High Temperature, High Pressure Electrolysis

Giner, Inc
Cortney Mittelsteadt
Jason Willey
Robert Stone

Virginia Tech
Judy Riffle
Jarrett Rowlett
Amin Daryaei

Jim McGrath

Project PD117

Project Overview

Timeline

- Project Start Date: 2/18/2014 (PI)
- Project End Date: 12/17/2016

Budget

- Fast-track $1.0M
  - Giner $780k
    - $421 k Spent
  - Virginia Tech $370k
    - $134k Spent
    - Contract delayed with passing of J.McGrath

Partners

- Virginia Tech

Barriers Addressed

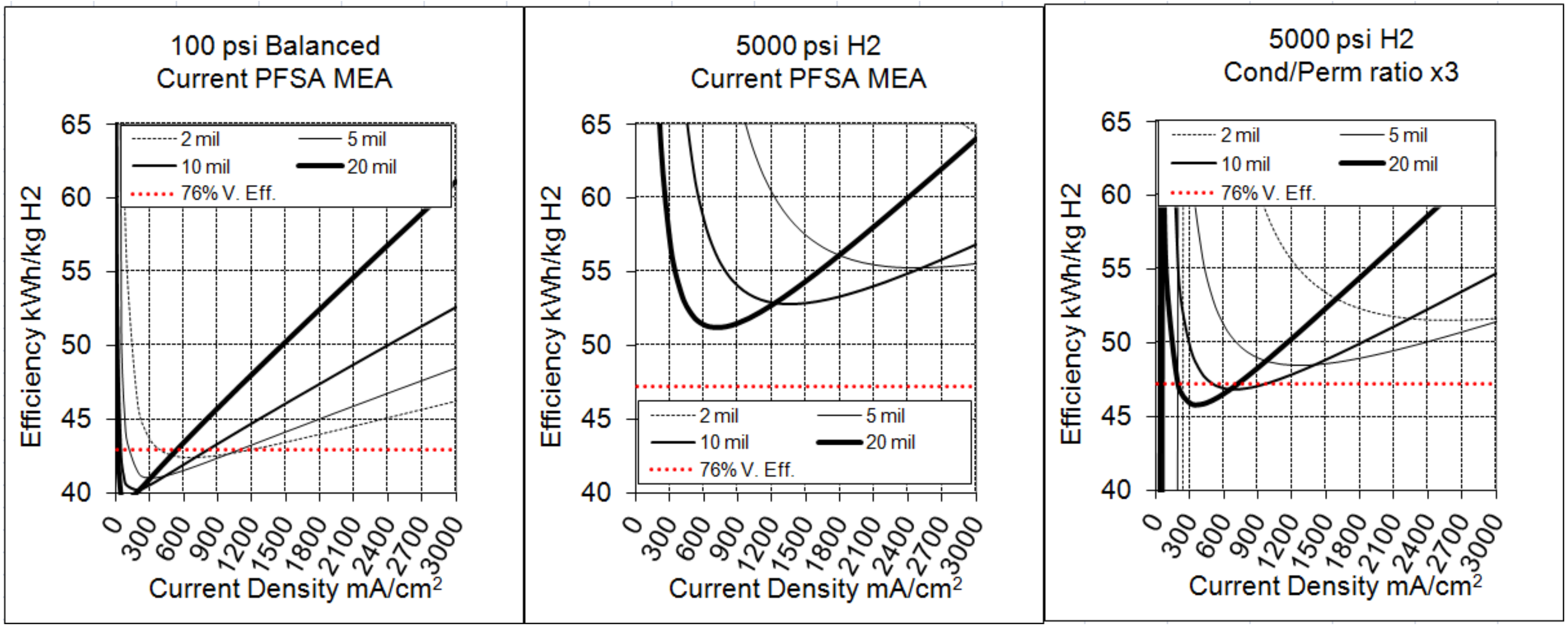
- Hydrogen Cost $4-5/kg

Technical Targets

Phase I

- 2x Conductivity: Permeability Ratio at end of Ph I
- **Phase II**
- 3x Ratio
- 95°C Operation for 1000 h 5000 psi operation for 1000 h
- Stack Delivery to DOE (NREL?) at end of PhII

Relevance: Pressure



Not Possible to have high efficiency at high pressure with current membranes

Increasing ratio is key to having large operating range: Essential for Renewables!

