Polyvinylidene Fluoride-Based Membranes for Direct Methanol Fuel Cell Applications

Wensheng He, David Mountz,
Tao Zhang, Chris Roger
July 17, 2012

ARKEMA
The world is our inspiration

Outline

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

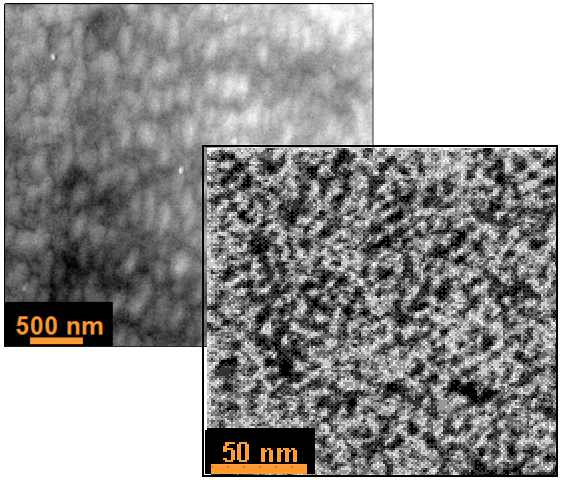
Membrane Technology

Polymer Blend

- Kynar® PVDF $-\!\!\left[CH_2\text{-}CF_2 \right]\!\!-$
  - 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



