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Engelhard Corporation

May 18, 2006

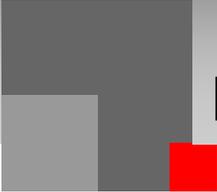
Platinum Group Metal Recycling Technology Development



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FC36

ENGELHARD



Fuel Fuel Recycling - Project Recapitulation

- In aggregate, fuel cells will represent a large inventory of platinum
 - This Pt inventory will have to be recycled to meet ongoing demand for new fuel cells
- Recycling of Pt via MEA combustion is counter-productive
 - The high fluorine content is converted to HF, a hazardous and corrosive vapor
 - The potential value for recovered perfluoropolymer is lost
- Engelhard was awarded a DOE funding for a five-year project to circumvent environmental issues, while developing a commercially-viable Pt recycling process.



Overview

Timeline

- Start - 11/2003
- Finish - 10/2008
- 70% Complete

Budget

- Total project funding
 - DOE share = \$4.8MM
 - Engelhard share = \$1.2MM
- \$875,000 received in FY05
- \$1.3M Funding for FY06
 - FY06 funding reduced 20% from budget

Barriers

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

Partners

Virginia Tech, Ceralink

Collaborators

- W.L. Gore, Etek
- MMT and Autoclave Engineers
- Milestone Scientific
- Pall Corporation
- Wyatt Technology, Malvern



Objectives

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
2005-2006	Evaluate the practicality of recovery of Nafion® polymer as part of a fuel cell recycling process
2006-2007	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**

- 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

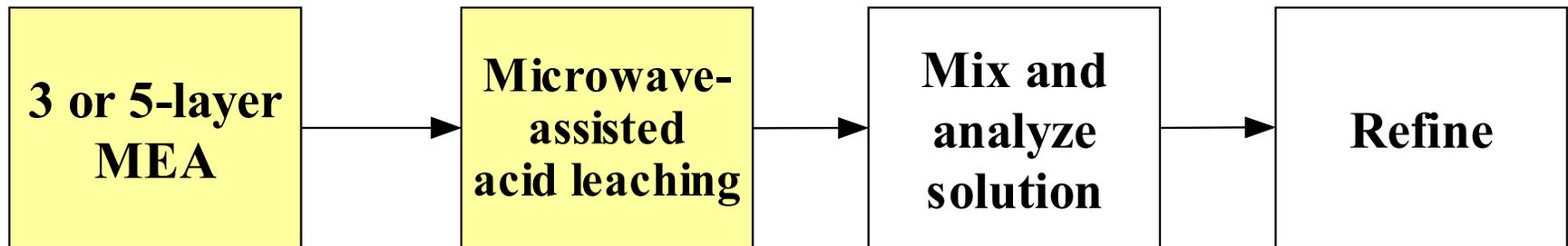
• **Task 5: Process Economics**

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

• **Task 6: Process demonstration**

- Build recycling prototype

Approach - Preliminary PM Recycling Process (No HF evolved)



Engelhard's preliminary work focused on Pt recovery from MEA's by leaching Pt from the carbon layers on the membrane; the membrane was left intact.

Nafion® recycling was not included in the process.

Technical Accomplishments

- Task 1 and 2 (Pt recovery and Sample Preparation)
 - Conflicting conditions for near quantitative Pt recovery determined

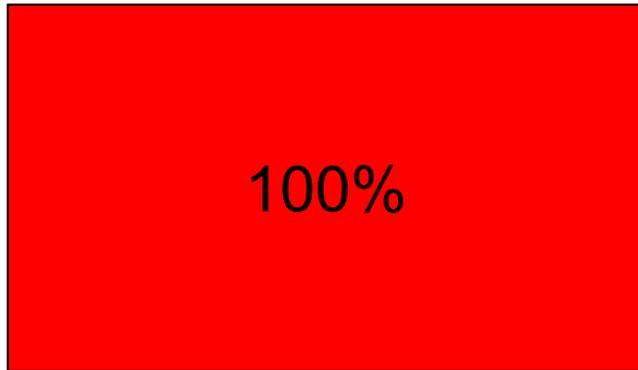
Results of Microwave-Assisted Acid Leaching

Sample	GDL present?	Temperature / Pressure	% Pt removal (based on residue)
3-layer MEA	no	200 / 10 bar	100, 100
5-layer MEA	yes	200 /10 bar	82, 65

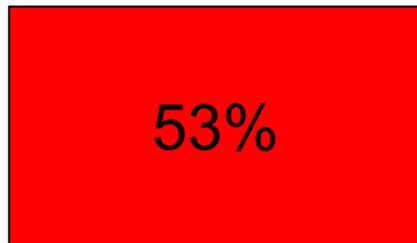
- Removal of the GDL increases Pt leachability from the membrane.
- However, 1.5 to 10% of Pt left on GDL 'dry' stripped from aged MEA

Conclusion - A process that reconciles this contradiction is needed.

