Procedure for Performing In-Plane Membrane Conductivity Testing

Work Performed by
the Florida Solar Energy Center
under DOE Contract # DE-FC36-06G016028

June 9, 2008

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EXECUTIVE SUMMARY

This document outlines, in detail, a test protocol for performing in-plane conductivity measurements on membranes for PEM fuel cells. Responsibility for developing this test protocol was tasked to the Topic 2 awardee under DOE Contract #DE-FC36-06GO16028. Under this award, FSEC was to work with the fuel cell community to develop standardized methodologies to membrane conductivity as a function of temperature and relative humidity (RH) and to measure membrane mechanical properties.

This conductivity protocol is used at FSEC for all membrane testing. FSEC follows the conductivity protocol established by BekkTech; and while different equipment was used for the samples that have been compared, this test protocol reproduced BekkTech conductivity results. BekkTech performs the DOE protocol using the BekkTech Conductivity Test System, Model BT-552. FSEC has reproduced the BekkTech test results using FSEC's existing test equipment with the only significant modification to the BekkTech procedures being the length of time at each RH. (BekkTech holds for 15 minutes at each RH. FSEC holds for 60 minutes at each RH.)

Researchers following the test protocol will be able to reproduce results that have been obtained by both FSEC and BekkTech.

Contents

1. Test Protocol for Membrane Conductivity Screening Test

Conductivity testing for the DOE program Milestones are conducted by BekkTech Corp. and reported to the individual teams and to FSEC Program Management for presentation and review with DOE. The purpose of this protocol is to provide the individual Task 1 team members with a verified protocol for their screening tests. This document outlines the conductivity test procedures used at FSEC. FSEC follows the conductivity protocol established by BekkTech, and while different equipment was used, for the samples that have been compared, this test protocol reproduced BekkTech conductivity results.

2. Gas, Equipment & Software Requirements

FSEC uses the equipment, and software listed below to perform conductivity measurements.

2.1 Gas Flow and System Pressure

- **Gas -** Hydrogen
- **30 ^{o}C Tests**
  - **Gas Flow Control -** Two Mass Flow Controllers from the Fuel Cell Test Station: Model 850C, Scribner Associates, Inc. are used for gas-mixing to achieve dew points for 30 ^{o}C testing.
  - **System Pressure -** 100 kPa absolute. This is approximately atmospheric pressure in Florida.
- **80 ^{o}C Tests**
  - **Gas Flow Control –** One Mass Flow Controller from the Fuel Cell Test Station: Model 850C, Scribner Associates.
  - **System Pressure -** 100 kPa absolute. This is approximately atmospheric pressure in Florida.
- **120 ^{o}C Tests**
  - **Gas Flow Control –** One Mass Flow Controller from the Fuel Cell Test Station: Model 850C, Scribner Associates.
  - **System Pressure -** 230 kPa absolute. This is approximately 130 kPa gauge in Florida. Pressure is provided by a Scribner and Associates backpressure regulator.

2.2 Equipment

- Fuel Cell Technologies 5 cm^2 fuel cell test hardware with longer bolts supplied by BekkTech
- BekkTech Conductivity Cell – Part # BT-112
- BekkTech Saturator – Part # BT-104
- BekkTech Heated Gas Line – Part # BT-125
- Princeton Applied Research 263 Potentiostat/Galvanostat
- Temperature Controllers & Thermocouples
  - Omega CSC32 Temperature Controller with a K-type thermocouple in the saturator
  - Self-tune Plus Love Controls with a K-type thermocouple in the heated gas line
  - Love Controls with T-type thermocouples in the fuel cell
- In-house-made water condensers on the gas exit
- Scribner Associates backpressure regulator

2.3 Software

- Conductivity is monitored as a function of time using CorrWare (Scribner Associates)
- Gas flow and cell temperature are controlled using Fuel Cell Software (Scribner Associates)
- Data is analyzed using Excel (Microsoft)

3. Preparing a Membrane Sample for Testing

Clean all work surfaces and test hardware with ethanol and compressed air. Wear properly specified gloves while handling the membrane to prevent contamination.

3.1 Equilibrate Sample to Room Conditions

Place membrane sample on a clean counter surface for 24 hours to allow equilibration to room temperature and room humidity.

FSEC Facility Room Conditions: Room temperature of approximately 21 ^{o}C and average room relative humidity of 60%.

3.2 Cut Sample

Use the *Sample Punch* (BekkTech part number ACC-960, Figure 1) to cut a piece from the membrane for testing. Sample to be tested measures approximately 5 mm x 25 mm. Sandwich the membrane between thin sheets of Teflon when cutting the sample.

Figure 1. Sample Punch

Alternative Cutting Method: Use an Exacto knife and a straight edge to cut the sample. The sample must be long enough to extend slightly beyond the platinum mesh of the conductivity cell.

3.3 Verify Sample Width

Use a *Width Measurement Tool* (BekkTech part number ACC-940) to verify the width of the sample being tested. The *Width Measurement Tool* has magnification of 11x and a reticule with 0.1mm gradients.

Figure 2: Width Measurement Tool

3.4 Sample Length

Sample length is set by the BekkTech Conductivity Cell. We use a length of 4.25 mm for all conductivity calculations.

3.5 Measure Sample Thickness

Use a Mitutoyo Gauge (Figure 3) is to determine sample thickness. Measure the equilibriated (according to section 3.1) thickness of the membrane using an average of at least 10 readings taken over the entire membrane. Sandwich the membrane between thin sheets of Teflon of known thickness when making the caliper readings.

Figure 3. Mitutoyo Gauge

3.6 Assemble Sample in the Conductivity Cell

The BekkTech conductivity cell is shown in Figure 4. Place the Teflon support (square Teflon piece) under the clamp of the BekkTech conductivity Cell. This prevents unnecessary bending of platinum wires during assembly.

Remove all four screws holding the top membrane clamp. Then remove the top membrane clamp from the bottom membrane clamp. Use tweezers to gently lift the platinum wires up from the bottom clamp.

Insert the membrane sample under the platinum wires. Place the membrane sample perpendicular to the voltage measurement probes in the main body. Ensure there is adequate overlap between the ends of the membrane and platinum gauze at either end of the sample. A schematic of a side view of the membrane sample assembly is shown in Figure 5. The conductivity cell is designed for a minimum of 3 mm of overlap with the gauze. For thick samples that will be run at high humidity, place the membrane above the platinum wires. For thin samples or dry operating conditions, place the membrane below the platinum wires.

Use tweezers to place the top membrane clamp onto the top surface of the membrane sample. Use the notches on the top membrane clamp as a guide. Gently secure the membrane clamp using the four fasteners. A picture of the conductivity cell with the top clamp secured is shown in Figure 6. Be careful to apply only light torque (finger tight) when tightening fasteners, as threads in main body are easily stripped-out.

