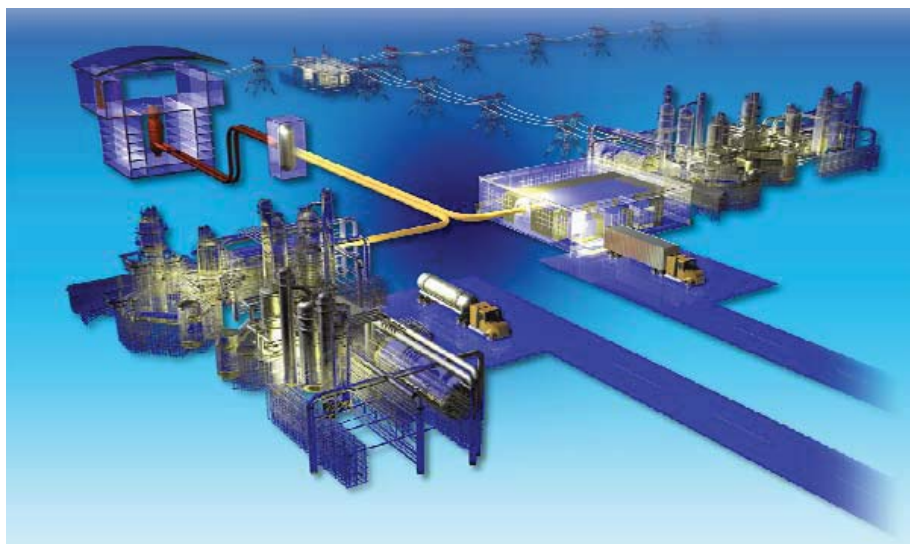# 2500-Hour High Temperature Solid-Oxide Electrolyzer Long Duration Test

C. M. Stoots
J. E. O'Brien
K. G. Condie
L. Moore-McAteer
J. J. Hartvigsen
D. Larsen

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The INL is a U.S. Department of Energy National Laboratory
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Idaho National
Laboratory

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C. M. Stoots
J. E. O'Brien
K. G. Condie
L. Moore-McAteer
J. J. Hartvigsen[1]
D. Larsen[1]

[1]Ceramatec

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Idaho National Laboratory
Idaho Falls, Idaho 83415

http://www.inl.gov

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Approved by:

Carl M. Stoots	Date
Principal Investigator	

James E. O'Brien	Date
Principal Investigator	

ABSTRACT

The Idaho National Laboratory (INL) has been developing the concept of using solid oxide fuel cells as electrolyzers for large-scale, high-temperature (efficient), hydrogen production. This program was sponsored by the U.S. Department of Energy under the Nuclear Hydrogen Initiative. Utilizing a fuel cell as an electrolyzer introduces some inherent differences in cell operating conditions. In particular, the performance of fuel cells operated as electrolyzers degrades with time faster. This issue of electrolyzer cell and stack performance degradation over time has been identified as a major barrier to technology development. Consequently, the INL has been working together with Ceramatec, Inc. (Salt Lake City, Utah) and other manufacturers of solid oxide cells to improve the long-term performance of high temperature electrolyzers. As part of this research partnership, the INL conducted a 2500 hour test of a Ceramatec designed and produced stack operated in the electrolysis mode. This report will provide a summary of experimental results for this long duration test.

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ACRONYMS

ASR	area-specific resistance
ILS	integrated laboratory scale
INL	Idaho National Laboratory
MIT	Massachusetts Institute of Technology
SCR	silicon-controlled rectifier

1.   INTRODUCTION

In spite of being the most abundant element in the universe, for the most part, molecular hydrogen is not available on earth. The US currently produces approximately 11 million tons of H_2 per year, almost entirely from natural gas. World production of H_2 is currently about 42 million tons per year: 48% from natural gas, 30% from oil, 18% from coal, and 4% from electrolysis [1]. About half is used to produce ammonia, which is then used for fertilizer. The other half is used to convert heavy petroleum sources into lighter fractions suitable for use as fuels.