Approach – Alternate Process with Combustion



1 kg of 5-layer MEA has
~360g of F



335g of 3-layer MEA has
~190g of F

5%

100g of electrode catalyst has
17g of F



Why Consider the 'Combustion' Option

Commercial settlement depends on a homogenous sample, an accurate assay of Pt content and a known lot weight.

- Commercial settlement is facilitated using a metal or metal oxide with a low moisture content.
- Commercial settlement using a 'wet' carbon sample or a solution is not preferred.
- Representative sampling of a shredded 5-layer MEA is difficult to achieve.

While adding complexity to the process, igniting the filtered electrode catalyst is in line with current refinery protocol for handling carbon catalysts.



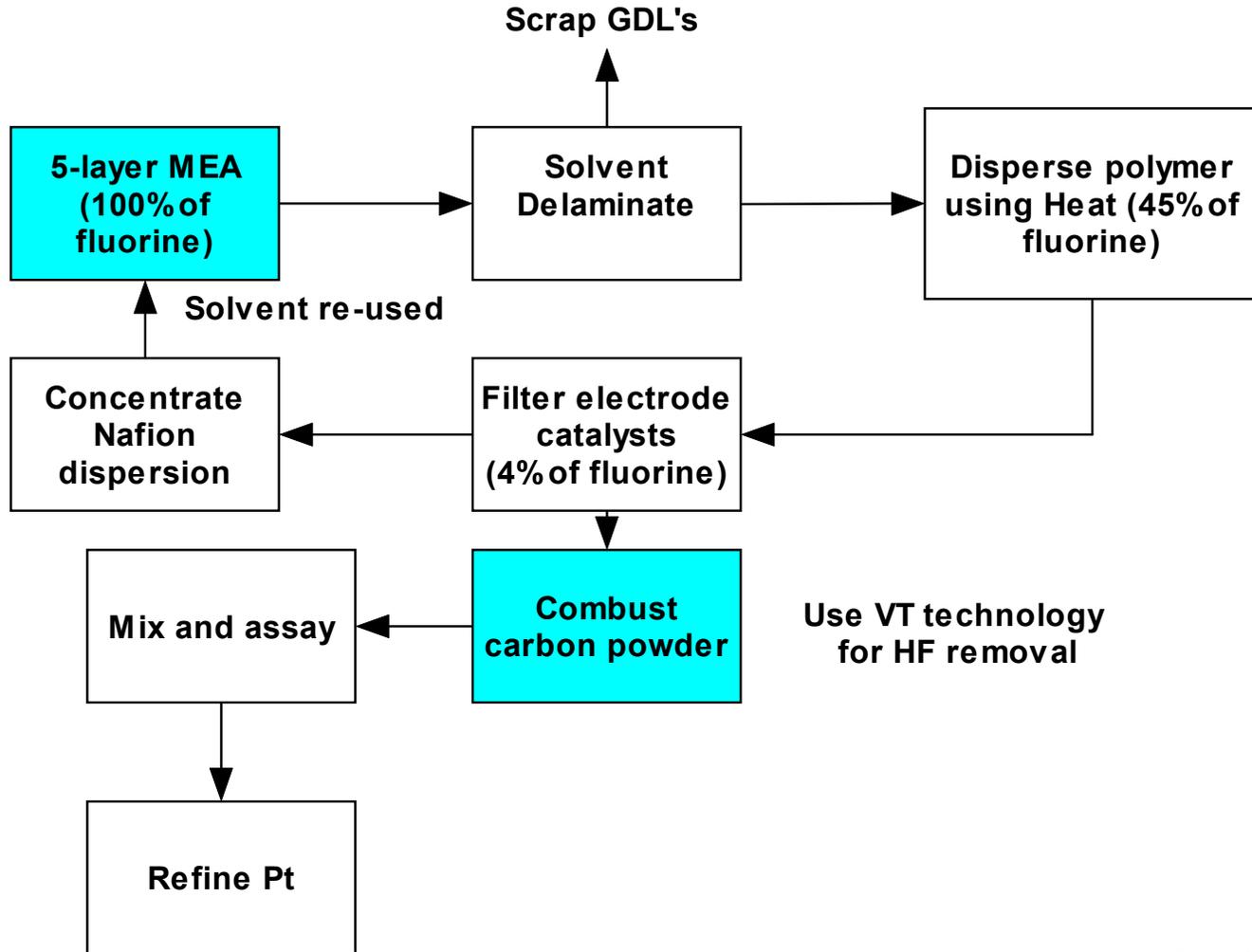
Critical Evaluation of Microwave Combustion of 'GDL' MEA's

Engelhard has experience in purifying Pt obtained from carbonaceous material.

