

Platinum Group Metal Recycling Technology Development

Lawrence Shore

BASF Catalysts LLC

May 18, 2007

FC30

Overview

Timeline

- Start - 11/2003
- Finish - 10/2008
- 85% Complete

Budget

- Total project funding
 - DOE share = \$4.8MM
 - Engelhard share = \$1.2MM
- \$743,000 received in FY06
- \$1.24 M budgeted for FY07

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
- Cabot, ONR, NECC
- Milestone Scientific, Pall Scientific
- Hosakawa Micron

Objectives/ Timeline

| | |
|-----------|----------------------------------------------------------------------------------------------------------------------|
| Overall | Develop and demonstrate a process for recycling of PEM fuel cell MEA's without HF emission |
| 2003-2006 | Determine the processing steps necessary to optimize Pt recovery from aged fuel cell MEA's |
| 2005-2006 | Develop a solid-state adsorbent that will capture HF and COF ₂ vapors (discontinued) |
| 2005-2006 | Evaluate the practicality of recovery of Nafion® polymer as part of a fuel cell recycling process (priority dropped) |
| 2006-2007 | Re-design process so that CCM and GDEs are processed together |
| 2007-2008 | Determine process economics and build a prototype |

Plan and Approach

■ Task 1: Pt recovery

- Compare acids used to dissolve Pt
- Compare conventional vs. microwave heating

■ Task 2: Sample preparation

- Balance MEA handling requirements with Pt yield

■ Task 3: HF remediation (Abandoned)

- Develop solid-state adsorber
- Modify process to minimize amount of adsorber required

■ Task 4: Process integration

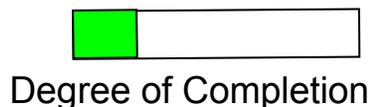
- Integrate unit operations based on results of Tasks 1-3

■ Task 5: Process Economics

- Estimate scale of pilot-sized plant
- Identify capital costs using process identified in Task 4

■ Task 6: Process demonstration

- Build recycling prototype

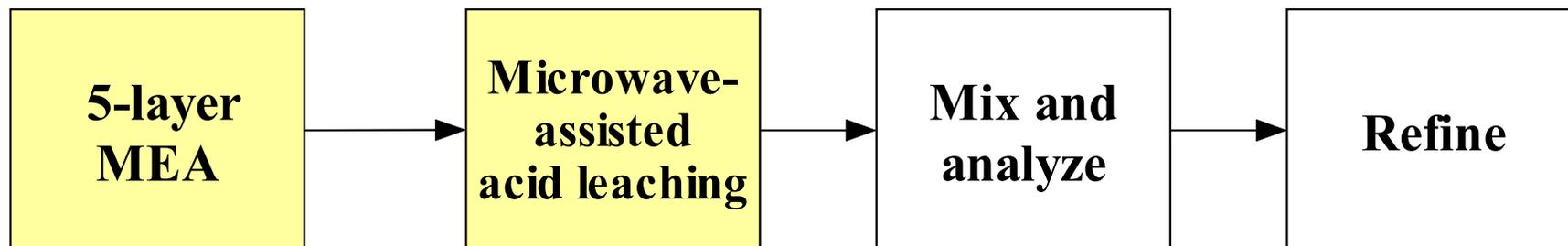


Technical Accomplishments for the last year

Developed a simple, environmentally-benign, 'universal' process to recover Pt from fuel cell MEAs with the following features:

- ✓ No organic solvent required
- ✓ No need for combustion
- ✓ Removal of GDL from membrane no longer necessary
- ✓ Applicable to both CCM and GDE architecture
- ✓ High Pt yield with base metal-alloyed cathode catalysts indicated

Approach #1- Preliminary PM Recycling Process (No HF evolved)