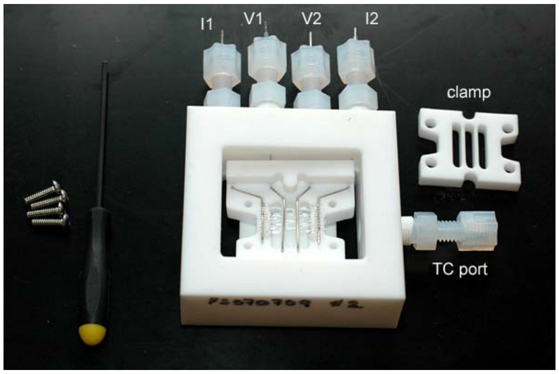

Figure 4. BekkTech Conductivity Cell shown with Teflon support (not labeled) beneath the membrane/platinum wire probe configuration. The membrane has been inserted properly in the Main Body with top clamp off to the side.

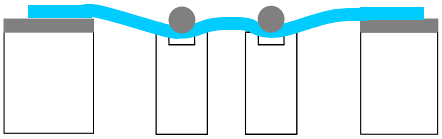

Figure 5: Assemble Sample Under Pt Wires

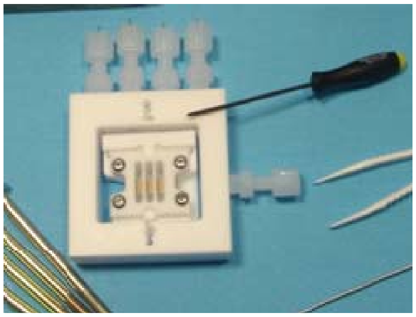

Figure 6. Replace Top Clamp

3.7 Insert Thermocouple

Insert **Type T** internal thermo couple (TC) into the Bottom Membrane Clamp beneath the membrane as shown in Figure 7. The TC should be positioned so that the junction is directly below the membrane. The junction is typically ~0.5 mm to 1 mm from the end of the TC. Once placed, snug the fitting around the TC.

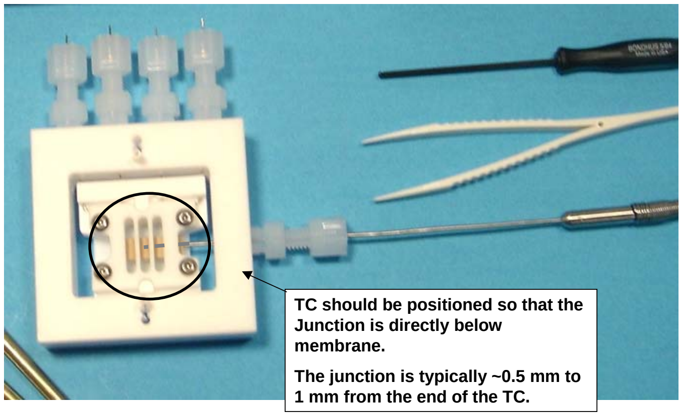

Figure 7. Internal Thermocouple Placement

3.8 Assemble Conductivity Cell with Cell Hardware

Place the Bekktech Conductivity Cell onto the graphite end plate of the Fuel Cell Technology test hardware as shown in Figure 8. The current collectors that extend from the ends of the graphite end plates must be aligned in the same direction as the voltage/current external ports of the Conductivity Cell. Place the remaining graphite end plate on top of the Conductivity Cell. Re-assemble the cell hardware. Using the longer bolts provided by BekkTech, secure the graphite/Conductivity Cell/graphite sandwich (Figure 9). You will use only 4 bolts to secure the assembly. The Conductivity Cell makes a good seal with the 4 bolts. Install the bolts in a diagonal pattern with a very light torque of about 20 in-lbs to make a good seal. The Teflon conductivity cell will expand upon heating, so if the sandwich is bolted too tightly, the Teflon will deform between the plates and begin to "flow out" the sides.

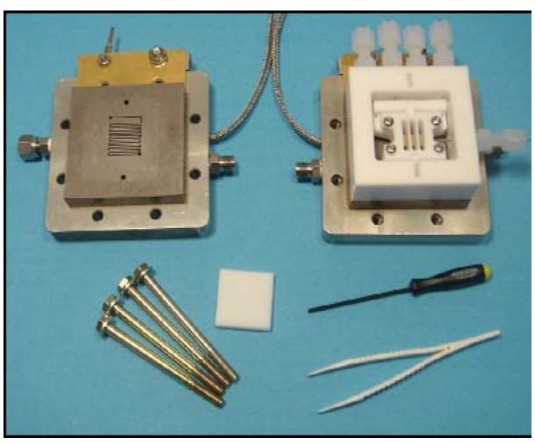

Figure 8: Conductivity cell with cell hardware

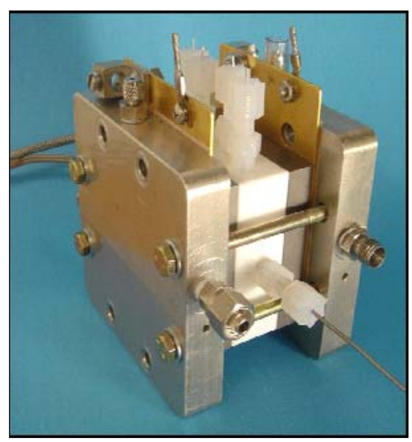

Figure 9: Assembled conductivity cell in cell hardware

3.9 Connect to Heated Gas Lines

Serious injury or death can occur if hydrogen and oxygen are combined within the conductivity cell. Therefore, only one source of gas is used in performing conductivity tests regardless of the "environmental system" used.

FSEC uses a combination of BekkTech and Scribner components to conduct membrane conductivity tests. The BekkTech Conductivity Cell hardware and BekkTech Saturator are used in conjunction with the Scribner 850C and a backpressure regulator located after the condenser on the gas exit line. In this case, FSEC uses the Scribner test stand for flow control and membrane temperature control and the BekkTech saturator for rapid humidity control. The backpressure regulator is used for pressure control. FuelCell® SOFTWARE is used control the flowrates and cell temperature.

Connect the gas outlet from the BekkTech saturator to the anode gas inlet of Fuel Cell Technology test hardware. Plug the anode outlet of the fuel cell test hardware with a ¼" stainless steel cap. Connect the cathode gas outlet of the cell hardware to the cathode exhaust line (which is connected to a condenser followed by a pressure regulator). Plug both cathode supply at the 850C station and cathode gas inlet of fuel cell test hardware with ¼" stainless steel caps. Doing this, and purging the system with N_2 prior to application of hydrogen, will eliminate the chances of accidental gas mixing. The setup described above with the gas lines, condenser and backpressure regulator connected to the fuel cell is shown below in Figures 10 and 11.

