Standard Operating Procedure (SOP)

Porous Transport Layer Resistance, Porosity, and Porosimetry Measurements

Test ID # LTE-P-17

Ryan Ouimet
Prepared By: NAME / TITLE

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Date

Approved By: NAME / TITLE

Date

Approved By: NAME / TITLE

Date

Date: 08/14/2023

Revision History

This page documents the revisions over time to the SOP. The most recent iteration should be listed in the row space, with consecutive versions following.

Date of Revision	Page(s)/Section(s) Revised	Revision Explanation
07/06/2021	-	Initial Release
08/14/2023	Title, 4, 5	Adjusted the summary to explain how contact angles measured are inferred rather than measured with a direct external process. Added a note in the procedure that listed material dimensions are for reference.

Outline/Table of Contents

3. Procedures

a. Scope and Applicability –

The purpose of this procedure is to determine the electrical bulk resistance of the porous transport layer (PTL) as well as the pore size distribution (PSD), mean flow pore diameter, and water contact angle of the PTL. This protocol assumes that the PTL has been thoroughly cleaned prior to testing. This protocol also assumes that the PTL being tested has uniform thickness and is defect-free.

b. Summary of Method –

This protocol will utilize a potentiostat with four probe measurements to determine the bulk resistance of the PTL. Following the resistance measurement, capillary flow porometry (CFP) will be performed on the PTL which will provide information on the porosity of the PTL. When using a wetting liquid with a low contact angle (such as POREFIL™ or Porofil™), the CFP will show the smallest pore, largest pore, and the mean flow pore of the PTL. When comparing CFP data from the low contact angle measurement to CFP data taken with deionized water as the wetting liquid, calculations can be made to determine the internal contact angle of the deionized water on the PTL. It should be noted that this method infers internal PTL contact angles and transport properties through a theory-based porosimetry method rather than measurement of external contact angles.

c. Definitions –

capillary flow porometry (CFP); microporous layer (MPL); pore size distribution (PSD); porous transport layer (PTL); safety data sheet (SDS)

d. Health & Safety Warning –

While this protocol assumes that the PTL has been cleaned prior to testing, the cleaning process may involve strongly corrosive solvents. Be aware of all hazards and thoroughly read through all safety data sheets (SDS) when preparing and cleaning the PTLs. When performing the resistance measurement, a current will be momentarily passed through the test setup. Ensure that the area is dry and free of any shock hazards. Additionally, during the resistance test, the sample will be pressed to high pressures (~100psi). Be aware that the lab press is a pinch hazard.

e. Cautions –

When handling the PTL, be sure to keep the PTL clean and avoid contamination. The introduction of foreign object debris to the PTL may result in higher resistance and could negatively impact the water properties of the PTL. Also, be sure not to introduce any bends or cracks into the PTL as that may also result in higher resistance.

f. Interferences –

The instrumentation used for this protocol should be calibrated prior to testing to ensure the accuracy of these tests. If pores are not completely wetted prior to CFP experiments, data may be inaccurate or incomplete.

g. Personnel Qualifications / Responsibilities –

Users should have basic laboratory knowledge and experience. Users should be trained to use all equipment listed in section (h). Users have the responsibility of ensuring that they have read through all pertinent SDS related to this protocol.

h. Equipment and Supplies –

Resistance Measurements: Potentiostat arranged for 4 probe measurements, carbon gas diffusion layers with a microporous layer (Freudenberg H23C8 or similar), 2 pieces of gold-plated copper with tabs where the potentiostat probes can be attached, laboratory press

Porosimetry Tests: Capillary flow porometer, POREFIL™ or similar wetting fluid, deionized water

i. Step by Step Procedure

Note: Material dimensions listed throughout the protocol are for reference only. Refer to your instrument manufacturer to ensure that the correct sample size is being used.

Resistance Measurements

1. Cut a piece of cleaned PTL to a dimension of 50mm x 50mm by using a cutting die. Ensure that the sample is flat and without defects. (If a cutting die is unavailable, cut the PTL using an alternative method to the specified dimension and then clean the PTL.)
2. Place the cleaned PTL between two pieces of carbon GDL material with a microporous layer (MPL). (The microporous layer should be adjacent to the PTL).

