NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Extended, Continuous Pt Nanostructures in Thick, Dispersed Electrodes

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FC007

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Overview

Timeline

Start: July 2009
End: September 2013
% complete: ~30%

Barriers

A. Durability (catalyst; MEA)
B. Cost (catalyst; MEA)
C. Performance (catalyst; MEA)

Budget

DOE Cost Share	Recipient Cost Share	TOTAL
$8,384,342	$867,763	$9,252,105

Budget ($K)

FY 2009	1480
FY 2010	1203
FY 2011	2177
FY 2012	2015
FY 2013	1508

Partners – Principle Investigators

Oak Ridge National Laboratory (ORNL) – Kelly Perry, 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
University of Tennessee (Tenn) – Tom Zawodzinski
University of Texas-Austin (Texas) – Jeremy Meyers
Nissan Technical Center North America* (NTCNA) – Kev Adjemian
Cabot Fuel Cells* (Cabot) – Paolina Atanassova
Tanaka Kikinzoku Kogyo* (TKK) – Fumiaki Ogura

*non-subcontracted collaborators

Relevance

ETFECS/Dispersed Electrodes

Review Period Objectives:

- **Produce novel extended thin film electrocatalyst structures (ETFECS) with increased activity and durability, moving towards meeting all 2015 DOE catalyst targets simultaneously.**

- **Begin studies of electrode incorporation of ETFECS with highest potential to address MEA Targets.**

Table 3.4.12 Technical Targets: Electrocatalysts for Transportation Applications

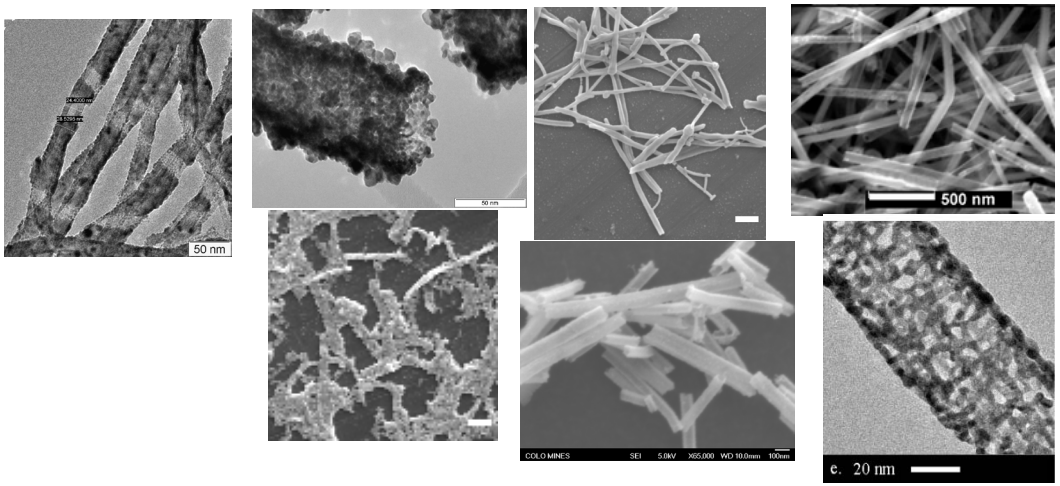
Characteristic	Units	2005 Status [a]		Stack Targets	
		Cell	Stack	2010	2015
Platinum group metal (pgm) total loading [b]	mg PGM / cm^2 electrode area	0.45	0.8	0.3	0.2
Cost	$ / kW	9	55 [c]	5 [d]	3 [d]
Durability with cycling					
Operating temp ≤80°C	hours	>2,000	~2,000 [e]	5,000 [f]	5,000 [f]
Operating 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 [i]	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	200	300	300
	mW / cm^2	160	250	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
ETFECS/Dispersed Electrodes

Synthesis of novel ETFECS
- These materials have demonstrated enhanced specific activity and exceptional durability (3M, others).
- Screen several synthesis techniques for relevance.



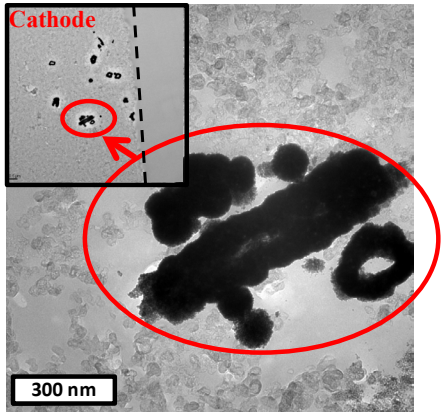
Focus on increased Pt utilization
- Low Pt ECAs (electrochemically accessible surface areas) are common (~10m^2/g_{Pt}), resulting in limited mass activity.

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%

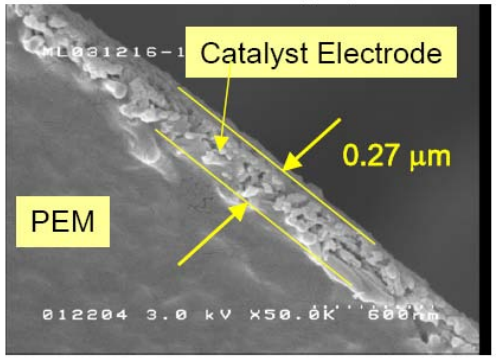
Electrode studies involving ETFECS
- Effectively incorporate extended Pt catalysts into more traditional, thick, dispersed electrodes for mass transport/water management.

Supplemental modeling
- Modeling of catalyst particles, electrode structure and electrode performance.

NREL ETFECS



3M NSTF

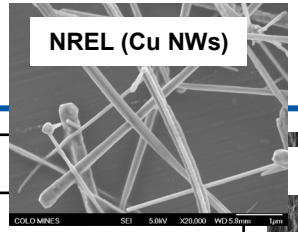


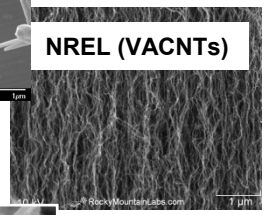
http://www.hydrogen.energy.gov/pdfs/review04/fc_4_debe.pdf

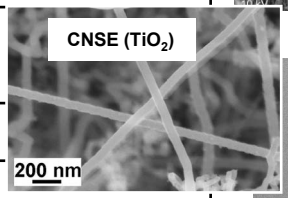
Approach: ETFECS Synthesis

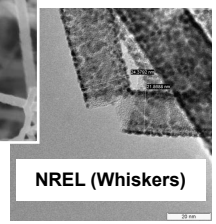
Templates/Pt Deposition

Template	Status
Metal (wires, tubes, etc) NREL, UC-R	Cu nanowires synthesized routinely Ag nanowires have been synthesized, now commercially obtained Ag nanoplates synthesized
Carbon Nanotubes (CNTs) NREL	Continuous thin films only obtained by sputtering Down selected work in synthesis to short, dispersed tubes.
Metal oxides (CNSE, NREL)	Focus on TiO_2 coated Si nanowires.
Whiskers	Avoided due to extensive 3M optimization







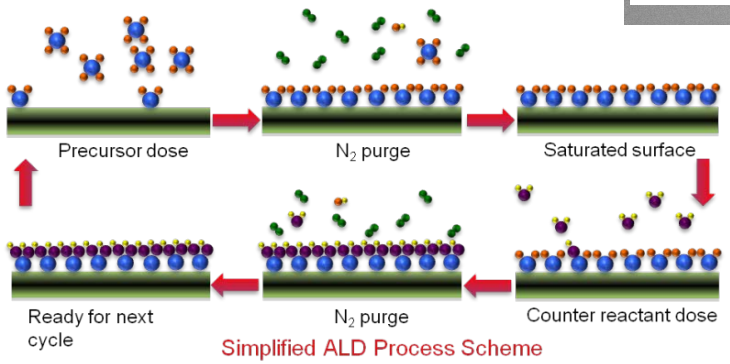


Discovery synthesis of cores/templates is ~90% complete.