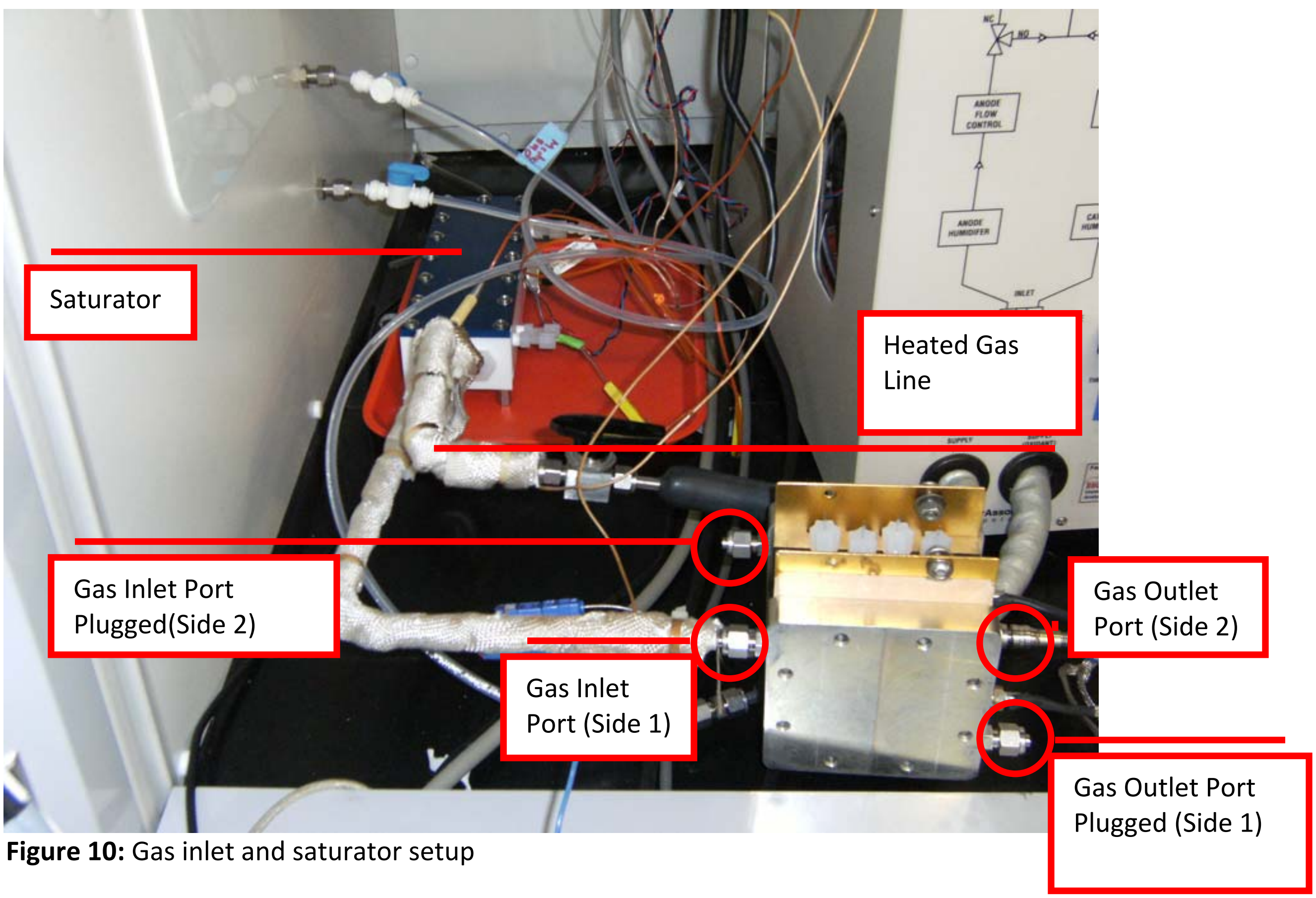

Figure 10: Gas inlet and saturator setup

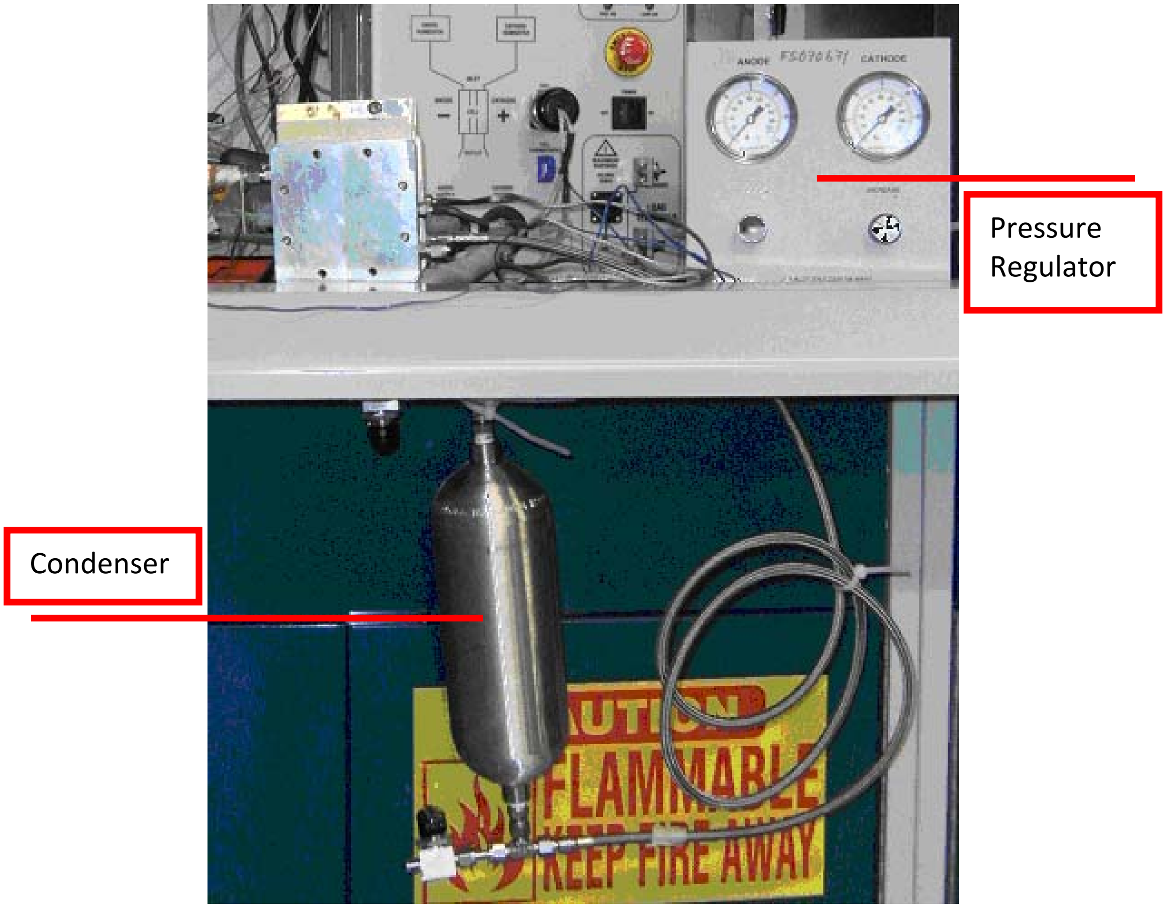

Figure 11: Condenser and pressure regulator setup

3.10 Electrical Connections to the Conductivity Cell

Figure 12 shows the Fuel Cell Technologies Cell Hardware with the BekkTech Conductivity Cell in place and the electrical connections attached to perform a 4-probe measurement. The electrical connection is made to a Princeton Applied Research Potentiostat/Galvanostat, Model 263.

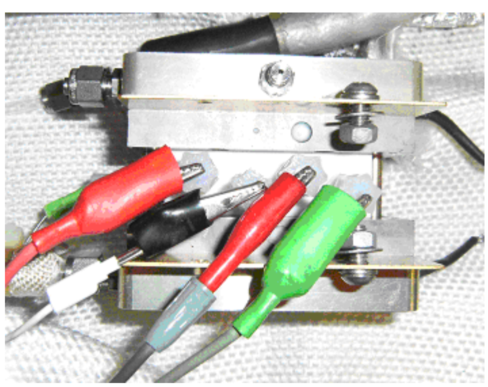

Figure 12: Wiring for a four electrode measurement. Connectivity from Left to Right is: Counter, Reference, Sense, Working

3.11 Measuring Resistance

FSEC uses a Princeton Applied Research Galvanostat/Potentiostat, Model 263 to set a voltage and measures the resulting current for conductivity tests. We perform a Scanning DC Sweep from 0.3V to -0.3V. The linear Voltage-Current data is fit for resistance.

3.12 Connect Cell Hardware to Heater Power and Heater Thermocouple

Plug the internal cell thermocouple (TC) into the thermocouple outlet. Plug the power cable from the cell hardware heaters into the power outlet on the test stand.

CAUTION: We recommend that you always wait to connect the cell hardware heaters to power until after you have verified that the cell hardware internal TC is properly placed in the cell hardware. If this TC is accidentally left out of the cell hardware or improperly installed, the TC will communicate an incorrect temperature to the cell hardware temperature controller. Irreparable damage to the cell hardware and conductivity cell may result.

