta}$
MIEC	Mixed ionic electronic conductor
NCC	Nano-composite cathode
SEM	Scanning electron microscopy
SOFC	Solid oxide fuel cell
TFV	Tanner, Fung and Virkar
TGA	Thermogravimetric analysis
TPB	Triple phase boundary
XRD	X-ray diffraction
YSZ	Yttria stabilized zirconia

LIST OF SYMBOLS

δ	oxygen nonstoichiometry
σ	IC scaffold ionic conductivity
θ	the angle between the incident X-ray and the sample plane
λ	wave length
A	GDC pellet area
A_{ind}	individual MIEC nano-particle surface area
A_{IC}	total IC surface area
A_{MIEC}	total MIEC surface area
A_G	cathode geometric area
d	MIEC particle diameter
D	diffusivity
h	cathode thickness
h_C	characteristic cathode thickness
k_B	Boltzmann constant, 8.617×10^{-5} eV/K
l	GDC pellet thickness
$N_{nano-particle}$	MIEC nano-particle number
N_r	repeat unit number
p	porosity
r	repeat unit thickness

T	temperature
R_a	roughness
R_{int}	MIEC-IC interfacial resistance
R_{ohmic}	ohmic resistance
R_p	polarization resistance
R_S	intrinsic MIEC surface exchange resistance
w	half width of IC scaffold column
x	water of hydration number

1 Introduction

1.1 Fuel Cells and Solid Oxide Fuel Cell (SOFC)

A fuel cell is a high efficiency (up to 80%) (1) energy conversion device, which can directly turn the fuels' chemical energy into electricity. Compared to combustion, which has an average efficiency of 20% only because it needs to turn fuels' chemical energy into heat first and then turn heat into mechanical energy and finally into electricity, fuel cells avoid lots of energy loss during the conversion process. Thus fuel cells are favored to become one of the most attractive solutions for the worldwide increasing demand for electricity and the exhaustion of primary energy sources problem(2). Compared to batteries, fuel cells can continuously generate electricity as long as the fuel and oxygen are fed to the cell continuously. The primary fuel used especially in research is hydrogen. With the development of technology, more and more hydrocarbons such as methane and propane can be used as fuels especially for the high-temperature fuel cells (3). Fuel cells consume fuel and oxygen, and produce electricity and water through some electrochemical process, as well as some heat.

Fuel cells consist of an anode, cathode and electrolyte (see Figure 1.1) (4). There are many different types of fuel cells, and they are characterized and denominated by their electrolyte materials. The major fuel cells are summarized and compared in Table 1.1.

Among the different types of fuel cells, solid oxide fuel cell (SOFC) has superior advantages. SOFCs provide high-quality waste heat for cogeneration applications due to its high operation temperature (600 ~ 1000 °C); it does not need to use a precious metal as the catalyst, and it is

flexible toward fuels. The most important point is that it has very high electrical efficiency (50~60%).

Table 1.1 Comparison of Major Types of Fuel Cells From Reference (1)

Fuel cell type	Electrolyte	Operation temperature (°C)	Catalyst	Fuel compatibility	Electrical efficiency (%)
Phosphoric Acid Fuel Cell	Liquid H ₃ PO ₄	200	platinum	H ₂	40
Polymer Electrolyte Membrane Fuel Cell	Polymer membrane	80	platinum	H ₂ , methanol	40-50
Alkaline Fuel Cell	Liquid KOH	60-220	platinum	H ₂	50
Molten Carbonate Fuel Cell	Molten carbonate	650	nickel	H ₂ , CH ₄	45-55
Solid Oxide Fuel Cell	ceramic	600-1000	perovskite	H ₂ , CH ₄ , CO, other hydrocarbons	50-60

SOFC has a relatively long history. The galvanic solid electrolyte gas cell was first discovered by Gaugain in 1853 (5). In 1937 Baur and Preis studied several materials for electrolyte and finally found “Nernst-Mass” which consist of 85% ZrO₂ and 15% Y₂O₃ had lowest conductivity among several materials they studied (6). They tried to improve the “Nernst-Mass” and proposed a new cell with the improved Nernst-Mass as the electrolyte. The calculated power density of this cell was competitive compared with the power plants at that time. Another revolutionary event in the SOFC history is that Weissbart and Ruka made a tubular fuel cell at Westinghouse Electric Corporation in 1962 (7). This fuel cell used (ZrO₂)_{0.85}(CaO)_{0.15} as the electrolyte material, and porous Pt as the electrodes. Oxygen was

fed to the cathode, and hydrogen or methane was fed to the anode. This fuel cell gave a current density of 10 mA/cm^2 at 810°C and at 0.7 V (3, 5).

A schematic of a SOFC is provided in Figure 1.1 (4). In microscopic view, the hydrogen is continuously fed and decomposed at the anode and gives electrons to the cathode side through external circuit. On the cathode side, one oxygen molecule gets into the cathode materials' vacancies and is reduced to two oxygen ions in the oxygen ion sites. The oxygen ions sites migrate across the cathode and the electrolyte to the anode, and combine with H_2 forming H_2O .

The half cell reactions can be expressed in Kroger-Vink notation:

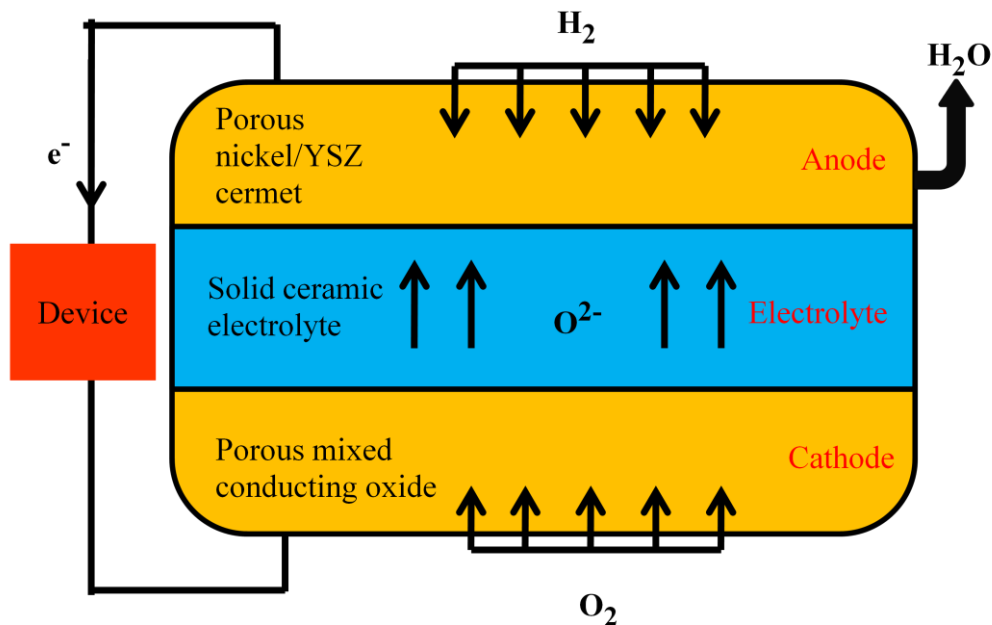
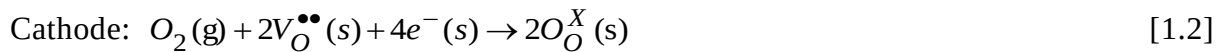
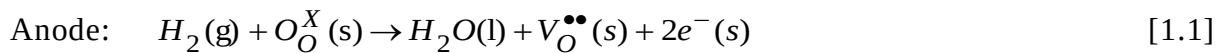


Figure 1.1 Schematic of a solid oxide fuel cell (For interpretation of the references to color in this and all other figures, the reader is referred to the electronic version of this thesis)

1.2 SOFC Infiltrated Cathodes

The oxygen reduction reaction has very sluggish kinetics, which limits the whole reaction rate of the SOFC. Thus SOFCs always have to operate at very high temperature ($\sim 1000^{\circ}\text{C}$) to thermally activate the electrolyte conductivity and accelerate the oxygen reduction reaction at the cathode. In order to improve the cathode performance, micro-composite cathodes which consist of micron-sized mixed ionic electronic conductor (MIEC) and ionic conductor (IC) have been made because it greatly increases the oxygen reduction rate by increasing the reaction sites and accelerate the oxygen ion conduction (8). The composite cathode provides paths for all the three components – oxygen gas, electrons and oxygen vacancies (Refer to Equation [1.2]), thus extends the oxygen reduction reaction from the interface between electrolyte and cathode to the whole cathode. The operation temperature for a typical LSM-YSZ micro-composite cathode based SOFC has to operate above below 950°C to ensure the R_p is below $0.1\ \Omega\text{cm}^2$. Further, nano-composite cathodes (NCCs) made by the infiltration method have received much attention in the literature (9-19) due to their excellent low-temperature performance. In particular, Nicholas and Barnett (16) fabricated $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ (SSC) – $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (GDC) infiltrated cathodes with a polarization resistance (R_p) of $0.1\ \Omega\text{cm}^2$ at 600°C . Further, Zhao et al. (14) fabricated $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ – $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ (SSC-SDC) cathodes with a R_p of $0.1\ \Omega\text{cm}^2$ at 570°C via the infiltration technique (20).

1.3 Introduction to the SIMPLE Model

There is a model of composite electrode derived by Tanner, Fung and Virkar in 1997 (21). It is the first one that derives the relationship between charge-transfer resistance R_{ct} of SOFC composite electrodes and cathode microstructure as well as cathode material intrinsic properties. The Tanner-Fung-Virkar (TFV) model describes micron-sized electron conductor/micron-sized IC composite cathodes, by assuming that the resistance associated with the triple phase boundary (TPB) reaction can be uniformly spread over the ionic-conducting surface. Recently, a Simple Infiltrated Microstructure Polarization Loss Estimation (SIMPLE) model has been used to describe nano-sized MIEC/micron-sized IC composite cathodes and model the performance of $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ – $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ (SSC-SDC) (16) $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSFC) – GDC (22) and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (LSCF) – GDC (23) cathodes. The SIMPLE model is a modification of the TFV model (22). The MIEC/IC cathodes have a surface reaction mechanism (8), and the MIEC materials have a higher ionic transference number than EC has. The SIMPLE model approximates the symmetric MIEC/IC cathodes geometry into uniform hemispherical MIEC particles on IC column shaped scaffold as shown in Figure 2.1.

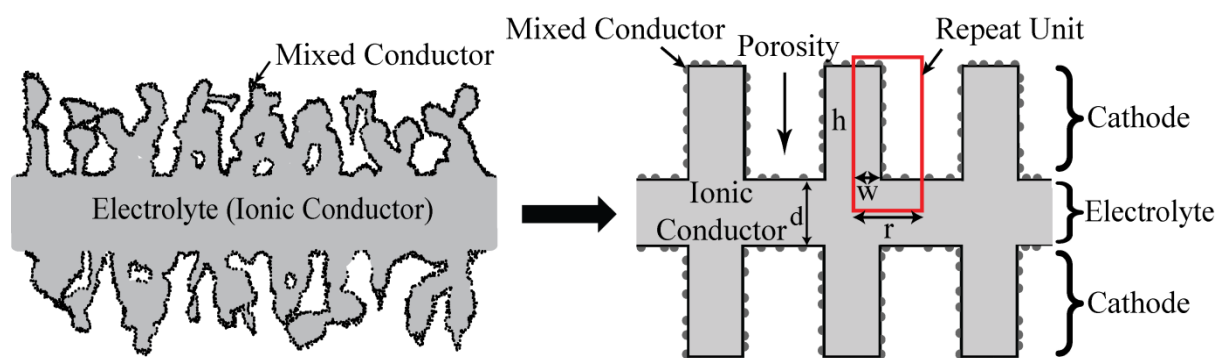


Figure 1.2 Approximation from a schematic of composite cathode (left) to an idealized

Figure 1.2 (cont'd)

SIMPLE Model cathode geometry (right), see Table 3.2 for variable definitions. (Figure not drawn to scale)

The SIMPLE model accounts for polarization resistance losses due to the difficulty of incorporating oxygen ions into the MIEC and the difficulty in diffusing oxygen ions through the bulk of the IC. It assumes that the interfacial resistance R_{int} between the MIEC and IC is negligible which is true for all the cobaltite MIEC-ionic conductor interfaces measured to date since it is about 10-100 times less than the ionic surface exchange resistance below 700°C (the oxygen surface exchange resistance R_S and the MIEC-IC interfacial resistance, R_{int} , of LSCF on $Y_{0.16}Zr_{0.84}O_{1.92}$ measured between 600 and 700°C, the R_S and R_{int} of LSCF on CGO measured at 500°C and the R_S and R_{int} of BSCF on $Y_{0.16}Zr_{0.84}O_{1.92}$ measured between 500 and 700°C are discussed in Baumann et al.(24)). The SIMPLE model also neglects the resistance contributed from the gas phase diffusion within the cathode and the current collector. The SIMPLE model also assumes that the electronic conductivity of MIEC is high enough so that the resistance from electron transfer can be neglected; the ionic transport in MIEC can also be neglected because the particle size is below the characteristic thickness of the materials. Since 1) the oxygen flux is small, 2) the porosity of the cathode is large, and 3) predictions are made at open circuit condition, the concentration polarization resistance resulting from poor gas-phase diffusion should have little contribution to the total resistance. The electron transfer resistance is not expected to be significant for heavily infiltrated cathodes because the MIEC is well connected and the MIEC has high electronic

conductivity. The MIEC materials provide better performance than electron conductor since they expand the reaction sites to the whole surface of the MIEC instead of the TPB only.

