**Investigation and Design Studies of SOFC Electrode Performance at
Elevated Pressure**

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Abstract

An experimental program was set forth to study fuel cell performance at pressure and under various compositions. Improvement in cathode electrode performance is on the order of 33-40% at pressures of 6.4 Bara compared to atmospheric pressure. Key cathode operational parameters are the concentration and partial pressure of O_2 , and temperature. The effect of partial pressure of oxygen (P_{O_2}) decreases the activation polarization, although there appears to be a secondary effect of absolute pressure as well. The concentration of oxygen impacts the diffusion component of the polarization, which is largely insensitive to absolute pressure. The effect of pressure was found to reduce the total polarization resistance of full fuel-cells beyond the reduction determined for the cathode alone. The total reduction in ASR was on the order of 0.10 ohm-cm^2 for a pressure increase from 1 to 6.5 Bara, with about 70% of the improvement being realized from 1 to 4 Bara. An important finding was that there is an effect of steam on the cathode that is highly temperature dependent. The loss of performance at temperatures below 850°C was very large for the standard LSM + YSZ cathodes.

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Executive Summary

The operation of the Rolls-Royce solid oxide fuel cell (SOFC) system is at pressures up to 7 atmospheres. The original Roll-Royce SOFC system featured anode recycle and anode off-gas combustion that creates unique gas conditions, especially at the cathode, that are outside the range of that typical for SOFCs: lower oxygen fractions, steam and carbon dioxide on the cathode and high steam contents on the anode. There is limited data on the performance of electrodes under such elevated pressure conditions and compositions.

Test apparatus to study cathode performance at pressure and under various compositions was constructed as part of this program. In addition, this program utilized existing test capability which included both ambient and pressurized test stands for full fuel cells. These stands are capable of supplying fuel cells with a range of anode and cathode compositions which encompass the operation of the Rolls-Royce system.

Improvement in cathode electrode performance is on the order of 33-40% at pressures of 6.4 Bara compared to atmospheric pressure. Key cathode operational parameters are the concentration and partial pressure of O_2 , and temperature. CO_2 showed negligible impact on short term electrode performance. Steam at levels below 20% also showed negligible impact on short term electrode performance, but has been found to cause a longer-term loss of performance, especially at lower temperatures.

The effect of partial pressure of O_2 (P_{O_2}) decreases the activation polarization, although there appears to be a secondary effect of absolute pressure as well. The concentration of O_2 impacts the diffusion component of the polarization, which is largely insensitive to absolute pressure.

The effect of pressure on long term cathode performance was not established. In general, due to the non-prototypic nature of the current collecting for the button cell samples compared to the full cells, and their apparent instability during long-term testing, the degradation tests were not considered to be as valuable as hoped for deconvolution of degradation results.

The effect of pressure was found to reduce the polarization resistance of the full fuel-cell beyond the reduction determined for the cathode alone. The total reduction in ASR was on the order of 0.10 ohm-cm^2 for a pressure increase from 1 to 6.5 Bara, with about 70% of the improvement being realized from 1 to 4 Bara. The effect of the change in fuel composition is on the order of 0.09 to 0.10 ohm-cm^2 , although the degree to which fuel composition affects performance is highly dependent upon the permeability of the substrates.

An important finding was that the effect of steam was highly temperature dependent. The loss of performance at temperatures below 850°C was very large for the standard LSM + YSZ cathodes. Steam is also a major factor in the degradation rate. Data at pressure was insufficient to substantiate the effect of pressure on degradation.

The test facilities in use and the data produced by them provide sufficient detail and range of operation to provide a robust set of data for model development and validation.

1.0 Background and Introduction

The operation of the Rolls-Royce solid oxide fuel cell (SOFC) system is at pressures up to 7 atmospheres. The Roll-Royce SOFC system features anode recycle and anode off-gas combustion that creates unique gas conditions, especially at the cathode, that are outside the range of that typical for SOFCs: lower oxygen fractions, steam and carbon dioxide on the cathode and high steam contents on the anode. There is limited data on the performance of electrodes under such elevated pressure conditions and compositions. Further investigations of the performance of electrodes at high pressure, and while under the system prototypic gas compositions present in the Rolls-Royce design, is a critical research area for Rolls-Royce in its development and commercialization of a 1MW distributed power plant, as well as for the US Dept. of Energy in its emphasis on large combined cycle centralized power stations using SOFC technology.

The fundamental building block of the 1MW power system is individual substrates containing a large number of small cells connected in series as shown in Figure 1.1.

Figure 1. 1 - Rolls-Royce Series Connected Cells on Substrate

The cells consist of printed active cell layers on a substrate as shown in Figure 1.2. The cells progressively build up voltage for as many cells as are connected in series. This design is amenable to mass manufacturing techniques and also provides flexibility in scale-up and material changes as technology improvements are made. The high voltage low current also minimizes ohmic losses.