4. Test Protocol for Samples under the DOE Program

Each sample is tested for approximately six days - first at 30 °C, then 80 °C, then 120 °C. A membrane sample is assembled into the conductivity cell/cell hardware fixture and tested at 30 °C, 80 °C, and 120 °C without removal from the cell hardware.

This section is intended to give nut & bolts instruction on how to start up or change gas supply conditions using the Scribner 850C test stand and Fuel Cell SOFTWARE, adjust system pressure using the backpressure regulator, and take V vs. I data using the PAR potentiostat and Corrware software.

5. Environmental Control of Membrane/Gas Supply Operation

Open FuelCell® SOFTWARE. Figures 13a and b show initial dialog boxes for setup cell and setup fuel with settings for a 30 °C run. The cell temperature (i.e. membrane temperature) and fuel flow control will change based on the scheduled testing condition (either 30, 80 or 120 °C). The initial dialog boxes for 80 and 120 °C runs are shown in Figures 14 and 15, respectively.

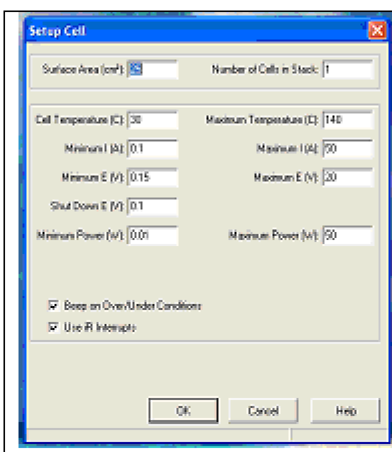

Figure 13a. Setup Cell menu in FuelCell software showing 30 °C test startup conditions

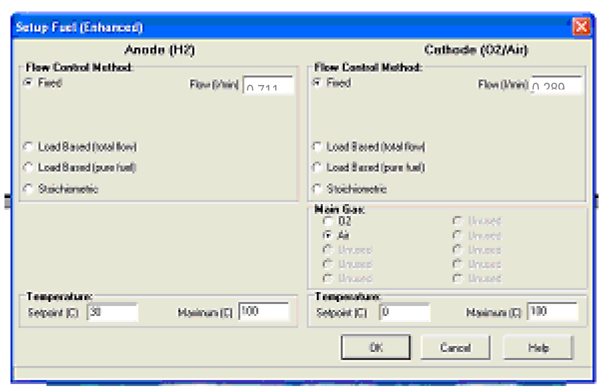

Figure 13b. Setup Fuel menu in FuelCell software showing 30 °C startup conditions

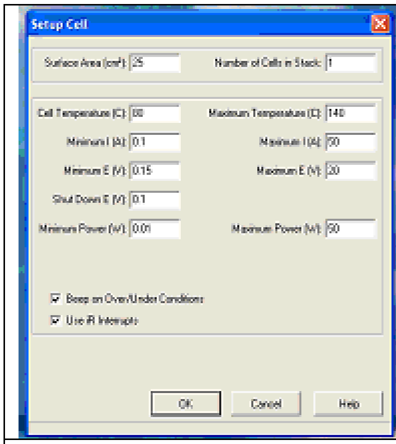

Figure 14a. Setup Cell menu in FuelCell software showing 80 °C test startup conditions

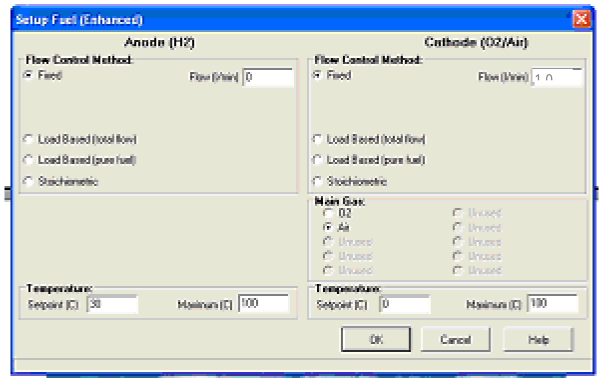

Figure 14b. Setup Fuel menu in FuelCell software showing 80 °C startup conditions

