Standard Operating Procedure

(SOP)

Proton Exchange Membrane

Ion Exchange Capacity

Test ID # LTE-P-3

Rev 3

Kelly M. Meek	03-06-2019
Prepared By:	Date
Approved By:	Date
Approved By:	Date

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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	Formatting, minor edits
03/04/2020	All	Revised procedure with minor edits Distributed for review

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. Validation of the SOP using Nafion™ 212 and RPI's Bae Group PEM (BP-SArSA) by following conventional acid-base titration method.
6. Reference Section

3. Procedures

a. Scope and Applicability – The purpose of this SOP is to describe the method for measuring the ion exchange capacity (IEC) of a proton exchange membrane (PEM). The membrane sample for evaluation must be in dry solid-state form, in the sodium cation form, and have a dry mass greater than 100 mg.

b. Summary of Method – A PEM sample is exchanged to the proton form by immersing in a 200 mL of 1.0 M sulfuric acid solution at 80 ºC for 1 hour, followed by washing with deionized water. The membrane is then immersed in hot DI water (80 °C) for 30 minutes to remove residual acid. After rinsing the membrane with room temperature DI water, remove the surface water with lint-free tissue (e.g., Kimwipes) followed by vacuum dry (see Figure 1A for recommended vacuum dry set up) for at least 12 hours without heating; heating under vacuum (Figure 1B) causes change in color of Nafion^{TM} 212 sample as shown in Figure 2). Then the dry weight of the membrane sample is obtained. The PEM sample is rolled or stirred in a 20 mL glass vial containing 1 M NaCl solution for at least 12 hours. The PEM sample and the 1 M NaCl solution from the rolling process are added to a Mettler Toledo (MT) sample cup. Rolling vials are rinsed with DI water which is also added to the MT cup. Mettler Toledo (MT) T90 is used for titration with a freshly prepared standard 0.01M NaOH solution (better to use within 24 h after preparation). Sensor DG111-SC is used to monitor titration. IEC and consumption results are displayed. Sample cup is removed and stirring arm is washed with DI water. Alternatively, the NaCl solution containing the PEM sample could be titrated with 0.01 M NaOH solution using phenolphthalein as an indicator to monitor titration.

c. Definitions – ion exchange capacity (IEC); proton exchange membrane (PEM), sodium chloride (NaCl); deionized (DI); sodium hydroxide (NaOH), potassium chloride (KCl).

d. Health & Safety Warning – Review safety data sheets for all chemicals used. All solutions should be handled with care, using appropriate PPE.

e. Cautions –Review safety data sheets for all chemicals used. Clean equipment after each use. Solutions used are not generally corrosive to the system, but they should still be removed immediately after experiment for best practices. Lint and powder free gloves should be worn at all times while handling solutions and membrane samples.

f. Interferences – instrument calibration is necessary to ensure accuracy of results. Excess sodium ions from insufficient washing with DI water (step 2) can result in falsely a high IEC. Freshly prepared 0.01 M NaOH solution should be used for titration.

g. Personnel Qualifications / Responsibilities – users should have basic laboratory knowledge and skills and should be led through operations of the Mettler Toledo T90 and accompanying software before performing this experiment.

h. Equipment and Supplies – NaCl, DI water, NaOH, phenolphthalein indicator, Mettler Toledo T90, KCl, sensor DG111-SC.

