The Science And Engineering of Durable Ultralow PGM Catalysts

Fernando Garzon
Los Alamos National Laboratory
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FC010

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Overview

Timeline

- Project start date: 03/2010
- Project end date: 03/2014
- Percent complete: *100%*

PGM total loading:	0.125 mg/cm^2 (2017 target)
PGM total content:	0.125 g/kW (2017 target)
Loss in initial catalytic activity	< 40% mass activity loss (2017 target)
Electrocatalyst support stability:	< 10 % mass activity loss (2017 target)
Durability: OCV hold 500 h	< 20 mA/cm^2 H_2 X-over < 20 % OCV loss (2017)
Durability with cycling:	5000 h (2017 target)

Budget

- FY13 DOE Funding: $1,100K
- Planned FY14 DOE Funding: $275K
- Total Project Value: $6,000K
- Cost Share Percentage (if applicable): 9%

Barriers

- DURABILITY: Free-radicals degrade membranes and catalyst supports
- COST: Unique catalyst microstructures and additives improve utilization and durability of ultralow precious metal loadings that reduce cost
- PERFORMANCE: More efficient catalyst layer structures improve transport properties and performance

Partners

- Ballard Fuel Cells, UNM, UD
- LANL

Project Objectives – Relevance- Collaborations

- Development of durable, high mass activity Platinum Group Metal cathode catalysts -enabling lower cost fuel cells - *Synthesis and characterization of Low PGM catalysts: LANL & UD Low loading Pt on carbon-nitrogen nanowires: LANL & ORNL*

- Elucidation of the interconnected relationships between PGM, nucleation, growth catalyst shape, particle size and activity will help design better catalysts - *Pt nucleation and dispersion on carbon research enabled well-dispersed Pt deposition on novel carbon nanowires: LANL & UNM*

- Optimization of the cathode electrode layer to maximize the performance of PGM catalysts- improving fuel cell performance and lowering cost – *Nanowire supports: LANL, Advanced microstructural catalyst layer model development- provided information on optimization of support geometry: Ballard*

- Understanding the performance degradation mechanisms of high mass activity cathode catalysts – provide insights to better catalyst design. *DFT models for particle reactivity: LANL, Free Radical scavenging MEAs; enhanced oxygen free radical elimination using size-optimized doped ceria nanoparticles: LANL & UNM*

- Development and testing of fuel cells using ultra-low loading, high activity PGM catalysts-Validation of advanced concepts. *Fuel cell testing of low-loading Pt carbon nanowire support derived from molecular templated polypyrrole: LANL & Ballard*

- IMPACT: This project will help lower the cost and the precious metal loading of PEM fuel cells and improve catalyst durability

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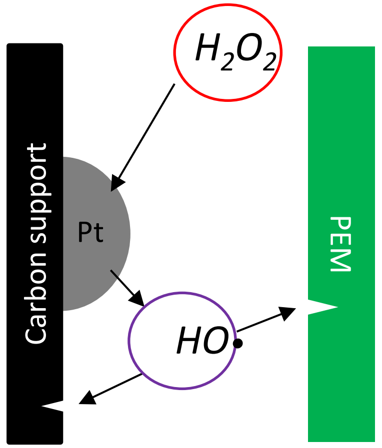
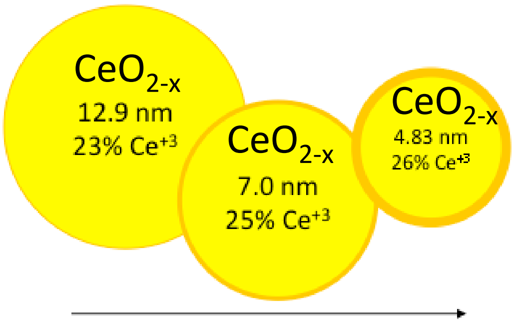
Approach: Ceria & Doped Ceria additives for Improving Durability

- **Problem:** Fuel cell degradation rates are higher at low PGM loadings-increased free radical generation results in more ionomer attack
- **Previously**: Originally developed ceria impregnated carbon supports, switched to additives
- **Progress**: Controlled synthesis of ceria crystallite size. Determined peroxide decomposition and free radical generation rates for CeO_2, Gd-CeO_2 Pr-$CeO_2$and Zr-CeO_2. Performing OCV tests and accelerated stress tests of fuel cells w/ and w/o ceria.



Peroxide generation and degradation into free radicals that attack the carbon support and PEM



Ceria Ce^{3+} / Ce^{4+} ratio varies with crystallite size

- Cerium cation exchanged membranes are currently used to stabilize PEMs
  - leaching observed from the membranes
- Ceria *nanoparticles* offer a relatively acid stable peroxide decomposition catalyst
- However, free radical formation is also destructive
  - Characterized relative decomposition/formation rates (right)
- Determine how chemical substitution changes ceria free radical scavenging properties

Cerium Oxide Nanoparticles for Stabilization

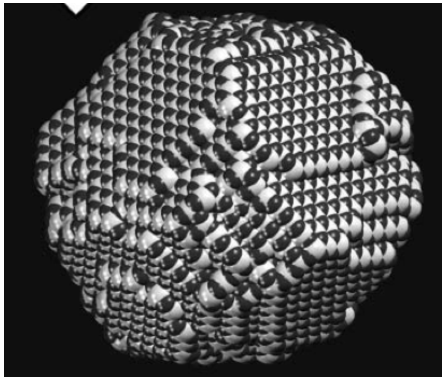
$$Ce^{+4} + H_2O_2 \longrightarrow Ce^{+3} + HOO\bullet + H^+$$

$$Ce^{+4} + HOO\bullet \longrightarrow Ce^{+3} + O_2 + H^+$$

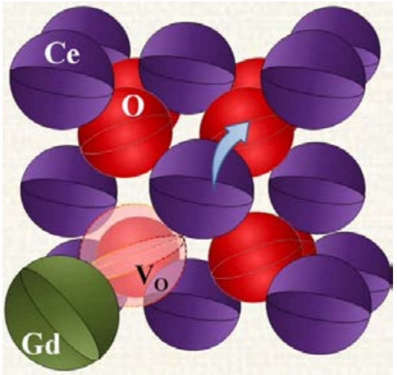
$$Ce^{+3} + HOO\bullet + H^+ \longrightarrow Ce^{+4} + H_2O_2$$

For Cerium ions in Solution

Karakoti et al.



