National Renewable Energy Laboratory
Innovation for Our Energy Future

Extended, Continuous Pt Nanostructures in Thick, Dispersed Electrodes

Bryan Pivovar (PI)

National Renewable Energy Laboratory

Sept 30, 2009

Objectives

To assist the DOE Fuel Cell Technologies (FCT) Program in meeting cost, durability, and performance targets in the areas of Electrocatalysts and MEAs.

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 / cm^2 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 [i]	A / mg Pt @ 900 $mV_{iR\text{-}free}$	0.28	0.11	0.44	0.44
Specific activity [j]	μA / cm^2 @ 900 $mV_{iR\text{-}free}$	550	180	720	720

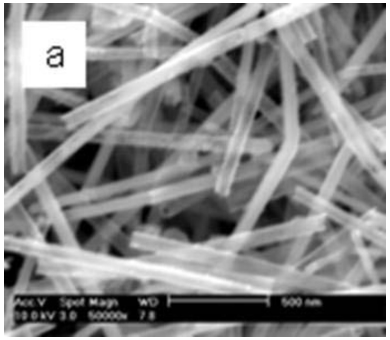
Table 3.4.13 Technical Targets: MEAs

Characteristic	Units	2005 Status [a]	2010	2015
Operating temperature	°C	<80	<120	<120
Inlet water vapor partial pressure	kPa	50	<1.5	<1.5
Cost [b]	$ / kW	60 [c]	10	5
Durability with cycling				
At operating temp of ≤80°C	hours	~2,000 [d]	5,000 [e]	5,000 [e]
At operating temp of >80°C	hours	N/A [f]	2,000	5,000 [e]
Unassisted start from low temperature	°C	-20	-40	-40
Performance @ ¼ power (0.8V)	mA / cm^2 mW / cm^2	200 160	300 250	300 250
Performance @ rated power	mW / cm^2	600	1,000	1,000
Extent of performance (power density) degradation over lifetime [g]	%	5 [h]	10	5
Thermal cyclability in presence of condensed water		Yes	Yes	Yes

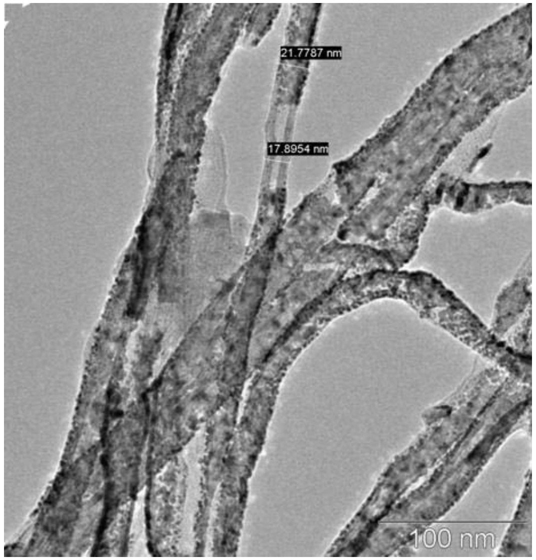
Approach: Novel Synthesis and Electrode Studies

Novel Synthesis

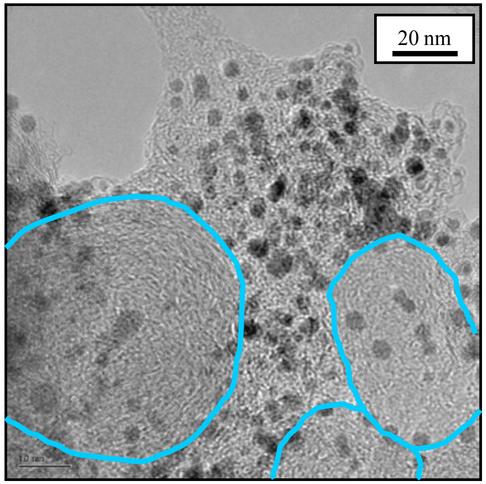
Synthesis of novel catalysts based on extended surfaces due to 3M's demonstrated improvements in specific activity and durability using similar systems.



