

Standard Operating Procedure (SOP)

Assessing the oxidative stability of anion exchange membrane in oxygen saturated aqueous alkaline solutions

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3. Procedures

a. Scope and Applicability – This SOP describes experimental methods for characterizing the chemical and mechanical stability of anion exchange membranes (AEMs) exposed to oxygen saturated concentrated alkaline aqueous solutions. The stability testing condition is aggressive, akin to an accelerated stress test (AST), and is used to assess the viability of a given AEM material to be stable in the presence of alkaline solutions containing dissolved oxygen at near saturation level. The testing procedure is based on a previous publication by Ramani and co-workers¹. Their work showed accelerated degradation of quaternary ammonium based AEM materials in oxygen saturated aqueous alkaline solutions when compared to nitrogen saturated alkaline solutions. Because water electrolyzers using AEMs generate oxygen at the anode and operate under an alkaline environment, this SOP allows stability assessment of AEM materials under AEM electrolyzer conditions without having to test an AEM in a water electrolyzer cell.

b. Summary of Method – This method carries out chemical stability experiments of AEMs by immersing AEM samples in oxygen saturated alkaline solutions at elevated temperatures (e.g., 1 M KOH or 1 M NaOH at 80 °C). Control experiments are performed by immersing AEM samples in nitrogen saturated alkaline solutions at elevated temperatures (i.e., identical conditions). After exposing the samples for a period time to the oxygen saturated and nitrogen saturated alkaline solutions, post-mortem analysis is performed on the AEMs to assess degradation. This includes measuring ionic conductivity, ion-exchange capacity via titration, collecting NMR spectra (and/or FTIR spectra), and assessing mechanical properties (e.g., tensile test). The properties and spectra of the AEM samples before exposure to the alkaline solutions are compared against the AEM samples exposed to oxygen and nitrogen saturated alkaline solutions. The change in AEM properties when compared to the pristine AEM are quantified over exposure time to the said alkaline solutions to determine degradation modes and rate of degradation.

c. Definitions –

AEM = anion exchange membranes

AgNO₃ = silver nitrate

AST = accelerated stress test

d6-DMSO = deuterated dimethyl sulfoxide

DI = deionized

Fe(NO₃)₃ = iron(III) nitrate

FTIR = Fourier transform infrared spectroscopy

IEC = ion-exchange capacity

KOH = potassium hydroxide

KSCN = potassium thiocyanate

M = molar

MΩ = megaohm

NaNO₃ = sodium nitrate

NaOH = sodium hydroxide

NMR = nuclear magnetic resonance
ppb = parts per billion
PP = polypropylene
PPE = personal protective equipment
PTFE = polytetrafluoroethylene
SOP = standard operating procedure
TOC = total organic carbon

- d. Health & Safety Warning – Be cautious working with NaOH, KOH, and HCl containing solutions as they are corrosive and can cause skin burns and damage metals and other equipment. d6-DMSO is flammable, and it can be adsorbed by skin and should not be inhaled. Other chemicals dissolved in d6-DMSO can penetrate the skin and body if direct contact with DMSO is made.
- e. Cautions – AEM samples that are too brittle to handle after removing from the jar with alkaline solutions should be discarded appropriately. Note that the sample did not mechanically survive the alkaline stability test at the specified temperature and time point.
- f. Interferences – Do not use glass containers for storing or hold NaOH and KOH solutions as the caustic media can etch the glass leading to precipitates that interfere with the degradation analysis.
- g. Personnel Qualifications / Responsibilities – The person performing this SOP should have basic training in chemistry at the college level (e.g., taken general chemistry class and lab and organic chemistry and lab).
- h. Equipment and Supplies –
Personal protective equipment (PPE) – lab jacket, safety gloves that protect against d6-DMSO and caustic solutions, and safety glasses.
- 150 mL empty high-density polyethylene, polypropylene, or polytetrafluoroethylene jars with lids. You need one jar for each sample to be tested with oxygen saturated alkaline solutions and with nitrogen saturated alkaline solutions.
- KOH or NaOH pellets. The water content of the pellets should be noted so accurate 1 M solutions can be prepared.
- Polytetrafluoroethylene or polypropylene tweezers for handling AEM samples in and out of the jar.
- Deionized (DI) water (18.2 MΩ, < 10 ppb TOC). Water should be withdrawn the day the alkaline solutions are prepared.
- Items and equipment for AEM characterization –

NMR - NMR tubes, d₆-DMSO, and NMR spectrometer

Conductivity - 4-point conductivity probe, 500 mL beaker for ionic conductivity measurements, DI water, and potentiostat/galvanostat for conductivity measurement, 1

IEC titration - 1 M sodium nitrate (NaNO₃) in DI water, 0.1 M AgNO₃ in DI water (standardized), 14wt% of iron (III) nitrate (Fe(NO₃)₃) in DI water (indicator), 0.1 M potassium thiocyanate in DI water

FTIR spectrometer with transmission sample holder.