This idealized microstructure involves the definition of “repeat unit”. All the other parts are just the same with the “repeat unit”, thus the whole cell’s R_P is the product of the number of repeat units and the R_P in a single repeat unit. The R_P in a single repeat unit is calculated by Nernst-Planck equation which reduces to the Laplace equation. Finally, the analytically solution is:

$$R_P = \frac{r \left(\frac{R_S A_{IC}}{A_{MIEC}} \right)}{\left(\frac{1+\beta}{1+\beta \text{Exp}\left(\frac{-2h}{\alpha}\right)} \right) r(1-p) \text{Exp}\left(\frac{-h}{\alpha}\right) + \left(\frac{1+\beta \text{Exp}\left(\frac{-h}{\alpha}\right)}{1+\beta \text{Exp}\left(\frac{-2h}{\alpha}\right)} \right) \alpha \left(1 - \text{Exp}\left(\frac{-h}{\alpha}\right) \right) + pr} \quad [1.4]$$

with

$$\alpha = \sqrt{\sigma r(1-p) \frac{R_S A_{IC}}{A_{MIEC}}} \quad [1.5]$$

and

$$\beta = \frac{\sigma \frac{R_S A_{IC}}{A_{MIEC}} - \alpha}{\sigma \frac{R_S A_{IC}}{A_{MIEC}} + \alpha} \quad [1.6]$$

The definition of each parameter can be found in Table 3.1, which will be fully discussed in Chapter 3.

1.4 Objectives

This work aims at validating the SIMPLE model, which calculates the R_p of the SOFC cathode and consequently reflects the performance of the cathode, by fitting both the literature cathodes and the fabricated cathodes. Another goal is to understand the structure - properties - performance relations by using the SIMPLE model. This work also aims to identify optimal conditions for the SOFC cathodes from the predictions of the SIMPLE model. This will result in that SOFC can be operated at intermediate temperature.

2 Experimental Techniques

2.1 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) is a technique used to analyze the mass change of a sample with temperature. Generally, the sample used in this method will either decompose or react with the atmosphere at elevated temperature due to gas formation, oxidation and so on (25). The equipment used for TGA always contains a furnace and a balance. The furnace is controlled by a computer program, and can elevate the temperature at a certain speed. The pan of the balance is made of inert material such as Pt and ceramics, so that it will neither react with the sample nor decompose by itself. A TA Instruments Q500 thermogravimetric analyzer was used in the experiments to analyze the water of hydration number of nitrates. The furnace of this analyzer has the temperature range from room temperature to 1000⁰C (26). The reaction of the nitrates and the maximum temperature are known beforehand. From the initial weight and the final weight of the sample and the molecular weight, the water of hydration number can be determined. Taking La(NO₃)₃ · xH₂O as example, the decomposition reaction can be written as:



According to the conservation of La ion in the initial and final solid phases, the following relation exists:

$$\frac{\text{Molecular weight of La(NO}_3)_3 \cdot x\text{H}_2\text{O}}{\text{Molecular weight of } 1/2 \text{ La}_2\text{O}_3} = \frac{\text{Initial weight of the sample}}{\text{Final weight of the sample}} \quad [2.2]$$

Thus,

$$\frac{324.92032 + 18.01528x}{162.9046} = \frac{23.93983 \text{ mg}}{8.89407 \text{ mg}}$$

$$x = 6.304$$

Thus this sample had 6.304 water of hydrations per mole.

2.2 Three Roll Mill

The three roll mill is used for mixing the powdered material (which in our case is either GDC powder or LSM powder) and the organic dispersant in order to distribute the powder uniformly in the liquid phase making a homogeneous paste.

As shown in Figure 2.1, there are three different functioning rolls in a three roll mill. The distance between the feed roll and the center roll controls the input quantity and consequently the throughput quantity, while the distance between the center roll and the apron roll directly controls throughput quantity. Overall, the smaller the rolling gap, the finer the dispersion will be and the lower ink throughput (27).

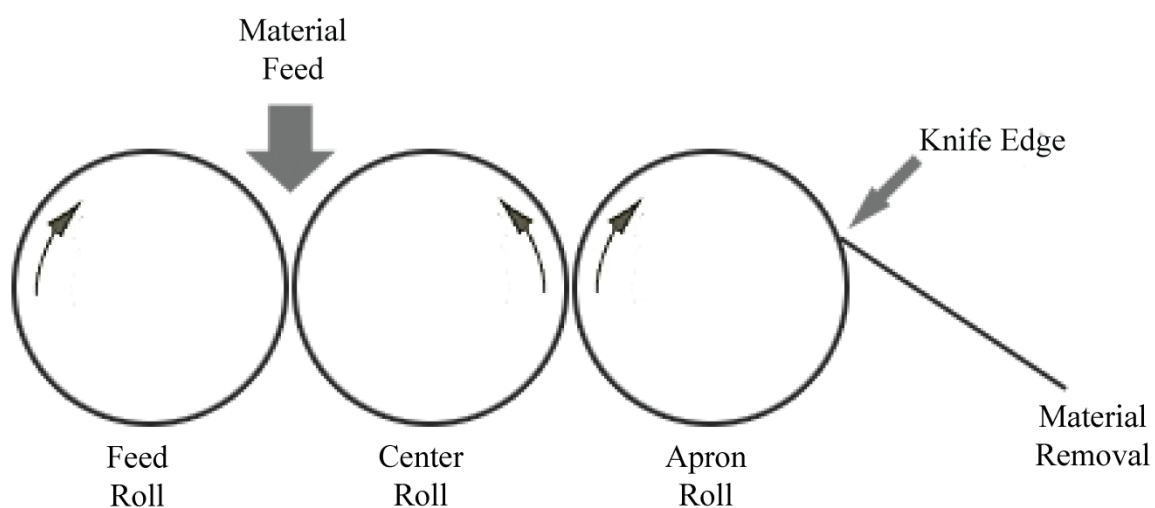


Figure 2.1 Schematic of a three roll mill from reference

The steps of making ink with three roll mill are as follows. The desired amount of the GDC or

LSM with organic vehicle is weighed and mixed by using a stir rod. The raw mixture was dropped in between the feed roll and the center roll by using a plastic spatula. Adjust the rolling speed by the speed control system and adjust the distance between the rolls by turning the particular knobs. A Thrifty Trowel 1 1/2 inch putty knife was used as a scraper. The well milled ink was scraped manually and collected into a vial.

2.3 Screen Printing

Screen printing is an important process in SOFC cathode fabrication. It is a method that creates a thin porous layer film on substrate. The screen printed thin film layer can be anywhere between 1~100 μm thick, which is not thick enough to support itself. Thus supporting substrate is mandatory. In our case, the substrate is a dense supporting electrolyte made by hydraulic pressing, firing and polishing of GDC powder

Here an AMI Presco Model CP-885 screen printer is used. The screen printer includes several important parts. The screen is a 12 inch $\times$ 12 inch screen, with a warp wire direction 22.5 degree from the frame. The wire diameter and mesh count control the aperture size and open area percentage. The thinner the wire and the smaller the mesh count number, the larger the open area percentage and the thinner the printed layer thickness will be. Here we use the wire diameter of 0.008 inch and a total of 290 wire/inch screen, which leads to a 60% open area. The underside of the screen has an emulsion layer which prevents the ink penetrating the screen except in the image area. The image is a 0.5 cm^2 circle positioned in the center of the screen and producing an exact 0.5 cm^2 printed layer. The distance between the screen and the

substrate is called the “snap-off distance”. A 0.023 inch snap-off distance was employed for the experiments described in this thesis.

The squeegee blade is used to print the ink on the substrate as shown in Figure 2.2, which has many important variables influencing the process. There are many variables to control the squeegee and consequently the screen printing process (Figure 2.3). The squeegee hardness is represented by variable a; b is thickness; c is free height; d is angle; e is pressure; f is speed and g is edge. The harder the squeegee and the faster the printing speed, the less ink that will be deposited on the substrate. The closer the angle is to 90° from the substrate, the less ink that will be deposited. The greater the pressure, the rounder the squeegee edge, the more ink deposit. In our setup, the squeegee had a diamond shape with sharp edge and 0 free height, and 45° angle from the substrate surface. The printing speed was 5 in/sec.

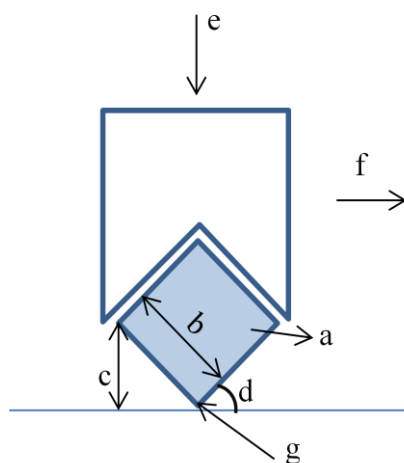


Figure 2.2 Squeegee variables (28)

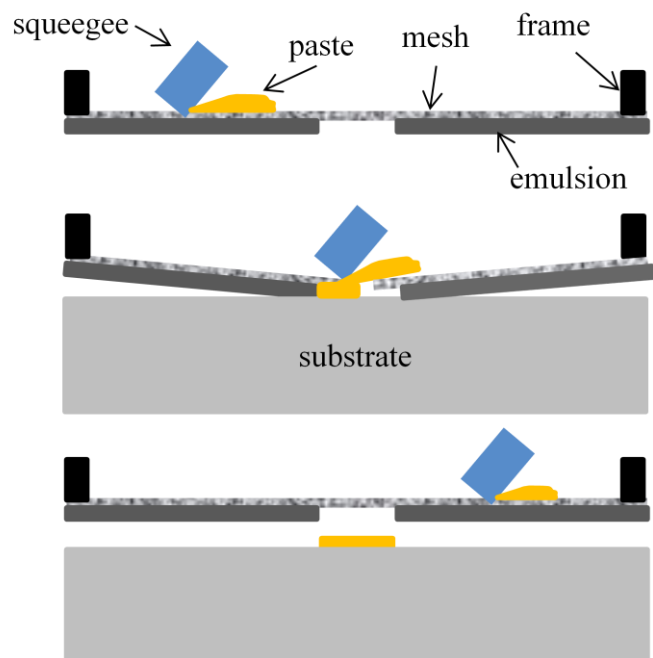


Figure 2.3 Screen printing process (29)

The operation of the screen printer is shown in Figure 2.3 (29). The substrate which is GDC electrolyte pellet in our case was positioned in the center of the carriage. The vacuum generated in the carriage would pin the pellet firmly and make it stable on the station during printing cycle. Send the station back under the screen. The print head assembly was raised in order to clean the screen. A little ink was put on the screen. The print head assembly was lowered. Make sure the mode was set at “run”. After the “cycle” pedal was hit, the screen printer would automatically do the following as shown in Figure 2.3 (29): lower the squeegee, give the squeegee downward pressure as well as push the squeegee forward. The squeegee would push the ink forward and spread it over the screen. When the ink reaches the circular imaged region, the ink will go through the screen opening, reach the substrate and adhere to it, leaving a uniform thin layer. Then the squeegee will rise up, step back to return to the original position before print. The well printed pellets would be aged at the room temperature for 5 min to let the ink flow around, and then placed in the 80 °C oven for another 5 min to remove the solvent. If multiple layers are needed to achieve a certain thickness, the above steps should be repeated.