From the above discussion, 96% of the world's hydrogen is produced from fossil fuels. And the demand for hydrogen is increasing at a rate of more than 10% per year. Long-term supplies of nonrenewable resources such as natural gas and oil for hydrogen production are in question, and their prices are volatile. Furthermore, when fossil fuels are used for hydrogen production, significant quantities of greenhouse gas CO_2 are produced as a byproduct. The majority of this CO_2 is currently released to the environment. Obviously this is not a sustainable means of satisfying H_2 demand for the future.

R&D efforts are underway to develop suitable renewable energy powered and/or nuclear powered water-splitting technologies for carbon-free sustainable hydrogen production. Water-splitting for hydrogen production can be accomplished via high-temperature electrolysis or thermochemical processes, using high-temperature nuclear process heat and electricity. In order to achieve competitive efficiencies, both processes require high-temperature operation. High-temperature electrolytic water-splitting supported by nuclear process heat and electricity has the potential to produce hydrogen with an overall system efficiency near those of the thermochemical processes [2], but without the corrosive conditions of thermochemical processes and without the fossil fuel consumption and greenhouse gas emissions associated with hydrocarbon processes. The Idaho National Laboratory (INL) has been researching the use of solid-oxide fuel cell technology to electrolyze steam for large-scale nuclear-powered hydrogen production. The scope of activities includes computational fluid dynamics modeling, process flow sheet analyses, and experimental testing. Scales of experimental testing extend from ~2 watt button cell tests to 15 kW multi-stack tests.

Utilizing a fuel cell as an electrolyzer introduces some inherent differences in cell operating conditions. For instance, the process heat requirements differ: electrolysis is endothermic while fuel cell operation is exothermic. Furthermore, the direction of the oxygen flux is opposite in the electrolyzer mode of operation versus in the fuel cell mode. Finally, cell performance degradation tends to be faster in the electrolytic mode than in the fuel cell mode. This issue of electrolyzer cell and stack performance degradation over time has been identified as a major barrier to technology development. Consequently, the INL has been working together with Ceramatec, Inc. (Salt Lake City, Utah) and other manufacturers of solid oxide cells to improve the long-term performance of high temperature electrolyzers. As part of this research partnership, the INL conducted a 2500 hour test of a Ceramatec designed and produced stack operated in the electrolysis mode.

1.1   Experimental Testing Facility

A comprehensive discussion of the INL high temperature solid oxide electrolysis bench scale experiment is presented elsewhere [3]. This same facility is used for button cell testing as well as stack testing. The facility incorporates 5 independent button cell / stack testing stations that can be used for steam electrolysis as well as steam / CO_2 coelectrolysis testing. A photograph of the laboratory is found in Fig. 1-1 and a simplified schematic of one stack testing station follows in Fig. 1-2. Primary components include gas supply cylinders, mass-flow controllers, a humidifier, dewpoint measurement stations, temperature and pressure measurement, high temperature furnace, and a solid oxide electrolysis stack. Nitrogen is used as an inert carrier gas. The use of a carrier gas allows for independent variation of both the partial pressures and the flow rates of the inlet steam and hydrogen gases while continuing to operate near atmospheric pressure.

Figure 1-1. INL high-temperature electrolysis laboratory.

The flow rates of nitrogen, hydrogen, and air are established by means of precision mass-flow controllers. Air flow to the stack is supplied by the shop air system, after passing through a two-stage extractor / dryer unit.

Downstream of the mass-flow controllers, the nitrogen hydrogen gases are mixed. Hydrogen is included in the inlet flow as a reducing gas in order to prevent oxidation of the nickel cermet electrode material. The nitrogen / hydrogen gas mixture is mixed with steam by means of a heated water bath. The humidifier water temperature is maintained at a constant setpoint value using computerized feedback control. The dewpoint temperature of the nitrogen / hydrogen / steam gas mixture exiting the humidifier is monitored continuously using a precision dewpoint sensor. Pressure is also measured at the dewpoint measurement stations using absolute pressure transducers. Local stream pressure information is required to determine the mole fraction of steam in the gas mixture at the dew point measurement station. Since the nitrogen and hydrogen flow rates are fixed by the mass flow controllers, and the steam partial pressure is fixed by the bath temperature, the complete inlet gas composition is precisely known at all times. All gas lines located downstream of the humidifier are heat-traced in order to prevent steam condensation. Gas line temperatures are monitored by thermocouples and controlled by means of computer-controlled SCRs.

