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***Development of Single Chamber Solid Oxide Fuel Cells with Porous
Samaria Doped Ceria Electrolytes***

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Abstract

Single chamber solid oxide fuel cells generate electricity using hydrogen and hydrocarbon fuel mixed with oxygen at intermediate temperatures (400-800°C) without using seals to separate the gases. A single-chamber solid oxide fuel cell was fabricated with a porous samaria doped ceria (SDC) electrolyte, nickel oxide anode, and a lanthanum strontium cobalt iron oxide (LSCF) cathode. Instead of separately sintering the different components at different temperatures, the electrolyte and electrodes were co-sintered at 1100°C. The porous SDC electrolyte approached 84% theoretical density when sintered at 1100°C. The fuel cell had a maximum open circuit voltage of .65 V at 550°C. The conductivity of the porous SDC electrolyte was greater than dense yttria-stabilized zirconia (YSZ) electrolytes but less than that of dense SDC electrolytes. Further studies will be conducted to determine the durability and to refine the heating schedule for simultaneous sintering of these fuel cells.

Introduction

A solid oxide fuel cell (SOFC) can efficiently convert hydrogen and hydrocarbon gases to electricity and thus provide power to various devices. When SOFCs are more fully researched and developed, they may be used in such widespread applications as generators, batteries, and power plants.

A SOFC relies on many basic catalytic reactions at high temperatures (400-1000°C) that ionize hydrogen and oxygen on the surface of the electrodes (Figure 1). Once the gases are ionized, the oxygen ion travels through the electrolyte to complete the circuit. The circuit is finally completed when the oxygen ion bonds with the hydrogen ions to release electrons and form a water molecule (a harmless byproduct).

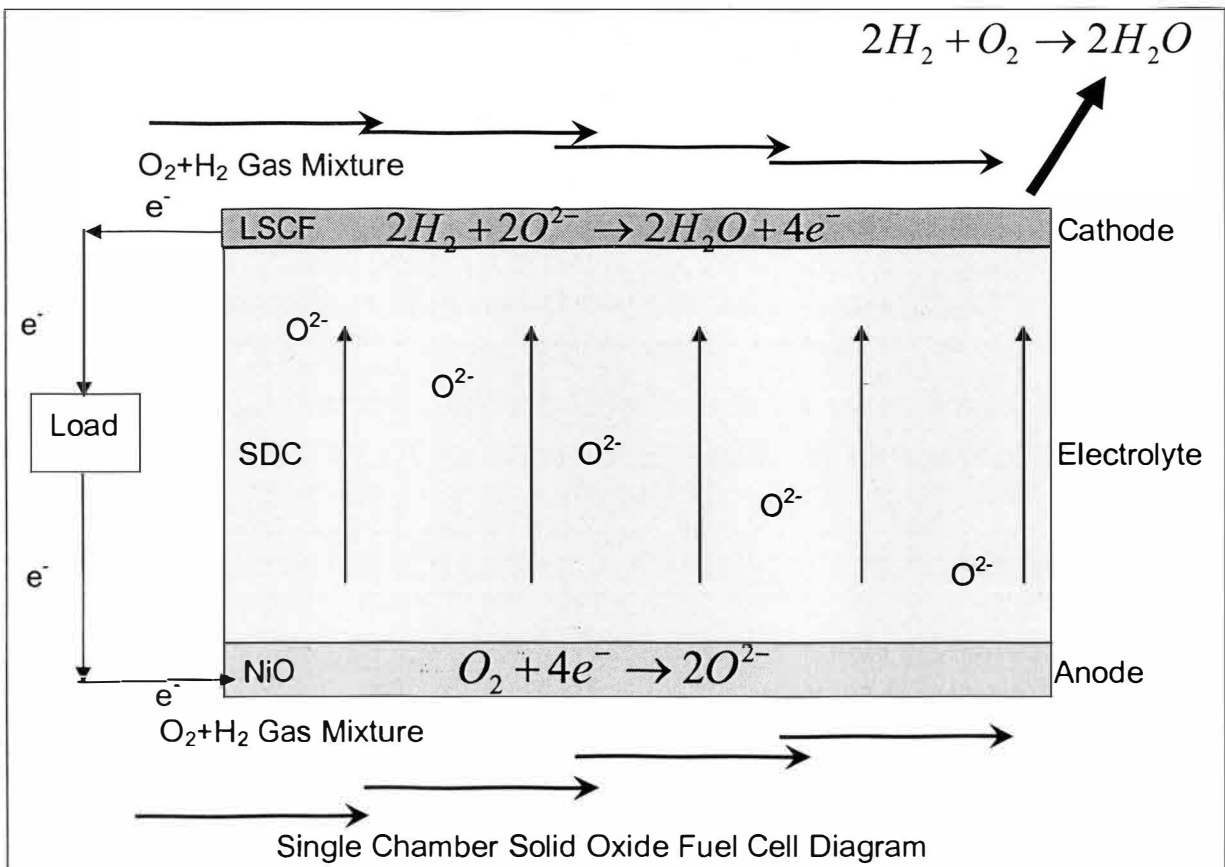


Figure 1. SC-SOFC Diagram

One of the major setbacks to the widespread utilization of solid oxide fuel cells is cost. One advantage of a single chamber SOFC is the ability for it to operate in a mixture of both fuel and air, while still maintaining a power density similar to that of a traditional double chambered SOFC. The single chamber solid oxide fuel cells (SC-SOFC) could become more economical due to the saved cost from unnecessary interconnects and seals which keep the gas mixtures separated.¹