2.4 Profilometry

A profiler is used to provide the information of sample's surface thickness and roughness. The profiler used here is Dektak 3 surface profilometer, which is a contact profilometer. The general operation steps are as follows. The sample is located on the stage, which can be moved in the X and Y directions, rotated, and/or tilted. The stylus will be lowered down and the tip will contact the sample surface. The stylus will scan along the surface of the sample at a given

scan speed over a given scan length to show the profile of the surface. When the scan is done, the stylus will rise up and step back to its original position. This type of profiler measures the vertical displacement of the stylus, which reflects the sample's surface profile.

The Dektak 3 profiler has a 0.5 nm vertical resolution. It can accept sample thickness up to 19 mm, a measurement range up to 65 microns and a scan length up to 30 mm. It can automatically give the roughness of the scanned region(30). The roughness is arithmetic average, which is defined as the arithmetic average deviation from the mean value. The equation is as follows

$$R_a = \frac{1}{n} \sum_{i=1}^n |y_i| \quad [2.3]$$

R_a is arithmetic average; y_i is the i th data point's absolute value of deviation from the mean line.

2.5 Scanning Electron Microscopy (SEM)

Scanning Electron Microscope (SEM) is a kind of device which is used to form magnified images of a sample by scanning it with a beam of electrons. Compared to light, electrons have the advantage of providing much larger resolution, which means that the SEM can distinguish finer details in nanometer scale. The SEM can also provide wider magnification range and higher depth of field than the reflected light microscope (31, 32).

The theory of generating images is as follows. The electron beam will interact with the surface atoms of the sample, forming a teardrop shaped interaction volume. The higher the accelerating

voltage of the electron beam and the smaller the average atomic number of the sample, the larger the interaction volume will be. If the incident electrons interact with the orbital shell electrons in the sample, there will be secondary electrons produced. The energy of the secondary electrons is low, so that they are easily attracted by the positive charged Faraday cage in the detector. The scintillator in the detector has a higher positive voltage in order to convert the secondary electrons to photons. The light information will be magnified and the output which can be converted to signal and displayed on the monitor (32).

The equipment used in the experiments in this thesis was a Zeiss Auriga dual-column focused ion beam/field emission scanning electron microscope. It had a 1.0 nm resolution when the voltage is as high as 15kV and the specimen is placed at optimum working distance, and a 1.9 nm resolution when the voltage is 1kV and the specimen is placed at corresponding optimum working distance. The magnification range is from $12\times$ to $1,000,000\times$. The electron source is the Schottky field emitter (33).

For taking images of the LSCF-GDC cathodes by SEM, the symmetric cathode was fractured in order to expose the cathode-electrolyte-cathode interface. The sample was then mounted vertically on the stub. Since the sample is not a good conductor, ~ 10 nm of gold was sputtered on the sample with Denton Vacuum Desk II under vacuum before taking SEM images. The chamber was evacuated in order to guarantee electrons generation and prevent the electrons from colliding with the gas molecules. A high quality image of area of interest can be generated by toggling the “aperture” and the “stigmator” knobs and adjusting the sample stage.

2.6 X-Ray Diffraction (XRD)

X-ray diffraction (XRD) was used for the determination of phases and phase crystal structure. X-rays used in diffraction have the wavelengths between 0.5 and 2.5 Å (34). The basic principle behind XRD is Bragg's law. As shown in Figure 2.4, a beam of parallel X-ray with wavelength λ is shot on the crystal plane. The angle between incident beam and the sample plane is defined as θ . The diffracted beam will scatter in all directions, but only in the direction like line 1' and 2' is in phase, so that in this direction the beam will add up and reinforce. This geometric relation can be represented by Bragg's law(34):

$$n\lambda = 2d'\sin\theta \quad [2.4]$$

where the variables are defined in Figure 2.4. In a perfect crystal, the atoms have a periodic order in the lattice, so that the diffracted beam has relations with the atomic arrangements.

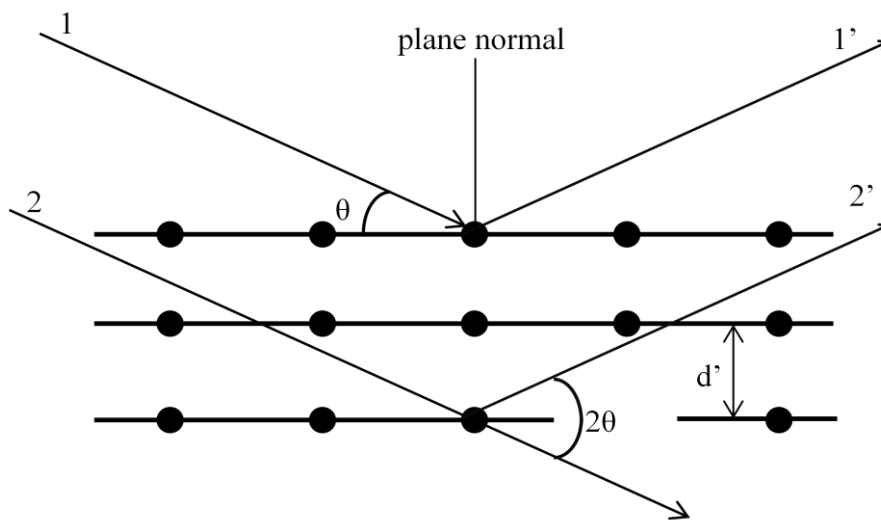


Figure 2.4 X-ray diffraction of a crystal (34)

By using known wavelength X-rays and measuring θ , the spacing d' can be determined. The principle of operation is that X-rays from the X-ray generator T with a certain angle θ from

the plane of the sample are emitted on the sample C (Figure 2.5). The diffracted beam will be detected by a detector D located at the other side of the plane normal, which has a corresponding intersectional angle θ from the sample. In practice, the sample is fixed, and both T and D can rotate around the center O (34). The intensity of the diffracted beam will be measured and spacing d' will be calculated from Braggs' law. This procedure will be repeated for a range of angles θ . In a measured XRD spectrum, the peak position provides the information of d' spacing, the phase identification, and the lattice constant. The integrated intensity provides the information of percent crystallinity. The peak widths give the information of crystallinity and particle size (35).

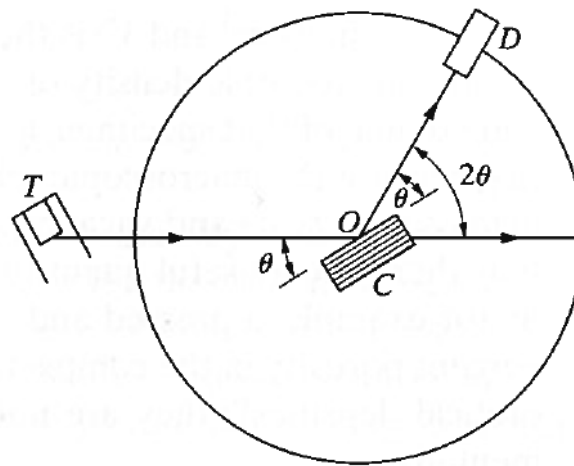


Figure 2.5 Schematic of an X-ray diffractometer (34)

The X-ray diffraction equipment used is Rigaku MiniFlex II Desktop X-ray diffractometer. This XRD equipment uses Cu as the target, Ni as $K\beta$ suppression filter, producing $K\alpha$ radiation(35). The tube output voltage was fixed at 30kV, and the current was fixed at 15 mA. In the experiment, 2θ ranged from 20° to 80° . The scanning speed was $0.5^\circ/\text{min}$, and the sampling width was 0.05° .

2.7 Impedance Spectroscopy

Impedance spectroscopy is a technique used to measure materials' impedance as a function of frequency f . Generally, a low amplitude sinusoidal perturbation

$$\eta = E \cos 2\pi ft \quad [2.5]$$

will be imposed on the test material (36) where η is the overpotential, t is time, E is amplitude of the imposed perturbation. The induced current will be measured at various frequencies. A Nyquist plot is used to present the measured impedance, in which the real part of the impedance is as the x axis and the minus of imaginary part is as y axis (37). The graph is generally an arc along the x axis. The left intersection point with x axis represents the value of ohmic resistance, and the distance between the arc represents the polarization resistance (38). Zahner IM6 was used for the experiments. The frequency range used was from 100mHz to 100kHz. The overpotential was set as 0. The amplitude is 100mV .

3 SIMPLE Model Validation by Comparing Against Literature Data

3.1 Introduction to the SIMPLE Model Calculation Method

The SIMPLE model R_P predictions of heavily infiltrated cathodes were made from all literature sources containing enough information to do a calculation. The calculations were only performed on heavily infiltrated cathodes because past studies (23, 39) have shown that poor connectivity of the MIEC infiltrate at low infiltrate loadings can lead to electronic conduction losses not accounted for by the SIMPLE model. Table 3.1 indicates the data sources for each parameter and Table 3.2 shows the literature-extracted values of the geometrical parameters used for the SIMPLE model calculations.

To model the situation where the polarization resistance of a NCC is completely dominated by the high surface resistance of the MIEC nano-particles (i.e. there are no significant bulk transport losses through the ionic conducting backbone), the polarization resistance is modeled, based on the definition of area specific resistance, as:

$$R_P = \frac{R_S A_G}{A_{MIEC}} \quad [3.1]$$

where A_G is the geometric (a.k.a. footprint) area of the cathode, and the other variables have their previously defined meanings.

The data extraction method and the input data sources are summarized in Table 3.1.

Table 3.1 SIMPLE model parameters and data sources

Parameter	Definition	Data Source
w	Half width of ion conducting scaffold column	Estimated from published scanning electron micrographs
d	MIEC hemispherical diameter	Value stated in publication text or estimated from published scanning electron micrographs
r	Repeat unit thickness	Estimated using the relation $r=w/(1-p)$ from Reference (21)
h	Cathode thickness	Value stated in publication text
p	Non-infiltrated cathode porosity	Value stated in publication text
A_{IC}	Total IC surface area	Calculated from w , h , p and the published electrode geometric area
A_{MIEC}	Total MIEC surface area	Calculated from infiltrate loading level and d
σ	Ion conducting scaffold ionic conductivity	Values taken from Reference (40) for $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$, Reference (41) for $\text{Y}_{0.8}\text{Zr}_{0.92}\text{O}_{1.9}$, Reference (42) for $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$, Reference (43) for $\text{Y}_{0.06}\text{Al}_{0.4}\text{Zr}_{0.77}\text{O}_{2.23}$ and $\text{Sc}_{0.2}\text{Zr}_{0.9}\text{O}_{2.1}$
R_S	Intrinsic MIEC surface exchange resistance	Values taken from Reference (24) and (44)

Table 3.2 SIMPLE model parameter values of literature existing cathodes

Author	Infiltrated Cathode Abbreviation	d (nm)	r (nm)	h (μm)	A_G (cm^2)	p (%)	Infiltrate/ Cathode Vol.(%)	Ref .
Zhao et al	$\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta} - \text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.95}$ SSC-GDC	46	1700	100	1.77	60	31	(39)
Zhao et al	$\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta} - \text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ LSC-SDC	80	9000	50	1.0	65	30	(13)
Huang et al	$\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta} - \text{Y}_{0.8}\text{Zr}_{0.92}\text{O}_{1.9}$ (Graphite pore former) LSC-YSZ(g)	200	1100	60	0.5	65	18	(9)
Huang et al	$\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta} - \text{Y}_{0.8}\text{Zr}_{0.92}\text{O}_{1.9}$ (Polystyrene pore former) LSC-YSZ(p)	200	22000	60	0.5	60	20	(9)
Nicholas et al	$\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta} - \text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ SSC-GDC	38	82	15	0.5	32	10	(14)
K üngas et al	$\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_{3-\delta} - \text{Y}_{0.8}\text{Zr}_{0.92}\text{O}_{1.9}$	–	690	38	0.35	65	20	(45)
K üngas et al	$\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_{3-\delta}$ $- \text{Y}_{0.06}\text{Al}_{0.4}\text{Zr}_{0.77}\text{O}_{2.23}$ LSF-YAZ	50	800	50	0.35	65	20	(43)
K üngas et al	$\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_{3-\delta} - \text{Y}_{0.8}\text{Zr}_{0.92}\text{O}_{1.9}$ LSF-YSZ	50	800	50	0.35	65	20	(43)
K üngas et al	$\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_{3-\delta} - \text{Sc}_{0.2}\text{Zr}_{0.9}\text{O}_{2.1}$ LSF-ScSZ	50	800	50	0.35	65	20	(43)

3.2 SIMPLE Model Literature Data Comparison Results

Figure 3.1 shows Arrhenius plots of the experimentally measured and SIMPLE model

predicted R_p . The experimental measurements and the SIMPLE model predictions agree to within 87% for most compositions, at all temperatures, without the use of fitting parameters, even as the polarization resistance varies over 4 orders of magnitude, despite the geometric assumptions of the SIMPLE model and the possibility of unwanted phases produced by the infiltration technique. Only LSC-YSZ(g) has a maximum of 137% error due to lower experimental data than predicted. Figure 3.1 also shows that today's best MIEC-IC nano-composite cathodes, those of Ref. (14), achieve the $\sim 0.1 \Omega\text{cm}^2$ target cited as necessary for fuel cell operation (20) at a temperature of $\sim 570^\circ\text{C}$.