Pt Deposition

Vapor Deposition (evaporation (CNSE), CVD, PLD)

- sputtering (NREL)
- atomic layer deposition(ALD) (NREL, Stanford)

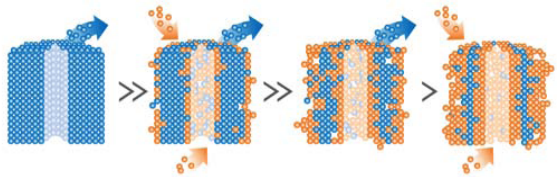


Simplified ALD Process Scheme

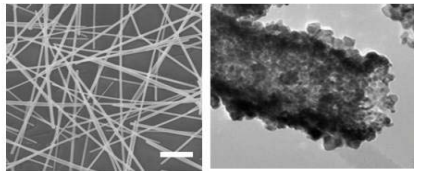
Solution Deposition (electrochemical, spontaneous, underpotential)

- spontaneous galvanic displacement (SGD) (NREL, UC-R)

Metal	E^0	# of e^-
$Au^{3+} + 3\ e^- \leftrightarrow Au$	1.498	3
$Pt^{2+} + 2\ e^- \leftrightarrow Pt$	1.180	2
$Pd^{2+} + 2\ e^- \leftrightarrow Pd$	0.951	2
$Ag^{+} + e^- \leftrightarrow Ag$	0.800	1
$Cu^{2+} + 2\ e^- \leftrightarrow Cu$	0.340	2



Simplified SGD Process Scheme



Approach
Electrode/Modeling Studies (NREL, UC-R, Tenn, Texas)

- Study the electrochemical behavior of ETFECs (RDE)
  - ECA, mass and specific activity
  - with and without carbon
  - Probe durability to cycling (both Pt dissolution and carbon corrosion)
- Investigate incorporation of ETFECS into MEAs
  - Nafion^{È}/ionic contact
  - Carbon
  - Electrochemical dealloying
  - Structural studies
  - Mass transport issues

Our development of novel catalysts and implementation in electrodes is supported with computational studies.

3 Thrusts (see Technical Backup Slides):

1. Simulations involving Pt film and extended Pt structure formation (Tenn).
2. Simulations of dispersed electrode architectures based on Pt ETFECS (Tenn).
3. Simulations of the performance of fuel cells based on thick electrodes with ETFECS (Texas).

Approach: Project Timeline/Milestones

1. Novel Synthesis
   a. Core/Templates
   b. Pt Deposition
2. Electrode Studies
3. Modeling

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

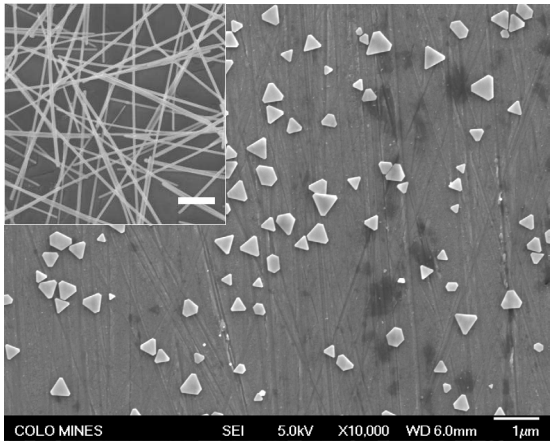
Milestones

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

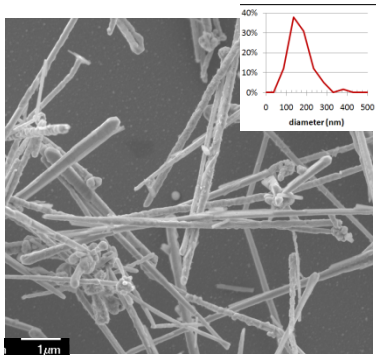
Go/no-go decision for 1st generation CNTs. Based on initial studies of CNTs by coating techniques if continuous coatings are not obtained begin 2nd generation CNT synthesis.	12/09 Complete
Complete parametric study of PtNT production as influenced by Pt supplied, reaction time, Pt surface area, and resulting wall thickness.	05/10 Complete
Demonstrate (at least 3) 1st generation continuous nanostructured Pt catalysts in fuel cell testing.	09/10 Complete
Demonstration of 2nd generation VACNTs, analogous to 3M's NSTF whiskers, based on low packing density and heights less than 2 microns.	**12/10** Complete
Joule Milestone – Demonstrate a continuous Pt nanostructured catalyst with specific activity greater than 720 µA / cm2 @ 900 $mV_{iR\text{-}free}$ (DOE 2010/2015 Target).	**3/11** Complete
Screening of at least 5 substrates and/or adhesion layers for their applicability to yield fast nucleation rates and form thin continuous films by ALD.	**05/11** On track
Go/no-go decision for down selection of carbon blacks included in electrode compositions containing extended surface Pt nanostructures based on ability to produce dispersed electrodes and electrochemical stability up to 1.5 V.	**09/11**

Technical Accomplishments and Progress
Metal Templates (NREL, UC-R)

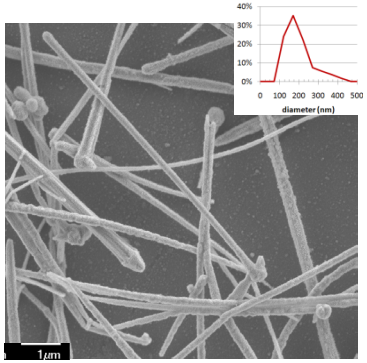
Ag Nanowires/plates



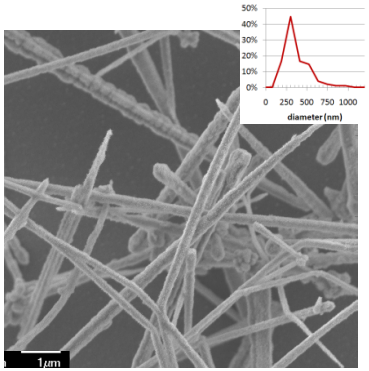
Cu Nanowires



167 nm mean dia.



197 nm mean dia.



238 nm mean dia.

Metal nanotemplate synthesis is not a primary project focus, rather our team leverages extensive recent work done in this area.

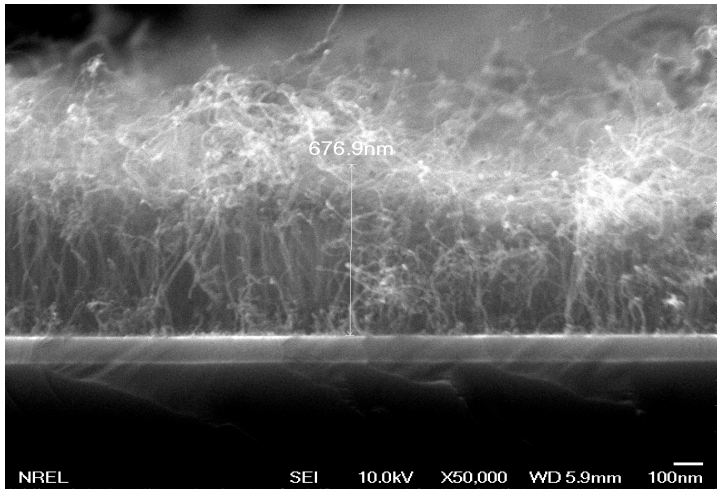
We have used Ag, Se, and Cu nanowires and Ag nanoplates as templates.

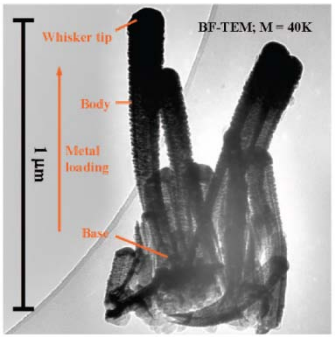
Wires 50-250 nm diameter, microns in length. Plates a few 100's of nm's width, ~20 nm thick. Similar aspect ratios, ~10x difference in scale.

Technical Accomplishments and Progress
Vertically Aligned (VA) Substrates (NREL, CNSE)

VACNTs (NREL)

- **Milestone: Demonstration of 2nd generation VACNTs, analogous to 3M's NSTF whiskers, based on low packing density and heights less than 2 microns. (~700nm height shown below)**



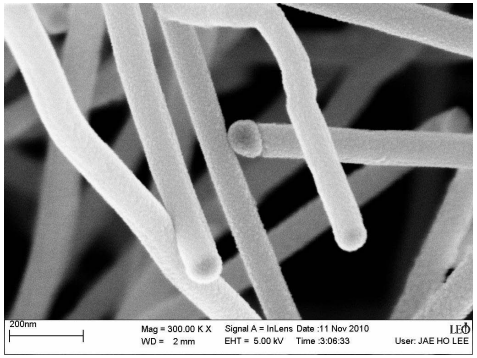


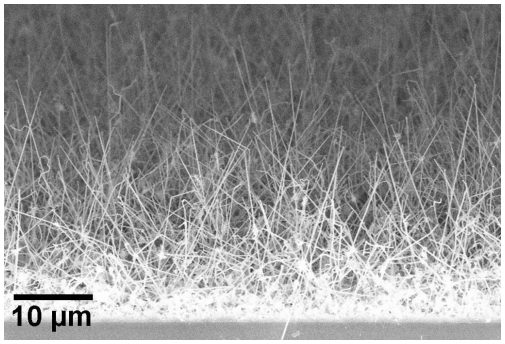
Pt coated 3m NSTF

Short, low density VACNTs not typical due to low (mass) yields.
Targeted here for the potential of continuous coating by sputtering.
VACNTs still less vertically aligned than whiskers.

VA TiO_2 coated Si nanowires (CNSE)

TiO_2 coated Si nanowires are more vertically aligned, have been synthesized at heights > CNTs/NSTF.

