# Standard Operating Procedure

# (SOP)

# Alkaline Stability of Anion Exchange Membranes (AEMs)

Test ID LTE-P-22

Rev 2

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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 |
|---|---|---|
| 05/12/2020 | All | First Release |
| 10/11/2024 | 3 - 10 | Protocol revision; updated Table of Contents; added details in procedure; replaced the characterization methods; updated the list of chemicals |
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3. Procedure

a. Scope and Applicability – This procedure is intended for *ex-situ* evaluation of alkaline stability of anion exchange membranes (AEMs).

b. Summary of the Method – The AEM samples are immersed in 1 M potassium hydroxide at 80 °C for 500 h. A higher temperature, a higher base concentration (e.g., 4 M potassium hydroxide, 1,000 h), and a longer time can be employed to accelerate the degradation. Ion exchange capacity (IEC), ionic conductivity, and nuclear magnetic resonance (NMR) of the samples are measured at regular time intervals.

c. Definitions – Anion exchange membrane (AEM); nuclear magnetic resonance (NMR); ion exchange capacity (IEC); electrochemical impedance spectroscopy (EIS); frequency response analyzer (FRA)

d. Health & Safety Warning – All solutions should be handled with care, using appropriate PPE. The operator should review the safety data sheets for the chemicals involved. The membrane should never be handled without gloves, as the chloride ions in the sweat can interfere with the measurement.

e. Cautions – Never touch the membrane with bare hands, as it will lead to interfering ions.

f. Interferences

- Reaction with carbon dioxide – May form carbonate and bicarbonate anions that can change membrane properties and conductivity readings.
- Insufficient DI water rinse – The residual KOH in the membrane may cause further degradation.

g. Personnel Qualifications / Responsibilities – Operators should have basic laboratory safety training per the organization's requirements.

h. Equipment and Supplies – An oven with temperature control, Polyethylene wide-mouth bottles, Inert gas, DI Water, KOH, NaCl.

i. Step by Step Procedure

- Instrument or Method Calibration and Standardization – Not applicable for this SOP.

- General Procedure – Prepare ~300 mL of 1 M potassium hydroxide in in 600 mL polypropylene wide-mouth bottles. Dry AEM samples of uniform thickness are cut into several pieces and placed in potassium hydroxide-containing bottles (e.g., 2.5 cm x 2.5 cm, ~55 mg). After placing the

membranes, the gas head space (approximately half the volume of the bottles) is flushed for 1-2 minutes with inert gas (e.g., nitrogen or argon gas). Close the bottles and seal with parafilm. The head space should be flushed with the gas used to keep the atmosphere every time a sample is taken. Place the bottles in an oven at 80 °C.

- Sample Collection – Collect the samples at regular intervals (e.g., 20, 50, 100, 200, 300, 400, 500 h). Modify the time intervals based on the chemical structure of the sample. Collected samples are washed with abundant DI water (3-5 washes) to remove the residual potassium hydroxide. Collected samples are exchanged to chloride ionic form by immersion in approximately 20 mL of 1 M sodium chloride. Preserve the membranes in 1 M NaCl solution in refrigerator after thorough DI wash. The solution should be replaced with fresh NaCl solution at least 2-3 times to allow complete ion exchange.

- Sample Handling and Preservation – The AEMs in chloride form can be stored in a refrigerator for at least 1 month without any significant degradation. Before analyses, dry all membranes completely and repeat ion exchange to their appropriate forms. For pristine membranes (i.e., 0 h), after exchanging chloride ionic form with 1 M NaCl solution, expose the membrane in water at 80 °C before conductivity measurement (e.g., 24 h).

- Sample Preparation and Analysis – Perform ion exchange capacity, ionic conductivity, and NMR characterization of collected samples. Procedures to measure IEC, ionic conductivity, and NMR are summarized below.

*Ion exchange capacity*

Refer to the LTE-P-7 IEC AEM SOP.

*Ionic conductivity*

Refer to the LTE-P-6 AEM Conductivity SOP to measure hydroxide conductivity. However, measuring the accurate hydroxide conductivity value of AEMs is challenging due to the formation of carbonate and bicarbonate anions that can change membrane properties and conductivity readings.