Figure 1. 2 - Schematic of Series Connected Cell

Program Summary

RRFCS has test facilities in North Canton, Ohio capable of testing both cathode symmetric cells and subscale substrates at the 1MW system prototypic pressures and gas compositions. The objective of testing cathode symmetric cells, at similar temperature and pressure conditions, is to compare to the full cell test data and aid deconvolution of the ASR contributions of the cell between the anode and cathode. Subscale substrates with 3 cells per substrate and having a high level of instrumentation are used to provide a breakdown of various cell components. Detailed electrochemical impedance analysis is also used to sort out ohmic and non-ohmic contributions of the active cell layers.

This project pursued a detailed investigation of the performance (ASR and degradation) of button cells and fuel cells under the full pressurized operating conditions and representative system gas compositions. The objective is to further define the performance difference for cells between ambient and pressurized operation. In both pressurized and ambient testing, anode and cathode side gas compositions were systematically varied to examine activation and concentration polarization processes for each electrode.

A limited number of longer-term tests (500-1000 hours) were also performed to compare degradation between ambient and pressurized operation, although this data was limited.

2.0 Literature Review of the Effect of Pressure on SOFC Performance

A brief summary of key observations from literature reviewed regarding SOFC performance is provided. In general, studies have shown benefits of pressure beyond nernst potential increases including reduction of anode and cathode activation as well as anode concentration polarizations.

“Parametric study of solid oxide fuel cell performance” Ni, Leung, Leung¹

This was a modeling study with comparisons to data in the literature.

Concentration Polarization

- Two parts, molecular and Knudsen diffusion
- Knudsen - If pore size is much smaller than the mean free path of the species, the molecule-pore wall interaction dominates
- Pore size is larger than mean free path – molecular dominates
- Pressure impact dependent on geometry and relative Knudsen/Molecular contributions

Activation Polarization

- Reduces with increased pressure due to higher molar concentration at triple point boundaries (TPBs)

Pore Size/porosity

- Concentration polarization decreases with increasing pore size up to 10 microns
- Optimal pore size of about 3 microns with 40% porosity

“On the mechanisms and behavior of coal syngas transport and reaction within the anode of a solid oxide fuel cell”, Gemmen, Trembly².

- Syngas compositions, 30% or less H₂, 30-60% CO
- 2 mm thick anode
- Tortuosity = 3.6
- Porosity = 56%
- Pore diameter = 1 micron

¹ “Parametric study of solid oxide fuel cell performance”, Meng Ni, Michael K.H. Leung *, Dennis Y.C. Leung, Department of Mechanical Engineering, The University of Hong Kong, 7/F Haking Wong Building, Pokfulam Road, Hong Kong, China, Energy Conversion and Management 48 (2007) 1525–1535, Received 17 May 2006; accepted 26 November 2006

² “On the mechanisms and behavior of coal syngas transport and reaction within the anode of a solid oxide fuel cell”, R.S. Gemmen, J. Trembly, National Energy Technology Laboratory, Journal of Power Sources 161 (2006) 1084-1095, Received in revised form 23 May 2006; accepted 6 June 2006

Concentration Polarization

- Concentration polarization reaches a minimum at 5 atmospheres for due to increased H₂ production
- As pressure increases, H₂ generation increases due to steam methane reforming (SMR) and water gas shift (WGS) reactions up to 7 atm
- At 8 atm and above methane is produced

“Characteristics of anodic polarization of solid oxide fuel cells under pressurized conditions”, Kikuchia, Yanoa, Takeguchib, Eguchia³

Experimental study was performed using anode symmetrical cell test setup.

Concentration Polarization

- Anode symmetric cell Ni-YSZ/YSZ/Ni-YSZ
- Anodic polarization increases with increasing pressure, decreases with increased P_{O₂} at interface.

“Electrode Studies at High Pressure”, Pederson, McCarthy, Chou, Coffey, Coyle, Marina, Nguyen, Thomsen, and Zhou⁴

Experimental and analytical study was performed on cathode symmetric cells with focus on effect of P_{O₂} on different cathodes up to 100 Bara.

Concentration Polarization

- Exchange current density followed P(O₂)^{1/2} dependence for LSM-20, Au
- LSM/Ceria and LSF show lesser dependence

“Oxygen electrode reaction on stabilized zirconia under high oxygen pressure (up to 100 bar)”, Drevet, He´nault, Fouletier⁵

Three electrodes were studied-Pt, Ag, LSM35

- Pt – Po₂ negative effect
- Ag – initial slightly decrease than increase greatly for Po₂ higher than 30bar
- LSM35 showed Rp decreases up to P_{O₂} < 20 bar

³ “Characteristics of anodic polarization of solid oxide fuel cells under pressurized conditions”, Ryuji Kikuchia, Tatsuya Yanoa, Tatsuya Takeguchib, Koichi Eguchia, Solid State Ionics 174 (2004) 111 –117, Received 5 February 2004; accepted 29 May 2004

⁴ “Electrode Studies at High Pressure”, Larry Pederson, Ben McCarthy, Matt Chou, Greg Coffey, Chris Coyle, Olga Marina, Carolyn Nguyen, Ed Thomsen, and Xiao-Dong Zhou, 8th Annual SECA Workshop, San Antonio TX, August 7-9, 2007

⁵ “Oxygen electrode reaction on stabilized zirconia under high oxygen pressure (up to 100 bar)”, C. Drevet, M. He´nault, J. Fouletier, Solid State Ionics 136–137 (2000) 807–812

3.0 Test Apparatus

Testing was performed on button cells and full fuel cells, both at atmospheric and pressurized conditions. The combination of cathode button cell and full cell testing is used to deconvolve performance of the whole cell. RRFCS has capabilities to test at system relevant conditions including pressure, temperature, and the full range of anode compositions experienced in service.