Instron or dynamic mechanical analyzer for AEM mechanical property testing.

i. Step by Step Procedure

1. Place 150 to 200 mg of AEM sample in a 150 mL empty high-density polyethylene, polypropylene, or polytetrafluoroethylene jar. The jar should be sealable using a screw lid. Replicate samples should be prepared for assessing sample stability at different time points, stability repeatability, and to benchmark against a control (i.e., alkaline solution saturated with nitrogen as opposed to oxygen).
2. For each sample being assessed, 100 mL of 1 M sodium hydroxide (NaOH) in deionized water (18.2 MΩ and < 100 ppb TOC) should be prepared. NaOH can be substituted for KOH. Split the 1 M NaOH (or 1 M KOH) solution in half. For one of the 1 M NaOH (or 1 M KOH) solutions, bubble pure oxygen gas through it continuously for over 30 minutes. The liquid volume should not exceed over 500 mL. If more than 500 mL needs to be saturated with oxygen, then have two separate contains for bubbling oxygen gas through it. The orifice for bubbling the oxygen gas should be near the bottom of the container holding the 1 M NaOH (or 1 M KOH) solution to ensure the gas bubbles make adequate contact with the volume of the liquid solution. For the other 1 M NaOH (or 1 M KOH) solution not saturated with oxygen, bubble pure nitrogen through it continuously for over 30 minutes. The liquid volume should not exceed over 500 mL. If more than 500 mL needs to be saturated with nitrogen, then have two separate contains for bubbling nitrogen gas through it. The orifice for bubbling the nitrogen gas should be near the bottom of the container holding the 1 M NaOH (or 1 M KOH) solution to ensure the gas bubbles make adequate contact with the volume of the liquid solution.
3. For each jar containing a sample, 50 mL of the 1 M NaOH (or 1 M KOH) saturated with oxygen should be added to the jar. The addition of liquid solution to the jar should occur within 5 minutes after bubbling the gas. After adding the liquid solution, the jar needs to be sealed shut with the screw cap. The immersed AEM sample in the liquid solution stored in the jar should be stored in a 60 °C temperature-controlled chamber. Alternatively, an 80 °C (or higher temperature) temperature-controlled chamber can be used to assess the stability of promising AEM candidates.

4. Repeat this procedure for replicate samples for assessing stability at various time points and with 1 M NaOH (or 1 M KOH) saturated nitrogen.
 5. After storing the AEM samples in gas saturated alkaline solutions for a given period at 60 °C or 80 °C, remove the jar sample from the oven. Let it cool for 30 minutes. Unscrew the lid. Remove the AEM sample from the jar with a pair of PTFE (or PP) tweezers/forceps. Immerse the sample in 0.1 M HCl for 30 minutes followed by 1 M NaCl for 12 to 18 hours. Then, rinse the AEM sample with deionized water and store in deionized water for 4 hours. During this 4 hour time period, remove the deionized water from the sample and add fresh deionized water. Then, store the AEM sample in an empty, clean jar with the lid open and let it dry in a fume hood for a day. The sample will be ready for IEC, NMR, ionic conductivity, and mechanical testing.
 6. The AEM samples should be stored at 60 °C or 80 °C over a 4 week period. A sample should be withdrawn from the oven at 7 days, 14, days, and 28 days.
 7. It is important to note that virgin AEM sample should be maintained in adequate quantities for characterization.
 8. The AEM samples, virgin and exposed to gas saturated alkaline solutions at elevated temperatures, should be characterized via the following methods²:
 - a. Ion-exchange capacity via Mohr or Vohlard titration².
 - b. NMR and/or FTIR spectroscopy to characterize the change in the chemical structure of the samples²⁻⁴
 - c. Ionic conductivity in deionized water at 25 °C with a 4-pt conductivity probe².
 - d. Stress-strain curve of the AEM by performing a tensile test or using a dynamic mechanical analyzer².
 9. Plot ionic conductivity, IEC, and mechanical properties (stress or elongation at break) versus time¹. Create separate traces for samples exposed to oxygen saturated alkaline solutions versus nitrogen saturated alkaline solutions. The zero-time point would be the properties of the virgin AEM sample. If NMR characterization is possible, the ¹H NMR for the AEM sample at different time points should be compared. Peaks associated with backbone and cation integrity in the virgin AEM sample should be assigned and monitored in the ¹H NMR. An internal standard should be added to the AEM sample dissolved in d6-DMSO to quantify cation and backbone degradation products. Similarly, FTIR spectra can be compared versus the samples exposed to alkaline solutions and the virgin AEM sample.
- Instrument or Method Calibration and Standardization – Ionic conductivity measurements can be calibrated by measuring a well-studied ion conducting membrane such as Nafion® 212. For IEC measurements, Vohlard titration can be calibrated by titrating 0.1 M

AgNO₃ solutions with no AEM samples and then titrating with 0.1 M KSCN. The volume of KSCN needed to reach the endpoint should be the same volume of added AgNO₃. Titration method can also be calibrated by measuring the IEC of a commercially available AEM such as Fumasep®. The same principle applies to the tensile test. When performing the spectroscopy methods, background corrections should be performed to account for environmental conditions.

- Sample Handling and Preservation – AEM samples should be cut so that the sample weight is approximately 150–200 mg. Enough samples should be cut so that samples can be placed in oxygen saturated alkaline solution, nitrogen saturated alkaline solution, and so that there are replicate samples that can be tested at various time intervals. During the IEC titration measurements, the samples should have an estimated dry weight of approximately 100 mg. For NMR measurements, the sample weight should be 3–5 mg. Samples that are to be used for measuring the ionic conductivity in water should be 10 mm × 30 mm so that they can fit within the PTFE conductivity cell. Samples to be used for the stress-strain measurement should have an approximate dimension of 50 mm × 5 mm × 0.05 mm. When preparing samples, ensure that there is enough virgin AEM material remaining for characterization.

4. Quality Control and Quality Assurance Section

Ionic conductivity measurements can be calibrated by measuring a well-studied ion conducting membrane such as Nafion® 212. For IEC measurements, Vohlard titration can be calibrated by titrating 0.1 M AgNO₃ solutions with no AEM samples and then titrating with 0.1 M KSCN. The volume of KSCN needed to reach the endpoint should be the same volume of added AgNO₃. Titration method can also be calibrated by measuring the IEC of a commercially available AEM such as Fumasep®. The same principle applies to the tensile test. When performing the spectroscopy methods, background corrections should be performed to account for environmental conditions.

5. Reference Section

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