SAND2008-2143P

DESIGN AND SYNTHESIS OF NOVEL ANION-EXCHANGE MEMBRANES FOR ENERGY APPLICATIONS

Michael R. Hibbs

Sandia National Laboratories

Albuquerque, New Mexico

mhibbs@sandia.gov

Sandia National Laboratories

SANDIA NATIONAL LABORATORIES

~8,000 employees

Albuquerque, New Mexico

Kauai Test Facility
Hawaii

Tonopah Test
Range,
Nevada

Yucca Mountain
Nevada

WIPP,
New Mexico

Pantex, Texas

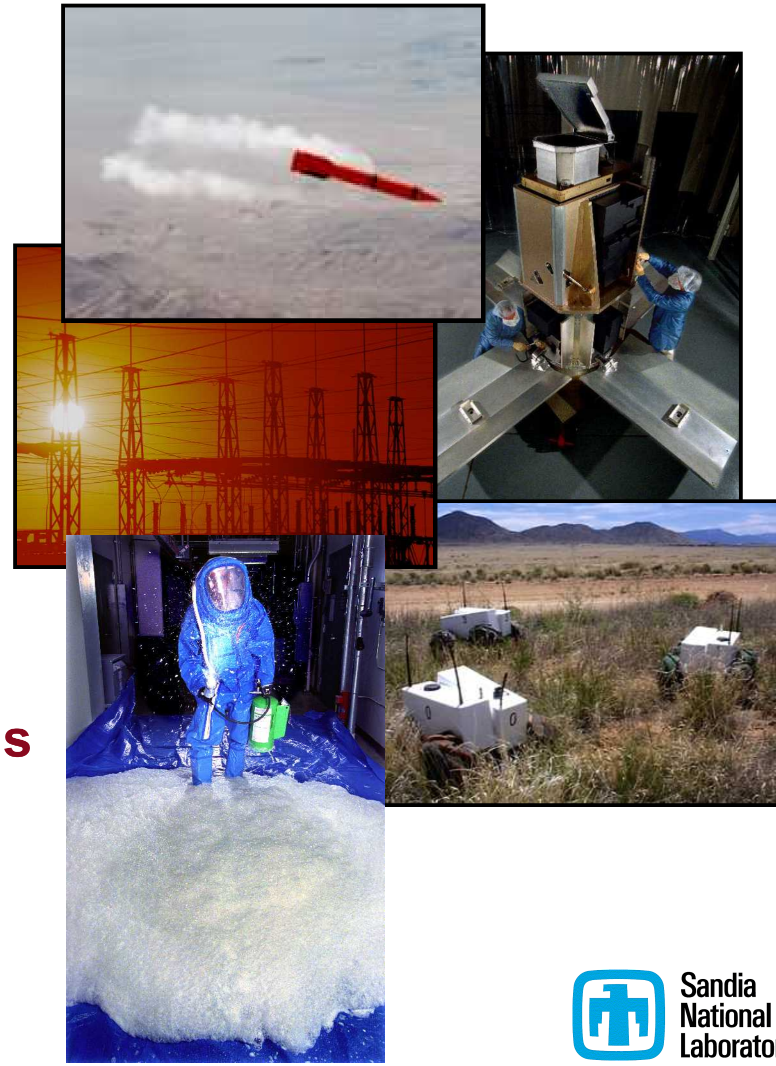
Livermore,California

Sandia
National
Laboratories

SANDIA RESEARCH AREAS

Our five Strategic Management Units:

- Nuclear Weapons
- Nonproliferation and Assessments
- Energy and Infrastructure Assurance
- Military Technologies and Applications
- Homeland Security

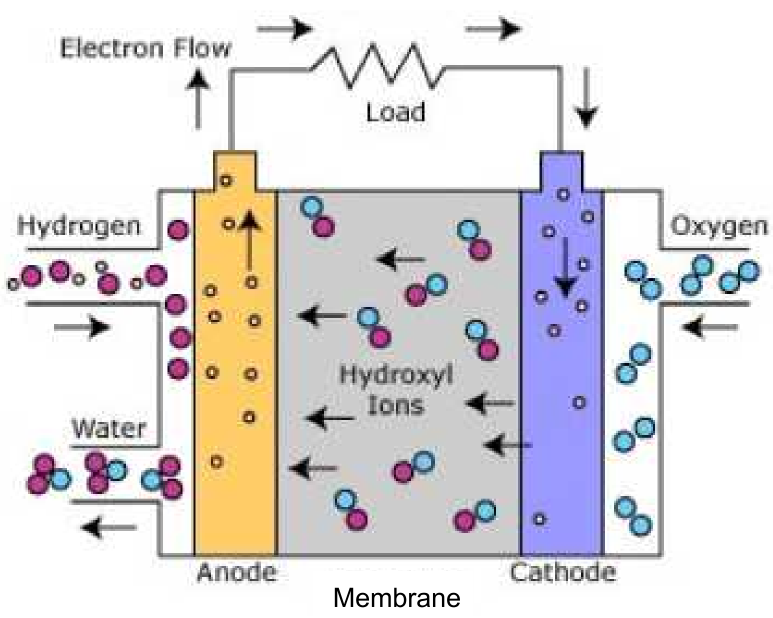


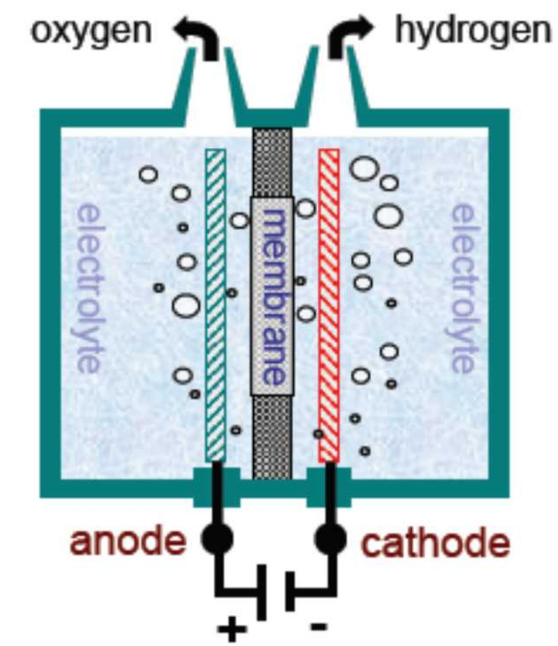
Sandia National Laboratories

OUTLINE

- Anion exchange membranes (AEM), applications and background
- First generation poly(sulfone) AEM synthesis
- Electrolysis testing results
- Second generation poly(sulfone) AEM synthesis
- Poly(pheylene)-based AEMs
- Preliminary fuel cell testing
- Plans for improving future generations

ANION EXCHANGE MEMBRANES: APPLICATIONS





(1) Alkaline fuel cells
(clean energy)

Anode: $2H_2 + 4OH^- \rightarrow 4H_20 + 4e^-$
Cathode: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$
Net: $2H_2 + O_2 \rightarrow 2H_2O$

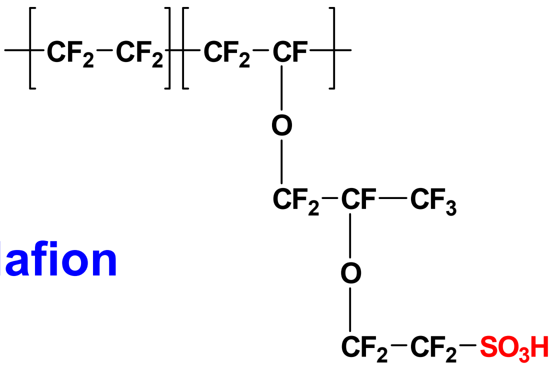
(2) Alkaline electrolysis
(H_2 production)