i. Step by Step Procedure for Titration Using Mettler Toledo T90

1. Instrument or Method Calibration and Standardization – Mettler Toledo T90 calibration check should be performed before experiments. This calibration is performed by dispensing 0.01M NaOH solution into a sample cup at a known volume (e.g., 2.0 mL, 10.0 mL), and running the IEC test. IEC test results should show the consumption matches the volume dispensed and the IEC is measured as 0.1, within 5% error.
2. **Ion exchange to proton form and hydration of membrane:** The PEM sample of weight > 100 mg is exchanged to the proton form by immersing in hot 200 mL 1 M sulfuric acid (80 ^{o}C) for 1 hour. The membrane is then rinsed with 100 mL room temperature DI water and immersed into the hot DI water (80 ^{o}C) for 30 minutes to remove the residual acid. The membrane is then soaked in room temperature DI water for 30 minutes, this is repeated 3 times with fresh DI water.
3. **Measurement of dry membrane weight**: The membrane sample is then blotted with lint-free tissue followed by 1 hour air dry at room temperature. The membrane is further dried for at least 12 hours in vacuum without heating (see Figure 1A for recommended vacuum dry set up). During vacuum dry process, the membrane sample is kept inside a loosely capped polypropylene bottle (see Figure 1A). Polypropylene bottle, which is hydrophobic in nature, can minimize the percentage error that could be caused by the absorption of the moisture if glass bottles are used. After vacuum drying for 12 hours, the desiccator is filled with nitrogen and the polypropylene bottle is immediately closed tightly. The bottle is then weighed. The membrane is removed, and the empty bottle is reweighed to determine the mass of the dry membrane. An analytical balance with tolerance of 0.1 mg and capacity of >1 g is used for measurement.
4. **Ion exchange of the membrane to Na+ form and release of H+**: The PEM sample is then placed in a clean 20 mL glass vial which is filled with a 1 M NaCl solution. The vial is rolled at 30 RPM in ambient temperature, or the solution gently stirred for at least 12 hours.
5. The NaCl solution is decanted into a clean sample polypropylene 100 mL cup from MT designed to be used with the instrument.
6. The vial is rinsed with ~5 mL DI water 3 times, with the rinse water captured in the sample cup.

7. Stir arm of MT is washed with DI water, which is discarded, and sample cup is screwed on.
8. A Mettler Toledo T90 charged with a freshly made 0.01 M NaOH solution at room temperature is used to titrate the rinse solution contained within the sample cup.
9. The mass of the PEM sample is entered into the software and the automatic titration begins.
10. Solution is continuously stirred and automatically titrated, while sensor DG111-SC containing a 3M KCl, as purchased, solution logs the results.
11. IEC and consumption results are displayed.
12. Sample cup is removed and stirring arm is rinsed with DI water.

ii. Step by Step Procedures for Conventional Titration Method

1. Follow the procedure of steps 2 to 4 from procedure i.
2. The NaCl solution of glass vial is decanted to a 250 mL beaker which contains a stir bar. The vial is rinsed with ~5 mL DI water 3 times, while the rinse water is collected in the same beaker.
3. 4-5 drops of phenolphthalein indicator is added to the NaCl solution containing beaker which was then titrated with freshly prepared 0.01 M NaOH solution while stirring the solution until the end point. The persistent of the pinkish color indicates the end point (see Figure 3).
4. The volume of the 0.01 M NaOH solution that is consumed until the end point is recorded and the IEC is determined by the following equation.

$$\text{IEC (meq./g)} = \frac{\text{Vol.of NaOH (mL) x molarity of NaOH(moles/L)}}{\text{mass of the membrane (mg)}} \text{ x } 1000$$

- Sample Collection –

Chloride exchange	Beaker containing 50 mL of a 1M NaCl solution
DI water washing	Beaker containing 50 mL of DI water
Sample	~100 mg sample recommended
Rolling	20 mL glass vial, 0.1M KCl solution
Sample Cup	100 mL polypropylene cup (included with the MT T90 analyzer)
Sensor	DG111-SC (included with the MT T90 analyzer)
Sensor solution	3M KCl solution, as purchased
Titrant	1L fresh 0.1M NaOH solution
Indicator	Phenolphthalein solution

- Sample Handling and Preservation – before and after experiment, PEM samples should be stored in clean, covered 20 mL glass vials of DI water.

- Troubleshooting – – instrument calibration is necessary to ensure accuracy of results. Excess sodium ions from insufficient washing with DI water (step 2) can result in reporting higher IEC values.

- Data Acquisition, Calculations & Data Reduction Requirements – calculations of consumption, IEC, and content are performed by LabX software.

- Computer Hardware & Software – LabX software should be loaded on the same computer operating the Mettler Toledo T90 hardware.

Data and Records Management – calculations of consumption, IEC, and content are performed by LabX software and should be recorded elsewhere both electronically and in a lab notebook by the user.