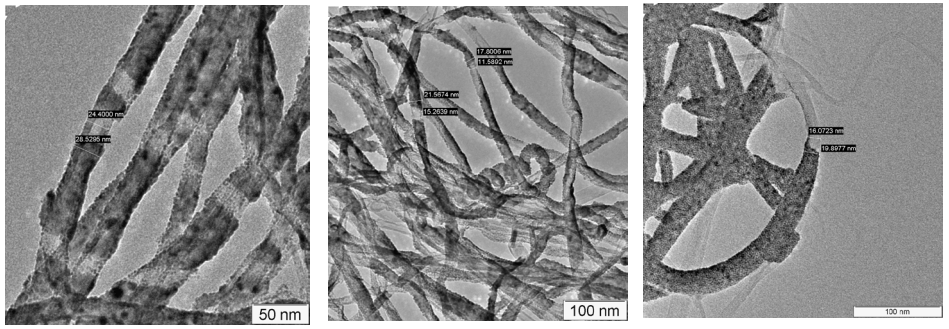




Low yields typical for our VA substrates.

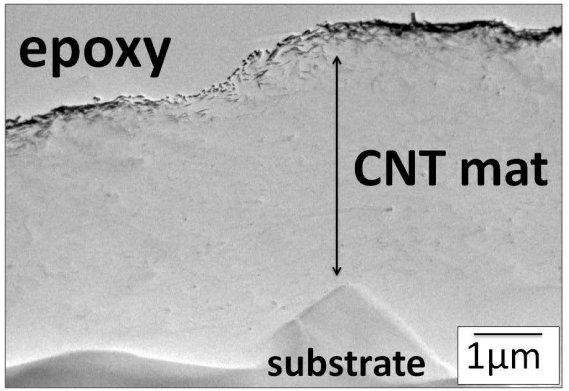
Technical Accomplishments and Progress
Pt Coating – Sputtering (NREL)

Focused on CNT mats where continuous Pt coatings have been observed

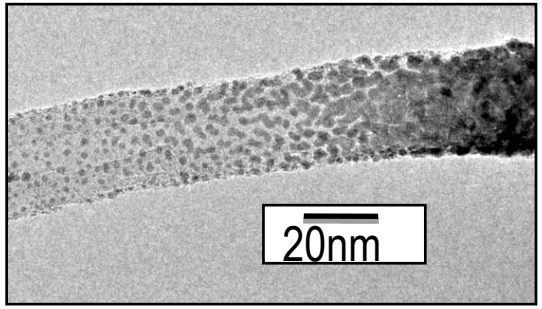


ORNL has performed high resolution TEM to further probe coating.

Target coating only occurs at top edge of mat as would be expected by (line of sight) sputtering. Yield is a major problem.

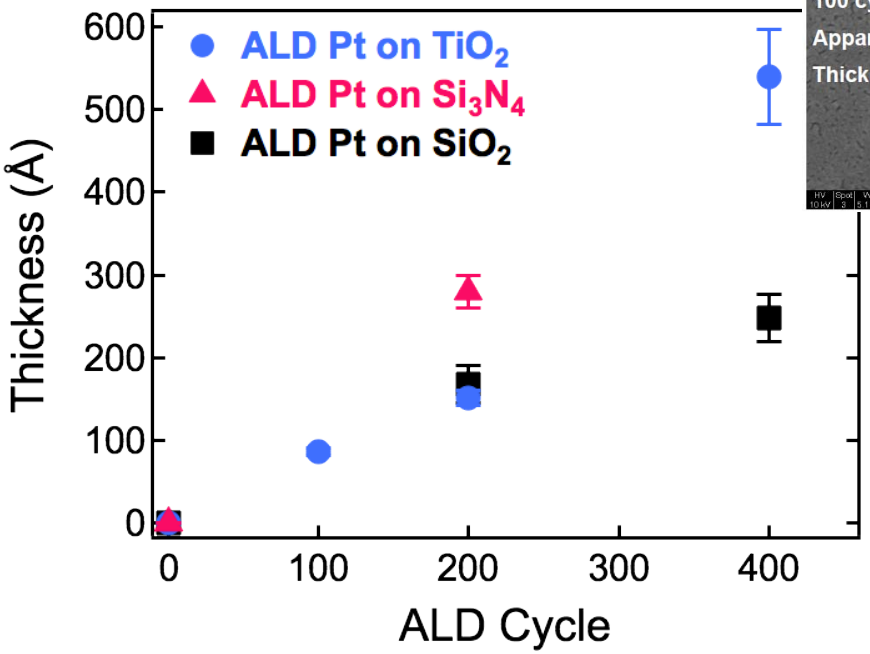


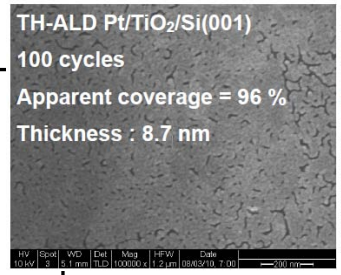
Microscopy shows transition between particles and continuous film. Particle size suggests continuous films ~2nm thickness.

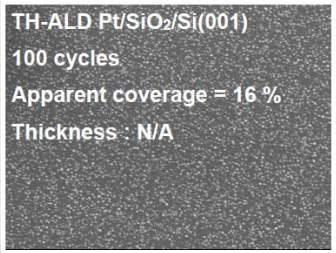


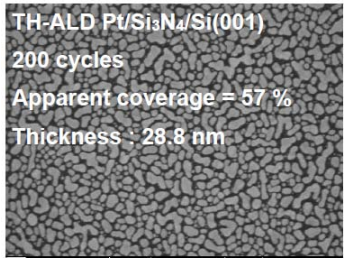
Technical Accomplishments and Progress
Pt Coating – ALD (Stanford, NREL)

As of 2010 AMR: our investigations showed significant non-conformality and slow nucleation rates: we have investigated temperature, pretreatment, and adhesion layers to increase Pt nucleation rates and conformality.



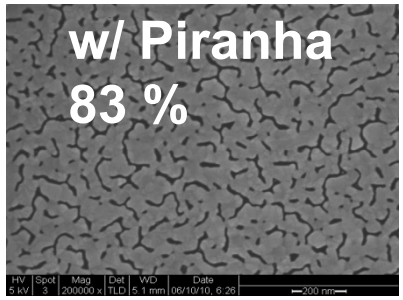


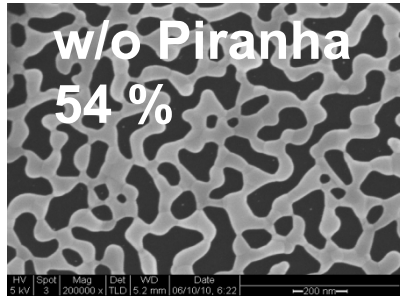




TiO_2 shows faster nucleation allowing coatings with measurable thicknesses to be obtained with only 100 ALD cycles.

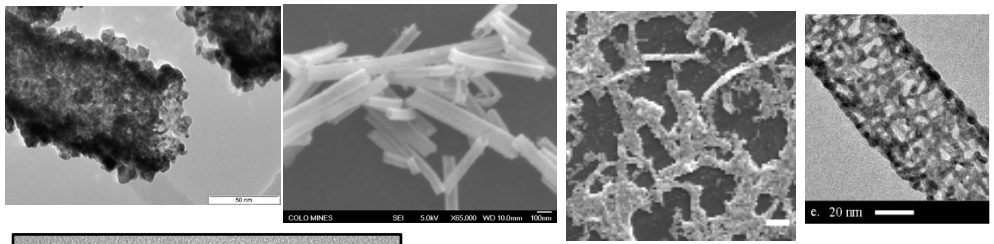
Effects of hydrophilicity on Pt growth

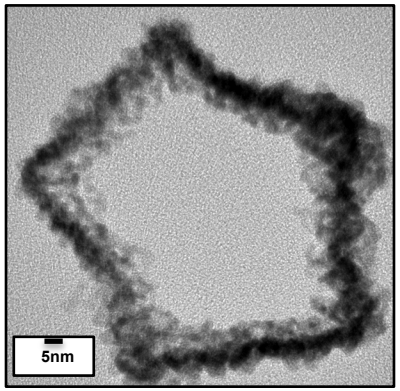


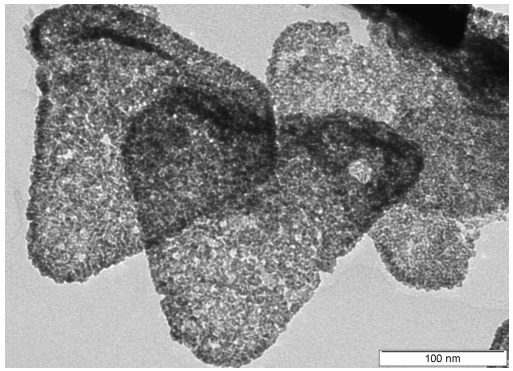


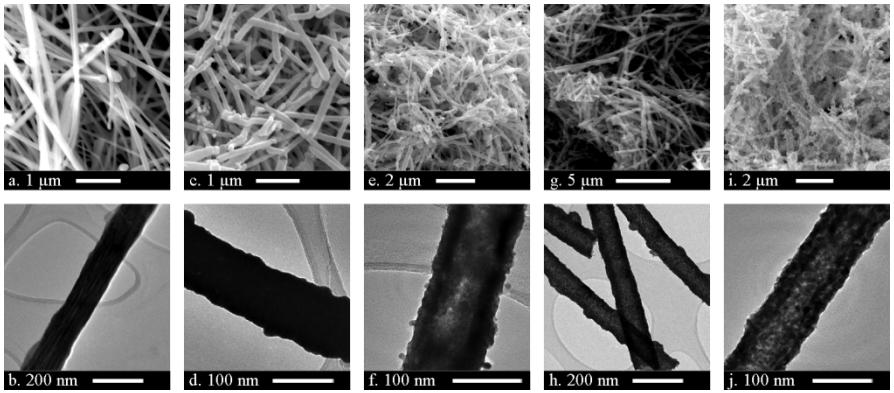
Surface pretreatment significantly impacts Pt deposition.