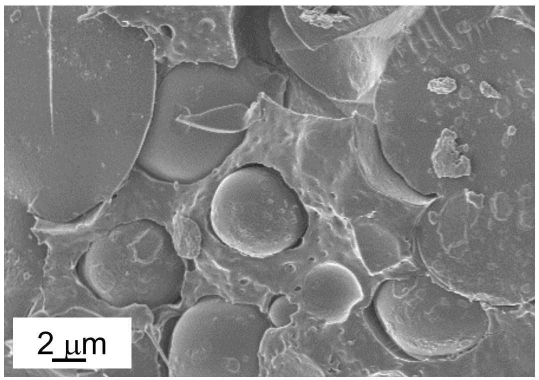
Property Control

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

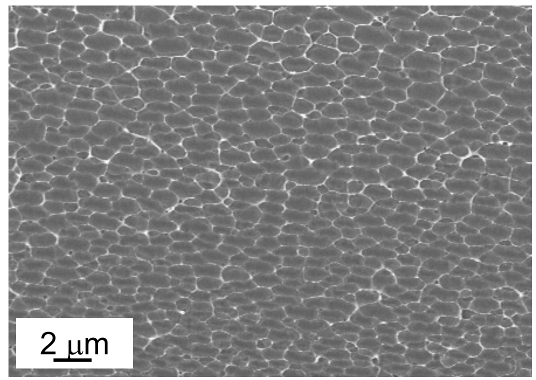
ARKEMA
The world is our inspiration

Morphology Control

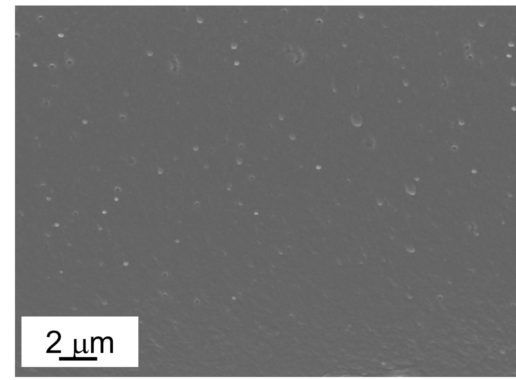
Increasing degree of compatibilization



σ = 10 mS/cm



σ = 90 mS/cm



σ = 140 mS/cm

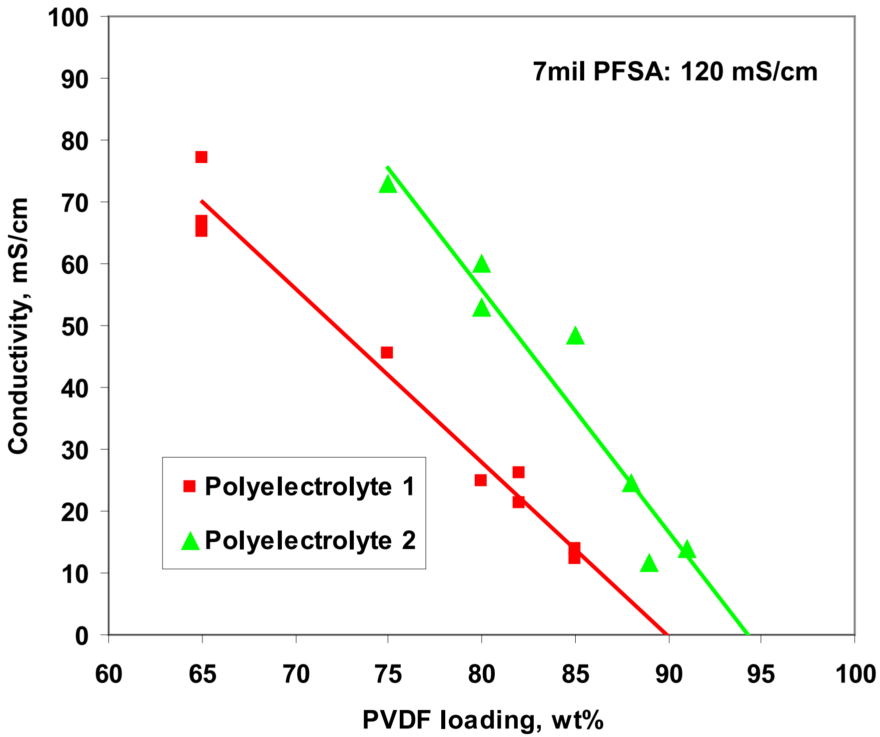
- Compatibilization
  - Polyelectrolyte and PVDF phase separate without compatibilization.
  - Compatibilizing agent allows for a tunable degree of mixing.
- Conductivity increases as the morphology becomes finer.
- The blending technology has been successfully used to incorporate more than 10 different families of polyelectrolytes into PVDF.