Another cost associated with SOFCs is the cost of manufacturing. The electrolyte material requires a high sintering temperature to completely densify the material in order for it to

be an effective ion conductor. However, it may be possible to sinter the electrolyte at lower temperatures in order to reduce energy costs in manufacturing although it is at the cost of net oxygen ion conductivity. Prior research has indicated that a porous yttria-stabilized zirconia (YSZ) electrolyte has a slightly lower open circuit voltage (OCV) than a denser, more highly sintered YSZ electrolyte. Because the electrolyte does not have to be sintered at such high temperatures, cost and processing time could be further reduced by sintering two or more components of the fuel cell simultaneously.²

Although porous YSZ electrolytes have already been investigated, SC-SOFCs with porous ceria electrolytes have not been studied extensively. The purpose of this project was to fabricate a single chamber, simultaneously sintered solid oxide fuel cell with a porous samaria doped ceria (SDC) electrolyte and to evaluate its performance against conventional single chambered and double chambered SOFCs. Many experimental variables were considered such as electrolyte thickness, fabrication technique, gas flow rate, temperature, and gas composition while comparing the OCV, impedance, and power densities of the fuel cell with the performance of other SDC and YSZ electrolytes.

Main Body

Procedure

The procedure was one of the most extensive parts of the research and was inherently vital to the success of the fuel cell. It can most easily be broken down into the fabrication of each of the components (electrolyte, cathode, and anode), the final sintering process, and testing.

Electrolyte

Samaria doped ceria (CeO_2) powder (#D1503 Daiichi, Kigenso, Kogyoco. LTD SDC-20) was chosen as the electrolyte material. The samaria doped ceria (SDC) had to be compacted in at minimal cost to form a wafer to be used as an electrolyte. Green density, green strength, and electrolyte thickness had to be considered for the electrolyte to be effective. Density is controlled both by the sintering temperature, time, and the pressure used to initially compact the material. Green strength primarily depended on the thickness of the electrolyte, although a thicker electrolyte increases the resistance of the cell. All of these factors had to be balanced for effective processing.

The SDC powder was compacted through uniaxial pressing. After some experimentation, 25 grams of SDC powder were pressed with a 56,000 lb load to form a wafer with approximately a .635 cm radius and a thickness of .05 cm. The wafer's thickness was measured with calipers, the variation was calculated. The wafers were inspected for impurities, cracks, and uniformity. After geometrically determining the density, the wafers were set aside until the cathode materials were pasted onto the SDC wafer.

Cathode

Lanthanum strontium cobalt iron oxide (LSCF, $(\text{La}_{.6}\text{Sr}_{.4})(\text{Co}_{.2}\text{Fe}_{.8})\text{O}_{3.5}$) was the material chosen for the cathode. The LSCF ink was obtained from NexTech Materials. After the ink was shaken by hand, a drop of BOE (ethylene, glycol, monobutyl ether; a volatile organic chemical compound) was mixed with LSCF ink. BOE reduces the viscosity of the ink so that it can be spread with ease and uniformity. A small disk of black LSCF ink was painted with a plastic tool onto the electrolyte.

The sample was dried for over two hours at ambient temperature as the volatile BOE evaporated from the cathode. Streaking and color variation in the deposited layer was an indication of excessive BOE in the ink, and the LSCF layer was too thin. If too little BOE was added, the cathode could not be spread evenly and areas of greater thickness would be present.

Anode

The final component added to the other side of the electrolyte was the anode. Nickel oxide (NiO) mixed with SDC formed the anode. Because no fine NiO powders can be obtained commercially, nickel (II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$) was calcined to form NiO at the lab. A few grams were placed in a crucible and covered before being placed into the furnace. The calcination schedule can be seen in Figure 2.

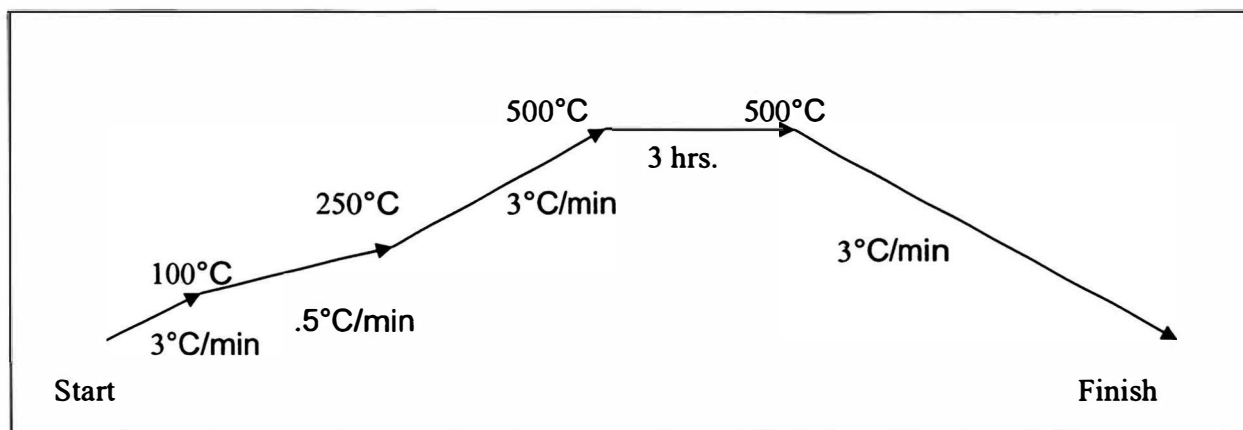


Figure 2. Calcination schedule of nickel (II) nitrate hexahydrate.

