

Optimizing Cathode Performance in Solid-Oxide Fuel Cells

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Abstract

In this proposed project, I will increase the output power of solid-oxide fuel cells. Specifically I will focus on planar cells composed of a yttria stabilized zirconia (YSZ) electrolyte, a lanthanum strontium manganate (LSM) anode, and the YSZ/LSM cathode. I will perfect the method of applying the cathode to the electrolyte and anode combination. After fabricating a complete cell, I will test its performance using electrochemical impedance spectroscopy (EIS). Once a successful construction and testing procedure has been developed, I will develop a better cathode to increase output power by changing compositions, application methods, and firing procedures.

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Introduction

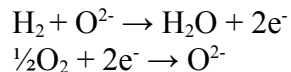
The purpose of this project is to develop a more efficient and powerful cathode for solid-oxide fuel cells. This task involves improving the output power (in Watts) per surface area (in square centimeters), W/cm^2 , through gaining better charge transfer through the cathode material.

There are five major kinds of fuel cells in research and development today: phosphoric acid fuel cells (PAFCs), polymer electrolyte membrane fuel cells (PEMFCs), alkaline fuel cells (AFCs), molten carbonate fuel cells (MCFCs), and solid-oxide fuel cells (SOFCs).¹ Of the five types, PEMFCs and SOFCs are the most widely studied. SOFCs have high potential in stationary applications such as powering and heating buildings because they are relatively highly efficient compared to the other fuel cell types and can take several input fuels. Also, while other fuel cell types such as PEMFCs must be air-tight to operate, SOFCs can run off atmosphere. The only disadvantage uncovered so far is that SOFCs must be run at high temperatures, between 600 and 1000 °C.¹

Solid-oxide fuel cells are composed of a ceramic electrolyte encased between a cathode and anode, also ceramic. In the fuel cells I will build and study, the electrolyte is composed of YSZ. Typically, there is about 8 % yttria in the mixture.¹ The anode is made up of LSM with a stoichiometric composition of $La_{0.8}Sr_{0.2}MnO_3$.² The current cathode composition used by many laboratories, including the Colorado Fuel Cell Center (CFCC), is a mixture of YSZ and LSM.

The typical fuel for an SOFC is gaseous hydrogen, $H_{2(g)}$, and oxygen from the surrounding atmosphere, $O_{2(g)}$. The YSZ electrolyte, when made correctly, is porous from the perspective of oxygen ions (O^{2-} , the charge carriers in SOFCs) moving through the electrolyte. When yttria (Y_2O_3) is added to zirconia (ZrO_2), pressed, and fired to make a YSZ electrolyte, high concentrations of oxygen vacancies in the zirconia crystal structure make the transport of the oxygen ions easier and more efficient than a pure zirconia electrolyte.¹

Two half-reactions take place in an SOFC, using air and hydrogen for fuel.



These reactions can occur on either the cathode or the anode, making the process reversible if the input fuel were switched to the other electrode.

The electrons in these half-reactions move around the electrolyte through wires connected to the load. The oxygen ions have a more difficult time moving through the electrolyte than the electrons around the circuit. This slower movement becomes the impedance of the cell, its resistance. The efficiency of an SOFC's electrode at breaking down the fuel into electrons and ions is where fuel cells lose efficiency to conventional

power systems.¹ Producing fuel cells with thinner electrolytes reduces the distance the ions must travel to complete the reactions.

Thin electrolytes are becoming easier and easier to make, but efficiency is still a problem in SOFCs. As research continues, it is now widely accepted that cathode performance is the primary concern when trying to increase the efficiency and power output of solid-oxide fuel cells. The mixture of YSZ and LSM in the cathode composition and uniformity of application to the electrolyte are major areas of focus in bettering the technology. If more power can be coaxed from fuel cells while maintaining low input energy requirements and fuel costs, SOFCs have the potential to reinvent power systems across industry and society.