Pressurized Button Cell Apparatus

As part of this program, RRFCS has developed the capability to test cathode symmetric button cells at pressures up to 7 Bara and temperatures up to 1000°C under various gas compositions consisting of O₂, N₂, CO₂, and steam.

The pressurized button cell test stand was designed and built on this program and is shown below in Figure 3.1. The test specimen is placed on a pedestal tube in the middle of the fixture which is then enclosed with a closed-one-end alumina tube which forms the pressure boundary. An inconel guard tube is placed around the alumina tube for safety. This assembly is placed inside of a furnace which heats the sample up to test temperature. The alumina tube is pressed onto a fixed base plate and is sealed on the bottom edge by means of a compressible gasket. Load is transferred to the alumina tube from compression springs and a loading plate through a load transfer insulation block. Additional personnel shields are placed around the fixture in case of a pressure boundary failure.

Figure 3.1 - Pressurized Button Cell Apparatus

The test setup – including the gas supply system, power control, and safety system which were developed separate from this program – is shown in the picture in Figure 3.2. The test arrangement is assembled and the test furnace lowered over the sample before adding seal load and personnel shield components. The test stand is supplied with gases including Air, N₂, CO₂, by a calibrated mixing station. Steam is added as required through a heated humidifier column, the effluent kept warm by means of a heated supply line. Data is collected for long-term tests with an automated DAS. EIS measurements were carried out using a Solartron 1286 or 1287 potentiostat with a Solartron 1255 frequency response analyzer. The applied frequency range was from 0.01 Hz to 150 kHz, with data collected by scanning from high to low frequencies. Polarization amplitude of 20 mV was applied at the open-circuit voltage (OCV) condition. Polarization value was obtained by dividing the difference of ASR and ohmic resistance by 2. A ventilated exhaust duct extracts the gases exiting the test stand. A safety system automatically shuts down the power to the test stand if there is an over-temperature or an electrical short detected.

Figure 3.2 - Pressurized Button Cell Test Setup

Fuel Cell Tests

Testing on fuel cell substrates was performed in both atmospheric and pressurized test stands. Five pressurized test stands are located in two separate ventilated enclosures, one of which is shown in Figure 3.3 below. Each test stand has a gas mixing station which blends air, N₂, and CO₂ on the cathode and H₂, CO₂, and N₂ on the anode. The streams can be passed through a heated humidification column to add steam on both

the anode and cathode. The blends can simulate the full range of anode and cathode conditions from inlet to outlet.

Figure 3.3 - Pressurized Test Stands in Ventilated Enclosure

The pressurized test stand arrangement is shown in Figures 3.4 and 3.5. Figure 3.4 shows the test rig consists of a hot-walled pressure vessel which sits inside a 3-zone furnace to control the temperature boundary condition of the test sample. The seal region is kept outside of the hot zone to permit the use of standard seal materials. Process connections for incoming anode and cathode streams are made at a fixed lower head, along with electrical and instrumentation lead outs. The electronic load which sets the steady state current condition is located in this region also. In addition, an external voltage tap patch panel is available for connecting a Solartron to acquire EIS data.

In Figure 3.5 we see the internals of the test section after the pressure vessel is removed. The lower section has a concentric anode and cathode gas preheat coil to bring the incoming gases to process temperature. The test sample sits inside the test chamber housing where two fuel cells connect to the fuel manifold and the cathode gas is directed over the samples. Above the test chamber the anode exhaust is routed and combined with the cathode exhaust to combust the unused fuel in a flare section before exiting the pressure vessel. The exhaust then flows out the top of the pressure vessel, passing through a cooling coil before venting into the enclosure.

Figure 3. 4 - Pressurized Test Stand Showing Pressure Vessel

Figure 3. 5 - Pressurized Test Setup with Vessel Removed

The samples tested were triple cells as shown in Figure 3.6. The samples consist of 3 cells with two cell primary interconnects (PICs). Fuel flows into the two cells by means of a manifold into which the two samples are connected, and exhausts into the flare section above through an exhaust tube. The cathode gas is directed over the face of the samples by means of a manifold nozzle. Voltages taps on the anode and cathode layers are used to measure the voltages at various points so as to separate out losses from the cells, cell interconnects, and the current collector layers. Current flows through the samples by means of the secondary interconnect wire (SIC) which connects to the current bus bars.

Figure 3.6 - Triple Cell Test Sample

The atmospheric stands used have similar functionality and are simpler in design than the pressurized test stands described above, so they are not detailed here.

4.0 Button Cell Testing

The button cells tested were cathode symmetric cells made of a screen printed cathode composed of LSM + YSZ and cathode current collector composed of LSM. A platinum mesh is attached to the CCC layer with additional LSM ink. Using the apparatus described above in Section 3, a sequence of tests was performed to examine the effect of composition, pressure, and temperature on cathode performance. The matrix of test conditions is shown below in Table 3.1.