Once the calcination was completed, the fine black Ni powder was removed from the crucible. After the powder was broken from its loosely conglomerated state, it was mixed in a 1:1 ratio with the SDC powder. The powder was then shaken by hand. The mixture was once again mixed in a 1:1.2 ratio with a generic binder. Modifier was then added to ensure a liquid consistency that could be painted onto the electrolyte. Approximately four drops for every 1.9 grams of the SDC NiO mixture were added or until a manageable viscosity could be reached. Glass beads (mixing media) were added to the mixture, and the mixture was shaken by a mechanical shaker. The viscosity of the mixture was observed. More modifier was added if the mixture did not have a milkshake consistency.

The NiO, SDC mixture was slurry painted onto the electrolyte with a plastic tool. Because of the greater viscosity of the mixture, more time was required to spread the mixture evenly. Some BOE was added as needed to ensure a more uniform anode layer.

Final Sintering Process

After the anode had completely dried on the electrolyte, the fuel cell was sintered. Normally, each component is sintered and requires three separate furnace cycles. For this project, the fuel cell was sintered in only one cycle.

A high temperature molybdenum disilicide furnace was used to sinter the fuel cell. The fuel cell was placed on larger ceria pellets to avoid any adverse reactions at the high temperatures. As seen in Figures 3 and 4, a multistep heating and cooling cycle was implemented for the best results.

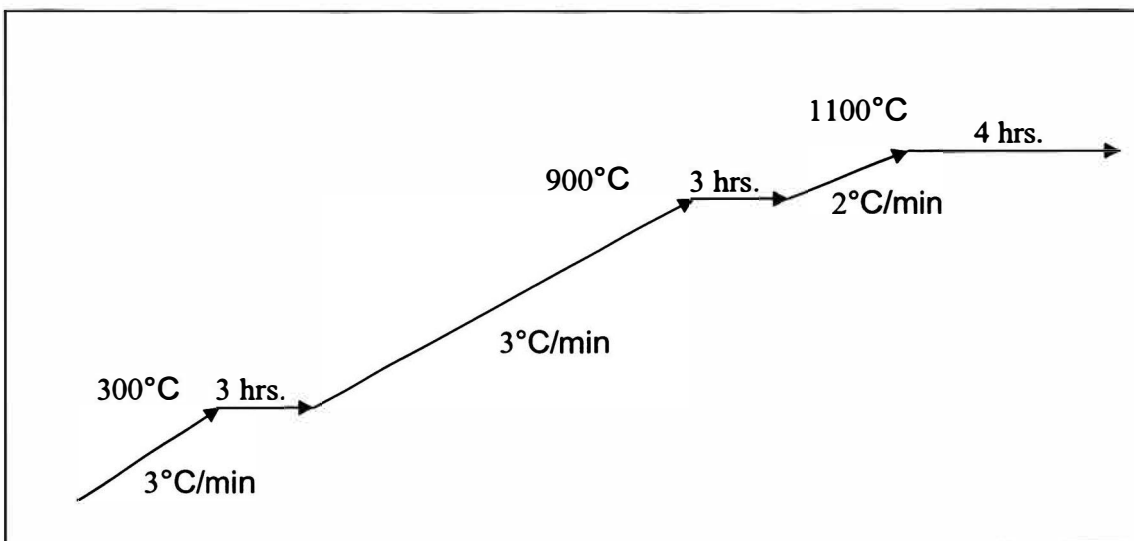


Figure 3. Heating schedule for the sintering of the SOFC.

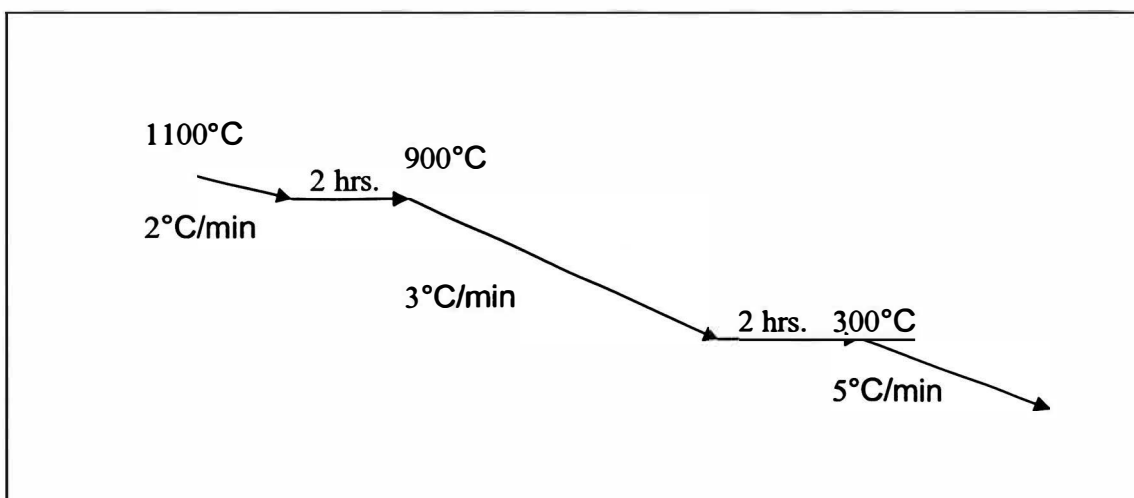


Figure 4. Cooling schedule after sintering the SOFC.