Ceria nanoparticle reconstruction



Gd doping creates vacancies

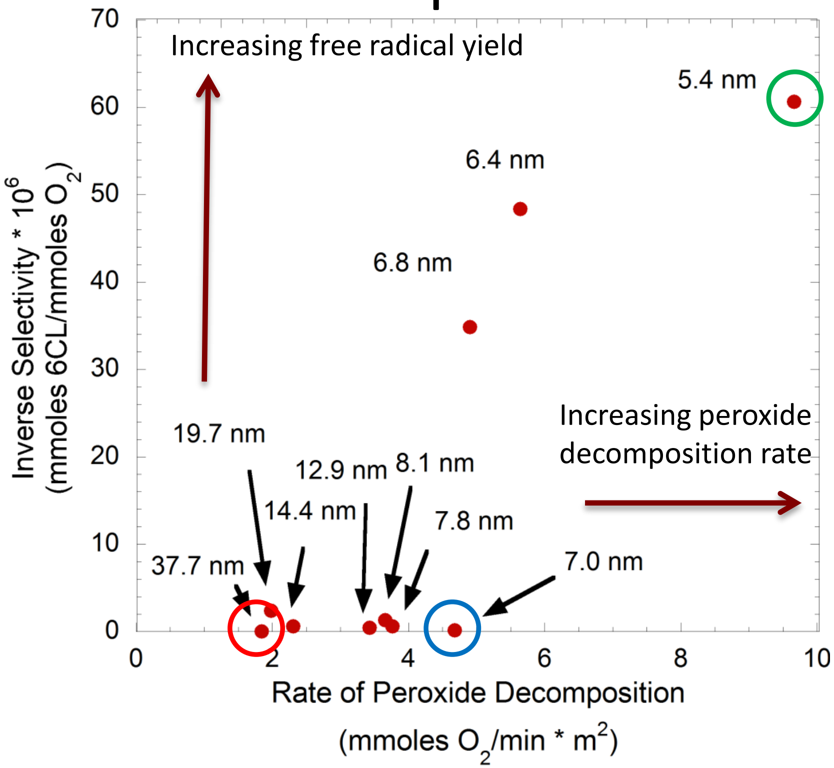
- *Cerium ions* are known to be both a good peroxide decomposer and a good radical scavenger[1] But:
  - *ions migrate and leach out of fuel cells*
  - *Cerium oxide nanoparticles slowly dissolve*
- Rate of peroxide decomposition increases with decreasing particle size, as does Ce^{+3} concentration
  - Ce^{3+} larger ionic radii and oxygen vacancy creation decrease surface energy of particle
- Is there an optimal size?
  - Does the increasing surface tension of small particles change the energetics of the Ce (IV) to Ce(III) reactions?
- How does doping Ceria affect selectivity, rate & particle stability?
  - Gd^{3+}, Zr^{4+},$Pr^{3+,4+}$

Karakoti, *Chem. Soc. Rev.*, 39, 4422, 2010
T X T Sayle, S.C. Parker and D Sayle, *Chem. Commun.* 2004, 2438-2439
Lubomirsky,http://www.weizmann.ac.il/materials/igorl/Inelastic-effects

Selectivity for Free Radical Production Versus Particle Size

- Large ceria (37.7 nm)
  - Good for scavenging radicals, poor for peroxide decomposition
- Medium ceria (7.0 nm)
  - Fastest peroxide decomposition with good peroxide selectivity
- Small ceria (5.4 nm)
  - Poor for scavenging radicals, good for peroxide decomposition

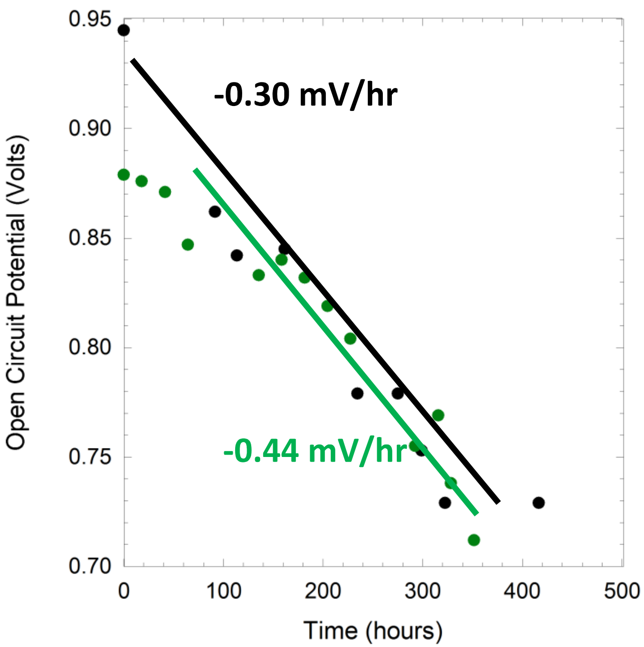
Selectivity^{-1} vs. Peroxide Decomposition