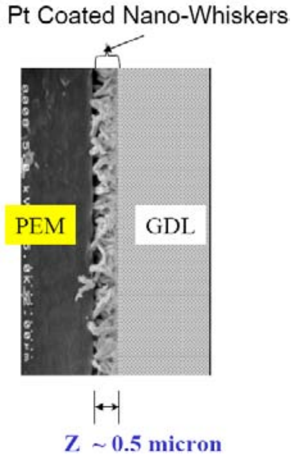
Pt nanotubes (UC-R)



Pt coated carbon nanotubes



HR-TEM Karren More ORNL



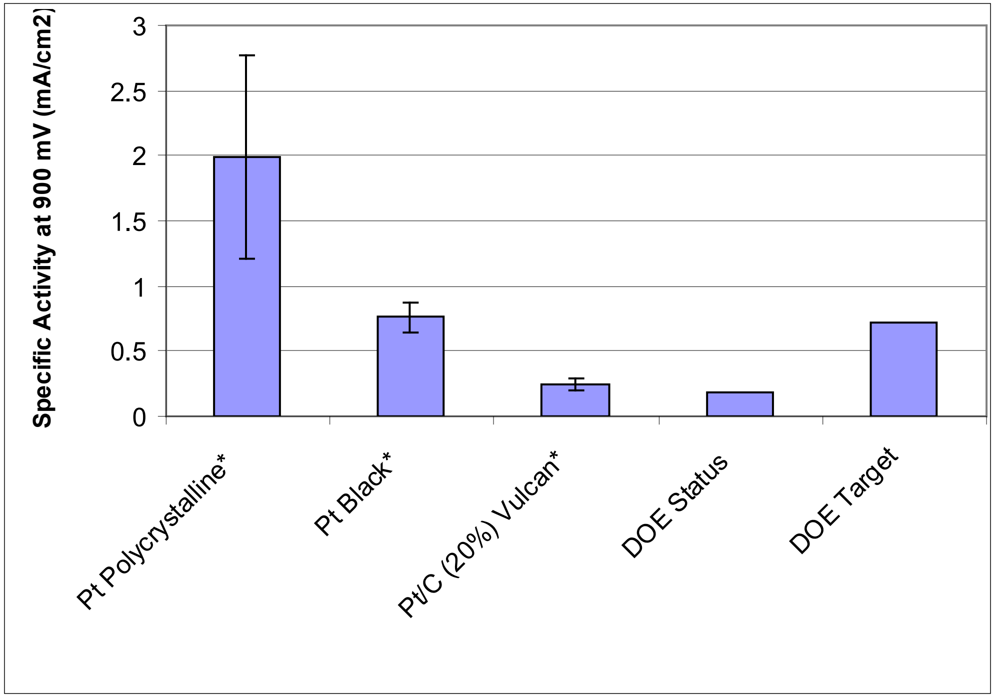
SEM of 3M's NSTF MEA

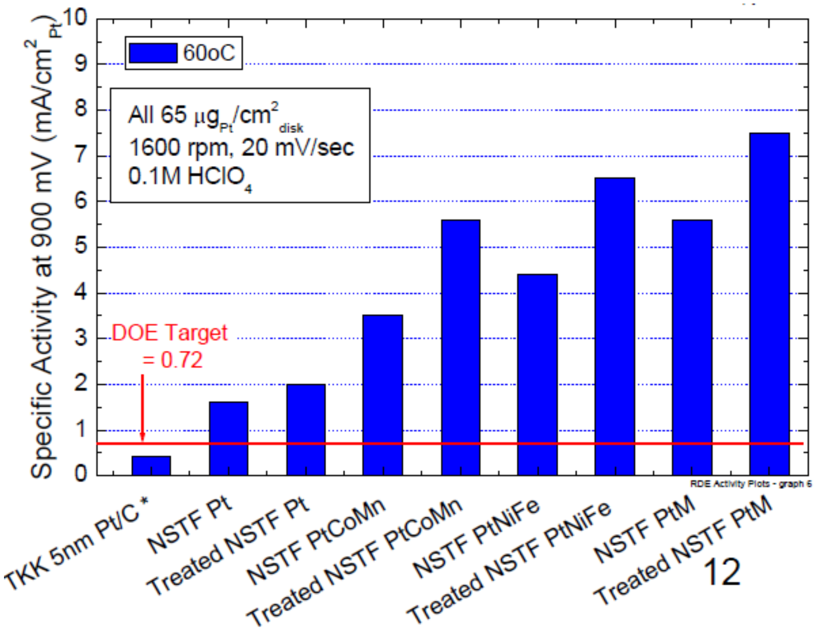
Electrode Studies

Electrode architecture design, based on novel catalyst structures that allow thick (~10 μm), dispersed electrodes to be fabricated that are more tolerant to ranges of operating conditions.