Technical Accomplishments and Progress
Pt Deposition – SGD (NREL, UC-R)









SEM images of a) CuNWs; c) PtNTs; e) Pt/CuNWs; g) PdNTs; and i) Pt/PdNTs. TEM images of b) CuNWs; d) PtNTs; f) Pt/CuNWs; h) PdNTs; and j) Pt/PdNTs.

A wide array of different structures and compositions have been obtained. Examples of nanotubes (NTs), nanowires (NWs) and nanoplates (NPs) all shown.

SGD has a number of controllable synthetic variables, including:

Surface ligand, sacrificial template, metal of deposition, solvent system, stoichiometry, temperature

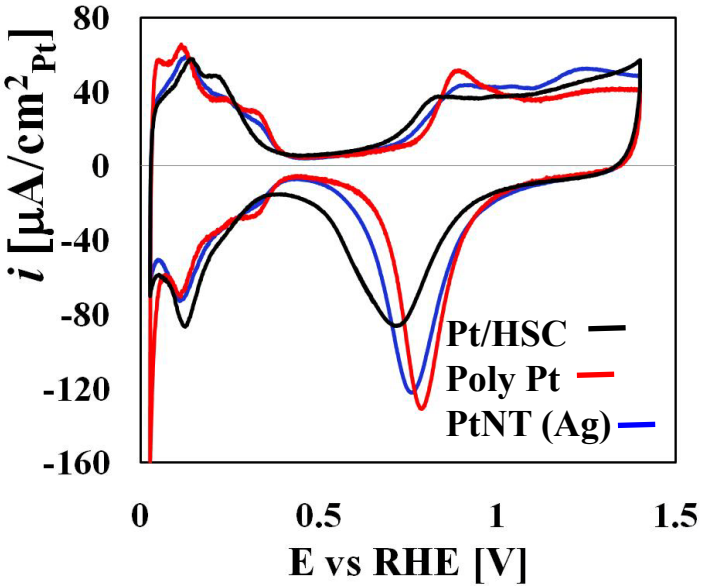
SGD as technique, allows:

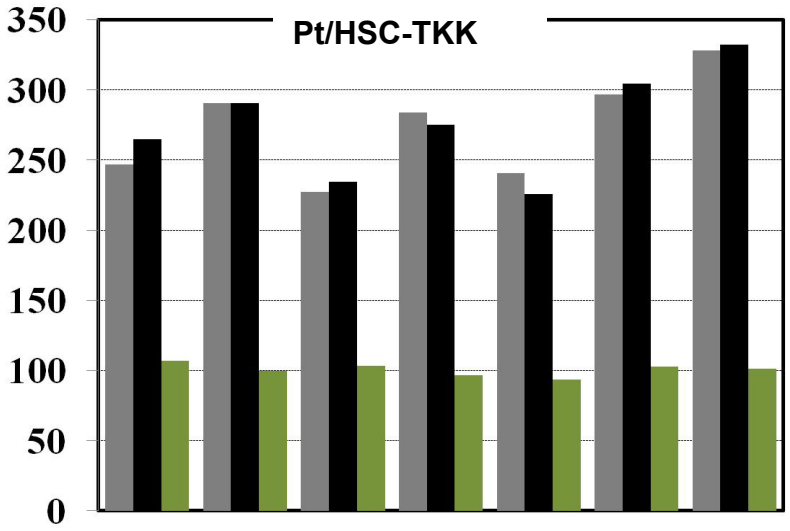
- synthesis of structures not directly obtainable
- thrifting of more noble metals
- ability to obtain extended structures with high electrochemically available surface area ECA

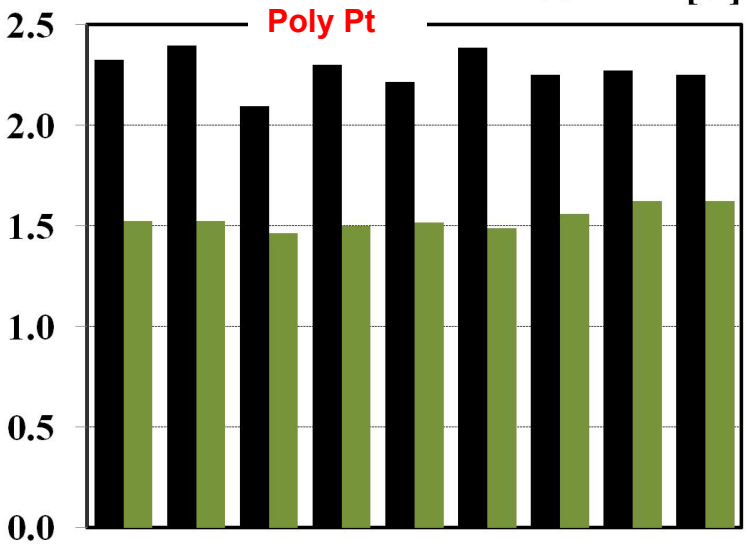
Technical Accomplishments and Progress
Electrochemistry (NREL)

No electrochemical characterization reported 2010 AMR. Baseline performance demonstrated reproducibly, in agreement with others. Multiple experimental results reported.

	$i_s^{0.9V}$ [mA/cm^2_{Pt}]	$i_m^{0.9V}$ [mA/mg_{Pt}]	ECA [m^2_{Pt}/g_{Pt}]	RF [cm^2_{Pt}/cm^2_{elec}]
Pt/HSC-TKK	270 ± 35	275 ± 35	100 ± 5	-
Poly Pt	2300 ± 100	-	-	1.5 ± 0.1