- Feasibility of combustion
 - Only 3-layer MEA's combust with microwave heating
 - GDL on 5-layer MEA's dissipate microwave energy
 - Preliminary stripping of the GDL from the membrane may result in Pt loss
- Capacity of Fluorine Adsorbent is limited
 - 3-layer MEA contains about 70% Nafion
 - Filtered electrode catalyst contains a small fraction of the total fluorine
 - Overall 90% reduction in fluorine emissions compared to 3-layer MEA

Conclusion – Combustion of filtered electrode catalyst is preferred

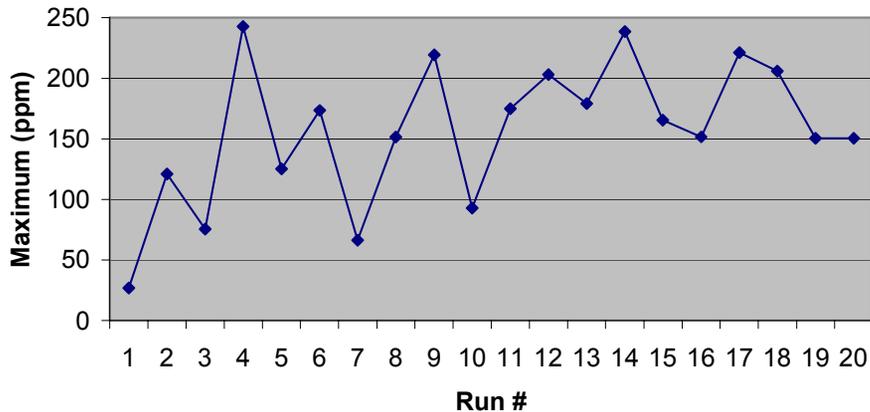
Approach – Alternate Process with Combustion



Technical Accomplishments –cont.

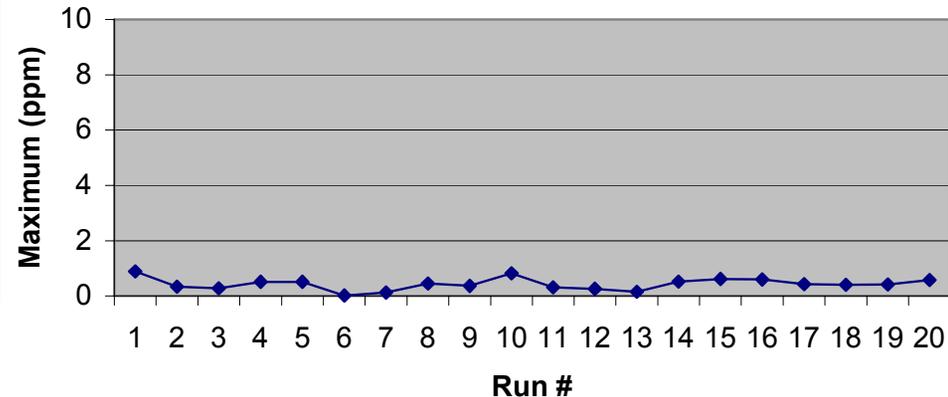
Task 3 – HF Remediation – 99.5% HF removal achieved

Maximum HF Emission, Empty Adsorbent Tube



No adsorbent,
0-250 ppm scale

Maximum HF Emission, Half Tube, 50% filled with adsorbent, 500°C



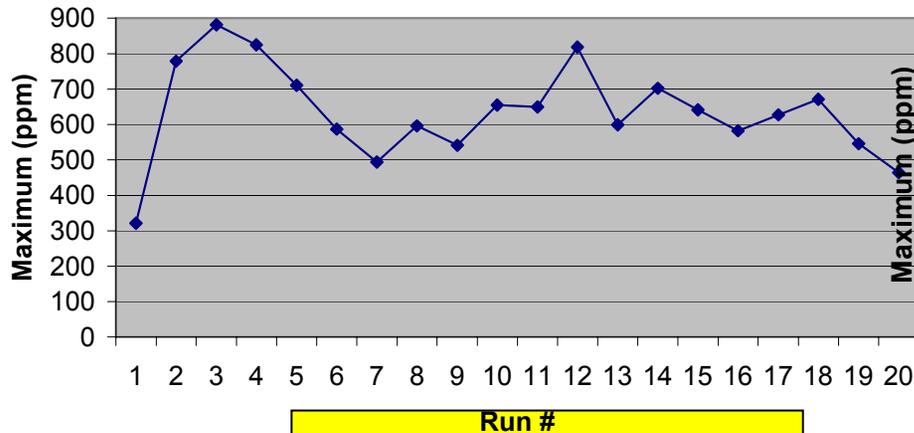
Adsorbent present,
0-10 ppm scale

Conclusion: Conditions have been identified to chemically remove fluorine-containing gases after Nafion combustion

Technical Accomplishments –cont.