Premise

Current catalysts - Pt is not particularly well used and has durability/performance issues that can be largely overcome.

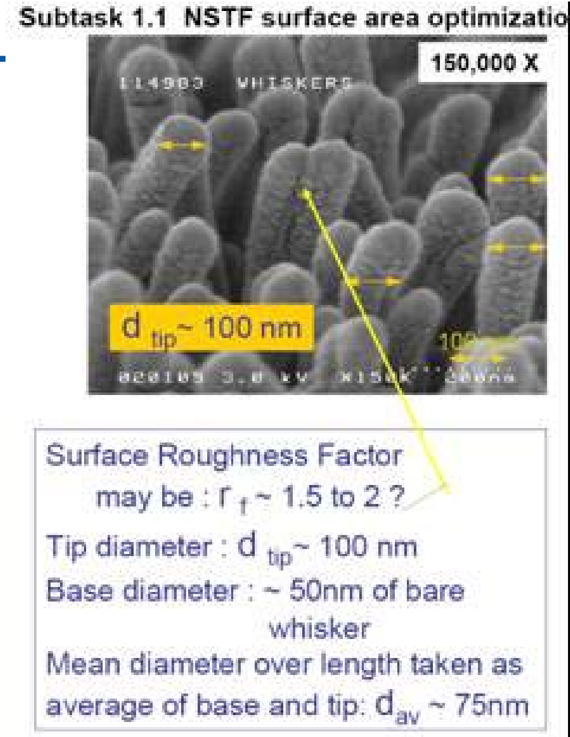


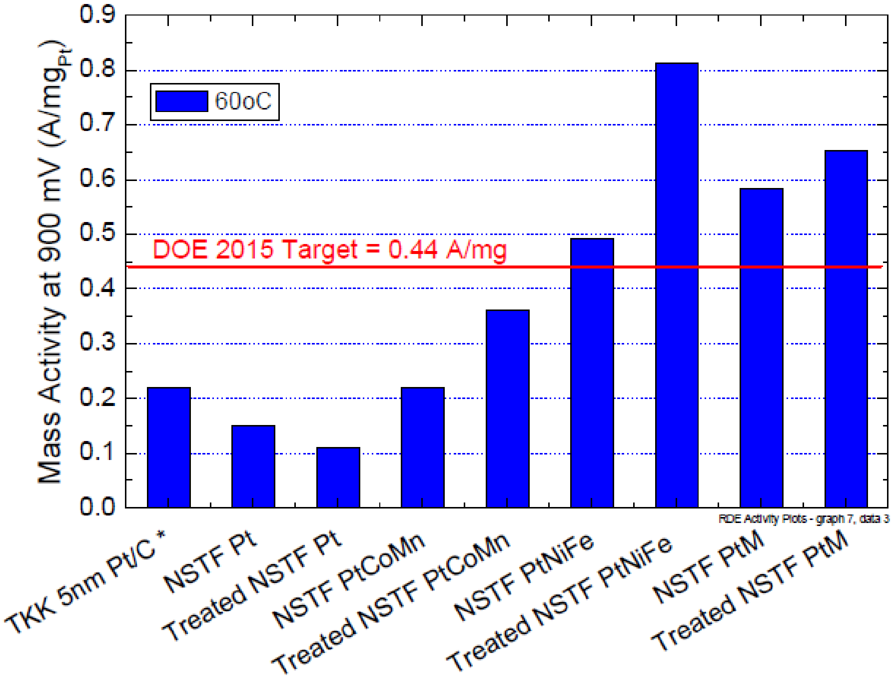


*Gasteiger *et al., Appl. Catal. B: Environ.*, 56, 9-35 (2005)

http://www.hydrogen.energy.gov/pdfs/review09/fc_17_debe.pdf

Limited mass activity





Particle	Pt Shells	Surface Pt
2 nm cubooctahedron	5	52%
5 nm cubooctahedron	12	24%
12.5 nm Pt coated(50 nm core) cylinder	29	~5%