Relevance: Pressure

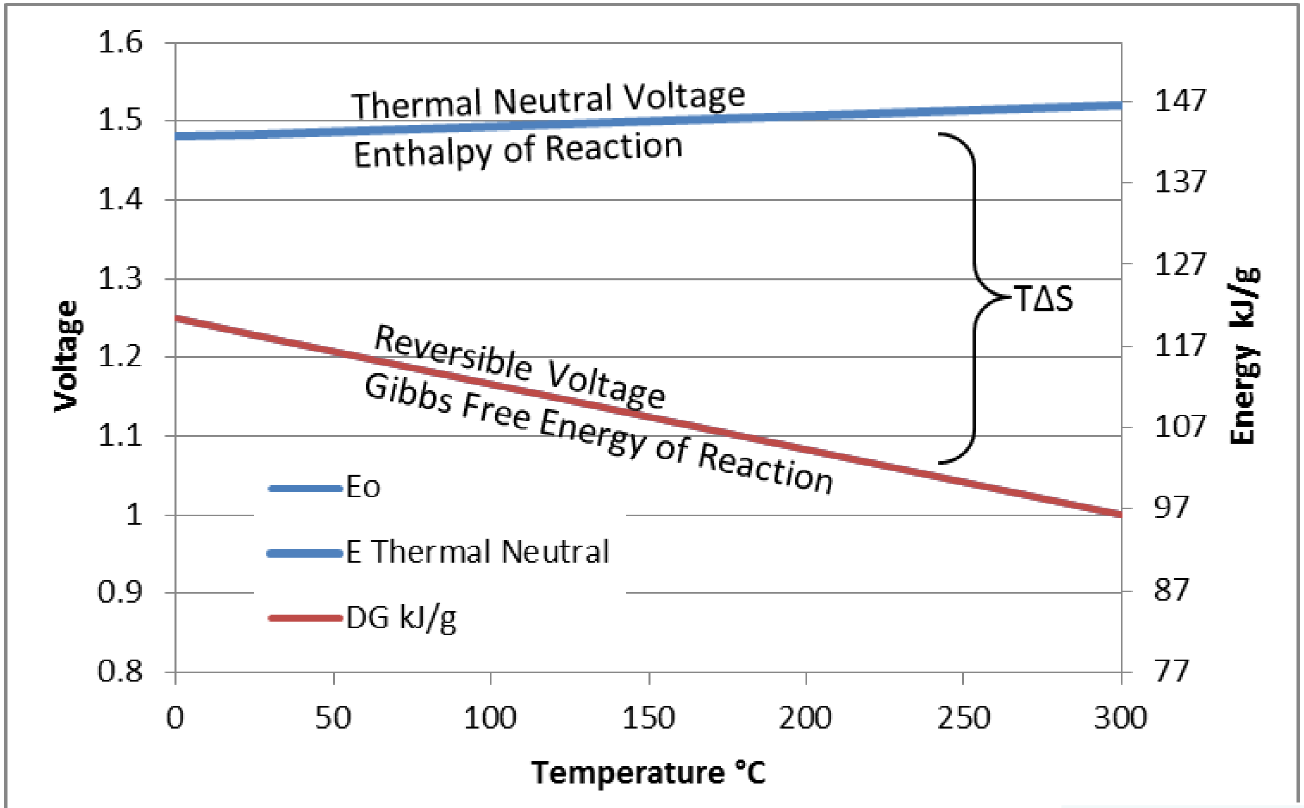
MEA
(After Disassembly)

Pressure always on to increase it!

Reduce Compression And maintenance costs

60°C 3500 PSI electrolyzer Nafion 110

Relevance: Temperature

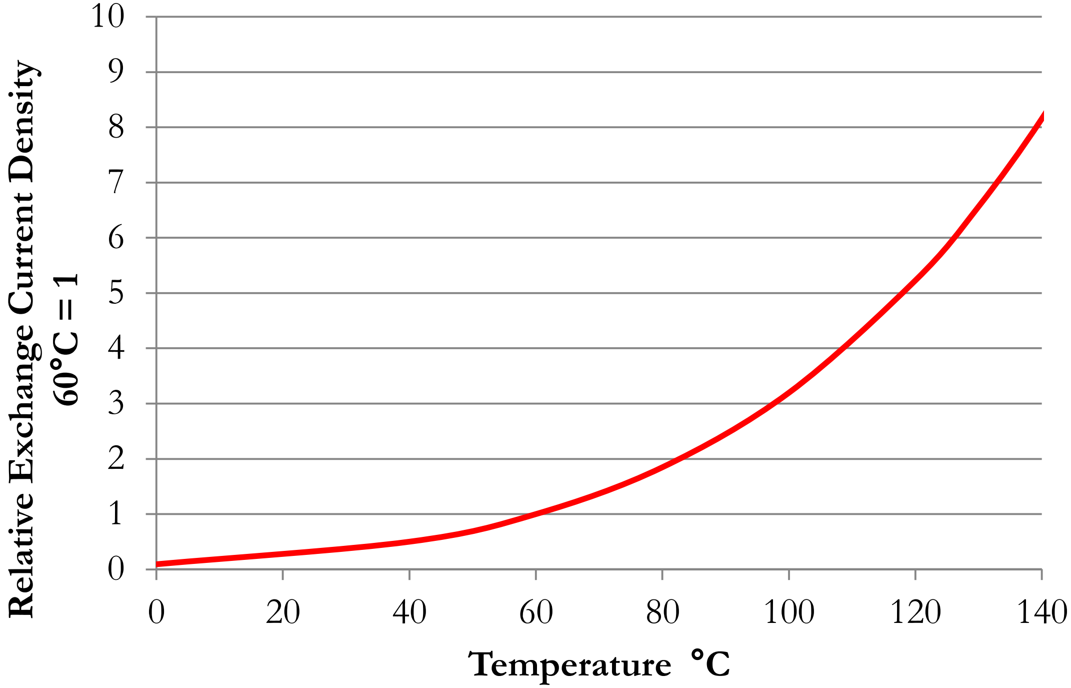


David Anthony, James Rand and Ronald Dell *Hydrogen Energy Challenges and Prospects* 2008.