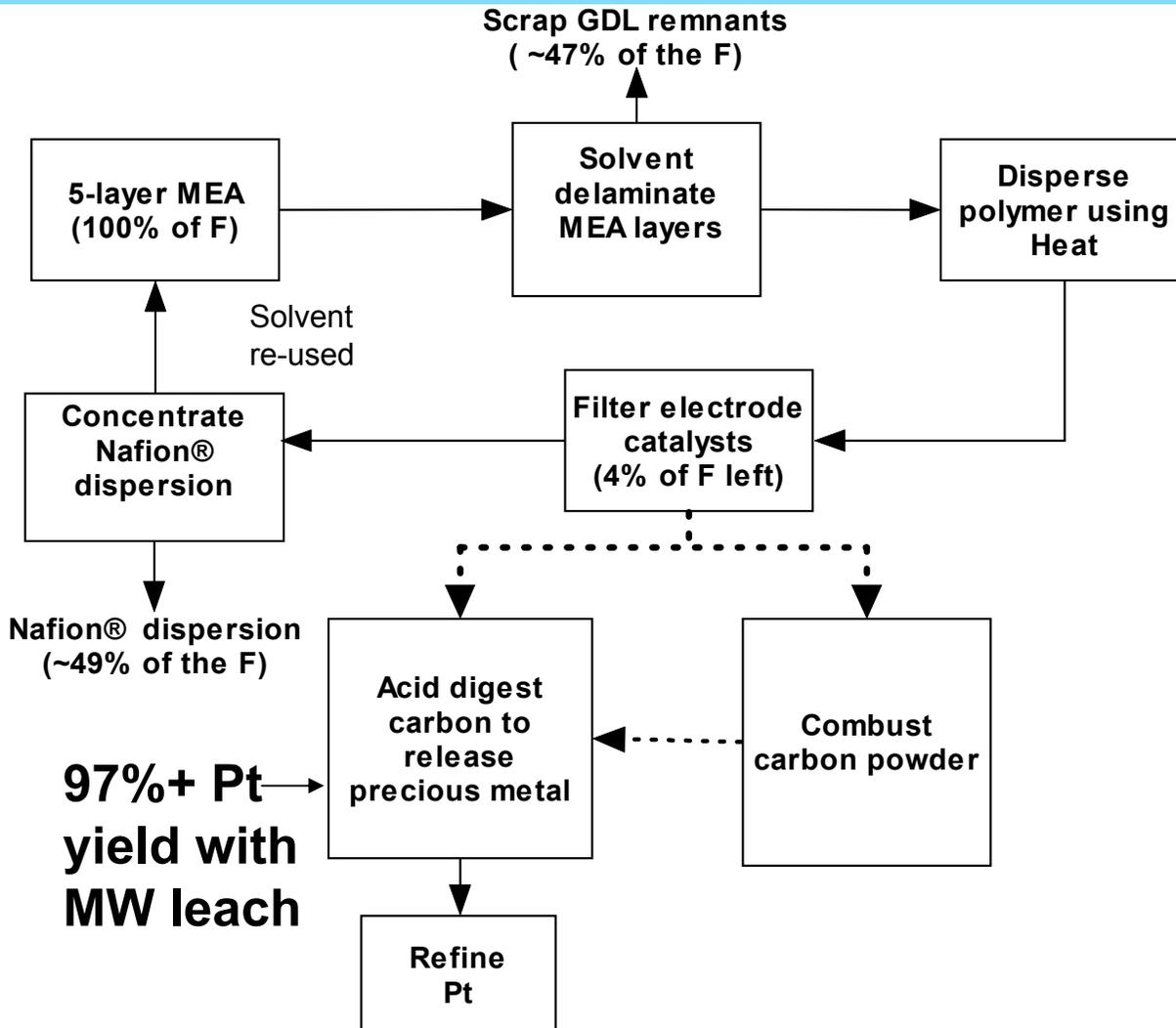


Engelhard's preliminary work focused on Pt recovery from MEAs using a direct leaching approach.

Nafion® recycling was not included in the process.

