Membrane Development for Hybrid Sulfur Electrolysis at High Temperatures

Sandia National Laboratories

Michael Hibbs[1], Kirsten Norman[1], Cy Fujimoto[1], Michael Hickner[2]

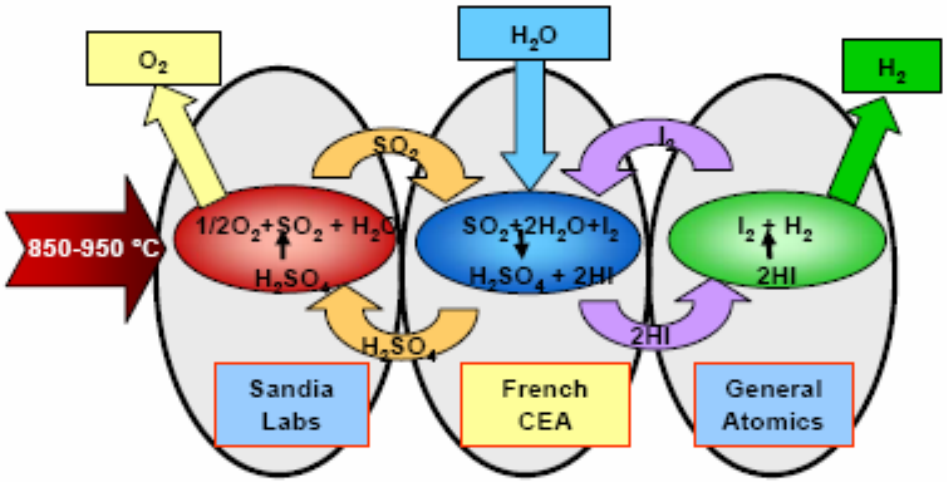
[1] 06338 Fuels and Energy Transitions
[2] Department of Materials Science and Engineering, The Pennsylvania State University

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Sulfur-Iodine versus Hybrid Sulfur Cycle

Hybrid-Sulfur (thermal and electrochemical reactors)

advantages	**disadvantages**
- fewer reactions	- electrochemical reactor cost
- no HI or I_2	- electricity needed (efficiency??)

