

2006 DOE Hydrogen Program Review Platinum Recycling Technology Development

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Project ID #
FC35

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Overview

Timeline

- Project start Aug 2003
- Project end Aug 2008
- Percent complete: 50%

Budget

- Total project \$3.31M
 - DOE share: \$2.65 M
 - Contractor: \$0.66 M
- FY05: \$0.48 M
- FY06: \$0.63 M

Barriers

- Barriers addressed
 - O: Stack Materials and Manufacturing Costs
 - P: Durability
 - (vitality measurements of materials recovered from end-of-life components will identify failure modes)

Partners

- DuPont, Delaware State University, NIST, Ballard, BCS Technology, Plug Power, Drexel University

Objectives

- To assist the DOE to demonstrate a cost effective and environmentally friendly recovery and re-use technology for PGM containing materials used in fuel cell systems.
- Use new processes that can also separate and recover valuable ionomer materials
 - DOE 2010 *targets* for membrane costs indicate membrane has value equal to the PGM

Approach

- Use solvents to “dissolve” ionomer and physically separate catalyst from ionomer solution in 1 sq meter batch sizes.
- Make best attempt to re-manufacture catalyst coated membrane with recovered materials; although may not be commercially acceptable
- Will learn failure modes of MEA materials used in fuel cells; ionomer and catalyst
- Use analytical techniques to determine the differences between used and virgin materials
- Determine the limits of separation technologies
- Economic analysis at pilot scale equipment will be used to determine feasibility of approach.
- Value of recovered NAFION® will likely be found in different application other than fuel cells; e.g. acid catalysis for organic synthesis.

Technical Accomplishments/ Progress/Results

- Examined batch materials from actual end-of-life systems of 4 different OEMs
- Identified Significant amounts of contaminations in end-of-life membranes, Ammonia, Sodium, Metals, and PGMs
- Identified methods to remove foreign cations during fuel cell operation.
- Demonstrated the end-of-life NAFION[®] membrane retains much of its original properties,
- Scaled-up the separation equipment, provides materials, and information for cost analysis.
- Improved catalyst vitality test to work in the presence of small amounts of NAFION[®]

End-of-Life NAFION®

Looks Like:



What's all that Brown stuff?

Where did it come from?

How much effect on FC Performance?

How to get rid of it?

Can the NAFION® be restored?

What's all that Brown stuff?

OEM A:

1) Determine foreign cation concentration via titration

→ 22% of Ion Sites occupied by non-H⁺ cations

2) Extract foreign cations with HCl and analyze with ICP:

Co: 1 ppm	Al: 60 ppm	
Cu: 5 ppm	Cr: 30 ppm	
Mn: 4 ppm	Fe: 130 ppm	
V : 3 ppm	Ni : 60 ppm	
Zr : 0.1ppm	Zn: 50 ppm	Na: 1700 ppm
=====	=====	=====
Total % of sites 0.048 %	2.1%	8.1%

3) Ammonium cation content measured separately to be 11%

4) Run Hours : High

5) When membrane is exposed to Hydrogen Peroxide it blisters

→ PGM's have migrated into interior of membrane during operation

Dissolved membrane and centrifuged out 0.026 mg PGM/cm²

Original MEA had 2 mg PGM/cm², thus 1.3% has migrated into membrane

Suspect this is large contributor to the brown color since it is a metal deposit

What's all that Brown stuff?

OEM B:

15% of IEC contaminated

Ammonia detected but less than our current quantification limit

PGM content inside membrane high, not yet quantified

Run Hours : High

OEM C:

13% of IEC Contaminated, Ammonia content faintly detected

PGM content inside membrane low,

Run Hours : Low

MEAs from DMFC

Acid Capacity Test*:

FRESH MEA : 0.914 meq/gram

*Analysis by Dennis E. Curtin of Dupont

FRESH MEA : after complete acid exchange 0.960 meq/gram

EOL MEA : 0.831 meq/gram (~13% capacity lost)

EOL MEA : after complete acid exchange 0.954 meq/gram

Contaminates Found*, ppm

Element	Fresh MEA	EOL-MEA Sample1	EOL-MEA Sample 2		% of Total IEC
NH ₃		Detected by Ion Power methods but not quantified			
K	170	303	348	ppm	0.8%
Na	170	331	341	ppm	1.6%
Ca	92.7	680	694	ppm	3.8%
Ni	10.2	352	353	ppm	1.3%
Fe	53.4	97.2	103	ppm	0.6%
Cr	9.8	15.6	15.5	ppm	0.1%
TOTAL:					8.2%

Conclusion: DMFC MEAs pick up contamination during life,
however they can be restored via a “cleaning” step

Where did it come from?

