2007 DOE Hydrogen Program Review
Platinum Recycling Technology Development

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This presentation does not contain any proprietary or confidential information
Overview

Timeline
• Project start Aug 2003
• Project end Aug 2008
• Percent complete: 70%

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

Budget
• Total project $3.31M
  – DOE share: $2.65 M
  – Contractor: $0.66 M
• FY06: $0.63 M
• FY07: $0.56 M

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 1-5 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

• Scaled up a new proprietary method that can effectively remove foreign cations from the recovered ionomer.
• Scaled up process and offered a 10 gallon 10% solution to DuPont for re-casting into re-manufactured membrane.
• Designed and purchased 4000 psi 50 gallon scaled up reactor, install scheduled May 07.
• Purchased and installed and demonstrated scale up equipment:
  – Continuous centrifuge
  – 40 gallon mixing/separation tank
  – “Tower of Purity” for ionomer enrichment/solvent recovery process
  – Used multiple small reactor batches to gather enough material
Technical Accomplishments

Previously discussed

• End-of-life NAFION® once cleaned up has properties similar to fresh NAFION®

• Catalyst vitality tests in the presence of small amounts of NAFION® is working at Del State University Subcontractor

• Separation Techniques at small scale are working
Scale-up of 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)

We purchased this reactor. Currently being modified at a local ASTM code Shop. Will be inspected by State of Del. Div. Of Boiler Safety. Scheduled start-up May 07
Scale up of NAFION®/Catalyst Separation Process

Operation:

Load Reactor discharge into Mixing Tank
Keep circulation liquid until it exits tank clear

- Catalyst in centrifuge
- Clear NAFION® solution drained for recovery

40 Gallon Mixing Tank

2 Liter Continuous Centrifuge

Coarse Screen
## Scale up Example

100 MEAs representing 3 sq meters at 1.0 mg PGM/cm^2

Gas Diffusion media removed separately and analyzed for PGM

<table>
<thead>
<tr>
<th>Processing Step</th>
<th>Total material</th>
<th>Total PGM Collected</th>
<th>Loading on MEA</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid &amp; DI water wash</td>
<td>1.5 Liters Acid</td>
<td>1.67 grams PGM,</td>
<td>0.11 mg PGM/cm^2</td>
<td>5.5%</td>
</tr>
<tr>
<td>Centrifuge top Discharge</td>
<td>2.04 kg Liquid “tinted”</td>
<td>0.6 grams PGM,</td>
<td>0.02 mg PGM/cm^2</td>
<td>2%</td>
</tr>
<tr>
<td>Centrifuge bowl solids</td>
<td>108 grams powder</td>
<td>27 grams PGM,</td>
<td>0.90 mg PGM/cm^2</td>
<td>88.2%</td>
</tr>
<tr>
<td>Centrifuge Bowl Liquids</td>
<td>1.045 kg black liquid</td>
<td>0.75 grams PGM</td>
<td>0.025 mg PGM/cm^2</td>
<td>2.3%</td>
</tr>
<tr>
<td>Diffusion Media</td>
<td>0.64 kg Carbon Paper</td>
<td>0.6 grams PGM</td>
<td>0.02 mg PGM/cm^2</td>
<td>2%</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td><strong>30.6 grams PGM</strong></td>
<td><strong>1.075 mg PGM/cm^2</strong></td>
<td><strong>100%</strong></td>
<td></td>
</tr>
</tbody>
</table>
Issues at Scale-up

• Does the separation equipment work?
• NAFION® solution is too dilute to be useful
• Screen gets plugged up with GDM fibers
• NAFION® solution is contaminated with Pt/C
Centrifuge Issues

• The centrifuge recovers 98% of the PGM fed to it
• The Catalyst can be scrapped as a solid cake from the centrifuge bowl
• The bowl capacity holds 5 sq meters worth of PGM, larger and/or continuous solids discharge centrifuges are available
• Centrifuge process time was 9 mins which is short compared to the reactor time of 4 hours
• NAFION® solution is contaminated with 2100 ppm of PGM. Will reduce feed rate and concentration to further reduce this.
Mixer Tank Issues

• NAFION® solution is too dilute
  – We need large volumes of liquid in order to get good mixing. E.g. 610 grams of MEAs requires 10 liters of liquid ➞ 1% NAFION® solution

• We have developed a proprietary enrichment / solvent recycle system to solve this problem
Issues Converting recovered NAFION® to a film

• Good film casting is achieved only from alcohol based solutions; however alcohols in the presence of catalysts is problematic.

• Water based recycling processing is preferred, makes low viscosity solutions.

• Conversion from water based to good film with good mechanical still a challenge.

• Will work with team member DuPont to assist in conversion of recovered solution into a mechanically robust film.
Project Summary

• Recovery and separation work at scale-up is being demonstrated. Challenges are being discovered and overcome.
Future Work

• Remainder of FY 2007:
  – Demonstration of vitality of separated materials
    • Incorporate membrane manufactured by DuPont into MEAs and build into fuel cell stacks and operate for performance and lifetime.

• FY 2007-2008:
  – Operate process equipment on larger scale to get real numbers on process costs.
  – Develop a robust process that is not dependent on type of membranes recovered
  – Develop applications that can purchase recovered end-of-life polymer