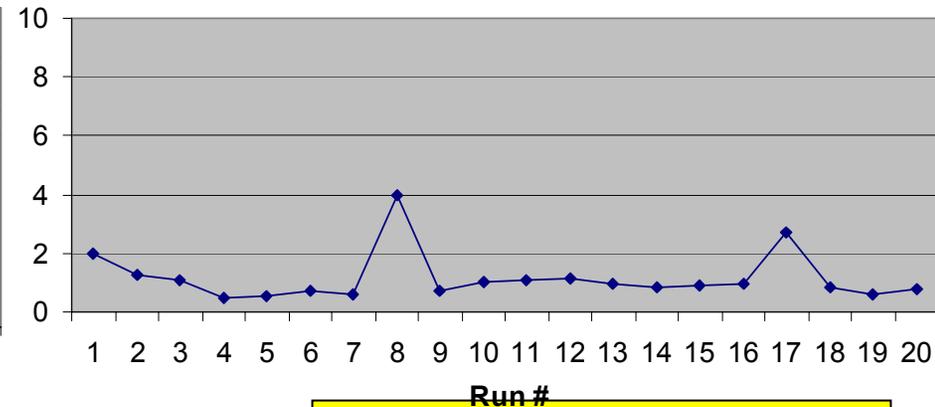
Task 3 – COF₂ Remediation – 99.8% HF removal achieved

Maximum COF₂ Emission, Empty Adsorbent Tube



No adsorbent,
0-900 ppm scale

Maximum COF₂ Emission, Half Tube, 50% filled with adsorbent, 500°C

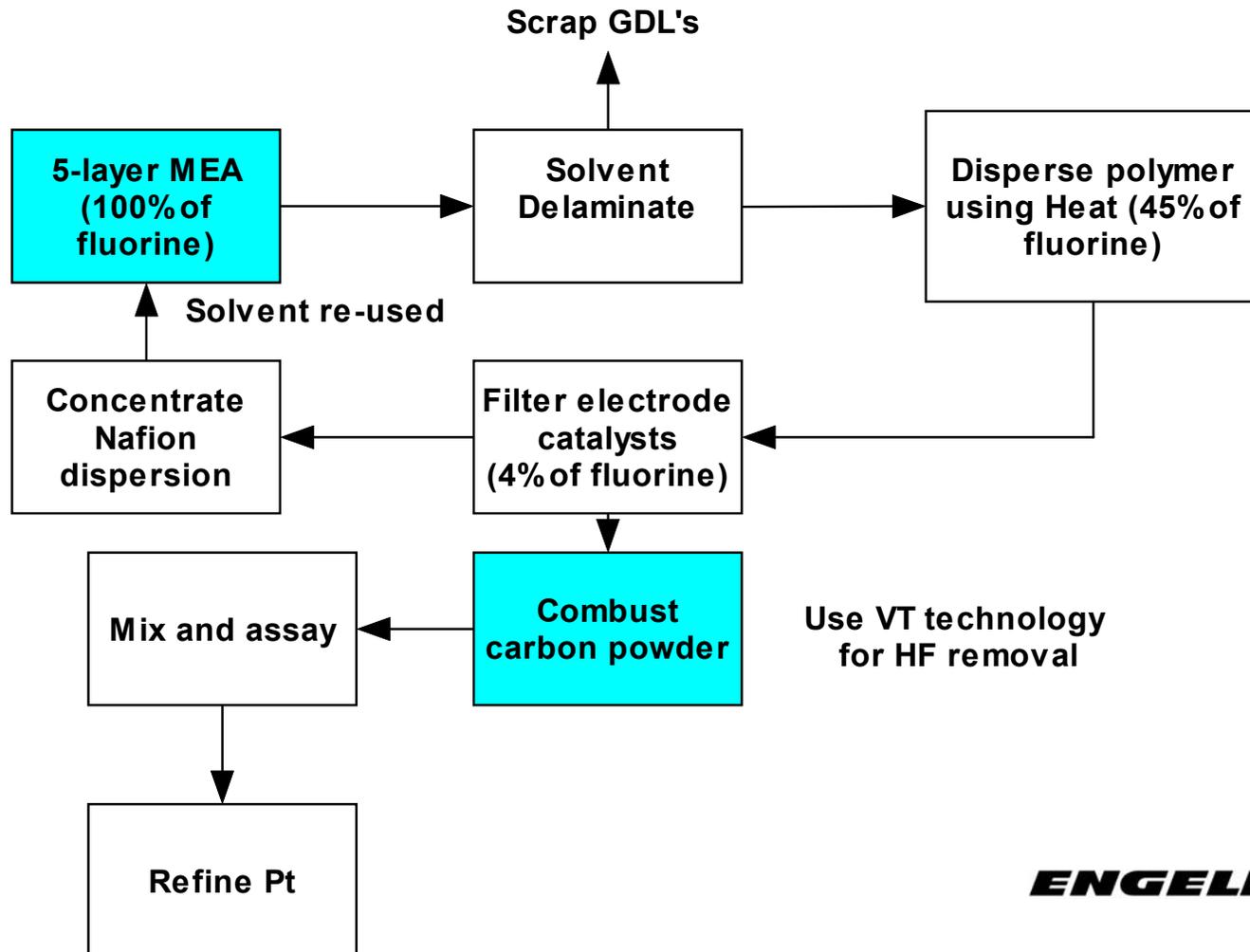


Adsorbent present,
0-10 ppm scale

Conclusion: Conditions have been identified to chemically remove fluorine-containing gases after Nafion combustion

Technical Accomplishments –cont.