- Sometimes ratio of the metals is close to 316 Stainless Steel

Cr: 30 ppm

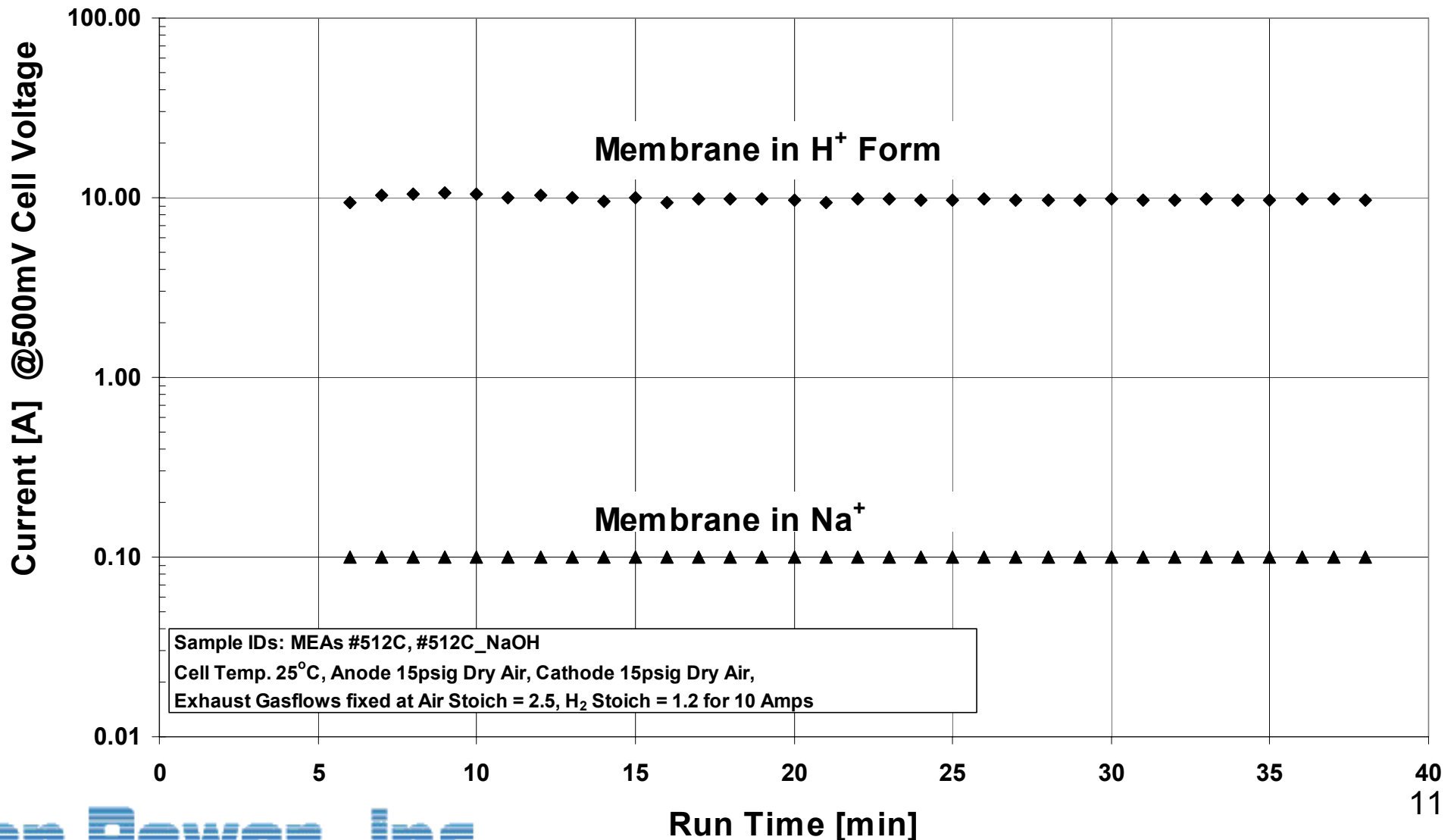
Fe: 130 ppm

Ni : 60 ppm

- Ammonia is likely coming from “Low quality Hydrogen”
- PGM is obviously coming from the electrodes, Should be considered a non-recoverable degradation
- Sodium is likely coming from incomplete acid exchange during membrane manufacture and/or during operation.