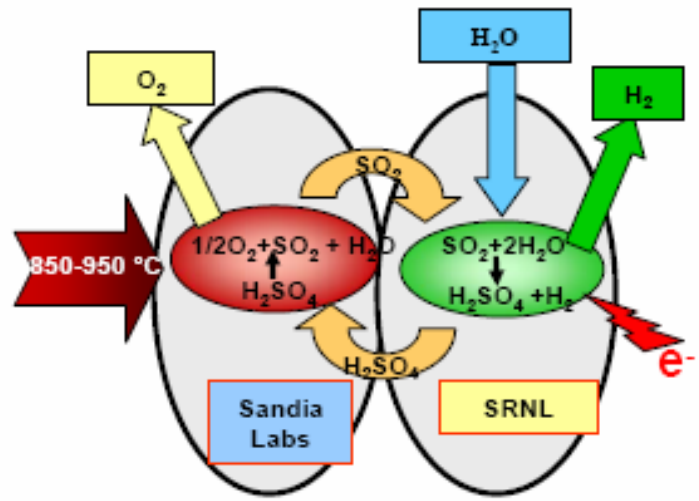


Sulfur Iodine

(1) $H_2SO_4 \rightarrow H_2O + SO_2 + 1/2O_2$

(2) $2HI \rightarrow I_2 + H_2$

(3) $2H_2O + SO_2 + I_2 \rightarrow H_2SO_4 + 2HI$



Hybrid-Sulfur

(1) $H_2SO_4 \rightarrow H_2O + SO_2 + 1/2O_2$

(2) $2H_2O + SO_2 \rightarrow H_2SO_4 + H_2$

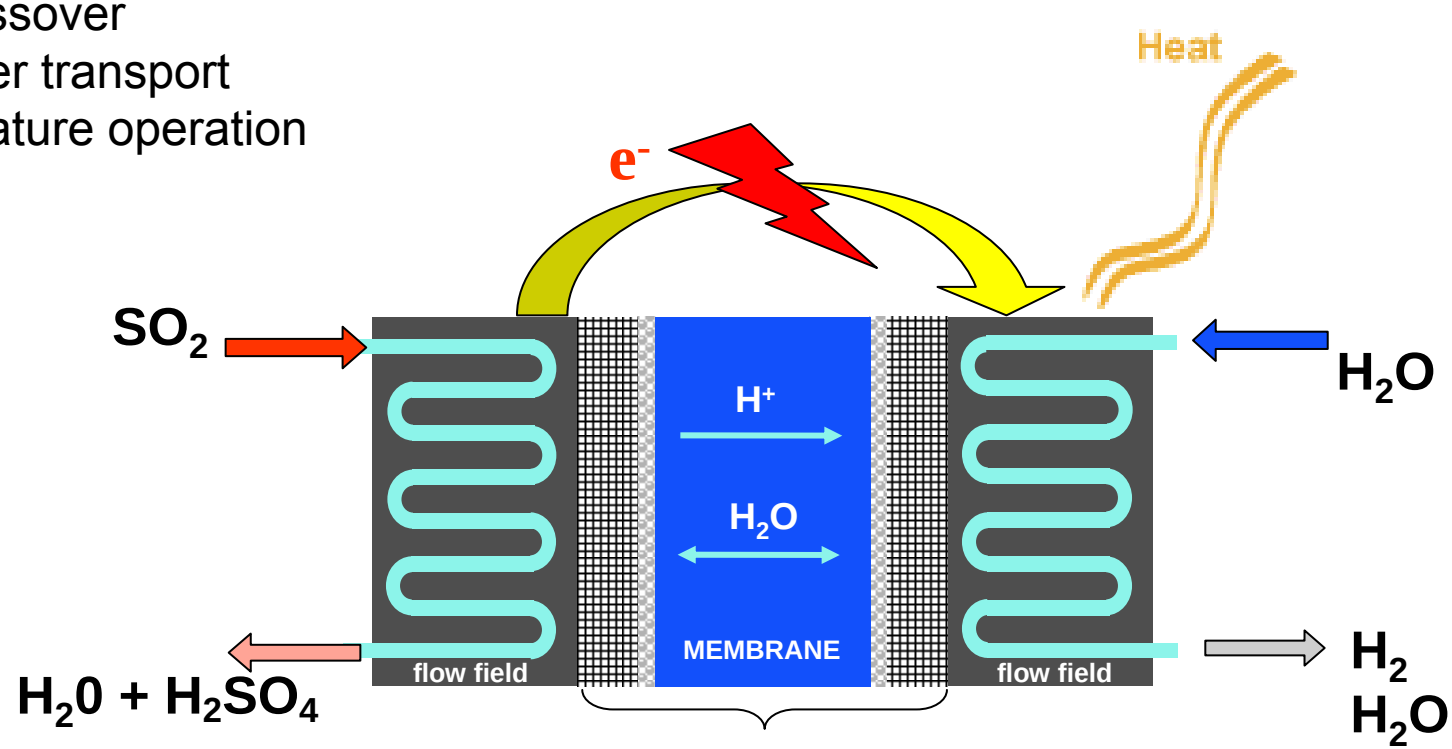
Sandia National Laboratories

Electrolyzer Schematic

$SO_2 + 2\ H_2O + \text{electric power} \rightarrow H_2SO_4 + H_2 + \text{heat}$

Membrane is critical for:

- low SO_2 crossover
- efficient water transport
- high temperature operation



Membrane Electrode Assembly – MEA

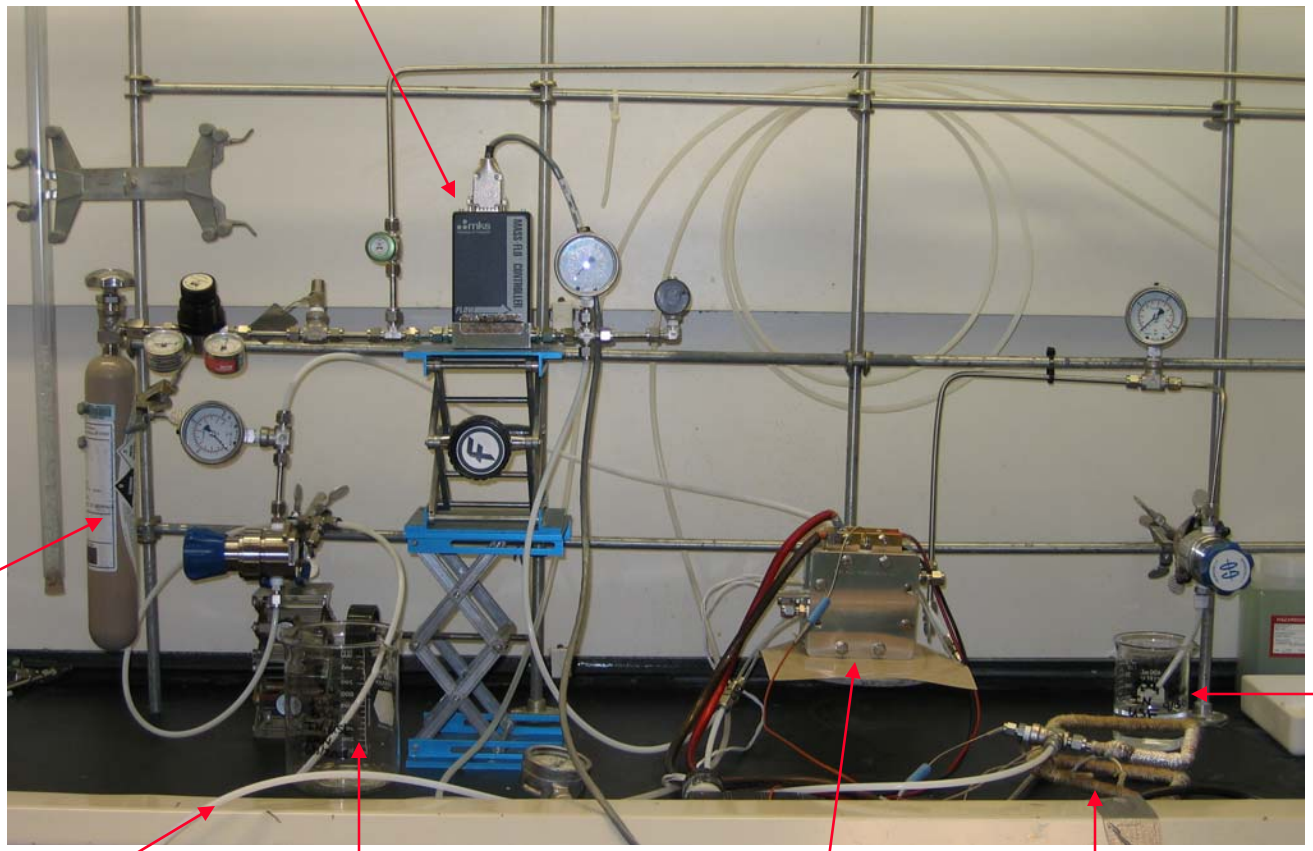
Membrane

Catalyst layers

Gas diffusion layers

Sandia National Laboratories

Electrolyzer Set-up



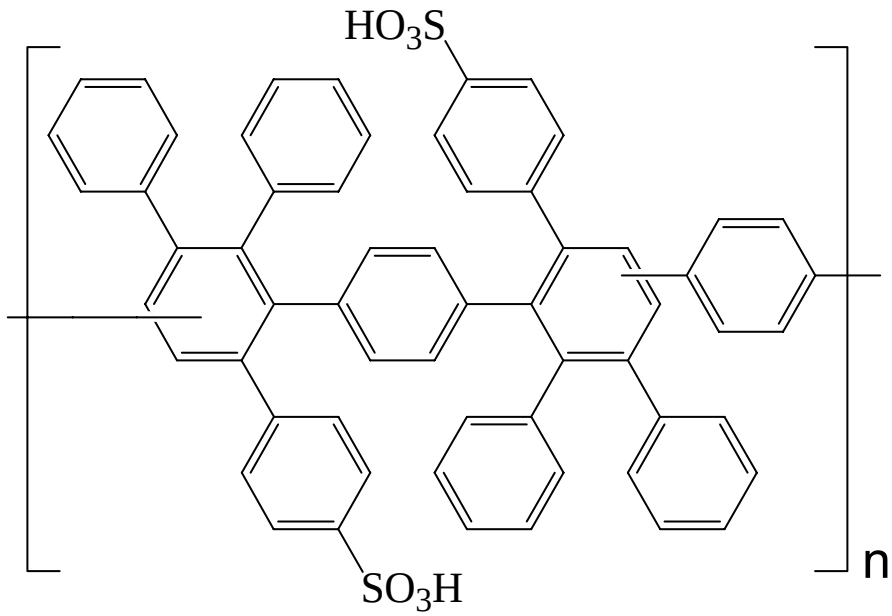
Sandia National Laboratories

High Temperature Polymeric Proton Conducting Membranes

Sandia-synthesized polymer membranes (SDAPP) have shown promise in high temperature electrochemical processes, e.g. fuel cells.