Pressurized BC Test Matrix

Test	Purpose	Pressure	Temp	Composition				Range
		Bara	°C	N ₂	O ₂	H ₂ O	CO ₂	
1A	Effect of Pressure	Varies	800	88%	12%	0%	0%	1 to 6.4 Bara
1B		Varies	800	85%	12%	3%	0%	1 to 6.4 Bara
2A		Varies	900	88%	12%	0%	0%	1 to 6.4 Bara
2B		Varies	900	85%	12%	3%	0%	1 to 6.4 Bara
3A	Effect of Temperature	6.4	Varies	88%	12%	0%	0%	750 - 950°C
3B		6.4	Varies	85%	12%	3%	0%	750 - 950°C
4A	H ₂ O Test	1	850	Varies	12%	Varies	0%	0 - 26%
4B	Constant P _{H2O} Test	Varies	850	Varies	12%	Varies	0%	P _{H2O} = 0.2 Bar
5A	O ₂ Variation	1	800	80%	Varies	0%	0%	8 - 20%
5B		6.4	800	80%	Varies	0%	0%	8 - 20%
5C		1	925	80%	Varies	0%	0%	8 - 20%
5D		6.4	925	80%	Varies	0%	0%	8 - 20%
6	CO ₂ Test	6.4	850	88%	12%	0%	Varies	0 - 25%
7	500 hours degradation	1bara		88%	12%	0%	0%	
		1bara		85%	12%	3%	0%	
		6.4bara		88%	12%	0%	0%	
		6.4bara		85%	12%	3%	0%	

Table 4. 1 Matrix of Test Conditions for Pressurized Button Cell Tests

Effect of Pressure

Figures 4.1 through 4.3 show the impact of pressure on the total cathode polarization (Rp) with a 12% O₂ feed at two temperatures. Figure 1 is at 800°C and Figure 2 is at 900°C. At 800°C, the cathode polarization is dominated by the activation loss, which is the higher frequency arc to the left of the x-axis. There is an approximate 40% reduction in the polarization with the increase in pressure from 1 to 6.4 Bara, although the majority of that reduction takes place with the pressure increase from 1 to 3 Bara. At 900°C the activation polarization similarly shows an approximate 40% reduction in overall polarization going from 1 to 6.4 Bara. There were two arcs in impedance spectra for the cathode symmetrical cells in which the high frequency arc was reduced with increased pressure but the low frequency arc (to the right of the x-axis) was nearly pressure independent. The effect of 3% steam on performance was negligible.

Figure 4.1 Effect of Pressure on Cathode Polarization at 800°C and 12% O₂ Figure 4.2 Effect of Pressure on Cathode Polarization at 900°C and 12% O₂

Figure 4.3 Summary of Pressure Effect Data at Two Temperatures.

Effect of Temperature

The cathode activation energy, calculated from slope of the Arrhenius plot, is shown in Figure 4.4 for constant O₂ concentration at 1 and 6.4 Bara. The data shows a linear activation energy over the temperature range of 750°C to 950°C and a moderate increase in activation energy with increased pressure.

Figure 4.4 Activation Energy at 1 and 6.4 Bara, 12% O₂

This was duplicated at a range of O₂ concentrations at 1 and 6.4 Bara on a second sample as shown in Figure 4.5, but only over the range of temperatures from 800 to 900°C. Activation energy value varies from 1.2 to 1.37 eV at 1 bara and 1.24~1.47 eV at 6.4 bara. Oxygen reduction reaction is strongly affected by surface adsorption step and then activation energy could be related to oxygen partial pressure effect on surface properties. The data demonstrates that activation energy shows a dependence upon %O₂ and P_{O₂} independently, with %O₂ being more dominant. This suggests that the simple dependence of current exchange density as a function of P_{O₂} alone is insufficient to describe the behavior.

Figure 4.5 Effect of Pressure and Oxygen Concentration on Activation Energy

Effect of O₂ Concentration

The effect of O₂ concentration on cathode R_p was investigated at different pressure (6.4 and 1 bar) and temperature (800, 850, and 900°C). R_p varies from 0.016 ohm-cm² at 6.4 bar and 900°C to 0.176 at 1.0 Bara and 800°C. The data is summarized in Figures 4.6 through 4.8.

The impedance data at 6.4 Bara and 900°C is shown in Figure 4.9. The R_p value was significantly reduced from 1 Bara to 6.4 Bara condition while R_s value remains constant under the pressure change at constant temperature. At constant pressure and temperature, as the oxygen concentration is decreased, both the high and low frequency arcs of EIS increased together. It is anticipated that the first and second arc of EIS could be related to charge transfer reaction, and diffusion mass transport (or some other mass transfer mechanism such as a surface adsorption) respectively. It appears to be reasonable that partial oxygen pressure change gives strong effect on both EIS arcs.

A typical button cell sample is shown in Figure 4.10 which shows a fairly thick layer which includes the cathode and current collector ink used to apply the platinum mesh current collector. The layer is estimated at 225 microns thick on average, with a porosity of 25% and a tortuosity of 2. From the impedance data at each condition, the low frequency (diffusion term) was estimated as shown in Figure 4.8. Based on the diffusion model (a more detailed discussion can be found in Section 7.0) for this arrangement we see that the data model indicates the low frequency portion of the impedance data is described by a gas diffusion model through the porous layer. The remaining polarization which composes the high frequency portion of the curve is shown in Figure 4.8. This is considered to be the activation portion of the cathode polarization.

