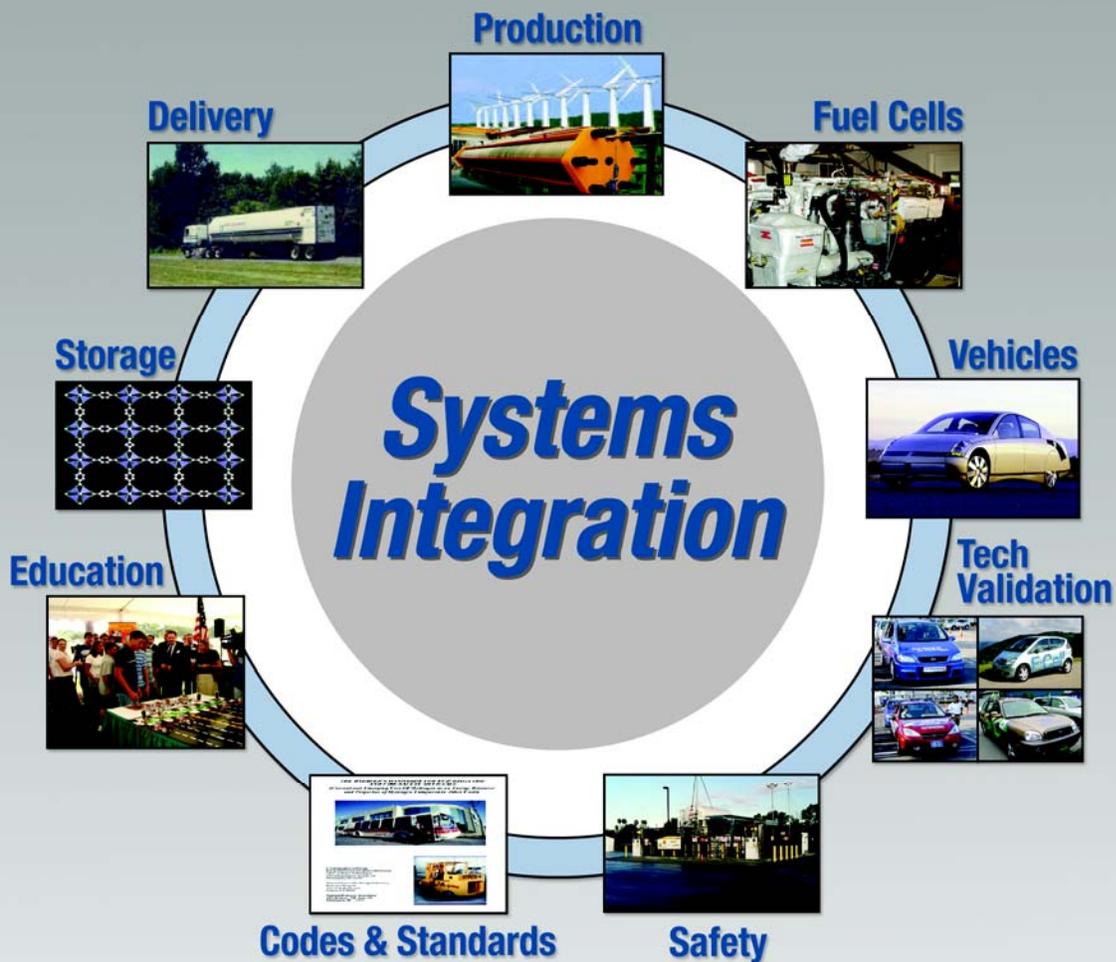




Measurement of Hydrogen Production Rate Based on Dew Point Temperatures



Independent Review

November 2007

National Renewable Energy Laboratory
1617 Cole Boulevard Golden, Colorado 80401-3393
303-275-3000 • www.nrel.gov

NREL is a U. S. Department of Energy Laboratory operated by Midwest Research Institute and Battelle
Contract No. DE-AC36-98-GO10337



NOTICE

This report was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or any agency thereof.

Available electronically at <http://www.osti.gov/bridge>

Available for a processing fee to U.S. Department of Energy
and its contractors, in paper, from:

U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831-0062
phone: 865.576.8401
fax: 865.576.5728
email: <mailto:reports@adonis.osti.gov>

Available for sale to the public, in paper, from:

U.S. Department of Commerce
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
phone: 800.553.6847
fax: 703.605.6900
email: orders@ntis.fedworld.gov <<mailto:orders@ntis.fedworld.gov>>
online ordering: <http://www.ntis.gov/ordering.htm>



Printed on paper containing at least 50% wastepaper, including 20% postconsumer waste

INDEPENDENT REVIEW TEAM SUMMARY REPORT



October 10, 2007

From: Independent Review Team (IRT), Hydrogen Production Rate Measurement
To: Mr. Carl Sink, Program Manager, Nuclear Hydrogen Initiative
Subject: Independent Review Team Report

Per your request for an independent verification of the approach being implemented by the Idaho National Laboratory (INL) to measure the rate of hydrogen production in INL's High-Temperature Electrolysis Project, this report presents the IRT's technical conclusions. We arrived at this consensus after reviewing documents and accompanying data, attending a detailed technical presentation made by INL staff, participating in a walkthrough of the test configuration, observing a hot experimental test, and interviewing both INL and Ceramatec staff.

Conclusion Statement

The IRT found the direct measurement in the change in dew point temperature approach, which the INL team is using as a surrogate for directly measuring the hydrogen production rate during high-temperature electrolysis, to be both reasonable and credible.

Rationale for Conclusion

The IRT believes that the INL process under review yielded appropriate and representative results within the framework of the thermodynamic analysis performed to justify the approach. The relationship between vapor pressure of water and dew point temperature is scientifically well established (and known as the Antoine correlation). As a result, the dew point measurements are an adequate means of determining water (H₂O) content. Specifically, the amount of H₂O converted to H₂ based on the vapor pressure measurement agrees with Faraday's Law for predicting hydrogen production rate from stack current.


Michael A. Duffy
Lead Systems Engineer


Kevin Harrison
Senior Engineer


Thomas Sheahan
Systems Integration Analyst

Contents

INTRODUCTION	1
OBJECTIVE.....	1
INDEPENDENT REVIEW TEAM APPROACH.....	1
HYDROGEN PRODUCTION RATE MEASUREMENTS	2
FINDINGS.....	4
ADDITIONAL OBSERVATIONS.....	6
RECOMMENDATIONS	9
BIBLIOGRAPHY.....	10
APPENDIX A: INDEPENDENT REVIEW TEAM.....	A-1
CONTACTS	A-1
APPENDIX B: TEST CONFIGURATION.....	B-1
APPENDIX C: THEORETICAL ANALYSIS.....	C-1
HYDROGEN PRODUCTION RATE BASED ON CURRENT	C-1
HYDROGEN PRODUCTION RATE BASED ON DEW POINT MEASUREMENTS	C-1
APPENDIX D: EXPERIMENTAL DATA.....	D-1
APPENDIX E: VAPOR PRESSURE OF WATER.....	E-1

Introduction

Over the last several years, the U.S. Department of Energy's (DOE) Office of Nuclear Energy (NE) has contracted with the Idaho National Laboratory (INL) to demonstrate the production of hydrogen from high-temperature electrolysis. Because the INL experimental team has implemented a novel approach for measuring the rate of hydrogen production, NE sought an independent verification of the approach. In turn, the DOE Hydrogen, Fuel Cells & Infrastructure Technologies Technology Analyst asked the National Renewable Energy Laboratory (NREL) to commission an independent verification of the approach being implemented by INL to measure the rate of hydrogen production in the laboratory's High-Temperature Electrolysis (HTE) Project.

