

Standard Operating Procedure (SOP)

Alkaline Stability of Anion Exchange Membranes (AEMs)

LTE-P-22

Rev 2

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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 membranes under evaluation will be immersed in 1 and/or 6 molar potassium hydroxide at temperatures ranging from 60 °C to 120 °C for a total time ranging from 1 week to 6 months. A higher temperature and base concentration will usually increase degradation rates. Higher temperatures and longer times are usually employed for very stable membranes to accelerate the degradation. In a typical test, samples are kept in 1 molar potassium hydroxide and the temperature is set at 80°C. Sample conductivity and ion exchange capacity are measured at regular time intervals.

c. **Definitions**

AEM -Anion exchange membrane
IEC -Ion exchange capacity
FRA -Frequency response analyzer

d. **Health & Safety Warning** – The procedure is generally safe, but all solvents should be handled with care, particularly 1M KOH (or NaOH) which is a caustic liquid, using appropriate PPE. The oven and polypropylene container surface will be hot so take appropriate precautions when opening and do not touch until temperatures are below 50 °C, or touch wearing insulated heat gloves. Take care when opening the polypropylene container that caustic solution does not spill onto the user. Please follow general chemistry safety rules in place at your laboratory

e. **Cautions** – Not applicable for this SOP

f. **Interferences** – Not applicable for this SOP.

g. **Personnel Qualifications / Responsibilities** – The user of this procedure should have basic laboratory safety training per the organization's requirements.

h. **Equipment and Supplies**

- An oven with temperature control
- 125 mL polypropylene wide-mouth bottles
- Oxygen and Argon gases
- Chemicals to prepare the alkaline stability solution: DI water and Potassium hydroxide

- A vacuum oven, an analytical balance, burettes, and beakers

i. Step by Step Procedure

- Instrument or Method Calibration and Standardization – Not applicable for this SOP
- General procedure – For all *ex situ* alkaline stability tests, dry AEM samples of uniform thickness are cut into several pieces and weighed. The conductivity of the AEM sample is measured using protocol P-6 and the ion-exchange capacity is measured using P-7. Following those measurements, the AEM samples are placed in 1 molar potassium hydroxide in 125 mL polypropylene wide-mouth bottles. The gas head space (approx. half the volume of the bottle) is flushed for 1-2 minutes with Argon or Oxygen, and the bottles closed, sealed with parafilm and placed in an oven at the temperature set for the experiment. The head space should be flushed with the gas used to keep the atmosphere every time a sample is taken or at least once per week. In a typical accelerated degradation test, the containers are kept at a constant temperature of 80 °C inside an oven for 1 month. Samples are taken after 1, 3, 7, 15 and 31 days. The AEM samples are washed with abundant DI water to remove the residual potassium hydroxide, ion exchanged to chloride form, and dried in an oven at 80 °C overnight before IEC and ion conductivity determination as determined from protocols P-7 and P-6, respectively.
- Sample Collection – Samples are taken from the oven at regular intervals and washed with abundant DI water. Three to five washes are required to remove completely the potassium hydroxide. Then, the AEM samples are exchanged to chloride ionic form by immersion in approximately 20 mL of 1 molar sodium chloride for at least 24 hours. The solution should be replaced (with fresh sodium chloride 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.
- The method for determining the ion exchange capacity and ionic conductivity can be found in protocols P-7 and P-6, respectively. Below we summarize the methods for H⁺-NMR spectra acquisition.

NMR characterization of the polymers

In some special cases it might be interesting to follow membrane degradation by using NMR spectroscopy. For the characterization of the

initial polymer and the degraded samples, ^1H NMR (spectra collected at 360 MHz, 48 scans) experiments were done. The samples were prepared by dissolving approximately 30-50 mg of polymer in 1 mL of deuterated solvent (typically, dimethylformamide- d_7 or dimethyl sulfoxide- d_6). 35 μL of tetramethylsilane (TMS) was added as the internal standard for calibrating the chemical shift ($\delta=0$ ppm for ^1H). Further details of the NMR methods can be found in Claridge's book (Claridge 2009) and in our previous works.(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.

5. References

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