Figure 4.6 Effect of Pressure and O₂ Concentration of Cathode Rp at 900°C

Figure 4.7 Effect of Pressure and O₂ Concentration of Cathode Rp at 850°C

Figure 4.8 Effect of Pressure and O_2 Concentration of Cathode R_p at 800°C

Figure 4.9 Impedance Data from O_2 Test Matrix at 6.4 Bara and 900°C

Figure 4.10 Cross-section of typical button cell sample

Figure 4.11 Low Frequency (diffusion) Portion of Cathode Polarization

Figure 4.12 High Frequency (activation) Portion of Cathode Polarization

Effect of CO₂ Concentration

CO₂ concentration effect (0, 6, 18, and 25%) on cathode Rp at 6.4 bara and 850°C was investigated. Oxygen concentration was fixed at 12%. Even though there was small Rp increment (0.0015 ohm-cm²) for the presence of CO₂, the CO₂ concentration effect from 6% to 25%-CO₂ was almost negligible.

Figure 4.13 Effect of CO₂ on Cathode Rp, 850°C, 6.4 Bara, Constant P_{O₂}

Effect of Steam Concentration

The effect of steam on cathode performance was of importance because the original RRFCS system design used a direct combustion of the unused anode fuel to pre-heat the incoming cathode air. This was found to cause an unacceptable loss of performance and the system configuration has since been modified to eliminate this feature. The effect of steam on cathode performance, was found to be a long-term effect, but did not manifest itself in short-term (hour long) tests. Figure 4.14 below shows little change in polarization at steam levels from 3% to 26%. Figure 4.15 shows the polarization at 1 and 6.4 Bara for the same P_{H_2O} and dry conditions, which again shows the steam addition has little impact on short-term performance.

Figure 4.14 Effect of Steam on Cathode Performance for Short Term Test

Figure 4.15 Effect of P_{H_2O} on Cathode Performance for Short Term Test

Degradation of Cathode Symmetric Cells

Longer-term testing was performed to begin investigating degradation trends with respect to pressure. Figure 4.16 below shows the traces of 4 tests conducted comparing pressure and cathode humidification (wet = 3% steam). The trends seem to show a small effect of the wet versus dry condition, but the effect of pressure is hard to discern. In general the degradation rate of these samples appears large.

Figure 4.16 Comparison of Degradation Traces under Constant Current Load

Figures 4.17 and 4.18 show the impedance traces at 0 and 500 hours for the dry cathode cases at 1 and 6.4 Bara. When the performance change is deconvolved we determine that most of this loss is due to ohmic change, likely indicating degradation of the current collection rather than the cathode polarization. The polarization loss decreases for the dry 1 Bara case and is very small for the dry 6.4 Bara case. The polarization loss increase is larger for both cases with humidified cathode air, again being slightly larger than for the case at pressure.

Figure 4.17 Impedance Traces at 0 and 500 hours at 900C, Dry Cathode, and a) 1 Bara, b) 6.4 Bara

Figure 4. 18 Impedance Traces at 0 and 500 hours at 900C, Wet Cathode, and a) 1 Bara, b) 6.4 Bara

Summary of Button Cell Testing

Improvement in cathode electrode performance is on the order of 33-40% at pressures of 6.4 Bara compared to atmospheric pressure. Key cathode operational parameters are the concentration and partial pressure of O₂, and temperature. CO₂ showed negligible impact on short term electrode performance. Steam at levels below 20% also showed negligible impact on short term electrode performance, but has been found to cause a longer-term loss of performance, especially at lower temperatures.

The effect of partial pressure of O₂ (P_{O₂}) decreases the activation polarization, although there appears to be a secondary effect of absolute pressure as well. The concentration of O₂ impacts the diffusion component of the polarization, which is largely insensitive to absolute pressure.

The effect of pressure on long term performance was not established. In general, due to the non-prototypic nature of the current collecting for the button cell samples compared to the full cells, and their apparent instability during long-term testing, the degradation tests were not considered to be as valuable as hoped for deconvolution of degradation results.

5.0 Triple Cell Testing

The testing of full fuel cells was performed in both atmospheric and pressurized test rigs. The effect of pressure, temperature, fuel composition, and cathode composition were examined. Longer term degradation effects were also examined considering the effects of pressure and cathode steam composition. Testing was performed on three-cell samples (triple-cells) which were fully instrumented to give a breakdown of cell and interconnect components under atmospheric and elevated pressures as described in Section 3.0.

Effect of Pressure

Figure 5.1 shows the effect of pressure for a test at 900°C which shows the total electrode polarization is reduced by about 0.09 ohm-cm² going from 1 to 6.5 Bara. Of note is that about 70% of the improvement takes place between 1 and 4 Bara.

