Platinum Group Metal Recycling Technology Development

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Iselin, NJ 08830
6/11/2008

FCP2

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Overview

Timeline
- Start - 11/2003
- Finish – extended to 3/2009
- 90% Complete

Budget
- Total project funding
  - DOE share = $4.25MM
  - Engelhard share = $1.07MM
- $579k received in FY07
- $993k budgeted for FY08

Barriers
- N (Cost)
- O (Stack Material and Manufacturing Cost)
- $45/kw for transportation
- $400-$700kw for stationary

Current Partners - Ceralink

Interactions/Collaborators
- W.L. Gore, 3M, Pemeas (MEAs)
- Parr Company, De Dietrich (reactor design)
- Hosakawa Micron (milling)
- New Wave, Cetac (Laser ablation)
Objectives for 2007-2008

- Determine
  - commercial practicality of cryo-grinding of MEAs
  - utility of the process for varied MEA architecture and materials

- Define unit operations for Pt recovery from MEAs, integrate them into a Process Flow Diagram and estimate process economics

- Identify apparatus/materials of construction for:
  - pilot plant (1 kg/day)
  - full-size (1000 MT/year) operation

- Develop a rapid process control method to determine Pt remaining in leached MEA residues
## Milestones

<table>
<thead>
<tr>
<th>Date</th>
<th>Milestone</th>
</tr>
</thead>
<tbody>
<tr>
<td>May-07</td>
<td>✓ Validated cryo-grinding with pre-embrittlement as best practice</td>
</tr>
<tr>
<td>Dec-07</td>
<td>✓ Completed ruggedness test with next-generation (alloyed) electrocatalysts and MEAs with PBI membranes</td>
</tr>
<tr>
<td>Oct-07</td>
<td>✓ Completed draft of Process Design</td>
</tr>
<tr>
<td>Nov-07</td>
<td>✓ Generated Process Cost estimate</td>
</tr>
<tr>
<td>Feb-08</td>
<td>✓ Identified Ti and Ta as possible corrosion-resistant reactor liners</td>
</tr>
<tr>
<td>Oct-08</td>
<td>Complete evaluation of Laser ablation-ICP for QC testing</td>
</tr>
<tr>
<td>Dec-08</td>
<td>Determine effect of mass transfer, T and P on Pt yield</td>
</tr>
</tbody>
</table>
Approach - Overview

- **Exploration**
  - Perform preliminary evaluation of potential processes for recovery of Pt from MEAs.
  - Rank and deselect non-competitive methods.
  - Concentrate effort on a process that is non-matrix specific.

- **Capability Validation**
  - Validate that the process works with CCM and GDE type MEAs.
  - Validate that the process works with base metal alloyed electrocatalysts.
  - Determine the impact of PBI substitution for Nafion®.

- **Process Development**
  - Integrate unit operations into a process flow diagram.
  - Identify capital requirements and perform economic analysis.
  - Resolve outstanding process issues and iterate analysis.
Technical Accomplishments (Summary)

- Using a hammer mill, LN$_2$ pre-embrittlement is shown to improve MEA cryo-grinding.

- Mass transfer limitation of current apparatus may limit Pt leachability
  - Heat and pressure help liberate Pt from ‘difficult’ samples

- Corrosion studies have identified passivated-titanium and tantalum as suitable for construction of high-pressure leaching reactors

- The proposed process incorporates an ‘azeotrope breaker’ that facilitates recovery of HCl above the concentration of the HCl/water azeotrope while concentrating Pt in the distillation bottom.
Pre-embrittlement with LN$_2$ reduces particle size distribution

A. CCM w/ gasket milled with LN$_2$.

$50\% < 263 \, \mu m, \; 90\% < 700 \, \mu m$

B. CCM w/ gasket chilled in LN$_2$ bath, then milled with liquid nitrogen.

$50\% < 63 \, \mu m, \; 90\% < 178 \, \mu m$
Excellent MEA Sampling Statistics Achievable Using Cryo-milling Procedure

MEA batch contained rigid gasket material, which made milling difficult.