Research Progress

I have begun preliminary research on my proposed project, starting August 26, 2007. Thus far, I have studied solid-oxide fuel cell concepts, basic fuel cell operation, equivalent circuit modeling of fuel cells, and performed some initial tests on sample cells by driving current through them in a furnace at high temperatures.

To begin, I gathered information resources to study SOFCs and how to model them as basic analog circuits. By drawing a diagram of a simple RC circuit, the fundamental workings of an SOFC reaction interface impedance as a function of input frequency can be explained. Figure 1 shows the equivalent circuit model of an SOFC reaction interface.

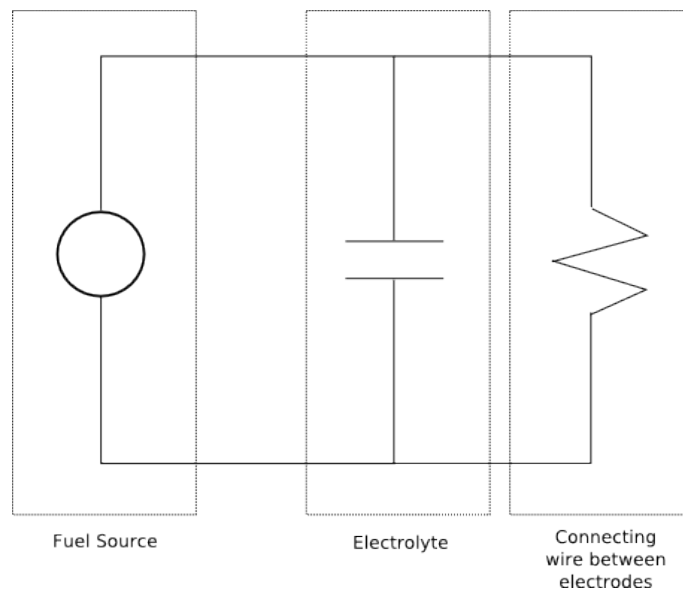


Figure 1: SOFC Equivalent Circuit Model

By the principles of an RC circuit, when there is a high input signal frequency ω all current will be shunted through the capacitor (roughly representing the SOFC electrolyte), because a capacitor blocks DC signals and passes AC signals of high frequency as if it were a short circuit. Conversely, when the frequency of the input signal is low, all current is channeled through the resistor (roughly representing the connecting

wire between electrodes that leads to whatever device the cell is powering).³ This frequency range can be displayed according to the impedance of the reaction interface in Figure 2.

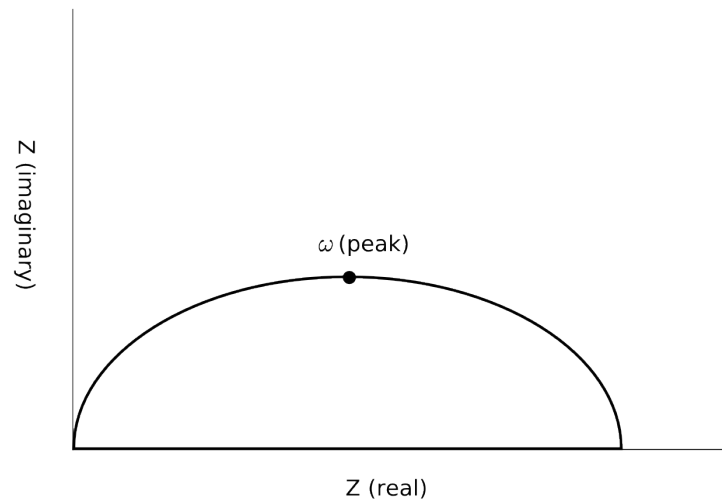


Figure 2: Complex and real impedance of cell as frequency varies

Figure 2 is the graph of the complex and real impedances of the SOFC as ω varies. There is an ideal ω value for which the current running through the cell will pass through both the electrolyte and the load (indicated by ω_{peak} in Figure 2). I will operate the cells at this frequency

I am using a Carver “Auto” Series Hydraulic Press to press YSZ powder into discs and have them fired. Ideally, I want to make 2.25 in discs for my tests, but have been making smaller 1.125 in discs to practice the procedure, using a steel die set. The larger dimension for the electrolyte discs was chosen after consulting with my project advisor. Before obtaining a 2.25 in die set, the available size was 1.125 in. For several weeks now, we have a 2.25 in die set and have made six larger discs.

