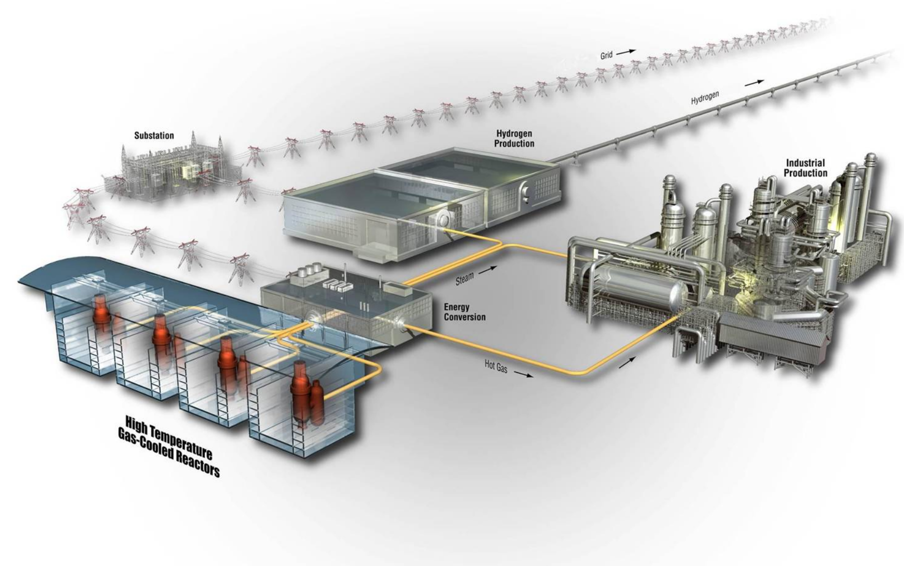
INL/EXT-12-27081

Summary Report on FY12 Small-Scale Test Activities High Temperature Electrolysis Program

James E. O'Brien and Xiaoyu Zhang

September 2012



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Prepared for the
U.S. Department of Energy
Office of Nuclear Energy
Under DOE Idaho Operations Office
Contract DE-AC07-05ID14517

VHTR TDO Program

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ABSTRACT

This report provides a description of the apparatus and the single cell testing results performed at Idaho National Laboratory during January–August 2012. It is an addendum to the Small-Scale Test Report issued in January 2012. The primary program objectives during this time period were associated with design, assembly, and operation of two large experiments: a pressurized test, and a 4 kW test. Consequently, the activities described in this report represent a much smaller effort.

SUMMARY

Results of an experimental investigation on the performance and durability of single solid oxide electrolysis cells (SOECs) from SOFCpower Inc. and MSRI Inc. are presented. Testing was completed during the summer of 2012. The test stand was the same one used for single cell testing from other vendors including St. Gobain, and NASA. SOFCpower provided electrode-supported, YSZ-based thin-film electrolyte, solid oxide fuel cells (SOFCs). A Ceria barrier layer is applied between the cathode and the electrolyte to improve durability. Although SOFCpower cells have been developed for the fuel cell application, they showed good durability operating in the electrolysis mode. The results of initial testing showed that SOFCpower cells had stable performance in the fuel cell mode, and 6.3% degradation under the electrolysis mode. With further optimization, SOFCpower cells will be good candidates for reversible fuel cell application. Additional testing was performed on a single cell from MSRI in the fuel cell mode to investigate the durability of a new electrode material. This cell exhibited good initial performance in the fuel cell mode, but had a relatively high degradation rate during long-term operation.

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ACRONYMS

ASME	American Society of Mechanical Engineers
ASR	Area Specific Resistance
BCTC	Bonneville County Technology Center
CEM	Controlled Evaporation and Mixing
DC	Direct Current
HTE	High-Temperature Electrolysis
ID	Inner Diameter
INL	Idaho National Laboratory
OD	Outer Diameter
P&ID	Piping and Instrumentation Diagram
MAWP	Maximum Allowable Working Pressure
MSRI	Materials and Systems Research, Inc.
NGNP	Next Generation Nuclear Plant
SOEC	Solid Oxide Electrolysis Cells
TC	Thermocouple
TRL	Technology Readiness Level

UNITS

cm^2	square centimeters
°C	degrees Celsius
khr	kilohour (1000 hours)
NL/hr	normal liters per hour
V	volts
A	amperes
kW	kilowatts
sccm	standard cubic centimeters per minute
Ω	Ohm
kPa	kilopascals

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1. INTRODUCTION

Large-scale hydrogen production is the most important factor impacting the hydrogen economy. An estimated 53 million metric tons of hydrogen was produced globally in 2010. An annual growth rate of 5.6% was forecasted for 2011–2016.[1] However, most hydrogen produced is from fossil fuels, including natural gas, oil, and coal.[2] Interest in increasing nonfossil-based, large-scale hydrogen production is growing around the world. High temperature electrolysis (HTE) is one of the most efficient technologies being considered for producing carbon-free hydrogen on a large scale.[3] Idaho National Laboratory (INL) has demonstrated HTE at the 15 kW scale with a hydrogen production rate in excess of 5,000 NL/hr.[4] However, technical barriers need to be resolved before HTE technology can be commercialized. The major issue for HTE is long-term performance degradation of the solid oxide electrolysis cells (SOECs).[5-8] Although common solid oxide fuel cells (SOFCs) can be reversely operated in electrolysis mode, they usually exhibit much higher degradation rates in the electrolysis mode than in fuel cell mode.[9,10] In previous stack tests, air electrode delamination, chromium vapor poisoning, microstructure degradation, and seal leakage were found to significantly affect the durability of the stack.[11,12] To understand the degradation mechanism and develop SOECs for strong durability, more single cell tests are needed.