- Low Pt recovery achieved because of restricted access to the electrocatalyst surface during leaching.
- No provision for recovery of valued polymer.

Approach #2 – Solvent Delamination/Acid Leaching with Combustion Option (for CCM)



1. Potential for Pt loss since mobilized nano-sized Pt particles formed by migration of Pt into the membrane can end up in UF retentate.

2. Separation of electrode catalyst by delamination ineffective with GDE MEAs

3. Solvent usage introduces safety and environmental issues

4. Importance of Nafion® recovery is questionable because of market/material issues.

Negative Aspects of MW Combustion of Delaminated Electrode Catalyst

- Combustion of harvested electrode catalyst yields minimal HF
- Combustion of carbon-containing materials is desirable because the product is favorable for downstream operations:
 - Low moisture content aids in the assay
 - Processing material with carbon content is avoided
 - The feedstock for refining operations is concentrated

However:

- **Combusted catalyst powder sinters**
 - Lower Pt yield compared to uncombusted material using Acid B
 - Controlled combustion at low temperature needed
- **Significant loss of ruthenium observed compared to starting material (~75%) [stationary or DMFC fuel cells]**

CCM Recycling – Loss of Ru during combustion

- Results show that $\frac{3}{4}$ of the ruthenium was loss during combustion
 - Values based on assay of leach solution using acid A
 - Acid B volatilizes ruthenium

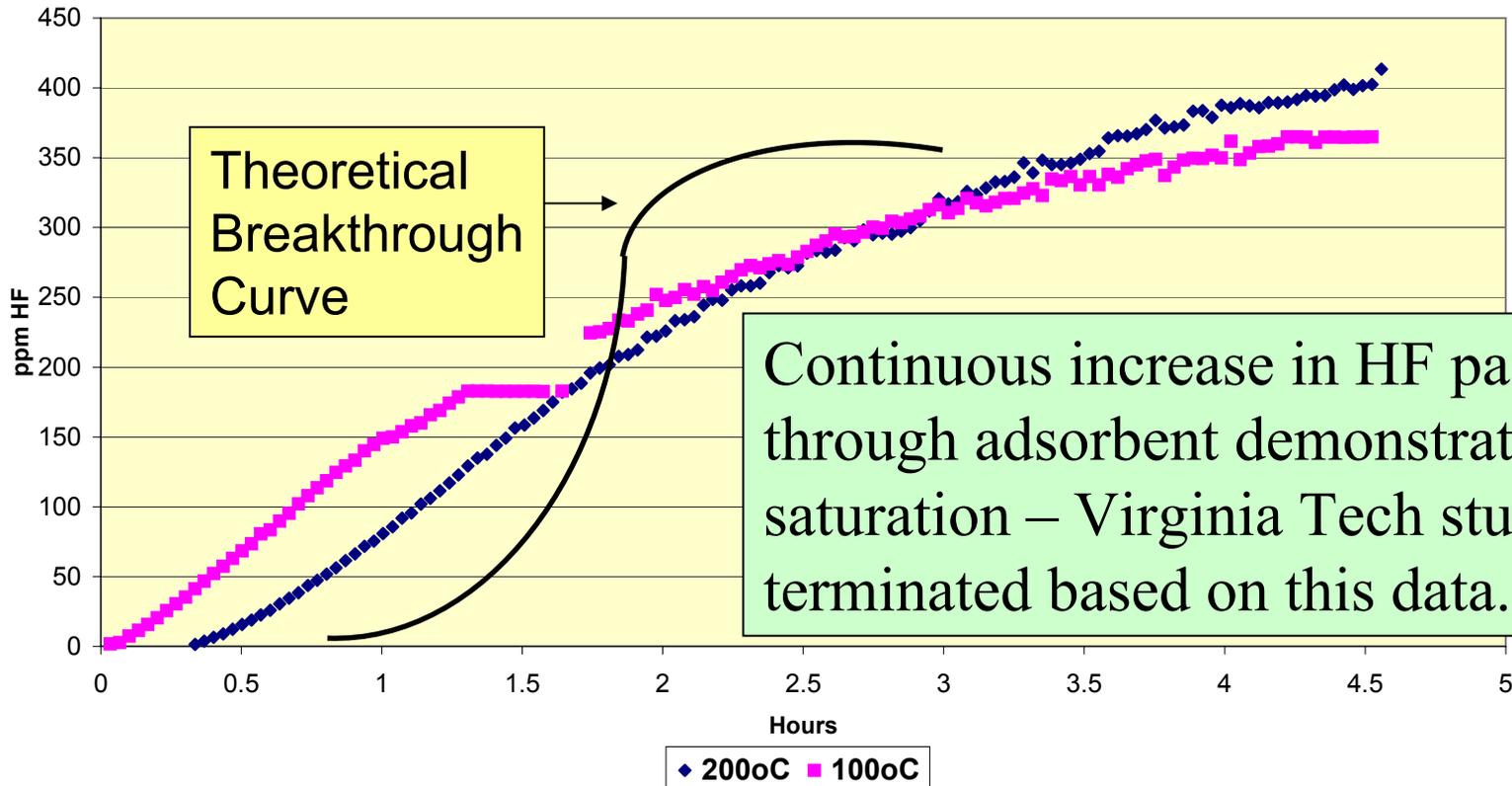
| Sample | Pt/Ru ratio | Ru loss | Pt yield |
|------------------------------------------|-------------|---------|----------|
| MW- Ashed (~1000°C) 3-layer MEA | 19.0 | 77%* | 94% |
| MW- Ashed harvested electrode catalyst | 15.6 | 72%* | 93% |
| Uncombusted harvested electrode catalyst | 4.4 | | 97% |