Run 7 had external embittance; run 6 performed with only cryo cooling of the mill.

<table>
<thead>
<tr>
<th>Run</th>
<th>Portion</th>
<th>wt.</th>
<th>mg F</th>
<th>mg R</th>
<th>mg T</th>
<th>% Pt</th>
<th>% yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>1</td>
<td>0.543</td>
<td>8.5</td>
<td>0.64</td>
<td>9.14</td>
<td>1.683</td>
<td>93.00</td>
</tr>
<tr>
<td>2</td>
<td>0.594</td>
<td>9.47</td>
<td>0.59</td>
<td>10.06</td>
<td>1.694</td>
<td>94.14</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>1</td>
<td>0.52</td>
<td>8.49</td>
<td>0.52</td>
<td>9.01</td>
<td>1.733</td>
<td>94.23</td>
</tr>
<tr>
<td>2</td>
<td>0.518</td>
<td>8.21</td>
<td>0.63</td>
<td>8.84</td>
<td>1.707</td>
<td>92.87</td>
<td></td>
</tr>
</tbody>
</table>
7% higher Pt leach yield achieved using GDE pre-embrittled with LN₂ (Material balance, expressed as % Pt, unchanged)

<table>
<thead>
<tr>
<th>Milling Condition</th>
<th>Open Vessel</th>
<th>Sealed Vessel</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% Pt</td>
<td>% yield</td>
</tr>
<tr>
<td>Cryo-cool mill only</td>
<td>3.08</td>
<td>81.1</td>
</tr>
<tr>
<td></td>
<td>3.2</td>
<td>77.2</td>
</tr>
<tr>
<td></td>
<td>3.25</td>
<td>84.3</td>
</tr>
<tr>
<td>avg.</td>
<td>3.14</td>
<td>79.15</td>
</tr>
<tr>
<td>Pre-embrittle, then cryo-cool mill</td>
<td>3.15</td>
<td>86.6</td>
</tr>
<tr>
<td></td>
<td>3.1</td>
<td>86.2</td>
</tr>
<tr>
<td>avg.</td>
<td>3.125</td>
<td>86.4</td>
</tr>
</tbody>
</table>
### Comparison of Experimental conditions

<table>
<thead>
<tr>
<th>Condition</th>
<th>BASF - Open Vessel</th>
<th>Ceralink – Sealed Vessel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reagents</td>
<td>Acid “A” only</td>
<td>Acid “A” or “B”</td>
</tr>
<tr>
<td>Temperature</td>
<td>Hot plate at 125-150°C setting</td>
<td>Variable to 200°C using microwave heating</td>
</tr>
<tr>
<td></td>
<td>Bulk temperature of 60-70°C</td>
<td>Measured in vessel</td>
</tr>
<tr>
<td>Pressure</td>
<td>Ambient</td>
<td>10-40 bar</td>
</tr>
</tbody>
</table>
Leaching Conditions (T and P) have Major Impact on Ability to Recover Pt from MEA Scrap Material

