2006 DOE Hydrogen Program Review
Platinum Recycling Technology Development

Stephen Grot, Frank Cimander, William Resende, Walther Grot,

Ion Power, Inc

May 18, 2006

Project ID #
FC35

This presentation does not contain any proprietary or confidential information

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/cm^2
Original MEA had 2 mg PGM/cm^2, 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

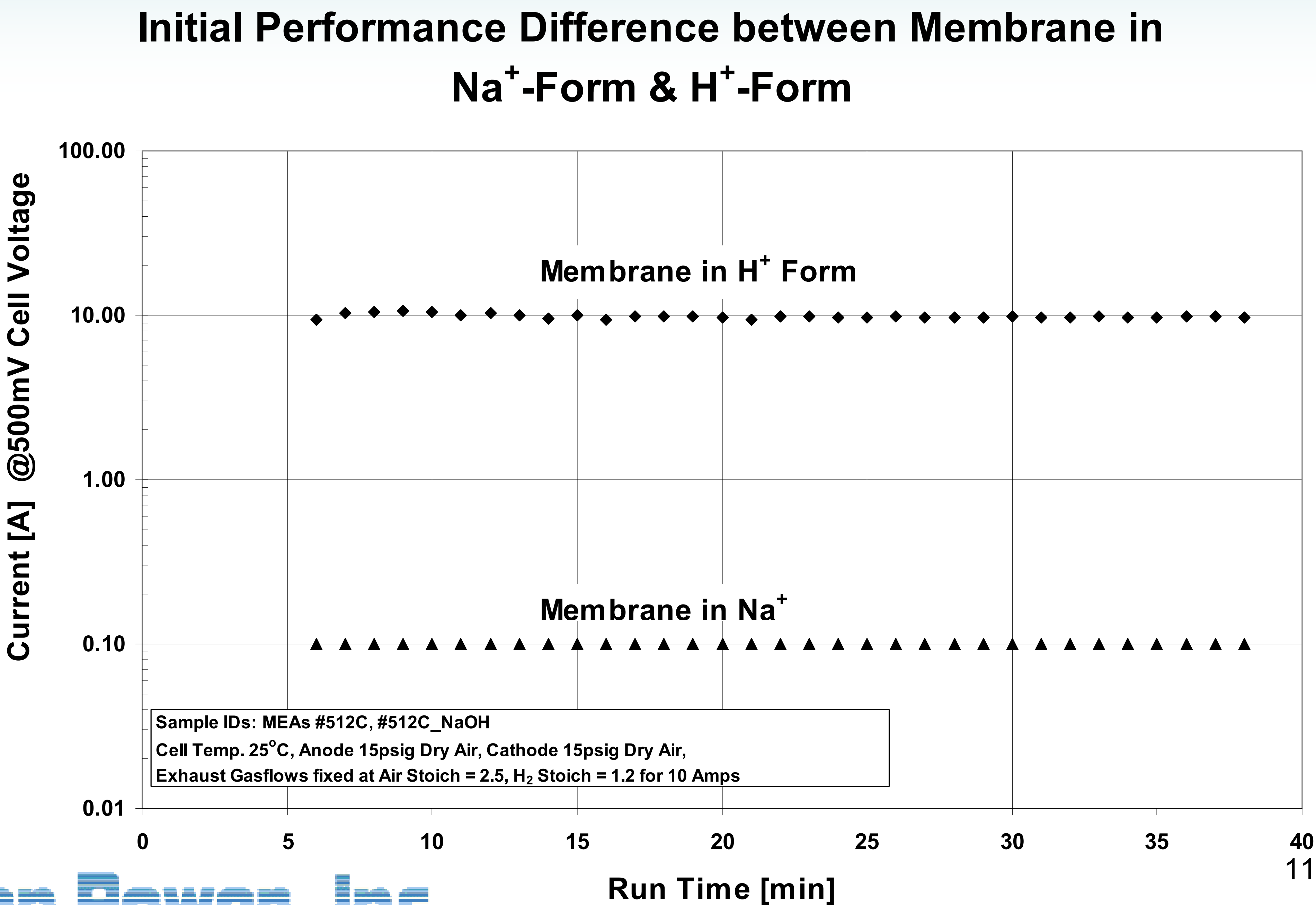
  Cr: 30 ppm

  Fe: 130 ppm

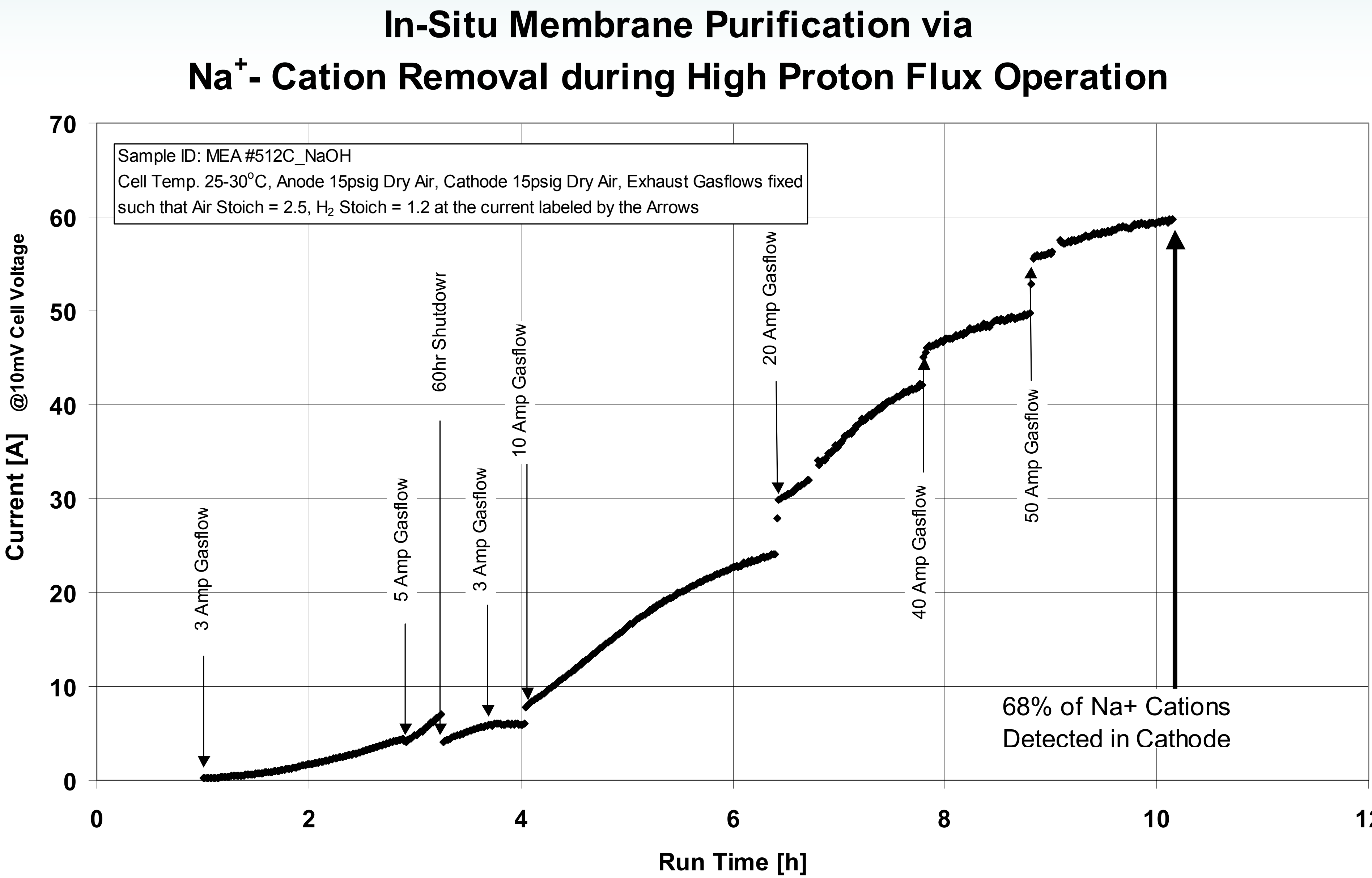
  Ni : 60 ppm

- 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?



Effect on Fuel Cell Performance?