After the fuel cell was sintered, it was examined for any cracks, dimples, or discolorations. Then, silver paste was painted with BOE on the cathode to increase current collection during testing. After the silver paste dried, the fuel cell was ready for testing.

Testing

To test the fuel cell, a small piece of the original sintered fuel cell was broken off and placed in between the gold current collectors. The fuel cell holder was then placed into the furnace. The sample was then heated to 700°C before being tested.

Results and Discussion

In order to fabricate a low-cost porous ceria electrolyte, it was decided to dry press a ceria disc that would support both the cathode and anode. Initially, a cylinder about 2 centimeters in length was uniaxially pressed and thin discs were then cut from the cylinder.

However, because the sample was over 2 inches thick when pressed, the discs cut from the center of the cylinder were weak and not fully compacted. With more experimentation, it was found that the discs could be uniaxially pressed individually with greater density and green strength. Additional experimentation was performed to determine if isostatic pressing would increase the density further. There was no significant difference between the two pressing procedures, and uniaxial pressing was the method of choice due to its simplicity.

An average density of 3.71 g/cm³ was obtained by uniaxially pressing approximately .25g of SDC at 11,000 PSI. The theoretical density of SDC (Sm_xCe_{1-x}O_{2-x/2}) was calculated by the following equation obtained from (Eq. 1):

$$\rho_{th} = \frac{4}{N_a a^3} ((1-x)M_{Ce} + x M_{Sm} + (\frac{2-x}{2})M_O) \quad (\text{Eq. 1})$$

Where ρ_{th} is the theoretical density, M is the molar mass and N_a is Avogadro's number.³ The theoretical density of SDC powder is 7.19 g/cm³. The average density of the green SDC discs was 3.71 g/cm³ (51.6% of the theoretical density of the powder) (see Table I).

Table I. Density measurements for porous SDC SC-SOFCs.

Density Measurements											
Sample	Load (PSI)	Mass (g)	Thickness (cm)				Avg Thickness (cm)	Radius (cm)	Density (g/cm ³)	Theoretical Density	% Theo. Density
A	11k	0.249	0.0612	0.0592	0.0591	0.0598	0.0598	0.635	3.28	7.19	45.7
B	11k	0.249	0.0469	0.0478	0.0483	0.0513	0.0486	0.635	4.05	7.19	56.3
C	11k	0.250	0.0551	0.0543	0.0526	0.0547	0.0542	0.635	3.64	7.19	50.7
D	11k	0.253	0.0497	0.0513	0.0510	0.0510	0.0508	0.635	3.94	7.19	54.7
E	11k	0.249	0.0532	0.0522	0.0535	0.0533	0.0531	0.635	3.70	7.19	51.5
F	11k	0.255	0.0618	0.0614	0.0589	0.0608	0.0607	0.635	3.31	7.19	46.1
G	11k	0.254	0.0628	0.0604	0.0608	0.0595	0.0609	0.635	3.29	7.19	45.8
H	11k	0.250	0.0498	0.0527	0.0495	0.0492	0.0503	0.635	3.92	7.19	54.6
I	11k	0.253	0.0492	0.0527	0.0500	0.0503	0.0506	0.635	3.95	7.19	55.0
J	11k	0.256	0.0491	0.0523	0.0510	0.0497	0.0505	0.635	4.00	7.19	55.6
K	11k	0.253	0.0550	0.0541	0.0552	0.0541	0.0546	0.635	3.66	7.19	50.9
L	11k	0.252	0.0536	0.0529	0.0546	0.0554	0.0541	0.635	3.68	7.19	51.1
M	11k	0.256	0.0513	0.0536	0.0525	0.0531	0.0526	0.635	3.84	7.19	53.4
			Center	Sides			0.0539		3.71		51.6

Two SDC discs were sintered separately at 1100°C for 5 hours and had an average density of 6.02 g/cm³ (83.9% theoretical density). An increase of 32% of the theoretical density was achieved through sintering. Density could be further increased at higher sintering temperatures of 1400°C, but the components of the fuel cell could not be simultaneously sintered.

At first, the cathode and electrolyte were co-sintered at 1100°C. Several cracks initiated and broke the sample. Also, the samples were dimpled from the stresses resulting in a mismatch in thermal expansion values. The SDC electrolyte was in compression and the LSCF cathode was in tension. To understand the causes of the cracking and dimpling within the samples, the ideal sintering temperatures of the different fuel cell materials were searched in journal and manufacturing data (see Table II).

Table II. Sintering and coefficient of thermal expansion (CTE) values for common SOFC Materials.

Sintering and CTE Values for Common SOFC Materials					
Material	Particle Size (nm)	CTE (ppm/ °C)	Source	Sintering Temperature (°C)	Source
LSCF	300-600	15	4	950	5,6
SDC	5-10	12.7	4	1200-1250	4
	100-200			1300-1350	4
GDC	5-10	13.4	4	1200-1250	4
	100-200			1300-1350	4
YSZ	300-500	10.5	4	1400	7
NiO		14.8	5	1350	
NiO-SDC		14	5	1200-1350	4

The dimpling and cracks in the co-sintered cathode, electrolyte sample was caused by the 2.3 ppm/°C difference in CTE values between the materials. Because the electrodes had such close thermal expansion values, it was hypothesized that perhaps co-sintering all of the components at once may reduce stresses in the sample if the difference in sintering temperatures did not debilitate the ability of the cathode to react with the fuel.