To measure the in-plane chloride conductivity in a 4-point (Fig. 1) or 2-point conductivity cell using electrochemical impedance spectroscopy (EIS), prepare 1 x 4 cm membrane sample. Ion exchange dry membranes into chloride form using 1 M NaCl for 2 days. Wash with DI water several times and immerse in DI water for 1 day. Measure the thickness and width of the membrane before the conductivity measurement. Load the

membrane into conductivity cell in contact with the platinum electrodes. Immerse the conductivity cell in a temperature-controlled DI water bath and connect the probes. Typical temperatures range from 30 °C to 80 °C. Equilibrate the conductivity cell at the selected temperature for at least 30 minutes. A potentiostat with frequency response analyzer (FRA) is used to measure the impedance in the frequency range 100 kHz to 0.1 Hz. The high frequency resistance is estimated from the Bode plots by selecting the modulus corresponding to a phase angle of zero. The membrane conductivity is calculated using equation [1]:

$$\sigma = \frac{L}{R \times t \times W} \qquad [1]$$

where, σ is the in-plane membrane conductivity (mS $cm^{-1}$); *R* is the in-plane membrane resistance (mOhm); t is the membrane thickness (fully hydrated, cm); *w* is the membrane width (fully hydrated, cm); L is the distance between the two inner voltage sensing electrodes (cm).

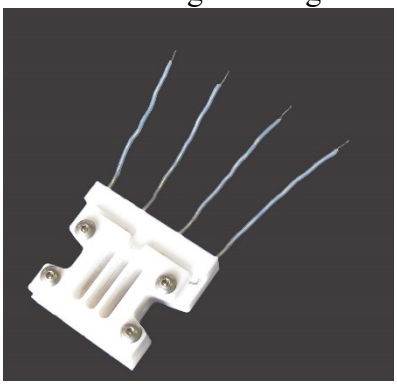


Fig 1. BT-110 cell for membrane conductivity measurement from Scribner and Associates

*NMR characterization*

Membrane degradation can be detected using NMR spectroscopy. Prepare samples by dissolving 30-50 mg samples in chloride form in 1 mL of deuterated solvent (e.g., dimethyl sulfoxide-$d_6$ or dimethylformamide-$d_7$). To calibrate the chemical shift (δ=0 ppm for $^1H$, add 35 µL of tetramethylsilane (TMS) as the internal standard. Collect $^1H$ NMR spectra (e.g., 400MHz, 128 scans) and compare results between the initial polymer and the degraded samples.

Further details of the NMR methods can be found in Claridge's book (Claridge 2009) and references (Arges and Ramani 2013, Arges and Ramani 2013, Arges, Wang et al. 2013, Parrondo, Arges et al. 2014, Parrondo and Ramani 2014).

4. Quality Control and Quality Assurance

All instrumentation used for measurements should be calibrated annually. Grade II or ASTM Type II DI water (conductivity ≤1 μS/cm) is required in all the processes.

## 5. References


Arges, C. G., et al. (2012). "Assessing the influence of different cation chemistries on ionic conductivity and alkaline stability of anion exchange membranes." Journal of Materials Chemistry **22**(9): 3733.

Arges, C. G. and V. Ramani (2013). "Investigation of Cation Degradation in Anion Exchange Membranes Using Multi-Dimensional NMR Spectroscopy." Journal of the Electrochemical Society **160**(9): F1006-F1021.

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Arges, C. G., et al. (2013). "Best Practices for Investigating Anion Exchange Membrane Suitability for Alkaline Electrochemical Devices: Case Study Using Quaternary Ammonium Poly(2,6-dimethyl 1,4-phenylene)oxide Anion Exchange Membranes." Journal of the Electrochemical Society **160**(11): F1258-F1274.

Claridge, T. D. W. (2009). High-Resolution NMR Techniques in Organic Chemistry. Oxford, UK, Elsevier.

Parrondo, J., et al. (2014). "Degradation of anion exchange membranes used for hydrogen production by ultrapure water electrolysis." RSC Advances **4**(19): 9875.

Parrondo, J. and V. Ramani (2014). "Stability of Poly(2,6-dimethyl 1,4-phenylene)Oxide-Based Anion Exchange Membrane Separator and Solubilized Electrode Binder in Solid-State Alkaline Water Electrolyzers." Journal of the Electrochemical Society **161**(10): F1015-F1020.


## 6. Required Chemicals

- Deionized (DI) Type 1 Ultrapure Water
  Thermo Scientific Smart2Pure 12 UV
  Milli-Q® Type 1 Ultrapure Water Systems
- Potassium Bromide (KBr)
  ReagentPlus®, ≥99.0% Sigma Aldrich (P9881)
  ACS reagent, ≥99.0% Sigma Aldrich (243418)
- Sodium Chloride (NaCl)
  ≥99.0% ACS, VWR Chemicals BDH® (BDH9286)
  https://us.vwr.com/store/product/9902221/sodium-chloride-99-0-
  ReagentPlus®, ≥99.0% Sigma Aldrich (P9881)