The electrolysis product stream exiting the furnace is directed towards a second dewpoint sensor upon exiting the furnace and then to a condenser through a heat-traced line. The condenser removes most of the residual steam from the exhaust. The final exhaust stream is vented outside the laboratory through the roof.
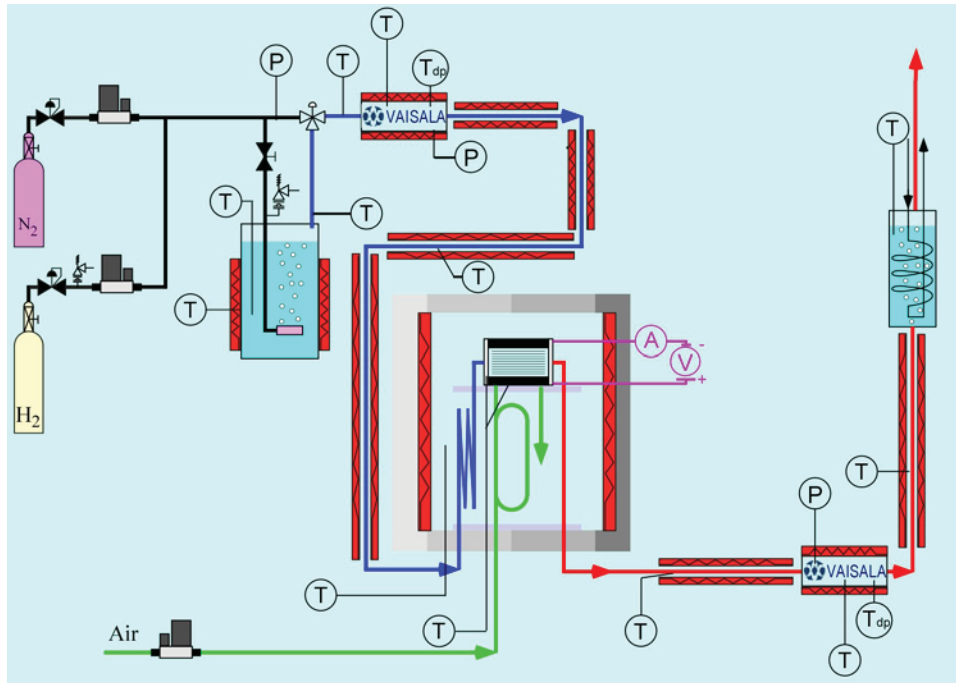
Figure 1-2. Simplified schematic of INL electrolysis / coelectrolysis stack test apparatus.

The rate of steam electrolysis is measured via two different, independent methods: 1) electrical current through the stack, and 2) the measured change in inlet and outlet steam concentrations as measured by the on-line dew point sensors.

The inlet gas mixture is directed to the high temperature furnace, which heats and maintains the electrolyzer at the appropriate test temperature via computer-based feedback control. The furnace also
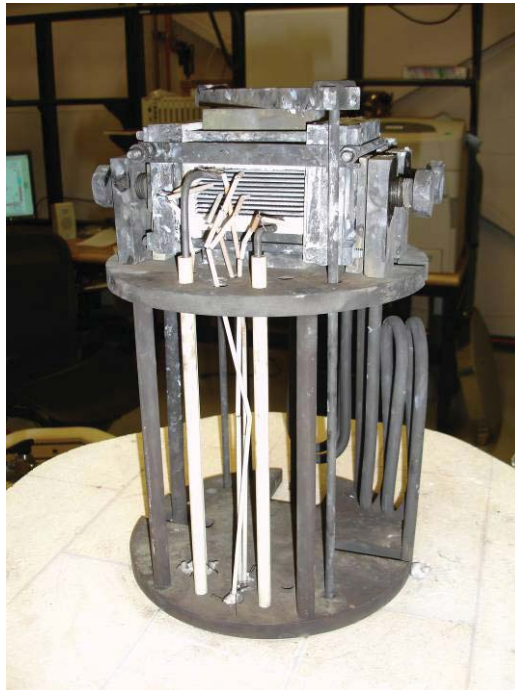