Anode: $4OH^- \rightarrow O_2 + 4e^- + 2H_2O$
Cathode: $4H_2O + 4e^- \rightarrow 2H_2 + 4OH^-$
Net: $2H_2O \rightarrow 2H_2 + O_2$

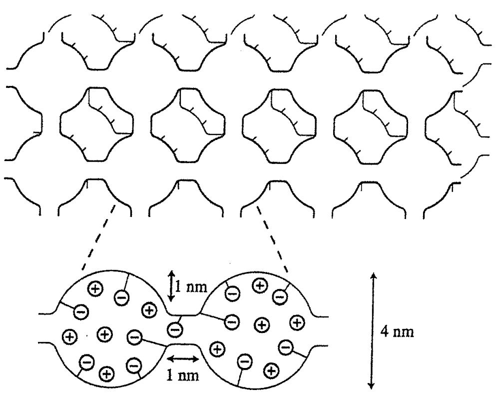
Sandia National Laboratories

PEM MATERIALS

The state of the art:

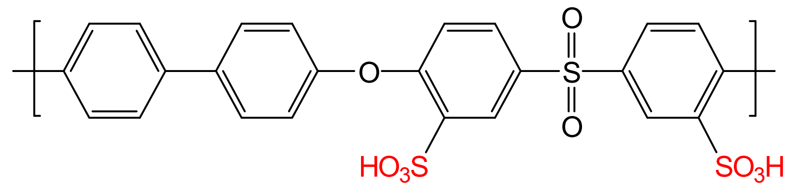


Nafion

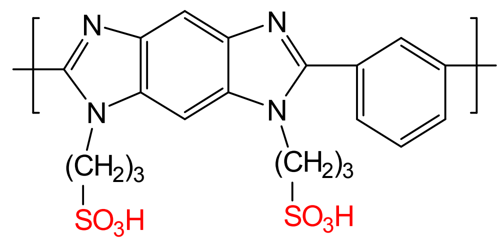


Proposed pore structure in Nafion membranes[1]

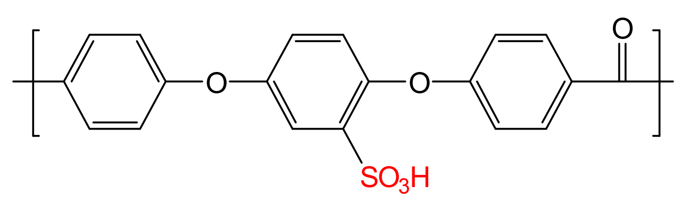
Hydrocarbon membranes:



Poly(ether sulfones)



Poly(benzimidazoles)



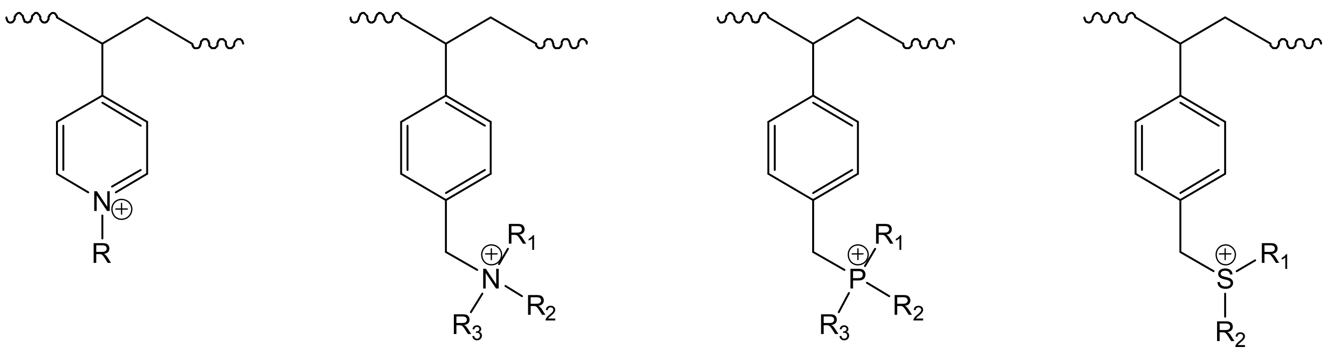
Poly(ether ether ketone)

[1]W. Y. Hsu and T. D. Gierke, *J. Membrane Sci.*, **13** (1983) 307.

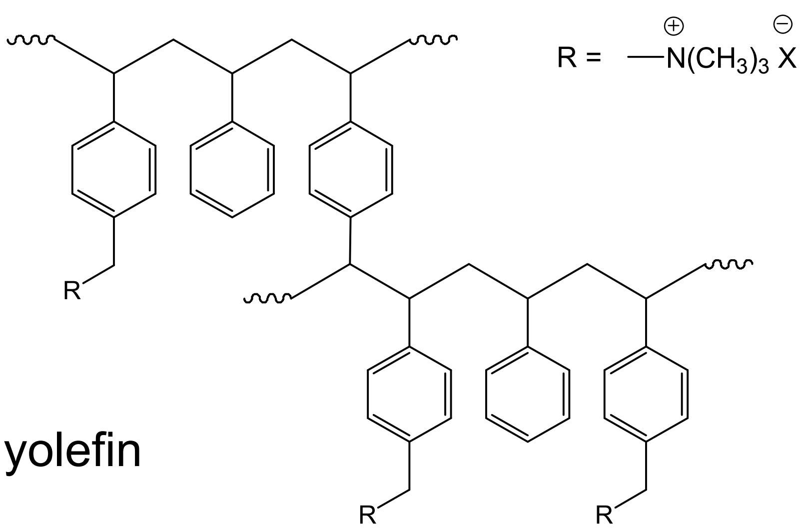
Sandia National Laboratories

ANION EXCHANGE MEMBRANES (AEMs)

Typical functional groups with fixed positive charges in AEMs:



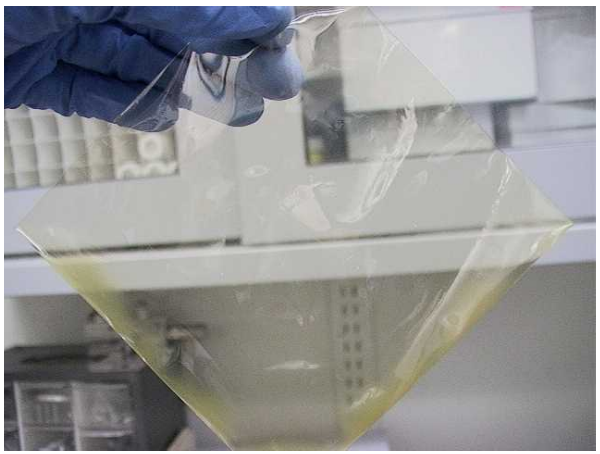
Commercially-available AEM:

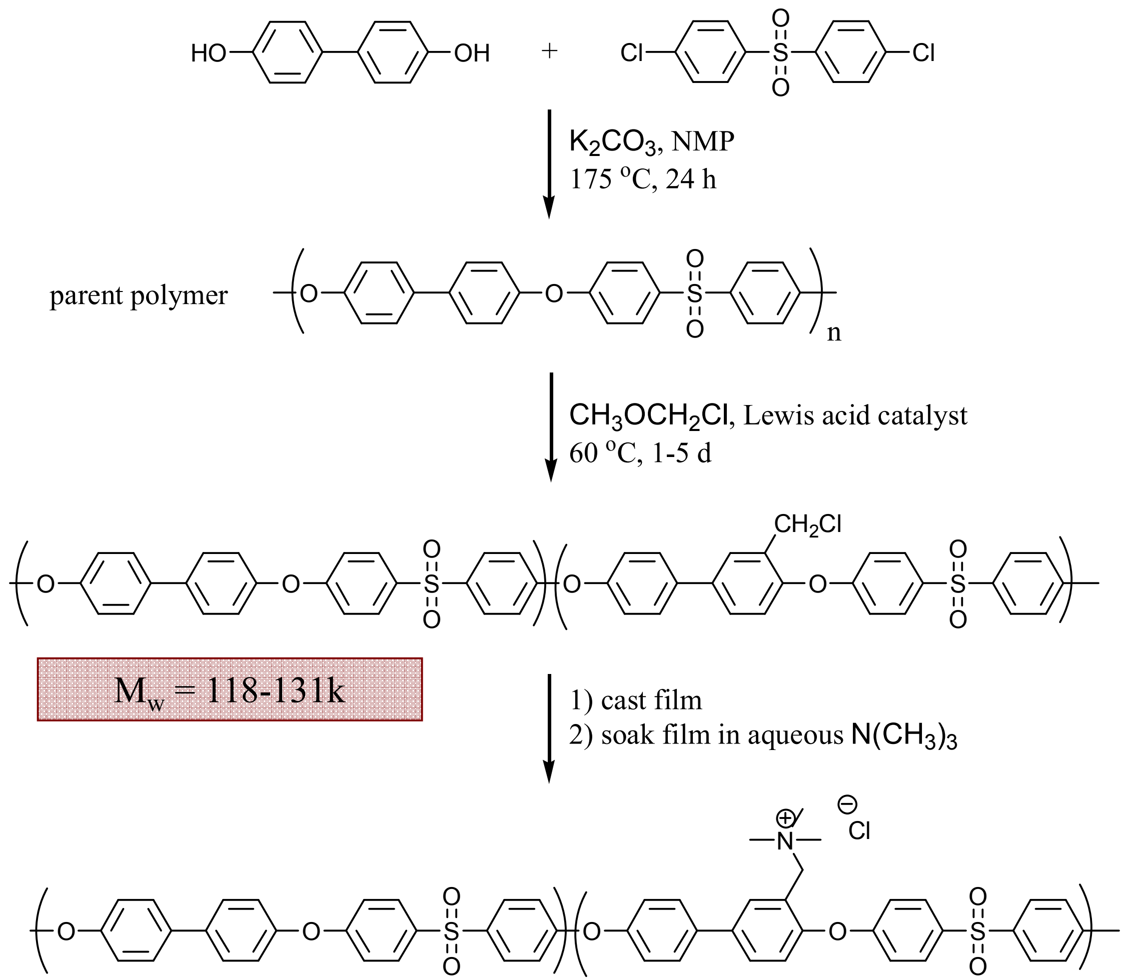


- Crosslinked polystyrene with benzyl trimethylammonium groups
- Typically blended with PVC or a polyolefin
- Cast on fabric support

Sandia National Laboratories

SYNTHESIS OF FIRST GENERATION AEM





CHEMICAL STABILITY

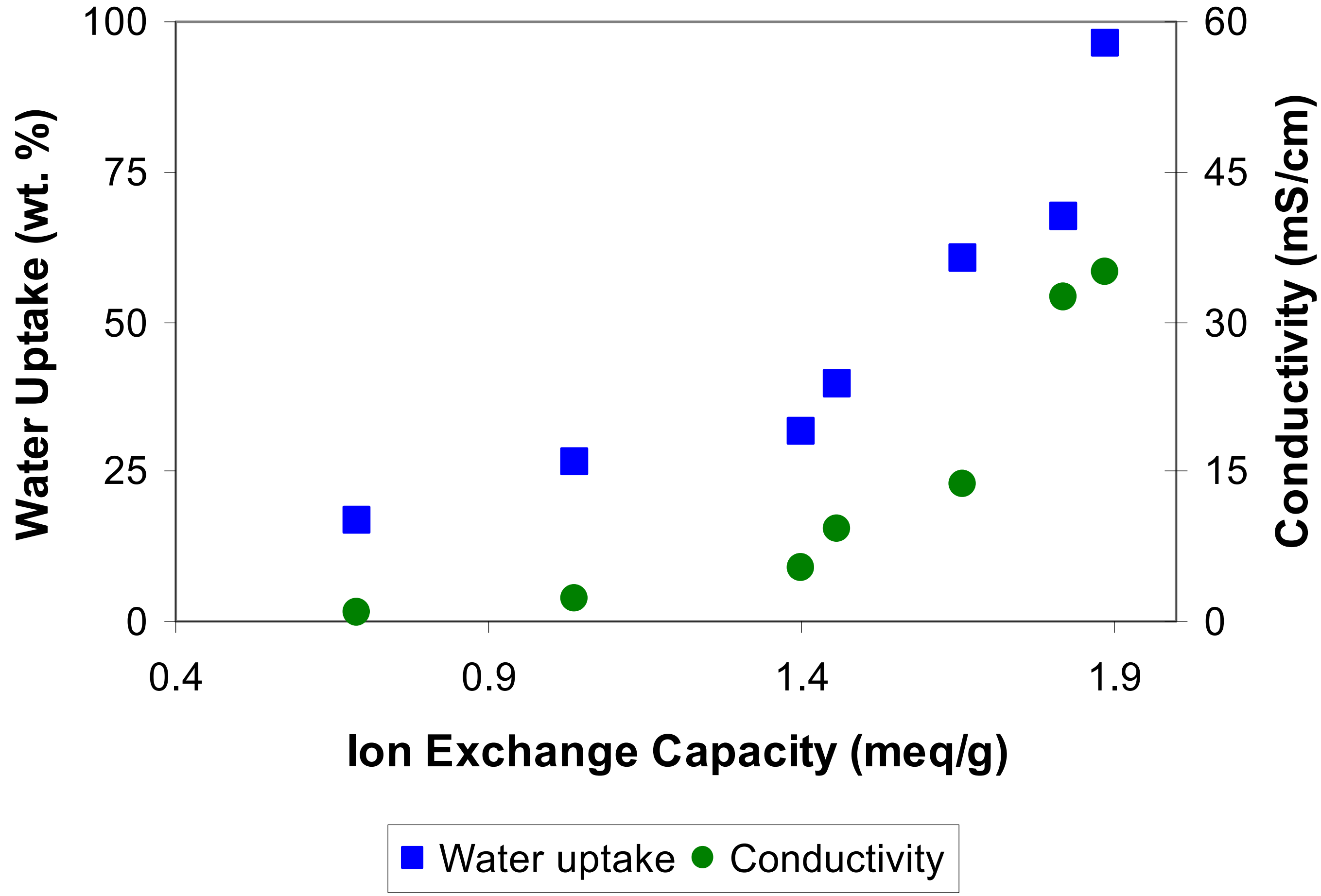
Commercial AMX membrane:

as received after 24 h in 1M NaOH

Sandia 1st generation membrane after 24 h in 1M NaOH

Sandia National Laboratories

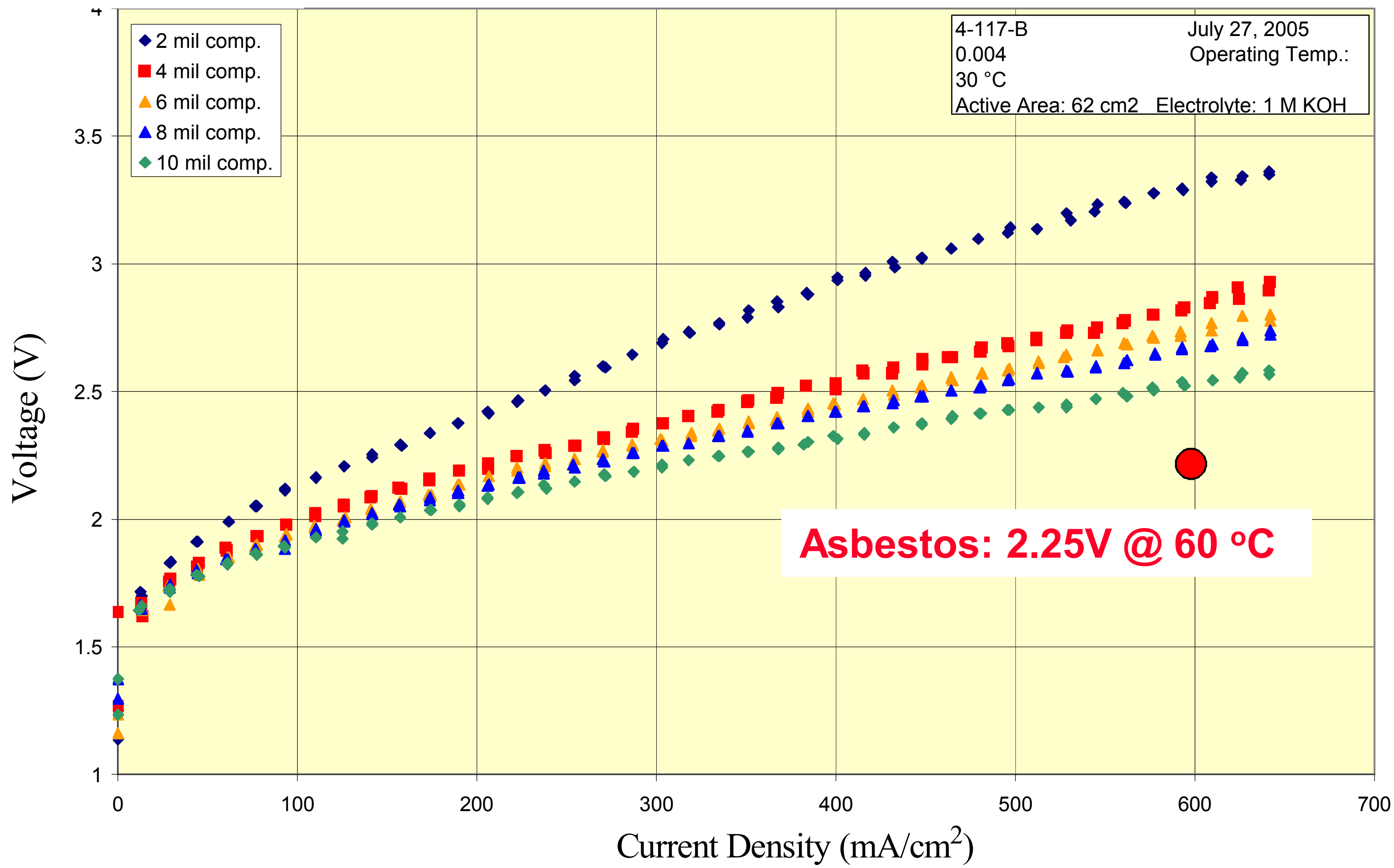
FIRST GENERATION MEMBRANE PROPERTIES



- Membranes in hydroxide form.
- Conductivities measured by impedance spectroscopy with a two-point probe immersed in water at room temperature.

Sandia National Laboratories

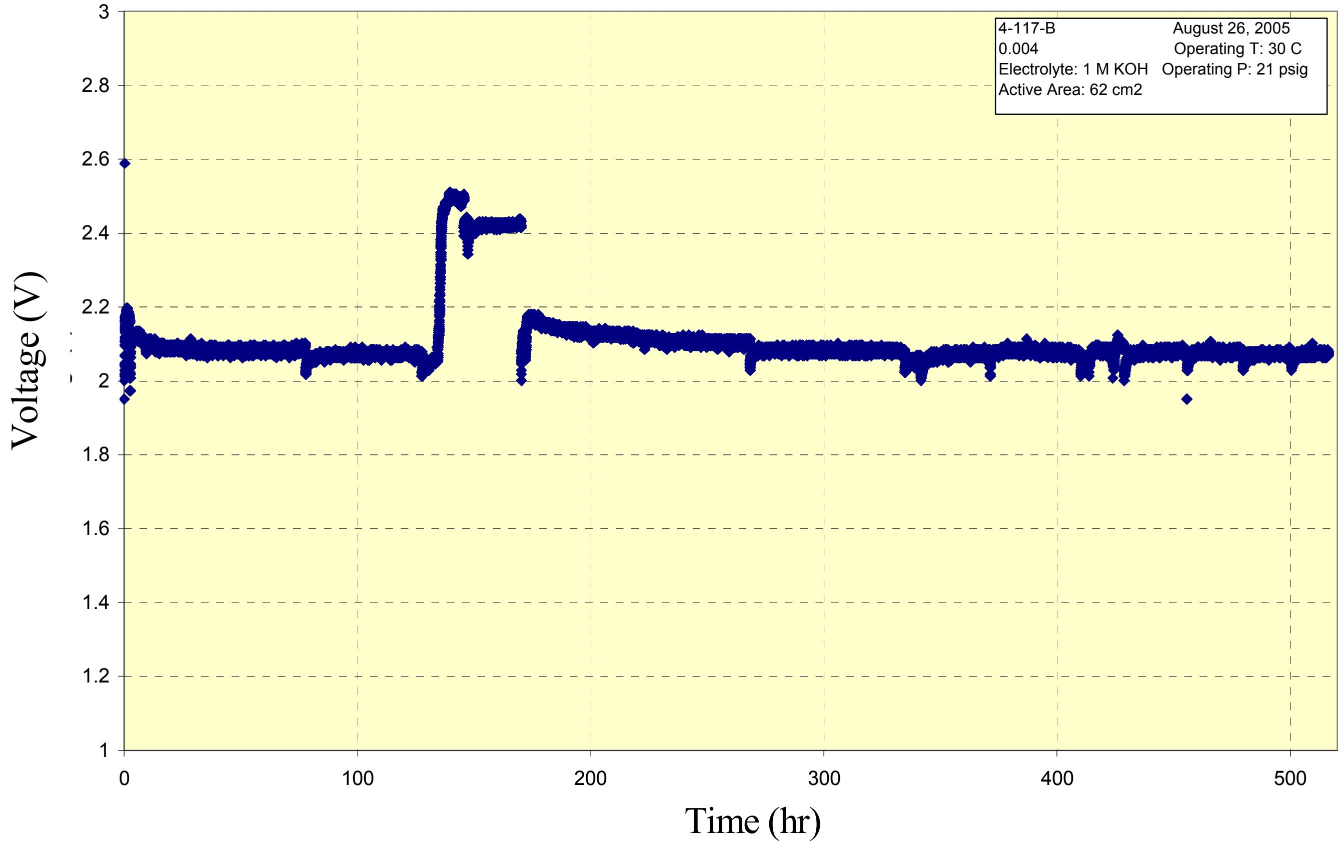
ELECTROLYSIS DATA: CELL COMPRESSION



- Cell conditions: 30 °C, 1M KOH, Active area = 62 cm^2, current swept from 0 – 40 Amps.
- Data collected by Teledyne Energy Systems, Inc.