SOFCs developed by SOFCpower Inc. for operation in the fuel cell mode were obtained by INL to evaluate their performance under the electrolysis mode. The SOFCpower Inc. cells are electrode-supported, YSZ-based, thin-film electrolyte SOFCs. A ceria barrier layer is applied between the cathode and the electrolyte to improve durability. Initial performance and long-term durability tests were conducted in both the fuel cell and electrolysis modes of operation. The SOFCpower Inc. cells showed the best durability in the fuel cell mode compared to previously tested cells from Ceramatec, Materials and Systems Research, Inc. (MSRI), and St. Gobain. In addition, although the cells were not optimized for electrolysis operation, they showed a respectable 6.3%/khr degradation rate in the electrolysis mode. However, cells obtained previously from MSRI which were optimized for the electrolysis mode of operation exhibited better performance in the SOEC mode.

One modified SOFC obtained from MSRI was tested at INL to evaluate the performance of a novel electrode material. This particular cell was only tested in the fuel cell mode and it showed poor performance.

This report provides a description of the apparatus and the single cell testing results performed at the INL during January–August 2012. It is an addendum to the Small-Scale Test Report issued in January, 2012.[13] The primary HTE program objectives during this time period were associated with design, assembly, and operation of two large experiments: a pressurized test and a 4 kW test. Consequently, the small-scale test activities described in this report represent a much smaller part of the overall programmatic effort.

2. SINGLE CELL TESTING

2.1 Materials and Experimental Apparatus

The solid oxide electrolysis cells provided by SOFCpower Inc. are fabricated as advanced SOFCs, which were operated at INL in the electrolysis mode. The SOFCs are electrode-supported cells with a YSZ electrolyte, Ni-YSZ based steam/hydrogen electrode, and lanthanum strontium cobalt ferrite (LSCF) air electrode with an active area of 23 cm^2. A gadolinium doped ceria (GDC) based diffusion barrier layer was applied between the electrolyte and the air-electrode to improve durability in the fuel cell mode.

A modified cell fixture was used to test the SOFCpower Inc. SOECs, as shown in an exploded view in Figure 1. This apparatus has a few advantages for fuel cell and electrolysis tests. It is versatile and robust so it can be used for both single cell and short stack tests; so far eleven single cells and two 3-cell short stacks have been tested on this apparatus without any post-test treatment. It is designed for operation at high current density and can be used for electrochemical impedance spectroscopy measurements. It minimizes the possibility of Cr poisoning. The degradation mechanisms are confined within the cell. The design details of this fixture are stated below.

