Applied Science for Electrode Cost, Performance, and Durability

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Project ID: FC10

Overview

Time Line

- Start: FY 05
- Status: ongoing

Barriers Addressed

- **A. Durability**
- **B. Cost**
- **C. Electrode Performance**

Funding

- Funding in FY07: $600 K
- Funding for FY08: $600 K
- Non-cost shared

Collaborators

- Oak Ridge National Laboratory

Objectives

- ***To assist the DOE Hydrogen, Fuel Cells & Infrastructure Technologies (HFCIT) Program in meeting cost, durability and performance targets by addressing issues directly associated with electrodes (electrode science not specifically called out in FY '06 call).***

Table 3.4.12 Technical Targets: Electrocatalysts for Transportation Applications						
Characteristic	Units	2005 Status [a]		Stack Targets	
		Cell	Stack	2010	2015
Platinum group metal (pgm) total loading [b]	mg PGM / cm² electrode area	0.45	0.8	0.3	0.2
Cost	$ / kW	9	55 [c]	5 [d]	3 [d]
Durability with cycling					
Operating temp ≤80°C	hours	>2,000	~2,000 [e]	5,000 [f]	5,000 [f]
Operating temp >80°C	hours	N/A [g]	N/A [g]	2,000	5,000 [f]
Electrochemical area loss [h]	%	90	90	<40	<40
Mass activity [j]	A / mg Pt @ 900 $mV_{iR\text{-}free}$	0.28	0.11	0.44	0.44
Specific activity [j]	μA / cm² @ 900 $mV_{iR\text{-}free}$	550	180	720	720

Pt cost is primary limitation to meeting targets.

Cost, performance, and durability intertwined.

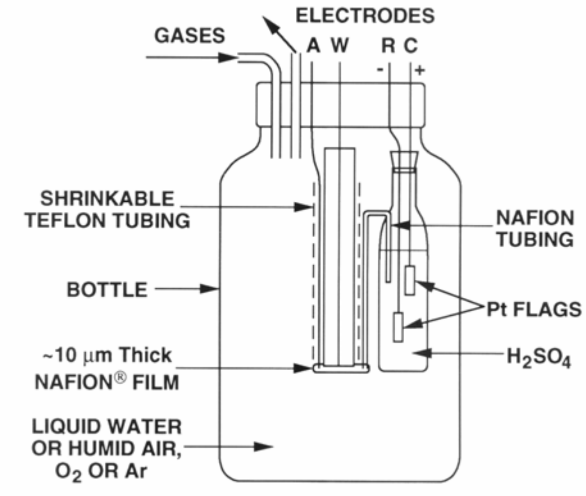
Milestones

Mon Yr	Milestone
Feb 07	Develop and validate a model of the oxygen reduction reaction on Pt catalyst that considers relevant intermediate oxide species and both dissociative and reductive adsorption reaction pathways (completed)
Apr 07	Determine peroxide generation rates at a minimum of three temperatures and three relative humidities (completed)
Mar 08	Perform gravimmetry experiments of H2S adsorption and CO adsorption to compare with heterogeneous surface area measurements obtained by ion selective electrodes (completed)
Jul 08	Modify MEAs processing to obtain electrochemical surface areas that vary by a factor of 3, and correlate these differences in surface area with fuel cell performance (in progress)

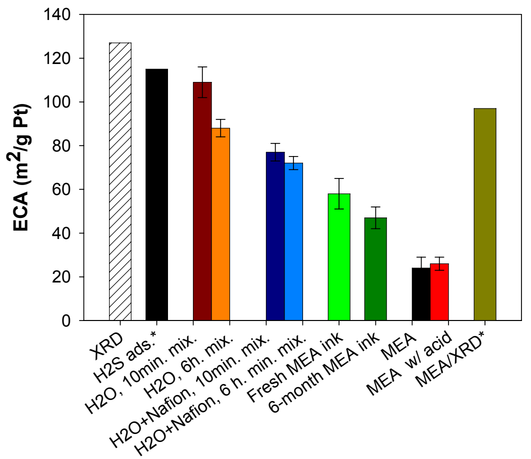
Approach

2007

Use micro-electrodes and interdigitated micro arrays to study ORR and peroxide generation.



Elucidating catalyst utilization in electrodes.



http://www.hydrogen.energy.gov/pdfs/review07/fc_7_pivovar.pdf

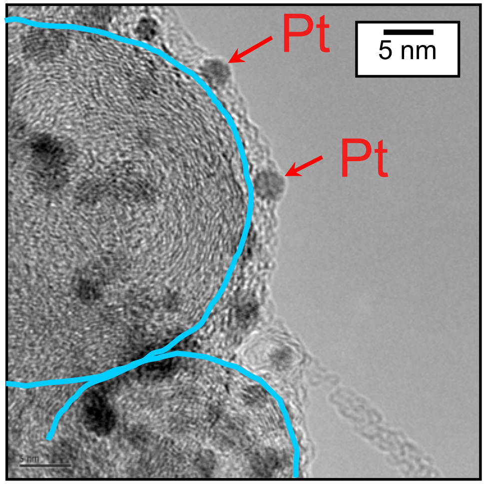
2008

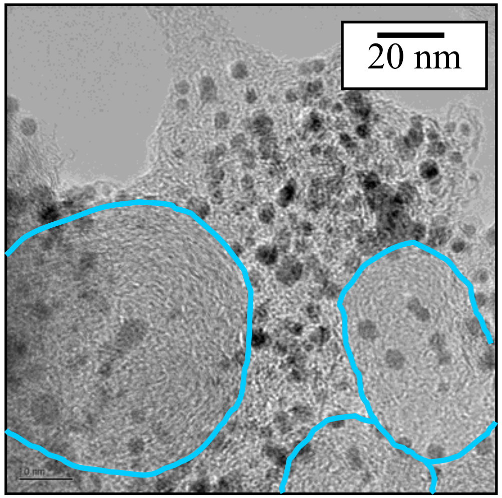
Explore effect of catalyst ink composition and processing on utilization and performance.

Use microscopy and other tools to better understand structure and impact on performance.