The firing of the electrolytes was done using a Lindberg/Blue 1200 °C box furnace with a profile of approximately 24 h rising to 1100 °C. The fired electrolytes shrink in diameter. After measuring the fired discs with a caliper, I observed 22.4 % shrinkage, going from 1.125 in to 0.872 in. The larger discs shrunk from 2.25 in to an average 1.71 in.

I roughly painted platinum electrodes on either side of three 0.872 in discs, making them rough test SOFCs, with the intent of only testing to see if current could be driven through the fired YSZ electrode at high temperatures. For a real cell, the electrodes will be YSZ/LSM and LSM and the electrolyte will be much thinner.

After the painting was complete and dried, I attached a 2-in length of silver wire to each side of the electrodes using silver paste and drying them in a Lindberg drying oven for approximately 2 hours. After removing the cells from the oven, I connected the short silver leads with longer silver wires (approximately 16 in) that ran to a Fluke PM2812

programmable power supply. I inserted the cell and most of the silver lead wires into a Thermolyne 21100 tube furnace. I heated the tube furnace up to 800 °C and measured the output current across the test cells. I have collected and tabulated data for each of the three test cells, seen in Table 1.

Table 1: Test data for linear response between input voltage and output current

Testing YSZ electrolytes with painted Pt electrodes						
Cell 1 (10/10/07), OD=0.874" Cell 2 (11/6/07), OD=0.875" Cell 3 (11/6/07), OD=0.875" Set Current at 10 A						
Vapp (V)	Iout 1 (A)	Iout 1 Rev (A)	Iout 2 (A)	Iout 2 Rev (A)	Iout 3 (A)	Iout 3 Rev (A)
0.25	0.03	0.04	0.05	0.05	0.05	0.05
0.50	0.03	0.05	0.06	0.05	0.05	0.07
0.75	0.05	0.07	0.08	0.06	0.06	0.09
1.00	0.12	0.11	0.13	0.11	0.10	0.11
1.25	0.17	0.16	0.17	0.16	0.17	0.15
1.50	0.23	0.22	0.22	0.24	0.25	0.22
1.75	0.32	0.31	0.29	0.28	0.32	0.27
2.00	0.49	0.45	0.33	0.37	0.42	0.34
2.25	0.59	0.55	0.36	0.41	0.55	0.43
2.50	0.70	0.70	0.43	0.50	0.62	0.50