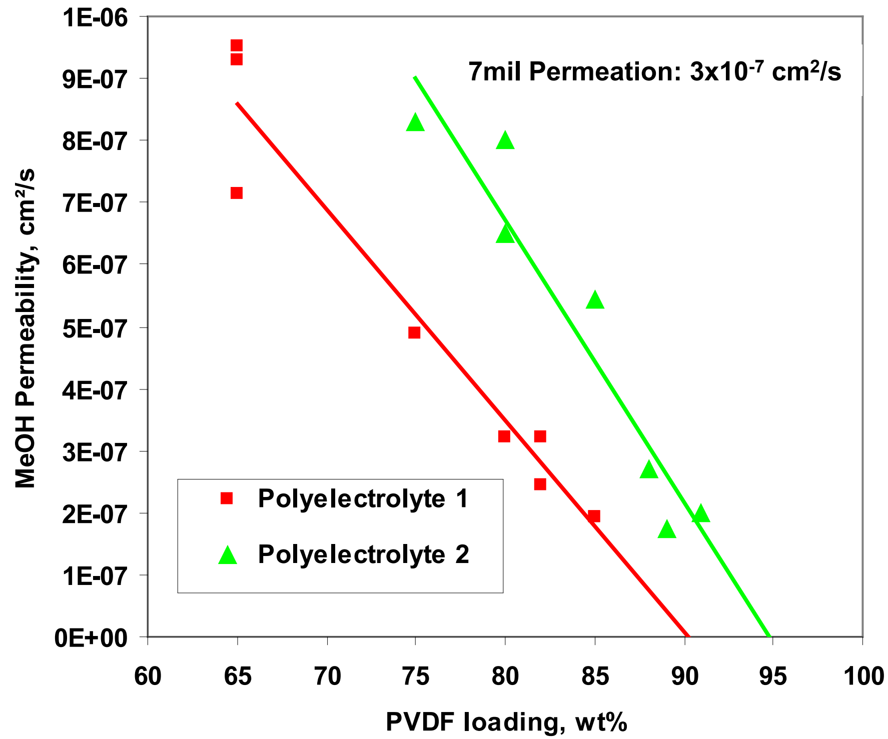
Membrane Development

- 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

In-cell data collected at 60° C

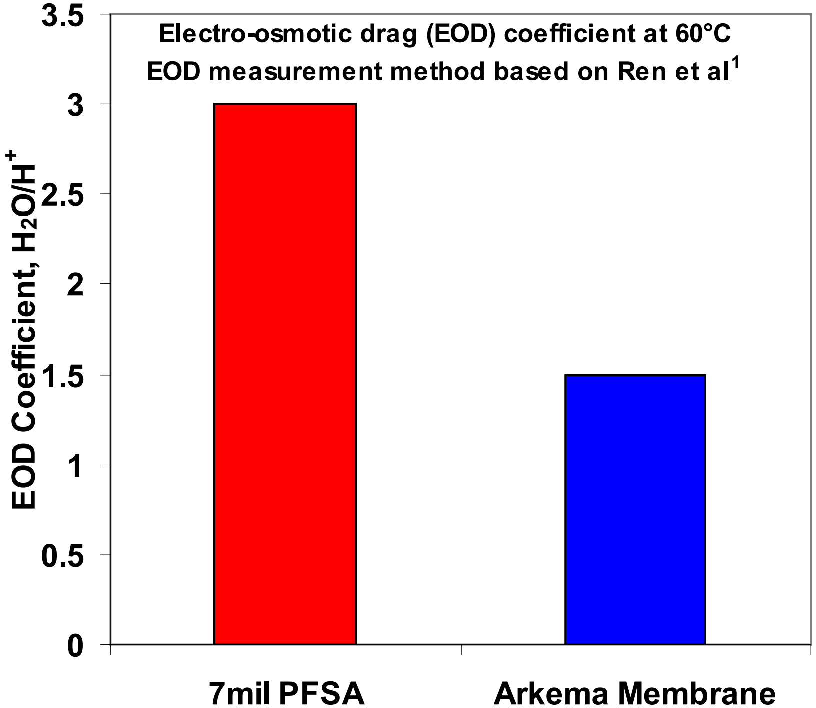


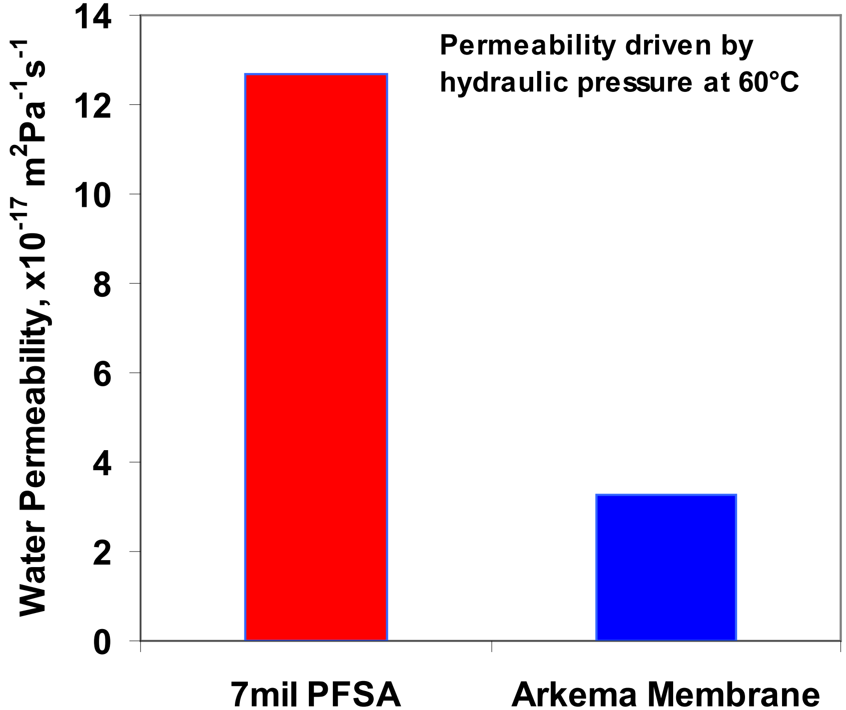


- PE 1 and 2 have the same selectivity, but PE2 achieves similar results to PE at lower loadings.
- Selectivity of the membranes is 3x better than 7mil PFSAs.