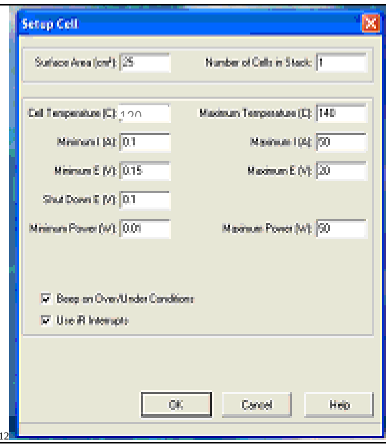

Figure 15a. Setup Cell menu in FuelCell software showing 120 °C test startup conditions

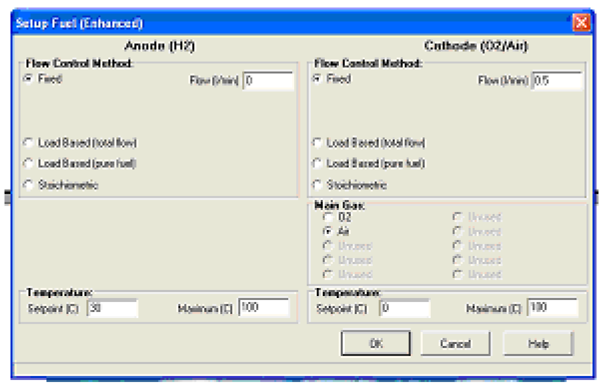

Figure 15b. Setup Fuel menu in FuelCell software showing 120 °C startup conditions

Hydrogen gas is used for all conductivity tests. Only nitrogen and hydrogen are connected to the test station. Fuel flow rates and temperatures are set based on test membrane temperature and test relative humidity (outlined in sections 7.2-7.4). Sections 7.2-7.4 contain more detailed information regarding flowrate settings. The temperature setpoint for the fuels is not critical because these temperatures will actually be controlled using the BekkTech saturator. The temperature of the saturator controls the relative humidity of the membrane. The relative humidity will be changed every 60 minutes based on the protocol for recommended conductivity test conditions, outlined in section 4.

In the Main Control dialog box of the FuelCell software, as shown in Figure 16, click “Cell” to control the temperature of the cell. Turn on the temperature control for the saturator and line. The temperature of the line should be 10-15 °C above the temperature of the saturator to prevent condensation. Then click the “Apply Fuel” button once the prescribed temperatures are reached. A click will sound from the 850C; indicating solenoid valves for flow control are in function.

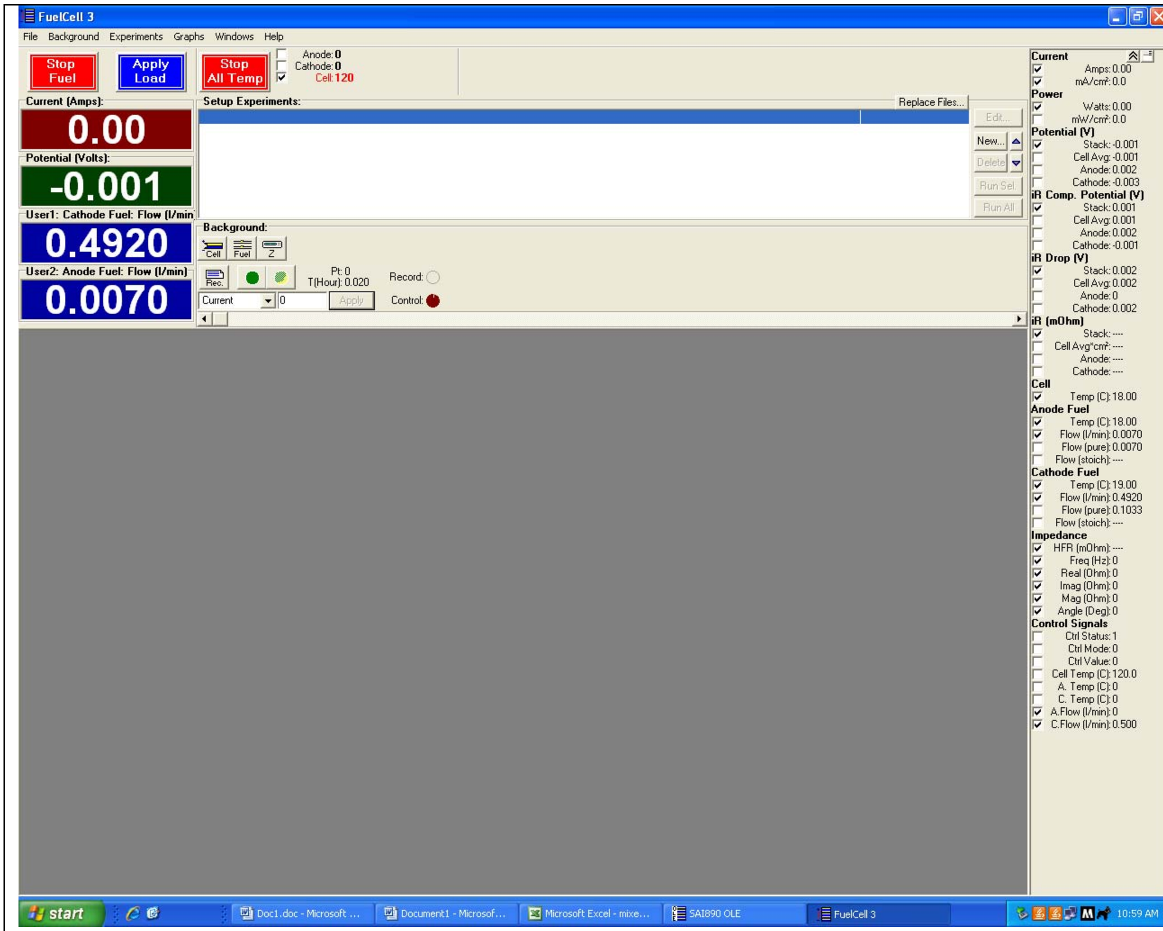

Figure 16. Main control and display menu in FuelCell® SOFTWARE.

6. System Pressure Regulation

When testing at membrane temperatures > 100 °C, the system must be operated at pressures above atmosphere in order to achieve 100% RH. System pressure is raised by restricting gas flow out of the system via a regulator placed after the exhaust gases pass through a condenser. The pressure is adjusted by dialing the regulator valve until the desired pressure is read off the gauge. A system pressure of 230 kPa is recommended for testing at a membrane temperature of 120 °C.

7. Data Acquisition and Analysis

Open Corrware2 data acquisition software to perform conductivity measurement (collect V vs I data) and following the steps shown below.