<table>
<thead>
<tr>
<th>Run</th>
<th>Condition</th>
<th>Open Beaker</th>
<th>Sealed Vessel</th>
<th>avg</th>
<th>SD</th>
<th>RSD</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>% Pt</td>
<td>% yield</td>
<td>% Pt</td>
<td>% yield</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>ambient</td>
<td>0.605</td>
<td>23.2</td>
<td>0.624</td>
<td>90.4</td>
<td>0.609</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.608</td>
<td>24.6</td>
<td>0.597</td>
<td>88.4</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Cool mill</td>
<td>0.584</td>
<td>9.9</td>
<td>0.609</td>
<td>88.1</td>
<td>0.596</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.582</td>
<td>14.9</td>
<td>0.61</td>
<td>84.2</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>ambient</td>
<td>0.725</td>
<td>23.8</td>
<td>0.753</td>
<td>85.5</td>
<td>0.739</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.705</td>
<td>23.9</td>
<td>0.774</td>
<td>86.8</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>ambient</td>
<td>0.608</td>
<td>45.0</td>
<td>0.622</td>
<td>87.7</td>
<td>0.623</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.606</td>
<td>44.5</td>
<td>0.655</td>
<td>91.5</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Cool mill</td>
<td>0.655</td>
<td>28.5</td>
<td>0.693</td>
<td>93.1</td>
<td>0.690</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.74</td>
<td>24.3</td>
<td>0.697</td>
<td>85.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.639</td>
<td>28.3</td>
<td>0.714</td>
<td>88.0</td>
<td></td>
</tr>
<tr>
<td>Avg.</td>
<td></td>
<td>0.642</td>
<td></td>
<td>0.668</td>
<td></td>
<td>26.445</td>
</tr>
<tr>
<td>SD</td>
<td></td>
<td>0.057</td>
<td></td>
<td>0.062</td>
<td></td>
<td>10.569</td>
</tr>
<tr>
<td>RSD</td>
<td></td>
<td>8.90</td>
<td></td>
<td>9.25</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Leaching efficiency not time-dependent-0.25g CCM sample in sealed vessel

<table>
<thead>
<tr>
<th>Minutes held @ 200°C</th>
<th>1st leach yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>94.40</td>
</tr>
<tr>
<td>20</td>
<td>93.47</td>
</tr>
<tr>
<td>30</td>
<td>93.60</td>
</tr>
<tr>
<td>40</td>
<td>94.15</td>
</tr>
</tbody>
</table>
>99% Pt Recovery achieved with two leaches 30 minute @ 200ºC with 0.5g MEA powder-
Data collected at Ceralink using sealed vessels

<table>
<thead>
<tr>
<th>Leach #</th>
<th>Cumulative %Yield</th>
<th>Leach #</th>
<th>Cumulative %Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid “A”</td>
<td>1g surfactant</td>
<td>Acid “B”</td>
<td>0.5g surfactant</td>
</tr>
<tr>
<td>1</td>
<td>96.9</td>
<td>1</td>
<td>90.3</td>
</tr>
<tr>
<td>2</td>
<td>99.8</td>
<td>2</td>
<td>99.4</td>
</tr>
</tbody>
</table>

CCM with either Acid “A” or “B”

<table>
<thead>
<tr>
<th>Leach #</th>
<th>Cumulative %Yield</th>
<th>Leach #</th>
<th>Cumulative %Yield</th>
<th>Leach #</th>
<th>Cumulative %Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>96.9</td>
<td>1</td>
<td>86.9</td>
<td>1</td>
<td>95.6</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>2</td>
<td>99.7</td>
<td>2</td>
<td>99.5</td>
</tr>
</tbody>
</table>

GDE with Acid “B”
1st leach yield decreases as sample size is increased – Acid “B” runs

<table>
<thead>
<tr>
<th>Sample/surfactant</th>
<th>Run time</th>
<th>% Pt yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25g/1g</td>
<td>36 min</td>
<td>94.4</td>
</tr>
<tr>
<td>0.5g/2g</td>
<td>36 min</td>
<td>92.5</td>
</tr>
<tr>
<td>1g/2g</td>
<td>16 min</td>
<td>81.2</td>
</tr>
<tr>
<td>1g/2g</td>
<td>36 min</td>
<td>77.4</td>
</tr>
</tbody>
</table>

![Graph showing 1st leach yield vs. sample weight]
Leaching Temperature influences Pt leachability – Kinetics vs. Cl₂ solubility?
Process Challenges

- Collect a powder sample suitable for determination of lot value
- Design for corrosive nature of leaching reagents
  - HCl, chlorine, trace HF
- Simplify process design
  - Eliminate transfers
- Close HCl loop
- Develop rapid QC method for process control
- Update business model based on new process
Precious Metal recovery from Membrane Electrode Assemblies,
Source: Fuel Cells for automotive applications
Part I MEA-Grinding