* Ru loss based on comparison of Pt/Ru ratio of ashed to non-ashed sample.

Rapid Breakthrough of HF Vapor From Simulated Combustion Observed Using Virginia Tech Adsorbent Conditions

0.6g High-Density gamma Alumina Supported on SiC Foam 500ppm HF,
1 LPM

Comparison of HF adsorption at 100°C and 200°C



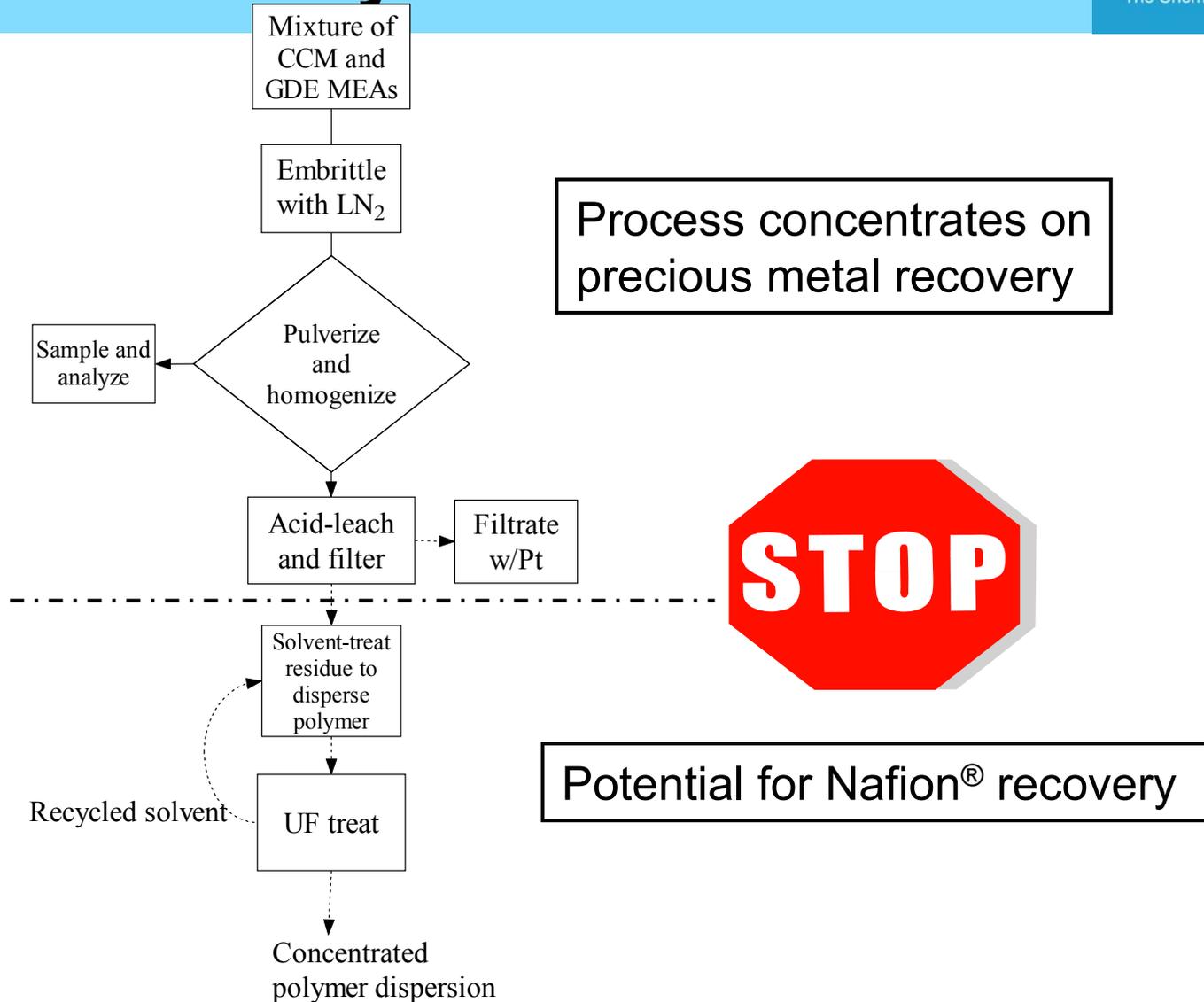
Continuous increase in HF passing through adsorbent demonstrates rapid saturation – Virginia Tech studies terminated based on this data.

Identification of the Conflict in Recycling CCM and GDE MEAs