Figure 5.1 Cell ASR reduction as a function of pressure at 900°C

The VI curves at 1 and 6.5 Bara are shown in Figure 5.2 which again shows the total electrode polarization is reduced by about 0.09 ohm-cm² going from 1 to 6.5 Bara. This is more than double the reduction observed for the cathode polarization alone. The impedance trace of another test is shown in Figure 5.3 which shows that the improvement in ASR is in the polarization term. As noted in Section 2.0 and as will be discussed in Section 6.0, it is expected that pressure impacts not only the anode activation but also the concentration polarization because of the small pore size and thickness of the substrate in which Knudsen diffusion will be a factor. This improvement results in a decrease in total ASR of over 20%, which when coupled with increased Nernst potential yields a much higher power density. For example, at an operating voltage of 0.8 volts, the power density at 6.5 Bara is double that at 1 Bara.

Figure 5.2 Effect of Pressure on Performance of a Triple-Cell Sample at 900°C

Figure 5.3 Impedance Trace of TCT26 at 900°C, 1 and 3.2 Bara

Effect of Fuel Composition

Figures 5.4 and 5.5 show the effect of fuel composition on performance. The fuel compositions tested are shown in Table 5.1. First, the effect of pressure is again shown to improve the total ASR by about 0.09 to 0.10 ohm-cm². Second, the effect of the change in fuel composition is on the order of 0.09 to 0.10 ohm-cm². It is discussed in Section 6.0 that the degree to which fuel composition affects performance is highly dependent upon the permeability of the substrates.

Table 5.1 – Fuel Composition at Bundle Inlet and Bundle Outlet

Constituent	Bundle Inlet	Bundle Outlet
H ₂	41%	21%
CO	23%	14%
CO ₂	12%	22%
H ₂ O	24%	43%

Figure 5.4 Effect of Fuel Composition at 900°C, 1 Bara

Figure 5.5 Effect of Fuel Composition at 900°C, 6.5 Bara

Effect of O₂ Concentration

Prior to performing this test, the sensitivity to total cathode flow was checked at an O₂ concentration of 8%. At flows above 20 slpm the ASR was not sensitive to flow, and a total flow of about 24 slpm was used for this test. Figure 5.6 shows the effect of oxygen concentration on performance. The effect is slightly larger than observed on the button cell testing described in Section 4.0. Note that at concentrations lower than 4% the ASR begins to increase rapidly.

Figure 5.6 Effect of Oxygen Concentration on Cell ASR at 6.4 Bara and 860°C

Effect of Steam Concentration

The original RRFCS system design used a direct combustion of the unused anode fuel to pre-heat the incoming cathode air. This was found to cause an unacceptable loss of performance and the system configuration has since been modified to eliminate this feature. Figure 5.7 shows the short term effect of 13% cathode steam on performance. The traces show that there was no significant effect of steam on short-term performance, confirming what was observed in button cell testing.

Figure 5.7 Short-term Effect of 13% Steam on Performance at 1 and 6.5 Bara

Figure 5.8 shows a time trace of a triple-cell test (TCT40) which was started up with steam on the cathode. At 40 hours, the steam was removed from the cathode stream, resulting in an immediate improvement followed by a continued gradual improvement. Impedance measurements were taken at about 38 and 59 hours. Figure 5.9 shows the two impedance curves, which show that the effect is a cathode polarization effect. Frequency analysis of impedance data showed that the increased polarization caused by steam is a slower process on the order of 10 Hz. This is similar to a mass transport process, and suggests a surface exchange phenomenon in the cathode.

Figure 5.8 Time Trace Showing Reduced ASR after Cathode Steam is Removed

Figure 5.9 Impedance Trace for TCT40A at 38 and 59 Hours

Effect of Temperature and Burn-In (plus steam)

The effect of temperature on the cells is shown in Figure 5.10 along with the effect of steam. An important finding was that the effect of steam was highly temperature dependent. The loss of performance at temperatures below 850°C was very large for the standard LSM + YSZ cathodes. Figure 5.10 is for a case early in the operation of the cells (less than 200 hours) before the cell “burn-in” takes place. This phenomenon is believed to occur due to the mix of materials used on the anode and anode current collector layers for the cell technology used at this time. After burn-in is completed, the cell ASR tends to be lower than at first, and is relatively stable for the remainder of the test. Figure 5.11 shows ASR data as a function of temperature with and without steam on the cathode after burn-in has occurred.

Degradation Testing

Degradation testing was conducted on several tests, however many were affected by rig related issues which cut tests short. Three test which ran 1000 hours without incident are shown in Figures 5.12 and 5.13. In these tests, triple-cell samples which were subjected to atmospheric and pressurized conditions, with high and low cathode steam concentration. Figure 5.12 shows the “burn-in” behavior described above, and shows that the atmospheric test with steam has a higher ASR from the start. Figure 5.13 shows that the effect of steam is a major factor in the degradation rate. The test at 6 Bara showed marginally higher degradation than at 1 Bara, but data was insufficient to substantiate the effect of pressure on degradation.