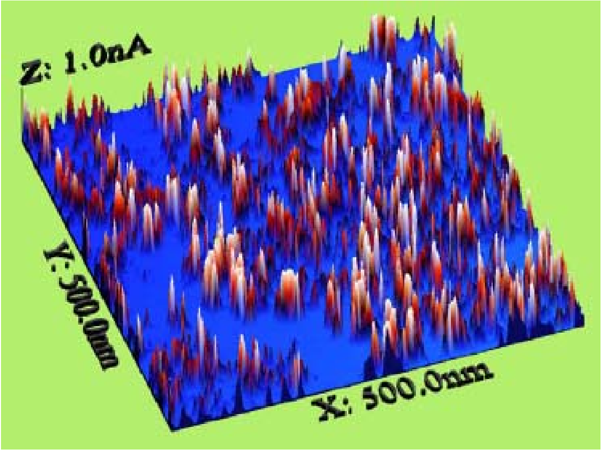
Electrodes

- ‘GE’ style electrode: Pt black steam-bonded with Teflon
- 1986: Raistrick (LANL): Impregnated catalyzed Prototech electrode (ELAT)
- 1990: Wilson (LANL): Intimately mixed ionomer/catalyst ink applied to membrane
- Mid 90’s – Present: Nanostructured electrodes (3M, carbon nanotubes, Pt nanotubes)





HR-TEMs courtesy of Karren More, ORNL



Emil Roduner, University of Stuttgart, Asilomar, CA, February19 –22, 2007

Catalyst Utilization

Definition

$$u = \frac{SA_{used}}{SA_{theoretical}}$$

SA_{used} → **utilized Pt surface area**

$SA_{theoretical}$ → **Theoretical Pt surface area**

- **Ralph *et al.*, *J. Electrochem. Soc.*, 144, 3845-57 (1997)**

  Catalyst: Johnson Matthey 20% Pt/C
  Utilization: $ECA_{\text{fuel cell electrode}} / ECA_{\text{fully flooded gas diffusion electrode w/o Nafion}}$
  Technique: Cyclic Voltammetry (CO stripping)
  Results: 40-50%

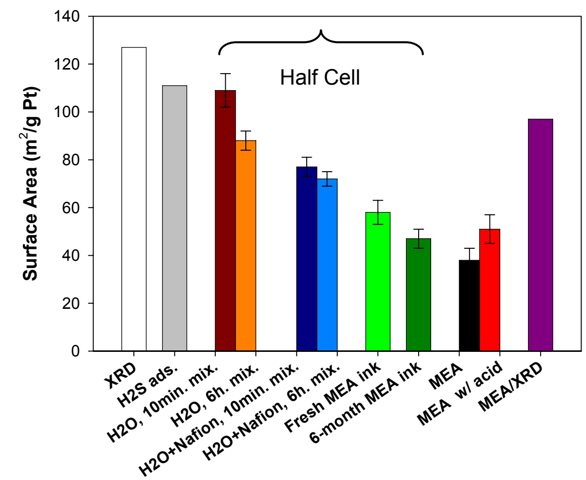
- **Gasteiger *et al.*, *Appl. Catal. B: Environ.*, 56, 9-35 (2005)**

  Catalyst: ETEK 20% Pt/C and TKK 47% Pt/C
  Utilization: $ECA_{\text{fuel cell electrode}} / ECA_{\text{Pt on glassy carbon w/ Nafion}}$
  Technique: Cyclic Voltammetry (Hydrogen adsorption)
  Results: 80-90%

- **Shinozaki *et al.*, the 212th ECS meeting (2007)**

  Catalyst: 45% Pt/Ketjen
  Utilization: #CO adsorbed on MEA/ #CO adsorbed on catalyst powder
  Technique: CO Stripping and CO pulse measurement
  Results: 88%

Results depend on techniques used.

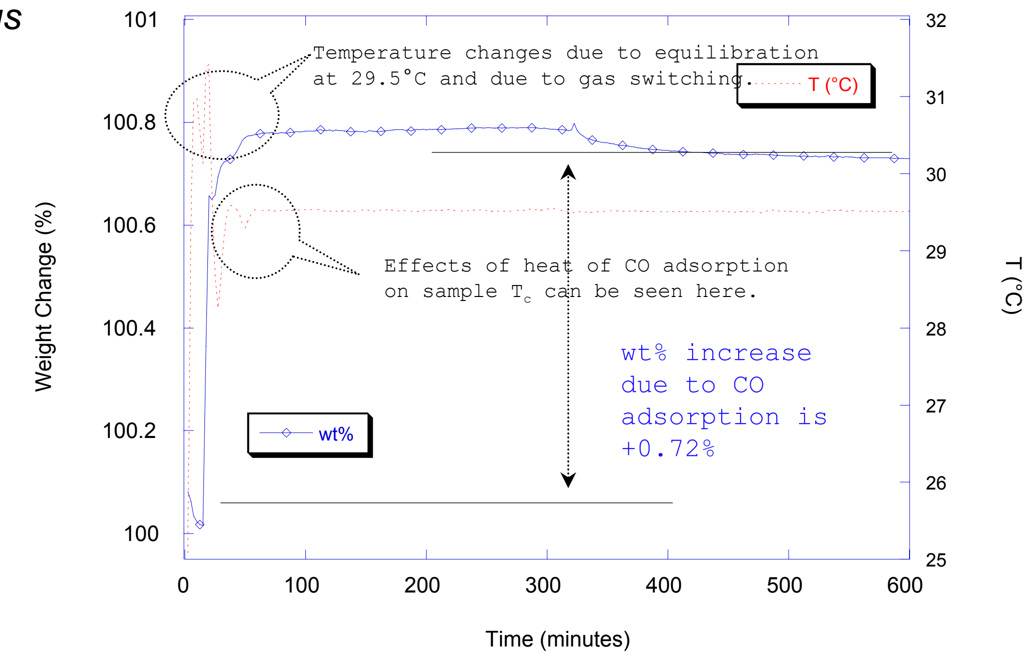


Our work

CO Gravimetric Experiments

- *Netzsch STA-449 high precision, simultaneous TGA/DSC*
  - *CO work required enhanced safety precautions - alarms, etc.*
- *Special Instrument*
  - *Rated vacuum tight at 10^{-4} torr operation (required for work with toxic gases)*
  - *Unique thermostatic controlled balance unit*
  - *Drift due to T&P (gas flow) variations amounts to less than 0.1% error*
- *2 Step procedure developed*
  - *1) clean surfaces*
  - *2) expose to CO and measure mass of CO uptake*

HiSpec 1000; Pt black cleaned; 128.522mg



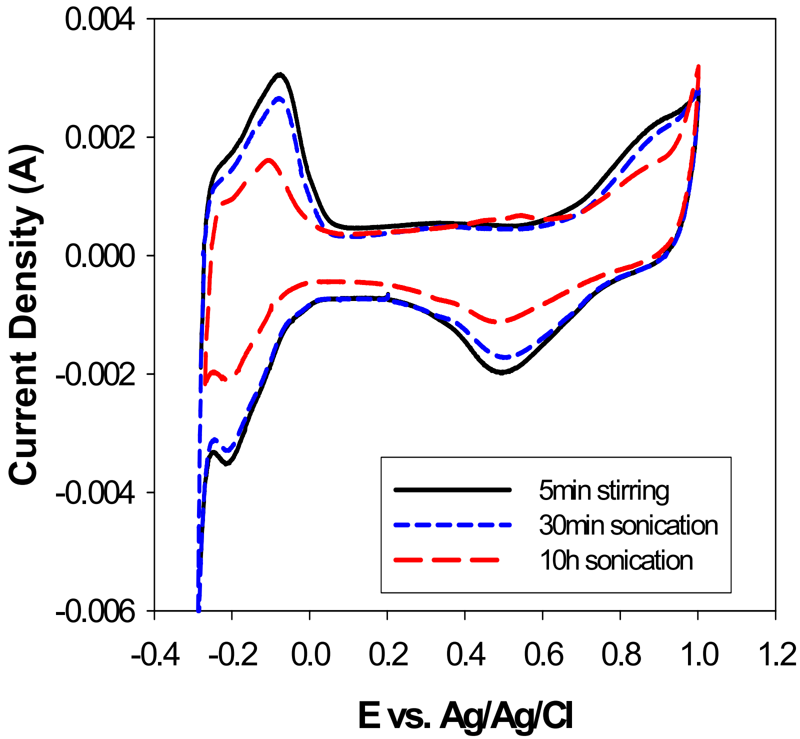
Surface Areas (m^2/g Pt)	CO*	Half cell	H2S	XRD
Pt Black	***26***	*29*	*73*	*35*
20% Pt/C (Etek)	***136***	*108*	*110*	*127*
Advanced Pt/C	***143***	*100*	*-*	*137*