Sandia National Laboratories

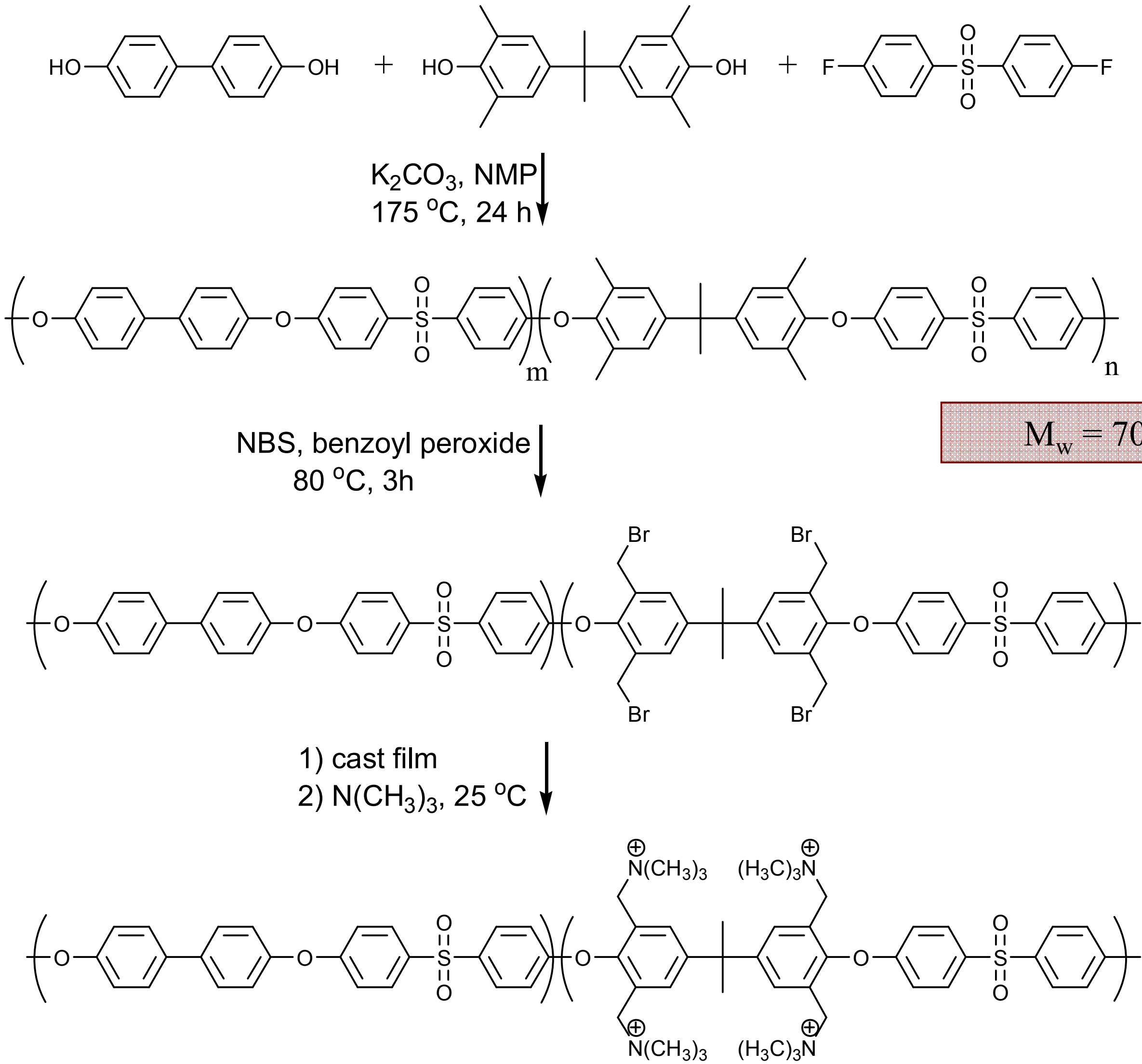
ELECTROLYSIS DATA: LIFETIME TEST



- Cell conditions: 30 ^oC, 1M KOH, 10 Amp. current
- Active area = 62 cm^2
- Data collected by Teledyne Energy Systems, Inc.