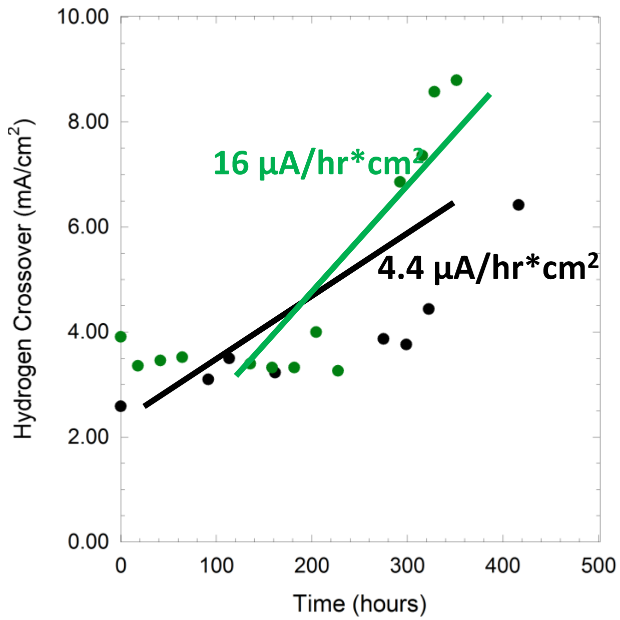
- Free radical generation measured using Carboxyfluorescein luminescence
- Peroxide decomposition rate measured by oxygen gas evolution rate
- Rates are normalized to surface area measured by gas adsorption

Accelerated Stress Test: Small Ceria Particles Added to Cathode

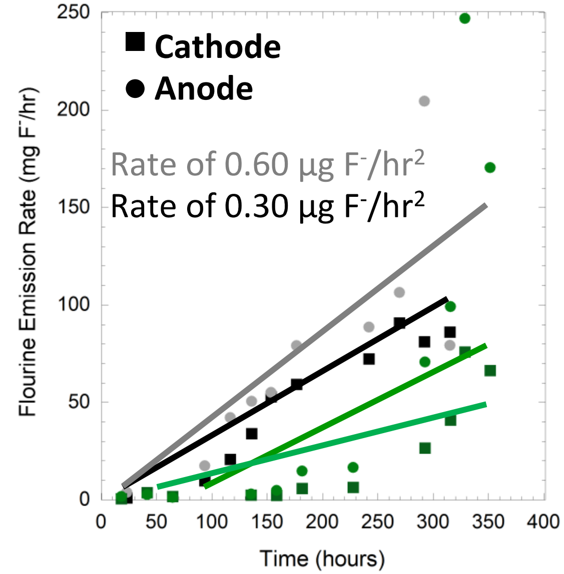
Open Circuit Potential



Hydrogen Cross Over



Fluorine Emission Rate



Rate of 0.70 µg F^-/hr^2
Rate of 0.23 µg F^-/hr^2

- Black dots- no particles added to non-stabilized MEA
- 5nm ceria nanoparticles (2 w/o) do not provide MEA stabilization despite their high surface area
  - Too many free radicals are produced by the decomposition of peroxide (previous slide)

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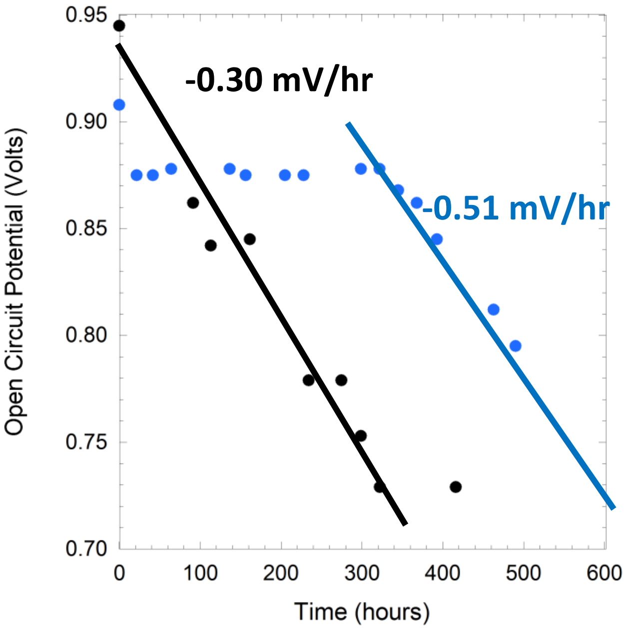
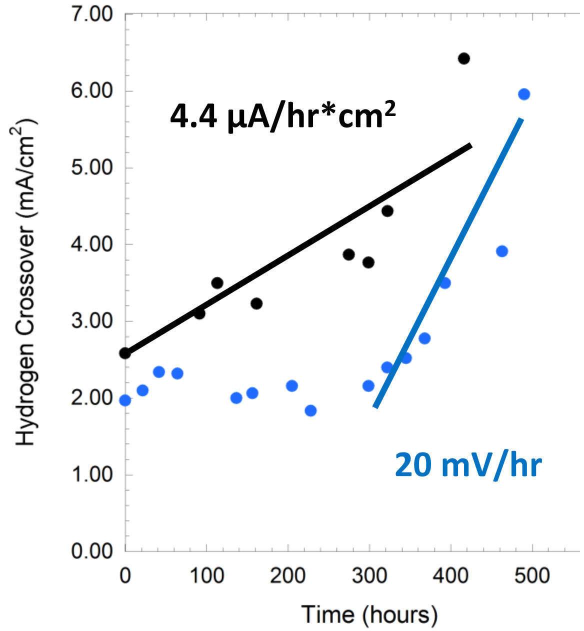
Accelerated Stress Test: Medium Ceria Particles Added to Cathode