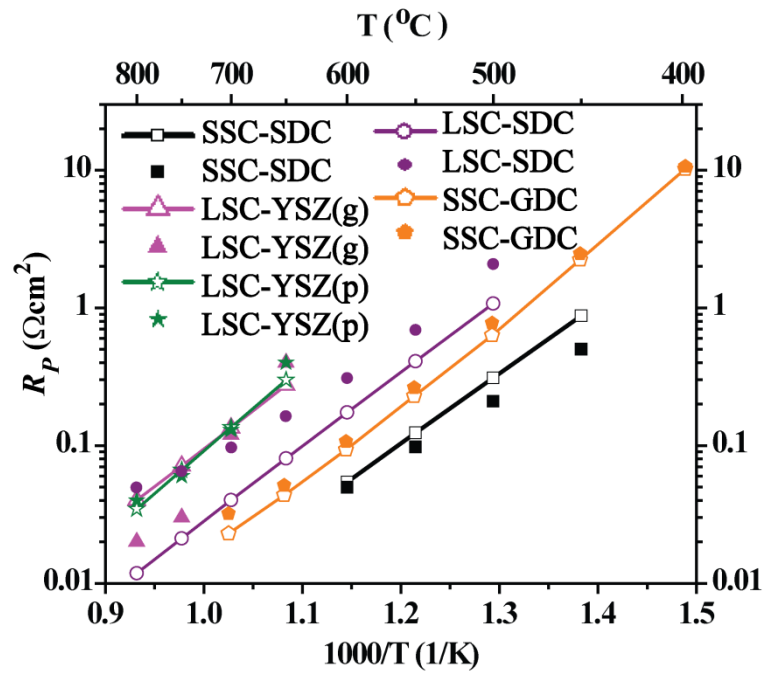


Figure 3.1 SIMPLE model polarization resistance predictions (lines with open symbols) and experimental measurements (closed symbols). See Table 3.2 for references.

Figure 3.2 shows the polarization resistance as a function of MIEC gravimetric surface area for LSF-YSZ NCCs. The closed squares are experimental measurements for Kungas et al's LSF-YSZ in Reference (45), and the solid line is the SIMPLE model prediction, assuming that

the scaffold is fully covered by MIEC. The different A_{MIEC} is achieved by varying the calcination temperature. Other geometrical values are listed in Table 3.2. A_{MIEC} is the product of the cathode total weight (which is calculated from the cathode geometry, LSF and YSZ volume ratio, and the theoretical density of LSF and YSZ) and the BET gravimetric surface area. The repeat unit thickness r is calculated from the scaffold surface area according to the equation:

$$(r + h) \cdot N_r \cdot \sqrt{A_G} = A_{IC} \quad [3.2]$$

where

$$N_r = \frac{\sqrt{A_G}}{r} \quad [3.3]$$

which is $0.48 \text{ m}^2/\text{g}$ (i.e. the total YSZ scaffold surface area A_{IC} is about 19.6 cm^2). r is 700nm here for all cases.

The SIMPLE model has a close prediction especially when the BET surface area is above $0.5 \text{ m}^2/\text{g}$, which is the percolation limit in this case. According to Nicholas et al (23), the SIMPLE model fails when the infiltrated particles are not percolated because the SIMPLE model assumes that the networks are so well connected that there will not be a percolation problem. The errors are still within 78% in all cases. Figure 3.2 also shows that the smaller the MIEC surface area, the fewer the reaction sites, and subsequently the lower the R_p will be. When the BET gravimetric surface area is $\sim 1.3 \text{ m}^2/\text{g}$, R_p can be decreased to about $0.1 \Omega \text{ cm}^2$ according to the literature extracted data. Since the cell was calcinated and then measured the surface area, and then calcinated at elevated temperature to decrease the LSF surface area, the scaffold may

be also coarsened after several thermal cycles and at high temperatures especially when the particles are in nano scale according to Reference (46). Thus the actual repeat unit thickness r might be larger than 700 nm when the surface area is decreased to lower than $0.5 \text{ m}^2/\text{g}$ by calcination. There may also be other geometric structure changes, thus more details are needed to give a more precise prediction.

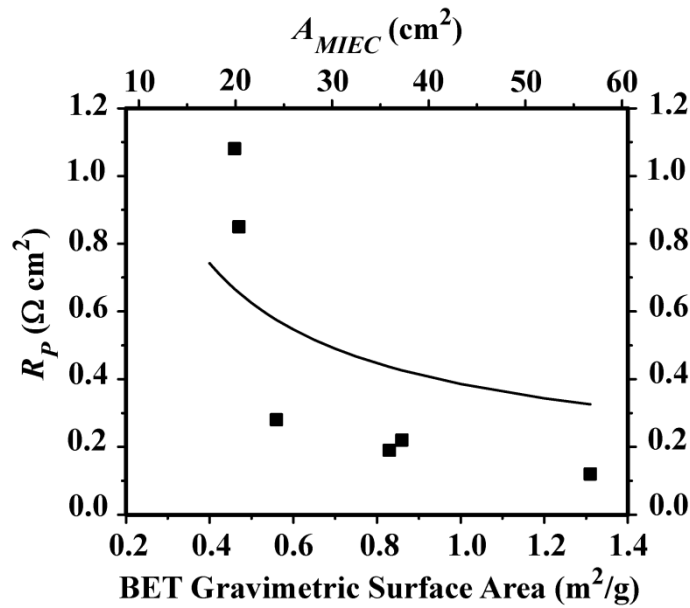


Figure 3.2 SIMPLE model polarization resistance predictions (solid line) and experimental measurement for LSF-YSZ nano-composite cathodes with various LSF surface areas (45)

Figure 3.3 shows the experimentally measured and SIMPLE model predicted R_p at 700°C by varying the scaffold ionic conductivity. The diamond data points are experimental data for the LSF infiltrated cathodes of Ref (43). Some commonly used ionic conductors' σ at 700°C are labeled. The SIMPLE model predictions have the same trend with the experimental measured results. The predicted value agrees with the experimental results to within 72%. Figure 3.3 also predicts the relation between R_p and IC conductivity at 700°C . As $\sigma \rightarrow 0$, according to Equation [1.4] R_p tends to

$$R_S A_{IC} / (p A_{MIEC}) \quad [3.4]$$

which indeed in the left y-intercept in Figure 3.3. When σ goes to infinity, R_P goes to SR limit in which case the resistance is totally dominated by the surface reaction resistance which indeed in the right y-intercept in Figure 3.3. This plot also shows the lower the surface resistance, the lower the R_P will be. When σ goes from 0 to infinity, the R_P can be lowered by 2 orders of magnitude.

According to Nicholas and Barnett, the nano-composite cathodes have a characteristic cathode thickness proportional to the σ of the IC, R_S of the MIEC, as well as A_G and $1/A_{MIEC}$, which is defined as:

$$h_C = \sigma R_S \frac{A_G}{A_{MIEC}} \quad [3.5]$$

When the characteristic cathode thickness h_C is exactly the same with the reported cathode thickness 50 μm in Figure 3.3, the characteristic conductivity σ has been calculated from Equation [3.5] and shown as bars in the plot, which is almost shown at the end of the straight line region. The region to the left of the bar is both surface and bulk controlled. The region to the right of the bar is completely surface controlled.

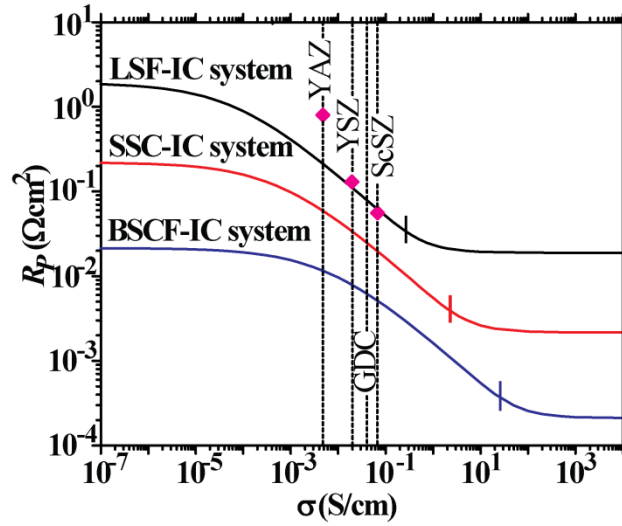


Figure 3.3 SIMPLE Model predictions for LSF, SSC, and BSCF infiltrated cathodes with different ionic conductor backbones at 700⁰C

3.3 Conclusions

The SIMPLE model has been applied to all the available NCCs reported in literature with enough information for a calculation. The SIMPLE model is able to predict the behavior of a variety of MIEC-IC NCCs to within 137% at all tested temperatures for all compositions even when the R_p varies four orders of magnitudes. The SIMPLE model is also able to predict the behavior of various MIEC-IC cathodes with various surface area and ionic conductivity within 78% error.

4 SIMPLE Model Validation by Comparing Against the RP of Fabricated LSCF-GDC Cathodes

4.1 Experimental

The LSCF solution which was infiltrated into the GDC scaffold was prepared in the following way. The appropriate amount of nitrates (Lanthanum nitrate 1.17068 g, strontium nitrate 0.38233 g, cobalt nitrate 1.03739 g, iron nitrate 0.35876 g) was dissolved in distilled water with the desired La:Sr:Co:Fe = 0.6:0.4:0.8:0.2 ratio. Thermo-gravimetric analysis was done on the starting nitrates in order to determine the exact hydration number of each nitrate. Citric acid was added to the nitrate solution with the total metal nitrate: citric acid molar ratio of 0.75:1. The citric acid acts as chelate agent, thus the metal cations can be locked in the polymer network stoichiometrically. After firing, the phase pure stoichiometric LSCF can be made. Then the precursor solution will be partially neutralized by adding aqueous ammonia to make the pH = 5. The final molarity of this LSCF precursor solution is 0.50M.

XRD spectrum was taken for the LSCF powder made *ex-situ* (i.e. outside an ionic conducting scaffold) to examine the phase purity. The *ex-situ* LSCF powder was made by spreading the LSCF solution on an alumina plate, gelling in an 80 °C oven for 5min, and firing at 800 °C for 1h. The LSCF powder was scratched off from the plate, ground and then put in the glass sample plate for XRD measurement.

For the symmetric cells, the dense electrolyte pellets were prepared by uniaxially pressing the coarsened GDC (Rhodia) powder in a 3/4 inch die with Carver hydraulic presser. The

coarsened GDC powder was prepared by firing the Rhodia GDC powder to 600 °C first for 1h with the ramping rate of 3 °C/min, then going to 800 °C with the ramping rate of 5 °C/min, and then staying at 800 °C for 4h. The pellets were fired at 1475 °C for 8h in order to ensure the pellets have the relative density above 95%. The pellets were then polished down to 0.0136 ± 0.0017 inch in thickness with SiC sandpaper. GDC ink for cathode scaffold screen printing was prepared by mixing the coarsened GDC powder and an organic vehicle (Heraeus V-737) with three-roll mill. Then the GDC ink was screen printed on both sides of the polished electrolytes pellet. After each screen printing, the cell was dried in the 80 °C oven for 5 min to remove the solvent. In order to achieve a certain cathode thickness, three cycles of screen printing/dry procedures were performed. The area of the scaffold is 0.50 cm^2 . The cells were fired at 1000 °C for 2h. The cathode thickness was measured with the Dektak 3 surface profiler before infiltration.