Sandia National Laboratories

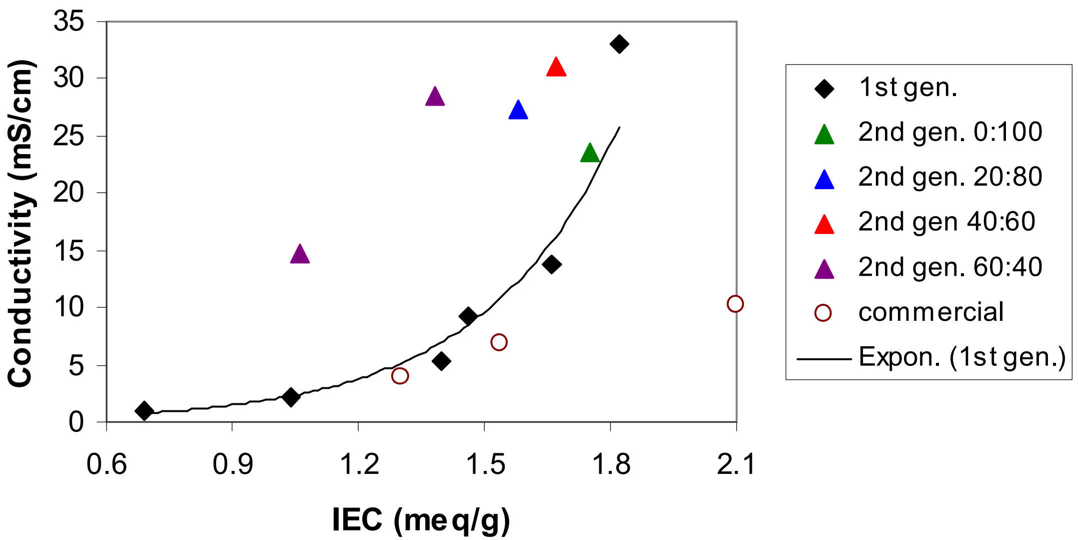
SECOND GENERATION MEMBRANES: SYNTHESIS

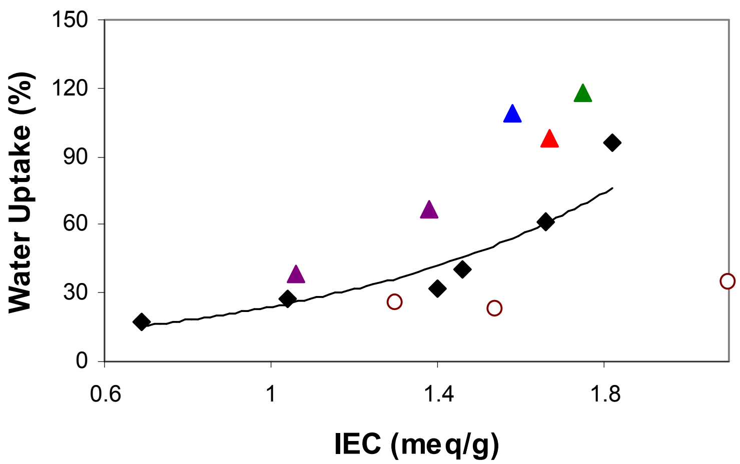


$M_w = 70\text{-}110k$

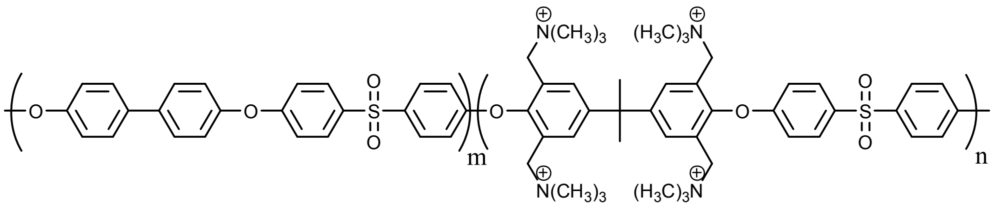
Sandia National Laboratories

SECOND GENERATION MEMBRANES: PROPERTIES

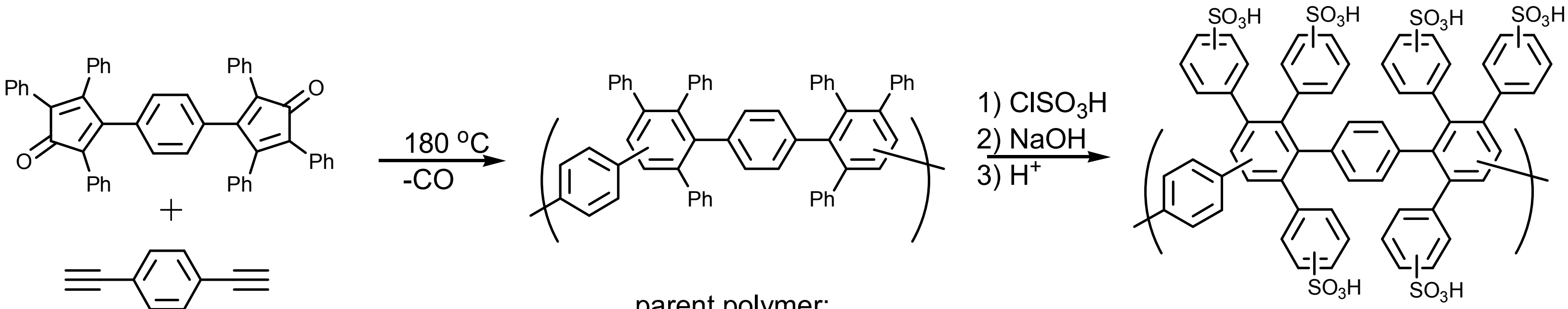




2nd generation AEM polymer repeat units

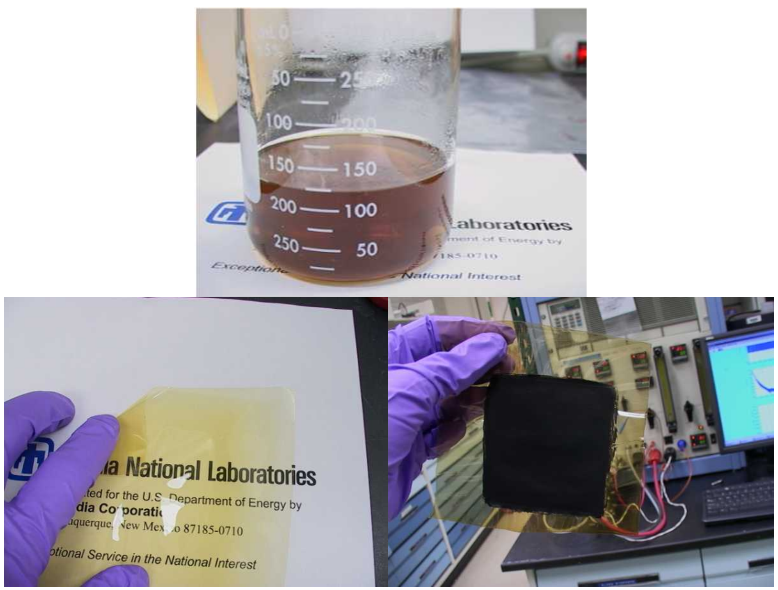


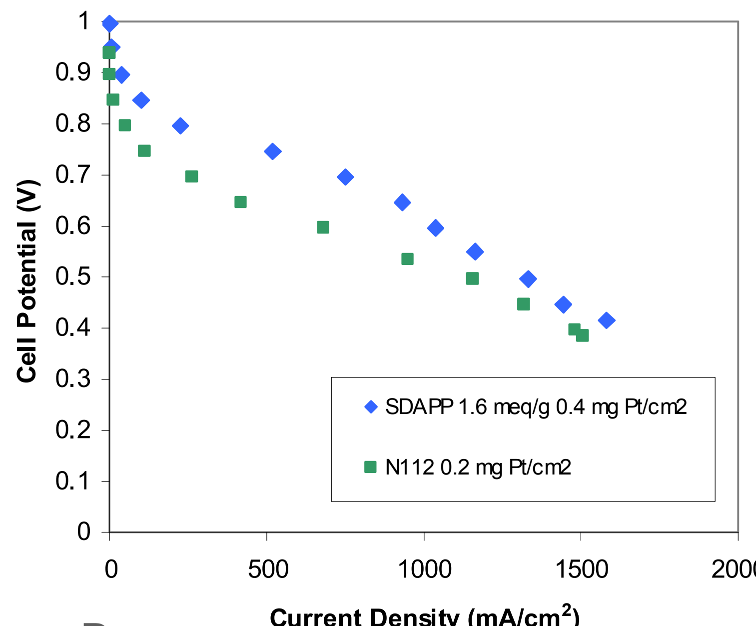
SANDIA POLY(PHENYLENES) FOR PEM FUEL CELLS



parent polymer:
Diels **A**lder **P**oly**P**henylene
DAPP

SDAPP
(cation exchange membrane)