Goals of HyS Membrane Project:

- Enable stable operation at T>120 ^{o}C
- Reduce SO_2 crossover
- Increase current density and/or reduce voltage as much as possible.
- Demonstrate durability.

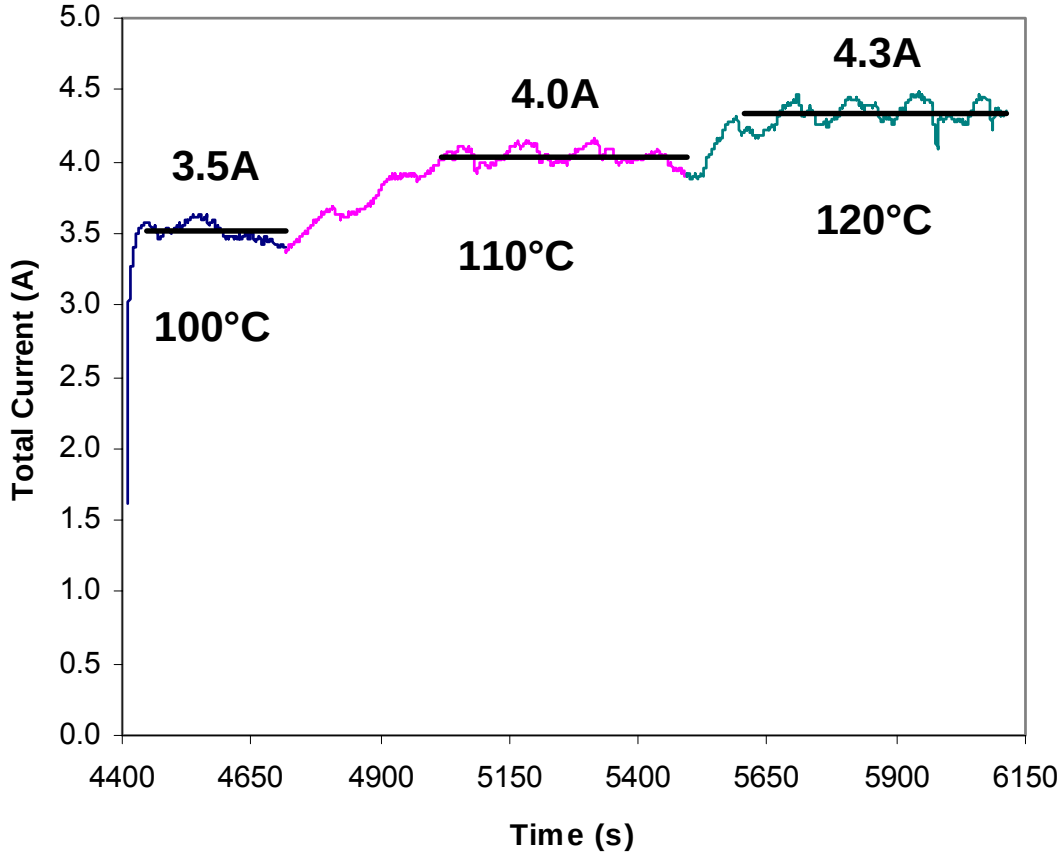


Sulfonated Diels-Alder Poly(phenylene) - SDAPP†

†Fujimoto, C.H, Hickner, M.A., Cornelius, C.J., Loy, D.A. *Macromolecules* **2005**, 38(12), 5010-5016.

Sandia National Laboratories

Increased Temperature Promotes Better Performance



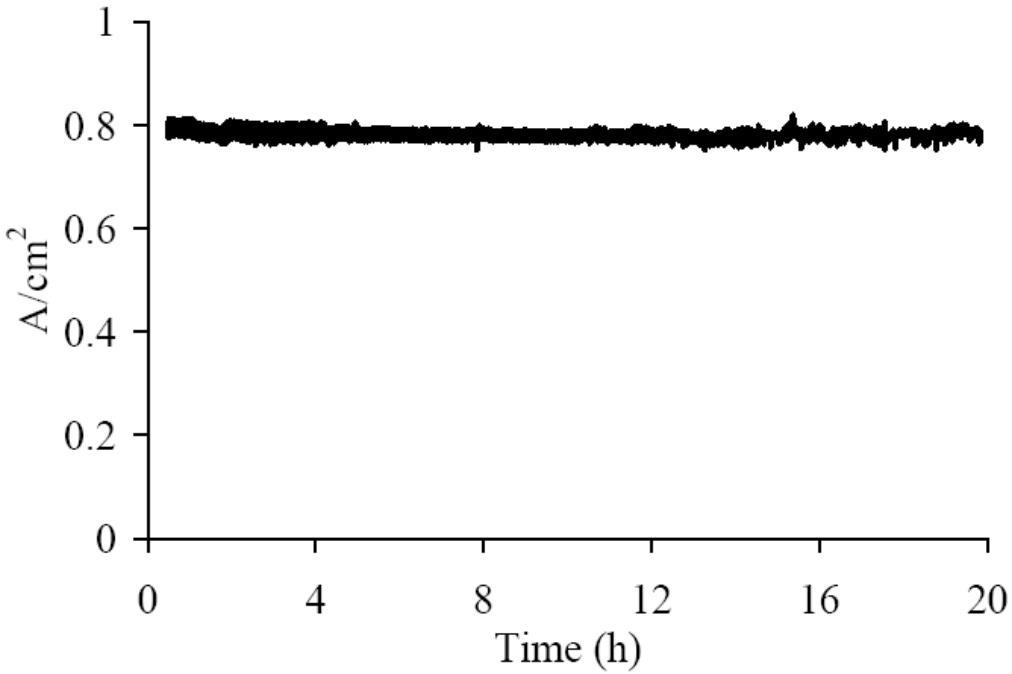
Note: Elemental sulfur melts at 114 °C.