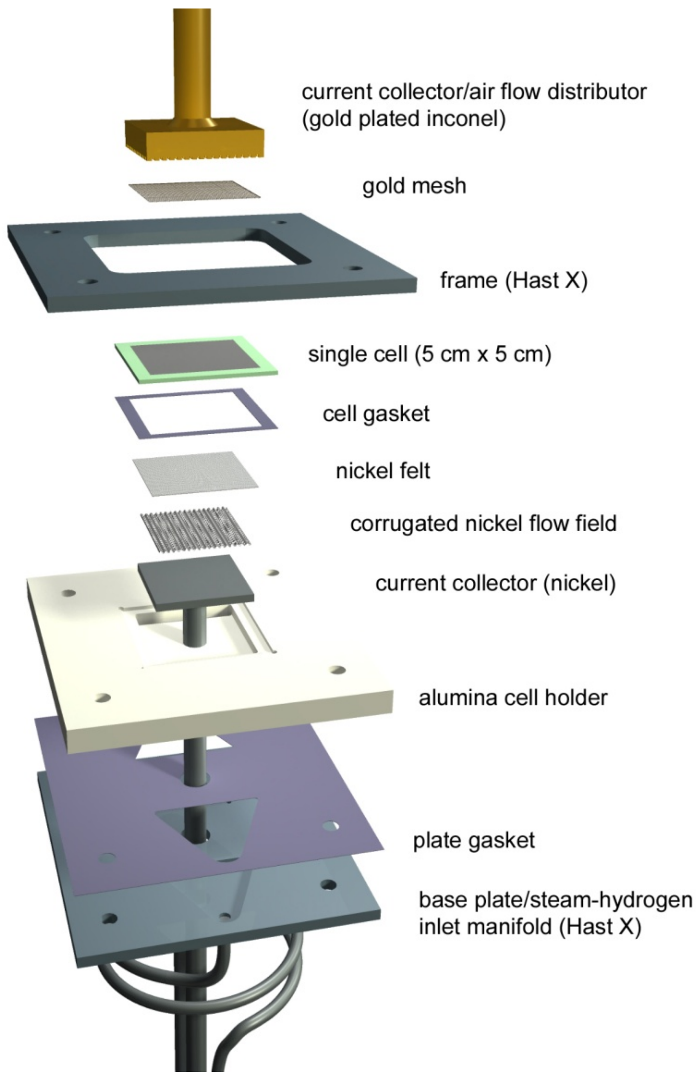


Figure 1. Exploded view of the cell fixture used for testing SOFCpower Inc. SOECs.

Referring to Figure 1, a hydrogen/steam mixture is fed from the bottom through a ¼-inch coiled inconel tube into the inlet hole in the bottom of the Hastelloy-X (HastX) base plate. The flow then passes through a slot at the bottom of the alumina cell holder. A mica/glass cell gasket is placed between the cell holder and the nickel current collector for sealing. A corrugated nickel flow field is used to manage the hydrogen steam flow and for electric conduction. Nickel felt is placed between the electrode and the nickel flow field to minimize the electrode/flow field contact resistance. The nickel felt and flow field are trimmed to fit the size of the nickel current collector sitting in the recess of the cell holder. After passing along the bottom of the cell, the flow exits through another slot and vents out via a 3/8 inch inconel tube. The outlet tube is sized larger than the inlet tube to minimize the back pressure on the cell seal.

A gold-plated inconel plate is used on the air side of the cell as the current collector and air flow distributer. Air is introduced through a tube that is welded to the inconel plate. Air flow is distributed along the air side of the cell through an array of flow channels milled into the bottom of the inconel plate. Air exhaust gas vents directly into the furnace. A gold mesh is placed between the air electrode and the plate to minimize ohmic loss and to further improve air flow distribution. The top conductor/air flow distributor consists of three parts. The tube is welded and protruded slightly into the center hole of the upper inconel plate. Another inconel plate is machined with the flow channels and through-plate holes. These two plates are then welded together. Gold plating is applied to the inconel surfaces that are exposed to the furnace hot zone to minimize oxidation.

A fixed compression load is applied to the solid oxide cell by means of weights as shown in the test stand overview in Figure 2. The use of weights for mechanical compression ensures a constant load while allowing for thermal expansion of components during heatup and thermal cycling. The mechanical load is transferred via an alumina tube from the dead weights to the top cell contact plate. This load simultaneously compresses the cell against the nickel felt, flow field and current collector on the bottom steam/hydrogen side of the cell and against the gold mesh on the air side. It also compresses the cell against the seal around the outer edge of the cell, which rests on the shelf milled into the alumina cell holder. The HastX weight plates are held in alignment outside of the furnace by the upper portion of the threaded rods extending upward for this purpose.

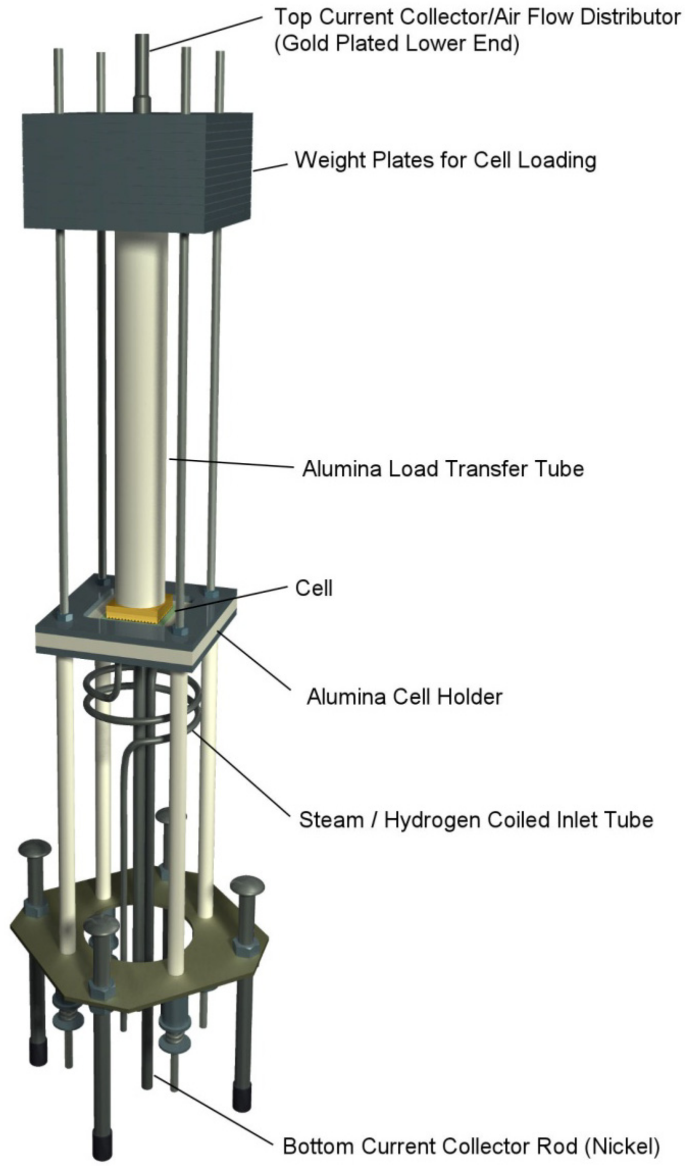


Figure 2. Test stand overview.