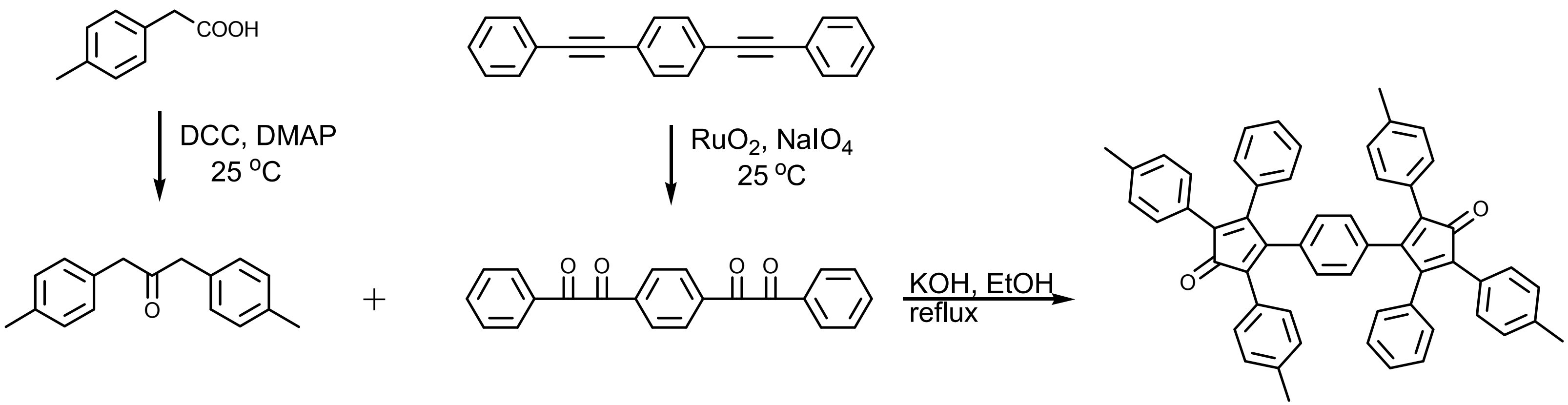




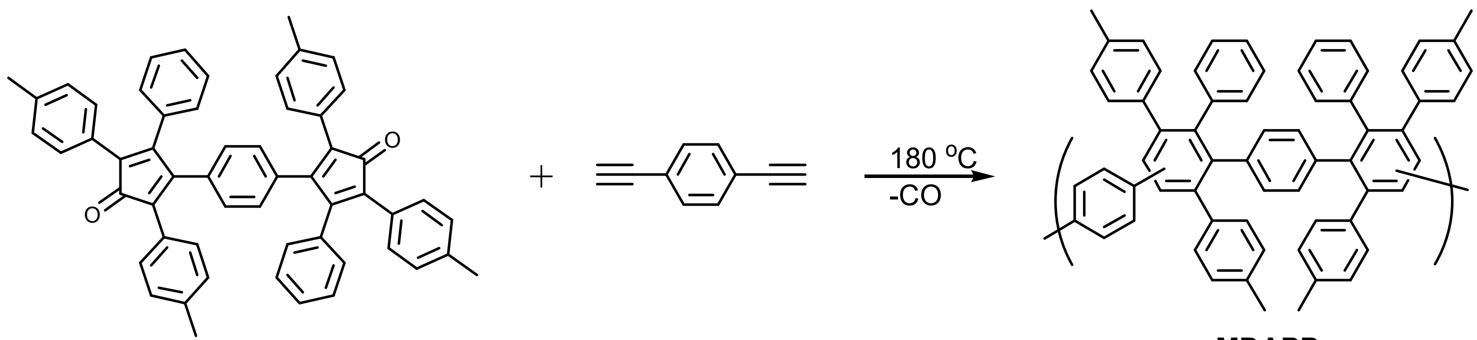
Fujimoto, C. H.; Hickner, M. A.; Cornelius, C. J.; Loy, D. A. *Macromol*. **2005**, *38*, 5010.

Sandia National Laboratories

SYNTHESIS OF METHYLATED DAPP



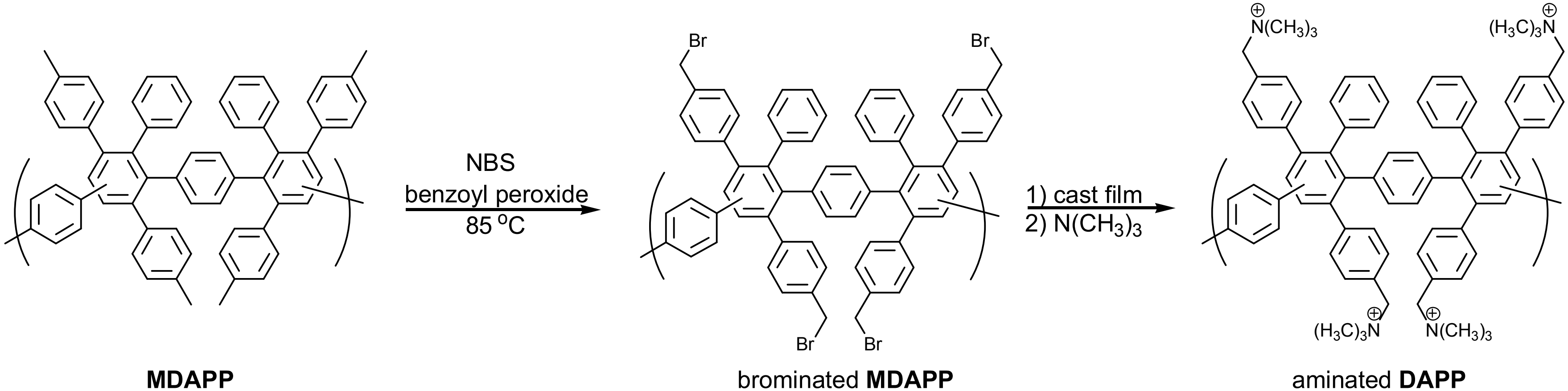
bis(cyclopentadienone)