Cell Conditions:

- 10 cm^2 cell
- Cell potential = 0.7 V
- SDAPP 2.2 meq/g membrane batch
- 2 mg Pt/cm^2 Pt Black anode and cathode
- Dry SO_2 gas anode, 100 sccm constant SO_2 flow rate with 15 psig backpressure
- Preheated liquid water cathode, 3 mL/min constant H_2O flow rate with 15 psig backpressure

Sandia National Laboratories

20-Hour Test with SDAPP Membrane



Cell: SDAPP 5-192-C, IEC = 2.6 meq/g (50 mm average thickness), ~1.5 mg/cm^2 Pt sprayed on anode and cathode, LT1400W GDL.

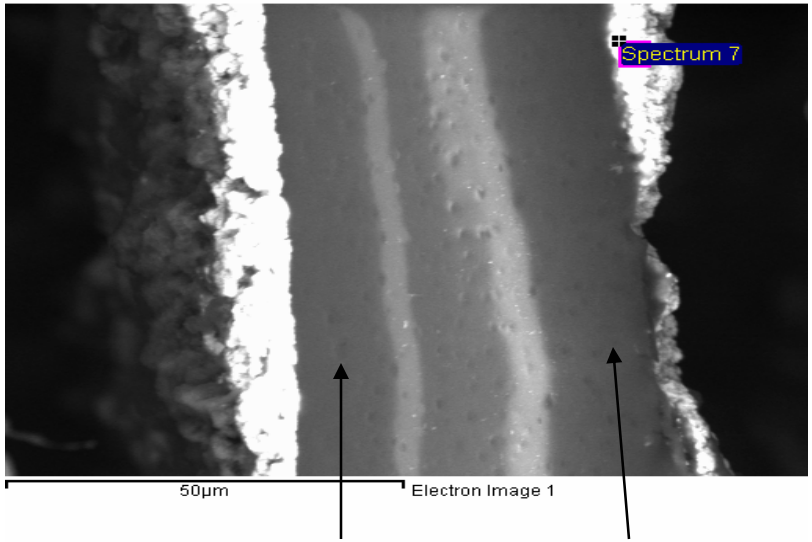
Operating conditions: 0.7 V, 120°C, 100 sccm SO_2, 10 mL/min H_2O, 25 psig backpressure.

SO_2 conversion was 56% (based on feed rate and total current).