Nearly 1 mV/°C decrease in Reversible Voltage

Larger TΔS means less heat to remove

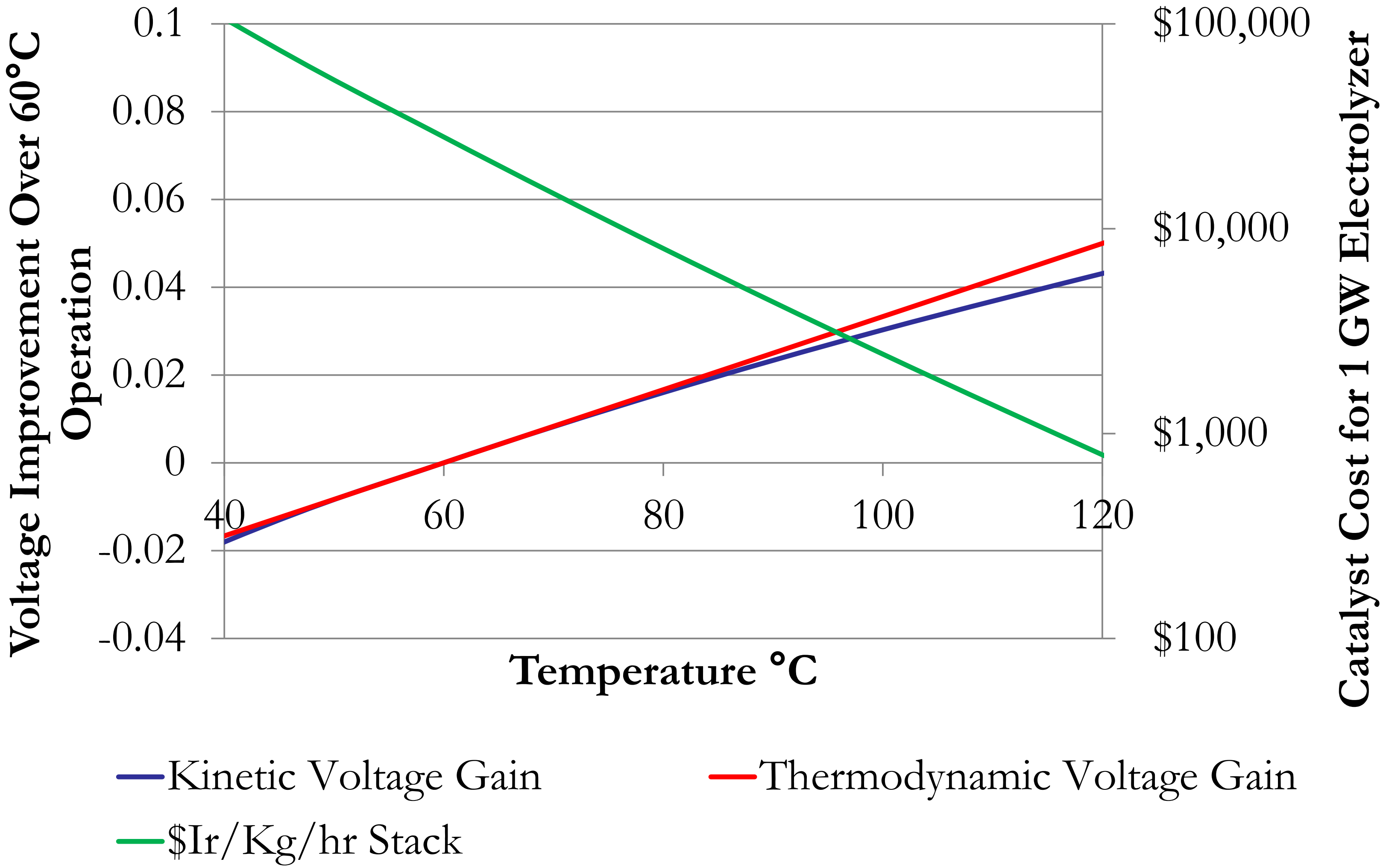
Relevance: Temperature



Oxygen Evolution Reaction
Has a High Activation Energy
~ 30 kJ/mol

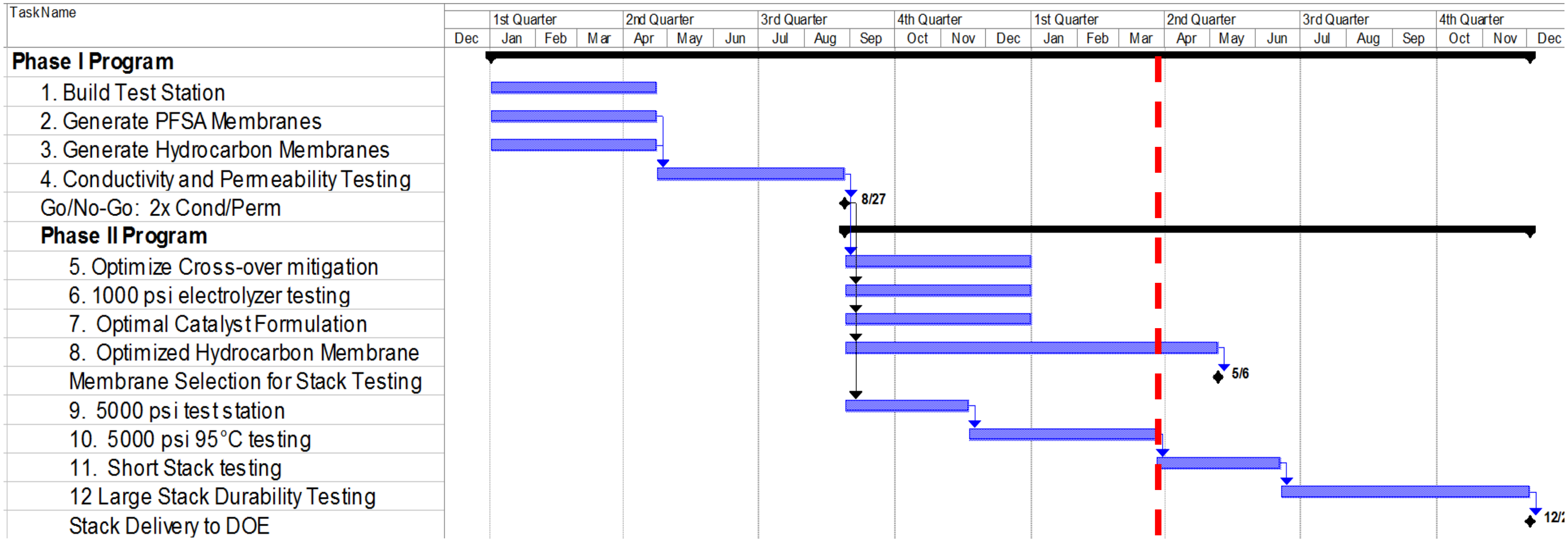
Going from 60 to 100°C results in an almost order of magnitude increase in kinetics

Relevance: $



Voltage Improvement Over 60°C Operation
0.1
0.08
0.06
0.04
0.02
0
-0.02
-0.04
40
60
80
100
120
Temperature °C
$100,000
$10,000
$1,000
$100
Catalyst Cost for 1 GW Electrolyzer
Kinetic Voltage Gain
Thermodynamic Voltage Gain
$Ir/Kg/hr Stack

Approach: Work Plan



Phase II is behind schedule in terms of timing, but not funding.

PFSA membrane selection has taken place

Catalyst formulation is complete