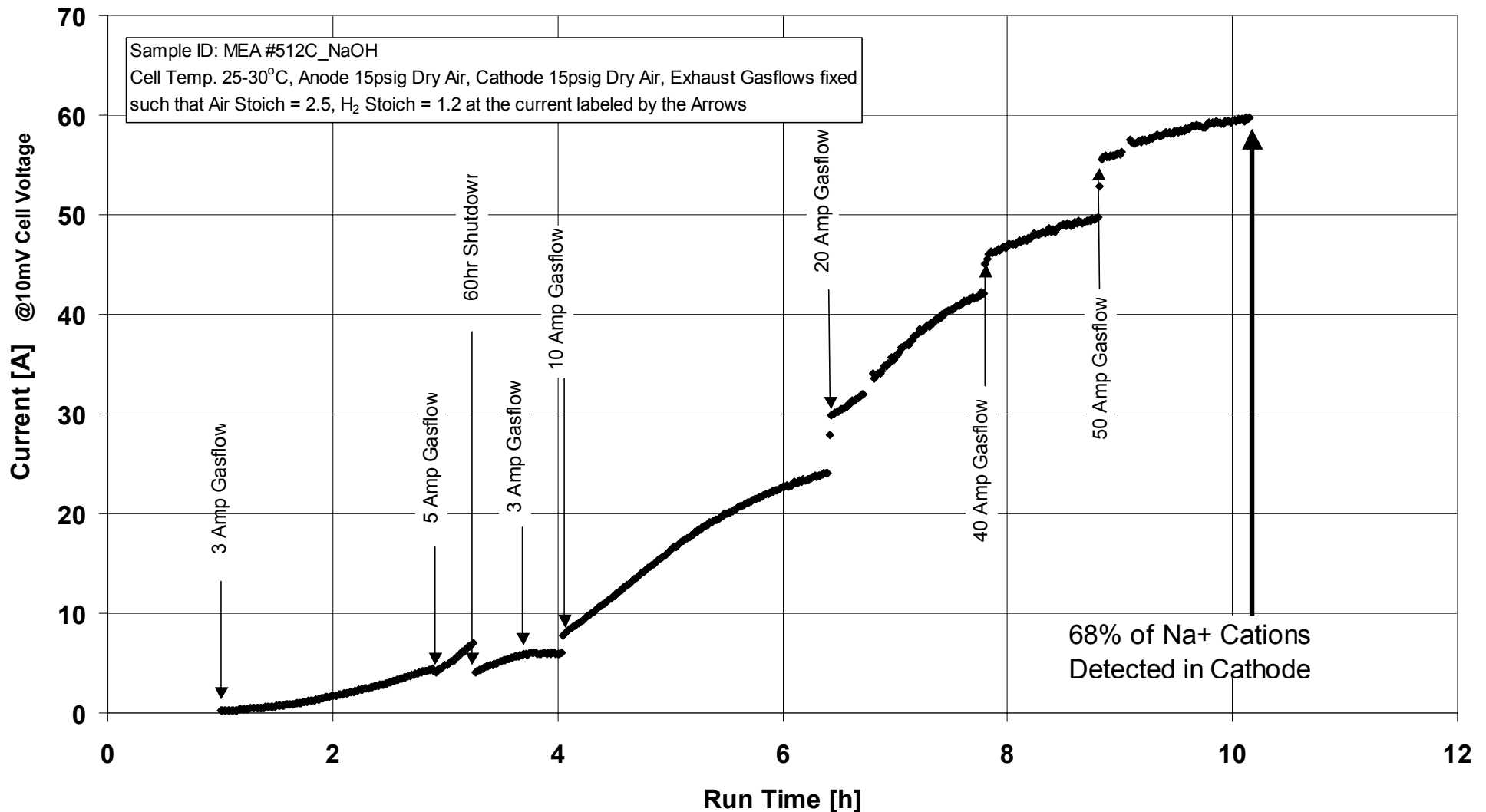
Effect on Fuel Cell Performance?