Objective

The NREL Systems Integration Office (SIO), which is responsible for conducting independent reviews of R&D results within DOE's Hydrogen Program, formed an Independent Review Team (IRT) to evaluate the dew point measurement process being implemented by INL.

Independent Review Team Approach

To assemble the IRT, the SIO tapped three staff members with expertise in hydrogen production and measurement, experimental physics, and systems engineering. Appendix A contains brief backgrounds for each IRT member.

The IRT assessed the INL approach for measuring hydrogen production rates by reviewing a number of technical documents (see Bibliography list). IRT members also developed discussion points and questions, attended a detailed technical presentation made by INL staff, observed an experimental run of the test configuration, and conducted interviews with both INL and Ceramatec staff.

Experimental Setup

Figure 1 is a schematic diagram of the stack-testing apparatus the INL team used for these measurements. Appendix B presents more details on the configuration and its operation. The primary focus for this review is on the *measurement* of hydrogen being produced in this process, notably the change in dew point temperature measurements between the input and exit gas stream of the electrolyzer stack.

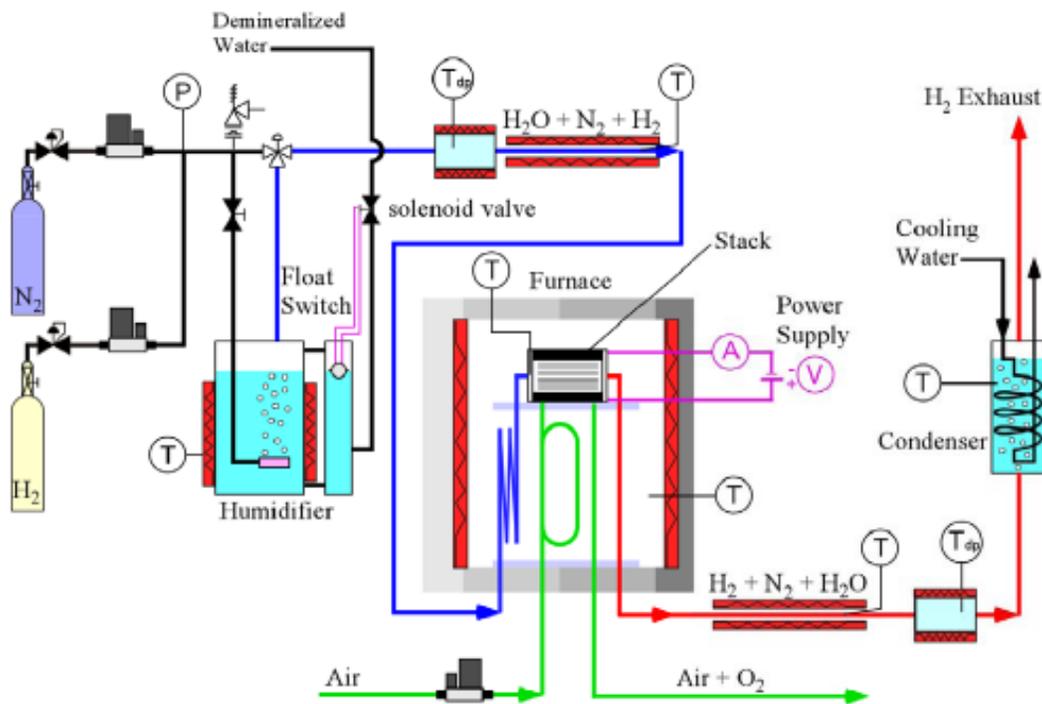


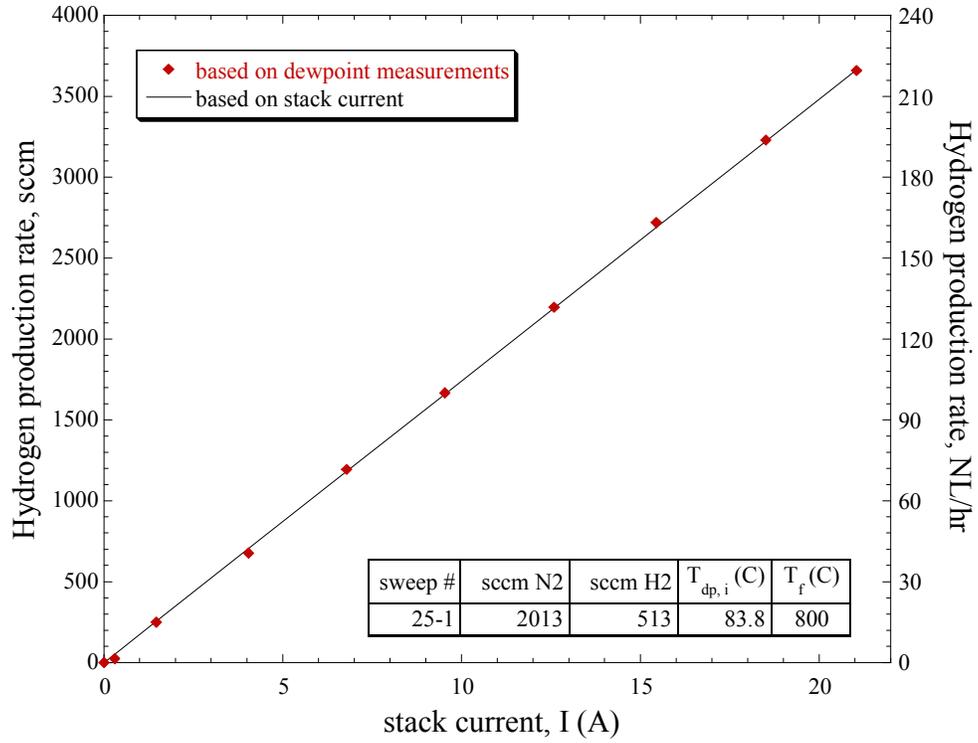
Figure 1. Schematic of experimental apparatus for electrolysis stack testing

Hydrogen Production Rate Measurements

The input gas flow contains primarily nitrogen, about 10% hydrogen, and water vapor measured by the dew point sensor that precedes the furnace. Combining that information with the subsequent measurement of the outlet dew point temperature (downstream of the electrolysis stack) allows the change in dew point to be determined. This, in turn, gives the change in water vapor and (following the theoretical derivation presented in Appendix C) the rate at which steam is removed; and, hence, the corresponding rate of hydrogen production by electrolysis.

Additional pressure measurements are made (not indicated in Figure 1). These measurements are necessary because, during stack tests, the INL team found pressure at the humidifier to be higher than the laboratory ambient pressure by an amount that depends on the flow rates of nitrogen, hydrogen, and steam. Because of flow losses in the line, higher flow rates yield higher back-pressure measurements. The actual pressure at the humidifier has to be taken into account when calculating the dew point-based hydrogen production rates.

Hydrogen production rates can be calculated directly from the stack electric current and independently from the measured inlet and outlet dew point measurements. Figure 2 shows a plot of hydrogen production rates measured during the stepwise sweep 25-1, which was taken before a 1,000-hour endurance test began. In the figure, the left-hand vertical scale is in standard cubic centimeters per minute (sccm) and the right-hand vertical axis is in normal liters per hour (NL/hr). The current-based hydrogen production rate is simply a straight line because hydrogen production is directly proportional to the stack current based on Faraday's Law. The dew point-based measurements exhibit excellent agreement with the current-based measurements. Hydrogen production rates as high as 220 NL/hr were achieved during this sweep.