ARKEMA
The world is our inspiration

Water Transport Properties



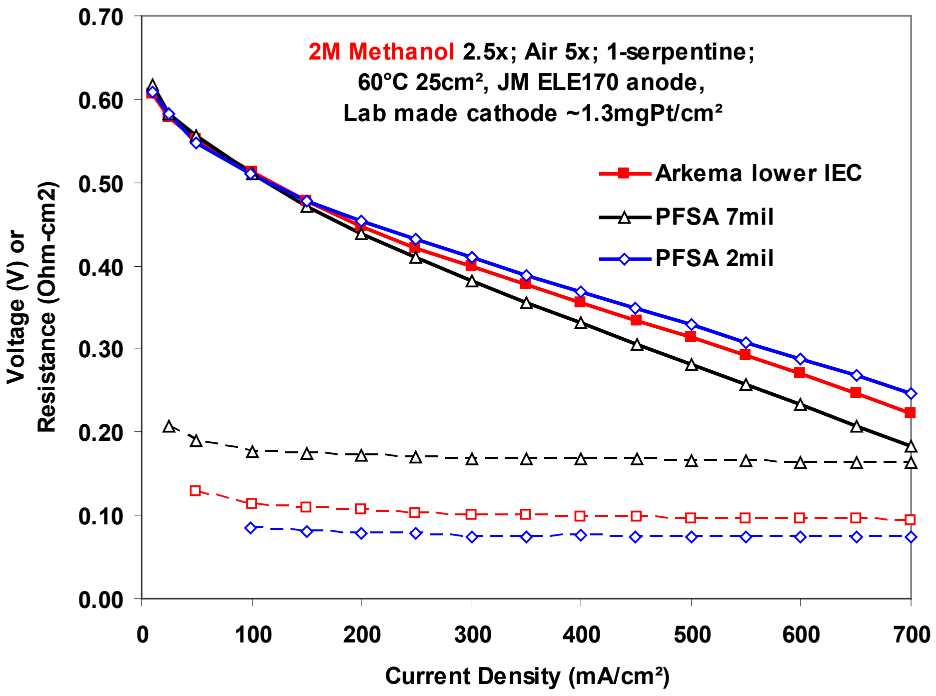


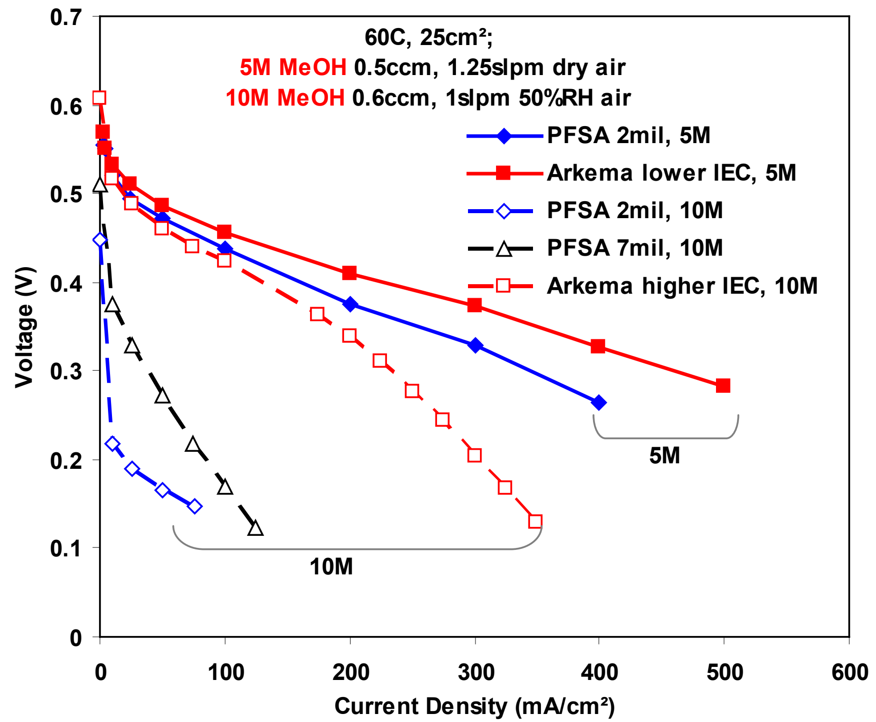
- Arkema membrane has a lower EOD coefficient and lower water permeability.
- A lower EOD coefficient is advantageous for DMFC applications.
  - Less cathode flooding and easier water management.
  - Reduced methanol crossover