A photograph of the test stand installed in the furnace base for testing SOFCpower Inc. SOECs is shown in Figure 3. Note that the upper part of the alumina load transfer tube is located outside of the furnace so the weights are located outside of the hot zone. Holes were drilled in the bottom of the kiln for the flow tubes, alumina spacer rods, nickel current collector rod, and instrumentation to pass through.

A piping and instrument diagram (P&ID) for the experimental apparatus used for SOFCpower Inc. single cell testing is presented in Figure 4. Primary components include gas supply cylinders, mass-flow controllers, a heated water-bath humidifier, online dew point sensors, temperature and pressure measurements, high temperature furnace, and the SOEC. Nitrogen is used as an inert carrier gas. Inlet flow rates of nitrogen, hydrogen, and air are established by means of precision mass-flow controllers. Hydrogen is included in the inlet flow as a reducing gas in order to prevent oxidation of the nickel cermet electrode material. Air flow to the cell is supplied by the shop air system, after passing through a two-stage extractor/dryer unit. The hydrogen-side inlet gas mixture, consisting of hydrogen and nitrogen is mixed with steam by means of a heated humidifier. The dew point temperatures of the nitrogen/hydrogen/steam gas mixture exiting the humidifier and downstream of the cell are monitored continuously using precision dew point sensors. All gas lines located downstream of the humidifier are heat-traced in order to prevent steam condensation.

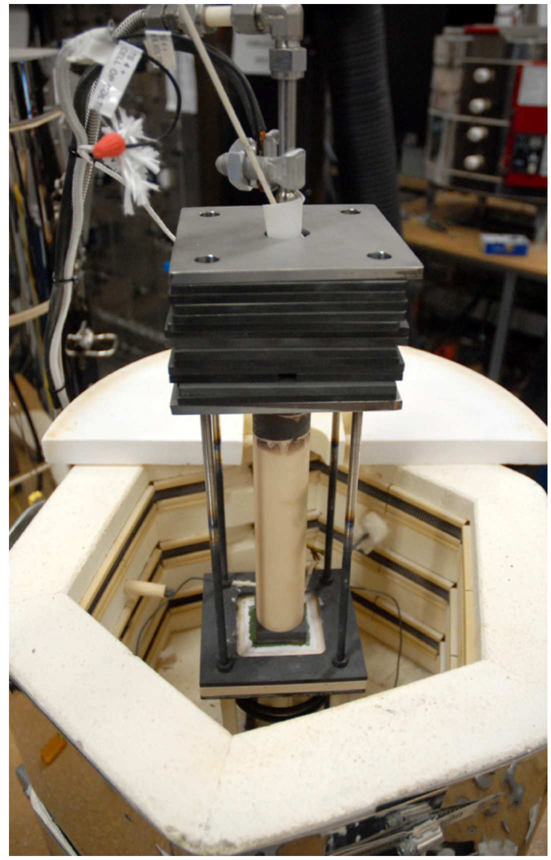


Figure 3. Single cell test stand installed in furnace.