Source: Reproduced from O'Brien et al. (2006)

Figure 2. Hydrogen production rates measured during initial sweep

Findings

The IRT's primary findings follow:

1. The IRT judged that the INL team members were fully competent in their field, and that this experiment was well planned and implemented.

The INL team members involved in the HTE are well qualified. They chose their experimental equipment well, and the IRT found no obvious weaknesses in the system's construction or operation. The INL team has carried out a series of experiments that incrementally lead toward a larger scale operation, with each step verifying another element along the pathway. For example, the INL team took care in designing the apparatus to verify the theoretical basis of the measurement system (i.e., why the change in dew point measurements will be correlated with hydrogen production).

Also, the INL researchers incorporated revisions to the experimental procedure as necessary based on earlier experimental results. For example, additional pressure (P_o) transducers (see Appendix D; Figure D-1) were added to eliminate the assumption of atmospheric pressure at the dew point sensors. Doing so improved the accuracy of the dew point sensor measurements.

2. The IRT found INL's approach to be in good agreement with the calculation based on stack current.

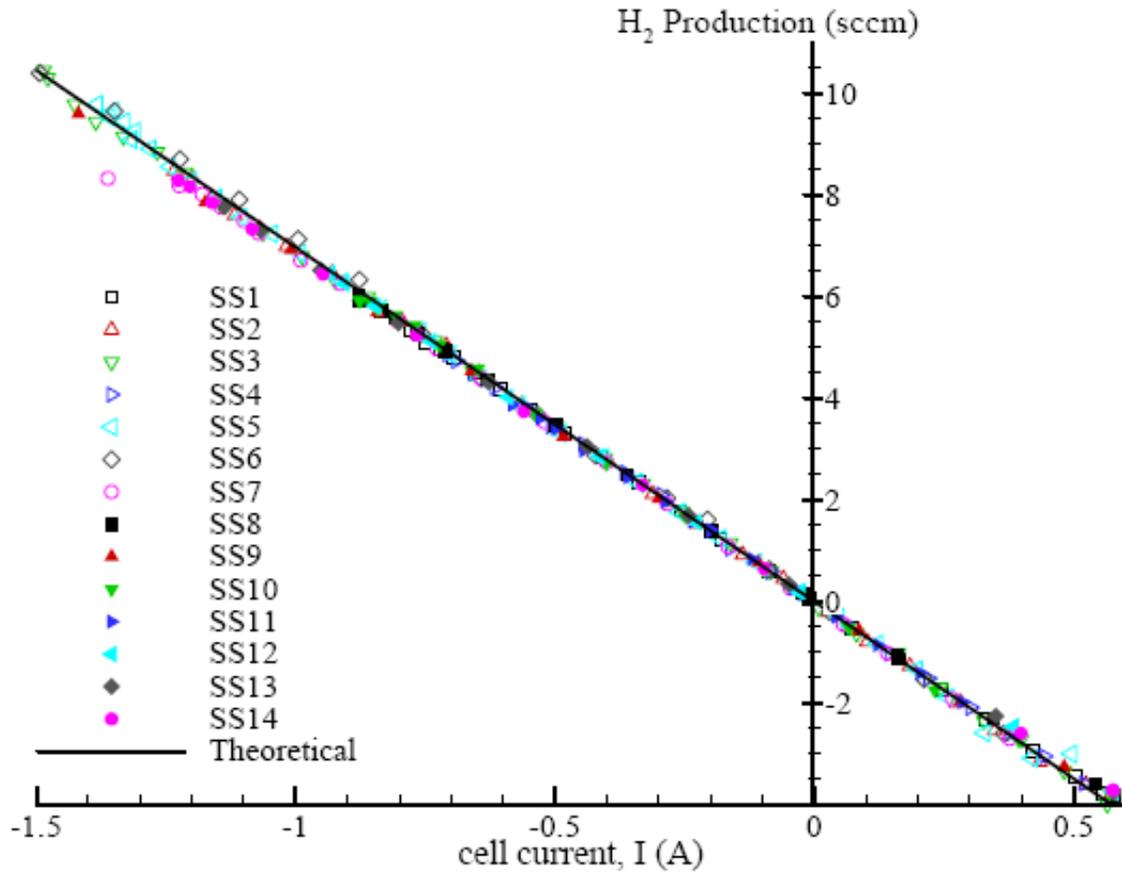
Hydrogen production is calculated in two ways: (1) from the current flowing through the cell; and (2) from the changing mole fraction of H_2O , which in turn comes from dew point temperature measurements before and after the H_2O flows through the $\sim 800^\circ C$ furnace chamber. These two results were in good agreement, lending credibility to the assertion that neither was contaminated by parasitic effects.

The theoretical relation of current-to-hydrogen-production is linear; it assumes that two electrons produce one H_2 molecule from H_2O . The theory relating dew point measurements to mole fraction is straightforward (see Appendix C), and assumes that when a mole of H_2O vanishes, a mole of H_2 is produced.¹ The post-furnace dew point temperature measurement is a good way to determine H_2 production. The precision of the dew point temperature measurement is the primary source of error in that method of determining hydrogen production. Once a measured temperature is chosen, the conversion to water vapor density is very accurate and adds no errors. The IRT estimates the error brackets of this dew point method to be less than $\pm 10\%$. The excellent agreement between the dew point temperature method and Faraday's Law (knowing stack current) justifies the change-in-dew-point measurement approach.

Fundamentally, one would consider using Faraday's Law and stack current measurements to be the more accurate means of determining H_2 production—as long as the system has no significant crossover losses or leaks. Leakage is discussed in more detail under "Additional Observations" later in this report. If hydrogen leaks out the side of the stack into an $800^\circ C$ surrounding environment, it will combine with oxygen and form H_2O again, and that water will escape with the air stream. In that case, the current drawn will be higher than expected for the amount of hydrogen actually contained in the outgoing gas stream. On the presumption that the electricity drawn does not do anything *but* electrolyze water, this immediately raises the question of where some of the hydrogen went. The ensuing discrepancy in the amount of hydrogen calculated separately by the dew point method and the stack current method would, therefore, indicate a possible leak.

¹ Extraneous chemical reactions are not a problem—no reactions of the form $N_2 + 3H_2 \rightarrow 2NH_3$, etc. take place at $800^\circ C$ and $P = 1$ atm. In other words, no loss of N_2 from the flowing stream takes place (Steve Deutch, NREL, personal communication).

When the system is leak-tight, the two methods of measurement correlate very well. Before beginning any testing of a stack of electrolysis cells, the INL team did some tests on “button cells” (single electrolysis cells) using argon as the carrier gas. The button cell testing showed excellent agreement between hydrogen production determinations via { Δ dew point} and {stack current}. No additional transducers—which monitor pressure at the dew point sensors—were used during the button cell experiments. This agreement is displayed in Figure 3.



Source: Reproduced from Figure 7 in INL (September 2004).