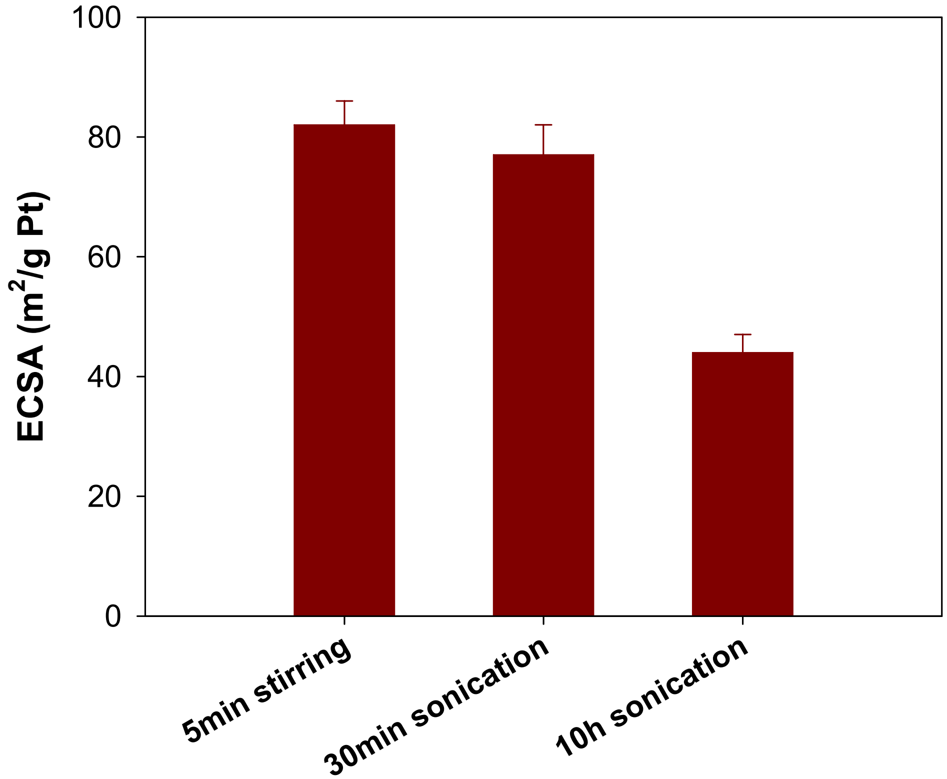
CO gravimetry yields reproducible results in reasonable agreement with other estimates of surface area. (milestone 1)
H_2S values unreliable (surface reorganization).

*16.3 A^2 used for surface coverage of CO molecule (**Shinozaki *et al.*, *ECS Trans.*, 11(1), 497 (2007)**).

Effect of Ink Processing on ECSA in Half Cells

Catalyst: Etek 20% Pt/C, mixed w/ Nafion (N:C=1:2)





ECSA decreases with increased mixing, HR-TEM shown on following slide.

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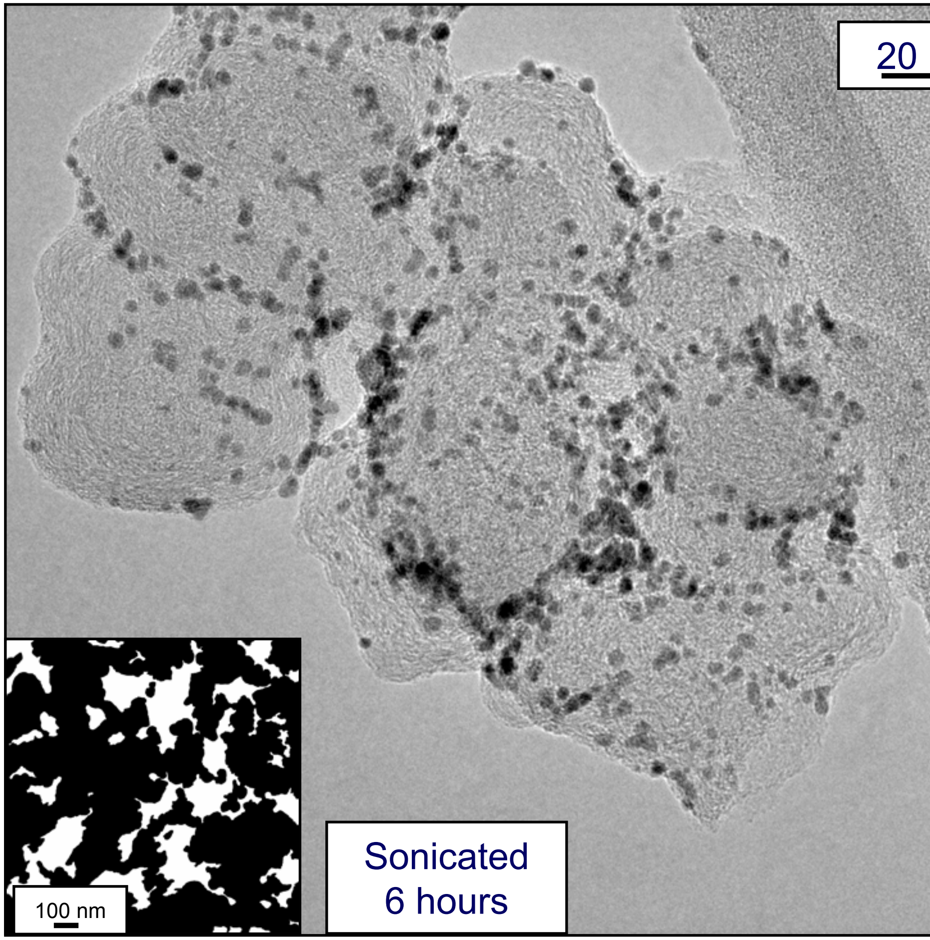
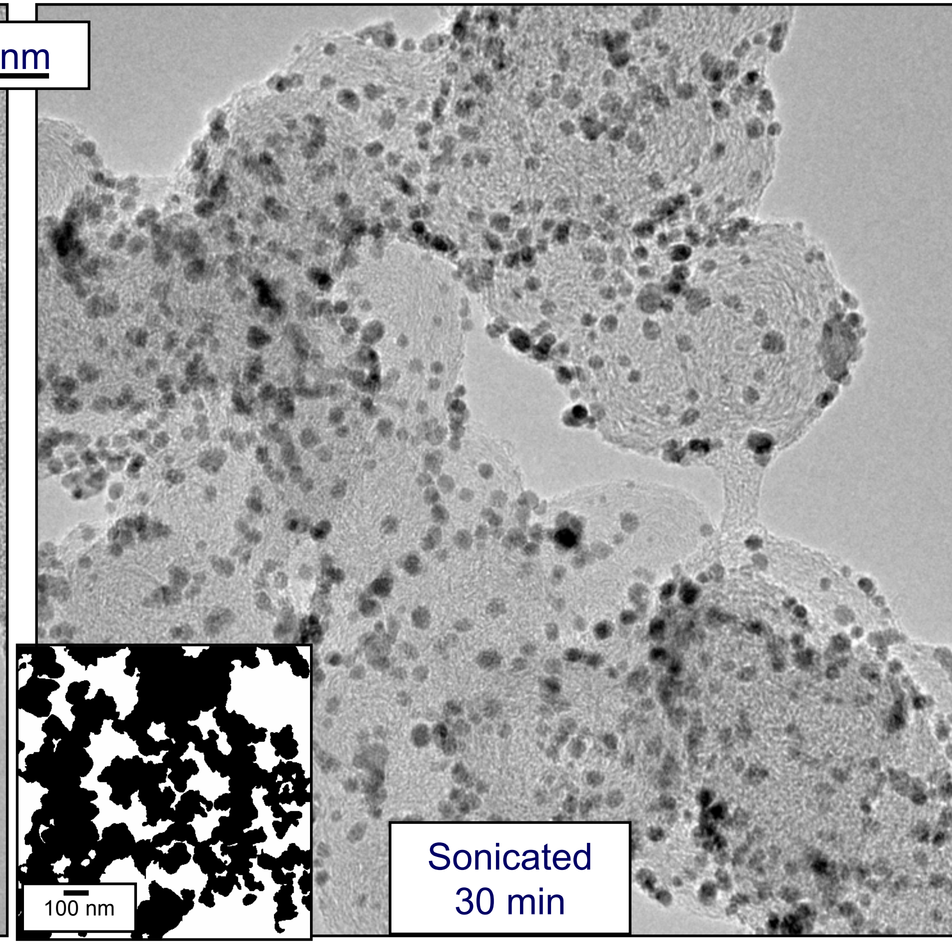
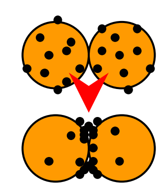
Effect of Sonication time