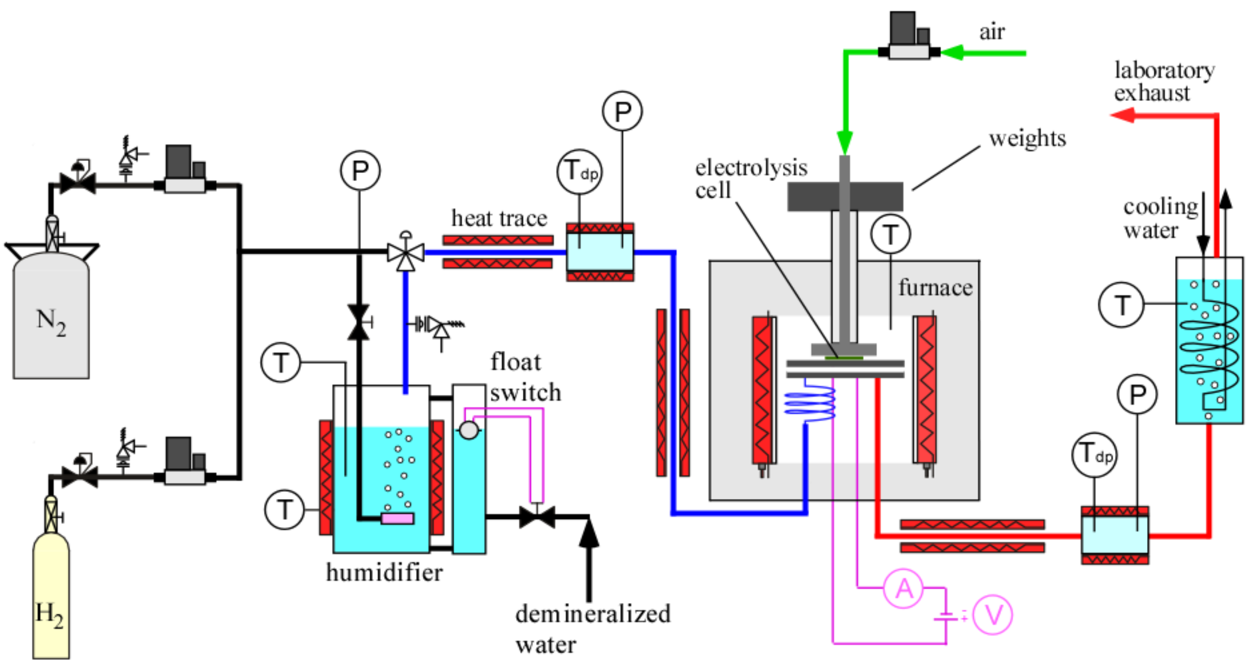


Figure 4. Piping and instrument diagram for single cell test apparatus.

2.2 Test Procedure

Each single cell undergoes three steps during the test: initial heatup and cell reduction, performance characterization, and long-term testing. During cell reduction, nickel oxide in the steam/hydrogen electrode is reduced to nickel metal by slowly introducing a dry hydrogen flow. Initial cell performance is evaluated by means of a series of voltage-current (V-I) sweeps with different steam content at the steam/hydrogen inlet.

After initial performance evaluation, the cells were operated in both the fuel cell and electrolysis modes, which is also termed reversible operation. Operating conditions during the long-term tests are listed in Table 1.

Table 1. Operating conditions during long term tests.

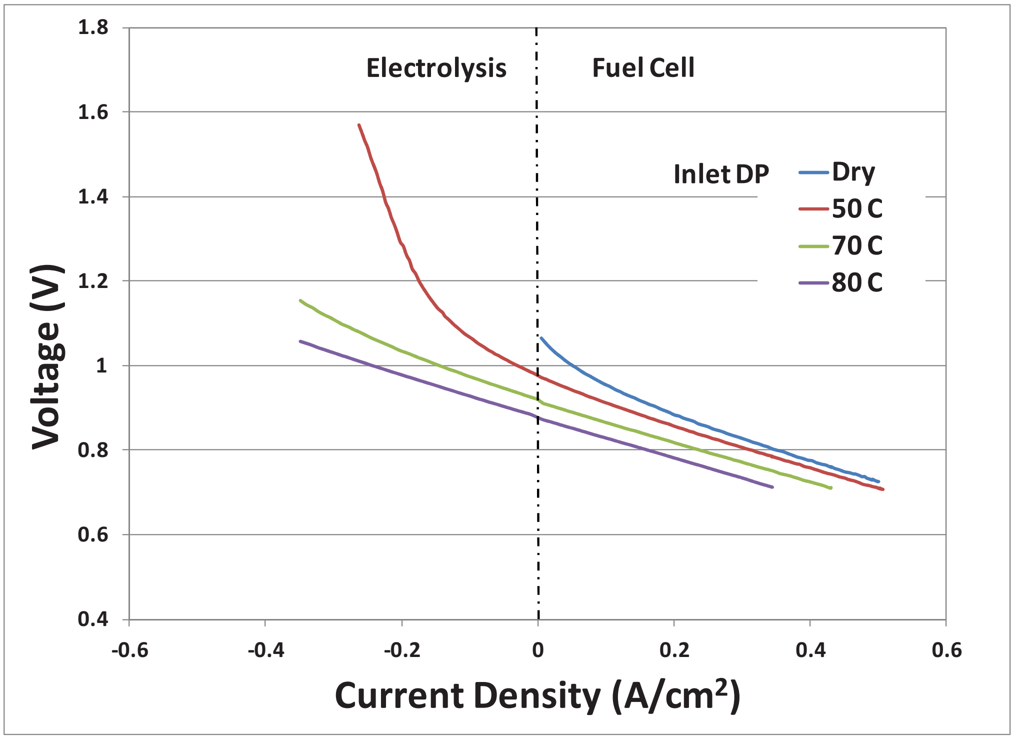
Cell No.	Temp (°C)	Flow Rate (H_2/N_2/Air sccm)	Dew Point (°C)	Control Mode
MSRI 1	800	280/120/660	0	CC*
SOFCpower 1	800	500/500/1000	80	CC*
SOFCpower 2	800	500/500/1000	80	CC*

* Constant current.