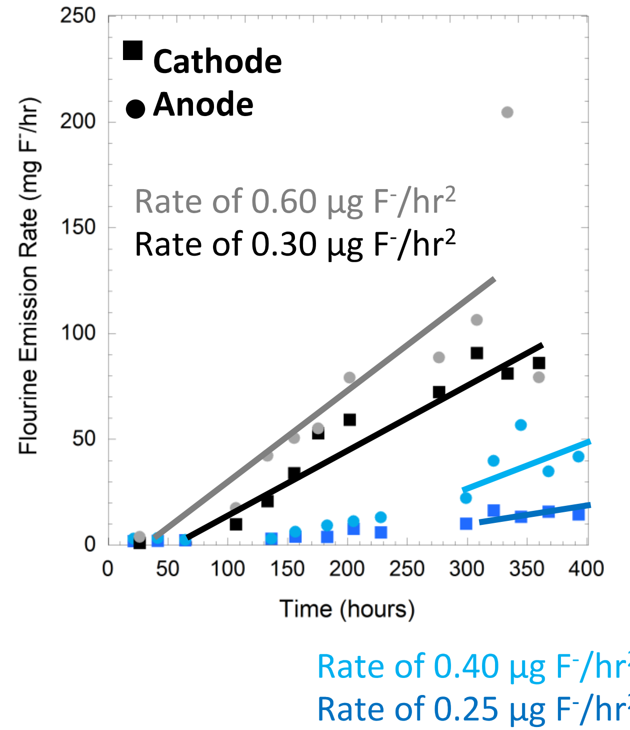
Open Circuit Potential



Hydrogen Cross Over



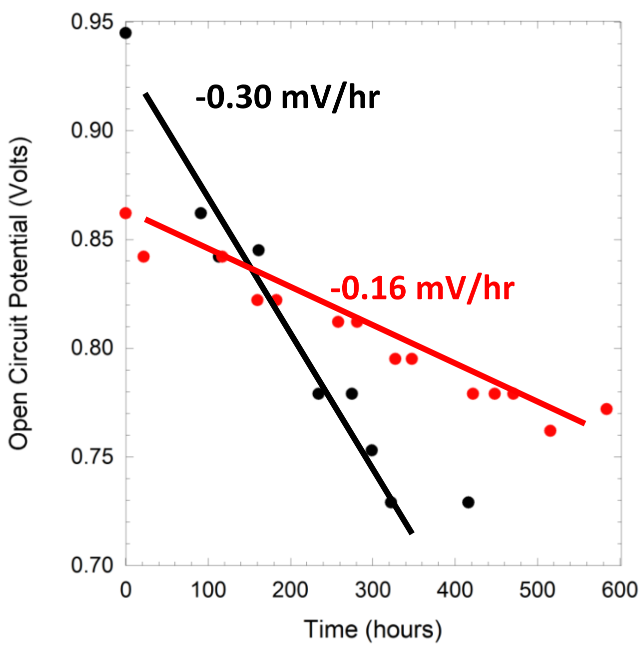
Fluorine Emission Rate



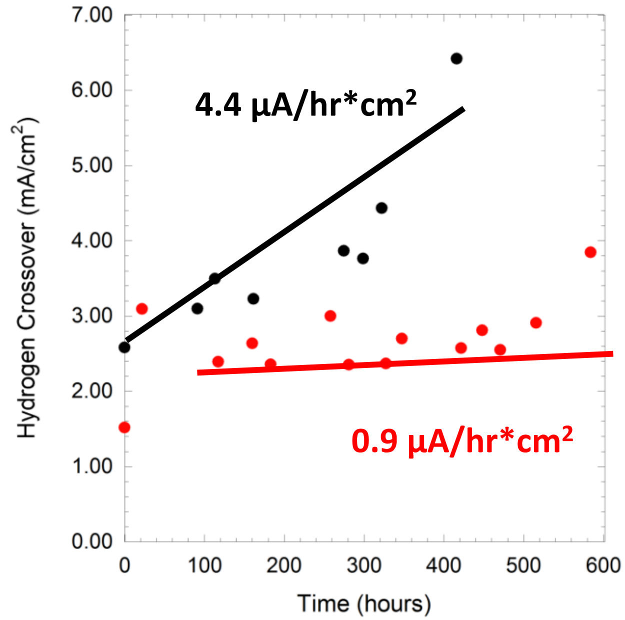
- 7nm particles provide good initial stabilization
- Over time they get smaller via dissolution causing increased free radical generation