Initial Performance Difference between Membrane in Na^+ -Form & H^+ -Form



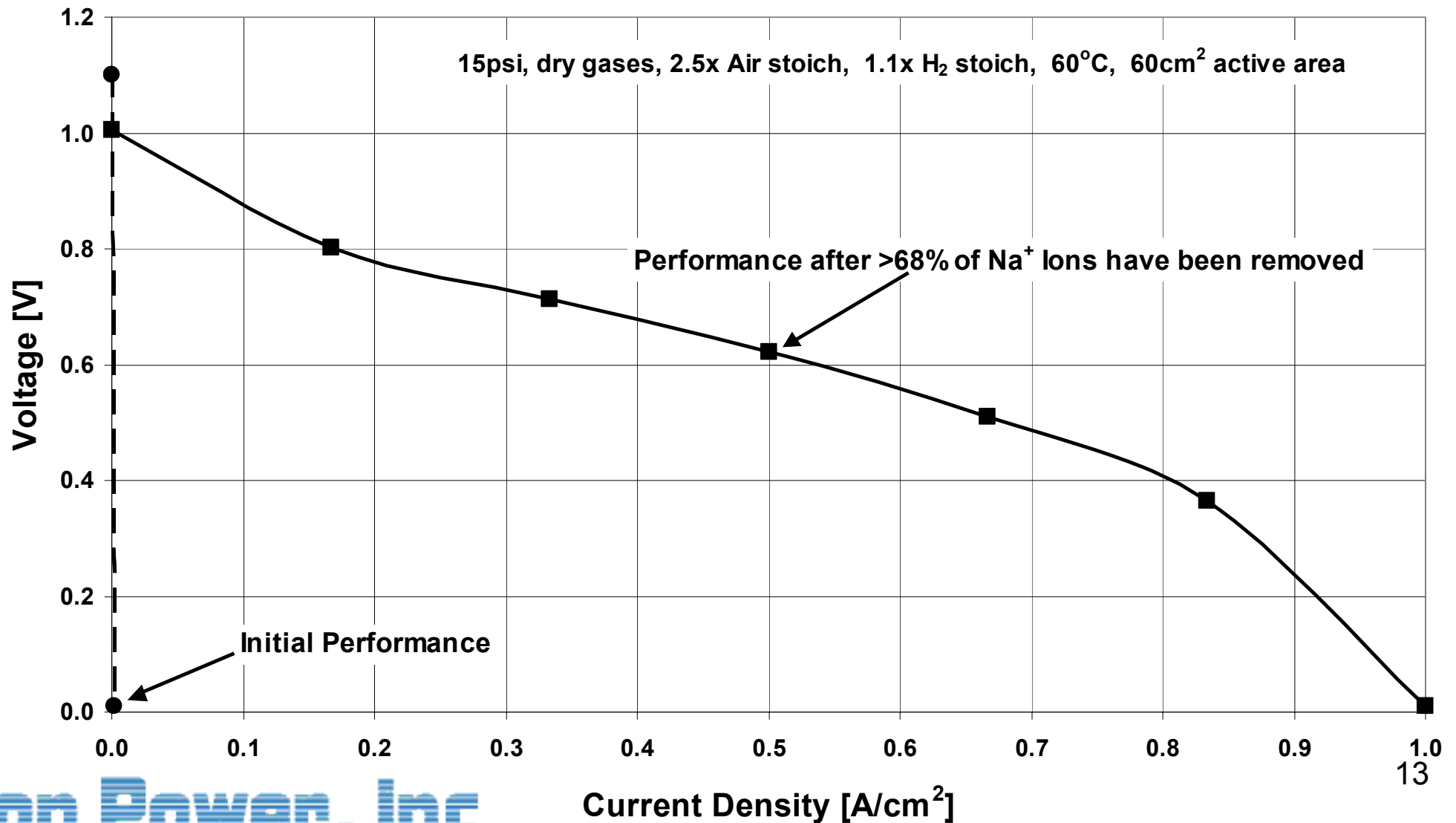
Effect on Fuel Cell Performance?

In-Situ Membrane Purification via Na^+ - Cation Removal during High Proton Flux Operation



Effect on Fuel Cell Performance?