1. Select the Cyclic Voltammagram experiment (Figures 17 and 18). Choose file name and where it will be saved. Then measure selected lines. In Figure 20, a typical plot is shown. When an appropriate amount of time has passed (one hour for each humidity and two hours for start up) press stop (the red octagon) to stop the experiment.

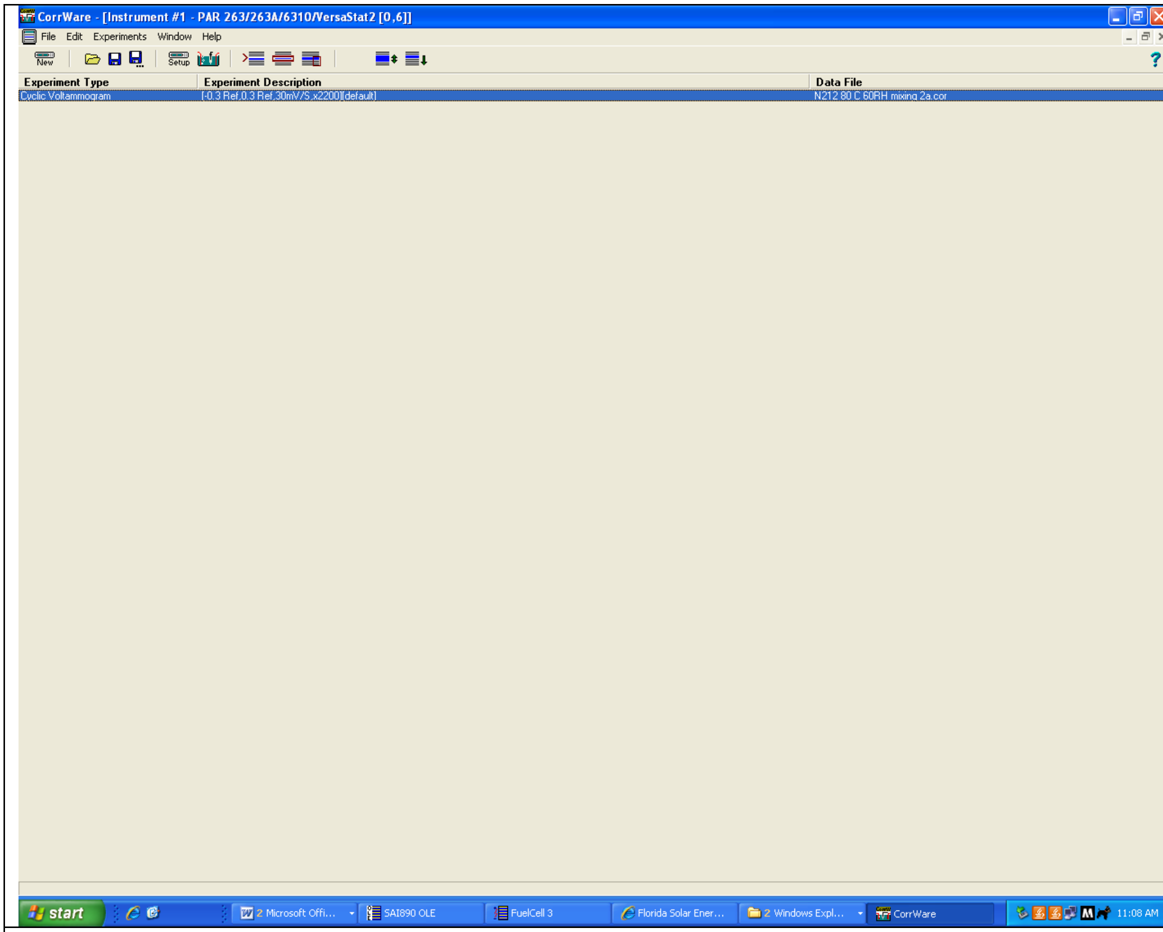

Figure 17. CorrWare experiment type page

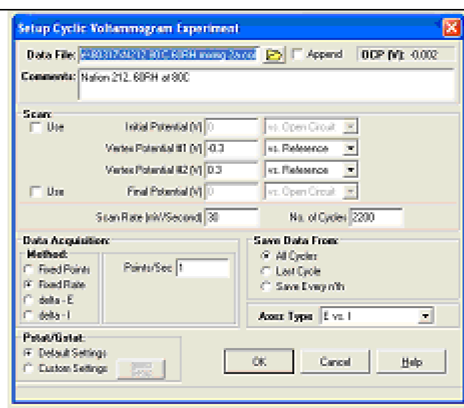

Figure 18. Cyclic voltammagram experimental setup

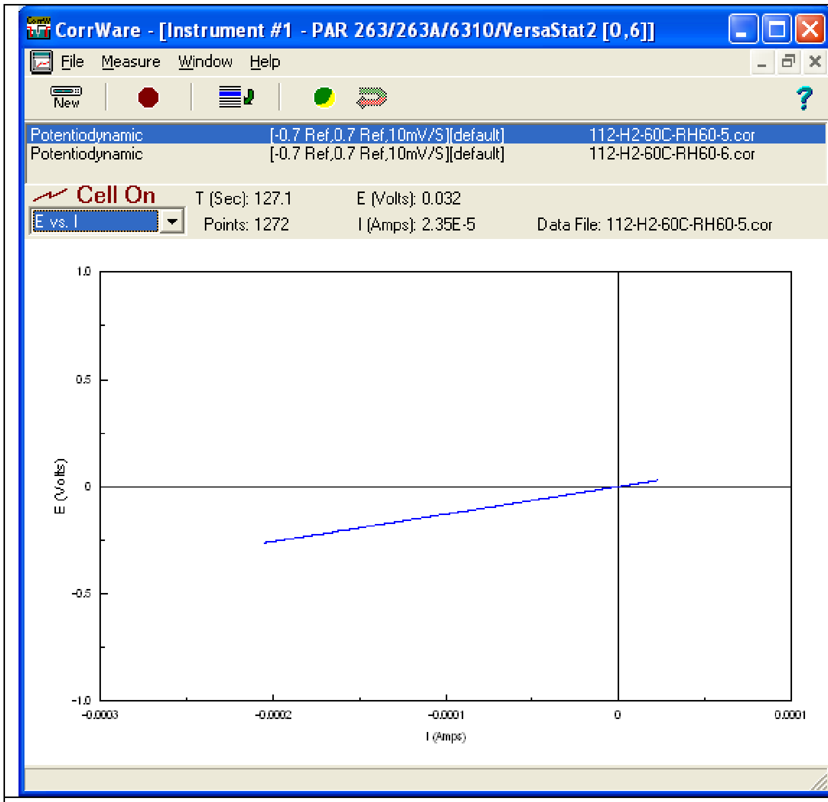

Figure 19. Typical plot of a cyclic voltammagram measurement.