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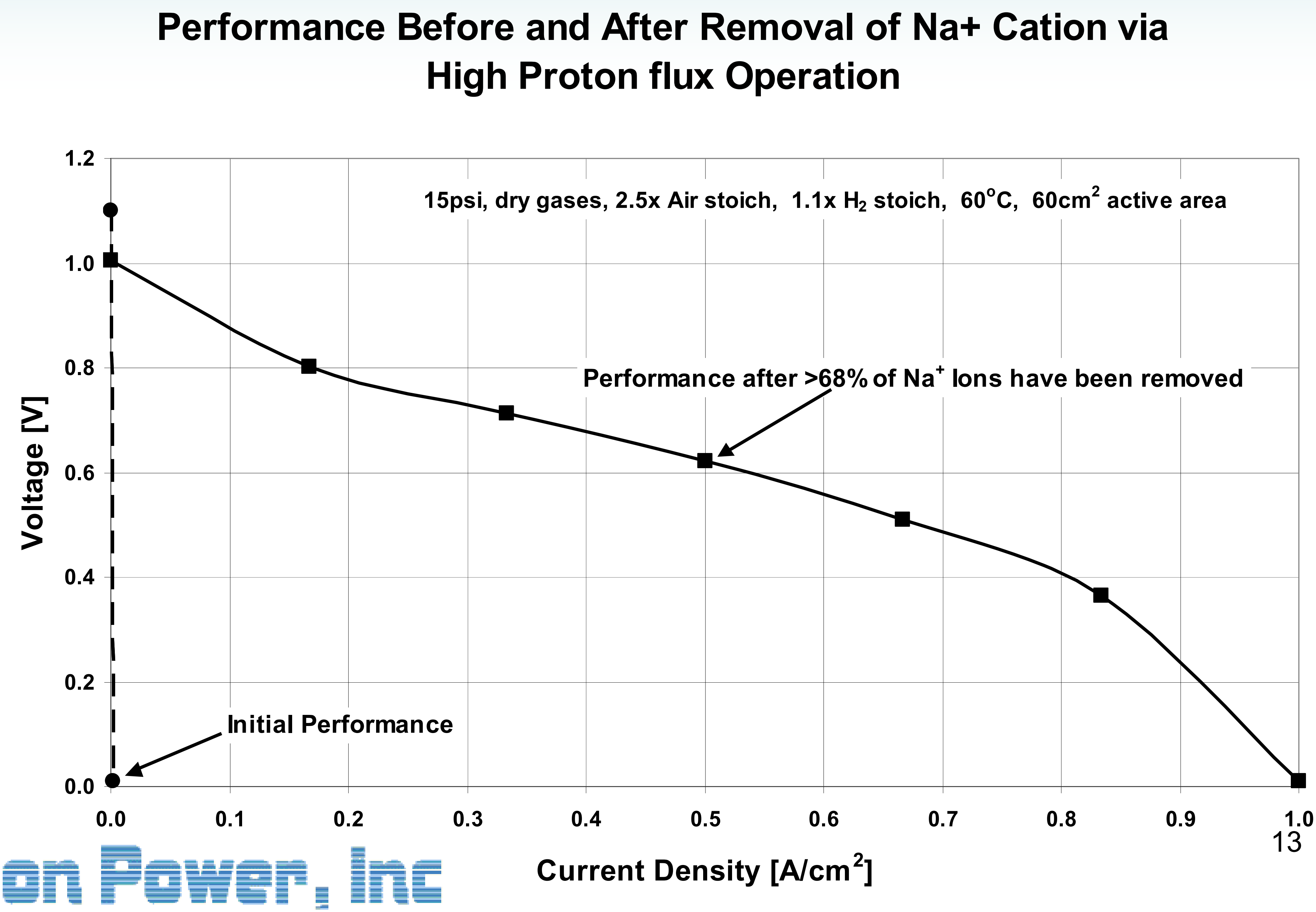
Effect on Fuel Cell Performance?



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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