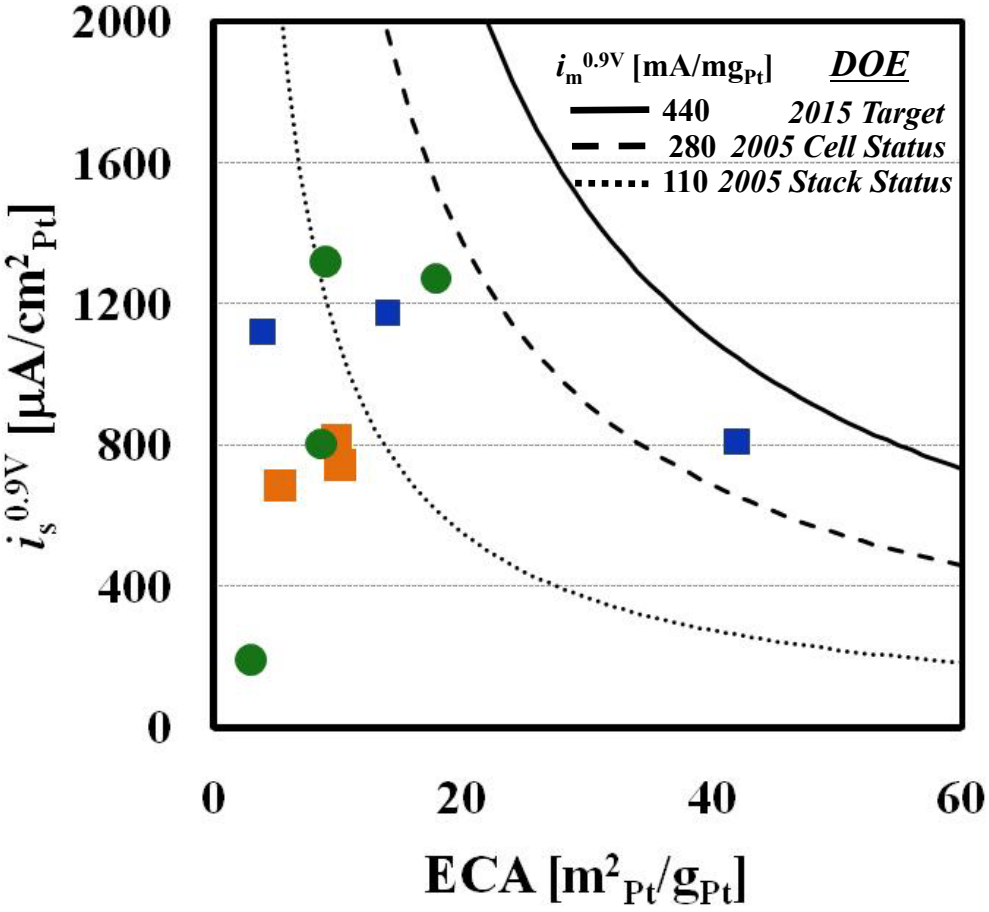






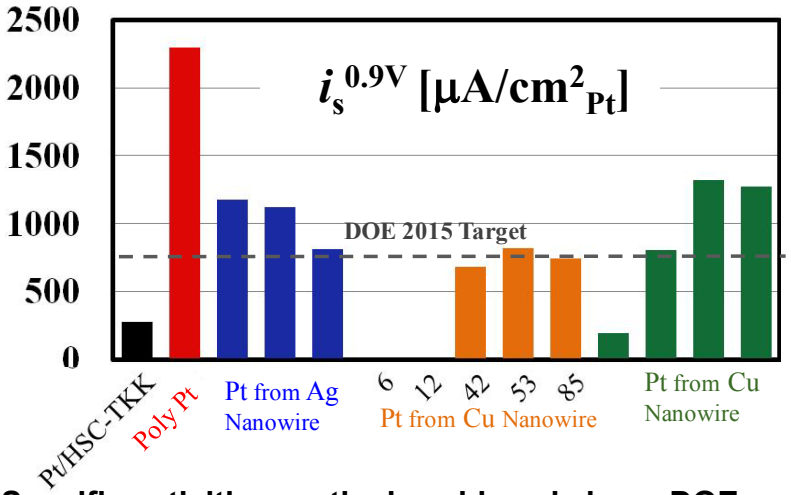
Technical Accomplishments and Progress

Electrochemical Characterization (NREL)

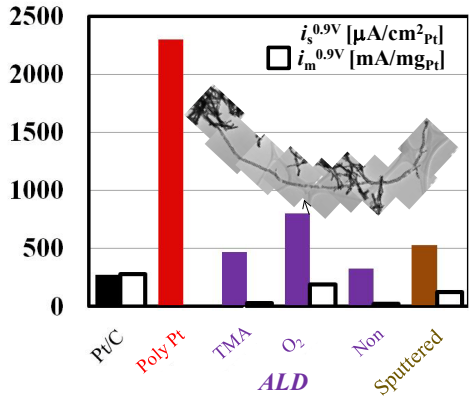


Parametric studies of SGD-ETFECS have yielded insight into factors that impact specific activity (i_s) and ECA. These have allowed mass activities approaching DOE targets to be obtained (330 mA/mg_{Pt}).

ECAs as high as 40 m^2/g_{Pt} have been obtained, a significant advancement for extended Pt surfaces.



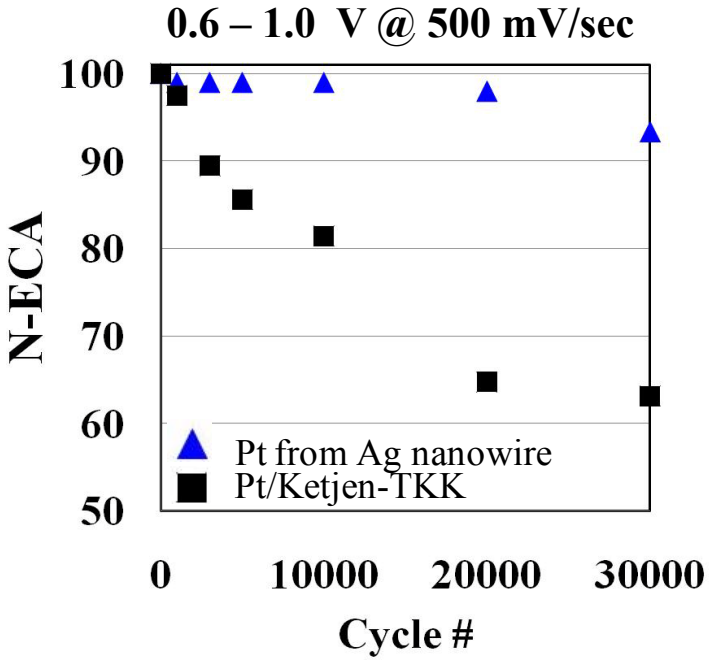
Specific activities routinely achieved above DOE 2015 Target, shows the impact of extended surfaces.

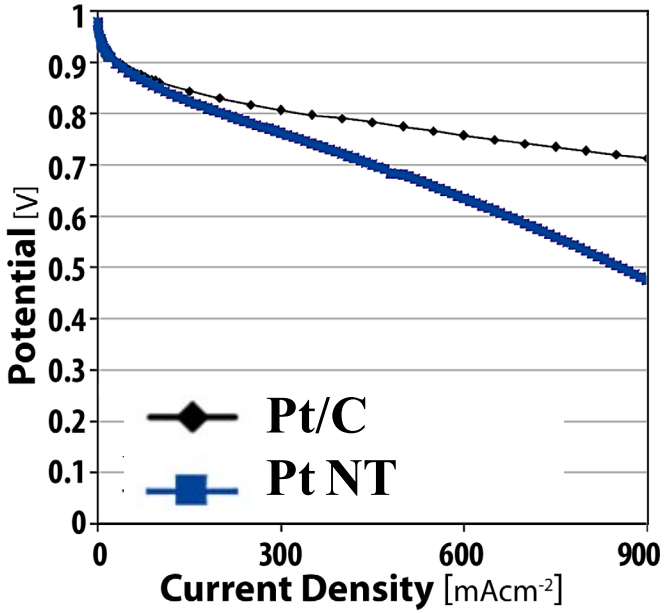


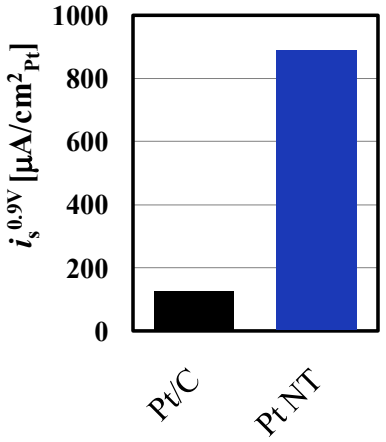
Pt on VACNT has not shown same degree of continuity.

Technical Accomplishments and Progress

RDE Durability, FC Performance of ETFECS (UC-R, NREL)







Pt nanowires synthesized to date have demonstrated excellent durability during potential cycling.

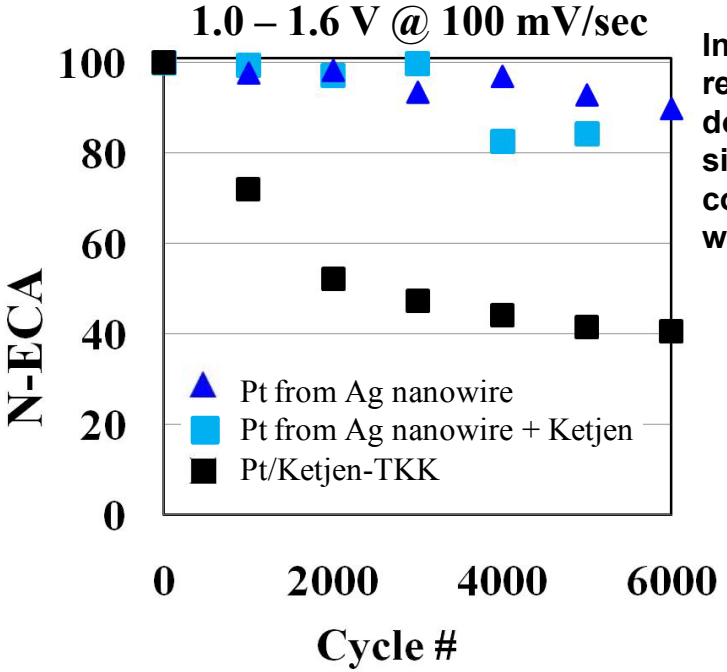
Limited studies to date need to be expanded to better understand impact of initial ECA and impact on specific/mass activity.

Limited testing in MEAs has shown that specific activity improvements demonstrated in RDE, can be maintained in fuel cell testing.