Hydrocarbon formulation is still undergoing

5000 psi testing has just begun

Accomplishments: Task 1. Build Test Station: 100% Complete

5000 PSI System Capable of Stack Testing is Available

Fabricated on DOE Home Refueling Program

Modified for diagnostic testing, individual cell monitoring

Accomplishments: Task 2. Generate PFSA Membranes 100% Complete

- Four Types of Membranes:

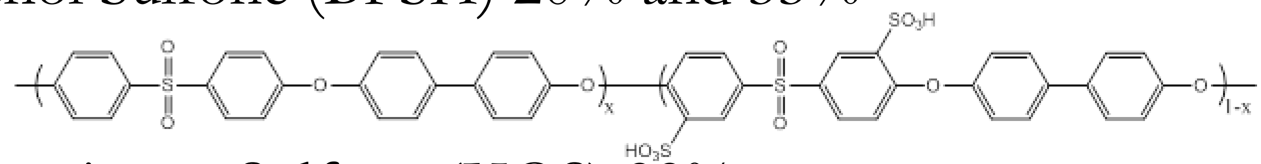
1. Different EW
2. Additives to limit crossover
3. Additives to limit degradation
4. Hydrocarbons

COMPLETED

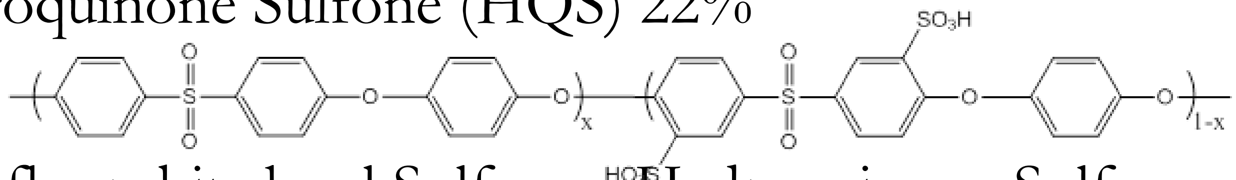
- Nafion 1100 EW
  - Used as the standard
- Nafion 1100 EW treated with cross-over additive
- Solvay Aquivion 790 EW
  - Short-chain PFSA
- 3M 825 EW
  - Short-chain PFSA