Accelerated Stress Test: Large Ceria Particles Added to Cathode

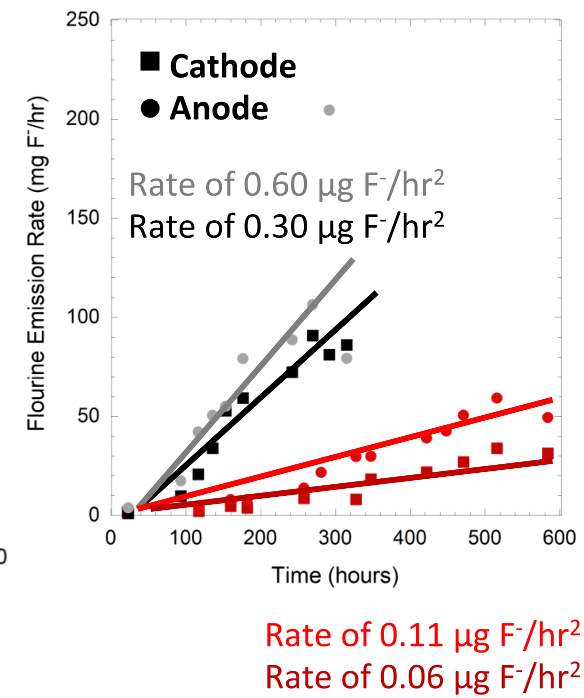
Open Circuit Potential



Hydrogen Cross Over



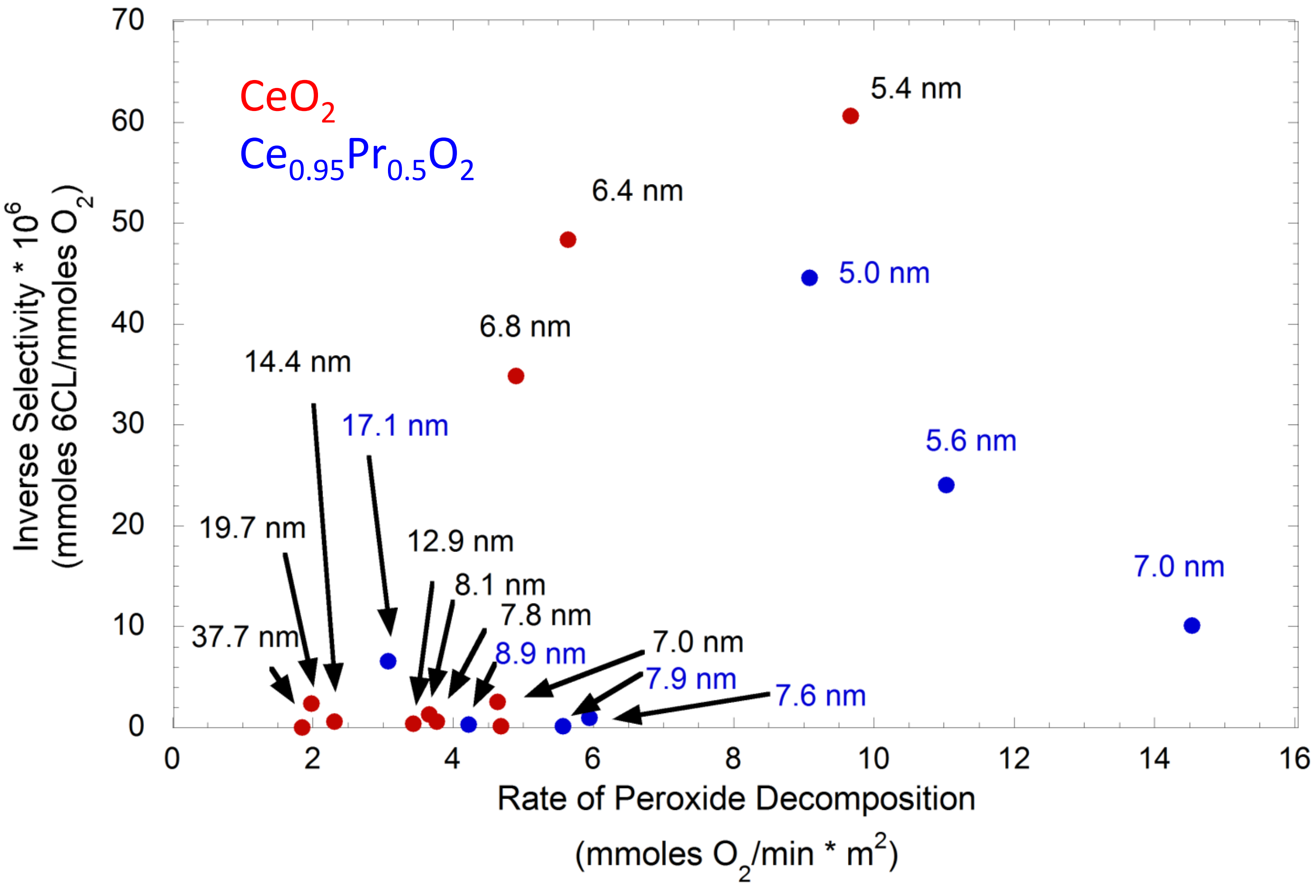
Fluorine Emission Rate



- Red 37nm particles
- Black- no particles
- Degradation reduced~5X
- Relatively large particles do not have much surface area