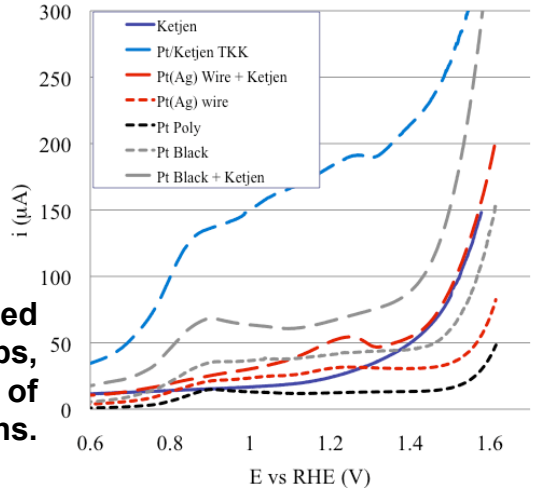
Results to date show viability of ETFECS when deployed as MEAs in fuel cells. Significant effort still required for electrode optimization.

Technical Accomplishments and Progress

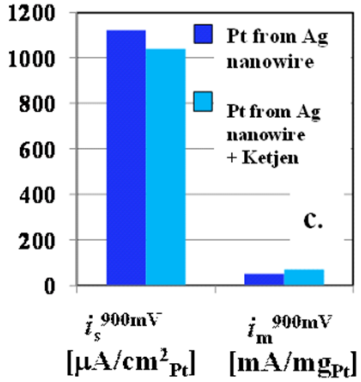
Carbon Incorporation into Electrodes (UC-R, NREL)



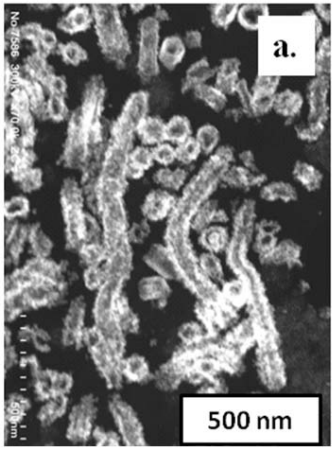
In the carbon corrosion region (start-up/shut-down), ETFECS show significantly improved corrosion resistance even with carbon inclusion.

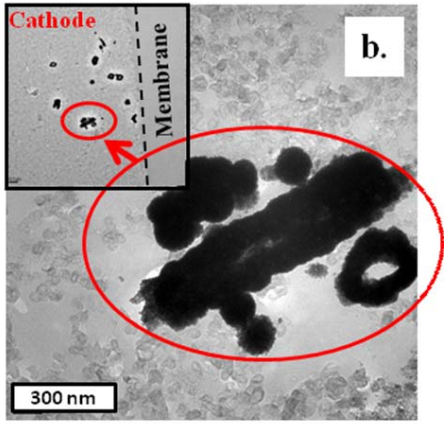


Similar trends witnessed in high potential sweeps, with onset and extent of oxidation reactions.



Specific and mass activities of ETFECS maintained in RDE tests when carbon is included.





MEA cross-sections without (a) and with (b) carbon (50% by weight), highlight electrode optimization challenges that remain. Lack of porosity and high packing density exist without carbon (a). Heterogeneity (diffuse Pt) are apparent with carbon (b).

Collaborations

Key Investigators/Major Participants

National Renewable Energy Lab: Bryan Pivovar (PI), Shyam Kocha, Huyen Dinh, Lin Simpson, Chai Engtrakul, Arrelaine Dameron, Jason Zack, Tim Olson, KC Neyerlin, Svitlana Pylypenko, Justin Bult, Brian Larsen, Niccolo Aieta, Jeremy Leong
Oak Ridge National Laboratory: Karren More, Kelly Perry
Los Alamos National Laboratory: Rod Borup
University of California-Riverside: Yushan Yan
State University of New York – Albany: Robert Geer
Stanford University: Stacey Bent
University of Tennessee: Tom Zawodzinski
University of Texas-Austin: Jeremy Meyers
Nissan Technical Center North America: Kev Adjemian
Cabot Fuel Cells: Paolina Atanassova
Tanaka Kikinzoku Kogyo: Fumiaki Ogura

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)

Proposed Future Work

Templates/Cores (1a): ~80% complete

- Metal oxide substrate development (4/11 – 10/11)

Pt deposition (1b): ~60% complete

- SGD process further optimization focusing on post-processing parameters (4/10 – 10/11)
- ALD studies investigating Pt growth on carbon and with reduced thickness/decreased nucleation cycles (4/10 – 10/11)

Electrode studies (2): ~10% complete

- Electrochemical (RDE) durability screening of ETFECS as a function of initial ECA (4/11 – 9/11)
- Incorporation of highest performing catalyst (330 mA/mg_{Pt}) into electrode studies (4/11 – 9/11)
- Expanded MEA fabrication and fuel cell testing of ETFECS (4/10 – TBD)

Modeling (3): ~10% complete (see Technical Backup Slides)

- Advancement of models to electrode structures incorporating model ETFECS – PtNT of 150 nm diameter, 2 micron length (ongoing)
- Expansion of porous electrode models to ETFECS incorporated electrodes (ongoing)

Summary

Relevance: Focused on overcoming the most critical barriers for fuel cell MEA development.

Approach: Developing extended surface Pt catalysts for their high mass activity and durability, and incorporating these structures into robust, high efficiency MEAs.

Technical Accomplishments and Progress: The project has synthesized many novel catalysts using materials and geometries not previously demonstrated. Synthesized several ETFECS that reach 2015 DOE specific activity targets. We have demonstrated ETFECS with ECA as high as $40 m^2/g_{Pt}$ and mass activities of 330 mA/mg_{Pt}. We have incorporated carbon into electrode structures that contain ETFECS while maintaining favorable durability and activity. We have demonstrated high specific activities of ETFECS in fuel cells.

Collaborations: We have a diverse team of researchers from several institutions including 2 national labs, 5 universities, and 3 industry.

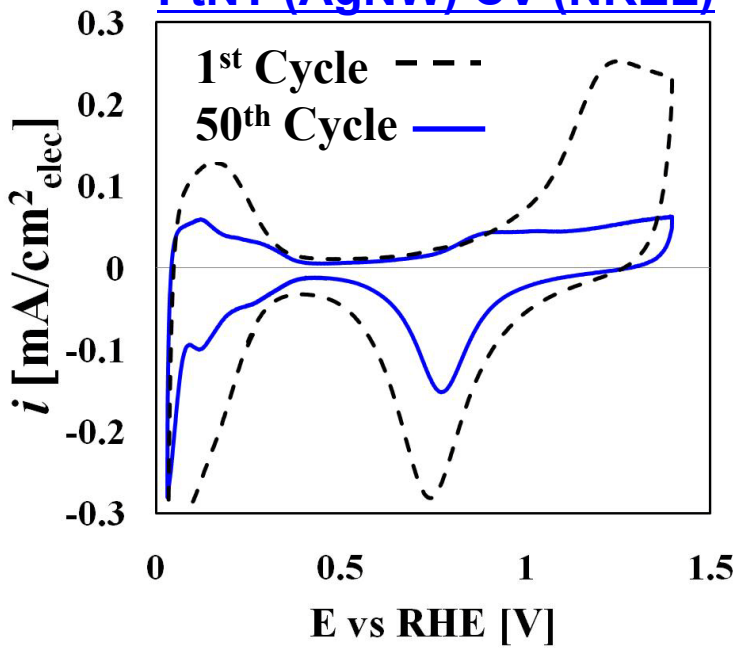
Proposed Future Research: Strongly focused on incorporating materials with improved mass activity and voltage cycling stability into highly performing electrodes.

Technical Backup Slides

Technical Accomplishments and Progress

Impact of Residual Ag (NREL, ORNL)

PtNT (AgNW) CV (NREL)

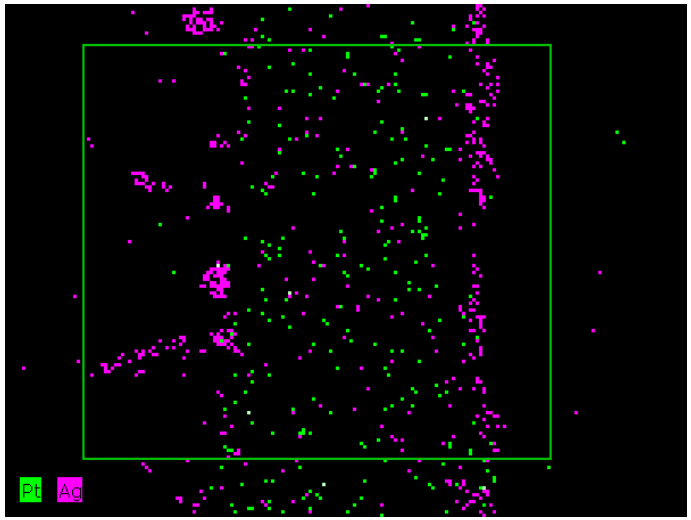


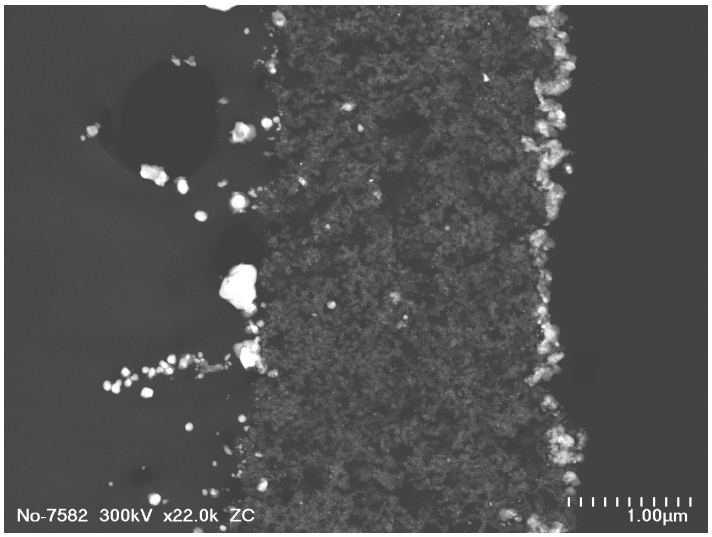
Cyclic voltammetry shows the stripping of Ag in early cycles followed by stable voltammograms suggesting lack of surface available Ag.