Figure 5.10 Effect of Steam and Temperature for Pre-Burn-in Case

Figure 5.11 Effect of Steam and Temperature for Post-Burn-in Case

Figure 5.12 Time Trace for 0 - 500 Hours on Triple-Cell Samples

Figure 5.13 Time Trace for 500 - 1000 Hours on Triple-Cell Samples

Summary of Triple-Cell Testing

The effect of pressure was found to reduce the polarization resistance of the full fuel-cell beyond the reduction determined for the cathode alone. The total reduction in ASR was on the order of 0.10 ohm-cm^2 for a pressure increase from 1 to 6.5 Bara, with about 70% of the improvement being realized from 1 to 4 Bara.

The effect of the change in fuel composition is on the order of 0.09 to 0.10 ohm-cm^2 , although the degree to which fuel composition affects performance is highly dependent upon the permeability of the substrates.

An important finding was that the effect of steam was highly temperature dependent. The loss of performance at temperatures below 850°C was very large for the standard LSM + YSZ cathodes.

Steam is also a major factor in the degradation rate. Data at pressure was insufficient to substantiate the effect of pressure on degradation.

6.0 Modeling

A basic electrochemical model was put together based partly on data generated in this program. The model is similar to one reported elsewhere⁶ and takes the basic form of:

$$V_{cell} = E_{Nernst} - \eta_{ohmic} - \eta_{conc,anode} - \eta_{conc,cathode} - \eta_{act,cathode} - \eta_{act,anode}$$

Where:

E_{Nernst} = nernst potential based on the bulk anode and cathode compositions

η_{ohmic} = the resistance of anode and cathode current collector layers and electrolyte

η_{conc} = concentration polarization for either anode or cathode

η_{act} = activation polarization for either anode or cathode

The approach to building this model was sequenced as follows:

- Nernst potential calculated from gas compositions
- Current collector layer ohmic losses based upon separately measured conductivities and analytical solution
- Electrolyte ohmic loss based upon theoretical material conductivity adjusted by measured cell ohmic loss data from EIS
- Cathode concentration polarization is calculated, and is small
- Anode concentration polarization is calculated based on a multi-component diffusion model
- Cathode polarization is based upon measured cathode symmetric button cell data
- Anode polarization is adjusted last to make overall loss match data measured from full cell test data

This process is described for each of these components below.

Nernst Potential

The nernst potential across the cell is calculated from the bulk anode and cathode compositions:

$$E = \frac{(R_J)(T_c) \ln \left(\frac{PO2cb}{PO2ab} \right)}{(4)(F)}$$

Where:

E = reversible voltage calculated with bulk gas properties (V)

R_J = Gas constant = $8.3145 \frac{J}{gmoleK}$

⁶ Electrochemical model of the integrated planar solid oxide fuel cell (IP-SOFC), Paola Costamagna, Azra Selimovic, Marco Del Borghi, Gerry Agnew, Chemical Engineering Journal 102 (2004) 61–69, 22 February 2004

T_C = temperature ($^{\circ}\text{C}$)

$\text{PO}_{2_{ib}}$ = oxygen partial pressure (atm) (i = anode, cathode) in bulk gases

F = Faraday constant = 96485 Coulombs/mole

Electronic Resistances

The anode and cathode current collector layer resistances are based upon the layer conductances of each layer and the current density. This is also shown in the reference⁶. Layer conductances are based upon separate effect tests for the anode and cathode layers.

The electrolyte resistance is based upon the fundamental conductivity for the zirconia based material and is modified based upon EIS data taken, such as shown in Figure 6.1. The left intercept represents the ohmic portion of the cell loss. So by calculating the anode and cathode current collector losses based on layer conductances the remaining portion is attributed to the electrolyte.

Figure 6.1 - Example Showing Impedance Data from Fuel Cell Test

Concentration Polarization

As the cell arrangement is anode supported, the cathode diffusion length is relatively small on the actual cells. However, the button cell data presented in Section 4.0 showed a clear diffusion loss which was accounted for in the modeling effort. In the model developed on this program, a standard two component diffusion resistance calculation is

performed to predict the equivalent voltage loss due to the P_{O_2} gradient through the porous cathode current collector and cathode layers.

On the anode side, there is a thick substrate as shown in Figure 6.2 through which fuel must flow into the active anode while the reaction products, H_2O and CO_2 , must flow back out into the bulk fuel stream. In the model developed on this program, an interpolation of component interactions was used to model the anode flows. Once the concentration of H_2 and H_2O at the anode are established, the concentration overpotential can be determined.

$$\eta_{\text{conc,a}} = \frac{(R_J)(T_K)\ell n(P_{O_{2a}} / P_{O_{2ab}})}{(4)(F)}$$

Where:

$$P_{O_{2ab}} = \text{partial pressure of oxygen in anode bulk,} = \left[\frac{(K_{Pa})(P_{H_2Oab})}{(P_{H_2ab})} \right]^2, (\text{atm})$$

$$P_{O_{2a}} = \text{partial pressure of oxygen at active anode,} = \left[\frac{(K_{Pa})(P_{H_2Oa})}{(P_{H_2a})} \right]^2, (\text{atm})$$

$$K_{Pa} = \text{equilibrium constant for fuel} = \exp \left\{ - \left[\frac{239500}{(R_J)(T_K)} - \frac{8.14\ell n(T_K)}{(R_J)} + \frac{9.25}{(R_J)} \right] \right\}, (\text{atm}^{1/2})$$