[1]Ren, X.; Henderson, W. and Gottesfeld, S., *J. Electrochem. Soc.*, 1997, **144**, L267.

The world is our inspiration

MEA Performance

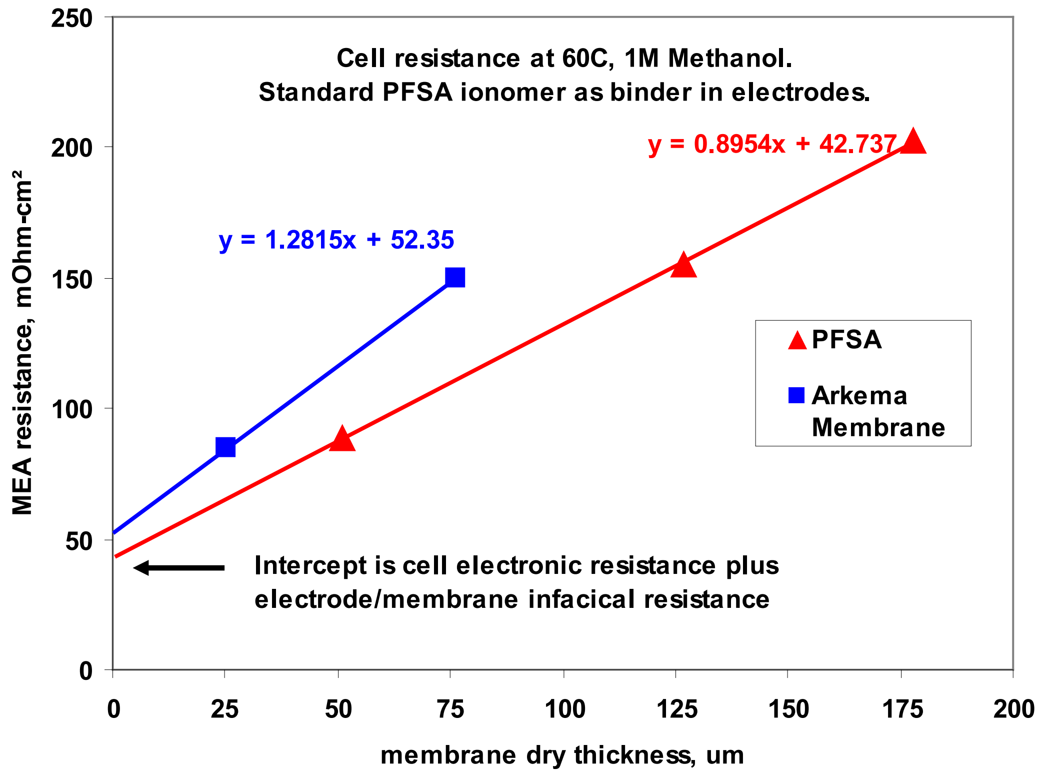




- In low concentration (≤ 3M) methanol operation, performance is largely determined by MEA resistance. Arkema membrane performance is between 2 and 7mil PFSA.
- At high methanol concentrations (>5M), the Arkema membranes outperform PFSA, due to significantly lower methanol crossover.