Performance Before and After Removal of Na⁺ Cation via High Proton flux Operation



How to Get Rid of it & Restoring the NAFION®

- PGM Removal from membrane interior likely difficult with aqua regia, However easy via ionomer dissolution and centrifuge.
 - represents 86 troy oz/tonne of membrane
 - \$100 Pt / kg of membrane
- After removal of the cations via acid exchange, the acid capacity is equivalent to the fresh NAFION®

Processing, OEM A,B,C, DMFC

OEM A: Catalyst applied to GDL (Cloth based)

Solvent swelling released membrane cleanly,

However catalyst largely remains on GDL

Hand peeling releases GDL free of PGM, Then solvent rinse catalyst

OEM B: Catalyst applied to GDL Paper based

Solvent swelling at room temperature releases membrane cleanly.

Some catalyst remains on GDL;

OEM C: Catalyst applied to GDL Paper based

Solvent swelling at room temperature releases membrane cleanly.

Some catalyst remains on GDL.

OEM DMFC : Solvent swelling of membrane at atmospheric pressure will release catalyst from the membrane with mild agitation. → separation can be done without autoclave

Process Energy Analysis

Worst Case Scenario

Reactor size: 300 Liters

1550 kg metal mass

Charge with 145 kg solvent, 30 kg MEAs (with GDL, Typical Lot)

Delta T: 250 C

60 kW-Hr required to heat Metal and contents

Centrifuge: 1 kW for 1 Hr (Estimated)

Output: \$54,500 / day → Will reduce by 10x if DOE 2015 goals are met → \$5,400

Pt: Typical of Today's MEAs at 0.8 mg Pt/cm² total

2-3% of MEA weight (0.75 kg) = \$27,500 (\$1100/try oz)

NAFION® : 30% of MEA weight (9 kg) = \$27,000 (\$300/sq meter)

GDL : 65% of MEA Weight (20 kg) = No value

Costs : Total: \$656/day

Energy: \$0.10/kW-hr : \$6.10

Man-Power: Estimate 8 Man-hours : \$300

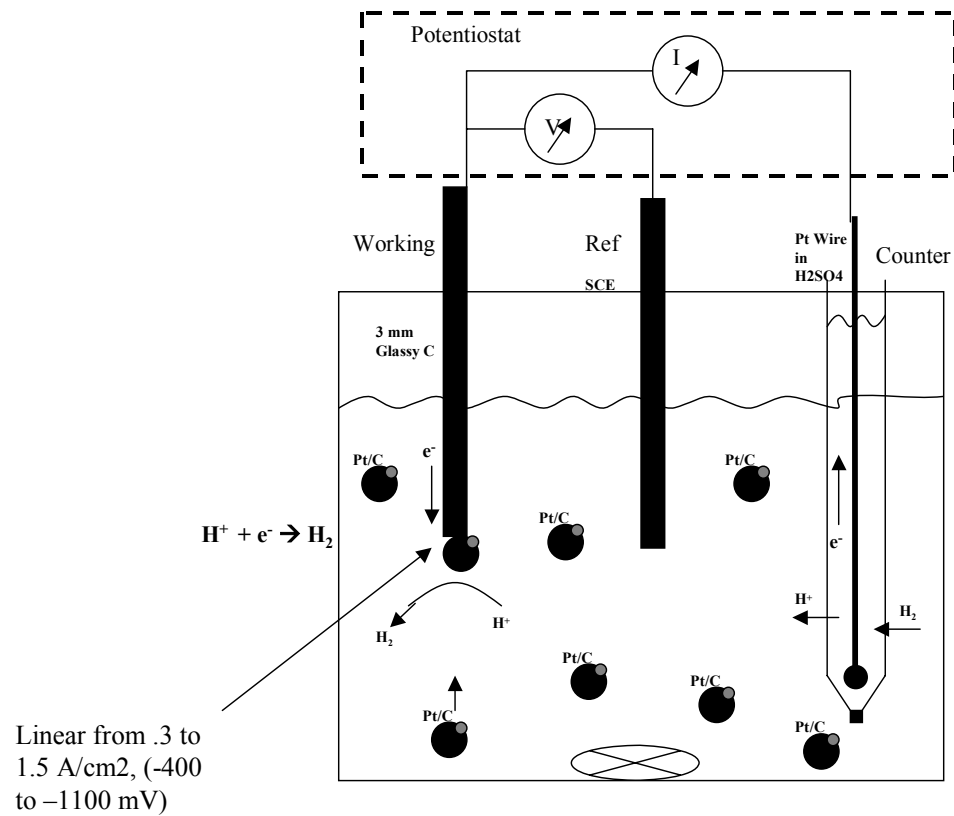
Solvents And Acids can be re-used; Estimate : \$100 cost