Task 4: Engelhard Preferred MEA Recycling Process

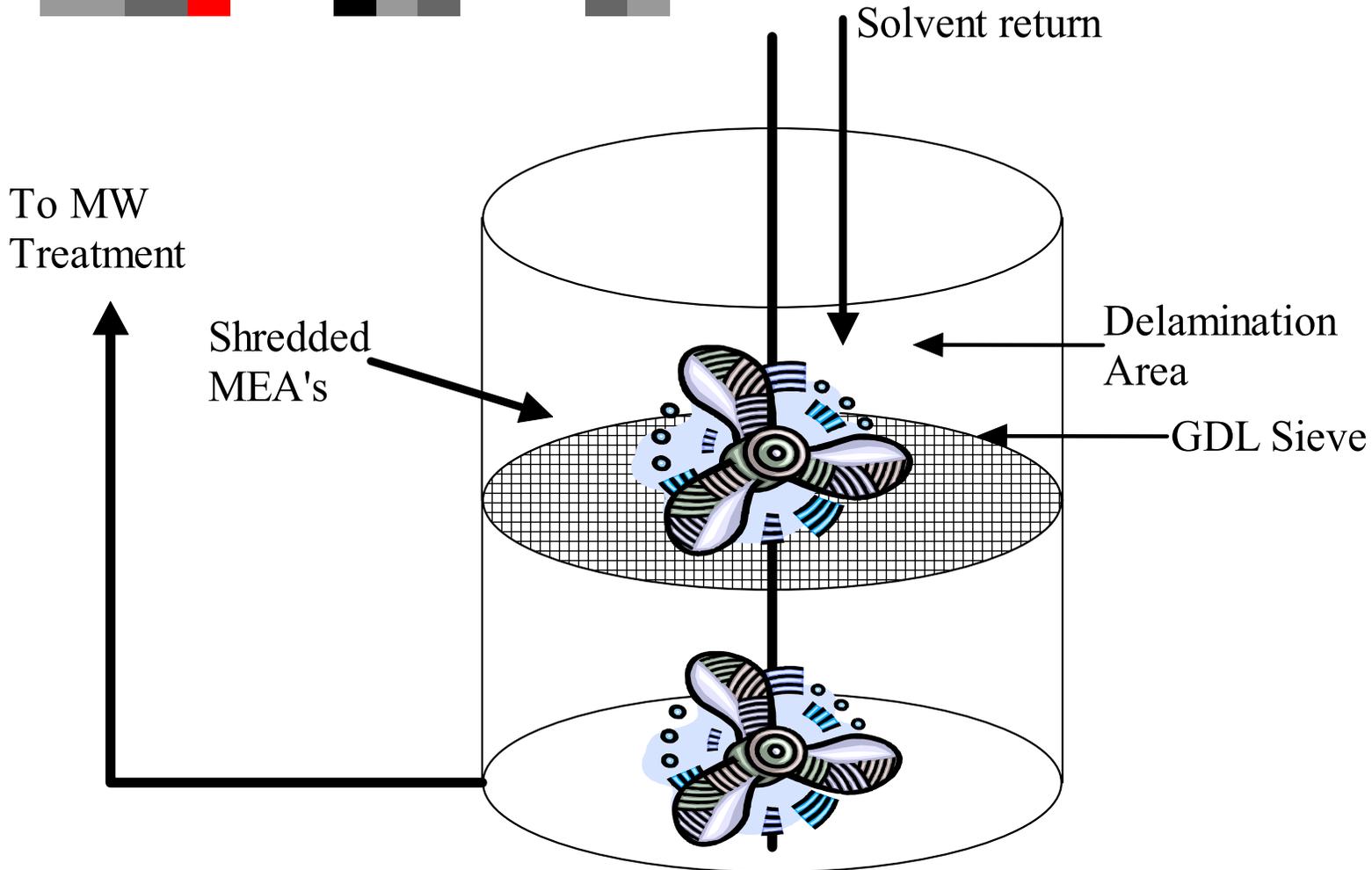




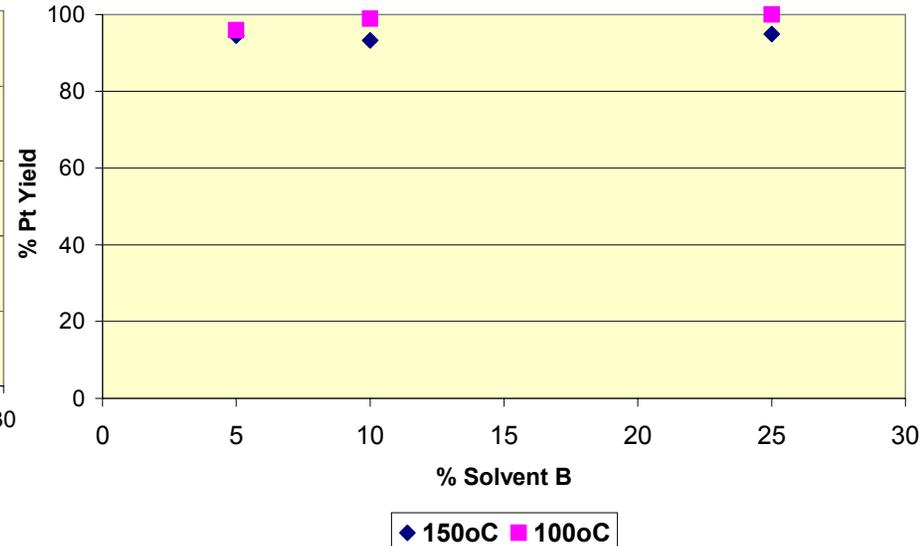
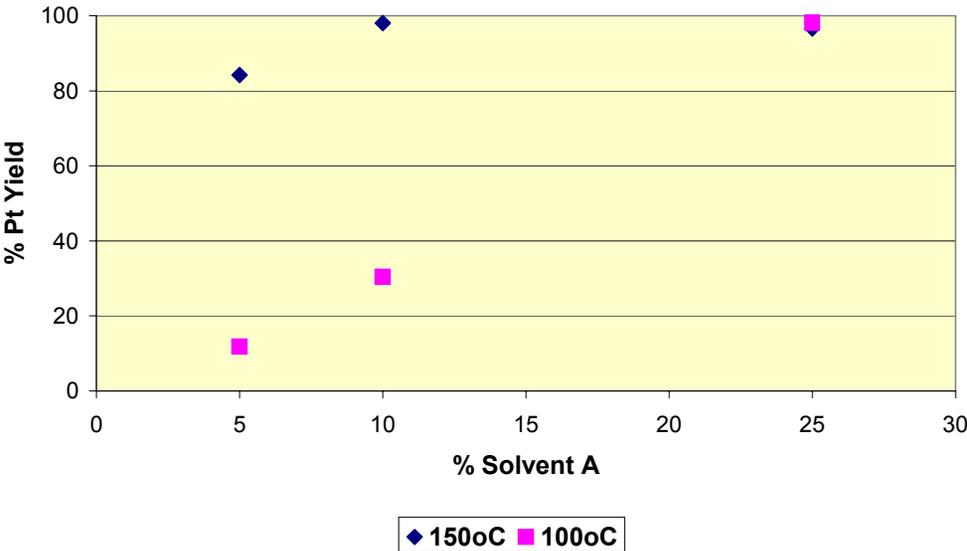
Process Explanation

- Used GDL-style MEA's have been shown to rapidly delaminate in alcohol/water mixtures, with partial membrane disintegration
- The membrane emulsion, with electrode catalyst, flows through a reactor and is heated with microwave energy to form a dispersion
- The carbon electrode particles are separated from the polymer dispersion for metal recovery
- The carbon is combusted, and the minimal HF emission is captured