Sandia National Laboratories

Analysis of MEA from 20-Hour Test

SEM of cross-section

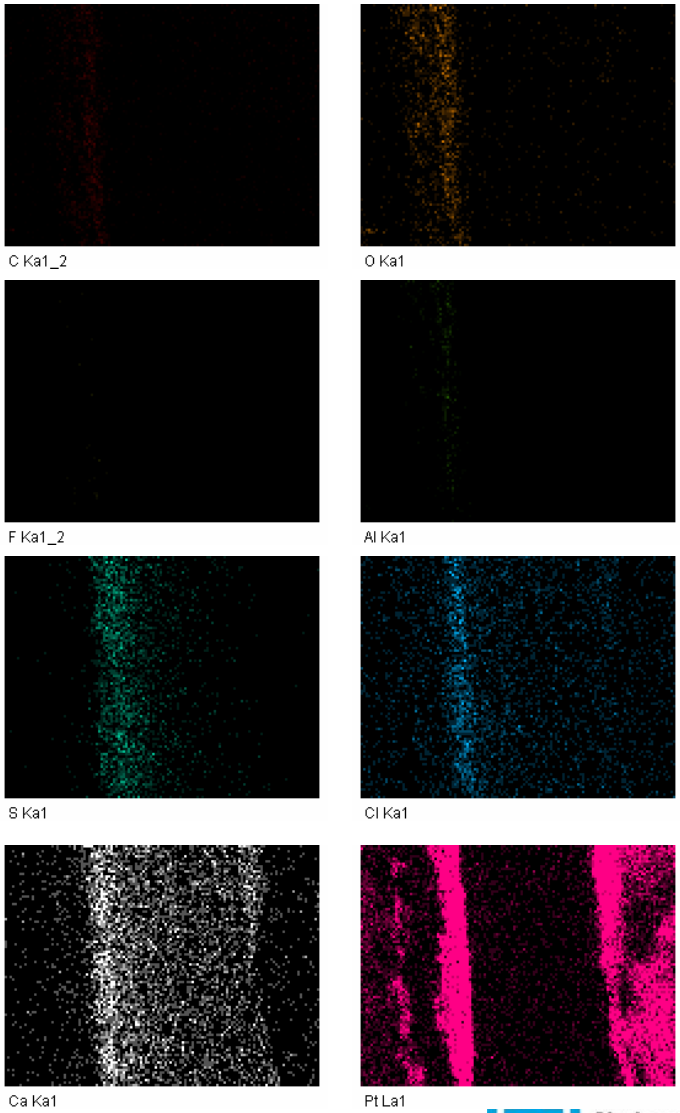


Anode

Cathode

6.08 wt.% S **2.25 wt.% S**

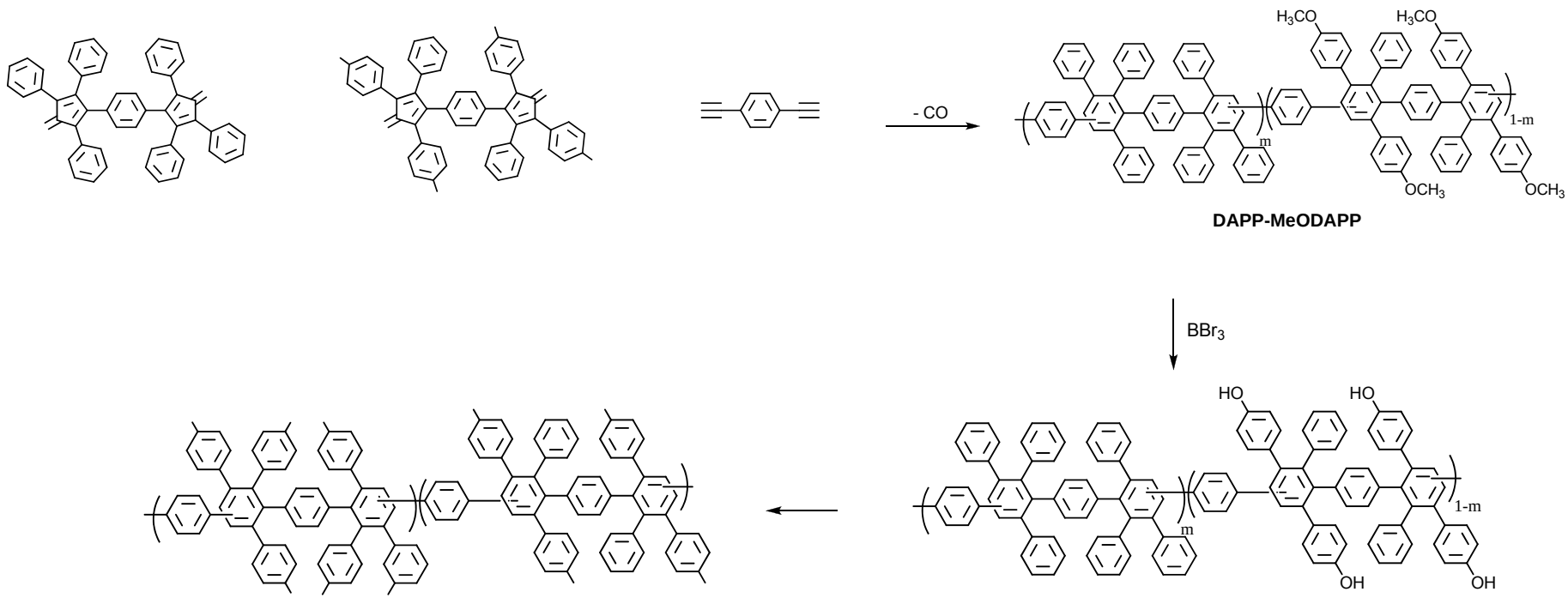
- No evidence of sulfur deposits on cathode side (or anywhere else).
- Small S gradient across membrane is probably indicative of H_2SO_4 flux through membrane.



National Laboratories

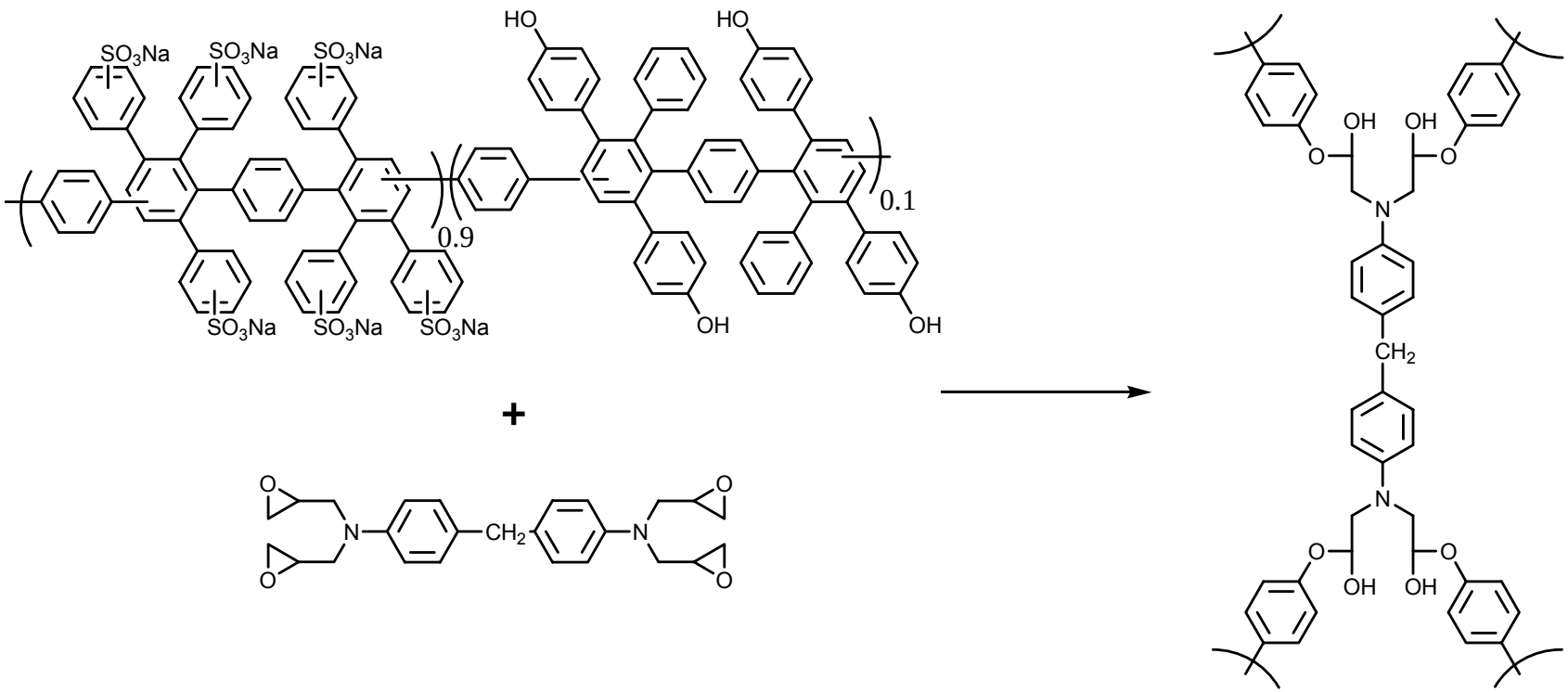
Synthesis of EXSDAPP

Objective:
Crosslink SDAPP in order to achieve higher IECs with mechanical integrity.