Capital Equipment Costs : ~ \$500k; or \$250/day (if used each day)

Catalyst Vitality

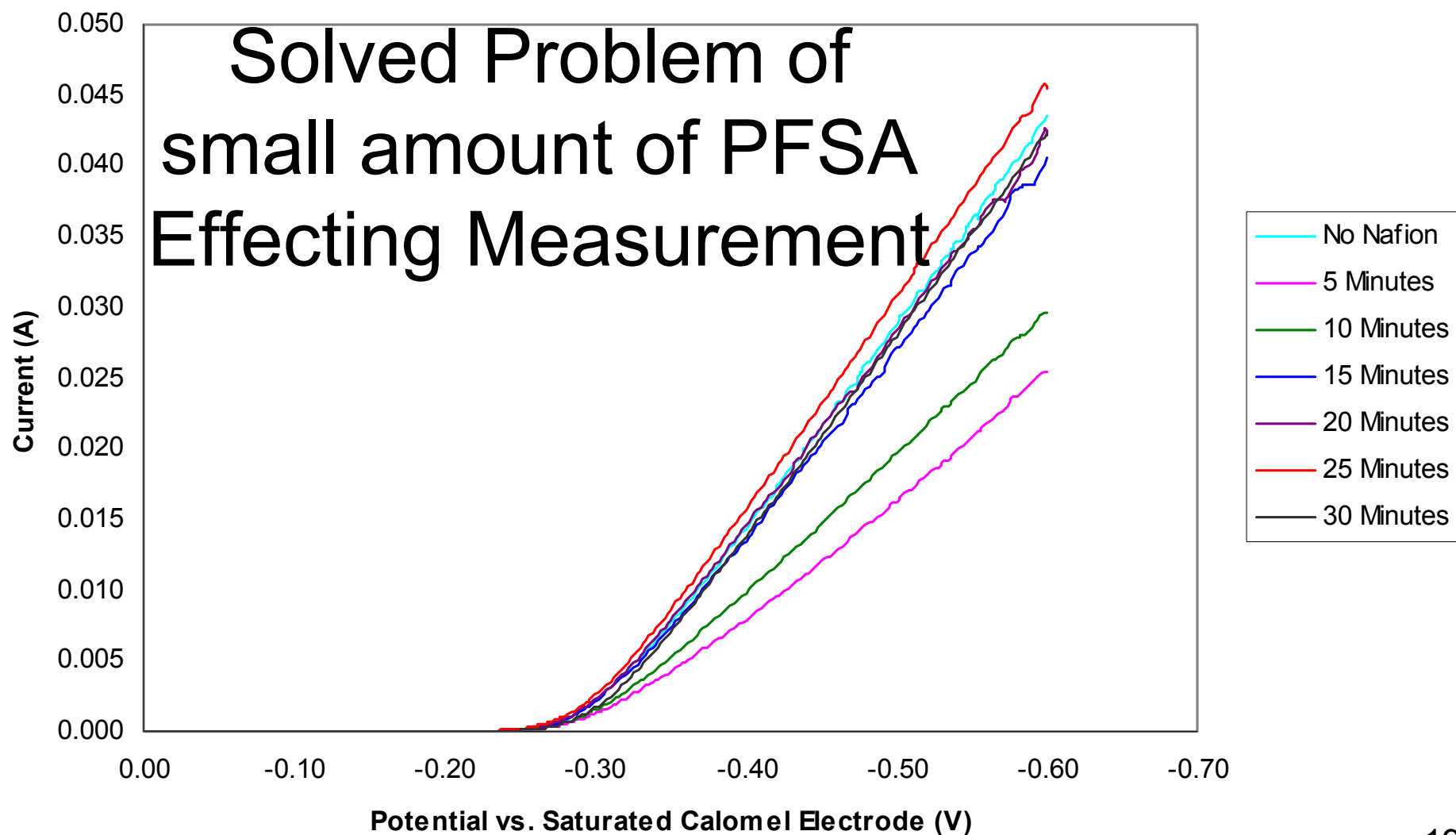
- Existing catalyst vitality tests are effected by the presence of small amounts of PFSA, e.g. CO Chemisorption
- Developed a new test that can be useful in the presence of small amounts of PFSA

Catalyst Vitality



Catalyst Vitality

Linear Sweep Voltammograms (LSVs) showing the effect of sonication on Nafion (0.82 mL of 1% w/v water based) solution added to 200 mL of 0.25g/L Pt/C suspension in 10% w/v H_2SO_4 . LSV with no Nafion label is before adding the Nafion solution.



