Standard Operating Procedure (SOP)

Anion Exchange Membrane Conductivity

Test ID # LTE-P-6

Rev 3

Yushan Yan, Santiago Rojas-Carbonell,
Brian Setzler, Matthew Ueckermann, Kelly Meek 02/28/2020

Prepared By: Date

________________________________ _____________________

Approved By: Date

________________________________ _____________________

Approved By: Date

Date: 02/28/2020

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
04/16/2019	All	First Release
09/24/2019	All	Clarifications, formatting
02/28/2020	All	Revised method and formatting

Outline/Table of Contents

1. Title Page
2. Table of Contents
3. Procedures
    a. Scope and Applicability
    b. Summary of Method
    c. Definitions
    d. Health & Safety Warning
    e. Cautions
    f. Interferences
    g. Personnel Qualifications / Responsibilities
    h. Equipment and Supplies
    i. Step by Step Procedure
        - Instrument or Method Calibration and Standardization
        - Sample Collection
        - Sample Handling and Preservation
        - Sample Preparation and Analysis
        - Troubleshooting
        - Data Acquisition, Calculations & Data Reduction Requirements
        - Computer Hardware & Software
    j. Data and Records Management
4. Quality Control and Quality Assurance Section
5. Reference Section

3. Procedures

a. Scope and Applicability – The purpose of this SOP is to provide a procedure for measuring the hydroxide conductivity of an anion exchange membrane (AEM). The membrane sample must be dry, in the solid-state form with dimensions of 8 mm wide by 30 mm long. Membrane should only be handled with nitrile laboratory gloves and clean, stainless steel or Teflon-coated forceps.

b. Summary of Method – The AEM sample in bicarbonate form is cut into a geometry of approximately 8.0 +/- 0.5 mm wide by 30 +/- 5 mm long. The membrane is placed in a four-electode in-plane conductivity cell (Bekktech BT-112) which is placed in fuel cell test hardware (Scribner, 5 cm^2) and attached to a gas humidification and temperature control system (e.g. Scribner 850e). A potentiostat with FRA (Solartron 1287A + 1260A) is used to apply a current across the cell to electrochemically exchange the membrane to hydroxide form, while simultaneously measuring resistance. After the membrane has been fully converted to hydroxide form, the relative humidity is stepped over a range of values to determine the dependence of in-plane conductivity on humidity. In-plane conductivity is calculated from the measured resistance using the measured dimensions of the cell and membrane, with corrections for swelling behavior as RH is varied.

c. Definitions – anion exchange membrane (AEM); deionized (DI); relative humidity (RH); high frequency resistance (HFR).

d. Health & Safety Warning – the procedure is generally safe, but all solvents should be handled with care, using appropriate PPE. The cell, gas lines, and gas exhaust will be hot. Do not touch until temperatures are below 50 °C.

e. Cautions – operate within the appropriate heating window of the gas humidification equipment and do not exceed the degradation temperature of your polymer membrane. Use conductivity cells made of PTFE, PEEK, or other high-temperature engineering plastics to prevent cell degradation or warping. If using homemade gas humidification equipment, ensure appropriate overtemperature and overpressure protections are in place.

f. Interferences – instrument calibration is necessary to ensure accuracy of results. CO_2 present in the carrier gas may prevent complete conversion to hydroxide and suppress conductivity. Temperature and dewpoints are absolutely critical. Therefore, cold spots on the junctions and lines must be eliminated.

g. Personnel Qualifications / Responsibilities – users should have basic laboratory knowledge and skills and should be led through operations of ZPlot and accompanying software before performing experiment.

h. Equipment and Supplies – chemicals: DI water, nitrogen gas; equipment: potentiostat with FRA (Solartron 1287A with 1260 A), PC with software (ZPlot) micrometer, caliper, four-electrode in-plane conductivity cell

i. Step by Step Procedure:

1. The AEM in the bicarbonate form is cut into a geometry of 8 +/-1 mm wide by 30 +/- 5 mm long. Prior to beginning the experiment, the membrane thickness is measured by a micrometer to a tolerance of +/- 1 µm. Their width is measured by calipers to a tolerance of +/- 0.1 mm. The membrane's dimensions are measured under an RH condition where water uptake and/or swelling is known.
2. Membrane is placed in a four-electrode in-plane conductivity cell with parallel platinum electrodes (Bekktech BT-112 or equivalent).
3. Conductivity cell is placed in fuel cell hardware (5 cm^2 single cell, Scribner) and attached to membrane test station which can control the cell temperature and RH. Heated cuffs must be used on any unheated fittings to avoid any cold spots in the gas flow path (this is important). The gas flow rate is set to 200 sccm nitrogen.
4. The conductivity cell is connected to a potentiostat with FRA (Solartron 1287A with 1260A FRA). If the electrodes are numbered 1-4 from left to right, the connections are made as follows (terms vary by brand, but I is a current carrying lead, and E is a potential sensing lead):
   Electrode 1: I- (CE)
   Electrode 2: E- (RE1)
   Electrode 3: E+ (RE2)
   Electrode 4: I+ (WE)
5. Resistance measurements are begun by setting the cell to either 0 V or 0 A in the potentiostat software (ZPlot) while continuously measuring impedance at 500 Hz during warmup (10 mV or 10 µA suggested amplitude). Resistance is taken as the real component of impedance at 500 Hz.
6. The cell is warmed to 80 °C and humidifiers to 77.4 °C (90% RH) while monitoring resistance. Take care that the cell temperature stays at or below the humidifier temperatures during the ramp so that potentially damaging low-RH exposure is avoided. The cell is held at 80 °C and 90% RH until resistance stabilizes (less than 30 minutes).
7. The cell voltage is changed to 3 V while continuing to measure impedance at 500 Hz (10 mV amplitude). This condition is used for the remainder of the experiment. The resulting current will generate hydroxide at I- and push bicarbonate and other anions to I+ and out of the membrane. Remember that the cell voltage and impedance are measured between E+ and E-, while current flows from I+ to I-.
8. The cell is equilibrated until the resistance has stabilized. A reasonable guideline for stability is a change in resistance of <2% of the last 20% of the elapsed time.