Sandia National Laboratories

Crosslinking SDAPP with Tetrafunctional Reagent

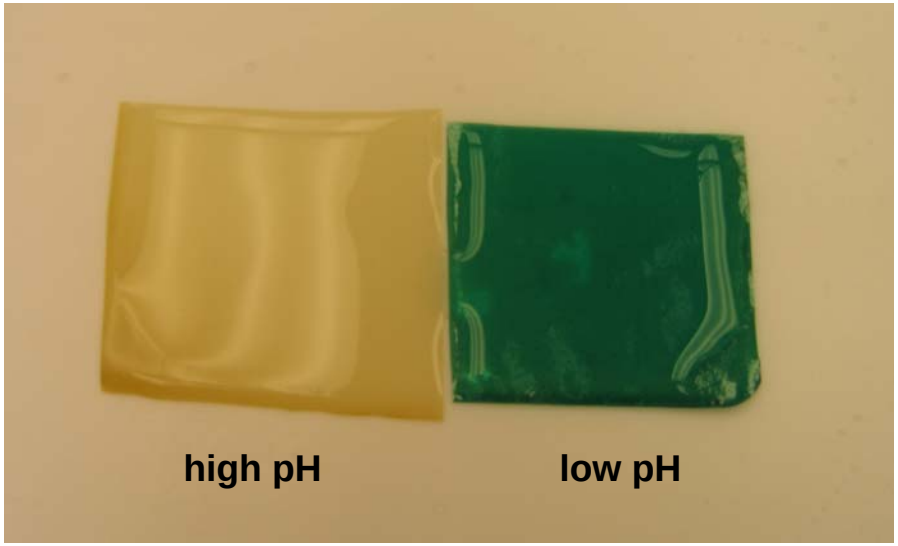


- Copolymer contains reactive hydroxyl groups.
- Copolymer and tetra-epoxide reagent are dissolved together in DMAc for casting.
- After casting, membrane is cured at 150 ºC for 90 min.
- Crosslinked membrane is soaked in solution of trimethylsilyl chlorosulfonate in CH_2Cl_2 to increase IEC without dissolving the membrane.

Sandia National Laboratories

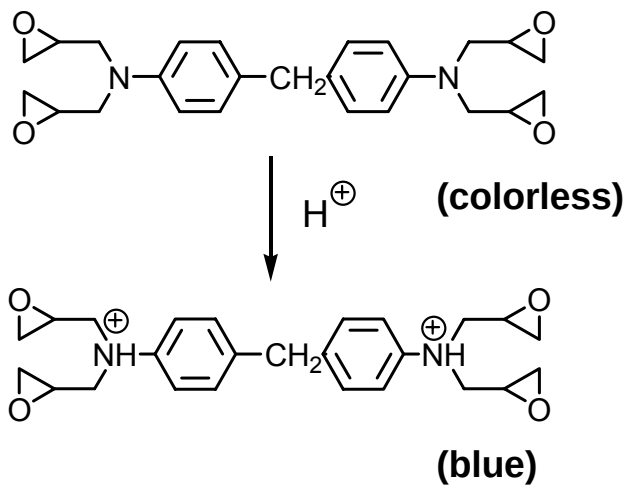
An Interesting Artifact

The color of the epoxy-crosslinked membranes is pH-dependant.



Color changes after soaking membranes in 1M H_2SO_4 and 1M NaOH

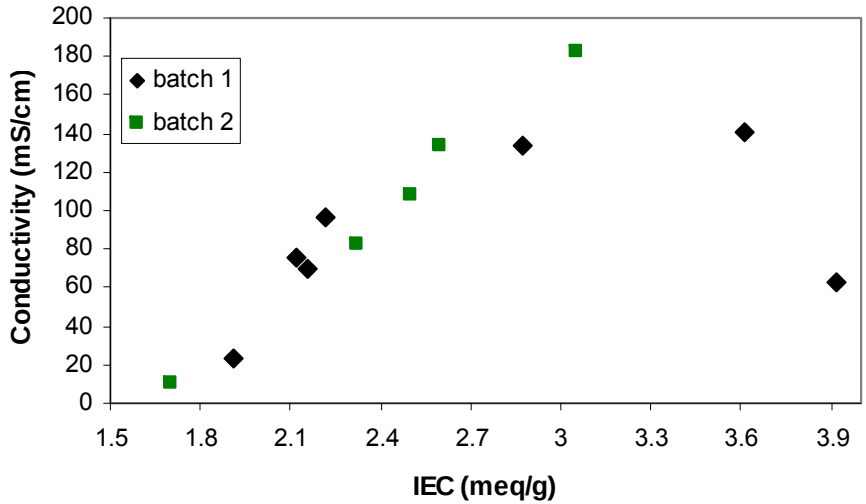
Protonation of crosslinking agent:



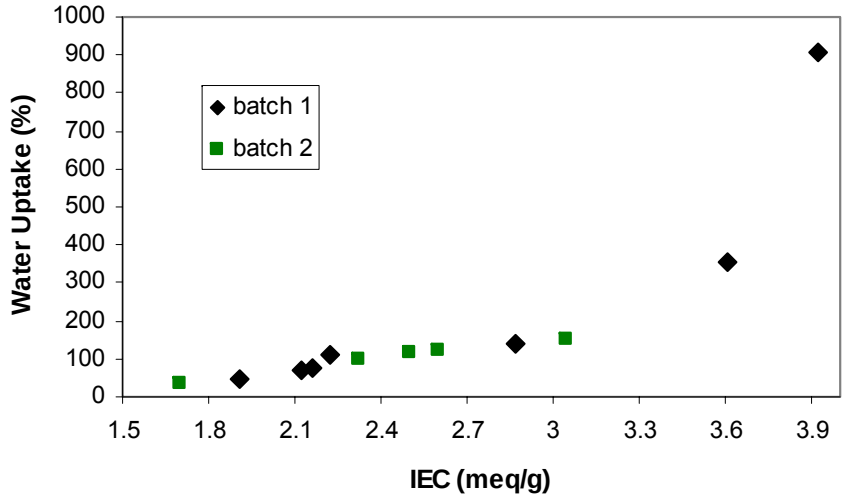
Sandia National Laboratories

EXSDAPP Properties

H^+ Conductivity at 25 ^oC in Water



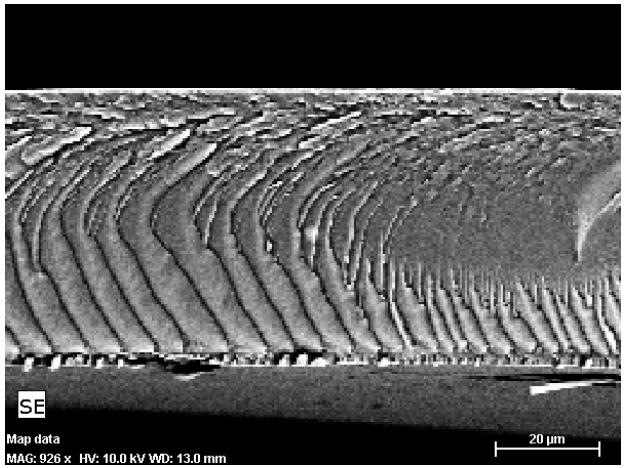
Weight % Water Swelling



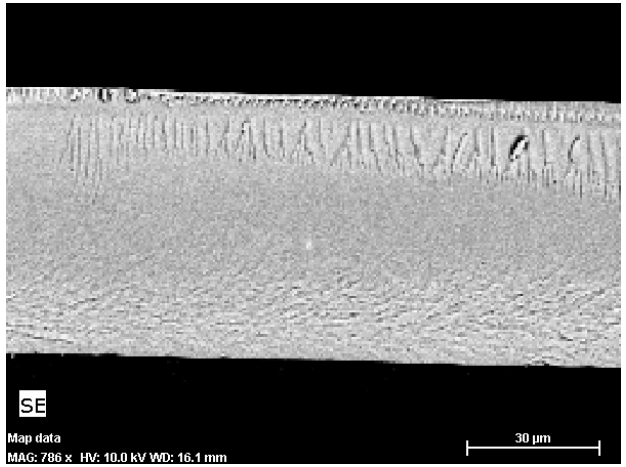
- Conductivity peaks at 180 mS/cm at IEC of ~3.1 meq/g.
- Conductivity decreases at higher IECs because of large water uptake.
- Uncrosslinked SDAPP dissolves in water at IEC of ~3.5 meq/g.
- EXSDAPP membranes with IEC ≤ 3.1 are tough and easy to process into MEAs.

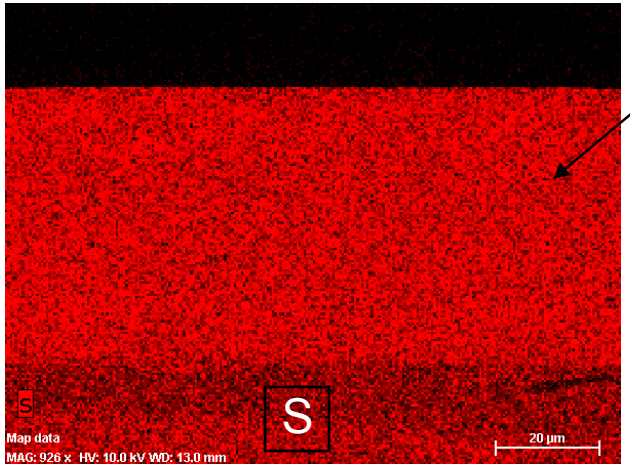
Sandia National Laboratories

SEM and EDS of EXSDAPP



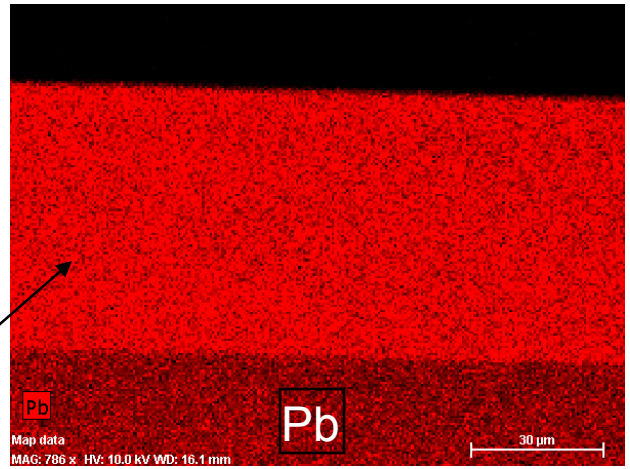
EXSDAPP with
IEC = 3





Even distribution of sulfur across membrane

Membrane stained with lead acetate and washed

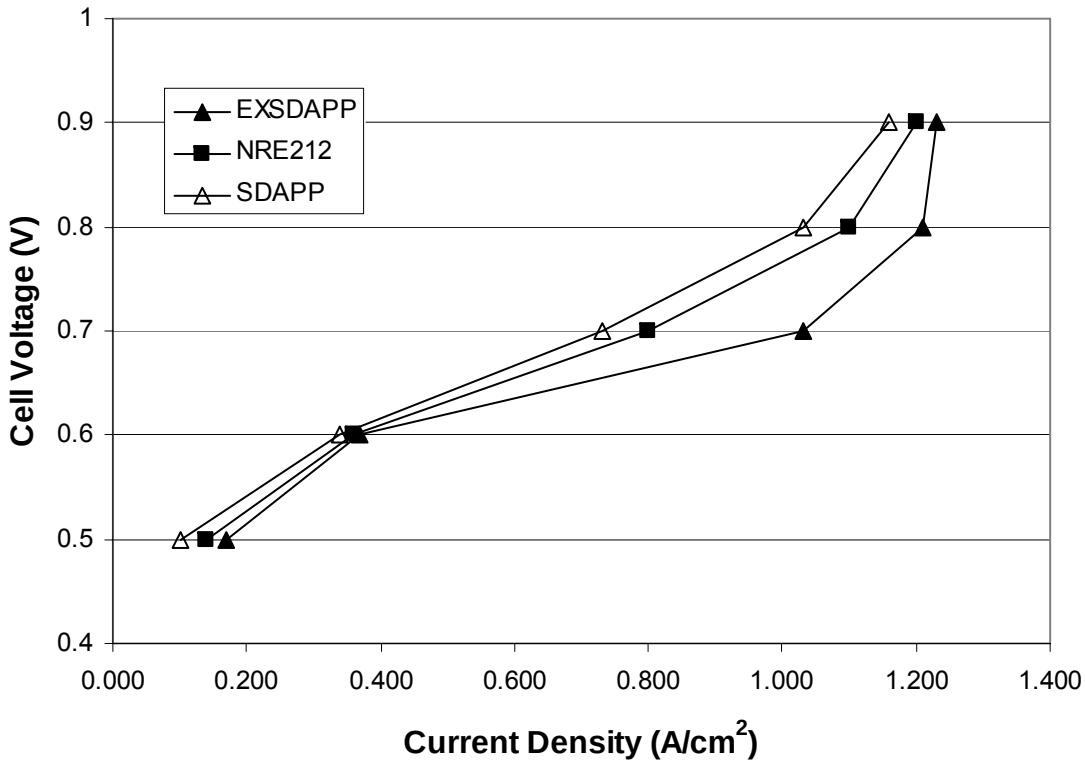


There is no indication of uneven sulfonation.

Sandia National Laboratories

Electrolyzer Performance

Operating conditions: 0.7 V, 120 ^{o}C 100 sccm SO_2, 10 mL/min H_2O, 25 psig backpressure.