Etek 20% Pt/C





Increased sonication time leads to more heterogeneous distribution of platinum, lower porosity, particle size growth (confirmed by XRD), decreased surface area, and decreased fuel cell performance (not shown).



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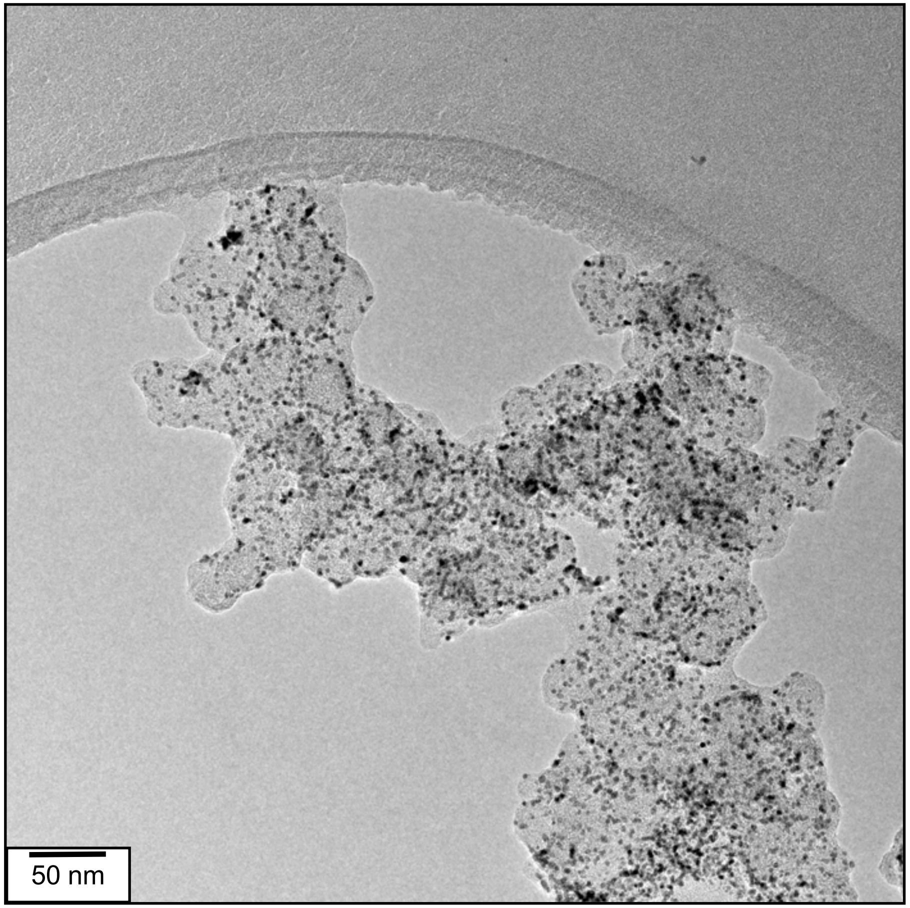
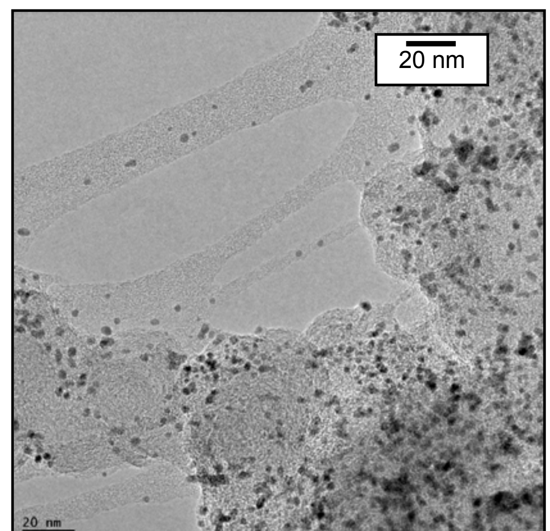
HR-TEMs courtesy of Karren More, ORNL