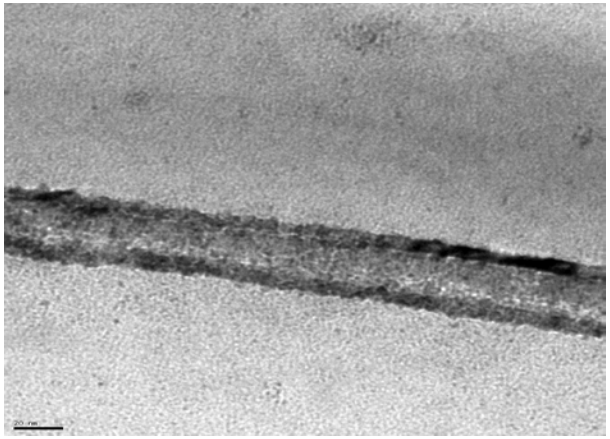
Significant improvements at least in part attributable to specific activity gains.

Further gains possible?

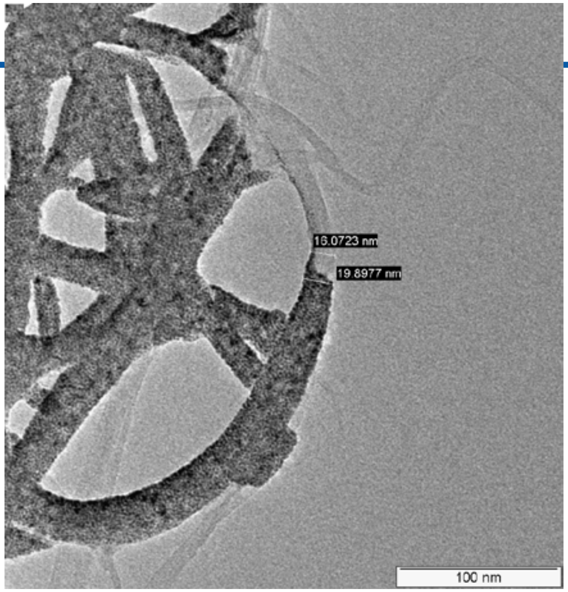
Nonconductive substrates and water management still a potential issue.

Mark Debe, 3M, DOE Annual Merit Reviews
http://www.hydrogen.energy.gov/pdfs/review08/fc_1_debe.pdf,
http://www.hydrogen.energy.gov/pdfs/review07/fcp_25_debe.pdf,
http://www.hydrogen.energy.gov/pdfs/review05/fc3_debe.pdf
http://www.hydrogen.energy.gov/pdfs/review09/fc_17_debe.pdf