Figure 1-3. 10-cell 10 cm x 10 cm stack mounted on fixture on furnace base, ready to test.
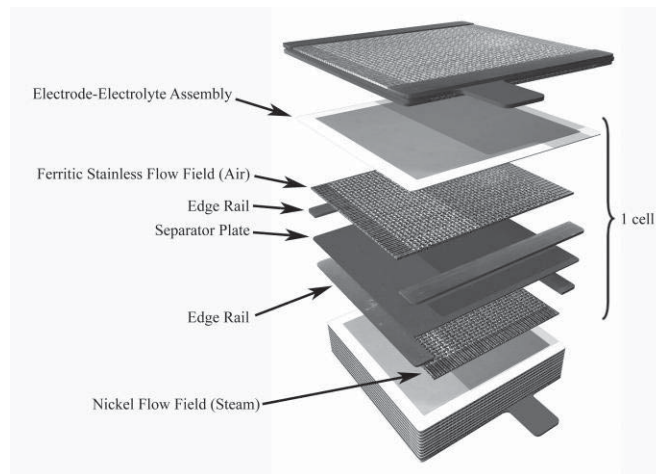
Figure 1-4. Diagram of solid-oxide stack components.

preheats the inlet gas mixture and the air sweep gas. A photograph of a 10 cm x 10 cm 10-cell stack, mounted on its inconel test fixture and resting on the furnace base, is shown in Fig. 1-3. The stacks were fabricated by Ceramatec, Inc., of Salt Lake City, UT. The stacks have a per-cell active area of 64 cm^2 for a total active area of 640 cm^2.

1.2   Electrolysis Stack

The internal components of a typical stack are shown in Fig. 1-4 and are comprised as follows. The interconnect plate is fabricated primarily from ferritic stainless steel. It includes an impermeable separator plate (~0.46 mm thick) with edge rails and two corrugated flow fields, one on the sweep-gas side and one on the steam / hydrogen side. The height of the flow fields is 1.0 mm. Each flow field includes 32 perforated flow channels across its width to provide uniform gas-flow distribution. The steam / hydrogen flow fields are fabricated from nickel foil. The air-sweep flow fields are made from ferritic stainless steel. The interconnect plates and flow fields also serve as electrical conductors and current distributors. To improve performance, the sweep-side separator plates and flow fields are surface-treated to form a rare-earth stable conductive oxide scale. A perovskite rare-earth coating is also applied to the separator plate oxide scale by either screen printing or plasma spraying. On the steam / hydrogen side of the separator plate, a thin (~10 μm) nickel metal coating is applied.

The electrolyte is partially-scandia-stabilized zirconia, ~140 μm thick. The steam / hydrogen electrode (cathode in the electrolysis mode) is graded, with a nickel cermet layer (~13 μm) immediately adjacent to the electrolyte and a pure nickel outer layer (~40 μm).

The sweep-side or oxygen-side electrode (anode in the electrolysis mode) in previously-tested stacks was composed of a base composition manganite perovskite adjacent to the electrolyte (14 μm) followed by a graded composition manganite perovskite (22 μm), and a cobaltite bond layer (38 μm). The performance of these earlier cells tended to degrade rapidly in the electrolysis mode.

Post-test examination of the cells used in the INL's three-module 15KW ILS test of 2008 [4] revealed that the O$_2$-electrode delaminated from the electrolyte near the electrode / electrolyte interface. One possible reason for this delamination is excessive pressure buildup due to high O$_2$ flow in the over-sintered region. Furthermore, electrochemical reactions were also identified as a cause of degradation. Two important degradation mechanisms were examined: (1) transport of Cr-containing species from steel interconnects into the oxygen electrode and cobaltite bond layers in solid-oxide electrolysis cells, and (2) cation segregation and phase separation in the bond layer [5]. To improve cell durability, Ceramatec

developed a new spinel coating for the oxygen-side of the interconnect and flow field to prevent Cr migration. Ceramatec also developed a new cobalt ferrite oxygen electrode and bond layer. These improvements were first tested in-house at Ceramatec. That testing showed that the spinel coating gave a significant reduction in stack degradation, but also resulted in a reduction in initial performance. The new oxygen-side electrode was more stable than the standard oxygen-side electrode. Based upon these promising results, the new coatings and electrode were incorporated into the 10-cell stack test discussed in this paper.