Figure 3. Comparison of hydrogen production rates as measured by dew point depression and as measured by cell current

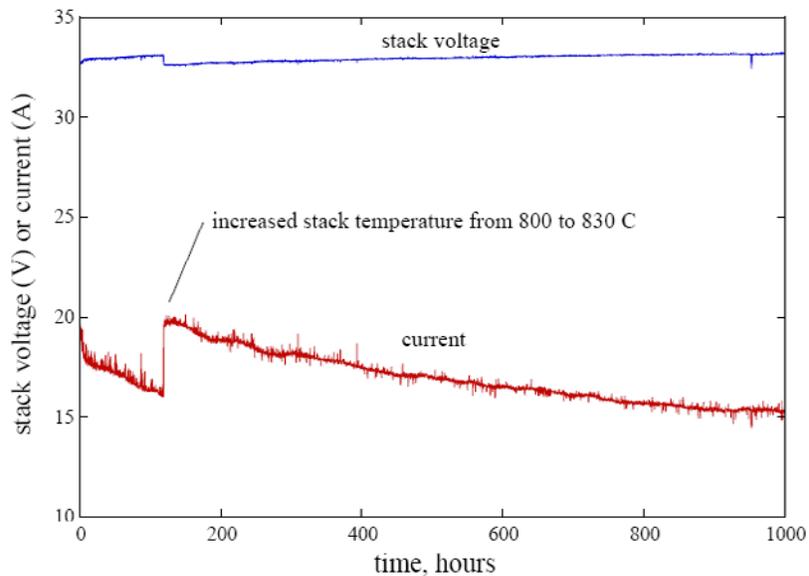
Because no hydrogen leakage concerns were present in the button cell testing, the hydrogen production rates calculated via the dew point measurements and the stack current were in excellent agreement. It is clear, then, that the change in dew point from inlet stream to output appears to be a reliable proxy for measuring hydrogen production.

Additional Observations

During their review, the IRT members noted several additional observations that, although not directly related to the dew point measurement process, may be of interest to the overall project:

1. Cell degradation over time

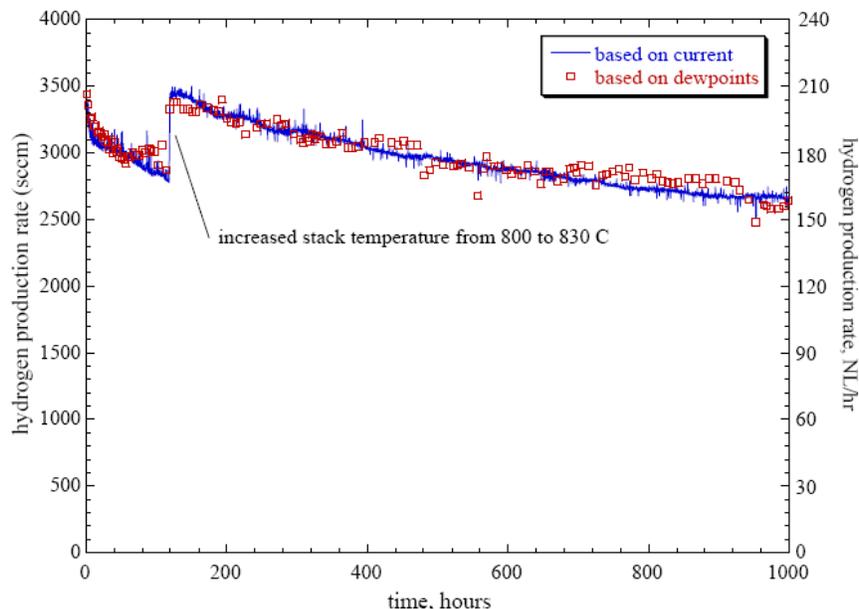
Figure 4 shows one very dramatic result from the 1,000-hour test. That figure shows a starting current of about 20 A. Then, in only one day, performance degraded about 10%, and after one week, performance degraded by about 20%. At that time the furnace temperature was increased from 800° to 830°C, and the current rose again to 20 A. The degradation that followed for the rest of the 1,000 hours appeared to follow a slope that was a continuation of the first week's curve. The improvement of performance when the temperature was raised is attributed to lower activation losses and higher conductivity through the electrolyte, but the steady deterioration seems to result from materials problems.



Source: Reproduced from Figure 10 in O'Brien et al. (2006).

Figure 4. Stack voltage and current measured during 1,000-hour test

The hydrogen production rate tracked well with the changing current, as shown in Figure 5.



Source: Reproduced from Figure 11 in O'Brien et al. (2006); see also Figure 6 from the same source.

Figure 5. Hydrogen production rates measured during 1,000-hour test

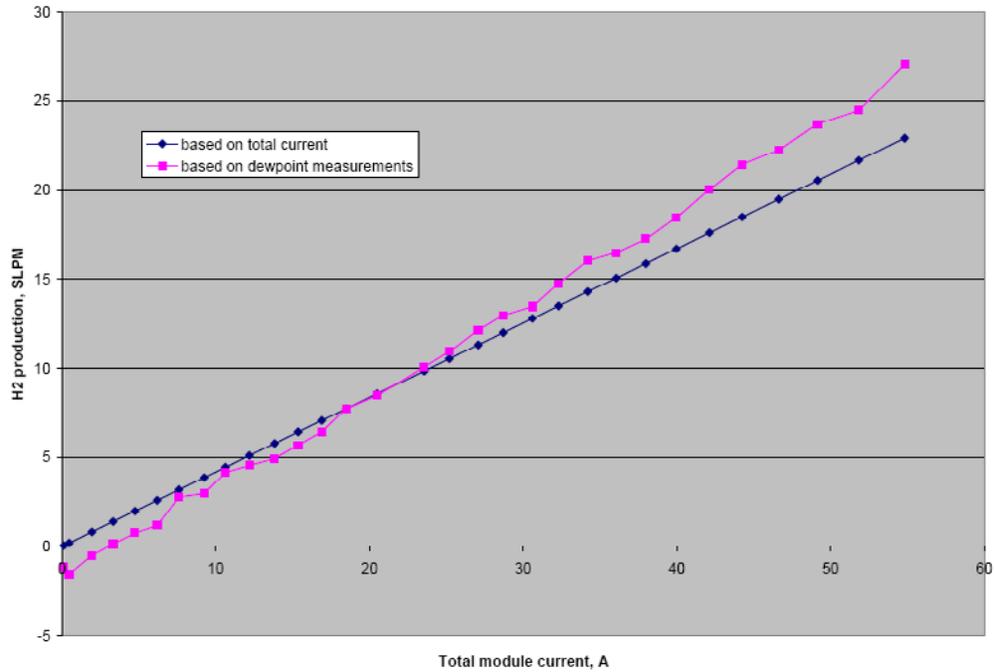
The ASR (area-specific resistance) degrades over time, which may be associated with delamination. Comparing two sweeps taken before and after 1,000 hours of operation shows about a 60% increase in ASR. Also, the per-cell operating voltage rose about 10% after the 1,000-hour run. More study is needed to explore these issues.

2. Leakage

In a system that is not perfectly closed (i.e., leaks), the H_2 calculated via the change in dew point temperature may disagree with that determined via stack current. For example, if H_2 preferentially leaks, H_2O will be a greater mole fraction of the outflowing gas, and H_2 will be a smaller mole fraction of the exit product stream. In that case the hydrogen calculation based on dew point temperature measurement would not agree with that based on the stack current measurement.

If the leakage of H_2O and H_2 are both at the same rate/ratio, though, the dew point temperature will give values for H_2 that are still in agreement with those based on current; however, some of the H_2 will be missing from the output stream. In that case, measuring total mass flow at the exit would be a way to detect any hidden leakage downstream of the inlet measurements to the stack. Such a mass flow measurement near the exit is to be part of the Integrated Laboratory Scale (ILS) experiment.

During the recent start-up (September 2007) of the ILS system, the INL team discussed the possibility that oxygen crossover may cause the variations in exit dew point measurements. The most recent data from the ILS show dew point versus stack current plots that are on different slopes and are diverging at higher stack currents (Figure 6). INL staff members noted that the stacks used in the ILS start-up might behave unexpectedly because they have been dormant at ambient conditions since March 2007.