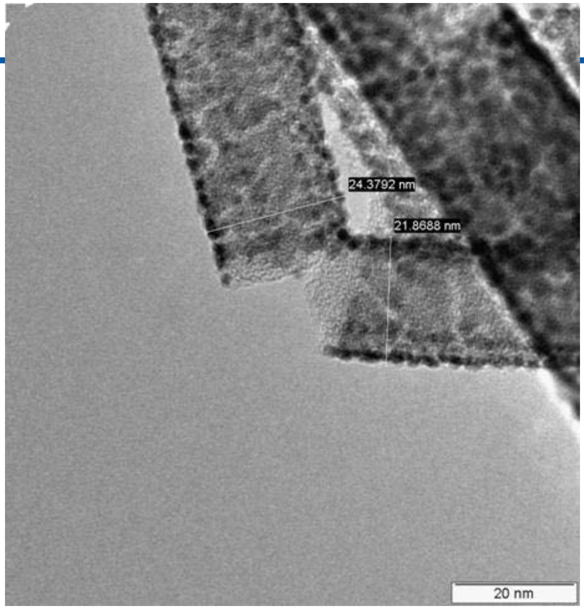
Continuous Pt-nanostructures



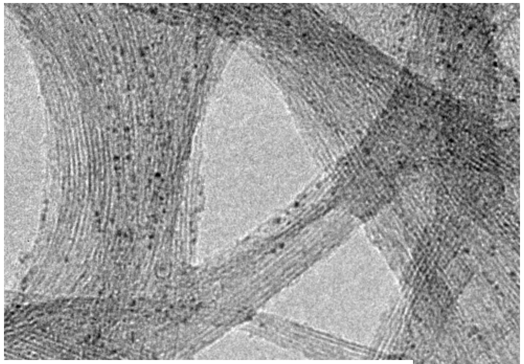
Pt nanotubes UC-R



Laser purified Pt coated SWCNT

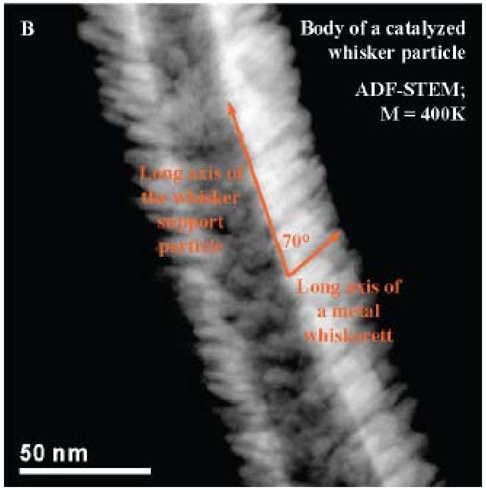


Pt coated perylene red whiskers

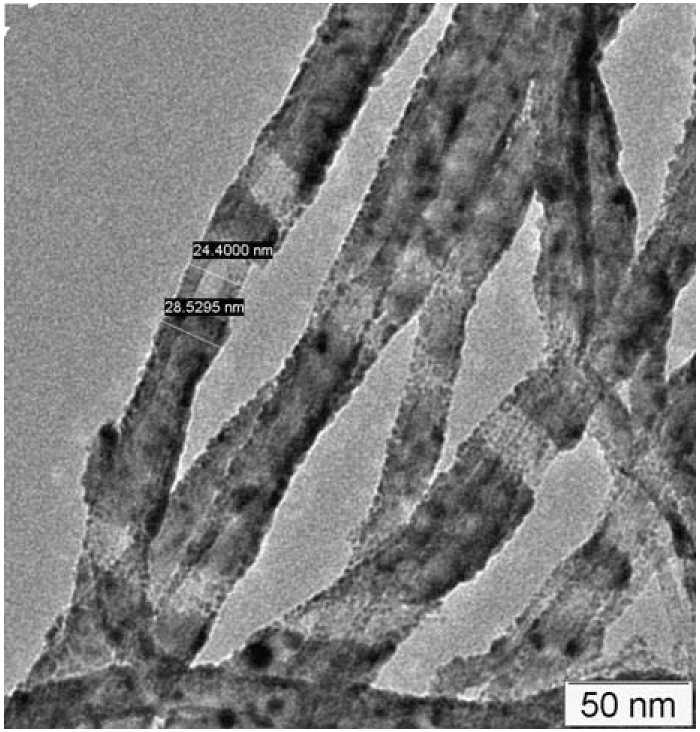


ISI literature search yielded 350 hits from 2007 and before for “carbon nanotubes” and “fuel cells”