- The polymer dispersion is then concentrated and the purified solvent reused
 - Engelhard is evaluating commercial outlets for recovered polymer
 - Applications will all be cost-driven
- The GDL's can be checked for residual Pt, then discarded

Visualization of Delamination Tank Using Alcohol/Water Mixtures



Technical Accomplishments- Effect of % Solvent and Temperature on Pt Recovery from Aged PEM MEA's is Solvent dependent -



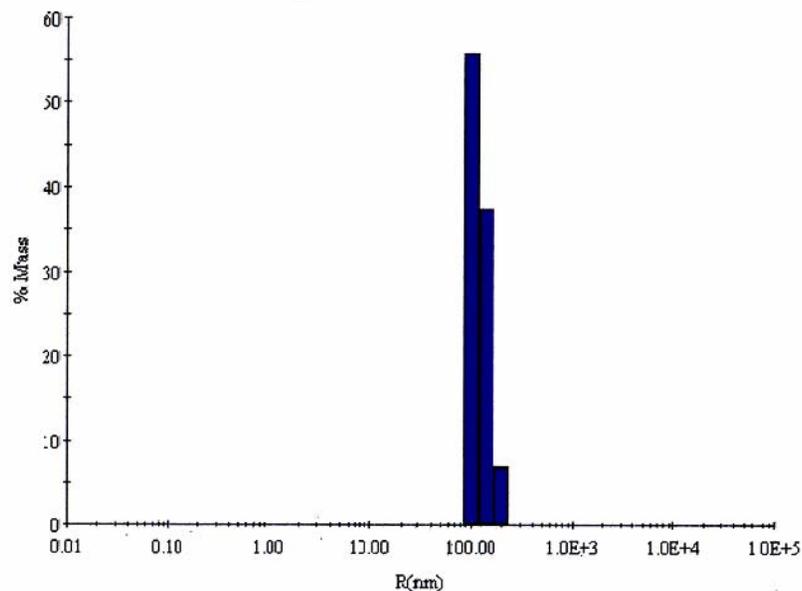
Influence of temperature important for Pt recovery using Solvent A Mixtures