Source: Reproduced from Figure 8 in Herring (2007).

Figure 6. Comparison of the hydrogen production rate as measured by the total current and by the change in dew point

Recommendations

The IRT is confident that the dew point measurements will yield credible results of the hydrogen production rates as the technology improves and cell degradation slows. Still, to offer even more reassurance to NE, the IRT recommends the following:

1. The INL team should conduct a thorough uncertainty analysis to bound minimum and maximum values of the hydrogen production rates as determined by the dew point measurements.

The accuracy of the dew point temperature sensors is good, but a detailed error analysis would be valuable. It is important to understand how an error associated with the measurement of T_{dew} will propagate through the analysis, thereby degrading the accuracy of the hydrogen production measurement.

2. The IRT agrees with the INL team that the output stream should be measured before it is vented to complete the mass balance.

Incorporating the mass flow meter in the ILS tests will yield a third independent measurement of the hydrogen production rate. Also, capturing the rate of water being condensed helps to determine the total mass flow balance. The amount of H_2O in the output stream provides a valuable comparison against the input stream. This is a way of double-checking the consistency of the process. Inlet and outlet mass flows of O_2 might also be a helpful correlative, but may be difficult to measure.

3. The IRT believes that voltage sweeps of the stack and corresponding dew point measurements should be taken more frequently.

Repeat measurements of H_2 production versus stack current at several different times during the lifetime of the test would be valuable, because the level of cell/stack degradation may vary over time. The evidence described in O'Brien et al. (2006) indicates that this is likely to reveal significant changes over time.

4. The IRT believes that additional measurements on the airflow into the furnace during ILS experiments may be useful.

An O_2 sensor could be placed in the airstream. Also, it may be helpful to include a T_{dew} measurement of the sweep air to determine whether any change in humidity would be attributable to leakage from within the stack.

Bibliography

- Herring, J.S.; O'Brien, J.E.; Stoots, C.M.; Lessing, P.; Hartvigsen, J.; and Elangovan, S. (2003). "Hydrogen Production through High-Temperature Electrolysis in a Solid Oxide Cell." Presented at the Second Information Exchange Meeting on Nuclear Production of Hydrogen, Argonne National Laboratory, Argonne, Illinois, October 2–3.
- Herring, J.S. (2007). E-mail to M. Duffy. Brief report on initial operation with single module. Attachment: Completion of Goal for High-Temperature Electrolysis, September 26, 2007; Sent October 1.
- Herring, J.S.; O'Brien, J.E.; Stoots, C.M.; Hawkes, G.; McKellar, M.; Sohal, M.; Harvego, E.; DeWalt, K.; and Hall, D. (2007). "2007 Laboratory-Scale High-Temperature Electrolysis System." Presented at the 2007 DOE Hydrogen, Fuel Cells & Infrastructure Technologies Program Review, Washington, D.C., May 16.
- INL. (September 2004). Completion of Button Cell Experiments for High-Temperature Electrolysis. PEMP PBI 13 1.12, Milestone 4.2 M2., INL submittal to DOE/NE.
- O'Brien, J.E.; Stoots, C.M.; and Herring, J.S. (October 2004). *Documentation of INEEL High-Temperature Electrolysis Milestone Demonstrating 50 NL/hr Hydrogen Production Rate*. Idaho Falls, ID: Idaho National Engineering and Environmental Laboratory (INEEL; now Idaho National Laboratory [INL]).
- O'Brien, J.E.; Stoots, C.M.; and Herring, J.S. (August 2005). *Documentation of INL High-Temperature Electrolysis Milestone Demonstrating 100 NL/hr Hydrogen Production Rate*. Idaho Falls, ID: INL.
- O'Brien, J.E.; Stoots, C.M.; and Herring, J.S. (April 2006). *Documentation of INL High-Temperature Electrolysis Milestone: Operation of HTE Stack at 100 NL/hr Hydrogen Production Rate for 1,000 Hours*. Idaho Falls, ID: INL.

Appendix A: Independent Review Team

Three NREL staff members participated in the IRT. A brief biography for each follows.

Dr. Michael A. Duffy is the lead systems engineer for NREL's Hydrogen Program. He has a Ph.D. from Ohio State University in systems engineering, an M.S. from Northeastern University in engineering management, a second M.S. from the Massachusetts Institute of Technology in mechanical engineering, and a B.S. from Tufts University in mechanical engineering. His background includes more than 30 years of systems engineering experience as a consultant and chief systems engineer in energy, safeguards and security, nuclear waste management, national defense, transportation, and space programs.

Dr. Kevin Harrison is a senior engineer at NREL. He leads research in the area of low-temperature (<100°C) electrolysis as it relates to integration with renewable energy sources. He also leads a project with Xcel Energy that is exploring renewable hydrogen production, compression, storage, and electricity generation via a hydrogen-fueled internal combustion engine. His work also includes testing and validating low-temperature electrolyzers and developing power electronics for wind- and solar-based electrolysis. He holds a Ph.D. and an M.S. in engineering and electrical engineering, respectively, from the University of North Dakota. His B.S. in electrical engineering was completed at the University of Rochester (UofR). Before joining NREL, Harrison worked for the UofR Laboratory for Laser Energetics and for Xerox Corporation.

Dr. Thomas Sheahen is a senior analyst in NREL's office in Washington, D.C. He holds both B.S. and Ph.D. degrees in physics from the Massachusetts Institute of Technology. He has been active in research related to measurements under difficult conditions since 1966, and his work has spanned a wide range of energy-related topics. He also wrote a well-known textbook entitled *Introduction to High-Temperature Superconductivity* (Plenum Press: 1994). Sheahen first became active in energy policy issues as a Congressional Science Fellow in 1978, and has remained current in that spectrum of issues, including the Energy Policy Act of 2005.

Contacts

INL

1. J. Stephen Herring, Ph.D., R&D Engineer
2. James E. O'Brien, Ph.D., Senior Research Engineer
3. Carl Stoots, Ph.D., Senior Research Engineer

Ceramatec

4. Joe Hartvigsen, Senior Engineer

NREL

5. Steve Deutch, Senior Scientist I

Appendix B: Test Configuration

The following description of the test configuration is reproduced from O'Brien et al. (2006):

An updated schematic of the stack-testing apparatus used for this test is presented in Fig. 1. Primary components include gas supply cylinders, gas mass-flow controllers, humidifier, dew point measurement stations, temperature and pressure measurement, high-temperature furnace, and a solid oxide electrolysis stack, condenser and exhaust. Nitrogen was used as an inert carrier gas. The use of a carrier gas allows us to independently vary both the partial pressures and the flow rates of the steam and hydrogen gases while continuing to operate at atmospheric pressure. The flow rates of nitrogen, hydrogen and air are established by means of precision mass-flow controllers (Hastings Model HFC-302, with Hastings Model 400 electronics). Air flow to the stack is supplied by the laboratory shop air system, after passing through a two-stage extractor/dryer unit.