Ball Milling



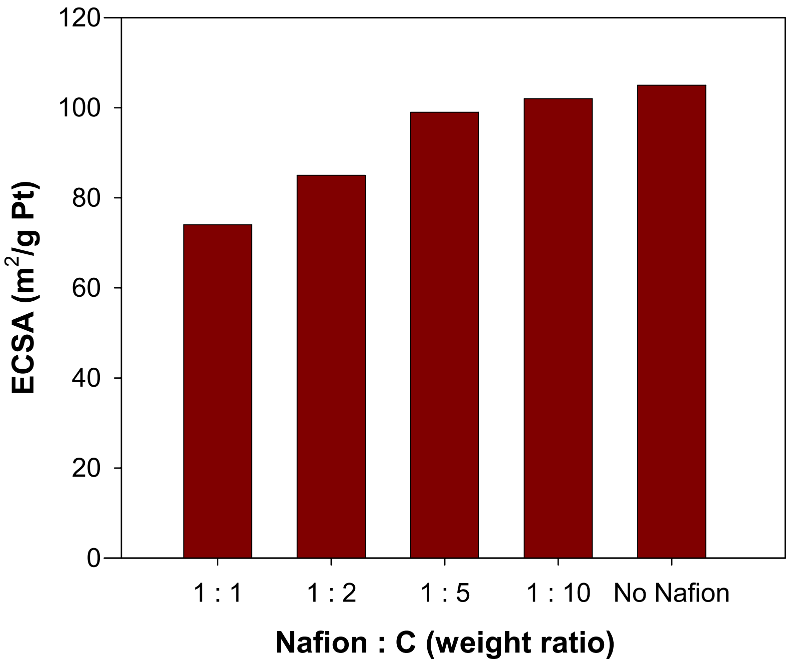
Ball milling gave relatively high surface area (electrochemical) measurements similar to short sonication times, but increased separation of Pt particles from carbon, and decreased build up at junctions evident from HR-TEM.



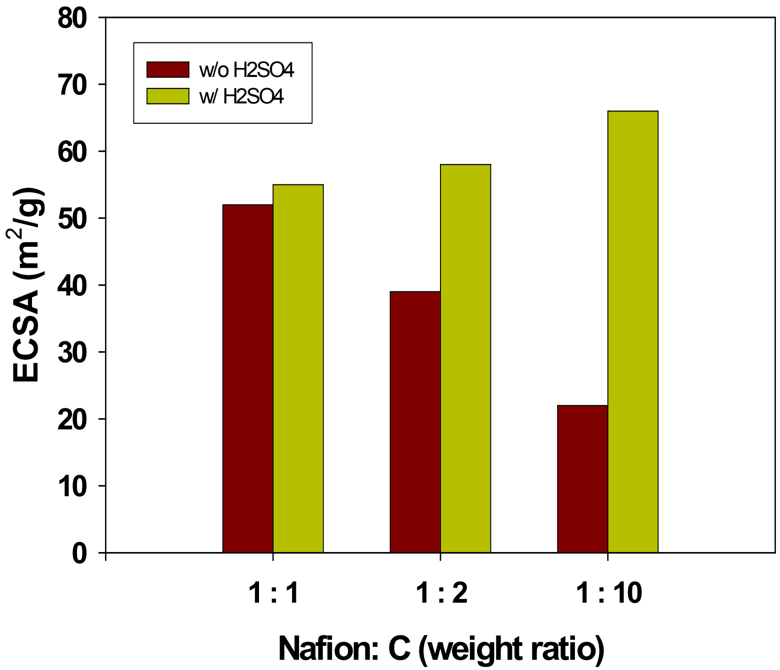
Etek 20% Pt/C

Effect of Nafion:C on ECSA

Half Cells



Fuel Cells

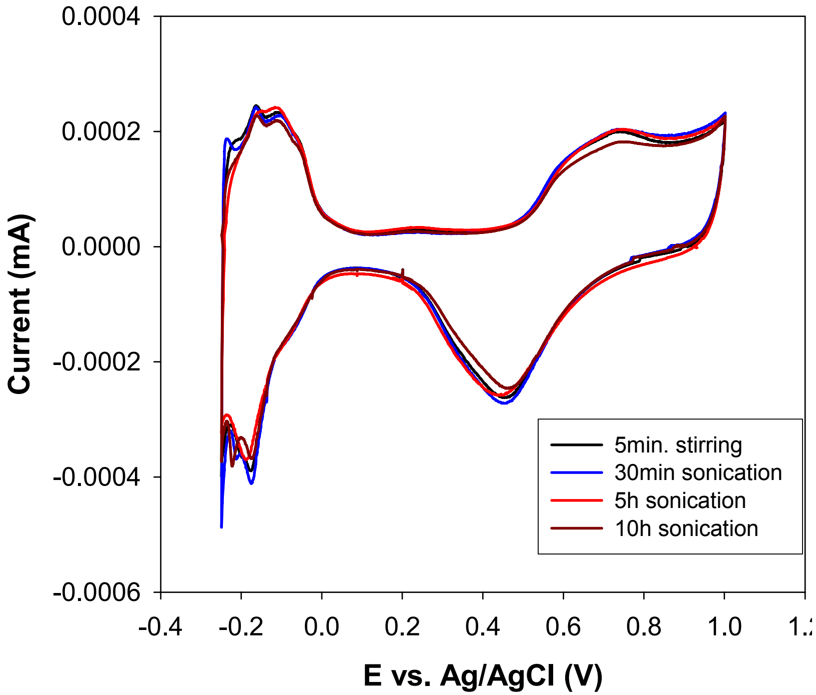


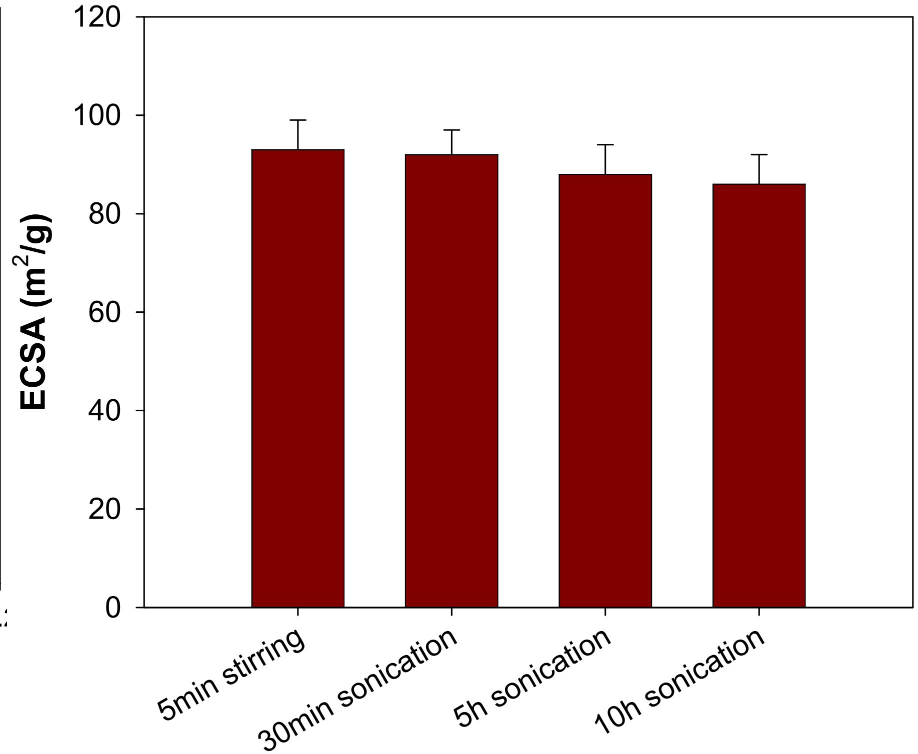
Catalyst: Etek 20% Pt/C, mixed w/ Nafion (N:C=1:2)

- In half cells, ECSA increases when Naf:C decreases but changes little when N:C is 1:5 or less;
- In fuel cells, ECSA decreases when Naf:C decreases but increases when free acid is circulated at cathode.