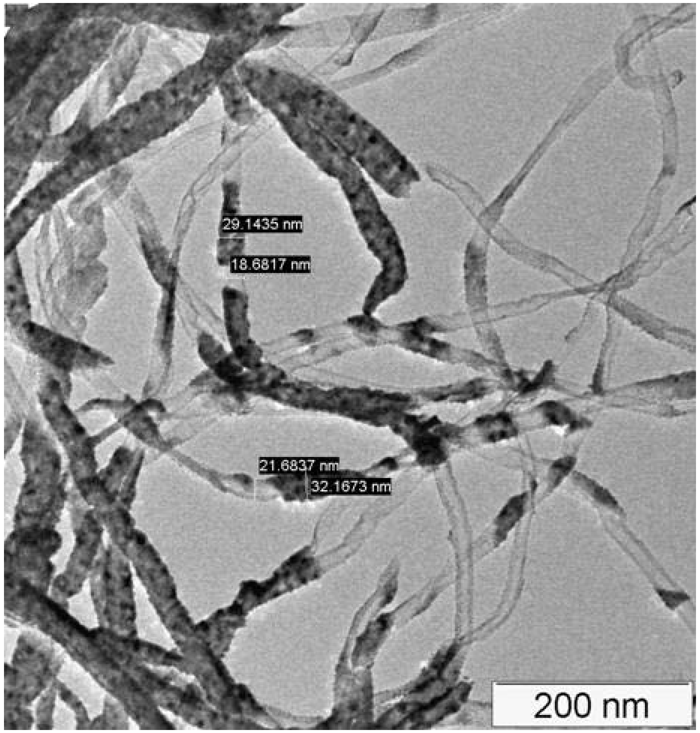
Gancs, L; Kobayashi, T; Debe, MK, Atanasoski, R., and Wieckowski, A., *Chemistry of Materials,* 20, 2444-2454, 2008



NREL Pt Deposition



Lower deposition parameters (thinner)



Increased deposition parameters (thicker)

Coatings obtained are reasonably continuous/conformal. Demonstrated some level of thickness control.

Electrochemical characterization issues, quantities increasing, testing forthcoming.

Novel Catalysts

Core-shell and free-standing, all with extended surfaces.

Core/Templates based on

- Metal Nanostructures (wires, tubes, etc)
- Carbon Nanotubes
- Metal oxides
- Whiskers