- Solvent delamination (Approach #2) liberates the electrode catalyst from both the GDL and membrane of a CCM, but is ineffective in releasing the electrode catalyst from the GDE.
- In the worst-case scenario, MEAs using both GDE and CCM design will:
 - acquire PEM fuel cell market share
 - and be indistinguishable to the recycler
 - and be mixed together when disassembled fuel cells are recycled.

This mixed lot of GDEs and CCMs cannot be efficiently recycled using processes tailored to MEA type.

Approach #3 - Simplified/Consolidated (CCM and GDE) Pt Recovery Process



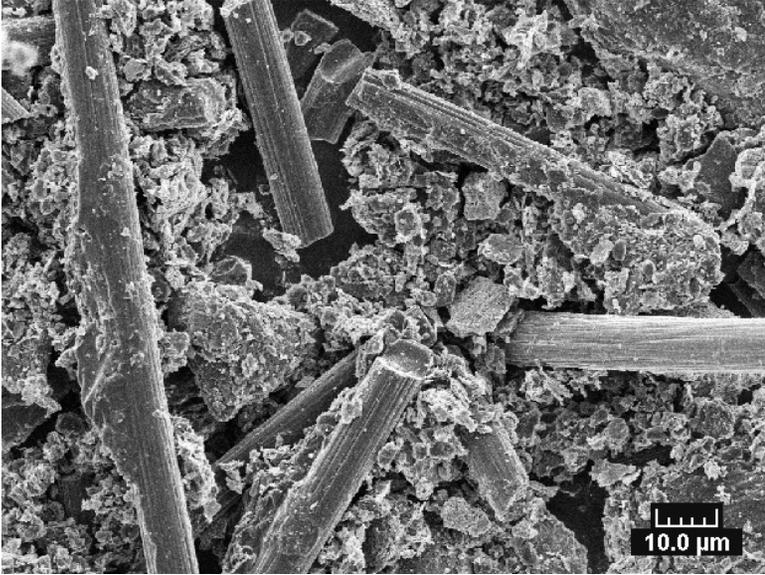
Options for Recovering Pt from Fuel Cell MEAs