3. Place the GDL|PTL|GDL between two pieces of gold-plated copper. One side of each Au-coated Cu plate should have an insulating layer applied. Ensure that the insulating layer is facing away from the GDL|PTL|GDL sample.
4. Place the Au-plated Cu|GDL|PTL|GDL|Au-plated Cu setup into a

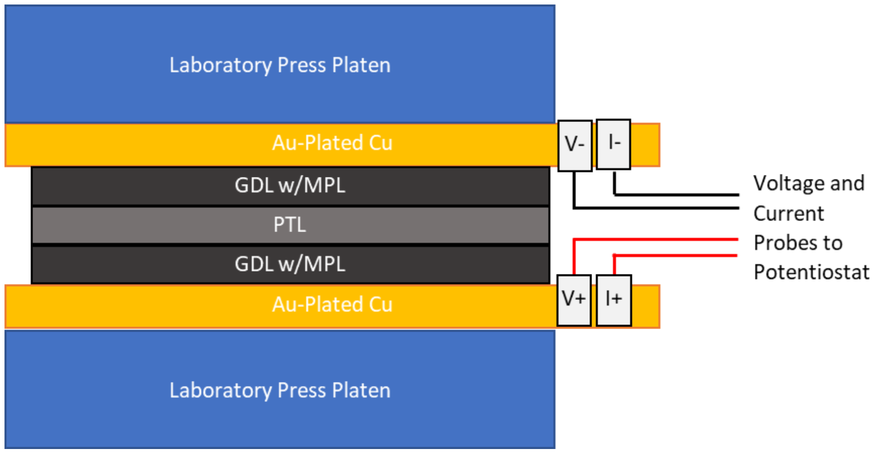

Figure 1: Test setup for the PTL resistance measurement

laboratory press. The setup should be similar to what is shown in Figure 1.
5. Press the sample to 100psi.
6. Once the sample is affixed in the press hardware, connect the positive voltage and current probes to one of the Au-coated Cu plates and the negative voltage and current probes to the other Au-coated Cu plate.
7. Once at the proper pressure, use the potentiostat to apply a 1A current across the sample and record the voltage.
8. Using ohm's law, calculate the resistance of the test setup with the sample: $R = V/I$
9. Once complete, remove the PTL and reassemble the Au-plated Cu|GDL|GDL|Au-plated Cu test setup.
10. Repeat the test again by pressing the test setup to 100psi. Apply a 1A current across the test setup and record the voltage.
11. Using ohm's law, calculate the resistance of just the test setup.
12. Subtract the test setup resistance from step 11 from the overall resistance in Step 8 to determine the bulk resistance of the PTL.

<u>Porosimetry Measurements</u>

1. Following the resistance measurements, cut out a piece of the PTL to a diameter of 47 mm.
2. Weigh the mass of the dry PTL sample
3. Immerse the PTL sample into a wetting liquid with a high wettability (ex. POREFIL™) so that the PTL sample is completely wet
4. Place the wet PTL sample into the sample holder of the capillary flow porometer, place an o-ring over the edge of the sample, and tighten the sample holder until it is closed.

5. Run the porometer with the pressure kept constant for 20s at each point to obtain stable data
6. Following the collection of the wet curve data, run the porometer again with the dry sample to obtain the dry curve.
7. In order to obtain the contact angle of water on the PTL surface, immerse the PTL sample into water in an ultrasonication bath. Sonicate the sample for 10 minutes or until the PTL is completely wet.
8. Place the wet PTL sample into the sample holder of the capillary flow porometer, place an o-ring over the edge of the sample, and tighten the sample holder until it is closed.
9. Run the porometer with the pressure kept constant for 20s at each point to obtain stable data
10. Following the collection of the wet curve data, run the porometer again with the dry sample to obtain the dry curve.

- Instrument or Method Calibration and Standardization –
  When operating the potentiostat for the resistance measurements, it may be helpful to use a multimeter to check that the voltage being measured between the sense probes is identical to what is being measured on the potentiostat. Additionally, the resistance of the GDL/MPL material should be obtained prior to measuring the resistance of the PTL sample. If the resistance of the GDL/MPL is not negligible, it should be subtracted from the PTL resistance measurements to have a more accurate PTL resistance value. The CFP should be calibrated against a standard material annually. Check with the porometer manufacturer for recommended calibration standards and procedures.

- Sample Collection –
  The cleaned PTL should be cut to 50mm x 50mm for the resistance measurement tests. The sample should then be cut to have a diameter of 47mm for the CFP tests

- Sample Handling and Preservation –
  After cleaning and prior to testing, the samples should be kept in a sterile container to ensure that no dust or foreign object debris contaminates the pores of the PTL. Handle with clean gloves to prevent contamination of the PTL.

- Sample Preparation and Analysis –
  The PTL sample should be prepped to 50mm x 50mm prior to the resistance measurement. Once cut, the sample should be flat and free of cracks or defects. Similarly, the sample should be cut to be a round disk with a 47mm diameter prior to the CFP measurements. The

sample should be flat and free of cracks or defects after the cutting step.

- Troubleshooting –
  To ensure the accuracy of the potentiostat during the resistance measurements, a calibrated multimeter can be used to measure the voltage across the sample which can be compared to the potentiostat measurements. If the voltage readings are different, additional troubleshooting of the potentiostat may be required to ensure accuracy.