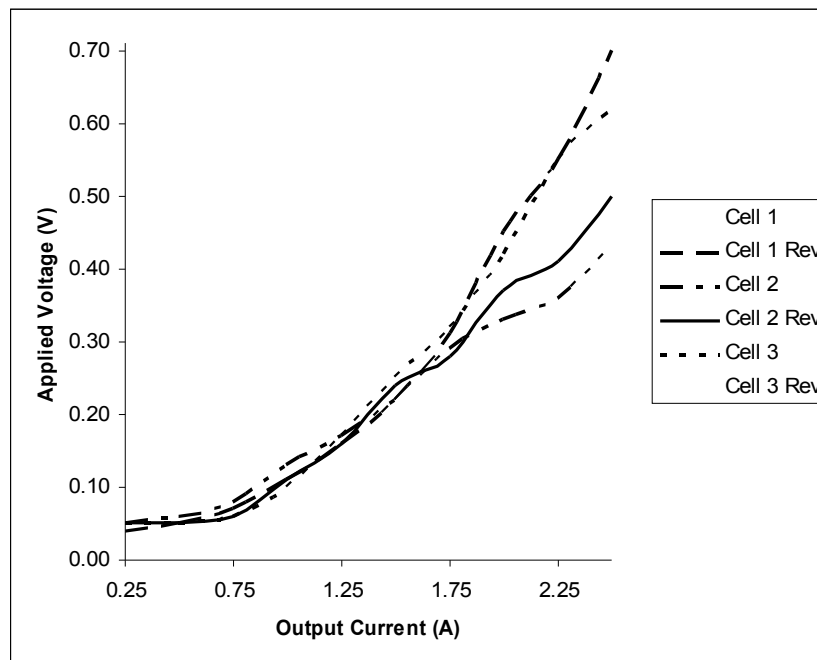


Figure 3: Output Current as a function of Input Voltage for three test cells

The relationship between output current and input voltage is seen to be roughly linear for three separate trials and when each of those trials have their leads reversed. When two 0.872 in discs were tested two before these three, I did not know what power supply

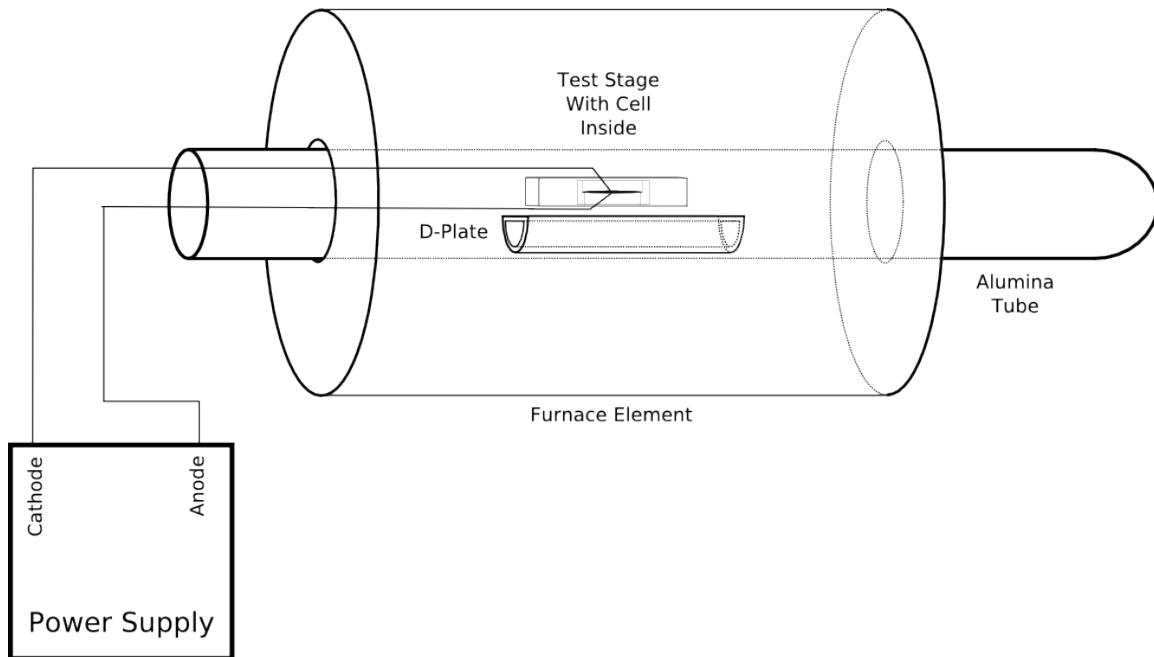


Figure 5: Initial Test Cell Set-up

Future Work

The mullite test stage is the first priority in the coming semester and will be built soon so experiments can continue.