Delivery of Membrane Electrode Assemblies (MEA) in drums or Big Bags

Storage in drums or Big Bags

Shredding

Cryo-grinding

Cooling screw feeder

Sub-sampling to make a lot composite

Drums

Big Bag

Liquid N2

Analyze lot sample to determine value of the lot

Store ground MEAs pending settlement
Obtaining a ‘Lot” Sample

- Current – Combust lot, then recover and blend ashes. Assay sub-sample (method must be free of interference from base metals).
  - Pros – gravimetric analysis of Pt-rich
  - Cons – loss of fine ash during blending; commercial settlement delayed by process steps.

- Proposed – Shred and grind a lot, then sub-sample and blend. Assay the final sample.
  - Pros – Settlement possible almost immediately
  - Cons – Instrumental analysis required; sample more likely to have a non-negligible moisture content
Representative Sampling Technologies

**Master sample**
Intersystems in-line cross-cut (‘pelican’) sampler (US)
Permission received from Intersystems for image reproduction.

**Sub-sample**
Retsch spinning riffler w/vibrating feeder (DE).
Permission received from Retsch for image reproduction.

**Sample Homogenizer**
Stomacher blender (UK)
Permission received from Fisher Scientific for image reproduction.
Even with silicon coating, ‘normal’ corrosion-resistant alloys like Hastelloy® do not survive exposure to chlorine.

Silicon coating reduced Hastelloy® corrosion 15 to 20-fold, but wt. loss was >0.05%.
Titanium Corrosion Resistance study – Silicon coating is an effective barrier*

<table>
<thead>
<tr>
<th>Experimental Conditions</th>
<th>mg Ti leached**</th>
<th>% wt loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Uncoated Ti – Acid “B”, 10 minutes @ 125°C</td>
<td>0.61</td>
<td>0.0074</td>
</tr>
<tr>
<td>2. Silicon-coated Ti – Acid “B”, 10 minutes @ 125°C</td>
<td>0.022</td>
<td>0.0003</td>
</tr>
<tr>
<td>3. Silicon-coated Ti – Acid “B”, 30 minutes @ 150°C</td>
<td>0.32</td>
<td>0.0039</td>
</tr>
<tr>
<td>4. Silicon-coated Ti – Acid “A”, 10 minutes @ 125°C</td>
<td>0.038</td>
<td>0.0005</td>
</tr>
</tbody>
</table>

Trials 2 through 4 run in order using the same Ti sample.
* Silicon coating commercially applied by Restek
** Leachable Ti determined by ICP determination of Ti in leachate.
Pt Recovery Anticipated to Require 2 Leaches and 2 Filtrations w/pumps, transfer lines, valves, etc.

Membrane electrode assembly (MEA)

- Warehouse
- Cryogrinding with precooling
- Sampling for pricing of lot
- Warehouse

125 kg/hr ground MEA

1 % of Pt

Surfactant

Blending of different lots for process stability

Leach 1

Solid-Liquid Separation

Leaching agents Option 1 Cl₂ and HCl

Solid residue (treatment?)

Concentration

Leach 2

Solid-Liquid Separation

Product 20 g/l Pt in dilute HCl to refining

Offgas treatment

20 g/l Pt in dilute HCl to refining
Single Apparatus for Leaching, Filtering, Washing, Neutralization and Solids Drying
Simplifies Process

Is low rpm agitator design sufficient for replenishment of oxidant (e.g. chlorine) in liquid phase?

Permission received from De Dietrich for image reproduction.
HCl content decreases as HCl is converted to Cl₂ by reaction with added oxidants.

HCL/water azeotrope has a BP of 109°C and a composition of 20% HCl vapor. By comparison, concentrated acid is 37% HCl.