2. To analyze the data, open CorrWare Data\MacroRev5.xls, found on the desktop. Select "enable macros." This program analyzes the CorrWare data by obtaining the slope of the V-I plots (i.e., the resistance) over time. Copy the name of the file that was just saved (.cor) in "Datafile to process". This file must be in the same folder as MacroRev5. Open the template file (.xls) whose name matches that in "Template file name". The output file will be that named in "New Data Analysis Name". Click on "Create New Data Analysis File". In a few seconds a new file is created that is the .xls version of the .cor file that was just obtained.

3. In the new .xls file open the "RH&4ElecCondVsTime" tab. This gives a plot of conductivity vs time. An example is shown in Figure 20. By examining this plot, it is possible to determine when the membrane's conductivity reached steady-state. In the plot in Figure 20, steady state was reached around 60 minutes. If steady-state is not reached, repeat the measurement using a new file name until a steady-state is reached.

4. Open the "data" tab in the .xls file. The final column (G) is the calculated 4 electrode conductivity. The file time is in column D. Take an average of the conductivity values that have been obtained in steady state. This value is the conductivity of this membrane in the conditions under study.

5. Repeat the test for various operating conditions.

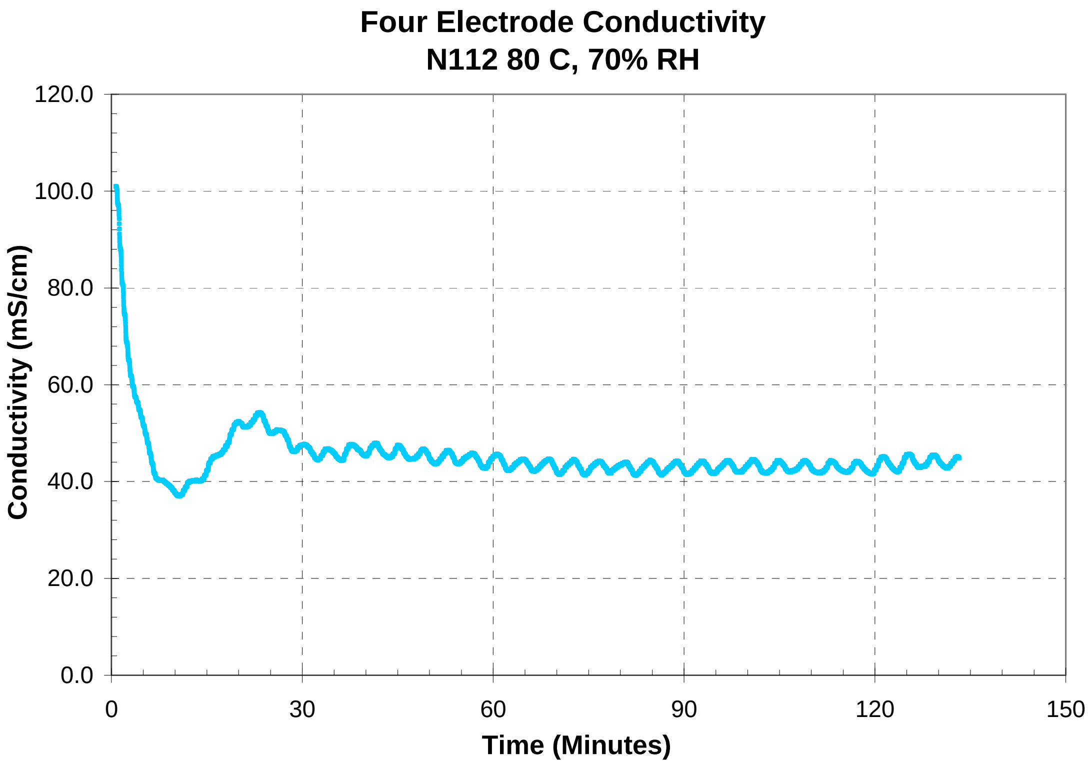

Figure 20. Sample conductivity plot.

7.1 Recommended Conductivity Test Conditions

The test includes both decreases and increases to the RH. This provides a more complete picture of the characteristics of the sample since the water content may change slowly with relative humidity and the conductivity may change with time.

- Load membrane into Conductivity Cell.
- Adjust Temperatures, pressures and flowrates to meet "wet-up" specifications
- Wet-up at desired temperature (30, 80, or 120 ^{o}C), 70% RH for 2 hours
- Follow RH steps allowing 60 minutes of stabilization for each, as follows:

Dew Point for 70 % RH ramping down to 20% in increments of 10% followed by a ramping up to 100% in increments of 10%.

7.2 Prepare Equipment & Software for 30 ^{o}C Test

Ensure that the valve on the dry gas line that connects into the wet gas line is open. Gas-mixing is needed for controlling dew points at 30 ^{o}C. Hydrogen gas is fed to both the anode and the cathode.

Gas Flow – 1000 SCCM Hydrogen
Gas Mixing - The dew points are set using a mixture of dry gas (-50 ^{o}C, anode, water was drained from the test station) with gas saturated to a dew point of 45 ^{o}C (cathode).
System Pressure -100 kPa absolute. This is atmospheric pressure in Florida
Sample Conditioning - Wet-up at 30 ^{o}C, 70% RH for 2 hours.

After 2 Hours of Conditioning - Operating conditions are adjusted every 60 minutes. Note that 2 Mass Flow Controllers are required for this temperature. One flows gas through the Saturator (Wet Gas, cathode). The second mixes with the saturated gas after the Saturator (Dry Gas, anode). Wet and dry gas flows are controlled using FuelCell software (Scribner).

The gas flow rates required to reach the desired relative humidities are outlined in Table 1. From 20-40% RH 2000 sccm of gas is used, while from 50-100% RH 1000 sccm of gas is used.

Relative Humidity (%RH)	Wet Gas Flow Rate (45 ^{o}C dew point) (SCCM)	Dry Gas Flow Rate (-50 ^{o}C dew point) (SCCM)
70	289	711
60	246	754
50	204	796
40	326	1664
30	243	1757
25	202	1798
20	161	1839
25	202	1798
30	243	1757
40	326	1664
50	204	796
60	246	754
70	289	711
80	331	669
90	375	625
95	396	604
100	418	582

Table 1. Wet and dry gas flow rates required to reach the desired relative humidities at 30 ^{o}C.

7.3 Prepare Equipment & Software for 80 ^{o}C Test

Ensure that the valve on the dry gas line that connects into the wet gas line is closed. Gas-mixing is not needed for controlling dew points at 80 ^{o}C.