- Data Acquisition, Calculations & Data Reduction Requirements–
  For the PTL resistance measurements, the resistance would be calculated using Ohm's law. With the current, I, set on the potentiostat, and the voltage, V, measured on the potentiostat, the resistance, R, can be calculated as:

$$R_{setup+PTL} = \frac{V}{I}$$

In order to extract the PTL resistance, the resistance of the test setup (Al plates with Au-plated Cu) must also be measured using the same method. Once the resistance of the test setup with the PTL, $R_{setup+PTL}$, is known along with the resistance of just the test setup, R_{setup}, then the PTL bulk resistance can be calculated as:

$$R_{PTL} = R_{setup+PTL} - R_{setup}$$

The CFP data should be plotted with the gas flow rate vs. pressure as shown below in Figure 2 from Bromberger et al.[2] Three curves should be plotted: the wet curve, dry curve, and half-dry curve. While the wet curve and dry curve is plotted from data collected by the CFP, the half-dry curve is typically calculated and plotted by the CFP software. The half-dry curve is equal to one half of the gas flow rate of the dry curve at a given pressure. When examining the plot, the intersection of the dry curve and wet curve indicates the smallest pore in the PTL. The first bubble point on the wet curve indicates the largest pore in the PTL. The intersection of the wet curve and the half-dry curve is the mean flow pore of the PTL.

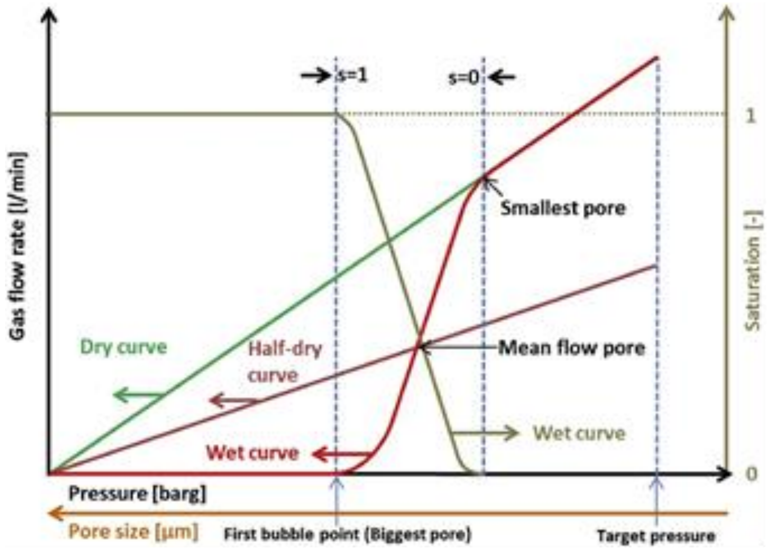

Figure 2: An example of a wet curve, dry curve, and half-dry curve obtained by capillary flow porometry.[1]

The pore diameter as a given pressure can be determined by:

$$d = \frac{4B\gamma \cos\theta}{p}$$

In this equation, d is the characteristic pore size (in m), B is the capillary constant, γ is the surface tension (in N/m), θ is the contact angle of the wetting liquid (in degrees), and p is the pressure (in Pa).

To calculate the contact angle of the water on the surface of the PTL, a specific pore diameter is examined and the equation above can be compared between the POROFIL™ CFP data and the water CFP data as:

$$\frac{\gamma_w \cos\theta_w}{p_w} = \frac{\gamma_p \cos\theta_p}{p_p}$$

where the w subscript is related to the water data while the p subscript is related to the POROFIL™ data. With θ_p=0°, the equation above can be rewritten as:

$$\theta_w = \cos^{-1}\left(\frac{\gamma_p p_p}{\gamma_w p_w}\right)$$

- Computer Hardware & Software –
  Software for the potentiostat should be provided by the potentiostat manufacturer. Software for the CFP hardware should be provided by the CFP manufacturer.

j. Data and Records Management –
Record PTL dimensions prior to testing. During the resistance testing, record the potentiostat current and voltage readings. During the CFP tests,

record the weight of the PTL before and after testing. Be sure to have all data recorded in a lab notebook and/or electronically.

4. Quality Control and Quality Assurance Section

The potentiostat and the CFP hardware should be calibrated annually according to the manufacturers' specified calibration standards and procedures. All data should be properly and securely logged to ensure repeatability and consistency among tests.

5. Reference Section

1. Vikram, A., Chowdhury, P.R., Phillips, R.K., Hoorfar, M. Measurement of effective bulk and contact resistance of gas diffusion layer under inhomogeneous compression – Part I: Electrical conductivity. *Journal of Power Sources* (2016), *320*, p 274-285.
2. Bromberger, K., Ghinaiya, J., Lickert, T., Fallisch, A., Smolinka, T. Hydraulic ex situ through-plane characterization of porous transport layers in PEM water electrolysis cells. *International Journal of Hydrogen Energy* (2018), *43*, p 2556-2569.