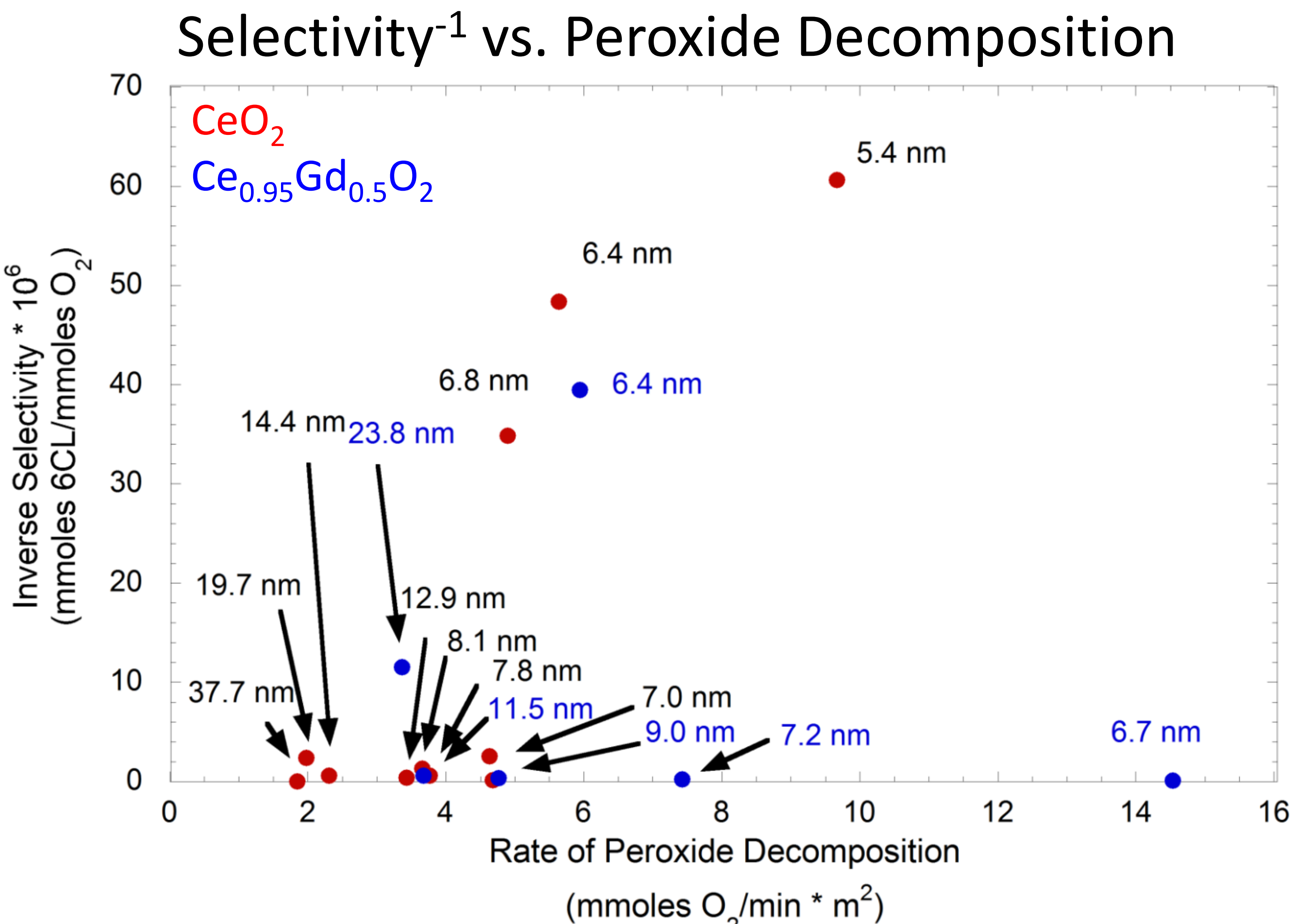
Effects of Pr Doping on Ceria Performance

Selectivity^{-1} vs. Peroxide Decomposition



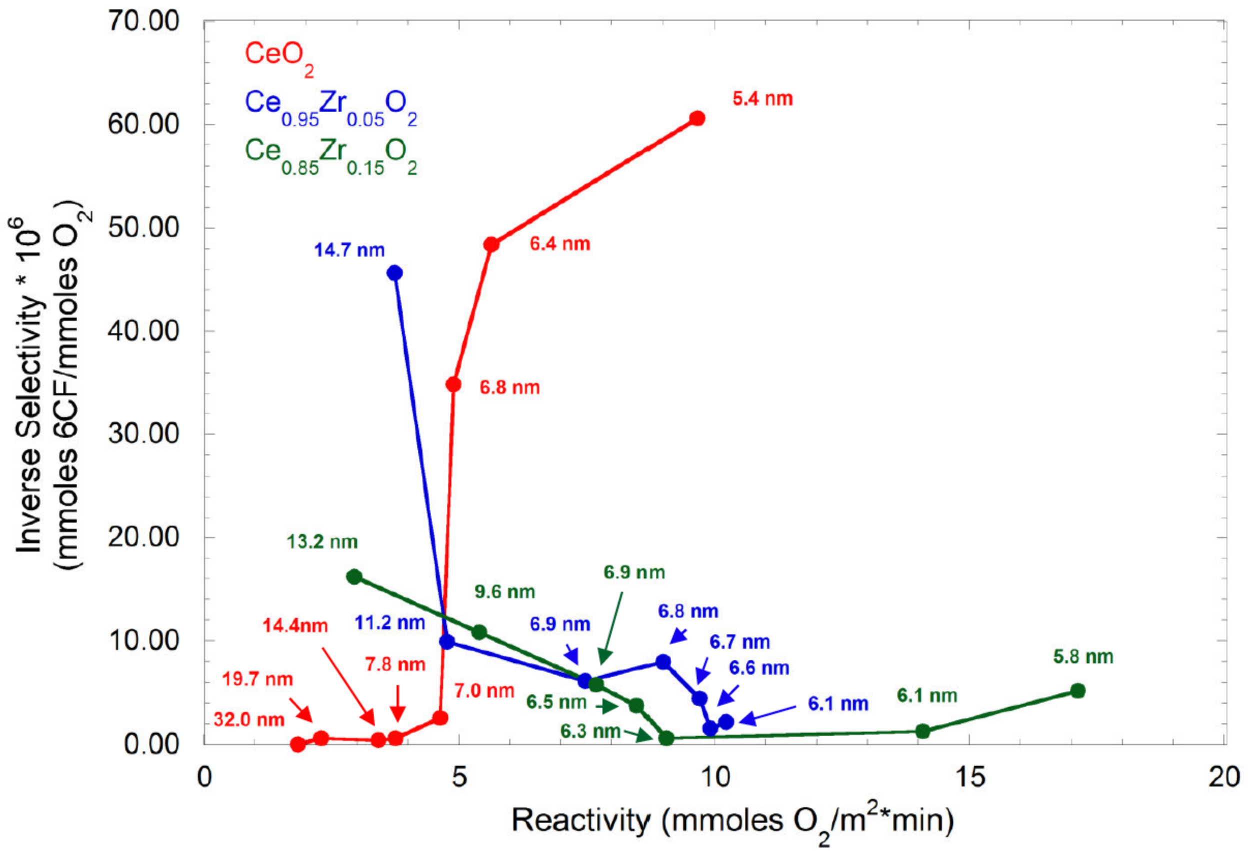
5 % Pr doping generally decreases free radical production but size results show scatter due to varies surface segregation of dopant, small sizes still generate significant amounts of free radicals