- Direct acid leaching of shredded MEAs (low yield - Approach #1)
- Acid leach solvent delaminated catalyst powder w/wo ashing (Specific to CCM's) (Approach #2)
- Acid leaching of delaminated MEA (Specific to GDE's) (Approach #2a)
- Direct acid leaching of powdered MEAs, ground after cryogenic embrittlement (Approach #3)
 - ✓ Universal
 - ✓ No solvent required
 - ✓ Leaching will recover Pt that migrated into the membrane

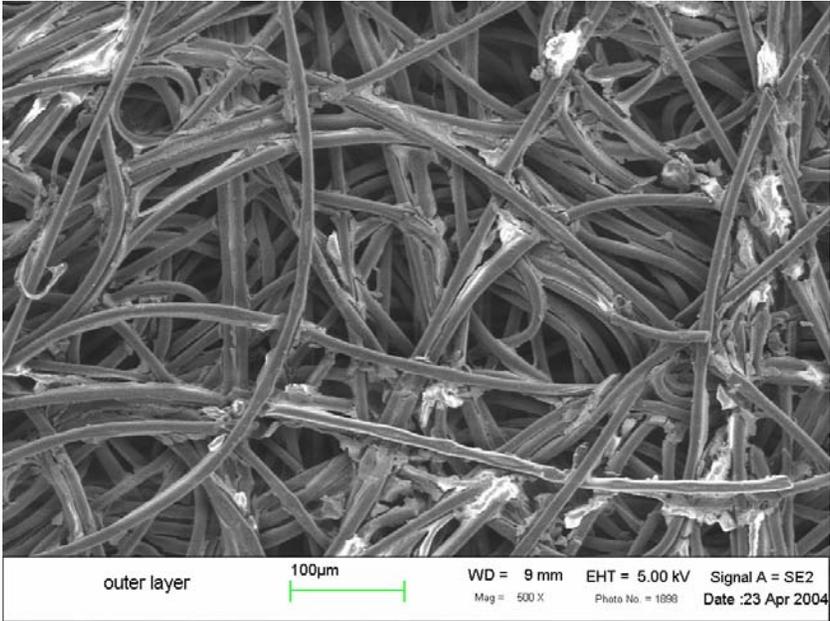
Only Cryo-Grinding Process (Approach #3) Yields High Pt Yield for both CCM and GDE MEAs

| Material | Acid Leach of 5-layer MEA | Acid Leach of Hand-stripped MEA | Leach of electrode catalyst (solvent-delaminated) | Leach of ashed electrode catalyst | MW Acid leach of solvent Delaminated GDE | MW Leach of Cryo-ground MEAs |
|----------|---------------------------|-------------------------------------------|---------------------------------------------------|-----------------------------------|------------------------------------------|------------------------------|
| Approach | 1 | 1a | 2 | 2 | 2a | 3 |
| CCM | 65, 82 | 98% on membrane (2-10% Pt left on GDL) | 97.2 (MW) 90 (Conv.) | 93, 99 | | 92 |
| GDE | | Catalyst split between GDL and membrane | NA | NA | 93.8 (86% w/conv. leach) | 97 |