Temperature has little effect on Pt recovery with Solvent B Mixtures

* Results obtained from batch experiments

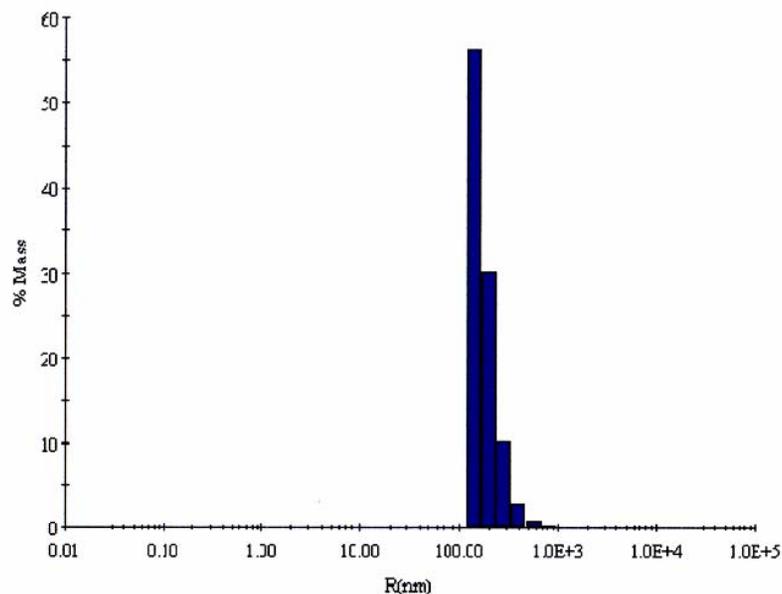
Technical Accomplishments – Dynamic Light Scattering Can be Used for Process Development and Quality Control

Nafion® Dispersed in 25% Solvent B @ 100°C (Batch)



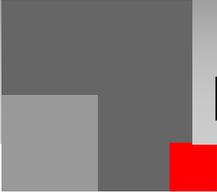
Item	D (cm ² /s)	R (nm)	%Pd	%Int	%Mass
Peak 1	1.97E-08	124.7	23.4	100	100

Nafion® Dispersed in 20% Solvent B, 5% Solvent A using a Continuous Method, 150°C



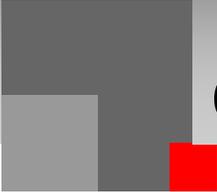
Item	D (cm ² /s)	R (nm)	%Pd	%Int	%Mass
Peak 1	1.30E-08	188.4	42.1	100	100

(Results courtesy of Wyatt Technology)
Data obtained using DynaPRO



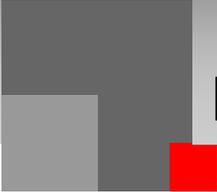
Future Work - Milestones

- Complete demonstration of scaled-up microwave digestion unit – 6/06
- Determine capacity of the VT adsorbent for fluorine gases – 9/06
 - Acid leaching of electrode catalyst will be substituted for combustion if fluorine gas removal is not scalable
- Validate the two-step filtration process for recovery of fuel cell catalyst and perfluoropolymer emulsion- 9/06
- Certify the process
 - Estimate economics, including combustion of electrode catalyst, based on daily rate of 100 kg of 5-layer MEA – 9/06
 - Purchase continuous reactor – 10/06
 - Integrate delamination, dispersion and filtration – 4/07



Critical Reviewer Comments From 2005

- Increase technical collaboration
- Continue with Nafion® recycling efforts (Value driven research)
- Why age MEA's? (500 vs. 2000 hours)
- What about GDE's? (This was a major concern of USCAR)



Recycling of GDE- style MEA's

- GDE's have electrode catalyst on the gas diffusion layer instead of on the membrane
- Layers of a fresh MEA do not split apart after exposure to hot water, steam or solvents
- The GDE has to be manually separated from the membrane to facilitate Pt recovery
 - **The electrode catalyst is partially left on the membrane during this process**
- After heating in boiling water, pulling apart the layers keeps all the electrode catalyst on the GDE
- High yields of Pt are achieved with microwave assisted acid-digestion of the GDE layers

Electrode catalyst is stripped from the GDE when the membrane is ripped from the outer (GDE) layers – No pre-treatment