Effects of Gd Doping on Ceria Performance



5 % Gd doping of ceria results in high peroxide decomposition rates with lower free radical generation for <u>most particle sizes</u>

Effects of Zr Doping on Ceria Performance



15 % Zr doping of ceria results in high peroxide decomposition rates with low free radical generation for <u>*small particle sizes*;</u> <u>Zr doping also improves nanoparticle acid stability</u>

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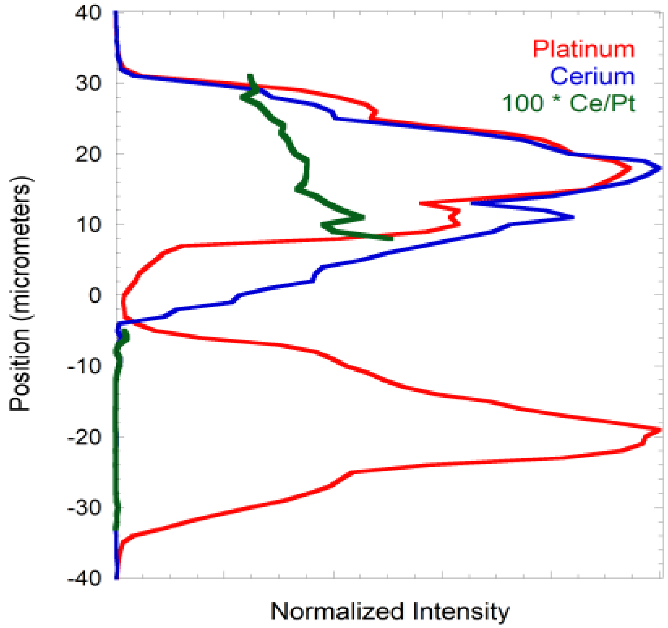
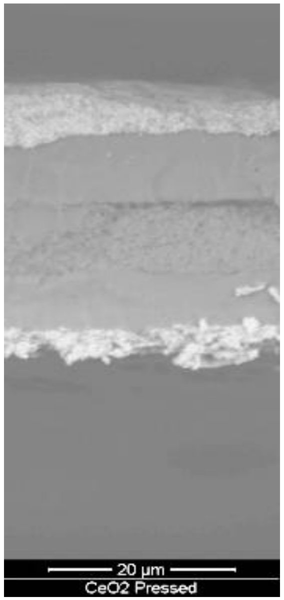
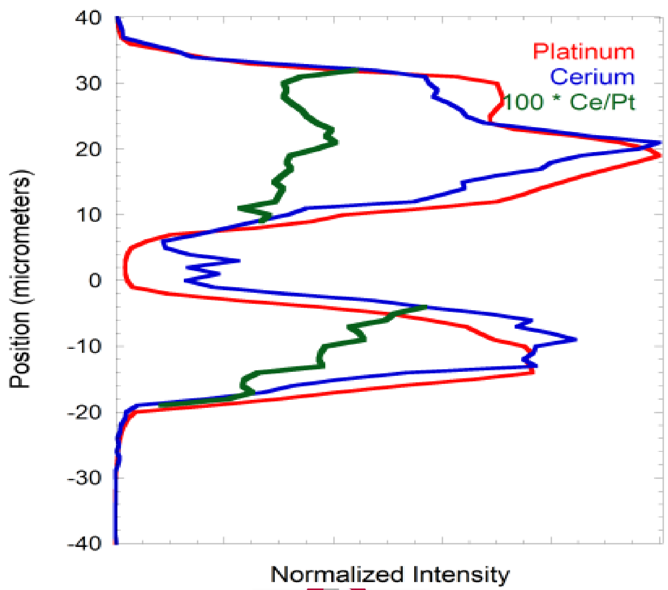
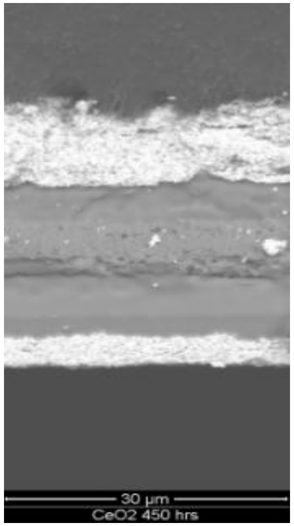
Ceria Migration studies at APS Argonne

- MEAs were prepared with 2% ceria nanoparticles in cathode layer
- AST OCV test performed
- APS X-ray Fluorescence microprobe used to characterize Ce migration
- 450 hr AST showed significant Ce migration from cathode to anode
- Note Ce does not stay in membrane