Processing Effect on Alternative Catalyst

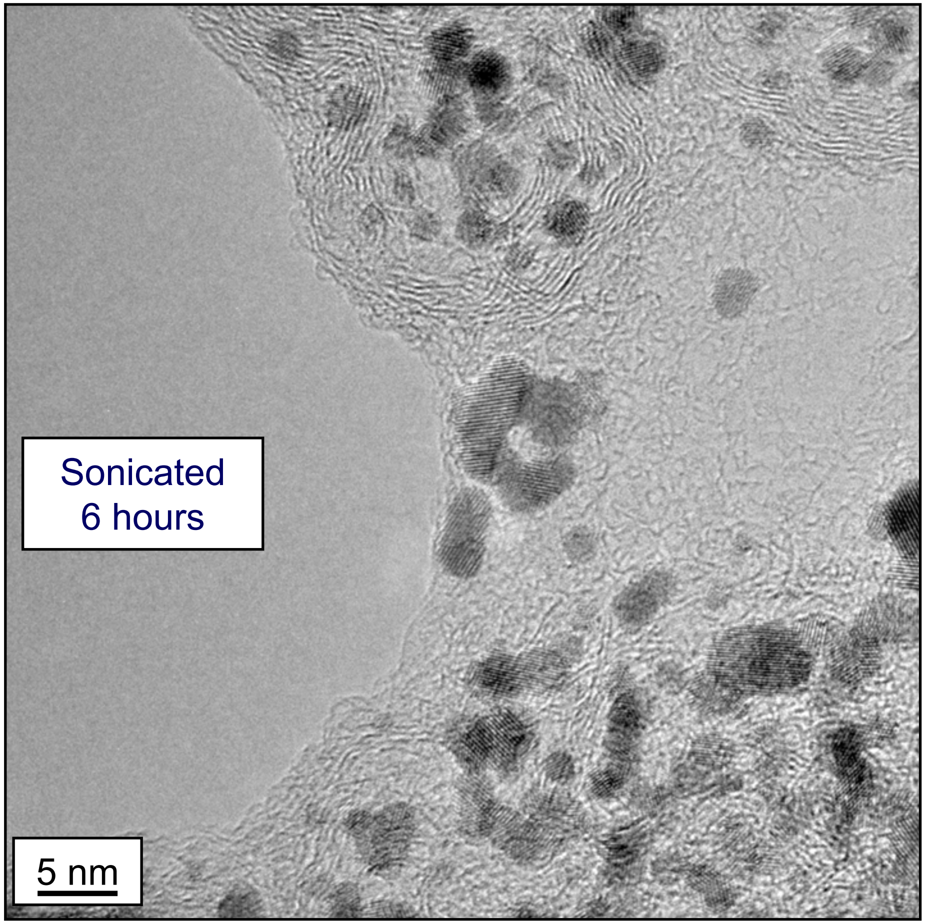
Catalyst: Pt (higher mass %)/alt. carbon support (Nafion:C=1:2)

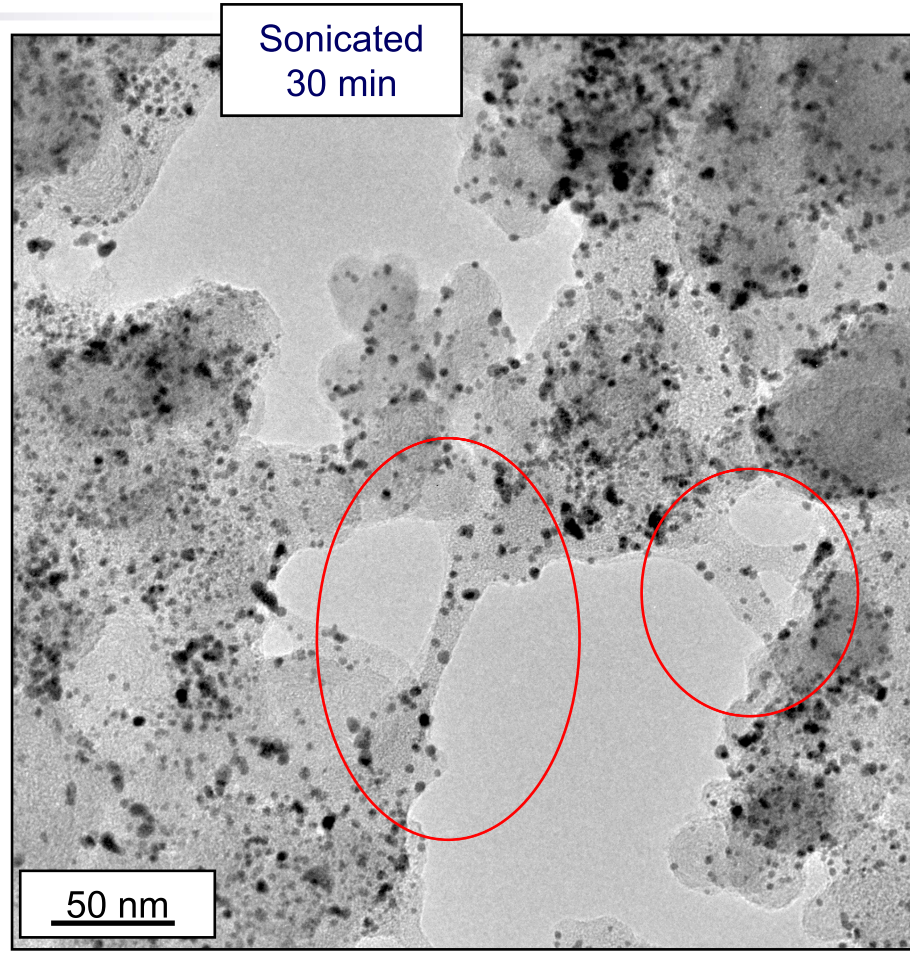




For “advanced” catalyst, ECSA changes very little with increased mixing-effect of processing is catalyst (support)-dependent.