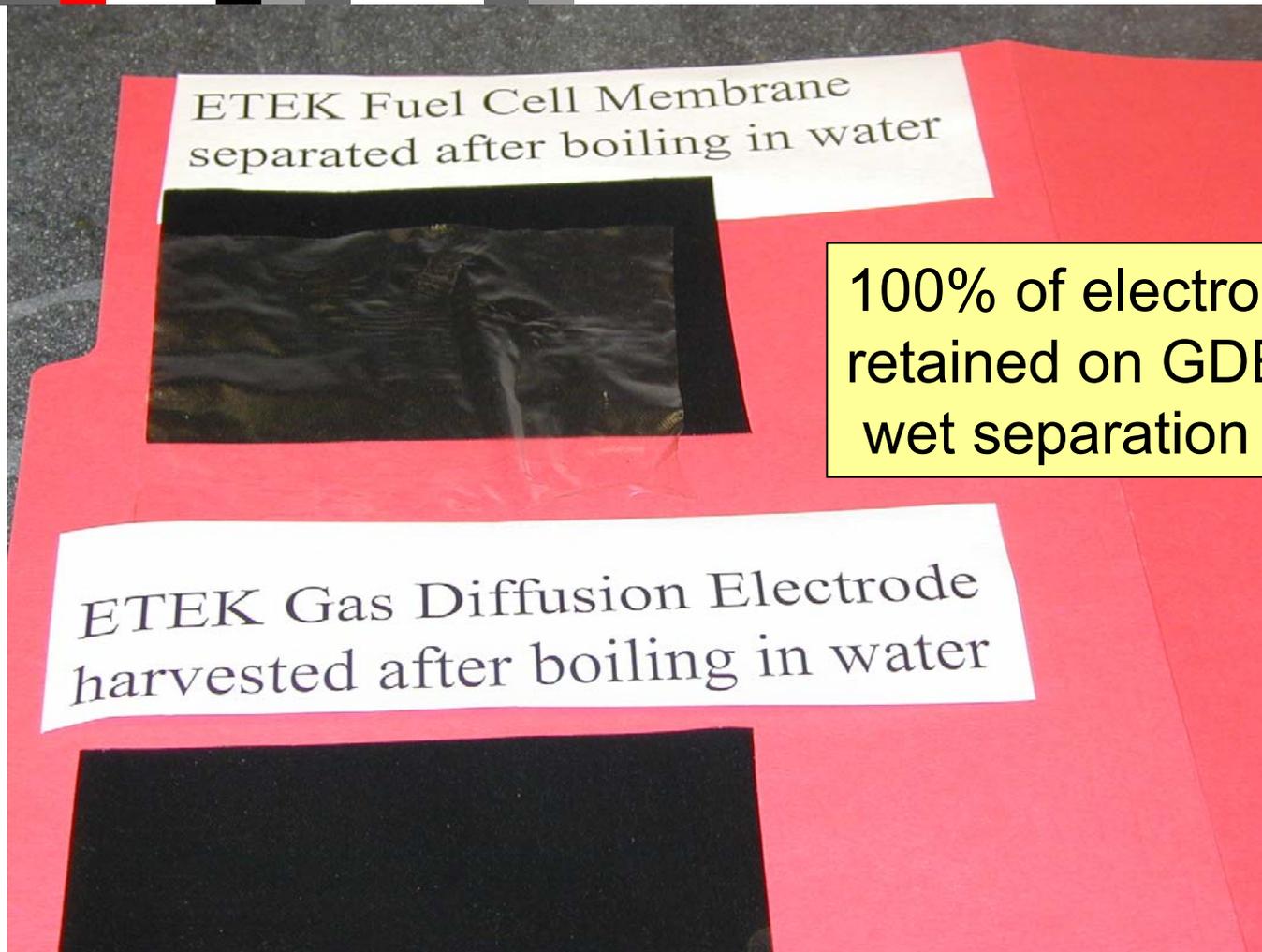
Exterior gas diffusion layers with electrode catalyst removed



Membrane partially Covered with electrode Catalyst stripped from GDE

Electrode catalyst ends up on all surfaces with dry dismemberment

Value of preliminary membrane separation in retaining electrode catalyst on the (outer) gas diffusion layer – Boil, then Strip



ETEK Fuel Cell Membrane
separated after boiling in water

100% of electrode catalyst
retained on GDE with
wet separation

ETEK Gas Diffusion Electrode
harvested after boiling in water

Recovery of Electrode Catalysts from new GDE MEA's (Etek) after membrane removal (except for Ignition Method)

- **U of K High T/P Autoclave process or Solvent Delamination**
- **Not viable- Most of the Pt/Carbon stays on the GDE**
- **Ignition (no pre-treatment)**
 - **High HF release**
- **Estimated >95% Pt recovery**
- Atmospheric acid leach (hot plate)
 - Nafion® membrane recycling possible
- **91% Pt recovered**
- Microwave assisted (under pressure) acid leach
 - **Nafion® membrane recycling possible**
- **96% Pt recovered**



Back-up slides

Highlights of Milestone Flowsynth Continuous Reactor (Courtesy of Milestone Scientific, Shelton, CT)



Pump



Reactor mixer

Reactor inside
Microwave oven





MATERIALS SCIENCE AND ENGINEERING



Tandem
Microwave
ovens