2.   TEST RESULTS

The stack was first characterized via polarization sweeps. The stack was then placed into a steady state long-duration mode for over 2500 hours. Test observations are discussed here.

2.1   Initial Stack Performance Characterization

Testing commenced with an inlet hydrogen flow rate of 800 sccm, nitrogen flow rate of 1600 sccm, and furnace temperature of 800 C. The inlet dew point temperature was 82 C. This corresponds to an inlet steam mole fraction of 0.6. The theoretical open cell potential for these inlet conditions was calculated to be 0.87 V. The measured open cell potential was 0.86 V.

Fig. 2-1 presents the results of an initial polarization curve / voltage sweep performed under the above conditions. The voltage was automatically swept from open cell to the thermal neutral voltage of 1.29 volts / cell for the operating temperature of 800 C. The peak current was measured to be 15.1 A, corresponding to a peak current density of 0.24 A/cm^2. Measured per-cell area specific resistance (ASR) values were around 2 Ωcm^2.
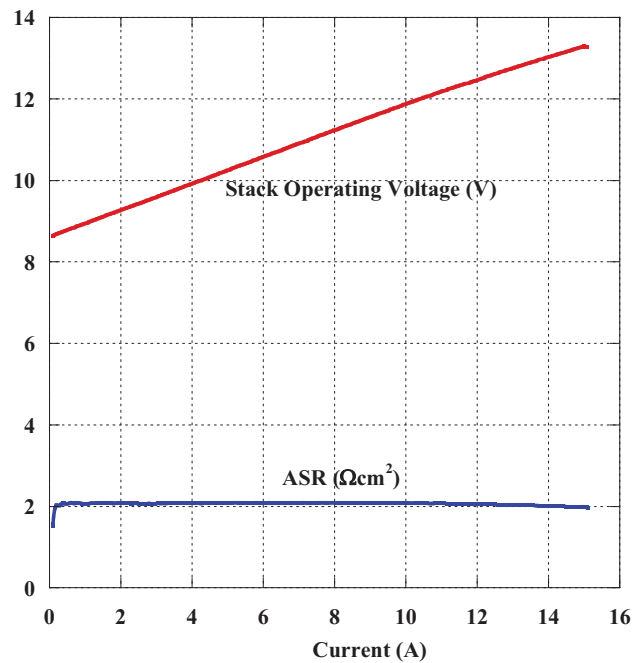

Figure 2-1. Initial polarization curve for stack.

2.2   Long Duration Test Results

Long-duration steady-state operations at the thermal neutral voltage of 12.9 V began on May 29, 2009, at 16:40. The stack completed 2500 hours at constant input on September 10 at 20:40. A summary graph of the results of the test is shown in Fig. 2-2. This graph shows the operating voltage, stack current and ASR with data recorded every five minutes. The stack operating conditions were kept constant at the same values as those for the polarization curve test discussed above.

Several events disrupted the steady-state testing. It is not clear whether these events affected the long-term performance of the stack. Most of these disruptions involved interruptions of inlet gas flows (N_2 and H_2), caused by problems with the gas mass flow controller electronics. Later in testing (beyond 1200 hours), the gas line exiting the humidifier would become occasionally clogged, also interrupting gas flows to the stack. When blockage of gas flow occurred, the stack would not receive sufficient steam and electrical current would drop drastically due to insufficient oxygen ions being available to carry the current through the electrolyte. Around 2100 hours elapsed test time, the problem gas line was replaced. A photograph of the hard water buildup within the humidifier line is in Fig. 2-3. Apparently the laboratory water demineralization system was not operating correctly. As a precaution, several analog pressure gauges were installed to monitor the humidifier back pressure such that lines could be replaced before gas flow was interrupted.

