Polyvinylidene Fluoride-Based Membranes for Direct Methanol Fuel Cell Applications

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Outline

- Background on Arkema’s polyvinylidene fluoride (PVDF) blend membrane technology
- Overview of membrane properties and performance
- Summary
Membrane Technology

**Polymer Blend**
- Kynar® PVDF \[
\left\{CH_2-CF_2\right\}
\]
  - Chemical and electrochemical stability
  - Mechanical strength
  - Excellent barrier against methanol
- Polyelectrolyte
  - H\(^+\) conduction and water uptake

**Flexible Blending Process**
- PVDF can be compatibilized with a number of polyelectrolytes
- Process has been scaled to a pilot line

**Property Control**
- Morphology: 10-100s nm domains
- Composition can be tailored to minimize methanol permeation, while optimizing conductivity and mechanical properties

*Kynar® is a registered trademark of Arkema Inc.*
Morphology Control

Compatibilization

- Polyelectrolyte and PVDF phase separate without compatibilization.
- Compatibilizing agent allows for a tunable degree of mixing.

Conductivity increases as the morphology becomes finer.

The blending technology has been successfully used to incorporate more than 10 different families of polyelectrolytes into PVDF.
Membrane Development

Under a grant from the Department of Energy (DE-EE0000474), Arkema has been developing DMFC membranes using this blending technology.

• One project goal is to develop membranes with optimized conductivity and methanol barrier properties for direct methanol fuel cells.

Variables studied:

• Polyelectrolyte composition, loading, and microstructure
• Crosslinking chemistry
• PVDF grade
• Incorporation of an inorganic phase to produce a membrane composite (in collaboration with Vijay Ramani at IIT)
• Membrane processing parameters (casting temperature, thickness, type of substrate)
Membrane Properties from Two Polyelectrolyte Candidates

PE 1 and 2 have the same selectivity, but PE2 achieves similar results to PE at lower loadings.

Selectivity of the membranes is 3x better than 7mil PFSAs.
Arkema membrane has a lower EOD coefficient and lower water permeability.

A lower EOD coefficient is advantageous for DMFC applications.
  • Less cathode flooding and easier water management.
  • Reduced methanol crossover

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In low concentration (≤ 3M) methanol operation, performance is largely determined by MEA resistance. Arkema membrane performance is between 2 and 7mil PFSA.

At high methanol concentrations (>5M), the Arkema membranes outperform PFSA, due to significantly lower methanol crossover.
Arkema membrane shows good compatibility to electrodes with standard PFSA ionomer binder.

Electrode/membrane interfacial resistance is slightly higher for PVDF blends.

Good adhesion between membrane and catalyst layers due to the partially fluorinated PVDF matrix.
Most membranes failed between 500-1000hr range due to performance loss (> 20%).
- Most performance losses came from the electrodes, but higher areal and resistance and lower methanol crossover developed over time.

Arkema membranes with a higher IEC and PFSAs lasted longer in durability test.
- Research is underway to understand the root causes.
Summary and Future Work

The PVDF membrane platform is very versatile
• A variety of polyelectrolytes can be blended with PVDF.
• The membrane composition can be easily tailored to deliver customized properties.
• Technology has been scaled up to produce pilot quantities of membrane.

Arkema membranes exhibit many of the properties required for DMFCs:
• Excellent methanol barrier properties – allows the membranes to be used with higher methanol concentrations than PFSAs.
• Good conductivity and mechanical strength.

Future Work
• Continue durability testing (including post mortem analysis).
• Development of a second membrane generation with better properties than the first generation.