Sample	Consumption (mL)	IEC (mmol/g)	Ion content (mol/L)

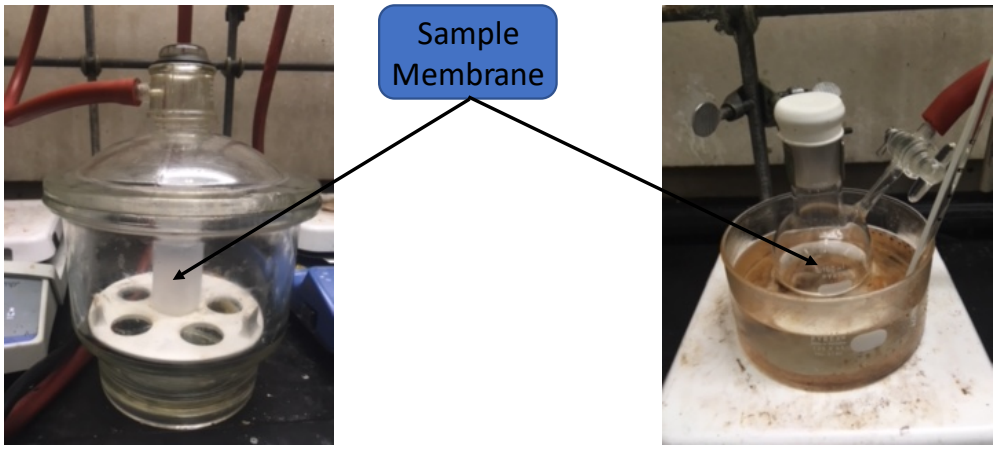
4. Quality Control and Quality Assurance Section

Mettler Toledo T90 calibration check should be performed before experiments. This calibration is performed by dispensing 0.1M NaOH solution into a sample cup at a known volume (e.g., 2 mL, 10 mL), and running the IEC test. IEC test results should show the consumption matches the volume dispensed and the IEC is measured as 0.1 mmol/g, within 5% error. Additionally, IEC of each PEM should be measured in duplicate for verification, as well as having a sample weight of ~100 mg to minimize error. If two sample IECs are not within 5% of one another, a third sample IEC should be measured, and all results should be recorded.

5. Validation of the SOP using Nafion™ 212 and Bae Group PEM (BP-SArSA) by following conventional acid-base titration method.

Using Nafion™ 212 (IEC = 0.95–1.01 meq./g)

Nafion™ 212 Sample	Vacuum Dry Mass (mg)	Measured IEC (meq./g)	Average IEC (meq./g)
1	133.5	1.01	0.96 ± 0.06
2	135.7	1.00	
3	144.8	0.90	



(A) (B)

Figure 1: (A) vacuum dry set up without heating (recommended), and (B) vacuum dry set up with heating at 80 °C (not recommended).

(A) (B) (C)

Figure 2. Pictures of the Nafion™ 212 membrane (A) after air dry for 1 hour, (B) after vacuum dry for 12 hours (from setup Figure 1A), and (C) after vacuum dry at 80 °C for 12 hours (from setup in Figure 1B).

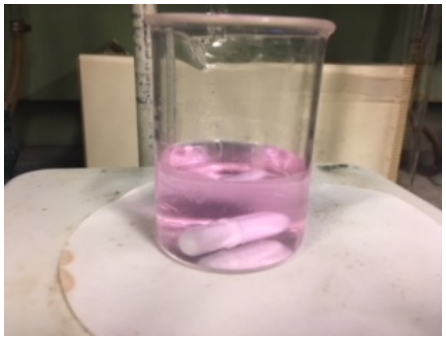


Figure 3: Pinkish color solution at the end point of acid-base titration.

Using Bae Group PEM (BP-SArSA) (Theoretical IEC = 2.01 meq./g)

BP-SArSA	Vacuum Dry Mass	Measured IEC (meq./g)	Average IEC (meq./g)
1	105.2	1.85	1.80 ± 0.05
2	109.1	1.82	
3	91.7	1.75	

6. Reference Section

R1. https://www.fuelcellsetc.com/store/N212