MEA cross-sections of traditional Pt/C anodes employed opposite PtNT cathodes (from Ag nanowires) shows significant Ag deposition at the anode.

We are employing routes that limit or avoid the potential to redeposit metals at the anode that can be detrimental.

Anode Microscopy (ORNL)





Approach/Future Work
Computational Studies (Tenn)

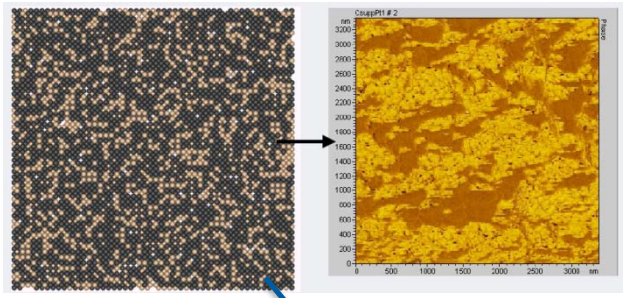
Current emphasis: electrode architecture simulation task

- 'Bottom-up' depiction of phase segregation, porosity
- Goal: extend this description beyond packing spheres
- Developing two approaches

1. Colloid interaction theory
2. Adapting dissipative particle dynamics

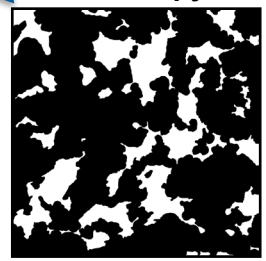
Using experiments (spectroscopy) for input validation w/each approach

Working with NREL to define model system as basis of studies



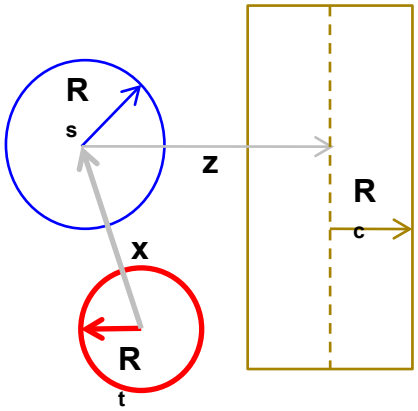
Traditional Pt/C Electrode Simulation

Pt/C Electrode Microscopy



Interaction energetics task:

- Using molecular-level descriptions of metal-substrate interactions

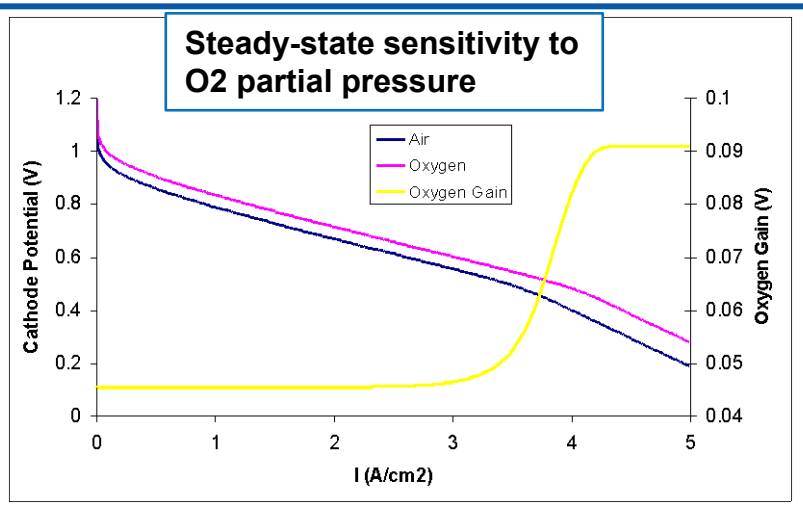


Expand demonstrated approach using interaction energies between spheres to include interaction energy between a sphere and an infinite cylinder under the Hamaker formalism

$$G_{s/c}(z;R_s;R_c) = -\frac{A_{Ham}\pi}{8} * \frac{R_s^3-(z+R_c)^2}{2(z+R_c+R_s)^2} + \frac{(z-R_c)^2-R_s^3}{2(z-R_c+R_s)^2} - \frac{(z-R_c)^2-R_s^3}{2(z-R_c-R_s)^2} + \frac{(z+R_c)^2-R_s^3}{2(z+R_c-R_s)^2} + \frac{2z+2R_c}{z+R_c+R_s} - \frac{2z+2R_c}{z+R_c-R_s} + \frac{2R_c-2z}{z-R_c+R_s} + \frac{2z-2R_c}{z-R_c-R_s} + ln\left(\frac{z+R_c+R_s}{z+R_c-R_s}\right) + \left(\frac{z-R_c-R_s}{z-R_c+R_s}\right)$$

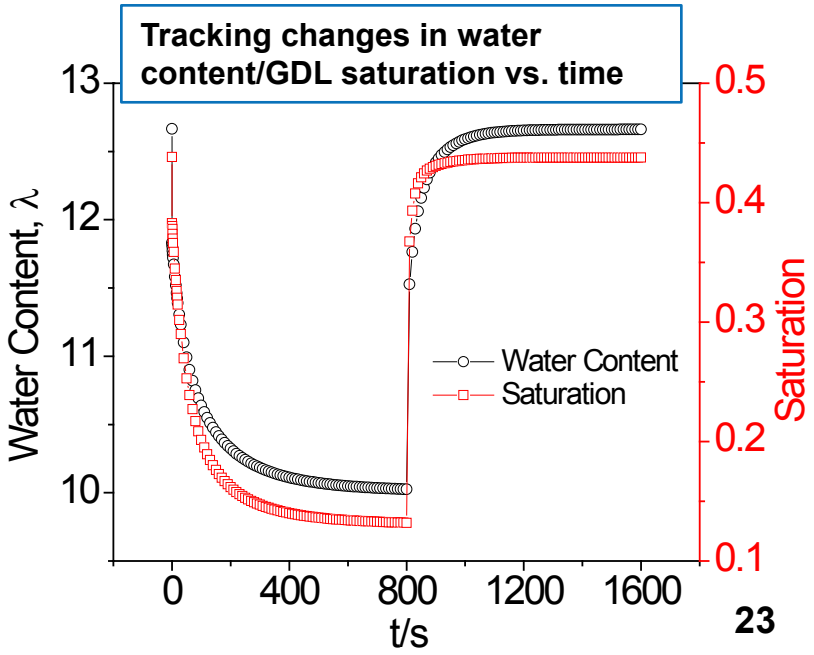
Approach/Future Work
Computational Studies (Texas)

Extension of established porous electrode models to highlight issues critical to the incorporation of extended surfaces in thick, dispersed electrodes



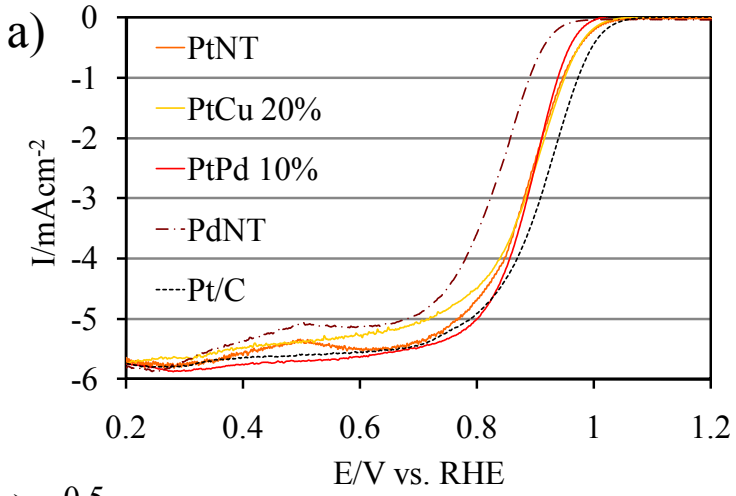
Simulating diagnostic techniques to develop consistent set of tests to identify key MEA transport/kinetic parameters