Accomplishments: Task 3. Generate HC Membranes 100% Complete

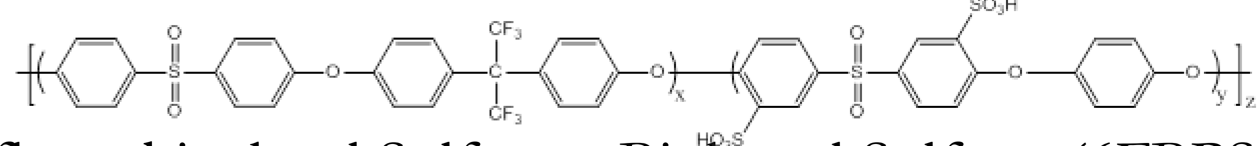
- Biphenol Sulfone (BPSH) 20% and 33%



- Hydroquinone Sulfone (HQS) 22%

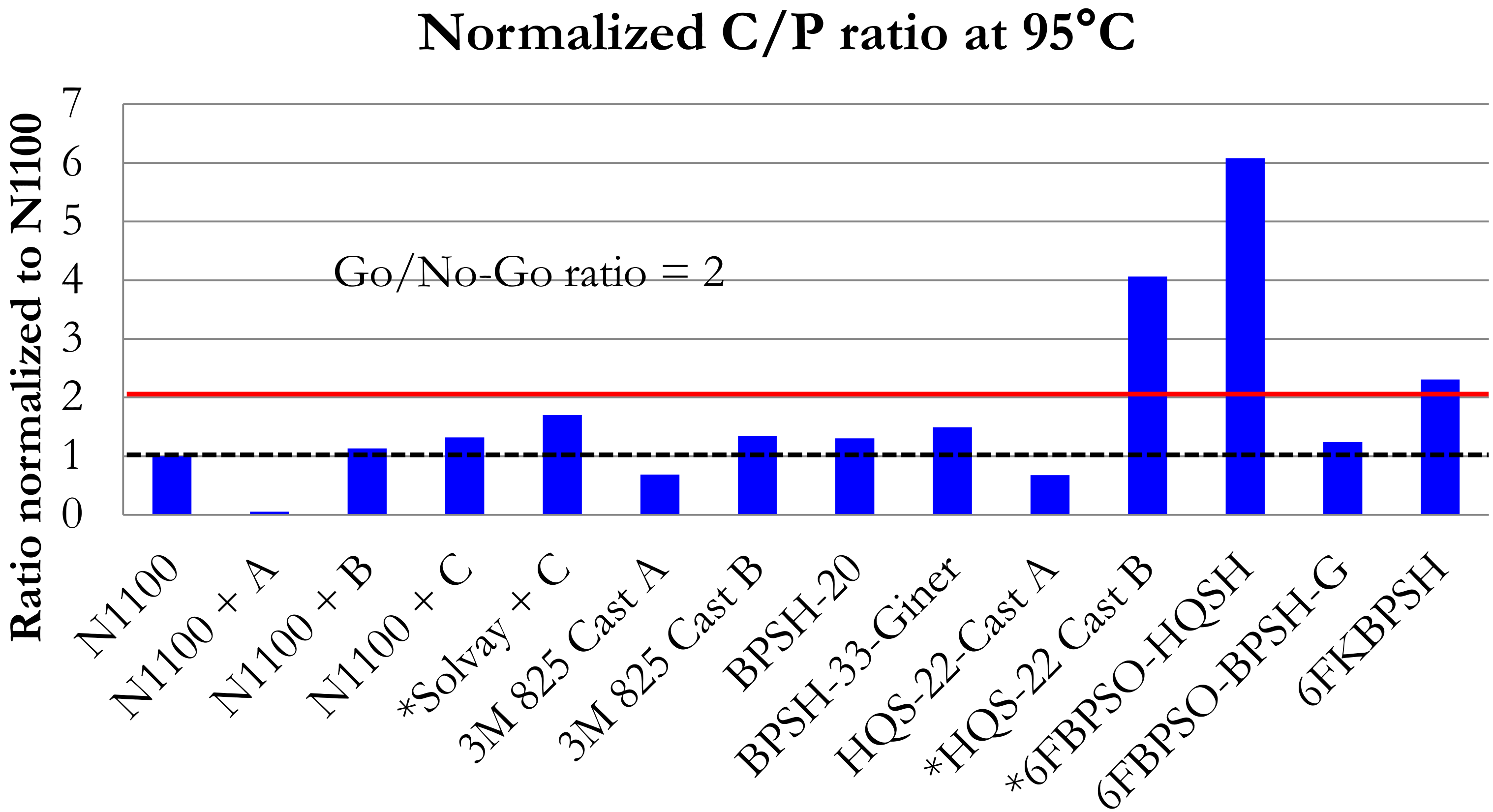


- Hexafluorobipehnol Sulfone - Hydroquinone Sulfone (6FBPS0-HQSH)



- Hexafluorobipehnol Sulfone - Biphenol Sulfone (6FBPSO-BPSH)
- Hexafluoroketone Bipehnol Sulfone (6FKBPSH)

Accomplishments: Task 4. Measure Conductivity to Permeability Ratio



Exceeded go/no-go with 3 membranes, almost 4.