9. Three RH sweeps are conducted with lower limits of 70%, 50% and 30%. Each sweep starts at 90% RH and steps down to the lower limit, then back to 90% using 10% increments with 30 minute holds. Between sweeps, the RH is held at 90% for 2 hours.
10. Conductivity is calculated by using the following equation: $\sigma = L/AR$, where L is the distance between two inner electrodes (E- and E+), measured by calipers, and A is the cross-sectional area of the polymer film ($A = WH$; W is the wet/humidified film width measured by caliper and H is the wet/humidified film thickness measure by micrometer). Resistance can be averaged over the last 10% of each RH hold.
11. Swelling of the membrane as a function of RH should be accounted for. If direct measurements are not available, a water uptake isotherm can be used to estimate volume swelling using a volume additivity assumption. Depending on membrane and cell, isotropic or anisotropic swelling may be appropriate. The corrected formula is $\sigma = \frac{L_0}{A_0}\left(\frac{V}{V_0}\right)^m \frac{1}{R}$, where L_0 and A_0 are the measured values at the reference condition and V/V_0 is volumetric swelling ratio relative to the reference condition. The exponent m is 1/3 for isotropic swelling and 1 for fully anisotropic swelling in the thickness direction only.

- Instrument or Method Calibration and Standardization – The potentiostat and FRA can be checked using precision resistors (1, 10, 100 kHz). The test station dewpoint should be checked using an RH probe in a heated chamber (Vaisala HMT 337). The cell thermocouple should be checked using an ice bath. The conductivity cell should be checked using Nafion membranes against literature values. A large disagreement that cannot be attributed to RH control or sample pretreatment could be an indication of a non-uniform current distribution within the conductivity cell. As non-uniform current distributions may vary from sample to sample, it is recommended to investigate and correct the defect in the conductivity cell, rather than use a calibrated cell constant.

- Sample Collection –

Sample	~8+/- .5 mm by 30+/-5 mm

- Sample Handling and Preservation – before and after experiment, samples should be stored sample bags. Handle only with nitrile gloves, as contact with bare hands will expose the membrane to chloride ions.

- Sample Preparation and Analysis – AEM (~5 mm by 30 mm) should be anion exchanged into bicarbonate form.

- Troubleshooting – instrument calibration is necessary to ensure accuracy of results. Excess ions from insufficient washing with DI water (step 1) can result in falsely high conductivity readings. Membranes should be measured at a condition with well-controlled water uptake to minimize uncertainty in the swelling correction. The humidified gas flow paths should be carefully checked for cold spots, which may result in inaccurate and unstable conductivity measurements.

- Data Acquisition, Calculations & Data Reduction Requirements – Conductivity is calculated by using the following equation: $\sigma = \frac{L_0}{A_0}\left(\frac{V}{V_0}\right)^m \frac{1}{R}$, where L_0 is the distance between two inner electrodes, measured by caliper, A_0 is the cross-sectional area of the polymer film ($A_0 = W_0H_0$; W_0 is the film width measured by caliper and H_0 is the film thickness measure by micrometer under the reference humidification conditions), V/V_0 is the volumetric swelling at the experimental temperature and relative humidity relative to the reference conditions, m is an exponent to account for anisotropy of swelling (m = 1/3 for isotropic swelling), and R is the measured resistance. R should be averaged over the last 10% of the RH hold.

- Computer Hardware & Software
  - i) ZPlot to control the potentiostat.
  - ii) Appropriate software to manage gas humidification equipment and program RH sweep, e.g. FuelCell if using Scribner 850e test station.

j. Data and Records Management – Record membrane dimensions and laboratory ambient RH both electronically and in lab notebook. Resistance data and conductivity calculations can be managed electronically.

4. Quality Control and Quality Assurance Section

Nafion membranes can be used for quality control and compared to literature values. However, the range of literature values reported for Nafion conductivity is large, so careful evaluation of the sources of uncertainty in both the present measurement and the literature measurement must be made, including effects of sample pretreatment.

5. Reference Section

Ziv, N.; Dekel, D. R. A Practical Method for Measuring the True Hydroxide Conductivity of Anion Exchange Membranes. Electrochem. Commun. 2018, 88, 109−113.

Muller, J., Zhegur, A., Krewer, U., Varcoe, J. R., & Dekel, D. R. A practical ex-situ technique to measure the chemical stability of anion-exchange membranes under conditions simulating fuel cell environment. ACS Materials Letter. 2020