During the first 60 hours, the nickel oxide in the hydrogen electrode is being reduced and all of the components of the cell are sintering. The ASR of the stack reached 2.3 Ω-cm^2 at 60 hours elapsed test time, at which point it stabilized. Beyond 60 hours elapsed test time, the average rate of degradation was 8.15 % per 1000 hours.
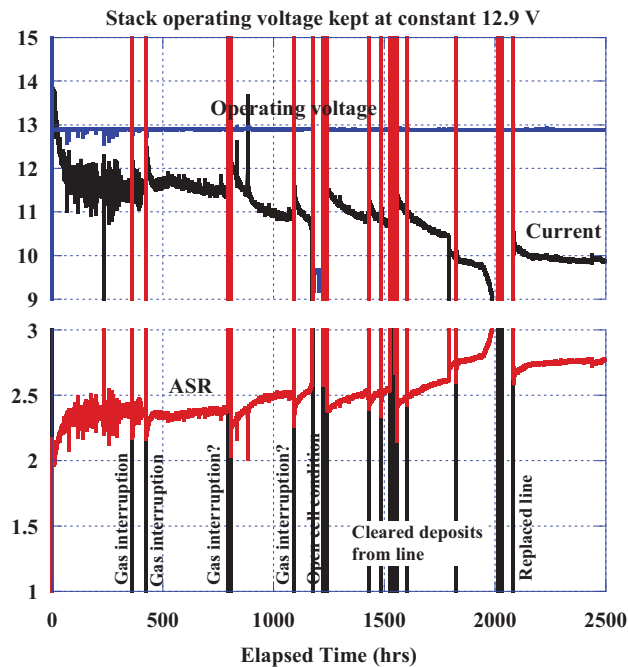

Figure 2-2. ASR, current, and voltage for the 2500 hour 10-cell stack test.

Figure 2-3. Photograph of mineral buildup in humidifier exit line.

At the conclusion of 2500 hours the stack had a per-cell ASR of 2.75 Ωcm^2. The hydrogen production rate as measured by the stack current (Faraday's Law) was 690 sccm (41.4 N-liters/hour, 3.7 g/h). The stack electrical current was 9.89 A.

Although the final determination of the cause of this improved performance must await a detailed examination of the cells after they are cooled and the stacked disassembled, it is thought that the spinel coating had the greatest effect on degradation rate. This statement is based upon this test and parametric studies conducted at Ceramatec. The revised formulation of the oxygen electrode had a more minor effect.

Also of interest is that the hydrogen product from the last several hundred hours of testing was intermittently compressed, stored, and subsequently used to produce methane. A methanation experiment was constructed under the INL Hybrid Energy Systems program. This apparatus consists of a ventilated enclosure, hydrogen compressor, hydrogen storage tank, heated methanation reactor, nickel catalyst, micro gas chromatograph, and various other instrumentation. Operating in a semi-continuous fashion, this experiment has successfully demonstrated in-line methanation of electrolysis products, and has provided reaction kinetics information to systems modelers.

3.   SUMMARY

Previous tests of solid-oxide cells as electrolyzers conducted at Ceramatec and at INL using Ceramatec technology have shown high rates of performance degradation (>20% / 1000 hours). Post-test studies conducted at MIT and at Argonne National Laboratory identified oxygen electrode delamination, transport of Cr-containing species from steel interconnects into the oxygen electrode, and cation segregation and phase separation in the bond layer as potential degradation mechanisms. Parametric studies conducted at Ceramatec helped identify improved metallic interconnect coatings and oxygen electrode materials. These materials were incorporated into a 10-cell stack which was subsequently tested for 2500 hours at the INL. After stack stabilization, the stack exhibited a long-duration performance degradation rate of 8.15% per 1000 hours based upon ASR. It is thought that most of the performance improvement resulted from the new metallic interconnect / flow field spinel coating. Overall, the test was quite successful, and demonstrated that good progress has been made in reducing the rate of cell degradation. Finally, the hydrogen product stream from this test was used to demonstrate a new methanation experiment.

4.   ACKNOWLEDGMENTS

5.   REFERENCES

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