Once I have developed a successful method for pressing and firing electrolytes I will work on a method of applying the YSZ/LSM cathode and the LSM anode. I have acquired a previous senior design report from the CSM Materials Science and Metallurgical Engineering (MME) department to study. In their project, the pair of students worked on a procedure for spraying a slurry of the cathode material onto a YSZ disc.⁴ They used a model airplane spray gun and masked the YSZ disc using tape so that the cathode material covered only a certain portion of the disc. After spraying, the mask was removed, leaving a painted circular area slightly smaller in diameter than the planar YSZ disc. This masking procedure prevents dripping of the cathode material over the edges of the disc, since both electrodes must be completely separated by the electrolyte so the cell can operate properly.

For using electrochemical impedance spectroscopy, I will need a more complicated mask for my project. EIS measures the change in current through a system using electrochemical reactions (like an SOFC) based on small perturbations in a constant input voltage. EIS can also measure the change in voltage due to small changes in input current.³ This test method will output an impedance graph, like the one in Figure 2. This graph will show how well the electrodes break down the fuel into ions and electrons over time.

To accurately measure the performance of an SOFC with EIS, I will make two electrodes on each side of a test cell, one a working and one a reference. The complete test cell, after spraying is seen below in Figure 6.

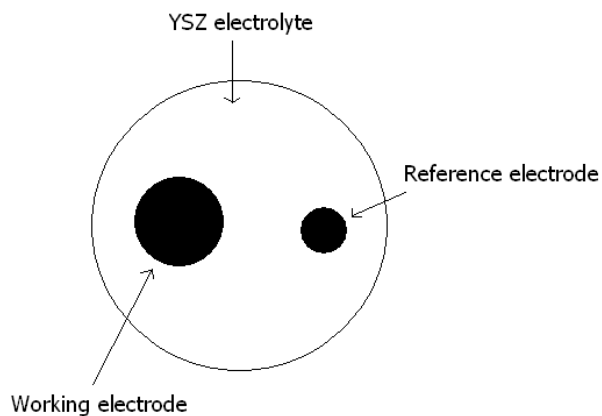


Figure 6: Test cell after masking to have two separate electrodes on its surface

The downside of this more complicated masking is that the working electrodes and reference electrodes must line up perfectly in placement and diameter on each side of the cell. I will develop a method of doing this matching consistently as the project continues.

The EIS measurements are taken through a machine called a Gamry. This machine is in the lab now and I will be interfacing with my test cells. The Gamry needs a working electrode and reference electrode on each side of a test cell, hence, the masking procedure above. The full setup of the EIS machine and the cell in its test stage can be seen in Figure 7.