Downstream of the mass-flow controller, nitrogen is mixed with a smaller flow of hydrogen gas. Hydrogen is included in the inlet flow as a reducing gas in order to help prevent oxidation of the nickel-zirconia cermet electrode material. The nitrogen/hydrogen gas mixture is mixed with steam by means of a heated humidifier. The humidifier consists of a heated stainless-steel vessel containing demineralized/deionized water through which the nitrogen/hydrogen flow is bubbled. A sintered stainless-steel filter was used as a sparger for this purpose. Note that an automated feedwater system was added to the apparatus to accommodate long-duration testing. This system includes a demineralized water supply, a modified humidifier with an auxiliary chamber, a float switch, and a solenoid valve. The dew point temperature of the nitrogen/hydrogen/steam gas mixture exiting the humidifier is monitored continuously using a precision dew point sensor (Vaisala Model HMP247). These measurements have indicated that the dew point temperature of the gas mixture leaving the humidifier is very close to the water bath temperature, but not necessarily equal to it. The humidifier is fitted with a clamp heater and is externally insulated. The temperatures of both the humidifier wall and the water bath are monitored continuously using thermocouples. The humidifier temperature is maintained at a constant setpoint value using feedback control. Since the vapor pressure of the water and the resulting partial pressure of the steam exiting the humidifier are determined by the water bath temperature, the water vapor mass flow rate is directly proportional to the carrier gas flow rate for a specified bath temperature. Also, 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 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 a variable transformers [sic]. During system cool-down, it is desirable to maintain nitrogen and hydrogen gas flows. In order to allow for the flow of a dry nitrogen/hydrogen mixture through the system during cool-down, without any possibility of steam condensation, a humidifier bypass was incorporated into the gas flow lines.

Humidifier bypass is achieved by closing the shut-off valve in the humidifier inlet line and changing the position of the 3-way valve located at the inlet to the first dew point measurement station (see Fig. 2). The humidifier also incorporates a pressure relief valve to avoid any possibility of over-pressurization. The inlet dew point measurement station is located immediately downstream of the humidifier. This measurement station consists of a stainless-steel vessel that houses the dew point sensor head, and a temperature probe. The sensors and the inlet and outlet gas lines are connected to the vessel using compression fittings. The outside of the vessel is fitted with a clamp heater and is maintained at a temperature above the gas mixture dew point value at all times using feedback control. The outlet dew point measurement station is identical to the inlet station.

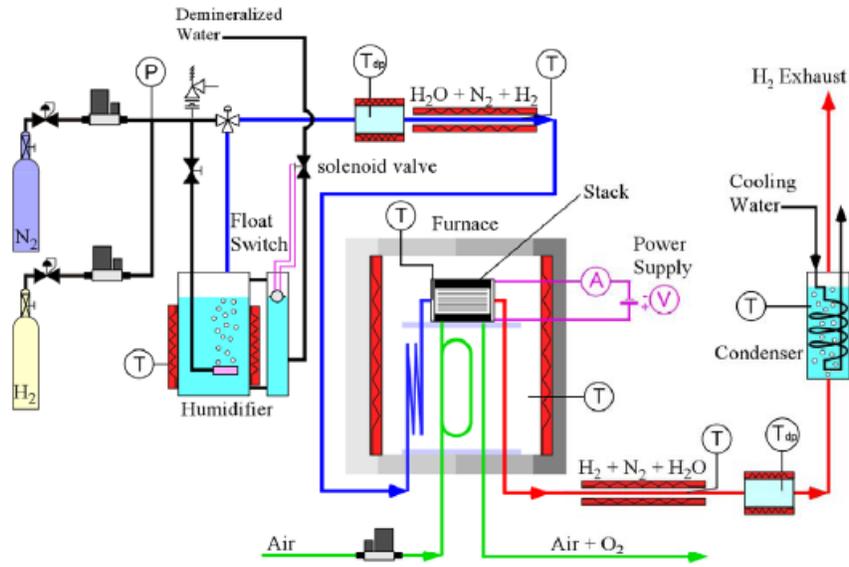


Figure 1: Schematic of experimental apparatus for electrolysis stack testing.

Appendix C: Theoretical Analysis

The following description is reproduced from O'Brien et al. (2004).

The principle [sic] question being asked in this independent analysis is: are the two methods of measuring hydrogen production equal? One method measures the current drawn by the electrolysis stack, and presumes that all H₂O that vanishes turns into H₂. The other method measures the dew point temperatures of the flowing gas before and after it enters the electrolysis cell, and thus determines the change in moisture content of the flowing gas. Whatever H₂O is lost is presumed to turn into H₂.

Here are the derivations of the relevant equations for both cases:

Hydrogen Production Rate Based on Current

The hydrogen production rate based on the stack ionic current is given by:

$$\Delta \dot{N}_{H_2} = \frac{I}{2F} N_{cells} \quad (1)$$

where I is the electric current to the stack, N_{cells} is the number of cells in the stack, and F is the Faraday number ($F = 96487 \text{ J/V mol}$). The product of I and N_{cells} is the stack ionic current. The molar production rate can be converted to a volumetric rate by invoking the ideal gas law:

$$\dot{V}_{H_2} = \Delta \dot{N}_{H_2} \frac{R_u T}{P} \quad (2)$$

Hydrogen Production Rate Based on Dew point Measurements

The hydrogen production rate can also be determined from the inlet and outlet gas stream dew point temperatures since one mole of steam consumption corresponds to one mole of hydrogen production. From the measured dew point temperatures, water vapor pressures may be calculated from an appropriate correlation (e.g., Antoine²). The inlet and outlet mole fractions of steam can then be obtained from:

$$y_{H_2O,i} = \frac{P_{H_2O,i}}{P}; \quad y_{H_2O,o} = \frac{P_{H_2O,o}}{P} \quad (3)$$

where P is the system pressure measured at the humidifier. It should be noted that since the mole fraction of steam in the inlet gas flow is determined by the dew point temperature and the system pressure, the total inlet flow rate of steam is therefore directly proportional to the sum of the molar flow rates of nitrogen plus hydrogen:

$$\dot{N}_{H_2O,i} = \frac{(\dot{N}_{N_2} + \dot{N}_{H_2,i}) y_{H_2O,i}}{1 - y_{H_2O,i}} \quad (4)$$

The magnitude of the total steam flow rate is important in determining whether or not steam starvation is likely to occur during electrolysis operation.

² Alternatively, see the vapor pressure table in Appendix E of this IRT report.

The inlet mole fraction of hydrogen, $y_{H2,i}$ is determined by the steam mole fraction and the ratio of the nitrogen flow rate to the hydrogen flow rate, both of which are determined by the setpoint values established on the mass flow controllers:

$$y_{H2,i} = \frac{1 - y_{H2O,i}}{1 + \dot{N}_{N2} / \dot{N}_{H2,i}}; \quad \dot{N}_{N2} = Q_{s,N2} \frac{P_{std}}{R_u T_{std}}; \quad \dot{N}_{H2,i} = Q_{s,H2} \frac{P_{std}}{R_u T_{std}} \quad (5)$$

Finally, the molar rates of hydrogen production and steam consumption may be determined from:

$$\Delta \dot{N}_{H2} = -\Delta \dot{N}_{H2O} = \dot{N}_{H2O,i} - (\dot{N}_{H2O,i} + \dot{N}_{H2,i} + \dot{N}_{N2}) y_{H2O,o} \quad (6)$$

Reproduced here is Figure 7 from O'Brien et al. (2006), documenting 1,000 hour performance. It shows a comparison between the two methods of measurement before the long-duration run was begun.