A heating and cooling schedule (see Figures 3 and 4) was developed to simultaneously sinter all of the components of the SOFC using the information in Table II. The heating schedule ensured that the cathode was sintered at the conventional temperature and to relieve the stresses within the SOFC in order to prevent dimpling and cracks. Holding the temperature at 1100°C for four hours allowed the electrolyte to sinter more completely without sacrificing the efficiency of the cathode at a higher sintering temperature of 1350°C. Several fuel cells were sintered with the heating and cooling schedules without any visible cracks or dimpling.

After several fuel cells were fabricated, two fuel cells were selected based on the uniform distribution of the electrodes on the electrolyte. The first fuel cell did not perform successfully. With hydrogen gas as the fuel, the fuel cell generated less than .1 V, far less than expected. Although it is not known for sure, it is thought that the cathode may have not been completely reduced, the fuel cell had a fabrication flaw, or that the fuel cell did not catalyze hydrogen well.

Propane was chosen as the fuel for the second attempt. At startup, as the fuel cell was held at 50°C increments from 700 to 400°C, the fuel cell had a potential greater than .5 V at 650°C (see Figure 5). After incrementally decreasing the temperature, it was again increased to 700°C in a second run in which there was a maximum potential of .65 V at 550°C (see Figure 6). In the third run, the fuel cell's performance decreased drastically as the temperature was decreased (see Figure 7). The cause of the failure is unknown, but it may be due to the degradation of the cathode. Its structural integrity and its ability to withstand the severe oxidation reduction cycle within the furnace may have been compromised by the 1100°C sintering temperature during processing.

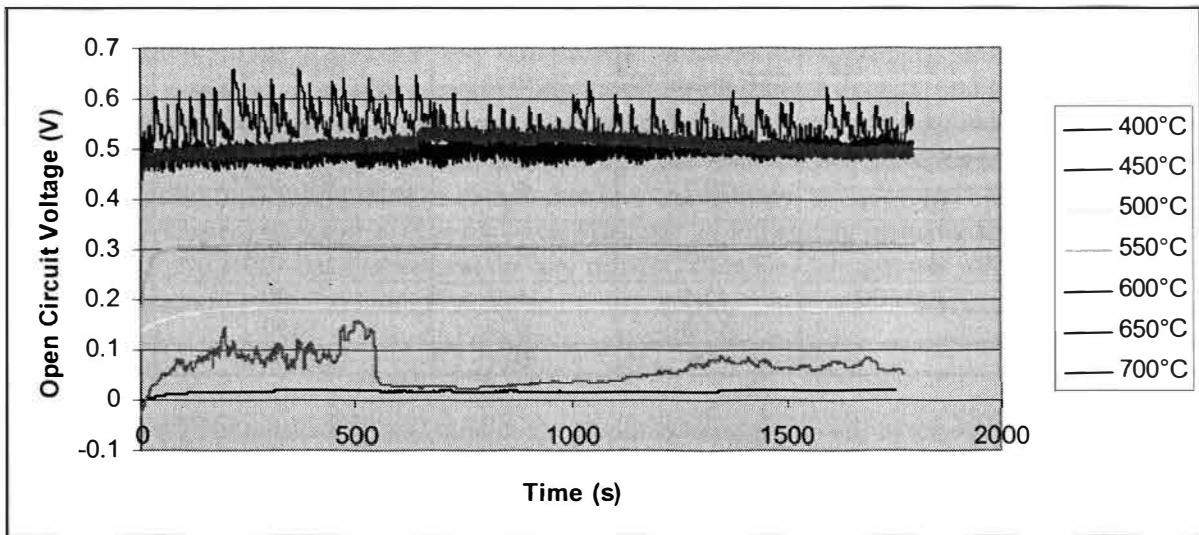


Figure 5. Open circuit voltage tests during startup (700-400°C)