Alternative Catalyst HR-TEM



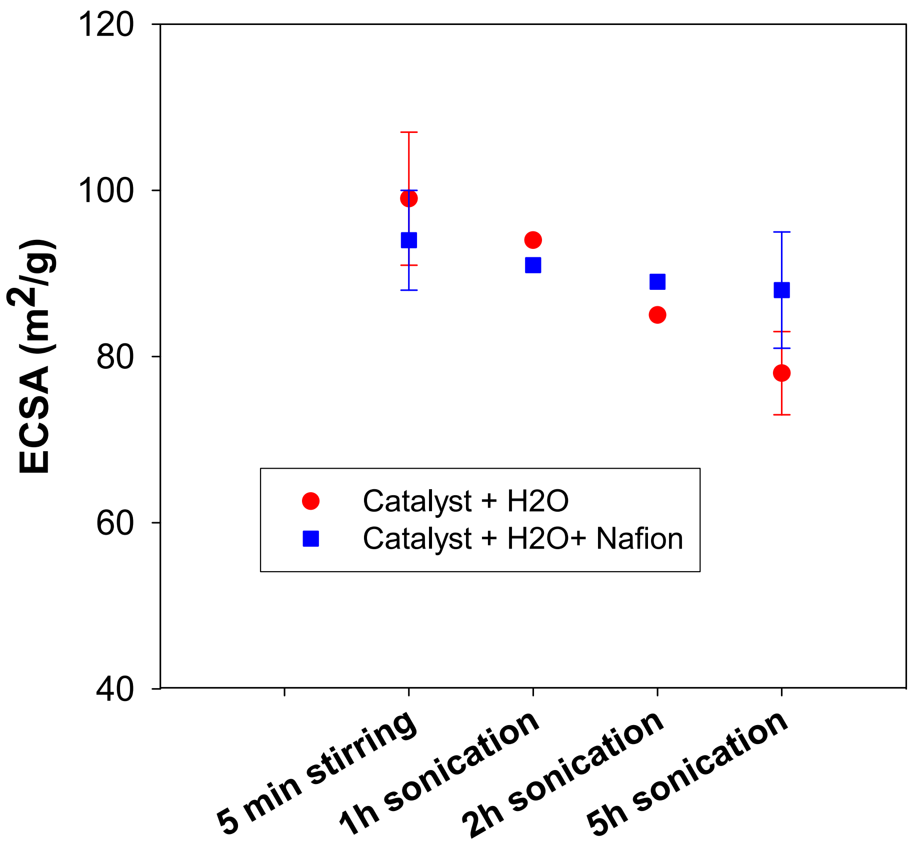


Relatively minor changes in TEM (and electrochemistry) as a function of sonication time, smaller Pt particles (confirmed by XRD) result in higher surface areas, significant Pt in ionomer webs.

HR-TEMs courtesy of Karren More, ORNL

The Effect of Nafion on ECSA Changes

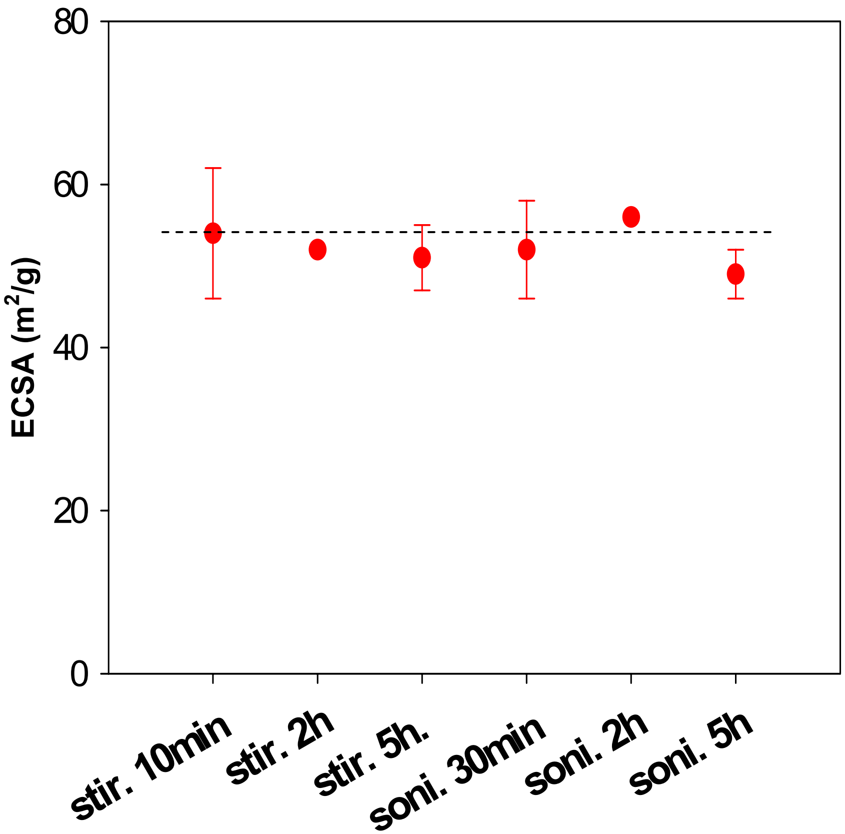
Catalyst: Pt/alternative carbon support (Nafion:C=1:2)



- w/o Nafion, ECSA is initially higher than w/ Nafion but decreases faster with increasing degree of processing.
- Presence of Nafion may cause initial Pt displacement, but actual act to prevent further displacement.
- Testing catalyst after water only sonication (microscopy and MEA is planned)

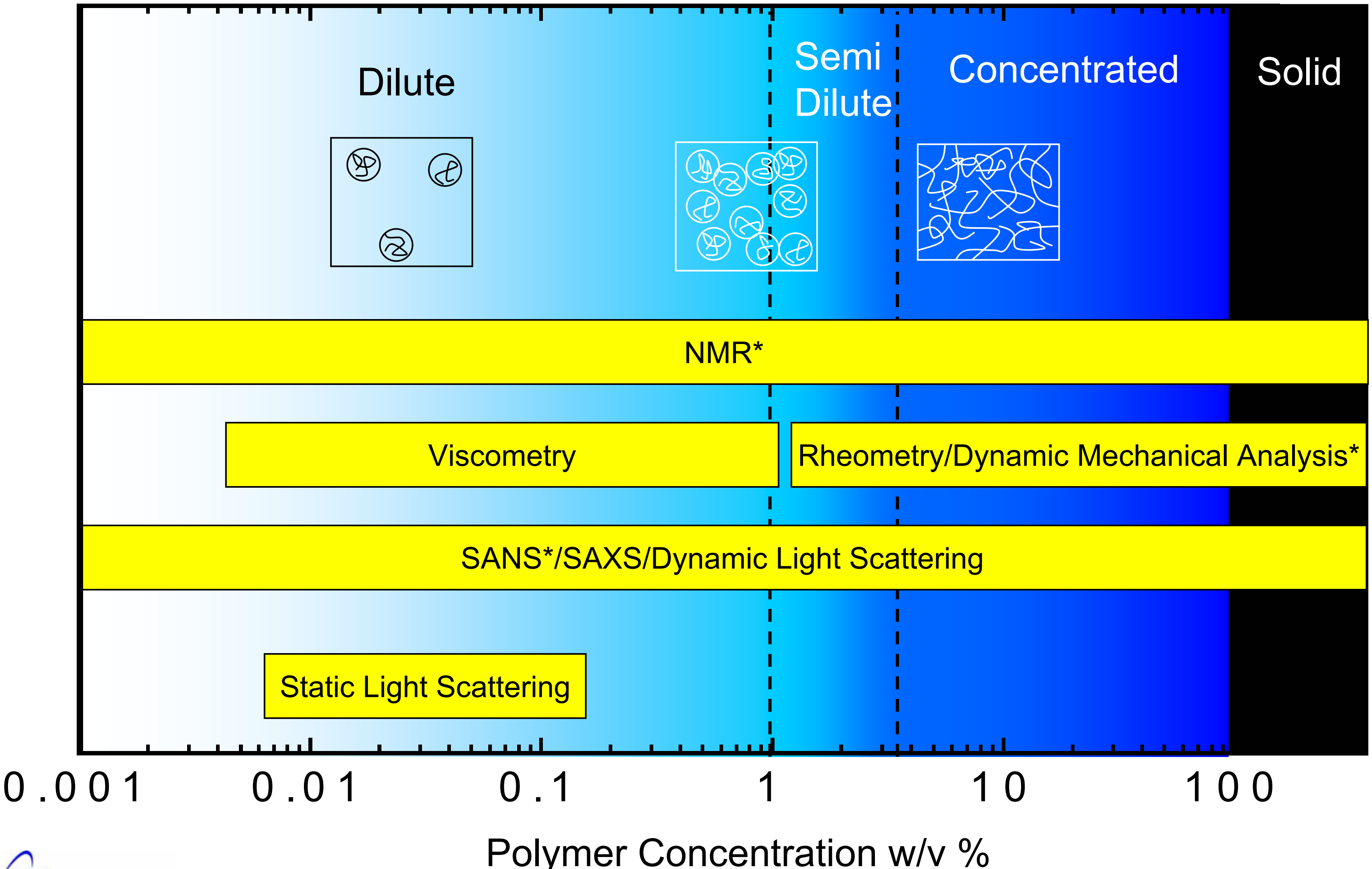
Processing Effect on Alternative Catalyst in Fuel Cells