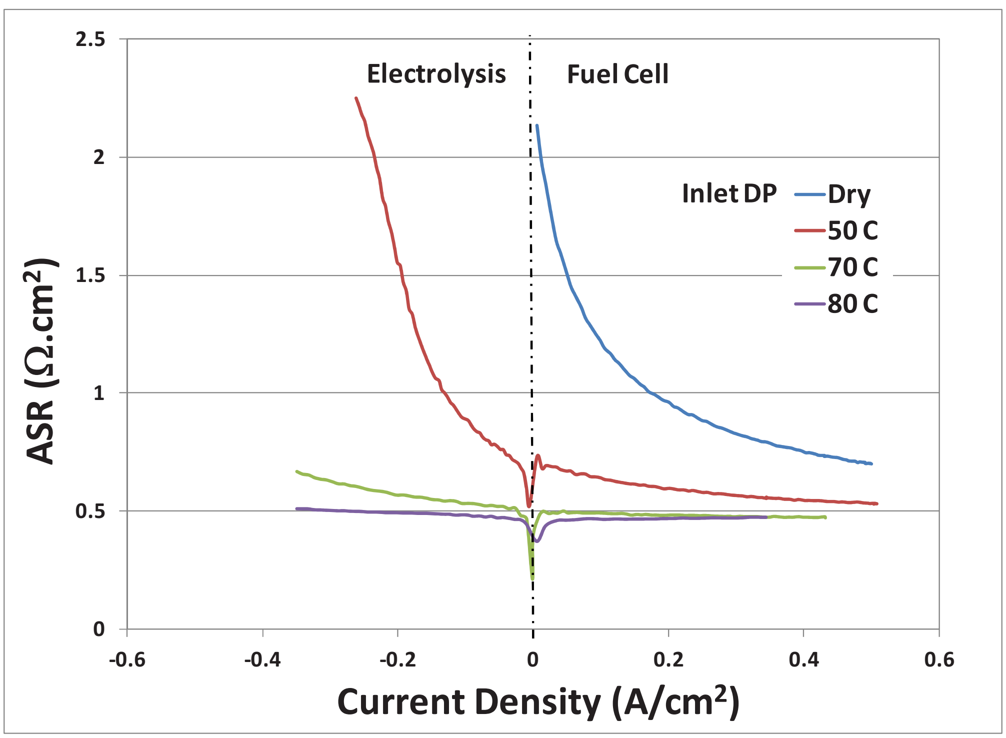
3. TESTING RESULTS

3.1 SOFC Power Single Cells

Two SOFCpower Inc. single cells were tested at INL. Figure 5 shows the results of the initial performance characterization of SOFCpower Cell 2. Figure 5(a) shows the polarization curve and cell voltage versus current density. Figure 5(b) shows the corresponding apparent area-specific resistance (ASR) as a function of current density. The curves show the effect of the steam content on cell performance. Curves representing higher steam content show more linear trends both in fuel cell and electrolysis modes. The nonlinearity in the curves at low steam content in the SOFC mode is associated with the high sensitivity of the Nernst potential to small changes in average steam content. Also, in the electrolysis mode, higher current densities can lead to steam starvation if the average steam content is low. The figure also shows that the ASR curves remain relatively flat at high steam content in both modes, while becoming significantly curved, especially in electrolysis mode as steam content decreases. At high steam content, the ASR values are similar in the fuel cell and electrolysis modes. At 80°C inlet dew point (56% steam content), ASR values remain below 0.5 Ω cm^2. Generally, SOFCpower Inc.single cells demonstrated initial performance similar to that observed with the St. Gobain cells.



(a)



(b)

Figure 5. Initial performance of SOFCpower Cell 2; (a) voltage polarization curves, (b) area-specific resistance