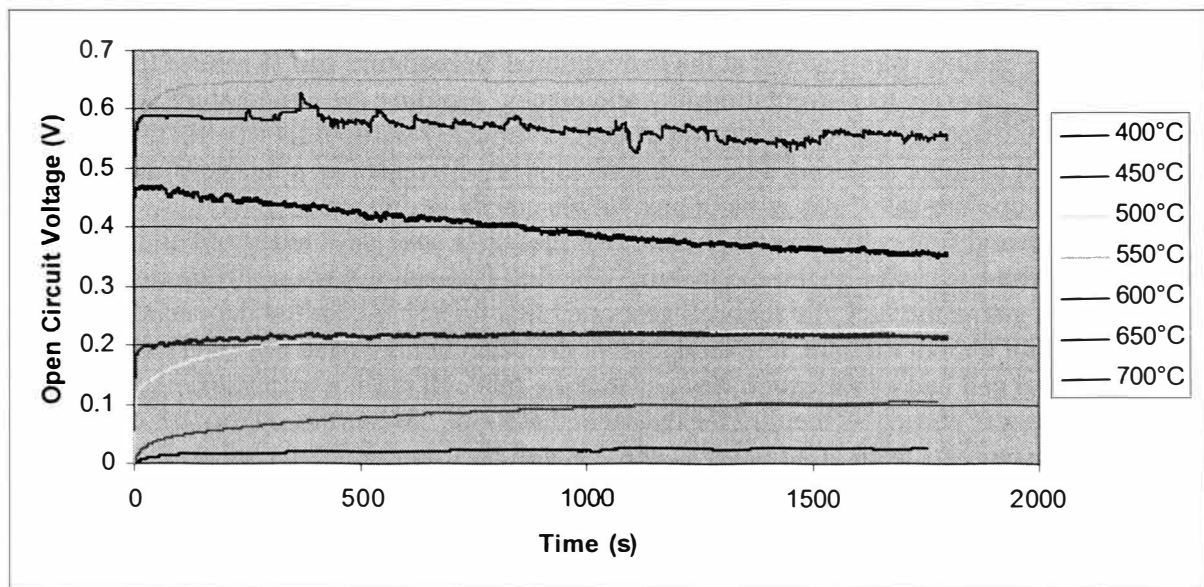


Figure 6. Open circuit voltage tests with increasing temperature (400-700°C).

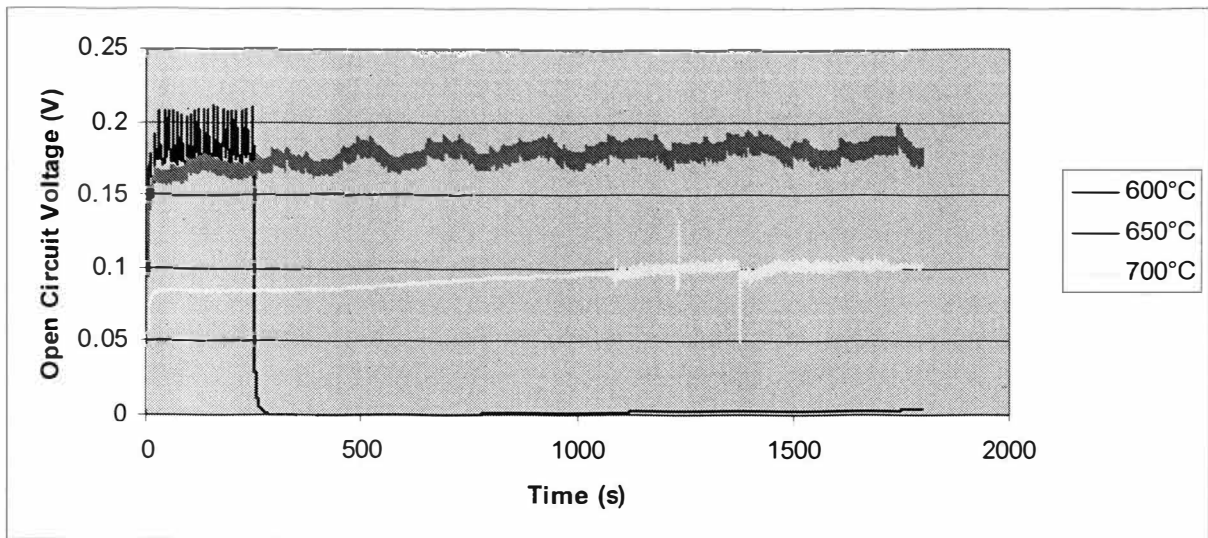


Figure 7. Open circuit voltage tests during second run with decreasing temperature before failure (700-600°C).

The impedance of the fuel cell was measured as well at different temperature increments (see Figures 6-8). Impedance can most closely be related to resistance. It is particularly interesting to note that the impedance was minimized at higher temperatures as expected and that the impedance actually decreased during failure (see Figure 7).

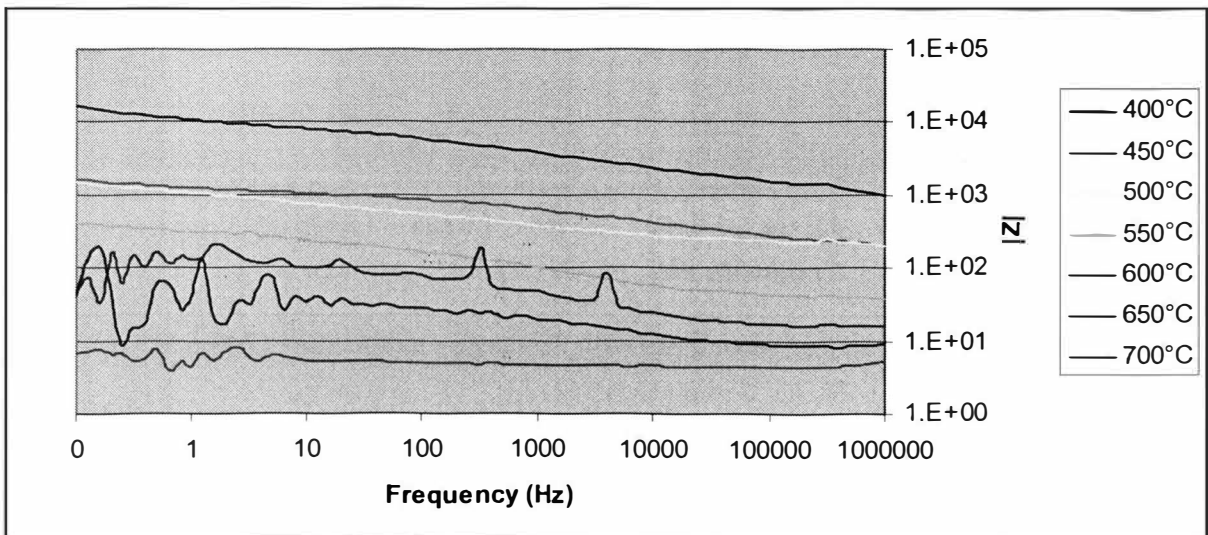


Figure 8. Impedance tests during startup (700-400°C).