Before infiltrating the LSCF precursor solution into the GDC scaffold, a solution of diluted acrylic paint (Liquitex) was painted on the electrolyte surface not covered by the GDC scaffold, so that the LSCF solution would not flow beyond the GDC scaffold during infiltration and firing. Then a certain volume of LSCF solution was pipetted into the GDC scaffold. After the solution gradually permeates into the interior of the scaffold, dry the cell in 80 °C oven for 5 min. The cells were then fired at 800 °C for 1h at 10 °C/min ramp rate in order to form the LSCF perovskite oxide. The infiltration/dry/fire cycle may repeat for several times in order to achieve the desired LSCF loading level (which is in the unit of volume percentage in the total cathode volume).

Finally, an LSM ink, which is used as the current collector, was prepared by mixing $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.98}\text{MnO}_{3-\delta}$ (Praxair) powder and the organic vehicle with a LSM weight percentage of 31.8%. The LSM ink is then screen printed on top both of the symmetric cathodes. Then the cells will be fired at 800°C for 1h to remove the organics and slightly sinter the LSM. A gold paste (Heraeus C5756) was screen printed atop the cathode, which was also used as a current collector. The cells were now ready for the EIS measurement.

The cathode polarization resistances were measured by EIS from 100mHz to 100kHz from 400°C to 700°C . The difference between the real intercepts on Nyquist plots is the polarization resistance. SEM microstructure analyses were performed on fractured samples after EIS. The average MIEC hemispherical particle diameter present in each infiltrated cathode was determined by taking the average of at least 100 infiltrate particles from 3 different regions.

In order to input the GDC conductivity σ to the SIMPLE model, the GDC conductivity was measured by EIS. The ohmic resistance on a dense, rectangular thick GDC block with 0.78 cm thickness and 1.17 cm^2 surface area was determined via EIS and the ionic conductivity σ was determined according to the equation:

$$\sigma = \frac{l}{R_{ohmic} \cdot A} \quad [4.1]$$

where σ is the GDC ionic conductivity, l is the thickness of the pellet, A is the geometric area of the pellet, and R_{ohmic} is the measured ohmic resistance of the pellet.

4.2 Characterization of LSCF-GDC Symmetric Cathodes

The water of hydration number of nitrates is summarized in the following Table:

Table 4.1 TGA results of the water of hydration number of starting nitrates

Sample	Stock# Lot#	TGA determined x	Certificate of Analysis x
La nitrate	44346 J30T011	6.304	5.984
Sr nitrate	10879 23338	0	0
Co nitrate	10694 J18W010	6.00	6.37
Fe(III) nitrate	10715 24000	8.54	8.56

Thus, the actual ratio of La:Sr:Co:Fe = 0.59:0.4:0.8:0.2 in the LSCF precursor solution, which is very closed to the desired value.

The *ex-situ* prepared LSCF powder is analyzed by XRD, as shown in Figure 4.1. Compared to the theoretical XRD pattern of LSCF in Reference (47), all the peaks agree with the standard peak positions. The absence of additional peak indicates that the LSCF was at least 97% phase pure (34).

Figure 4.2 shows the measured GDC conductivity from 300 °C to 750 °C compared with the literature data. The measured σ of the GDC agrees well with the literature data reported by Fergus (48)(the dash line), Huang et al (49) (the solid line), Jasper et al (50) (the dot line), and follows the Arrhenius behavior. The σ of GDC at different temperatures can be expressed by the following fitting equation:

$$\sigma = 53.1 \text{ S/cm} \exp\left(\frac{-0.597 \text{ eV}}{k_B T}\right) \quad [4.2]$$

where k_B is Boltzmann constant, which is $8.617 \times 10^{-5} \text{ eV/K}$

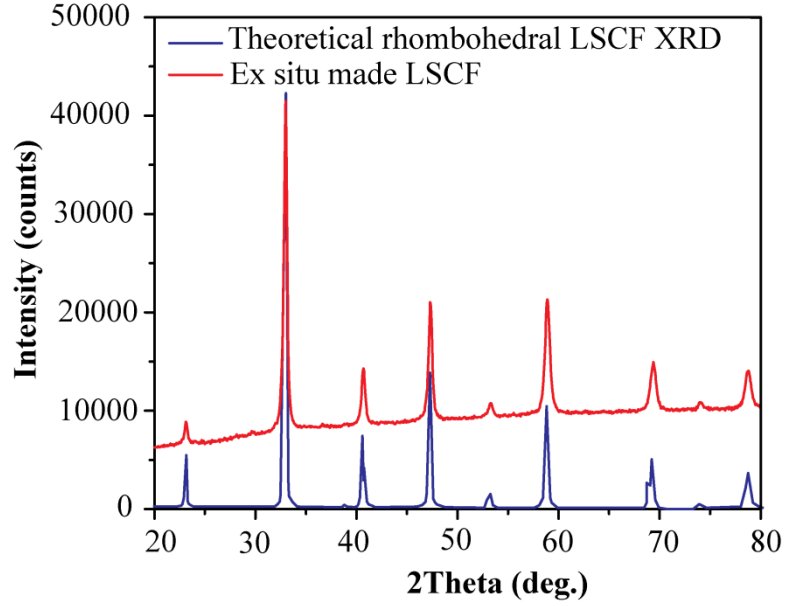


Figure 4.1 XRD analysis of ex situ prepared LSCF powder compared with a standard pattern

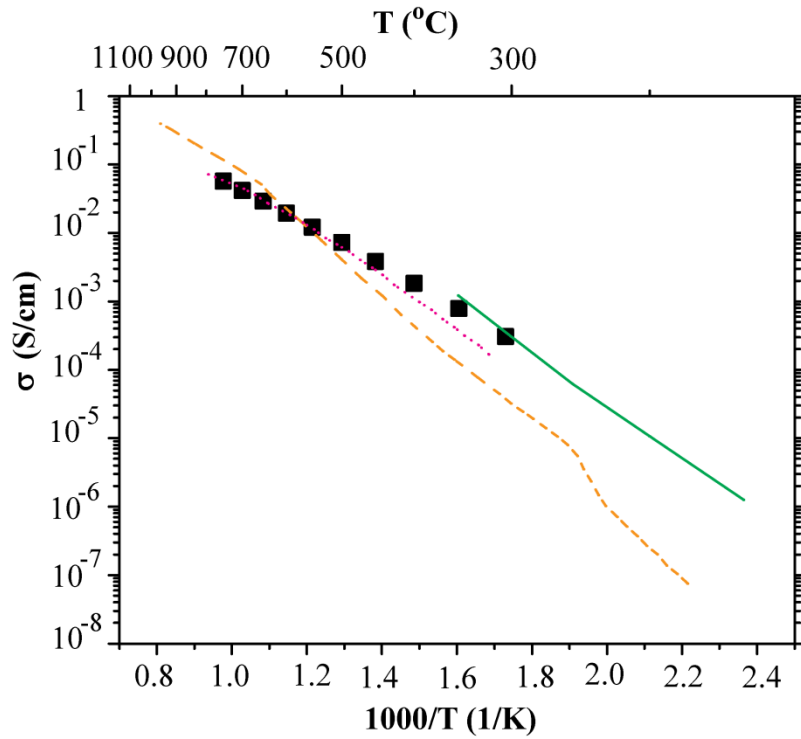


Figure 4.2 Measured GDC conductivity compared with literature reported data

Table 4.2 reports the symmetric cell geometric values. All the relative densities were calculated by taking the pellets density over the theoretical value which is 7.23 g/cm^3 as reported in Ref. (51). All the relative densities were above 95%. Table 4.2 also shows the scaffolds geometry. The scaffolds on both sides of the electrolyte are generally above $10 \text{ }\mu\text{m}$ and the thickness difference between the two sides does not exceed $2 \text{ }\mu\text{m}$. All the cathodes have a geometric area of 0.5 cm^2 .

Table 4.2 Symmetric cells geometry

Cell #	Mass (g)	Electrolyte Thickness (cm)	Electrolyte Diameter (cm)	Relative Density (%)	Cathode Scaffold Thickness (μm)	Cathode Scaffold Ra (μm)	Average Scaffold Thickness (μm)	Infiltrate Loading Level (%)
44	0.43638	0.036	1.505	96.6	11.5 10.2	1.62 1.75	10.9	0
10	0.41824	0.033	1.508	98.2	12.4 13.1	3.1 2.9	12.8	1.0
12	0.34336	0.028	1.493	95.9	11.4 11.6	2.8 2.8	11.5	2.0
16	0.38250	0.031	1.507	96.5	11.8 10.8	3.1 2.6	11.3	3.0
17	0.38376	0.031	1.500	96.1	12.3 12.1	3.0 3.0	12.2	4.0
18	0.53452	0.043	1.515	95.2	12.6 11.0	3.1 2.6	11.8	5.0
20	0.41727	0.034	1.488	99.0	9.1 10.9	2.4 2.3	10.0	8.0
21	0.45251	0.037	1.488	96.6	10.0 10.0	2.7 2.6	10.0	11.0
2	0.45587	0.037	1.506	96.5%	12.0 13.6	2.5 2.6	12.8	14.2

Figure 4.3 shows an FIB-SEM image of a cross-section of a non-infiltrated cathode, which is used to calculate the porosity of the scaffold. The grey area corresponds to the GDC scaffold particles, and the black area corresponds to pores. From the image, the GDC scaffold is well percolated, and there is enough space for gas diffusion. The porosity calculated based on stereological analysis (52) is 58.5%. The scaffold column width, $2w$, can also be determined from this figure, which is ~ 100 nm. In order to get the desired MIEC loading level, the number of infiltrations, the LSCF solution molarity, the cathode thickness h , the geometric cathode area A_G , a 6.463 g/cm^3 LSCF density at 394°C from Yashima and Komika (53)(the only data available in literature), and the ratio of LSCF solution nitrates and weight of LSCF which is 0.009095 mol/g are used to calculate the volume solution per infiltration.

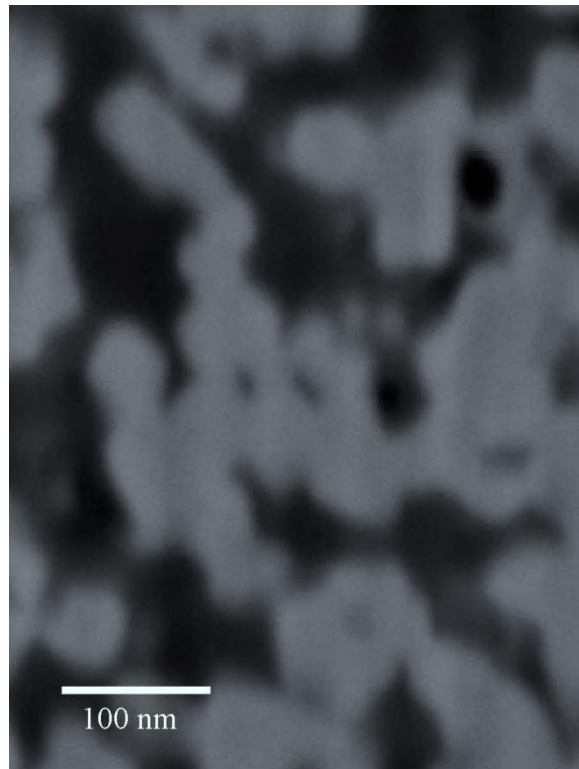


Figure 4.3 FIB-SEM image of a non-infiltrated scaffold

Figure 4.4 shows three representative images of LSCF nano-particles from different loading

LSCF-GDC NCCs. Figure 4.4A is for 1vol% LSCF loading, and B and C are for 4vol% and 11vol% respectively. The nano-particles become more and more well-connected when increasing the MIEC loading level. When the cathodes are very heavily infiltrated, the nano-particles are atop the existing particles. The nano-particle sizes at the cathode-electrolyte interface are analyzed instead of in the heart of the cathode, because it is hard to differentiate the GDC particles and LSCF particles due to very close particle sizes. The LSCF particle sizes are summarized in Figure 4.5. Error bars are $\pm$ a standard deviation. From the figure, the average LSCF infiltrate nano-particle diameters are around 50 nm for all infiltrate loading levels. This means that the infiltrate particle size did not grow during the multiple infiltrate/gel/fire cycles. This behavior suggests that a high surface area can be achieved by repeating the infiltration with a dilute (such as 0.5 M) precursor solution.