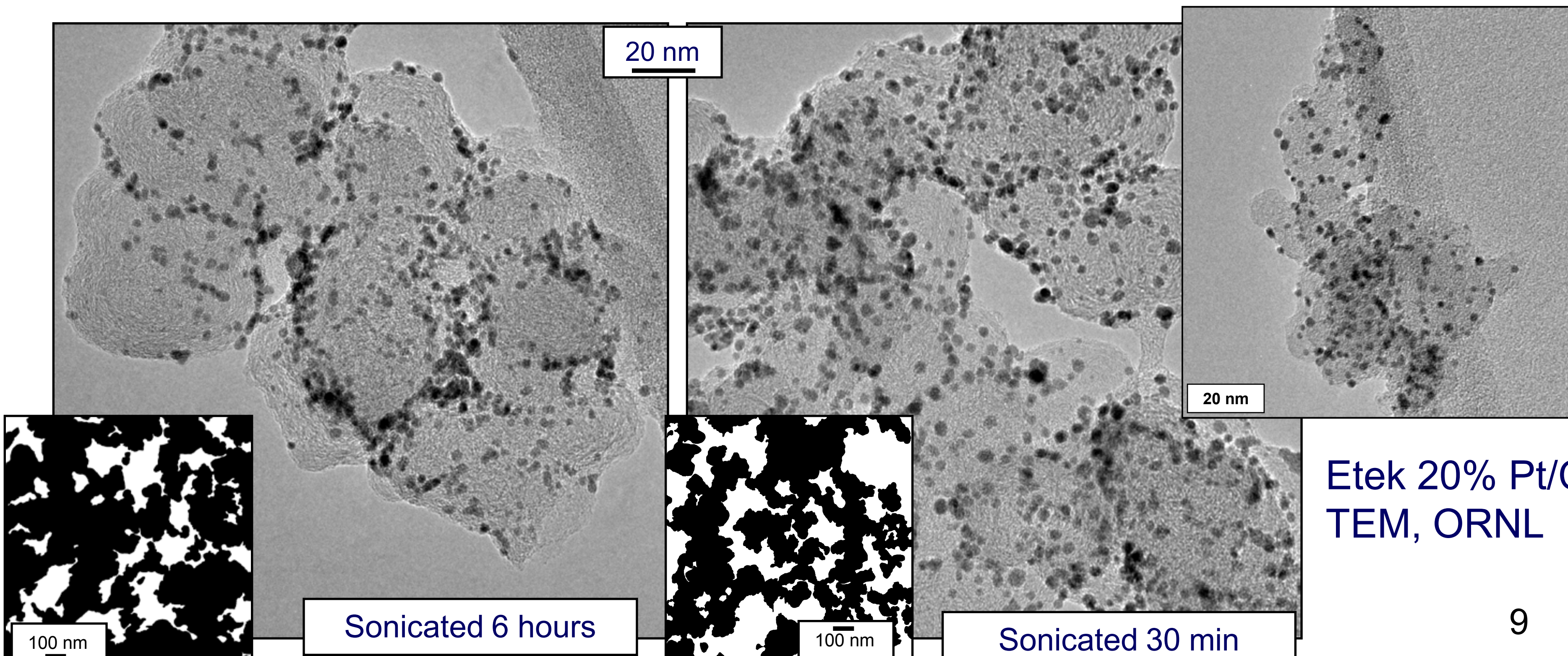
Pt Coating Techniques based on

- **Vapor Deposition** (sputtering, thermal evaporation, chemical vapor deposition, pulsed laser deposition, atomic layer deposition)
- **Solution Deposition** (galvanic displacement, electrochemical, spontaneous, underpotential)

Electrodes Studies

Novel extended-surface catalysts have yet to be incorporated into dispersed electrodes.

Factors investigated will include porosity, composition, and architecture (addressing durability and performance).



Etek 20% Pt/C TEM, ORNL

Timeline/Budget Overview

Timeline

Start: July 2009

End: September 2013

% complete: 2%

Project Timeline (Table of associated Milestones and Decision Points follows)

Task*	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12	Q13	Q14	Q15	Q16
1ai	M			MG				M				MG				
1aii	M	G				MG				M						
1aiii	M					MG		M				M				
1aiv	M					MG				M						
1bi[a]	M	M				MG										
1bi[b]						M				M		M		MG	MG	
1bii	M			M		M				M				MG	MG	
2a				M				MG				M				
2b				M						M				MG	MG	MG
3[c]				M						M						M
3[d]						M				M						M

*Task descriptions can be found in *Work Plan Outline*, [a] PVD coatings; [b]ALD coatings; [c]catalyst modeling; [d]electrode modeling

Q represents quarter from start date; M represents Milestones; G represents go/no-go decisions

Milestones due and go/no-go decisions enacted at end of quarter in which they appear

active task during quarter; active task during quarter pending go/no-go decision; inactive task

1. Novel Synthesis
   a. Substrates
   b. Deposition Methods
2. Electrode Studies
3. Modeling

Go/no-go decisions focus primarily on down selection of substrates and deposition processes to those of novel structures showing improved performance and durability.

Budget

DOE Cost Share	Recipient Cost Share	TOTAL
$8,384,342	$867,763	$9,252,105*
91%	9%	100%

Budget ($K)

FY 2009	1564
FY 2010	590
FY 2011	2177
FY 2012	2015
FY 2013	2033

***Final award amounts are subject to appropriations and award negotiations.**

Project Participants

Key Investigators/Major Participants:
National Renewable Energy Lab (NREL): Bryan Pivovar (PI), Huyen Dinh, Lin Simpson, Chai Engtrakul, Tom Gennett, Arrelaine Dameron, Tim Olson, KC Neyerlin, Jeremy Leong
Oak Ridge National Laboratory (ORNL): Karren More
Los Alamos National Laboratory (LANL): Rod Borup
University of California-Riverside (UC-R): Yushan Yan
State University of New York – Albany (CNSE): John Elter
Stanford University (Stanford): Stacey Bent
Case Western Reserve University (CWRU): Tom Zawodzinski
University of Texas-Austin (Texas): Jeremy Meyers
Nissan Motors (Nissan): Shyam Kocha
Cabot Fuel Cells (Cabot): Paolina Atanassova
Tanaka Kikinzoku Kogyo (Tanaka): Tomoyuki Tada

- Novel Material Synthesis and Characterization (NREL, CNSE, UC-R)
    - Continuous coating of Pt on substrates (NREL, Stanford, UC-R)
    - Electrode/Fuel Cell Studies (NREL, LANL, ORNL, Nissan, Cabot, Tanaka)
- Modeling of Catalysts and Electrodes (NREL, CWRU, Texas)