Accomplishments: Task 6.

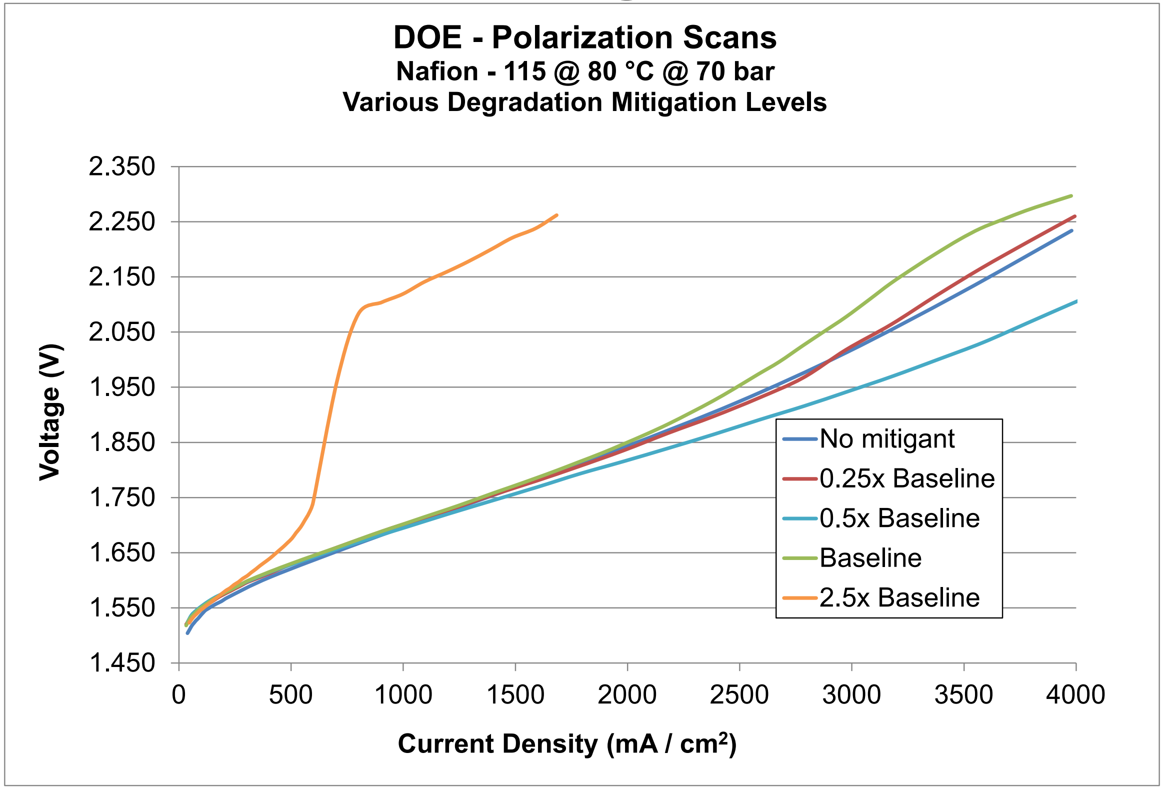
Temp 40-95°C, 7-70 bar

Test #	Membrane	Type	XM*	DM (%)**	Test length (hrs)	Failure	Est. Life (hrs)†
1	N115	PFSA	yes	0	518	no	7,000
2	N115	PFSA	yes	0.25	456	no	>100,000
3	N115	PFSA	yes	0.5	411	no	>100,000
4	N115	PFSA	yes	1	552	no	>100,000
5	N115	PFSA	yes	2.5	1017	no	>100,000
6	Solvay E79	PFSA	yes	0	697	no	4,000
7	Solvay E79	PFSA/DSM	yes	0.5	488	no	15,000
8	Solvay E79	PFSA	yes	0.5	356	yes	-
9	HQS-22	HC/DSM	no	0	25	no	-
10	HQS-22	HC/DSM	yes	0	41	yes	-
12	HQS-22	HC	yes	0	74	yes	-
13	HQS-22	HC/DSM	yes	0.5	20	yes	-
14	HQS-22	HC/DSM	yes	0.5	2	yes	-

* XM = Crossover Mitigation Added. ** DM = Degradation Mitigation Level as multiple of baseline amount.