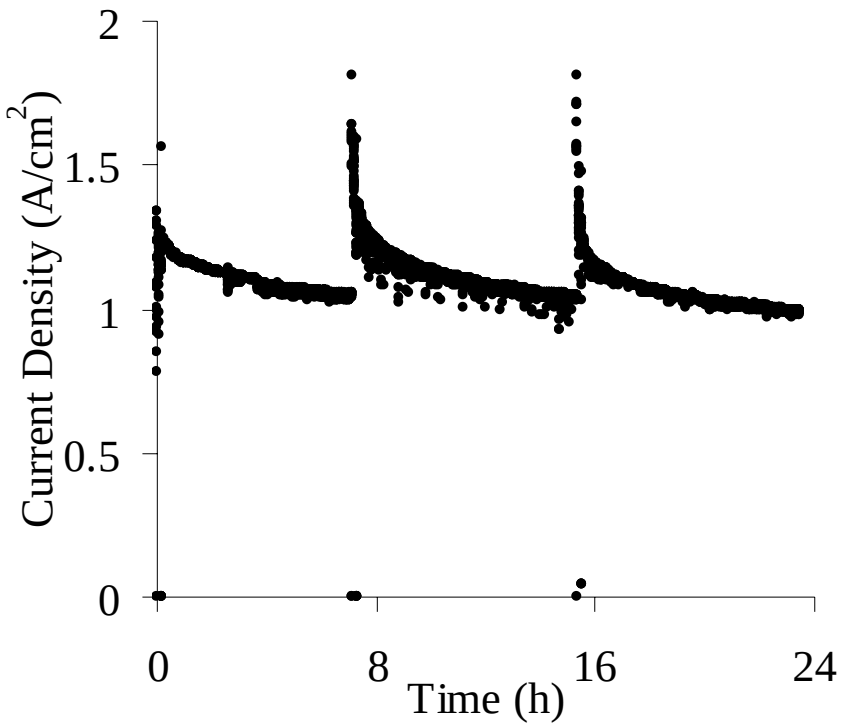


- All three membranes are 45–50 microns thick.
- At 0.7V, current density with EXSDAPP is ≥25% greater than for SDAPP or Nafion.
- In some tests with EXSDAPP, 1.3 A/cm^2 at 0.7V has been reached!

Sandia National Laboratories

24-Hour Test with EXSDAPP

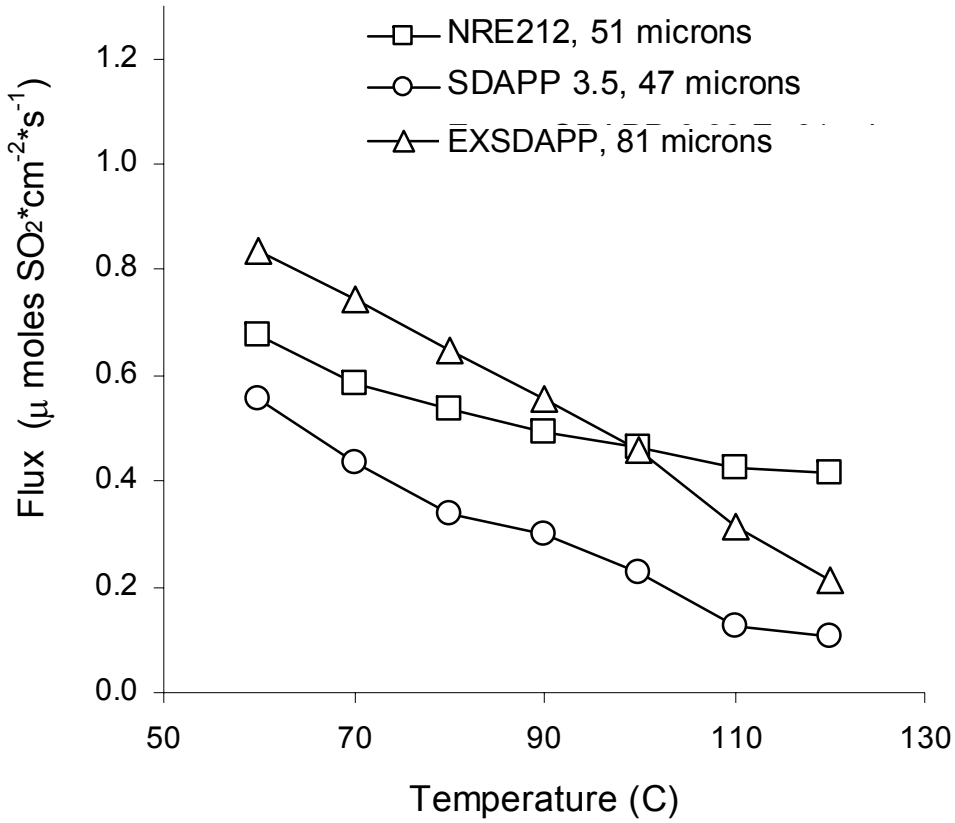
Operating conditions: 0.7 V, 120 ^{o}C 225 sccm SO_2, 10 mL/min H_2O, 25 psig backpressure.



- Cell was shut down after operating for 8 hours on 3 consecutive days.
- Current density slowly decreases but is fully recovered at each start-up.
- SO_2 conversion was 35% (based on feed rate and total current).
- High current density can be maintained at >1 A/cm^2 by increasing voltage to 0.9V for 10 minutes every 8 hours.

Sandia National Laboratories

SO_2 Crossover



- SDAPP and EXSDAPP have lower SO_2 fluxes than Nafion at T > 100 ^oC.
- EXSDAPP limits SO_2 crossover by enabling high conversion.

Sandia National Laboratories

Conclusions

Accomplishments

- Method for preparing crosslinked SDAPP membranes with high IEC has been developed (patent application filed).
- EXSDAPP membranes have at least 25% greater current density at 0.7V than SDAPP or Nafion with similar thickness.
- There is no evidence of elemental sulfur build-up when cell is operated at 120 ^{o}C.
- Cell with EXSDAPP has been operated for 24 hours with current density ≥1 A/cm^2 at 0.7V.

Issues

- Simplify membrane synthesis (1 sulfonation step instead of 2).
- Thinner EXSDAPP for even higher current densities?
- Stable operation at 0.6V?

Sandia National Laboratories

Acknowledgements

SEM imaging

Hector Colon-Mercado (SRNL)

Jiyoung Park (Clemson)

Bonnie McKenzie (SNL)

Help with SO_2 Crossover Measurements

John Staser (USC)

John Weidner (USC)

Sandia National Laboratories