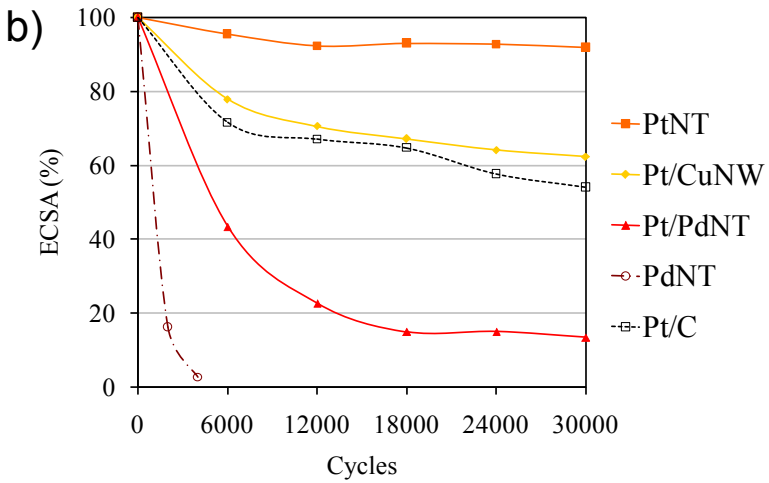
- Approximating "orthogonal" experiments
- oxygen gain, current interrupt, response to step changes in current to differentiate between GDL and CL limitations

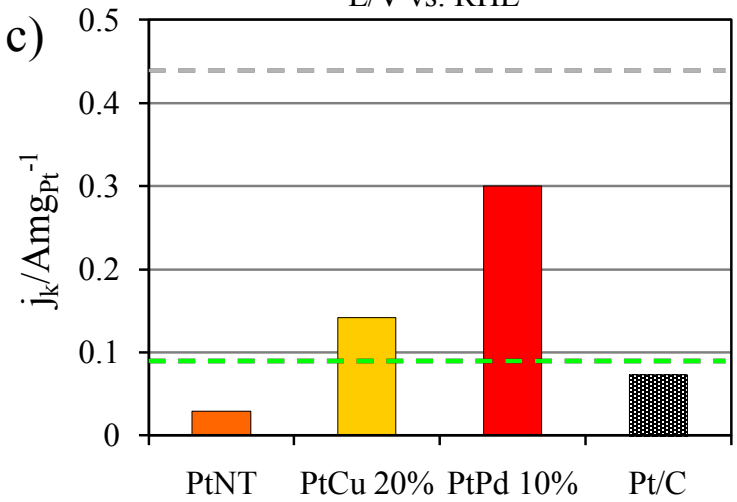


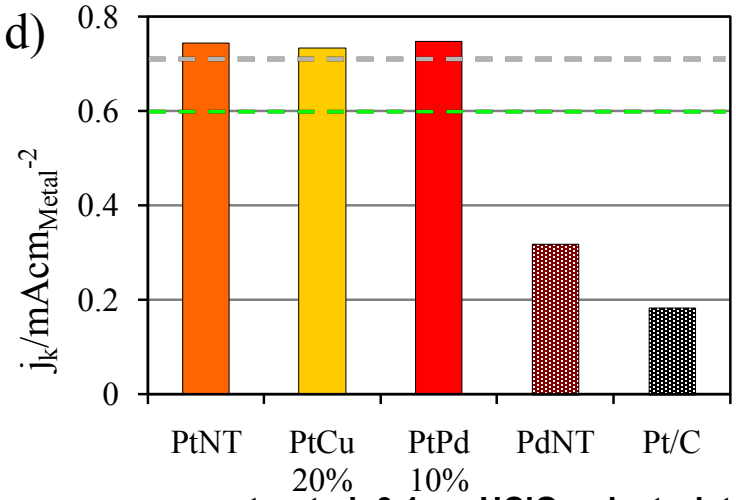
Technical Accomplishments and Progress

PtNTs (effects of Pd) (UC-R)









Pd incorporation into NTs results in significantly reduced performance and durability.

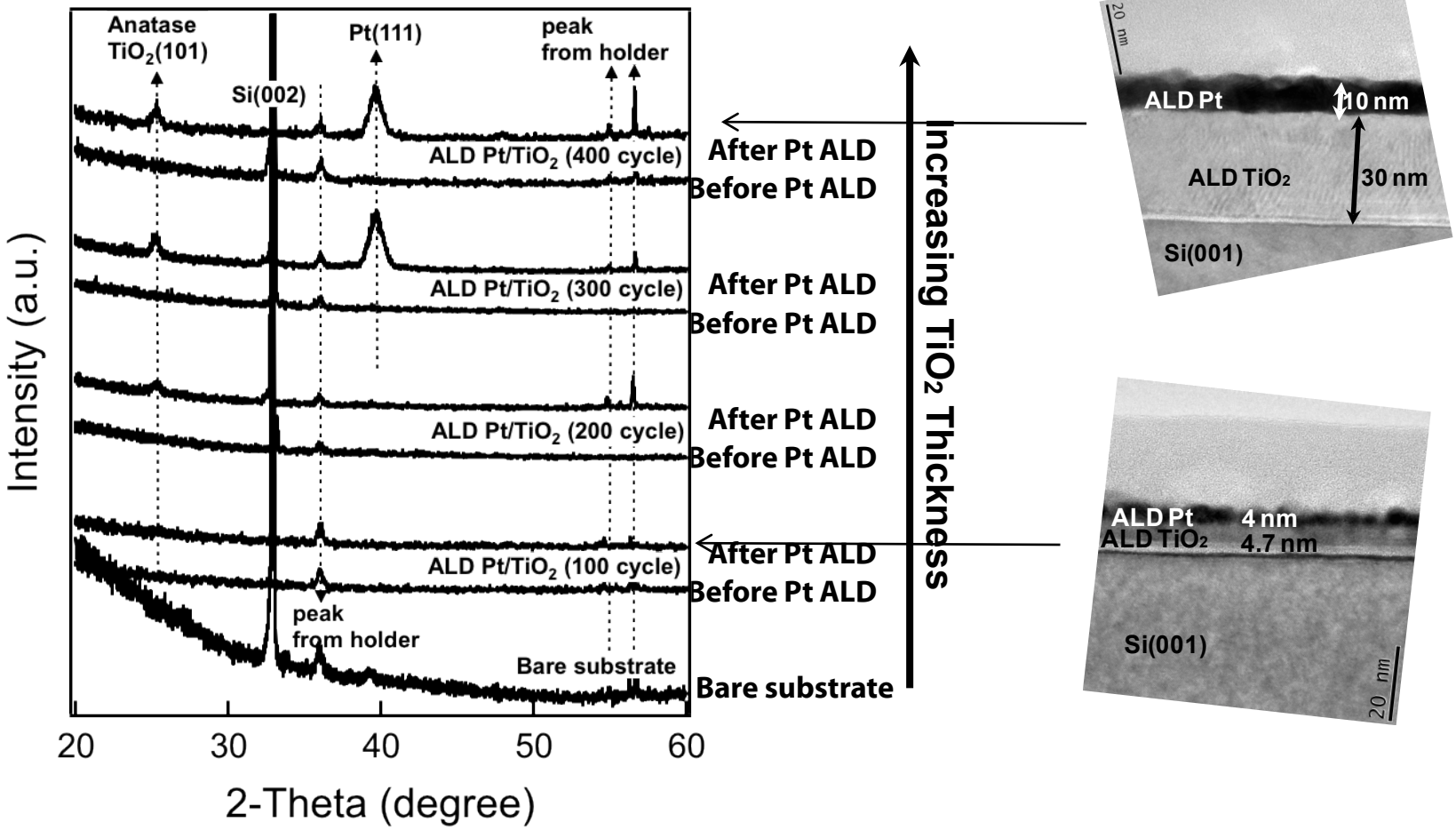
Incomplete Cu displacement also resulted in PtNTs with decreased durability.

Specific activity targets reached for 3 NTs presented.

a) Anodic polarization curves at 1,600 rpm in an oxygen saturated 0.1 M $HClO_4$ electrolyte of PtNTs, Pt/CuNWs, Pt/PdNTs, PdNTs, and Pt/C taken at a scan rate of 20 mVs^{-1}. b) Cyclic durability between 0.6-1.1V c) Mass (platinum normalized) and d) Specific ORR activity of aforementioned catalysts at 0.9 V vs. RHE.

Technical Accomplishments and Progress

Effect of TiO_2 layer on Pt ALD (Stanford)



Increasing TiO_2 coating layer leads to formation of anatase TiO2. Faster nucleation, enhanced conformality.