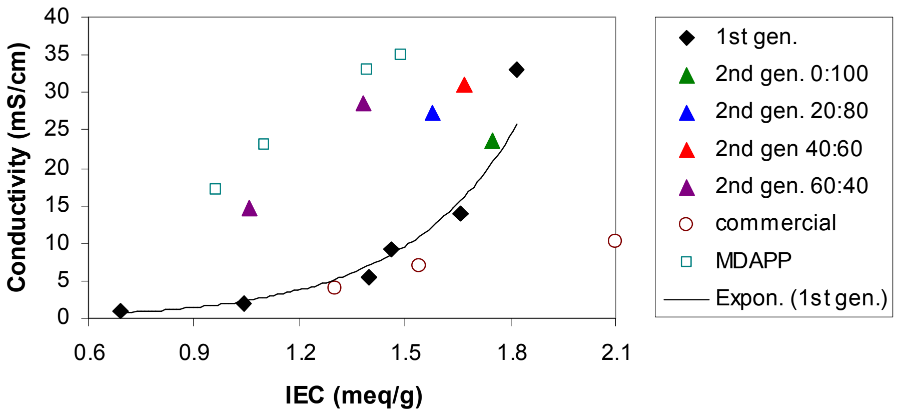


MDAPP

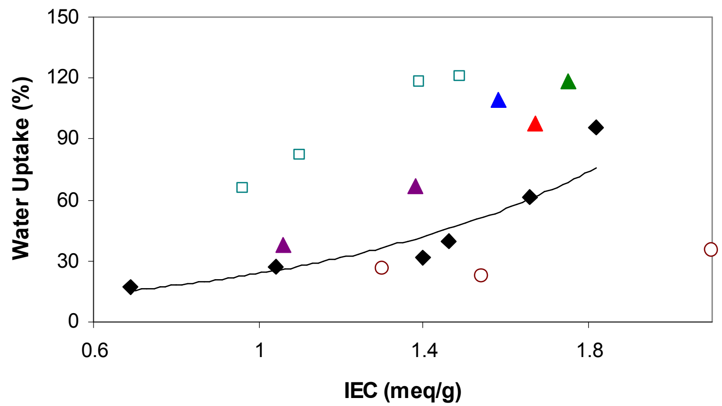
$M_w = 60\text{-}80k$

ADAPP MEMBRANES





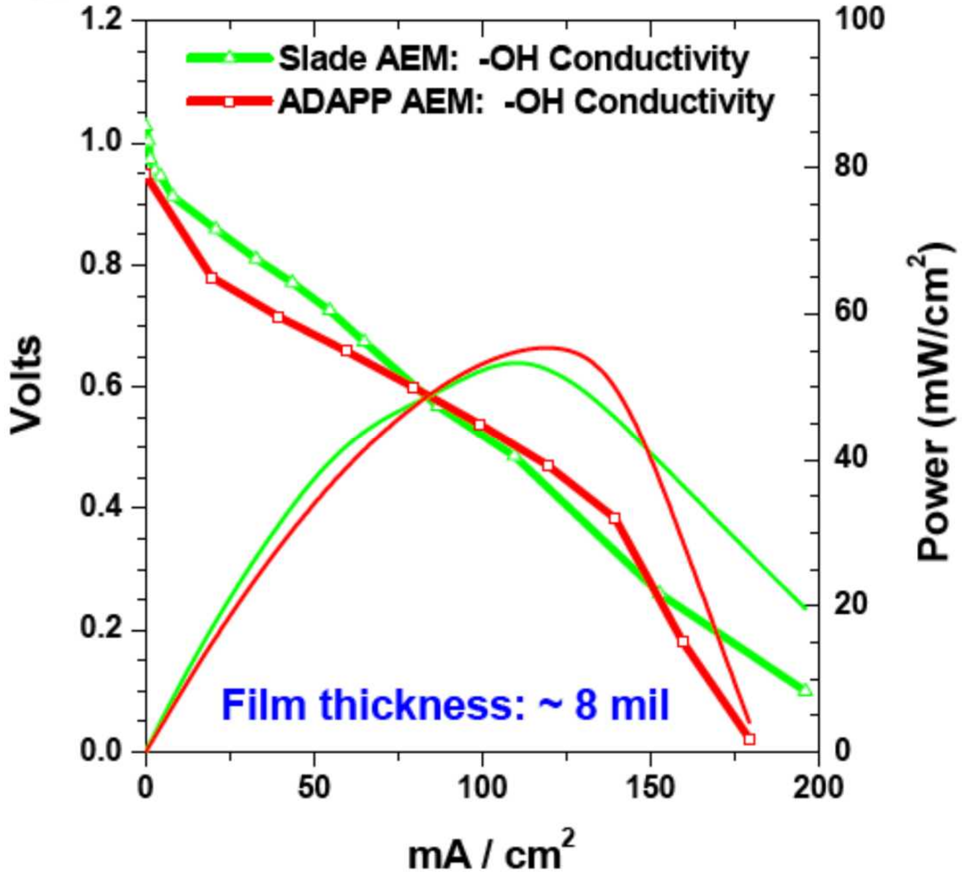
Ionic Conductivity



Water Uptake

Sandia National Laboratories

FUEL CELL TESTING



Comparison with state of the art:

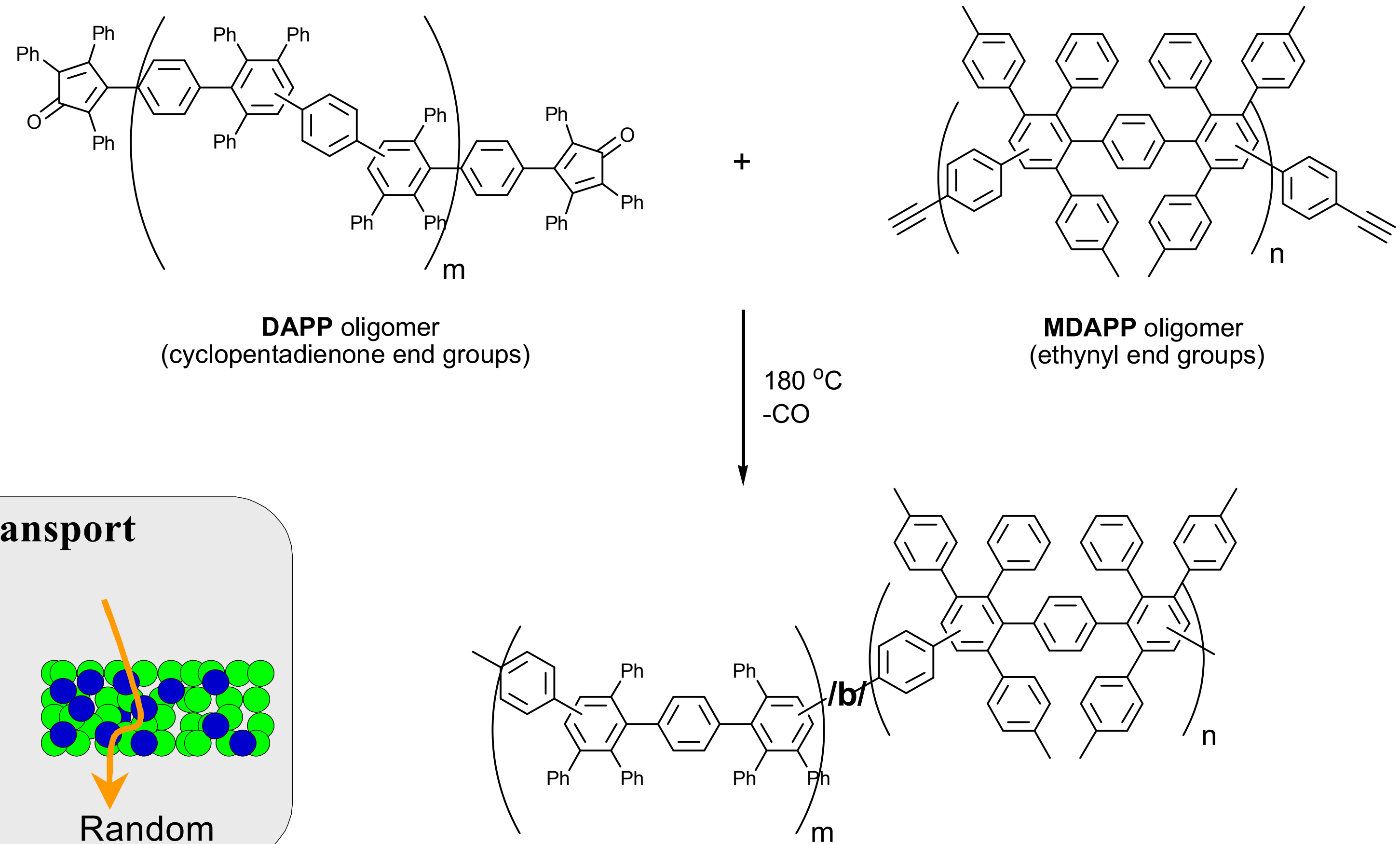
	SNL	Slade*
Temperature	80	50
Fuel	H_2/air	H_2/O_2
Anode	PtRu	Pt
Cathode	CoTMPP	Pt
Pressure (psig)	0	0

Conditions are different but the Sandia alkaline fuel cell performance is very similar to the best reported work.

*Varcoe, J. R.; Slade, R. C. T.; Lam How Yee, E. *Chem. Commun.*, **2006**, 1428.

Sandia National Laboratories

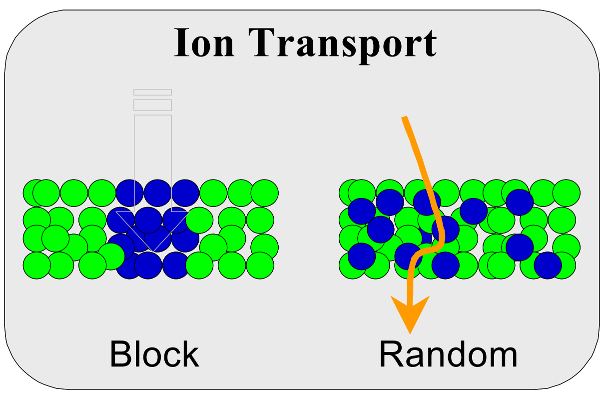
BLOCK COPOLYMERS



DAPP oligomer
(cyclopentadienone end groups)

MDAPP oligomer
(ethynyl end groups)

DAPP/MDAPP block copolymer



- **Better phase separation of hydrophobic and hydrophilic components.**
- **Higher ionic conductivity.**

CONCLUSIONS

- Three novel polymers with quaternary ammonium groups have been synthesized.
- Preparation of halomethyl groups has been simplified by using methylated monomers and then brominating the polymer.
- Ionic conductivities vary with IEC and can reach as high as 40 mS/cm.
- These AEMs have been shown to function in both alkaline electrolysis and fuel cell applications.
- Further improvements in ionic conductivity and chemical stability are needed to maximize the potential impact of these AEMs.

CONCLUSIONS

ACKNOWLEDGEMENTS

Sandia
Chris Cornelius
Cy Fujimoto
Mike Hickner (PSU)
Susan Altman
Lucas McGrath
Paul Clem
Adam Cook
Bonnie McKenzie
Doug Ruby

University of New Mexico
Plamen Atanassov
Tim Olsen
Elise Switzer

Teledyne Energy Systems, Inc.
Steve Cohen
Mike Miller

Sandia National Laboratories