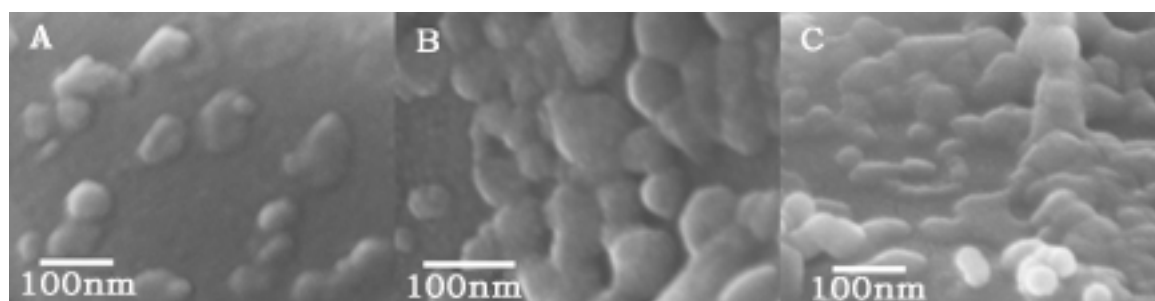


Figure 4.4 SEM images of cathodes with A. 1vol% loading; B. 4vol% loading; C. 11vol% loading

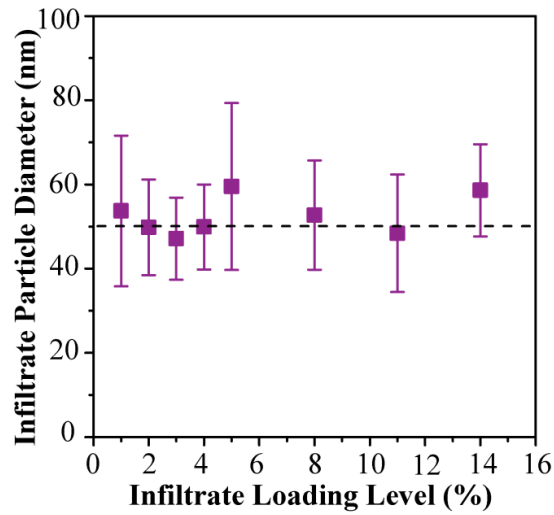


Figure 4.5 LSCF hemispherical particle diameters as a function of LSCF loading level. The bar represents the +/- standard deviation

4.3 SIMPLE Model Calculation of Fabricated LSCF-GDC Cathodes

Figure 4.6 shows the typical impedance spectra for 4.0 vol% LSCF-GDC NCC at 400 °C, 500 °C and 600 °C in air. The R_p of a single cathode can be obtained by dividing the distance between the two intersections on x-axis by 2 and then multiplying the geometric area of cathode which is 0.5 cm^2 in our case. The other LSCF-GDC NCCs with various loadings show similar changes in the spectrum shape.

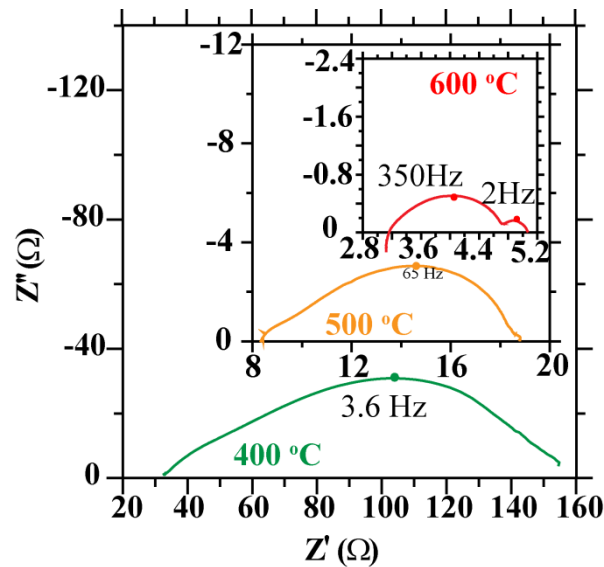


Figure 4.6 4 vol% LSCF-GDC impedance spectrum at various temperatures

Figure 4.7 shows three typical impedance spectrum of LSCF-GDC cathode measured in air at 700 °C. This figure shows that two orders of magnitude's decrease in R_p is due to increasing the LSCF loading.

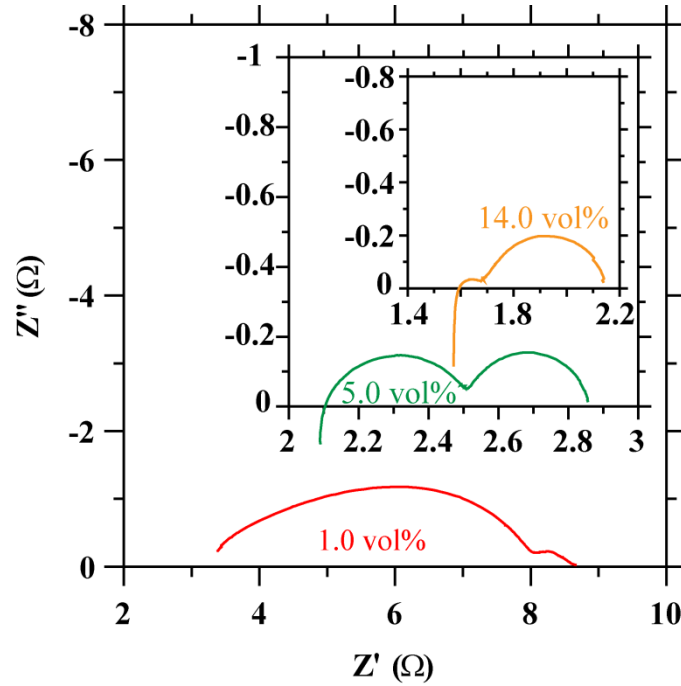


Figure 4.7 Typical impedance spectra for various LSCF loading levels at 700 °C

Figure 4.8 summarizes the SIMPLE model and SR model calculated R_p compared with the experimentally measured R_p of LSCF-GDC NCCs. The thin solid line is the SIMPLE model prediction by using Baumann et al's reported R_S values (24). The thick solid line is the SIMPLE model prediction by using Xiong et al's R_S values (44). The dash line is the SR model prediction by using Xiong et al's R_S values (44). The SIMPLE model predicted R_p using Xiong's R_S values converge with the measured when the MIEC loading is above the percolation limit. The SIMPLE model predicted LSCF-GDC R_p using the Xiong et al.(54) R_S values are within 73% error at all temperatures and various loading levels compared with experimentally measured R_p values. The error is calculated according to the following

equation:

$$\text{Error} = \frac{|\text{Literature Experimental Data} - \text{SIMPLE Model Calculated}|}{\text{Literature Experimental Data}} \times 100\% \quad [4.3]$$

The experimentally measured R_p slightly decrease for the 5.0-14.0 vol% LSCF-GDC cathodes, while the SIMPLE model predicts larger decrease with increasing loading. It is hypothesized that the additional infiltrated LSCF failed to largely lower the R_p as predicted may be due to the deposition of LSCF directly atop the existing LSCF particles, as suggested in Figure 4.4C. More accurate actual LSCF surface area measurements are needed in order to give a better agreement with the experimentally measured R_p for heavily infiltrated cathodes.

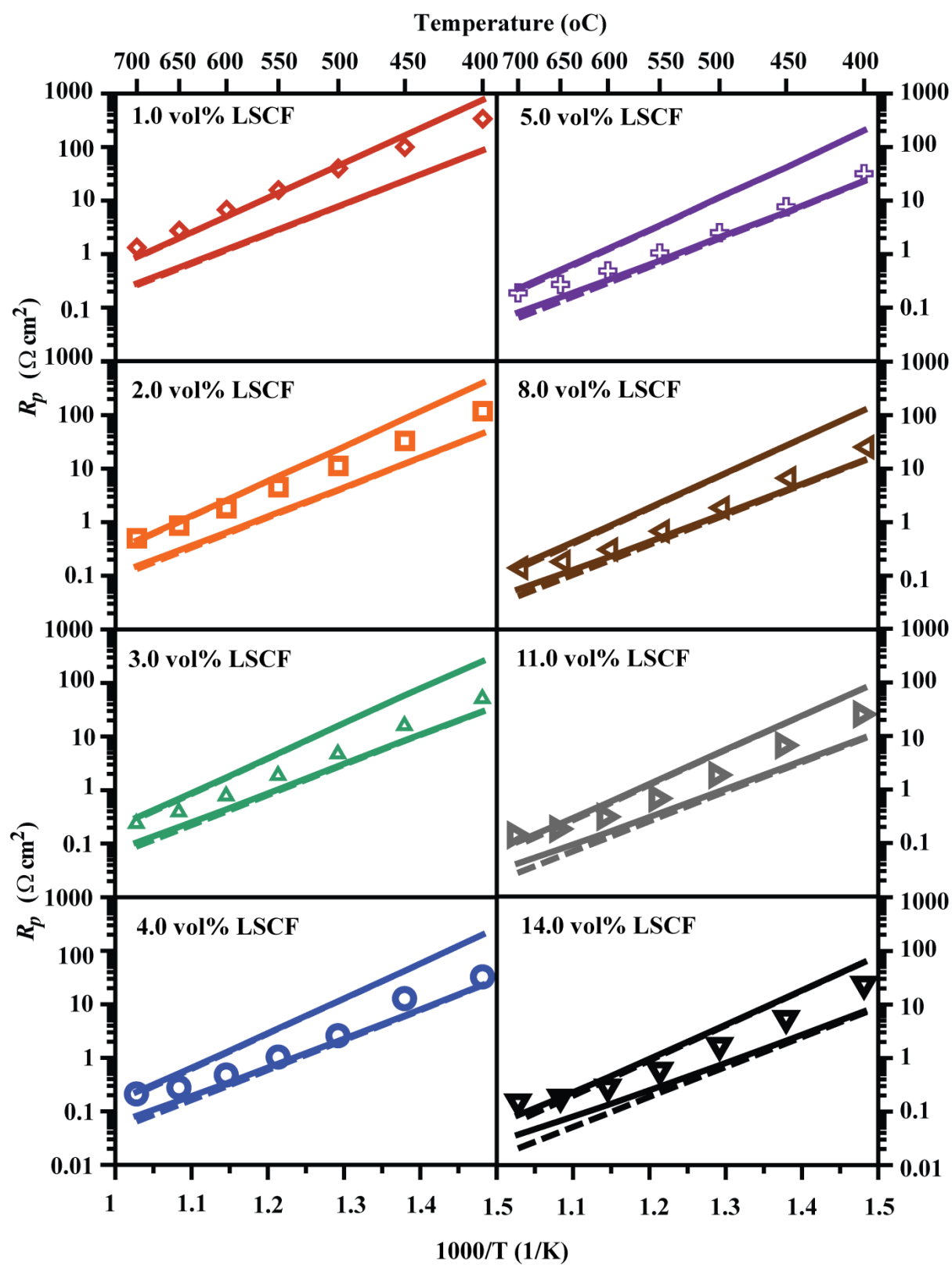


Figure 4.8 SIMPLE model and SR model predictions compared with measured R_p for LSCF-GDC nano-composite cathodes

4.4 Conclusions

LSCF-GDC cathodes have been made. The measured GDC conductivity agrees with the literature reported data. The LSCF particles are roughly hemispherical, with an average diameter of 50 nm. By varying the LSCF loading levels, the MIEC surface areas differ. The SIMPLE model is able to capture the R_p change of fabricated LSCF-GDC cathodes when varying the LSCF loading levels within 73% agreement. If more accurate surface area information is provided, a more closed fitting is expected. The SR model has a closed prediction with the SIMPLE model prediction especially at low temperatures.