Responses to Previous Year Reviewers' Comments

- Need to look at all MEA suppliers
 - Studied MEAs from 4 different major OEMs, all are close to commercialization
- Needs more emphasis on process costs
 - Scaled process further to estimated commercial batch size
 - Estimated costs of full size reactor, capital, labor, energy
- Needs more emphasis on fundamental properties of the NAFION[®] how it has changed
 - Studied in detail the cation contamination of the membrane this year, via ICP, and ammonia analysis.
 - Worked with NIST to study Neutron Scattering images of re-cast and virgin NAFION; work accepted at *Macromolecules*

Critical Assumptions & Issues

- Developing a market for recovered polymer. When PGM is recovered it is like cash, ionomer needs to find a customer to purchase; I.e. an application. @ current market price of \$2000-\$4000 \$/lb I think we can find one! Its more valuable than aluminum cans!
- Developing a process that is robust enough to easily handle the variety of materials being produced today and in the near term. Advantage: recycling is always working on last year's materials; and has foresight of adapting to new materials entering market.
- Collection of end-of-life systems, and education of consumers on where and how they get value out of returning end-of-life systems into recycling stream.

Future Work

- Remainder of FY 2006:
 - Demonstration of vitality of separated materials
 - Re-manufacture additional MEAs, test for lifetime
 - Further scale-up processing to refine process and gather more economic information
- FY 2007-2008:
 - Will search out different membrane manufacturers other than NAFION® and determine applicability of recycling process.
 - Remanufacture and Test
 - Demonstrate a fuel cell running on remanufactured CCMs
 - Both the catalyst and the membrane
 - Test for lifetime as well
 - Economic analysis
 - Based on best known pilot scale method estimate scale required to become competitive and profitable over existing methods of PGM recycling.

Publications and Presentations

- Patent filing for Recycling process, March 2005, Notification of Allowance of Claims
- USCAR/DOE Tech-Team Meeting, Feb 2006 Detroit MI Grot, et al. "*Platinum Recycling Technology Development*";
- Grot, et al. "*Platinum Recycling Technology Development*"; 2005 Fuel Cell Seminar, Palm Springs, CA, Nov 2005
- Fourteenth Annual Mid-Atlantic HBCU Science Research Conference, Princess Anne, MD, April 12, 2006, "Electrochemical Studies of the Suspension of Platinum Supported on Carbon (Pt/C) in H_2SO_4 . Effects of the Amount of Pt/C, Sonication, and an Alcohol on the H^+/H_2 Reduction Current", D. Boucek, S. Lamar, A. Amoako, B. Workie, A. Goudy, H. P. Hayward, S. Grot, and W. Grot.
- HBCU-UP 2006 National Research Conference, Baltimore, MD, February 9 – 12, 2006, "Electrochemical Studies of the Suspension of Platinum Supported on Carbon (Pt/C) in H_2SO_4 . Effects of the Amount of Pt/C, Sonication, and an Alcohol on the H^+/H_2 Reduction Current", D. Boucek, S. Lamar, A. Amoako, B. Workie, A. Goudy, H. P. Hayward, S. Grot, and W. Grot.
- American Chemical Society 230th National Meeting, Washington, DC, August 28 – September 1, 2005, "Simple Electrochemical Procedure to Test the Catalytic Activity of Platinum Supported on Carbon.", J. E Trower, A. Amoako, B. Workie, A. Goudy, H. P. Hayward, S. Grot, and W. Grot.

Submitted

- American Chemical Society 232nd National Meeting, San Francisco, CA, September 10-14, 2006, "Electrochemical Studies of the Suspension of Platinum Supported on Carbon (Pt/C) in H_2SO_4 . Effects of the Amount of Pt/C, Sonication, and an Alcohol on the H^+/H_2 Reduction Current", D. Boucek, S. Lamar, A. Amoako, B. Workie, A. Goudy, H. P. Hayward, S. Grot, and W. Grot.
- "SANS Study of the Effects of Water Vapor Sorption on the Nanoscale Structure of Perfluorinated Sulfonic Acid (NAFION) Membranes" Man-Ho Kim, Charles J. Glinka, Stephen Grot, and Walther Grot; *to Macromolecules*