Demonstration of MEA Cryo-grinding



Ground CCM MEA, 1000x magnification



Intact GDL from a CCM MEA, 500x magnification

Comparison of Leaching Cryo-ground MEAs using the MW method

| MEA type | Acid | 1 st leach yield | 2 nd leach yield | Total yield |
|----------|------|-----------------------------|-----------------------------|-------------|
| CCM | A | 92.0 | 5.7 | 97.7 |
| | C | 97.5 | 1.6 | 99.1 |
| GDE | A | 97.4 | 2.1 | 99.5 |
| | C | 96.4 | 2.2 | 98.6 |

Advantages and Challenges of Cryo-grinding MEAs

- Environmentally friendly – No HF released, no solvent used
- Practical - Both CCM and GDE-style MEAs are processed equally
- Efficient - Delamination (manual or solvent assisted) not required to expose catalyst particles to leach medium
- Accurate - Lot homogenization achievable through grinding and standard sampling procedures. TGA shows material has very low moisture content
- Clean - Reduced handling while obtaining high Pt yield – low potential for dust loss
- Economic - Process concentrates on Pt recovery - Polymer recovery is possible downstream, if justified
- **Hydrophobic – Poor wetting of PTFE and graphite needs to be overcome to achieve high yield during leaching**

Comparison of Leaching Methods for Cryo-ground MEAs- 1st yield

| MEA type | Conventional Leach with Acid C | | MW-assisted Leach @ 200°C | |
|----------|-----------------------------------|------------|------------------------------|---------------|
| | No surfactant | Surfactant | Acid A | Acid C |
| | | | No surfactant | No surfactant |
| CCM | 72.5 | 94 | 92* | 97.5* |
| GDE | 93 | 94-96 | 97 | 96.4 |

*Relatively high MW yield achieved but vessel damaged because of carbon adsorbed on walls, overheating the vessel.

CCM more hydrophobic than GDE so wetting sample is a problem.
Continuous-flow microwave reactor may be more efficient than autoclave.

Comparison of Pt yields for developmental electrode catalysts

- Experiments performed using either conventional or MW-assisted leaching.
- Sample presented as undispersed electrode catalyst powder (not on MEA.)

| Acid | | Pt-TaPO | Pt/Fe | Pt/Co | Pt/Cr | Pt/Ru (ref.) |
|-----------------|-----------------------------|---------|-------|-------|-------|--------------|
| A (MW leach) | 1 st leach yield | 95% | 90% | 89% | 94% | |
| | S.D | 1.3% | 2.6% | 3.0% | 0.5% | |
| | | | | | | |
| C (Conv. leach) | 1 st leach yield | | 95% | 97% | 97% | 78% |
| | S.D | | 2.0% | 0.1% | 0.9% | 0.7% |

Future Work - Milestones

■ Unit operations

- Demonstrate scaled-up cryogenic grinding of MEAs – 6/07
- Complete shakedown of scaled-up microwave digestion unit – 7/07
- Validate the ‘dewatering’ of MEA slurry required for continuous leaching approach – 8/07
- Optimize the selection of surfactant for MEA wetting and the order of material addition - 8/07
- Determine best approach (batch, continuous, packed bed) for MEA leaching - 10/07

■ Process

- Estimate economics of consolidated process (w/ MEA grinding) – 10/07
- Build prototype for leach scale-up with on-line QC capabilities –2/08

Summary of Key Accomplishments during past year

- Recognized shortcomings inherent in first-generation processes and validated a generalized Pt recycling process, based on cryo-grinding, that addresses DOE concerns regarding efficiency and environmental impact.
- Documented the increase in Pt leach yield using a surfactant and operating at elevated T and P.
- Demonstrated that the leach process was applicable to alloyed cathode catalysts.
- Cancelled the MEA combustion program at Virginia Tech because of sintering of Pt, loss of volatile Ru and the inability to sequester HF from the vapor phase.
- Produced an assay-quality (homogenous) sub-sample of MEA using a combination of cryo-grinding and blending.