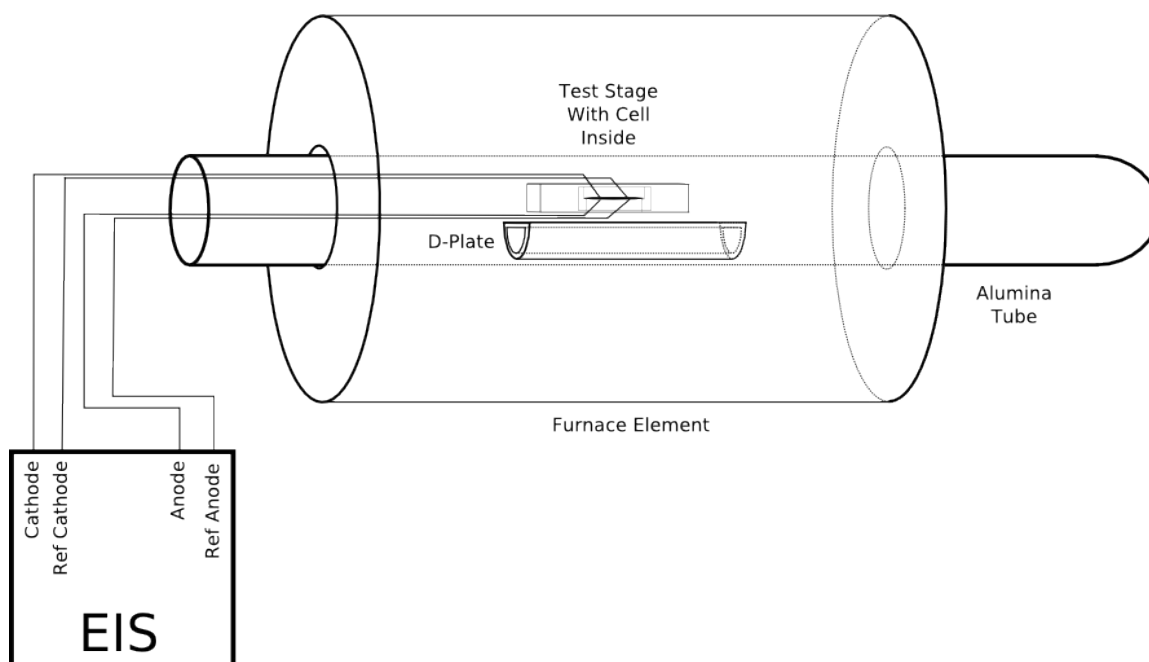


Figure 7: Full test set-up with EIS machine

After a successful EIS measurement run, I will study the impedance graphs and use this data to fabricate a better cathode. I will work on four aspects of the SOFC cathode to find a production process that generates more output power.

- Testing different compositions of LSM and YSZ powders to find ideal mixture.
- Perfecting the spray-on method of applying cathodes to a YSZ disc
- Searching for other methods of application to produce a more uniform electrode.
- Raising and lowering the temperature of the oven when the cathode and electrolyte are being fired.

Finally, I will write up my results and recommend a better cathode composition to produce and SOFC with greater power output.

Timeline

- November 30: Designed mullite test stage for SOFCs.
December 8: Constructed a mullite test stage.
January 15: Conducted a successful test of a 2.25 in. cast SOFC in the test stage and furnace setup at 800 °C, showing that current can be driven through the cell.
January 28: Developed a procedure for masking the cells such that the Gamry EIS machine can be used to test them in the tube furnace.
February 15: Conducted enough EIS measurements to have a reliable model for how an SOFC reaction interface behaves over a range of input frequencies.
February 20: Brainstormed ideas for a better cathode composition to maximize power output across the SOFC reaction interface based on collected data.
March 7: Start to write final report on results of attempt to increase power output of SOFCs.
May 10: Turn in final report for review.

Facilities/Equipment

I am using a portion of the CFCC to conduct my project. I have the tube furnace, power supply, wire connections, hydraulic press, and spraying apparatus at my disposal to carry out my research. Additionally, I have human resources such as professors in the MME department and Engineering department to assist me when I have questions. Finally, I have book resources given me by these professors as references for understanding concepts related to my project.

Proposed Budget

Many of the materials and devices, such as the tube furnace, spray gun, Gamry, mixing chambers, and power supply are already available in the CFCC for my use. I have tabulated an estimated cost analysis for the remaining items needed for my project. I will not be requesting money from the Physics department senior design program.

Table 2: Estimated Budget

Item	Cost
YSZ Powder	\$80
(New) Die Set	\$500
25 m Silver wire	\$200

References

¹R. O'Hayre, et al., Fuel Cell Fundamentals, 1st ed. (John Wiley & Sons, New York, 2006), pp. 10, 121.

²"Inframent Advanced Materials", <http://www.advancedmaterials.us/S5725SR.htm>, accessed 10/22/2007.

³E. Barsoukov, J. R. McDonald, Impedance Spectroscopy: Theory, Experiment, and Applications, 2nd ed. (John Wiley & Sons, New Jersey, 2005), p. 14.

⁴K. Leopoldt and C. Myers, "Cathode Deposition and Electrolyte Removal Processes for the Production of Planar Solid-Oxide Fuel Cells" (Colorado School of Mines, Materials Science and Metallurgical Engineering department), April 30, 2007, pp. 4-9.