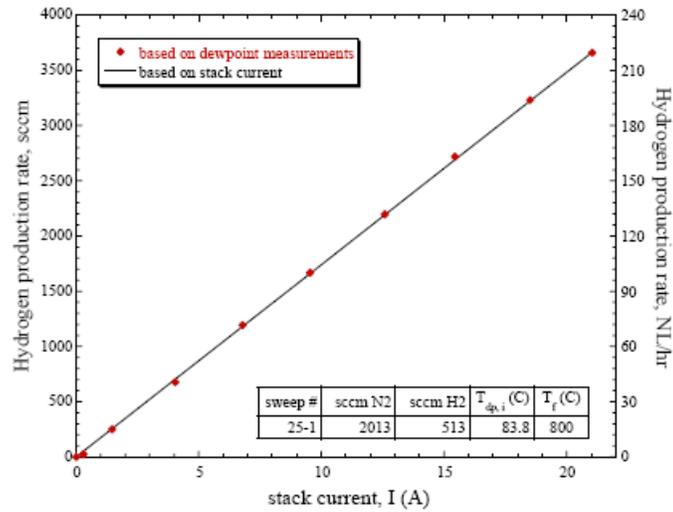


Figure 7. Hydrogen production rates measured during initial sweep.

The agreement between the two methods appears to be very good.

Appendix D: Experimental Data

Figures D-1 and D-2 show actual data from the experiment as it was running; that is, they are printouts from the screen of the monitoring equipment. Close scrutiny of either figure shows typical values for the many parameters recorded during the experiment. These screens were captured on August 28, 2007.

The addition of pressure sensors near the dew point measurements appears clearly in Figures D-1 and D-2, whereas that is not shown in an earlier publication (O'Brien et al. [2006]) from which Figure 1 (in the main body of this IRT report) is taken (nor does Appendix B mention additional pressure sensors). Adding such sensors improves the accuracy of the determination of water content.

