Status and Challenges of Hydroxide Ion-Conducting Polymers for Anion Exchange Membrane Applications

What energy-producing technologies can be envisioned that will last for millennia, and just how many people can they sustain?

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Solid Electrolyte in Fuel Cells: PEM vs. AEM

- **Since 1960s (most advanced fuel cells)**
  - Bipolar plate: titanium (*acidic* environment)
  - Catalyst: expensive Pt
  - PEM: insufficient H⁺ conductivity at low RH, high cost of Nafion

- **Since 2010s (new concept)**
  - Bipolar plate: stainless steel (*basic* environment)
  - Catalyst: non-noble metals possible (Ag, Ni)
  - AEM: insufficient OH⁻ conductivity, poor stability against OH⁻

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**Reaction at Anode:**
- H₂ → 2 H⁺ + 2 e⁻

**Reaction at Cathode:**
- ½ O₂ + 2 H⁺ + 2 e⁻ → H₂O
- H₂ + 2 OH⁻ → 2 H₂O + 2 e⁻

**Overall Reaction:**
- H₂ + ½ O₂ → electricity + H₂O
- H₂ + ½ O₂ → electricity + H₂O
Major Requirements for AEMs

- Key component in alkaline membrane fuel cells
  - Transport OH\(^-\) (and H\(_2\)O)
  - Separate H\(_2\) and O\(_2\)

- Required Properties in AEM
  - Hydroxide ion-containing polymer materials

  - **Synthesis**
    - Inexpensive, less hazardous chemicals
    - Short synthetic steps
    - Easily scalable, quality controlled process
    - High molecular weights

  - **Good ion conductivity (even at low RH)**
    - Low area specific resistance (thin membrane)
    - High IEC

  - **Good stability**
    - Chemical/electrochemical: 1M NaOH, >80 °C
    - Mechanical: High tensile strength with good elongation behavior

  - **Low H\(_2\) and O\(_2\) crossover**
Current Status & Challenges of AEMs for Electrochemical Energy Conversion & Storage

Unlike Nafion in PEM, there is no benchmark membrane in AEM yet!

» Limitation of commercially available AEMs for use in electrochemical energy conversion technology
  • Too thick: 100-200 micron (desired <20 micron)
  • Too high area specific resistance: >1 ohm cm² (desired <0.02 ohm cm²)
  • Moderate IEC: 1.0–2.0 mequiv/g (or mmol/g)
  • Poor stability (chemical & mechanical) at high temperature (>80 °C, 1M NaOH)
    1. to avoid HCO₃⁻ from OH⁻ and CO₂ in air
    2. to generate more power

AEM synthesis via chloromethylation

\[
\text{O} \quad \xrightarrow{\text{N(CH₃)₃}} \quad \text{O} \quad \text{N(CH₃)₃}
\]

Moon, et al. RSC Adv. 2015, 5, 37206
Tethered Cations in AEMs

Degradation Routes of Quaternary Ammoniums

(a) Nucleophilic Substitution Reaction by Hydroxide Ion: Dealkylation

\[
\begin{align*}
\text{OH}^- &\quad \text{SN}_2 \quad \text{OH}^- \\
\text{OH}^- &\quad \text{SN}_2
\end{align*}
\]

(b) N-ylide formations & Rearrangements

(c) Hofmann Elimination: Hydroxide Ion abstracts β-Hydrogen
Stability Comparison of Small Molecule Ammoniums

A. Mohanty, C. Bae

M.G. Marino, K. D. Kreuer
Polymer Backbones in AEMs

Thermally crosslinked

\[ R = H \text{ or } CH_2N^+Me_3 \]
Chemical Degradation of Polymer Backbone in AEM

» Cleavage at Aryl C–O bond

\[ \text{Chemical Reaction} \]

Ramani, *PNAS* 2013, 110, 2490
Hickner, *ACS Macro Lett.* 2013, 2, 49

\[ \text{Graph showing degradation processes} \]

- 0.5M HCl, 80 °C, 0.5 h
- 0.1M NaOH, 25 °C, 1 h
- 0.5M NaOH, 25 °C, 0.5 h
- 0.5M NaOH, 80 °C, 1 h

\[ \text{12% Cationic group degradation} \]

\[ \text{61% Polymer backbone degradation} \]

\[ \Delta G^\ddagger \text{ from DFT modeling (kJ/mol)} \]

1. 90.8  
2. 201.7  
3. 85.8  
4. 246.0
Poor Mechanical Stability of Polysulfone AEMs under Alkaline Conditions


Mohanty et al., *Macromolecules* accepted

Need polymer backbone structures with

- *Rigid backbone & elastic mechanical property*
- *High molecular weights*
- *Avoid aryl C–O bonds if possible*
- *Convenient synthesis (e.g., avoid metal catalyst in synthesis)*
Challenges in AEM: Mechanical Stability

Approaches to enhance mechanical stabilities of AEMs

1. Enhance polymer chain entanglement by increasing molecular weights
   - > 100,000 g/mol
2. Decouple the interactions of ionic groups and polymer backbone
   - Longer tether chain for ionic group
   - Phase separation of hydrophilic/hydrophobic domains
3. Crosslinking
4. Composite membranes

Pintauro, Macromolecules 2014, 47, 227
Improve Ion Conductivity with Minimum Swelling in Water: Lesson from Nafion

Kreuer, K. D.  
_J. Membr. Sci._ 2001, 185, 29

Hickner, Pivovar  
_Fuel Cells_ 2005, 5, 213

- Close packing of ionic groups
- **Wide channels & good connectivity**
- **Good phase-separated morphology**
- Promotes loosely bound water
- Good water (& H$_3$O$^+$) transport

- **Narrow hydrophilic domain channels**
- Highly branched & dead-end channels
- **Lower degree of phase separation**
- More tightly bound water
- Decreased water (& H$_3$O$^+$) transport
Morphology Control in Hydrophilic-Hydrophobic Sulfonated Block Copolymers

Proton conductivity depends on diffusion of $\text{H}_3\text{O}^+$

To improve transport of $[\text{H}_2\text{O}]$

Sulfonated random copolymer
IEC = 1.53 mequiv/g

Sulfonated multi-block copolymer
IEC = 1.51 mequiv/g

Kim, McGrath, Guiver, Pivovar
*Chem. Mater.* **2008**, *20*, 5636
Challenge in AEM: Morphology Control via Polymer Architecture

Morphology of polymer membrane depends on
- Structure of ionic groups: short vs. long, bulky vs. compact
- Distribution of ionic groups: random vs. block
- Polarity difference between hydrophilic/hydrophobic units
- Volume fraction ($f_x$) of hydrophilic/hydrophobic units
Summary

- **To enhance ionic conductivity (lower resistance)**
  - Add more ionic groups (higher IEC)
  - Create interconnected hydrophilic channels via morphology control
  - Thinner membrane (<20 micron)

- **To improve stability**
  - Avoid vulnerable functional groups at cation and backbone (chemical)
  - Decouple interaction of ionic groups and polymer backbone (chemical & mechanical)
  - High molecular weight polymer backbone, crosslinking, composite membrane (mechanical)

- **To reduce cost**
  - Avoid expensive and toxic chemicals (e.g., chloromethylation)
  - Avoid complicated synthetic process

- **Challenges ahead**
  - **Materials property**: achieve high ion conductivity and good mechanical strength simultaneously without sacrificing each other
  - **Synthesis**: practical process (low cost, easy scalability, quality control, high molecular weight)
  - **Characterization**: understanding of the relationship between polymer structures and membrane property (ion transport, mechanical)
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