By comparing against both the literature data and the fabricated cathodes' data, the SIMPLE model provides reliable predictions. Thus the SIMPLE model is capable of simulating the NCCs' performance, and it can be therefore used as a tool to guide the design of optimal nano-composite cathodes.

5 SIMPLE Model Predictions

5.1 Results and Discussions

Figure 5.1 shows the effect of varying MIEC nano-particle size on the R_P of SSC-SDC NCCs with other microstructure parameters the same with Reference (14) as shown in Table 3.2. For this NCC geometry, SIMPLE model predictions show that a reduction in the MIEC nanoparticle diameter from 200 nm to 6.25 nm decreases the polarization resistance by roughly one order of magnitude. When the particle size halves, for example, from 12.5 nm to 6.25 nm, the R_P decreases roughly 35%. The extent of reduction depends on particle sizes and temperatures. At extremely low temperature, such as 100°C, R_P will almost halve when particle size d reduced by half. This can be explained mathematically. At low temperature, the SIMPLE model results approach the SR limit, in which R_P is dominated by surface reaction resistance and can be calculated by Equation [3.1]. Also, the total MIEC surface area A_{MIEC} and nano-particle size d can be related through the following equation:

$$A_{MIEC} = A_{ind} \cdot N_{nano-particle} \quad [5.1]$$

A_{ind} indicates individual MIEC hemispherical surface area, which is proportional to d^2 . $N_{nano-particle}$ is calculated from total volume of infiltrated MIEC over individual particle volume, thus $N_{nano-particle}$ is proportional to $1/d^3$. As a whole, A_{MIEC} is proportional to $1/d$. Subsequently R_P is proportional to d . Even if extremely small nano-particles can lower the R_P , it may not be microstructurally stable at high temperature. Other solutions are needed to optimize the cathode performance.

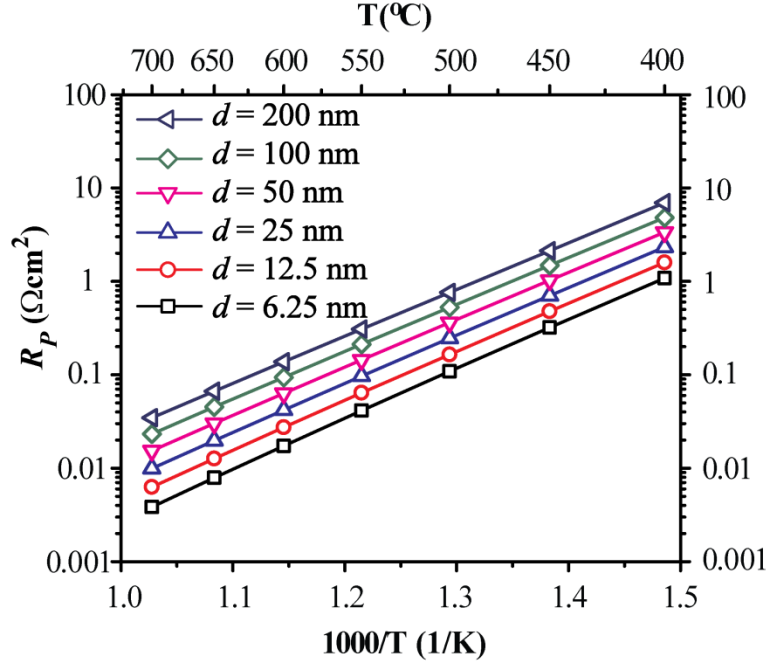


Figure 5.1 SIMPLE model predictions for SSC-SDC NCC with varying SSC particle sizes

Figure 5.2a shows both SIMPLE and SR Limit predictions for today's best performing cathodes, the SSC-GDC cathodes of Reference (39). The $\sim 250^{\circ}\text{C}$ kink in the Figure 5.2a SIMPLE model predictions represents a transition from a regime where the low MIEC surface resistance alone determines R_p (as indicated by the identical values of the SIMPLE model and SR Limit below $\sim 250^{\circ}\text{C}$) to a regime where both R_s and σ determine R_p . That is because the SR model only accounts for surface resistance losses, whereas the SIMPLE model accounts for both surface losses which dominate at low temperature and ionic conduction losses of the IC. Comparison of the SIMPLE model and SR Limit in the $500\text{--}700^{\circ}\text{C}$ range indicates that ionic conduction losses in the scaffold can appreciably raise R_p . Thus, despite the SOFC community's intense focus on developing lower R_s MIEC materials, performance increases in heavily infiltrated nano-composite cathodes can also be achievable through the development of improved ionic conductors.

Figures 5.2b, c, and d show the magnitude of the performance increases possible through improved materials properties (assuming the cathode microstructures equal to those of Reference (39) in Table 3.2 is maintained). Figure 5.2b shows SIMPLE model predictions when σ is increased by an order of magnitude, when R_S is decreased by an order of magnitude, and when both σ and R_S are improved by an order of magnitude, compared to their respective values in SDC and SSC (when only one of the variables is changed, the other variable has the value utilized in Figure 5.2a). Figure 5.2b also shows the SR Limit for the situation where both σ and R_S are improved by an order of magnitude. Nowadays, bismuth metal vanadium oxide materials can roughly achieve one order of magnitude higher ionic conductivity than SDC (55), and BSCF has one order of magnitude lower R_S than SSC (24). Figures 5.2c and 5.2d are identical to 5.2b, except that σ and R_S are improved by two and three orders of magnitude, respectively. Together, these figures show that it should be possible to achieve the target R_P value of $0.1 \Omega\text{cm}^2$ R_P at $\sim 450^\circ\text{C}$, $\sim 375^\circ\text{C}$, and $\sim 300^\circ\text{C}$ with simultaneous improvements in IC σ and MIEC R_S by one, two and three orders of magnitude respectively, although no known materials can currently achieve the 375°C and 300°C performance.

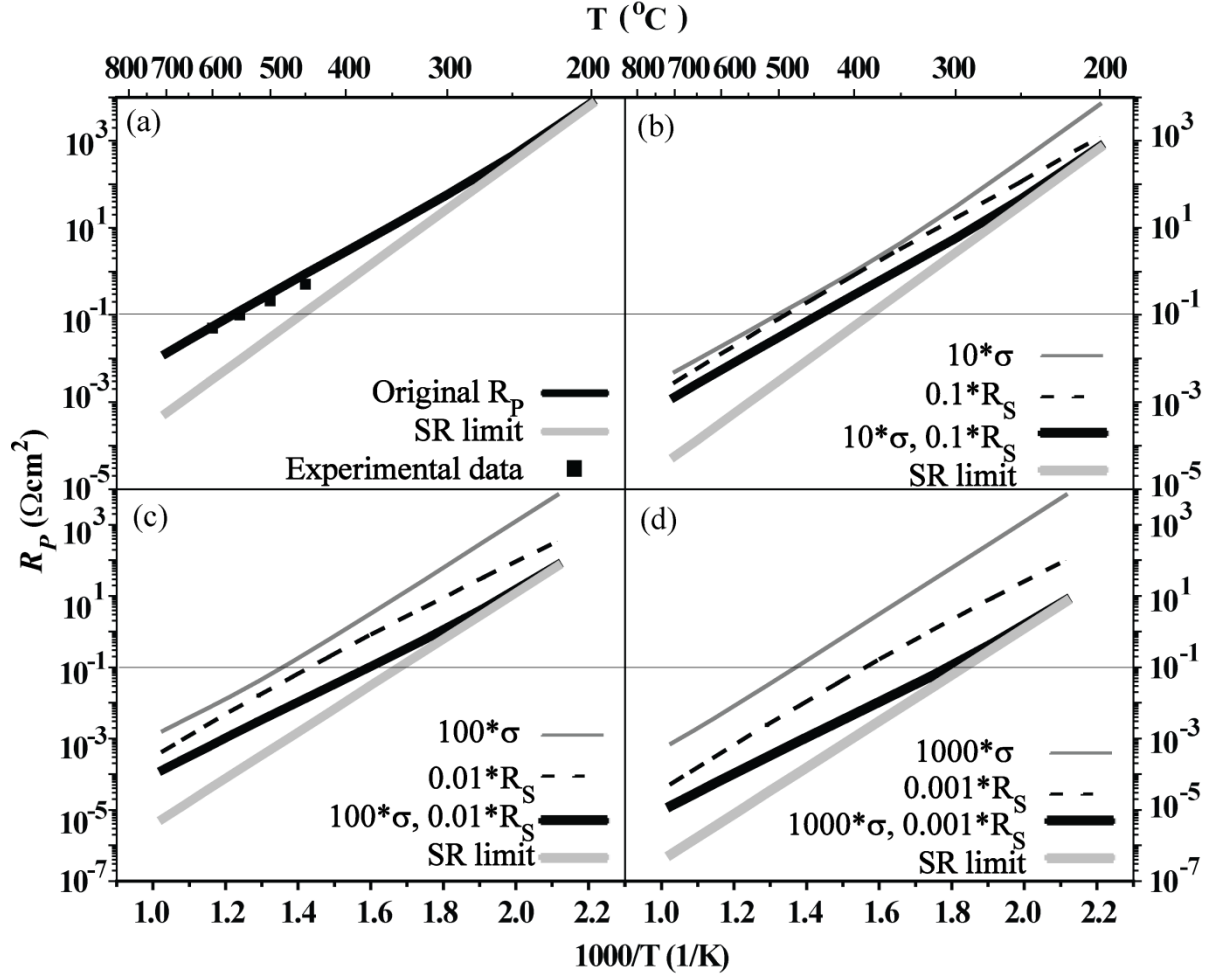


Figure 5.2 SIMPLE model predictions for the MIEC-IC NCC with varying σ of IC and R_S of MIEC. Refer Reference (14) for the experimental data in Figure 5.2a.

Figure 5.3 shows how infiltrated cathode performance changes as the thickness and porosity of the cathode are changed, assuming the MIEC nano-particle loading level and the microstructure are held constant (10vol%). Other parameter values are identical to those in Reference (39). The relatively flat R_p surface in the figure's front right corner yield nearly optimal performance. All the optimal performance cathodes have the cathode thickness h above their characteristic cathode thickness h_C according to Equation [3.5]. When increasing h with the loading level kept constant, the A_{MIEC} will go up, thus h_C will go down. Each h has its

corresponding h_C . The curve starts to transit from sharp decrease to plateau when h and h_C equal. Figure 5.3 shows that once h has equal value with h_C , additional cathode thickness increases do little to improve cathode performance (and probably hurt cell performance due to additional gas transport losses not accounted for in the SIMPLE model). Figure 5.3 also shows that the R_P decreases slightly as the cathode porosity is decreased. This occurs because as the porosity is increased the IC scaffold column width decreases (for constant repeat unit thickness) thereby increasing the amount of current focusing in the IC scaffold.

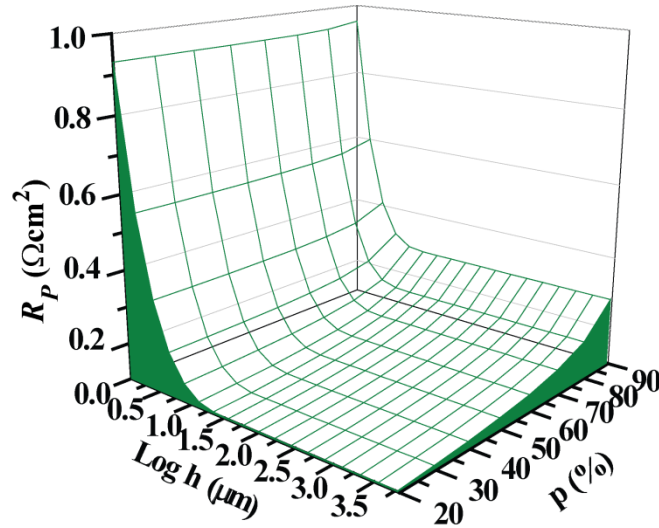


Figure 5.3 SIMPLE model predictions of a 600°C SSC-GDC nano-composite cathode when varying h and p with constant loading level. MIEC particle size d , repeat unit thickness r , footprint cathode area A_G , and MIEC loading level are identical to those of Reference (39) in Table 3.2

Figure 5.4 shows how MIEC-IC nano-composite cathode performance changes as the thickness and porosity of the cathode are changed, assuming that as much MIEC as possible is infiltrated into the pores. To preserve an interconnected gas transport network, this

“maximum possible” MIEC infiltrate loading level is assumed to be 20% less than the non-infiltrated IC scaffold porosity. Like Figure 5.3, Figure 5.4 has a relatively flat R_p surface when h is above its corresponding characteristic thickness level h_C . The characteristic thickness h_C decreases with MIEC loading level, thus the transition from R_p sharp change to plateau where also h and h_C converge shows at lower and lower h when p increases. In contrast to the Figure 5.3 constant loading situation where R_p always scales with porosity, for the “maximum possible” MIEC loading situation of Figure 5.4 R_p shows a minimum at an intermediate porosity for cathode thicknesses above the characteristic cathode thickness h_C . This occurs because at low loading levels the R_p is decreased with the additional surface reaction sites introduced with a higher MIEC loading level. However, above some loading level this benefit is overwhelmed by the R_p increases caused by increasing current focusing within the IC scaffold (as the loading level and p increase, w must decrease for constant r).