HCl in vapor phase can be enriched using an ‘azeotrope breaker’

In this example, a hygroscopic alkaline earth chloride reduces water in the vapor phase

After saturation with water, the salt is thermally regenerated and re-used
Halving added HCl has a small effect (~3%) on Leaching Efficiency

<table>
<thead>
<tr>
<th>Hot Plate Setting</th>
<th>% HCL Dosage</th>
<th>% Oxidant “A” Dosage</th>
<th>% Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>125°C</td>
<td>100</td>
<td>100</td>
<td>93.7</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>100</td>
<td>90.1</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>50</td>
<td>89.6</td>
</tr>
<tr>
<td>150°C</td>
<td>100</td>
<td>100</td>
<td>95.8</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>100</td>
<td>93.5</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>50</td>
<td>92.5</td>
</tr>
</tbody>
</table>

Water added in place of HCl to maintain volume.
Process Control Methodology - Laser Ablation – Inductively Coupled Plasma Emission

- Example of track of 213 nm laser through a layer of MEA powder deposited on a filter paper

- Note non-uniformity of sample layer
Laser Power has major impact on ICP signal derived from ablated sample

- Dramatic increase in Pt and Ru signal when laser power raised from 20 to 25% (minimum power required)
- Minimal change going from 30 to 35% (Layer completely ablated)
Internal Standardization Method Proposed for Improved Powder Analysis

- Laser ablation transfers MEA powder as an aerosol to the ICP torch, where the particles are vaporized.
- The ICP emission/MS signal will depend on the aerosol loading in the carrier gas.
- The expected non-spatially uniform deposition of MEA powder on a filter substrate will result in poor precision.
- Blending an internal standard powder with the MEA is shown to improve reproducibility of data.
internal standard method improves LA-ICP precision (CCM MEA powder w/Mg silicate)

<table>
<thead>
<tr>
<th>Run</th>
<th>Pt 1/ Si 1 Count Ratio</th>
<th>Pt 2/ Si 2 Count Ratio</th>
<th>Pt 1 Counts</th>
<th>Pt 2 Counts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run 1</td>
<td>0.209</td>
<td>0.0438</td>
<td>4383 (raw)</td>
<td>4485 (raw)</td>
</tr>
<tr>
<td>Run 2</td>
<td>0.205</td>
<td>0.0414</td>
<td>3330 (raw)</td>
<td>3316 (raw)</td>
</tr>
</tbody>
</table>

ICP Emission Wavelengths
Pt 1 = 214.4 nm, Si 1 = 212.4 nm
Pt 2 = 265.9 nm, Si 2 = 251.6 nm
8 sets of five-second integrations per run
Proposed Pilot Plant Layout
20’ x 40’ (Roughly $1MM cost)

- sink and bench
- DI water
- LA-ICP
- Hamilton sampler
- Shared PC/terminal
- 'Clean room' Temperature controlled
- PBI leach area
- 'Work bench/balance'
- Balance
- Oven area
- Blender and Splitter, balance
- Main processing room
- HCL storage
- Scrubber
- Filter
- Reactor
- HCl still
- HCl still
- Chiller
- Cryo-grinder
- LN2 Dewar
- Shredder
- Heater
- Chiller
- LN2 Dewar
- Shredder
- Heater
Future Work

- Install an agitated glass reactor and determine Pt yield at atmospheric pressure and $T \sim 100^\circ$C (BASF) -9/08

- Install an agitated titanium-lined reactor and determine Pt yield at elevated pressure and variable temperature $> 100^\circ$C (Ceralink) -12/08.

- Improve economic model for process based on reactor design-12/08.
Summary

- Pt recovery of >98% is achievable from milled MEAs using an oxidative leaching process.
- The process has been shown to work with all types of MEAs and electro-catalyst compositions.
- Operated commercially, the process requires little manual labor and generates minimal waste (solid residue of the leaching).
- Integration of unit operations will better define actual process costs.
- New, rapid technology has been invented to accurately analyze slurry solids composition.