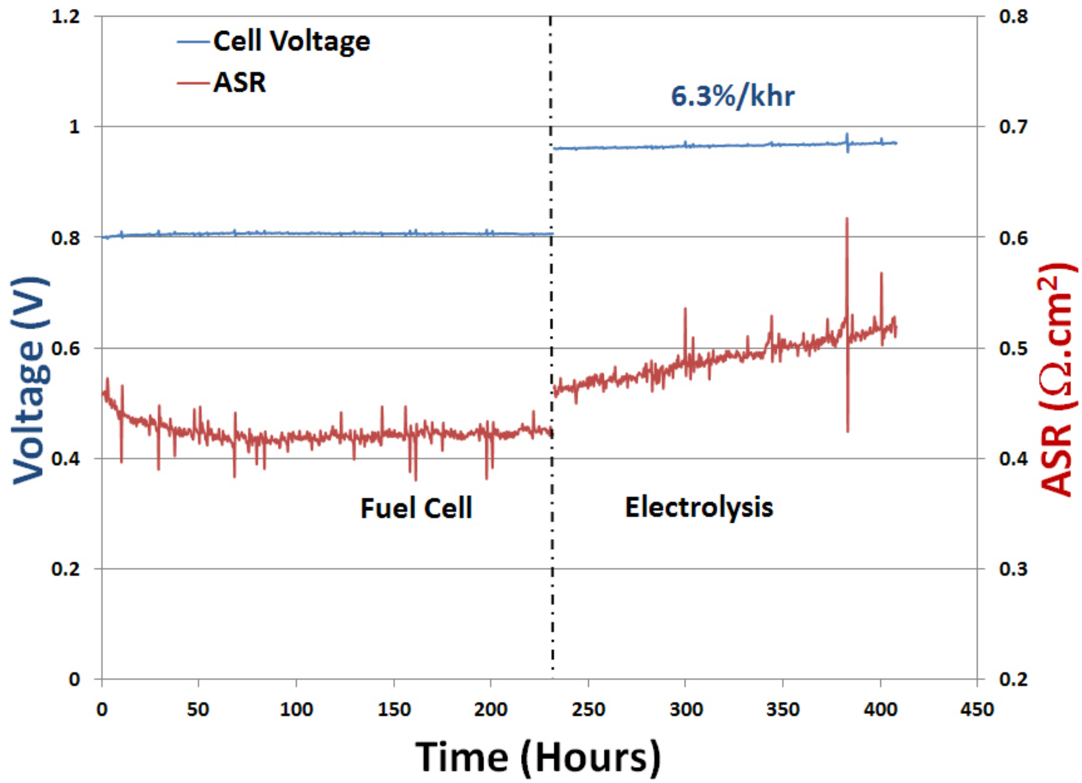


Figure 6. Long-term test of SOFCpower Inc. in the fuel cell and the electrolysis mode.

SOFCpower Cell 2 was operated in the fuel cell mode for 200 hours, followed by about 200 hours of operation in the electrolysis mode. Both modes were controlled galvanostatically at 0.174 A/cm^2 in order to compare the degradation between two modes. Figure 6 shows the result of the long-term test of SOFCpower Cell 2. Cell voltage was stable in the fuel cell mode after an initial drop during the first 50 hours, then there was no degradation. After switching to the electrolysis mode at 230 hours, significnat cell degradation was observed, as indicated by an increase in cell voltage with time. The normalized degradation rate for the 200 hours of electrolysis operation was 6.3%/khr. This degradation rate is relatively high, considering that the current density is low. Although the observed degradation rate was a little higher than Ceramatec and MSRI SOECs (i.e. cells that were optimized for the SOEC mode of operation), the tested SOFCpower Inc.cells were designed as SOFCs. With further optimization on the microstucture and materials, SOFCpower Inc.cells could be a good candidate for reversible operation.

3.2 MSRI Single Cell

Performance of a single cell from MSRI was evaluated to investigate the durability of a new electrode material. Figure 7 shows the results of the initial performance characterization of MSRI Cell 1. Three voltage polarization curves are shown, one for dry inlet gas (50% H_2, 50% N_2), one for an inlet dewpoint temperature of 20°C (2.5% H_2O), and one for an inlet dewpoint temperature of 80°C (56% H_2O). The curve for dry gas only shows operation in the fuel cell mode. The curves for 20°C and 80°C inlet dewpoint values extended into the electrolysis mode. For the highest steam content, performance in the two modes of operation was linear over the range of current densities shown (-0.5 to 0.5 A/cm^2). For the dry gas sweep, a curve representing the area-specific resistance as a function of current density is also shown. Note that the ASR decreases significantly with increasing current density in the fuel cell mode. At high current density, the ASR approached a value less than 0.5 Ω cm^2.

After initial characterization, the cell was operated for several hundred hours in the fuel cell mode with dry gas, 20% hydrogen utilizaiton; results are show in Figure 8. The current density for long-term testing was initially set at 0.25 A/cm^2. At 220 hours, the current density was increased to 0.5 A/cm^2. The degradation rate for the initial 220 was 6.6%/khr. At the higher current density, from 220 to 350 hours, the degration rate was 13.5%/khr. The ASR value associated with low current density operation was ~0.6 Ω cm^2. The ASR dropped significantly when the current density was increased at 220 hours, consistent with the observations made during the initial dry gas sweep. A temporary loss of air flow occurred at ~315 hours, resulting in a fluctuation in voltage. The effect was temporary.