ARKEMA
The world is our inspiration

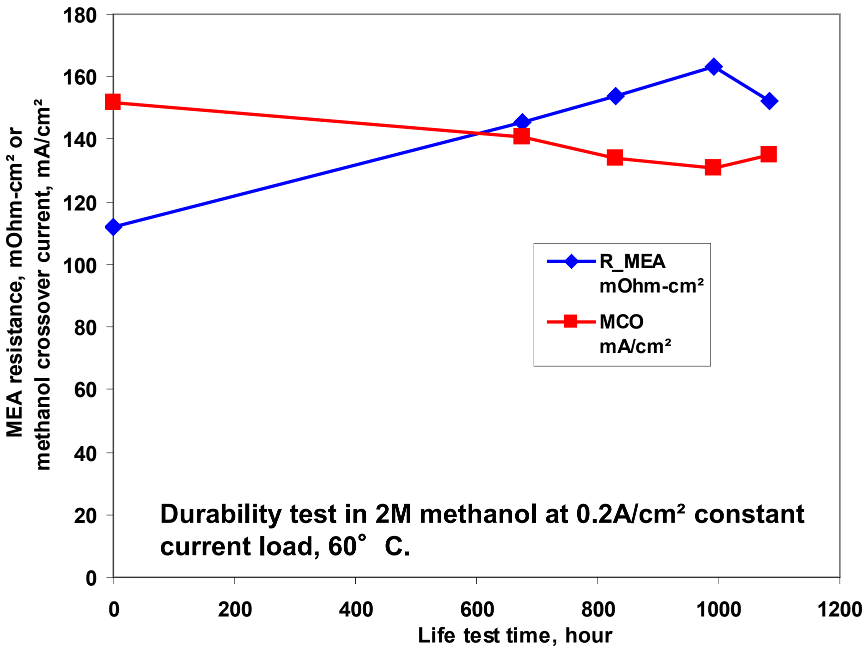
MEA Performance – Electrode/Membrane Interface

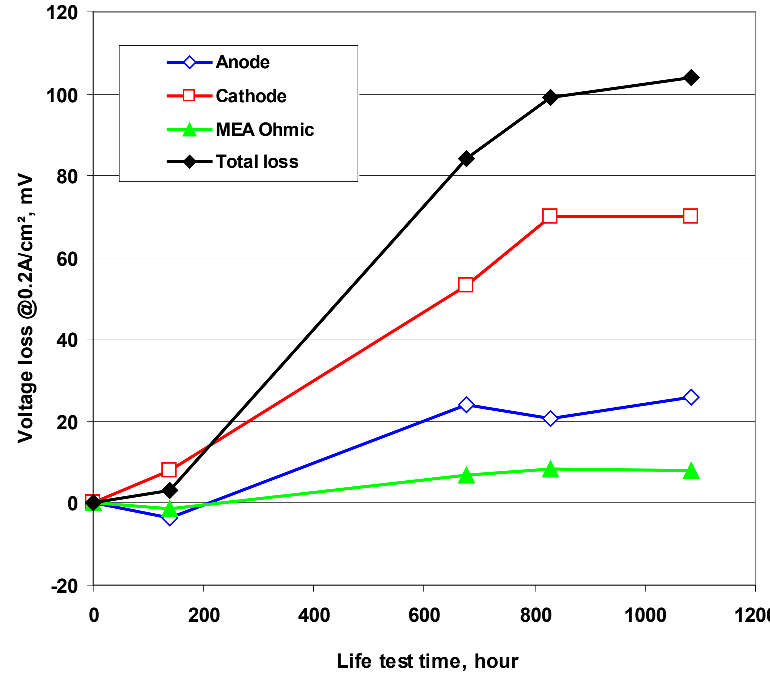


- Arkema membrane shows good compatibility to electrodes with standard PFSA ionomer binder.
- Electrode/membrane interfacial resistance is slightly higher for PVDF blends.
- Good adhesion between membrane and catalyst layers due to the partially fluorinated PVDF matrix.

ARKEMA
The world is our inspiration

MEA Performance – Arkema Membrane Durability Testing





- 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.

ARKEMA
The world is our inspiration

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.