Figure 6.2 - Porous structure of fuel cell for gas diffusion

Activation Polarization

Two terms remain to be defined, the anode and cathode activations. The cathode activation polarization was a primary area of study on this program as presented in Section 4. We start with the Butler-Volmer equation for cathode activation:

$$\eta_{act,i} = \frac{(R_J)(T_K)}{F} \ln \left[\frac{J}{\partial J_{o,i}} + \sqrt{\left(\frac{J}{\partial J_{o,i}} \right)^2 + 1} \right]$$

Where:

J = current density (amps/cm²)

J_{o,i} = exchange current density (i = anode, cathode) (amps/cm²)

The exchange current density on the cathode side is of the form:

$$J_{o,c} = (K_c) \left(\frac{PO_{2c}}{P_{ref}} \right)^N \exp \left[\frac{(E_{act,c})}{(R_J)(T_K)} \right]$$

Where:

K_c = pre-exponential constant

N = pressure effect exponent

E_{act} = cathode activation energy

P_{O_{2c}} = cathode partial pressure of oxygen, atm

P_{ref} = reference pressure, generally set at 1 atm

Fitting Cathode Data

Now taking the data presented in section 4.0 we can see that the equation form presented above is inadequate to match all the data sets collected. Figure 6.3 shows data for cathode R_p as a function of P_{O₂} at varying pressure and O₂ concentrations.

Figure 6.3 - Comparison of Cathode R_p Model to Data

The form of the equation was changed to include a function of the total pressure in place of the reference pressure term.

$$P_{ref} = C_1 + C_2 * P_T$$

Where:

P_T = total pressure, (atm)

C_1, C_2 = linear curvefit constants

The constants K_c , N , and E_{act} in the current exchange density equation are adjusted to fit the data. The new model comparisons to data are shown below in Figures 6.4 through 6.7 which show reasonably good agreement to the data. A more rigorous approach to determining an optimum fit could be employed but was not done on this program.

Figure 6.4 - Adjusted Model Comparison at 900°C

Figure 6.5 - Adjusted Model Comparison at 800°C

Figure 6.6 - R_p versus Temperature at 12% O₂ and 1.0 Bara

Figure 6.7 - Rp versus Temperature at 12% O2 and 6.4 Bara

Fitting Full Fuel Cell Data

Finally, after all other parts of the cell loss have been either fit to data or calculated the full fuel-cell data is used to determine the adjustment to the anode activation.

After going through the process for several sets of data, the model was set and then compared to test data taken over a range of conditions. Figures 6.8 through 6.10 show an example of the comparison for TCT35. As shown, the overall comparison is reasonable considering the variation in the two samples shown. The breakdown of the polarization and ohmic loss components is reasonable, although the limitations of the anode side diffusion model are exposed when a dilute fuel composition was used. This finding led to later enhancements using the Cylindrical Pore Interpolation Model, or CPIM⁷ to model the complexity of this process (work not sponsored by this program). The substrate thickness, porosity, and tortuosity are key parameters needed for this model.

In summary the facilities in use and the data produced by them provides sufficient detail and range of operation to provide a robust set of data for model development and validation.

⁷ “Modelling of multi-component gas flows in capillaries and porous solids”, J.B. Young *, B. Todd Hopkinson Laboratory, Cambridge University, Engineering Department, International Journal of Heat and Mass Transfer 48 (2005) 5338–5353, Received 2 March 2005

Figure 6.8 Comparison of Overall Model to Overall Cell ASR for TCT35

Figure 6.9 Comparison of Polarization Prediction to Data for TCT35

Figure 6.10 Comparison of Ohmic Loss Prediction to Data for TCT35

Conclusion

The data acquired in this program has shown a clear performance benefit to operating solid oxide fuel cells at pressure. The improved performance includes of course increased Nernst potential, but also includes cathode activation, anode activation, and anode diffusion (for anode supported type cells). Improvement in cathode electrode performance is on the order of 33-40% at pressures of 6.4 Bara compared to atmospheric pressure. Key cathode operational parameters are the concentration and partial pressure of O₂, and temperature. The effect of partial pressure of oxygen (P_{O₂}) decreases the activation polarization, although there appears to be a secondary effect of absolute pressure as well. The ASR reduction for the full fuel-cell was on the order of 0.10 ohm-cm² for a pressure increase from 1 to 6.5 Bara, with about 70% of the improvement being realized from 1 to 4 Bara.

This program shows that pressurized fuel cell operation can be a step toward increases power density as well as fundamental fuel cell efficiency.

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List of Acronyms and Abbreviations

RRFCS: Rolls-Royce Fuel Cell Systems
SOFC: Solid Oxide Fuel Cell
PO₂: Partial pressure of oxygen
MW: megawatt
TPB: triple point boundary
SMR: Steam methane reforming
WGS: Water gas shift
PIC: primary interconnect
SIC: secondary interconnect
LSM: Lanthanum-Strontium-Manganate
YSZ: Ytria-Stabilized Zirconia
EIS: electro-impedance spectroscopy
Rs: electronic resistance
Rp: electrode resistance due to polarization
TCT: triple-cell-test
CPIM: cylindrical pore interpolation model