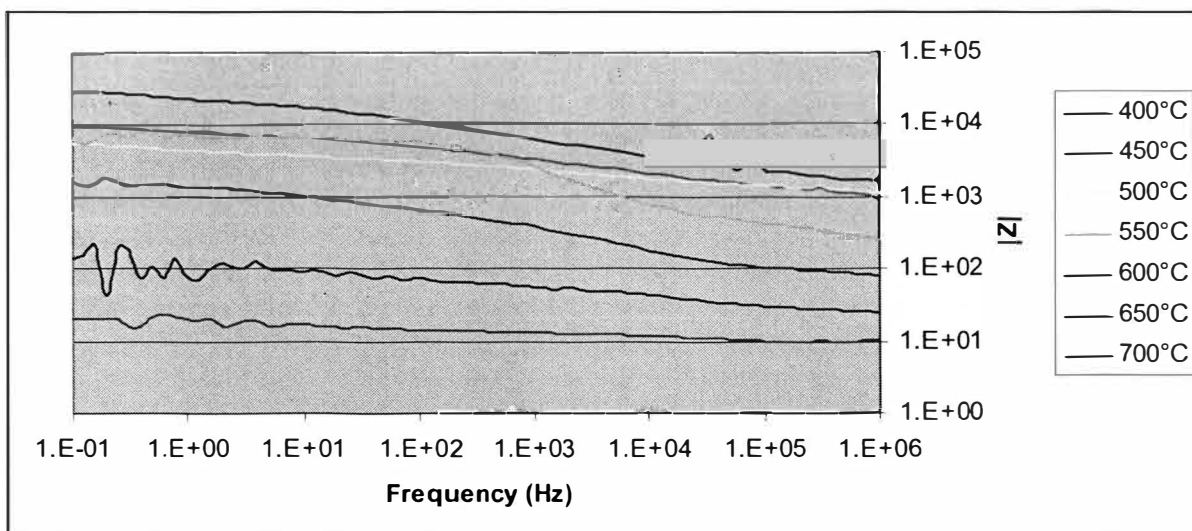


Figure 9. Impedance tests during first run with increasing temperature (400-700°C).

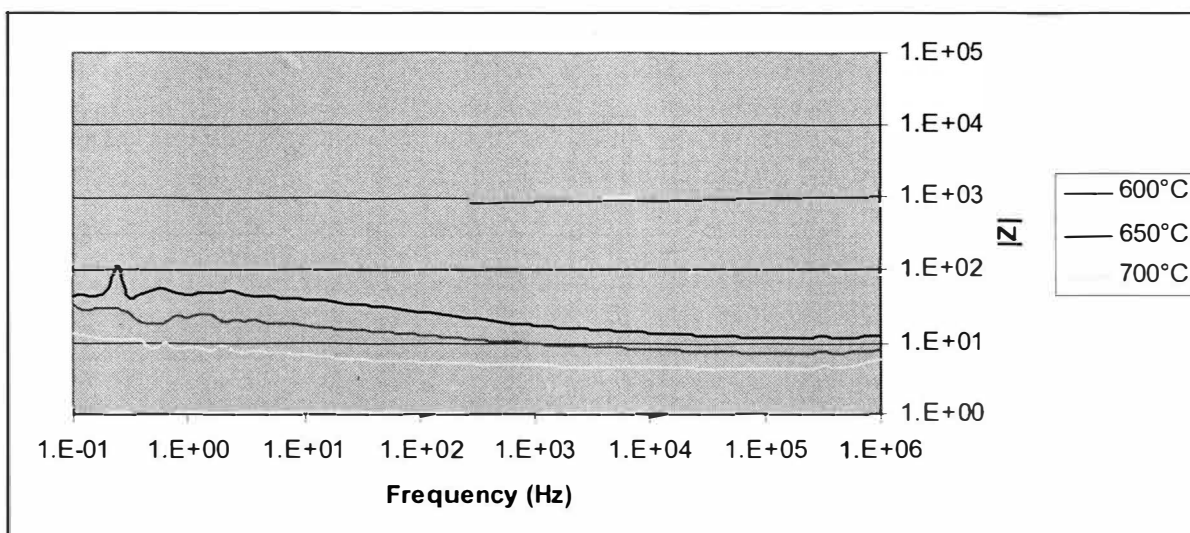


Figure 10. Impedance tests during second run with decreasing temperature (700-600°C).

Potentiodynamic tests were also performed in which the voltage is measured while the current is varied. However, there was an equipment problem and the tests were not completed. In order to calculate the conductivity of the electrolyte during each run, impedance test results were used in conjunction with some basic physics formulas. The resistance of the electrolyte was assumed to be the lowest impedance measurement for each temperature. At lower frequencies, the fluctuations in impedance are most likely caused by the oxidation reduction cycle of the electrodes. However, the electrolyte has relatively constant impedance since it is not being reacted with any gas or material.