Gas Flow - 1000 SCCM Hydrogen
Gas Mixing – None
System Pressure -100 kPa absolute. This is atmospheric pressure in Florida.
Sample Conditioning - Wet-up at 80 ^{o}C, 70% RH for 2 hours.
After 2 Hours of Conditioning - Operating conditions (saturator temperature) are adjusted every 60 minutes, as follows:

- Dew Point of 71.4 ^{o}C for 70% RH
- Dew Point of 67.9 ^{o}C for 60% RH
- Dew Point of 63.8 ^{o}C for 50% RH
- Dew Point of 58.9 ^{o}C for 40% RH
- Dew Point of 52.9 ^{o}C for 30% RH
- Dew Point of 49.2 ^{o}C for 25% RH

- Dew Point of 44.8 °C for 20% RH
- Dew Point of 49.2 °C for 25% RH
- Dew Point of 52.9 °C for 30% RH
- Dew Point of 58.9 °C for 40% RH
- Dew Point of 63.8 °C for 50% RH
- Dew Point of 67.9 °C for 60% RH
- Dew Point of 71.4 °C for 70% RH
- Dew Point of 74.6 °C for 80% RH
- Dew Point of 77.4 °C for 90% RH
- Dew Point of 78.7 °C for 95% RH
- Dew Point of 80.0 °C for 100% RH

7.4 Prepare Equipment and Software for 120 °C Test

Ensure that the valve on the dry gas line that connects into the wet gas line is closed. Gas-mixing is not needed for controlling dew points at 120 °C.

Gas Flow - 500 SCCM Hydrogen
Gas Mixing – None
System Pressure - 230 kPa absolute. This is approximately 130 kPa in Florida.
Sample Conditioning - Wet-up at 80C, 70% RH for 2 hours.
After 2 Hours of Conditioning - Operating conditions (saturator temperature) are adjusted every 60 minutes, as follows:

- Dew Point of 108.9 °C for 70% RH
- Dew Point of 104.4 °C for 60% RH
- Dew Point of 99.2 °C for 50% RH
- Dew Point of 93.0 °C for 40% RH
- Dew Point of 85.4 °C for 30% RH
- Dew Point of 81.1 °C for 25% RH
- Dew Point of 75.2 °C for 20% RH
- Dew Point of 81.1 °C for 25% RH
- Dew Point of 85.4 °C for 30% RH
- Dew Point of 93.0 °C for 40% RH
- Dew Point of 99.2 °C for 50% RH
- Dew Point of 104.4 °C for 60 % RH
- Dew Point of 108.9 °C for 70% RH
- Dew Point of 113.0 °C for 80% RH
- Dew Point of 116.7 °C for 90 % RH
- Dew Point of 118.4 °C for 95% RH
- Dew Point of 120.0 °C for 100% RH

7.5 Shut Down Procedures

- When the test has completed, stop fuel using FuelCell software.
- Cool the system by reducing the temperatures on the temperature controllers.
- When the system has cooled to below 100 °C, reduce back pressure to 100 kPa and allow system to depressurize.

- Turn off PAR 263 Potentiostat.
- When the system has cooled to ~50 °C, close FuelCell program, turn off test station, and turn off Nitrogen and Hydrogen.

7.6 Calculating Conductivity

The formula for calculating conductivity is included in the MacroRev5.xls file. To manually calculate conductivity, use the following information. R is calculated using a Least Squares Fit of the voltage-current data.

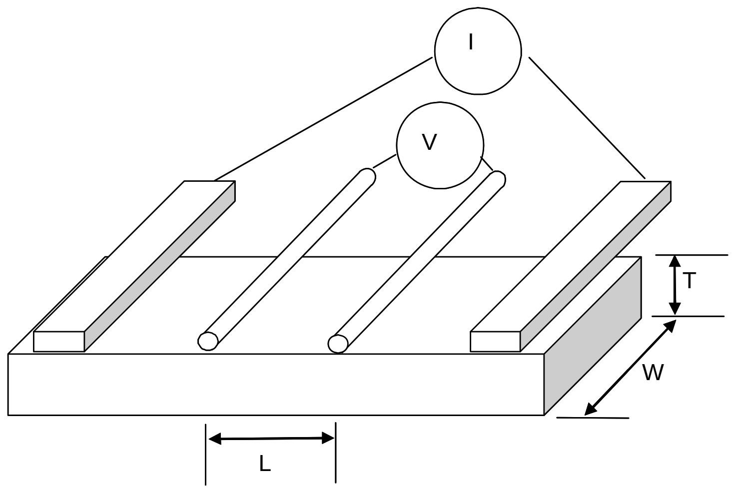

Figure 21. Schematic of conductivity cell.

The distance between V1 and V2 probe points (L) in the conductivity cell is 4.25 mm. The definition of Resistance in terms of bulk resistivity, **R**, is shown in equation 1.

$$R = \frac{\rho L}{A} = \frac{\rho L}{WT} \quad (1)$$

Where, **A** is the cross-sectional area perpendicular to the current flow, which in this case, is sample **W**idth * **T**hickness. **L** is the distance in the direction of ion flow, between voltage measurements. Solving this equation for resistivity, ρ results in equation 2.

$$\rho = \frac{RWT}{L} \quad (2)$$

Conductivity, σ, is the inverse of resistivity, as shown in equation 3.

$$\sigma = \frac{1}{\rho} = \frac{L}{RWT} \quad (3)$$

For example,

- Size of Nafion membrane sample: 0.5 cm wide, 0.005 cm thick
- Slope of current vs. voltage measurement (resistance): 2,230 Ohms @ 60C, 100% RH.

$$\rho = \frac{R \cdot W \cdot T}{L} = \frac{2,230 ohms \cdot 0.5cm \cdot 0.005cm}{0.425cm} = 13.11 Ohms \cdot cm$$

This yields a conductivity of:

$$\sigma = \frac{1}{\rho} = 0.076\ Siemens / cm$$

7.7 Basic Assumptions of Experiment

When assessing the accuracy of results, note the following assumptions:

- The length of the membrane between the platinum wire measurement probes connected to V1 and V2 is known to be 0.425 cm for the Conductivity Cell.
  - V1 and V2 are measured using platinum wire 0.75 mm diameter. The two wires are 5 mm apart, center-to-center. Thus, for a rigid sample, 5 mm may be a better distance to use. But, for a pliable sample, 4.25 mm is a better measurement.
  - Be aware that some membrane samples may swell or change dimension, impacting resistivity measurements.
- The interior humidity of the Conductivity Cell is exactly what is set *at* the humidifier.
  - Many humidifiers are inaccurate. Be sure to test the humidification system if results of these tests will be used for more than comparative analysis.
  - Low flows and condensing environments can lead to lower than expected humidity levels.

8. Contact Information:

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