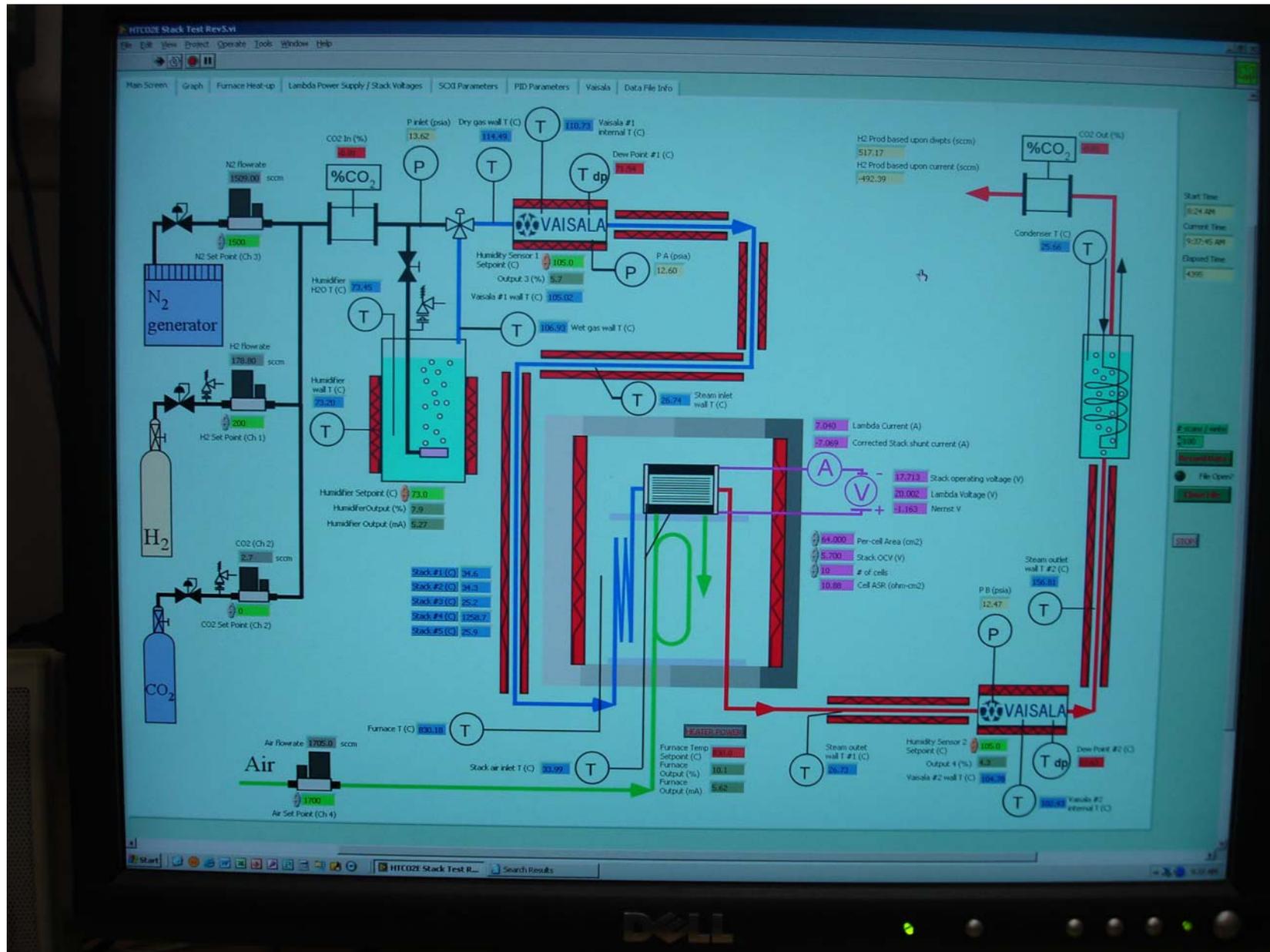


Figure D-1. Screen shot 1 showing real-time experimental data

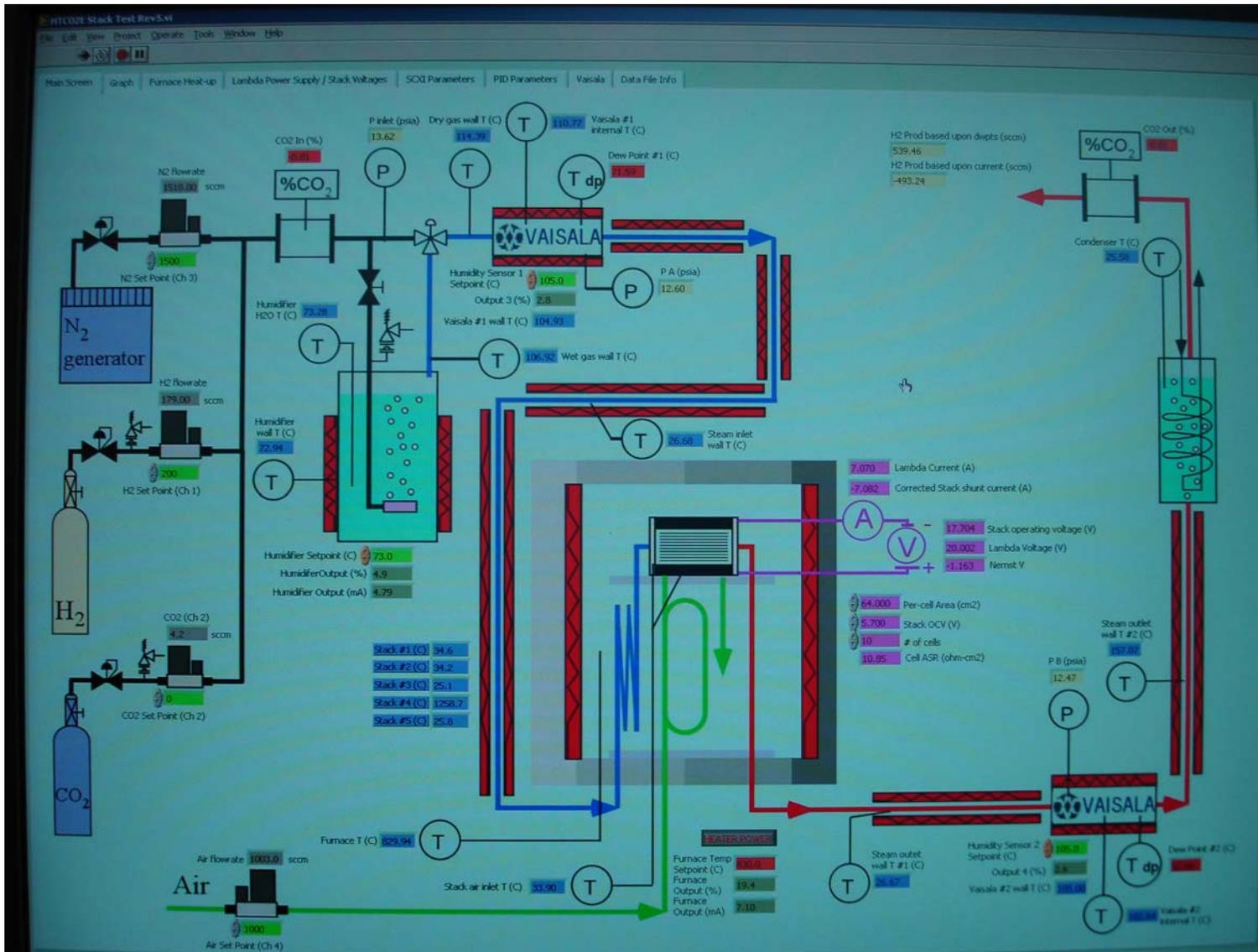


Figure D-2. Screen shot 2 showing real-time experimental data

Appendix E: Vapor Pressure of Water

This appendix discusses the relationship between vapor pressure of water and dew point temperature.

The HyperPhysics Web site (<http://hyperphysics.phy-astr.gsu.edu/hbase/kinetic/relhum.html#c3>) provides explanatory text about dew points, as well as the following data about water vapor at moderate temperatures. This table presents data for the relationship between saturated vapor pressure, saturated vapor density, and temperature.

Table E-1. Saturated Vapor Pressure, Density for Water

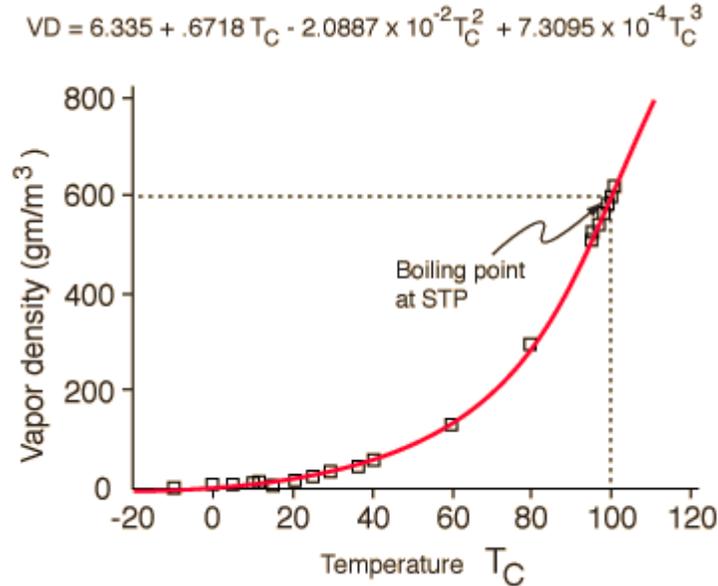
Temp (°C)	Temp (°F)	Saturated Vapor Pressure (mmHg)	Saturated Vapor Density (gm/m ³)	Temp (°C)	Temp (°F)	Saturated Vapor Pressure (mmHg)	Saturated Vapor Density (gm/m ³)
-10	14	2.15	2.36	40	104	55.3	51.1
0	32	4.58	4.85	60	140	149.4	130.5
5	41	6.54	6.8	80	176	355.1	293.8
10	50	9.21	9.4	95	203	634	505
11	51.8	9.84	10.01	96	205	658	523
12	53.6	10.52	10.66	97	207	682	541
13	55.4	11.23	11.35	98	208	707	560
14	57.2	11.99	12.07	99	210	733	579
15	59	12.79	12.83	100	212	760	598
20	68	17.54	17.3	101	214	788	618
25	77	23.76	23	110	230	1074.6	...
30	86	31.8	30.4	120	248	1489	...
37	98.6	47.07	44	200	392	11659	7840

Below are some selected values of temperature and the [saturated vapor pressures](#) required to place the [boiling point](#) at those temperatures. The pressures are stated in mega-Pascals, where a Pascal is a Newton per square meter, and as a multiple of standard [atmospheric pressure](#).

Temperature (°C)	Pressure (MPa)	Pressure (Atmospheres)
100	0.101325	1
150	0.4762	4.700
200	1.55	15.297
250	3.976	39.24
300	8.588	84.757
350	16.529	163.13
373.946	22.064	217.75

Source: HyperPhysics Web site: <http://hyperphysics.phy-astr.gsu.edu/hbase/kinetic/relhum.html#c3> . Used with permission from C.R. Nave, HyperPhysics.

The vapor pressure and vapor density are different (not merely a matter of units), because $PV = nRT$ doesn't apply (in this temperature range water is normally a liquid). Each is useful in certain applications. For the experiments studied here, the mass content of H_2O in the flowing gas is of interest, so vapor *density* is the important parameter. A polynomial is often used to fit the data for water vapor density up to $100^\circ C$:



Source: HyperPhysics Web site: <http://hyperphysics.phy-astr.gsu.edu/hbase/kinetic/relhum.html#c3> . Used with permission from C.R. Nave, HyperPhysics.

Figure E-1. Water vapor density (pressure) as a function of temperature

Uncertainty: It bears mentioning that the graph (as well as differentiating the formula), indicates that when $T \sim 20^\circ C$, an error in determining dew point of $\Delta T = 1^\circ C$ implies an error in vapor density of 1.5 g/m^3 , or 8.3%. And when $T \sim 80^\circ C$, an error of $\Delta T = 1^\circ C$ yields an error in vapor density of 11.3 g/m^3 , or 3.8%. If most dew point measurements are made on the incoming stream at slightly above room temperature, perhaps $33^\circ C$, the vapor density error would be about 6% for a $1^\circ C$ temperature error. Summing two such errors randomly still gives under 9% uncertainty.

To cover a wider range of temperatures, an alternative formula is

$$\ln(P) = A - [B/(C+T)] \quad \text{or} \quad P = \exp \{A - [B/(C+T)]\}$$

where P = vapor pressure in kilopascals (kPa), T = absolute temperature ($^\circ K$); and A , B , and C are constants. This representation is known as the *Antoine correlation* and gives vapor pressure for many substances.* For water, the coefficients are

$$A = 16.5362, \quad B = 3985.44, \quad C = -38.9974$$

For example, at $300^\circ K$ the vapor pressure of water is $0.00355 \text{ MPa} = 26.6 \text{ mm Hg}$.

By scaling A and B and sliding C , this formula can be converted into mm Hg, degrees C or F, etc.

* webMATHEMATICA in Chemical Engineering at UC Davis, Pure Component Vapor Pressure Calculator: <http://www.higgins.ucdavis.edu/webMathematica/MSP/Examples/VaporPressures>