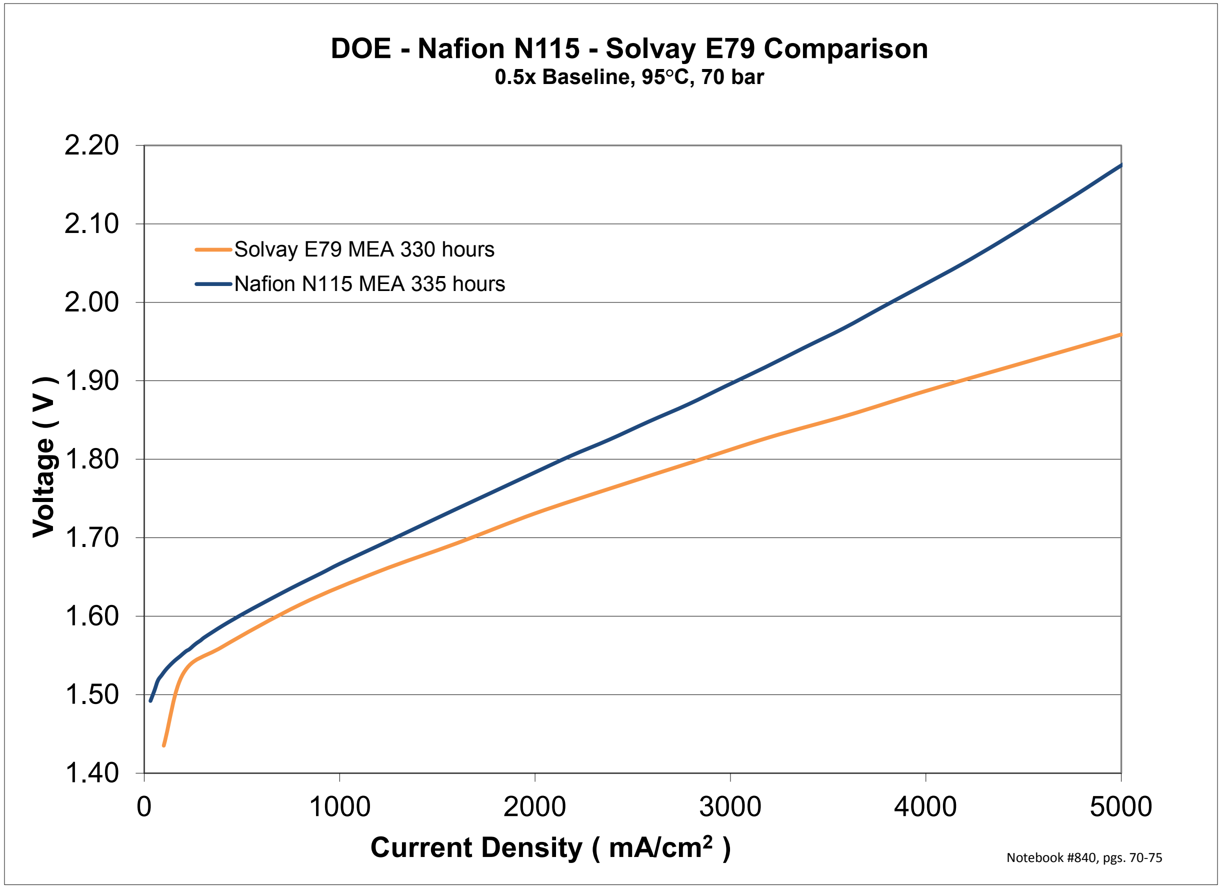
† Estimated Lifetimes are for MEAs operated at 95°C and 70 bar. Lifetimes are estimated by loss of 10% of membrane fluoride inventory as measured by F- release in cathodic water.