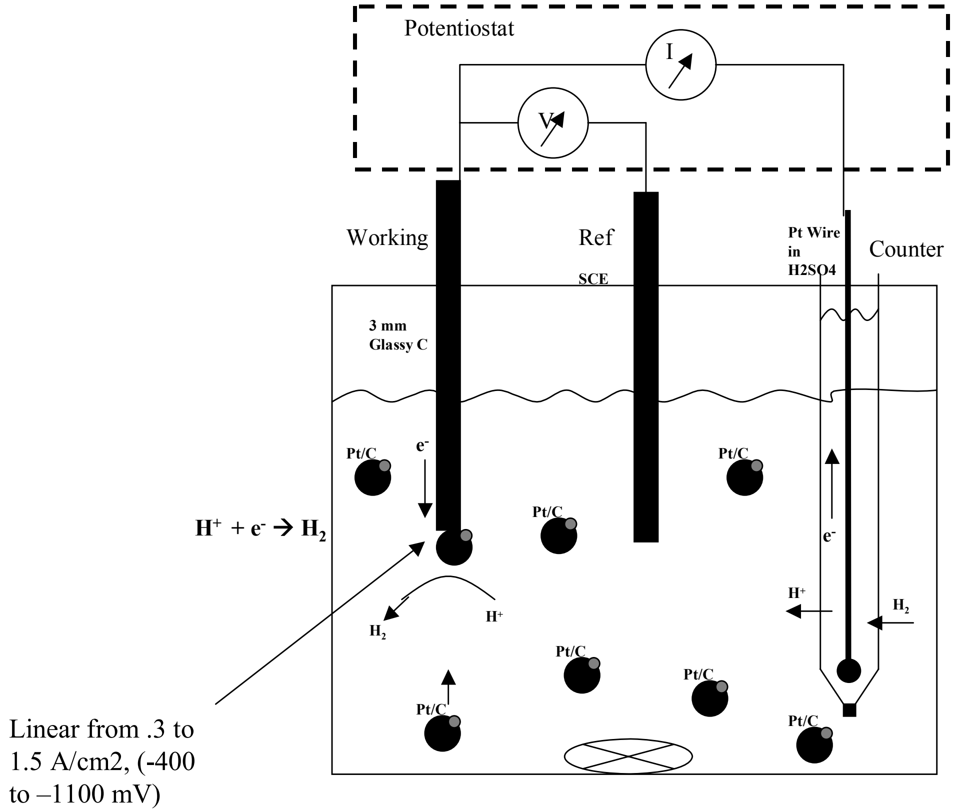
Costs : Total: $656/day

- 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



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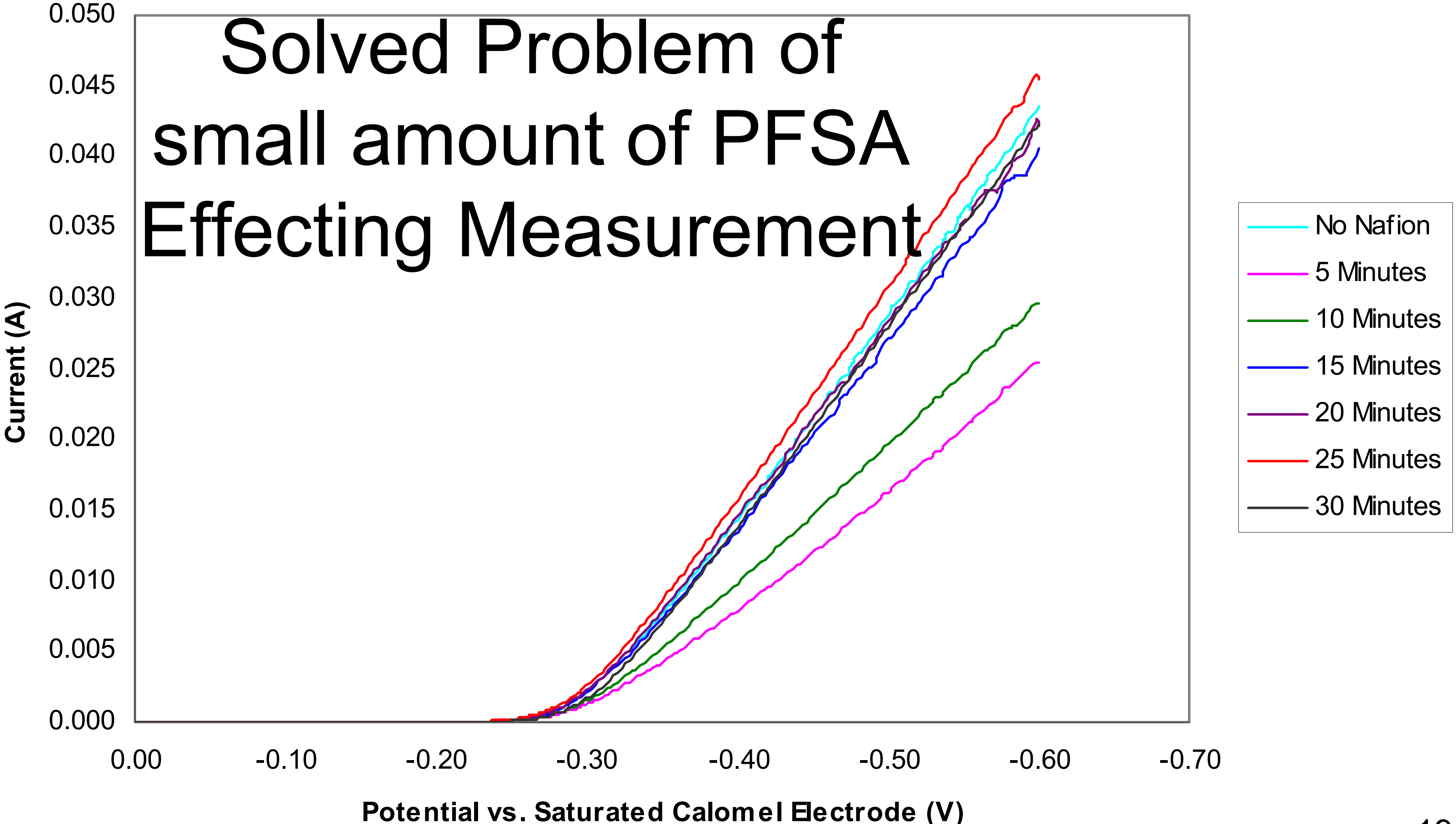
Catalyst Vitality

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*