Catalyst: Pt/alternative carbon support (Nafion:C=1:2)



- ECSA of fuel cell electrode changes little with processing time, similar to half cell.
- Significant loss of surface area compared to half cell studies (90 m^2/g).

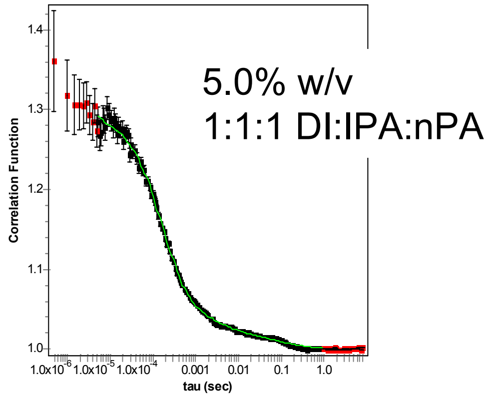
Characterization of Polymer Solutions



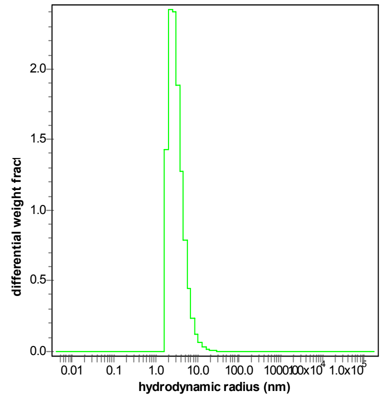
*Can be used to characterize catalyst dispersions

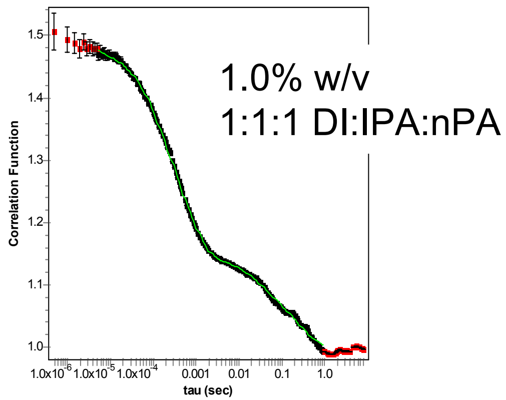
Dynamic Light Scattering of Polymer Dispersions

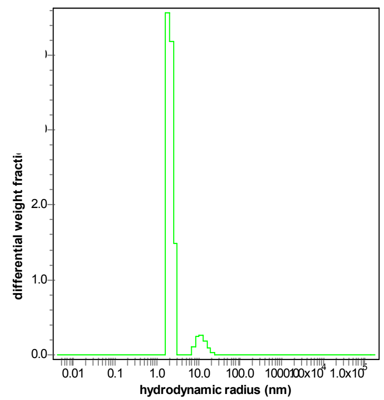
Correlation Function



Correlation Length ζ





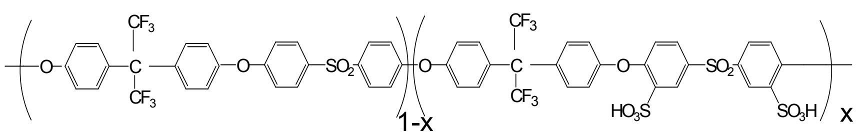


Initial studies focus on dynamic and static light scattering to yield information about characteristic length scales.

Changes in correlation lengths observed by changing polymer concentration.

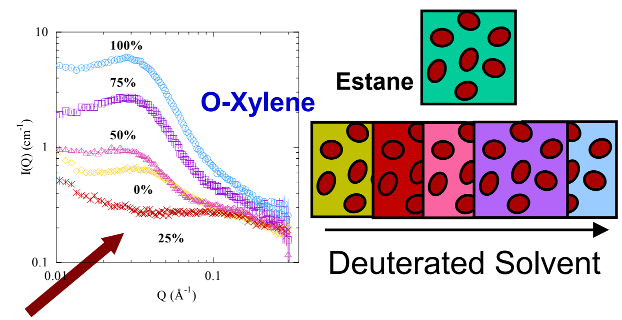
By spanning concentration ranges information on radius of gyration, hydrodynamic radius and other parameters effecting electrode preparation (ie, ink drying) can be explored.

6F-35 solutions



Future Work

- *Kinetic Studies*
  - *Coupling performance and durability with structure/composition*
    - *Measurements of mass activity*
    - *Effects of (accelerated) aging (particle size growth, migration)*
  - *Discerning activity within accessible Pt (not all sites are equal), can accessible sites be made more active?*
- *Advanced Supports/Novel Architectures*
  - *Corrosion resistant supports*
  - *Pt nanotubes, “whiskers”, pretreatment, etc.*
- *Ink/Solution Studies*
  - *Probing ionomer/catalyst in solution and inks*
    - *Scattering (x-rays, neutrons (beam time at LANSCE in June), light)*
  - *Effects of drying and wetting (polymer/ catalyst(support) interactions) on structure-performance relationships*
- *Modeling/Correlation with Models*



Project Summary

- *Pulsed CO absorption measurements validated as a probe of heterogeneous surface area (milestone 1).*
- *We have characterized platinum surface area as a function of processing and shown significant decreases in surface area occur.*
- *Loss of surface area dependent on the types of supports and conditions investigated.*
- *Incorporation of Nafion is necessary for ionic contact, but likely leads to Pt “displacement” from typical supports. Over longer times Nafion can have a protecting effect holding Pt in contact with support.*
- *Neutron time awarded for deuterated solvent based ink studies. Light scattering yielding preliminary results.*