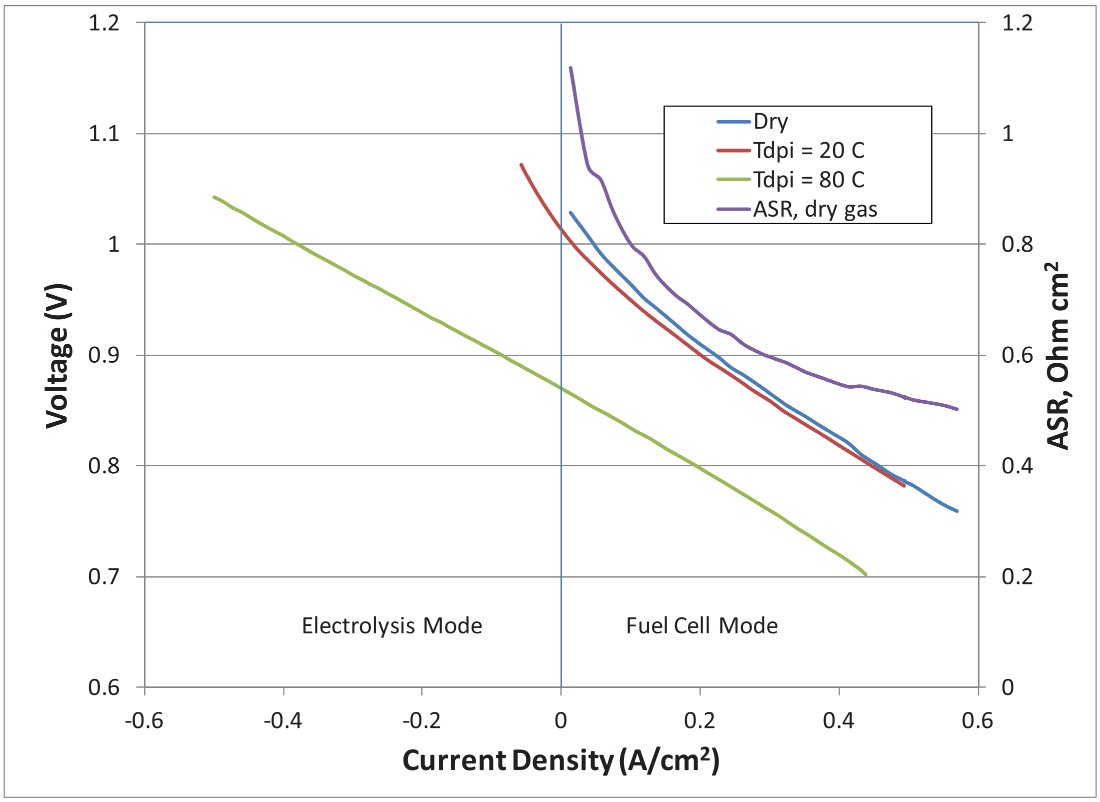


Figure 7. Initial performance of MSRI single cell #1.

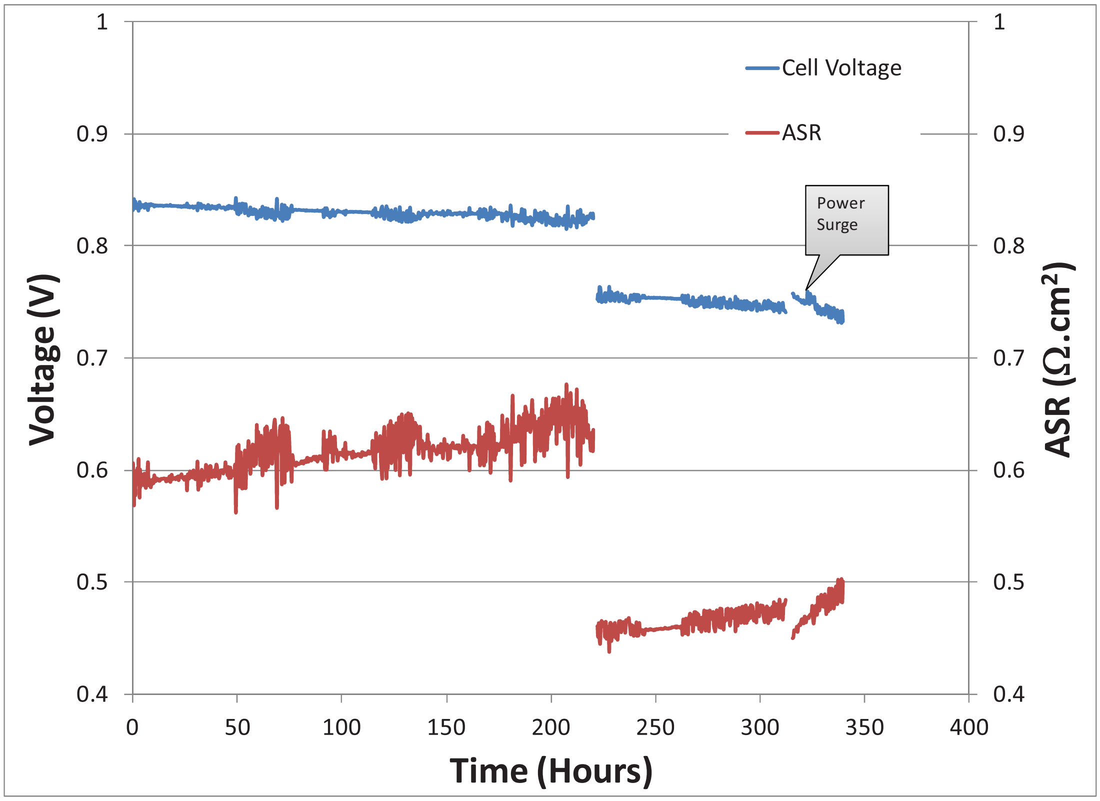


Figure 8. Initial performance of MSRI single cell #1.

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