Accomplishments: Task 6. Degradation Mitigation



Higher mitigant levels affect performance, especially at higher current density

Accomplishments: Task 6. Alternate PFSA



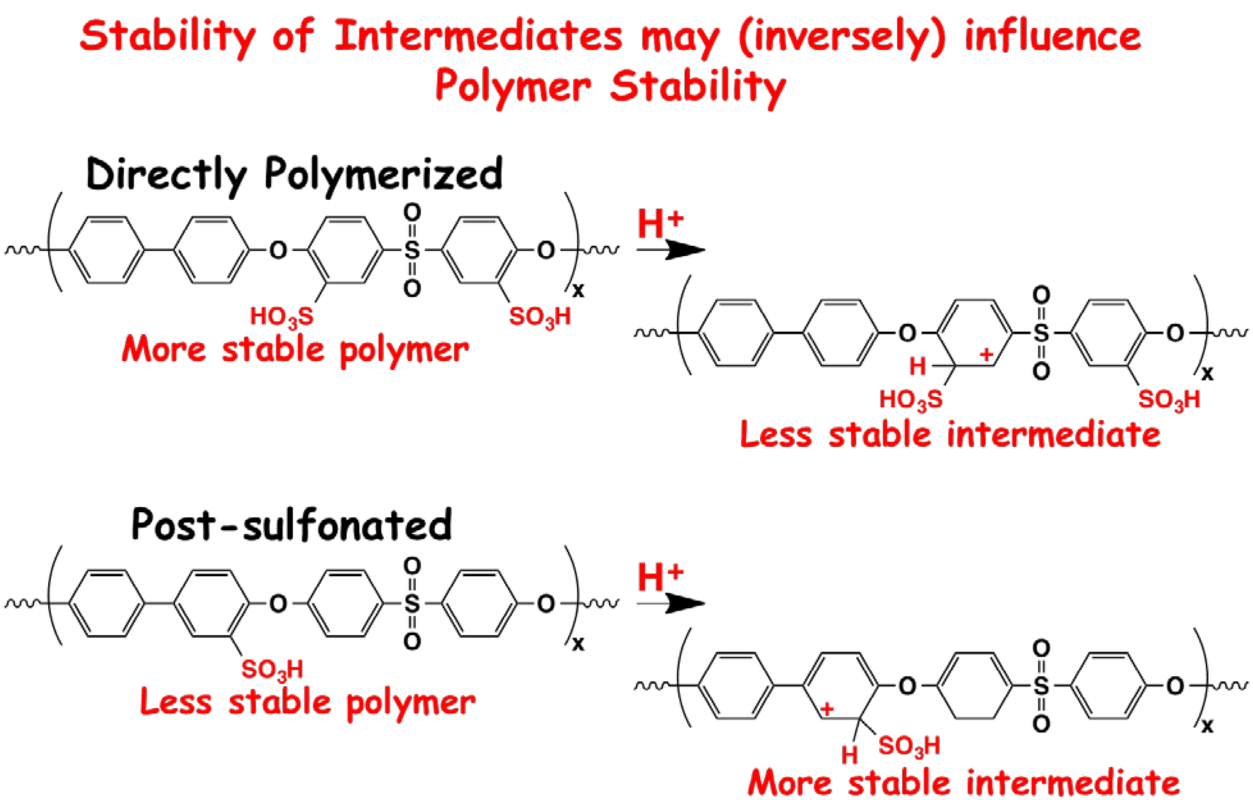
Performance of Solvay E79 MEA (100 μm thickness) is higher than N115 at the stated conditions

Accomplishments: Task 7. Optimize Catalyst Layer

- At high temperature the ionomer in the catalyst layer swells, reducing electrical contact of the catalyst particles and decreasing the performance gain
- Giner has started work on a catalyst layer with higher equivalent weight ionomer to reduce swelling at high temperatures

Accomplishments: Task 8. Develop Improved Hydrocarbon Membrane

Relative stability against loss of $-SO_3H$ by electrophilic aromatic substitution in strong acid: H^+



Future Work is to increase chemical stability of the chain itself

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Accomplishments: Task 9&10. 350 bar Testing

- A Solvay E79 DSM MEA has been fabricated for installation in the high pressure hardware to begin 350 bar operation.

Collaborations

- Virginia Tech
  - Subcontractor, generating alternative membranes
  - Employed Student at Giner for one Week to maximize interaction
- 3M
  - Supplying Ionomer

Future Work:

- Task 6. Two more test
  - Repeat of Solvay DSM
  - New hydrocarbon MEA
- Task 7. Optimal Catalyst Formulation
  - Effective lower loading
  - Higher EW ionomer
  - Post-mortem testing
- Task 9-10. 5000 psi, 95°C testing
- Task 11. Short Stack Testing
- Task 12. Long-term verification (5000h goal)

Summary

- Four membranes developed with a 2x Conductivity/Permeability Ratio improvement
- 1000 h at 95°C demonstrated
- 500 h at 95°C and 1000 psi demonstrated
- MEA testing of hydrocarbon materials
- 14 tests at 70 bar completed to determine high-pressure candidate
- High pressure (5000 psi) test to begin soon

Response to Reviewers Comments

- Overall reviews were quite positive, we report only on the constructive criticisms or where we believe there may be a misunderstanding. Comments are in black, our responses in red.
- While the C/P ratio is good for screening, it is also desired to simultaneously have high conductivity. Thus, screening for conductivity might be an important adjunct to the C/P metric.
  - We are confused by the reviewers comment. In order to obtain the conductivity/permeability ratio we must measure each. In the absence of mechanical failure, we can choose our membrane thickness based on acceptable permeability, each are equally important.
- Additional testing of the alternative membranes is both necessary and planned. Actual validation at 5000 psi (with comparison to the baseline membrane) is critical.
  - We will test at 5000 psi, we do disagree however as how critical this is to overall success of the program as we believe there are only few cases where direct electrolysis to 5000 psi are economical.
- It is not clear whether the proposed process to directly generate high-pressure hydrogen is more economically valuable than the existing techniques, which generate hydrogen at low pressures and then use compression
  - We agree with the reviewers comments that direct high pressure electrolysis is not always the most economical. In cases where footprint and maintenance are key drivers however it can be the difference between H_2 being accepted. We will do a more thorough case analysis this period