The conductivity of the electrolyte was calculated using Eq. 2.

$$\sigma = \frac{1}{R} \cdot \frac{T}{SA} \quad (\text{Eq. 2})$$

Where σ is the conductivity of the electrolyte, R is the resistance measured in the impedance measurements, T is the thickness of the electrolyte, and SA is the surface area of the electrolyte. Using Dr. Petrovsky's prio data of SC-SOFCs with non-porous SDC electrolytes, a graph with a comparison between the conductivities of the fuel cells at different temperatures and with different electrolytes was created (see Figure 11).

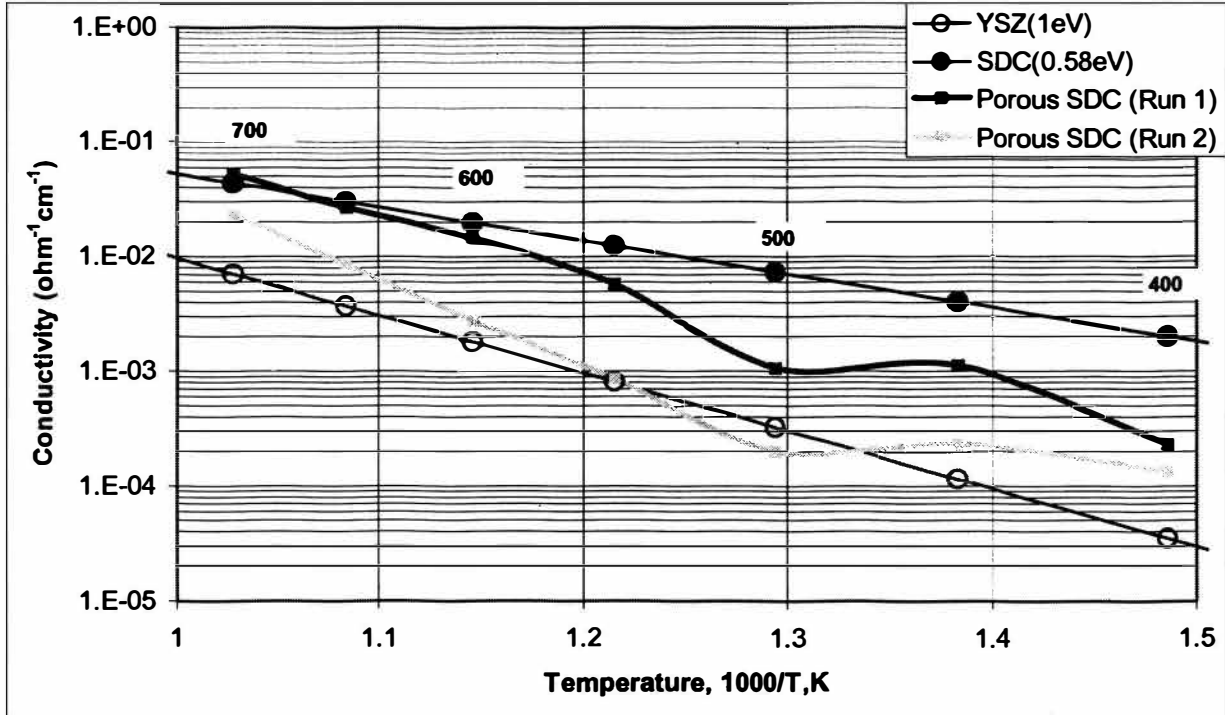


Figure 11. Comparison of conductivities electrolytic conductivities.

Although more fuel cells need to be tested to see if the results are repeatable, the performance of the simultaneously sintered single chamber SOFC was more conductive than a dense YSZ electrolyte but less conductive than dense SDC electrolytes. The conductivities have an exponential trend, but there is a slight deviation at 500°C. Also, the preliminary results show that there is significant degradation over a short period of time.

Future Work

Much was accomplished in this study including the successful development of a process to simultaneously sinter all of the components of a SC-SOFC. However, much work is left to be done in order to increase the efficiency of the fuel cells. More tests need to be run on a number of different fuel cells to determine the reproducibility and predictability of the results found in this report. Durability is a concern in the initial results and further tests need to be performed to determine the causes. Also, the open circuit voltage and conductivity may be improved by means of better uniaxial pressing technique to increase the density. A study is needed to

understand the versatility of the cell to operate efficiently in different hydrogen and hydrocarbon gases.

Conclusion

A fuel cell was successfully created by simultaneously sintering both electrodes and the electrolyte at 1100°C. The electrolyte was uniaxially pressed but was not completely densified due to the lower sintering temperature. The electrodes were evenly distributed onto the electrolyte using BOE to lower the viscosity of the paste. When tested at 50°C increments from 400-700°C, the fuel cell had a maximum potential of .65 V at 550°C. The porous SDC electrolyte had a conductivity lower than a dense SDC electrolyte as expected due to the increased diffusion of hydrogen ions into the electrolyte. One concern about the simultaneous SC-SOFCs with a porous SDC electrolytes is its durability. Initial tests show a significant decrease in voltage over time and less than 10 operational hours before failure. Many factors must be considered such as the effect of a higher sintering temperature on the durability of the cathode and the lower than ideal sintering temperature for electrolyte which might increase the amount of hydrogen diffusion through the electrolyte. Further studies need to be performed to determine the durability of the fuel cells and the causes of failure. With further studying, a simultaneously sintered single chamber SOFC with a porous SDC electrolyte may be more cost-effective alternative to traditional SOFCs.

Acknowledgements

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