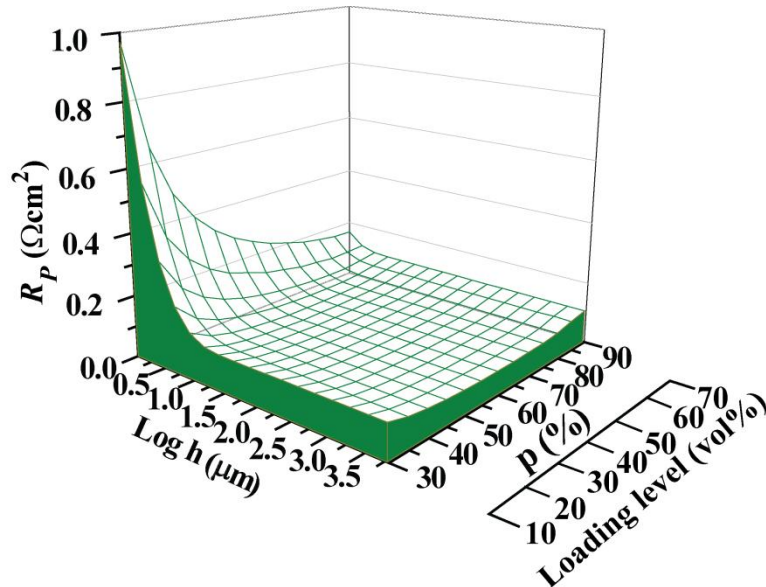


Figure 5.4 SIMPLE model predictions of a 600^oC SSC-GDC nano-composite cathode when varying h and p with loading level equal to $(p-20\%)$. MIEC particle size d , repeat unit thickness

r , and footprint cathode area A_G are identical to those of Reference (39) in Table 3.2.

Figure 5.5 shows the R_p change when r ranges from 100 nm to 100 μm , and p ranges from 10% to 95%, assuming that the MIEC loading level is held constant at 10 vol%. The R_p increases with r when p is low, and decreases with r when p is high. When p is held constant, r increase will lead to scaffold surface area A_{IC} decrease. The r increase dominates when p is low, however scaffold surface area A_{IC} decrease will dominate when p is high, thus the final trend will vary according to Equation [1.4]. Figure 4.5 also shows that R_p will increase with p when r is fixed and low. To the contrary, R_p will decrease with p when r is high. Mathematically, p increase will lead to α decrease and β increase. From the complexity of the denominator of Equation [1.4], the results caused by p increase will vary. Physically, the ionic currents will be limited by the thin IC column when r is small and p is high, thus R_p will go up. However, when r is very large, the larger the porosity, the less the total ionic conductor volume will be, thus less resistance contributed from IC. In addition, the black lines connect all the cathodes with the same column width w according to the relation between r , w , and p . The change of r , p or w will not result in a very significant change to R_p except at the very extreme conditions (p is larger than 80%).

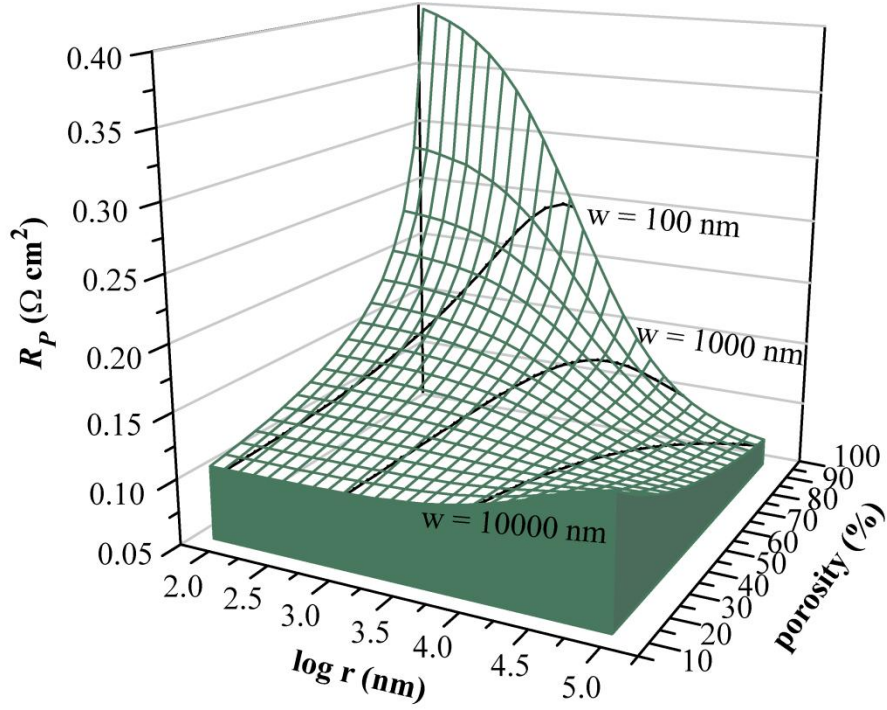


Figure 5.5 SIMPLE model predictions of a 600^oC SSC-GDC nano-composite cathode when varying r and p with constant loading level. MIEC particle size d , cathode thickness h and footprint cathode area A_G are identical to those of Reference (39) in Table 3.2.

Figure 5.6 shows the R_p change with r ranges from 100 nm to 100 μm , and p ranges from 20% to 95%, assuming that as much MIEC as possible is infiltrated into the pores. The MIEC infiltrate loading level is assumed to be 20% less than the non-infiltrated IC scaffold porosity in order to retain a percolated gas diffusion network. The R_p decreases with p first at low r due to more MIEC materials are infiltrated in the scaffold, subsequently more reaction sites will promote the surface reaction rates. However, the R_p will increase with p then due to current limitation. At very large r , the R_p will keep decreasing when p goes up because of both more MIEC and less ionic conductor resistance. Column width w could effect R_p but R_p is not very sensitive to the change in w . This figure enlightens that when r is between 80 nm to ~ 2000 nm (most SIMPLE model calculated cathodes have their r in this range), there is a

valley in the plot where the conditions are optimal. In those optimal conditions, the p is between 45% ~ 70%. The pore space should be fully taken advantage of (infiltrate maximum possible MIEC in the space) in order to promote the cathode performance.

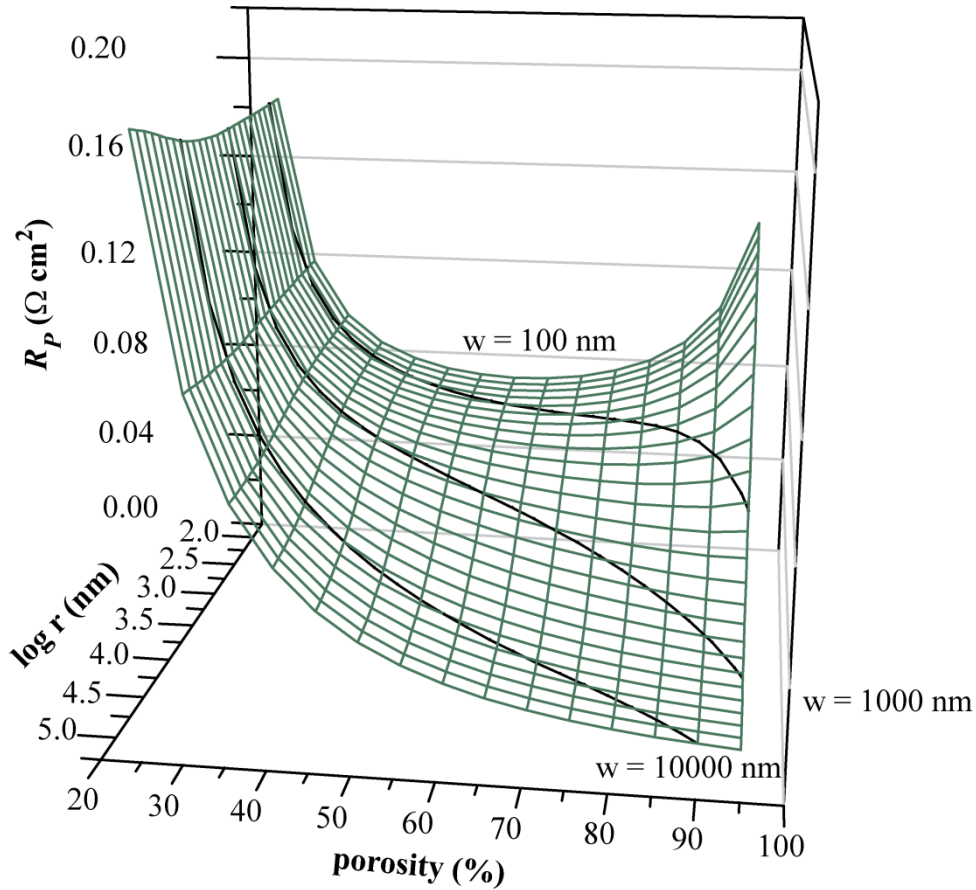


Figure 5.6 SIMPLE model predictions of a 600°C SSC-GDC nano-composite cathode when varying r and p with loading level equal to $(p-20\%)$. MIEC particle size d , cathode thickness h and footprint cathode area A_G are identical to those of Reference (39) in Table 3.2.

5.2 Conclusions

The SIMPLE model predictions show that smaller MIEC particles will lead to larger surface area and subsequently more reaction sites, which will help lower the R_p . However, considering the instability of nano-particles at high temperature, this may not be a favored

optimal condition. An effective way to lower the R_p is to utilize better MIEC and IC materials, which can largely decrease the operation temperature of SOFC. If MIEC and IC materials with, say, 100 times better properties than the SSC and GDC typically used today can be produced (something which seems quite likely given the many orders of magnitude these materials properties already span between different materials and temperatures), SOFC nano-composite cathodes operating at $\sim 375^\circ\text{C}$ should be possible. In the microstructure aspect, keeping the p at intermediate value (45% $\sim$ 70%) and keeping the h above the corresponding h_C will yield an optimal performance.

6 Conclusions

LSCF-GDC symmetric cathodes with various LSCF loading levels have been fabricated by using a nitrate solution infiltration method. The LSCF nano-particles have diameters ~ 50 nm, which do not show increases with multiple infiltration/gel/firing sequences, suggesting that the heavy infiltrated cathodes can be made by using dilute precursor solution and infiltrating several times. The R_p decrease when more MIEC is infiltrated into the scaffold, and the SIMPLE model is able to capture the change. The SIMPLE model is also able to capture the R_p changes with temperature, which follow the Arrhenius behavior. The SIMPLE model is validated also by fitting the literature existing NCCs, and the predictions are all within 137% errors for all compositions at all temperatures.

The SIMPLE model shows that reducing the MIEC particle size can help lower the R_p when the MIEC loading level is held constant. However, R_p decreases only one order of magnitude when the SSC particle size is brought down from 200 nm to 6.25 nm. Considering the coarsening feature of extremely small nano-particles at high temperature, reducing the MIEC particle size may not be an efficient way to lower R_p . In order to optimize the performance of NCCs, an efficient solution could be using high σ IC and low R_s MIEC materials. If MIEC and IC materials with, say, 100 times better properties than the SSC and GDC typically used today can be produced (something which seems quite likely given the many orders of magnitude these materials properties already span between different materials and temperatures), SOFC nano-composite cathodes operating at $\sim 375^\circ\text{C}$ should be possible. The

SIMPLE model also suggests that the cathode thickness should be above the characteristic thickness to get the optimal behavior.

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