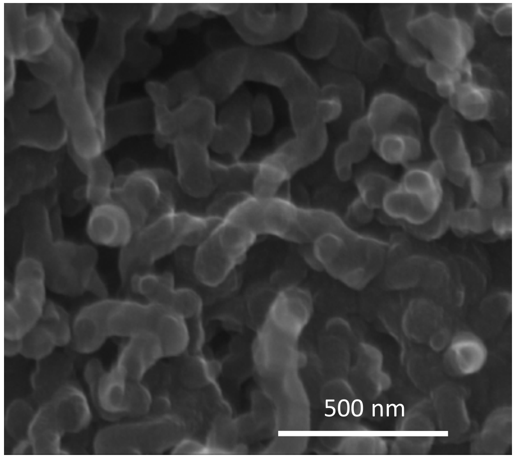






Molecular Templated Polypyrrole Nanowire Supports

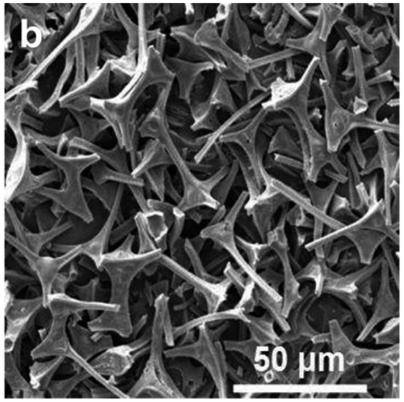
- **Previous Effort**
  - Process
    - Electropolymerize PPy nanowires onto a substrate
    - Pyrolyze
    - Platinize: sputter or impregnate
    - Hot press to membrane
  - Issues:
    - Achieving high Pt dispersions
    - Poor MEA performance (esp. Pt utilization & flooding)



Electropolymerized PPy nanowires

- **New Direction**
  - Process
    - Bulk synthesis of PPy nanowires
    - Pyrolyze to form powder
    - Platinize using polyol process
    - Prepare catalyst ink
    - Coat decals (or membrane)
    - Hot-press
  - Advantages
    - Conventional MEA manufacture
    - Greatly improved MEA performance

- Advantageous geometry of nanowire network supports
  - Tortuous branched networks maintain open pores but minimal "voids"
    - More free volume available for ionic and mass transport
    - Facilitates ionomer access and dispersion during fabrication
  - Enhances electronic conductivity (including "z" direction)
    - Minimizes electronically stranded catalyst
- Comparison with other carbon tube/fiber/wire support options
  - Nanotubes/fibers (vapor grown): expensive, not branched
  - Polyaniline nanowires: easily made, but pyrolyze poorly
  - Polypyrrole nanowires: readily graphitize
    - Synthesis by potentially low-cost "soft" template processes
    - Good results with Heparin:Methylene Blue soft template (Wei et al., *Synth. Met.* 160 (9–10), 849-854 (2010))
      - Some control of fiber diameter possible by varying the Hep:MB ratio



"Tetrapod" Catalyst Structure
Lee et al., Angew. Chem. Int. Ed., 52, 1026 (2013)

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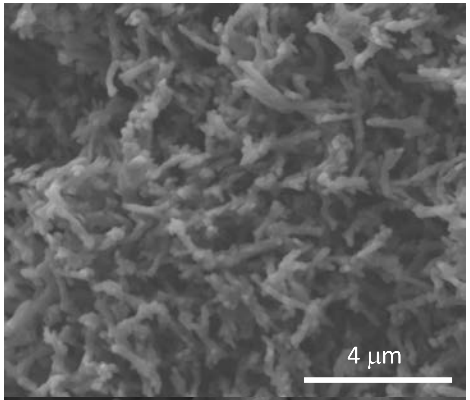
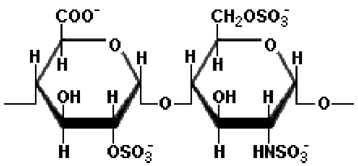
PPy nanostructures w/ various templates

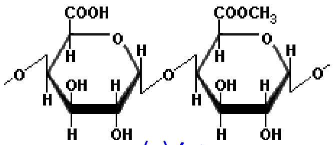




$2^{(-)}$/ring

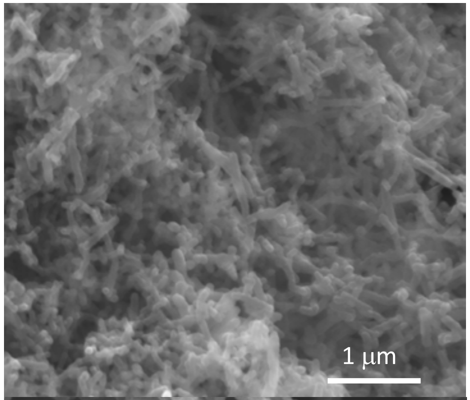
Heparin

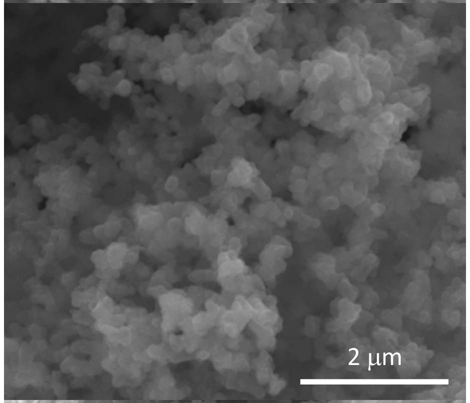
Pectin
(low methoxyl,
+ maltodextrin)

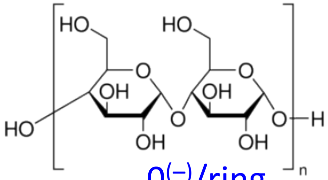


$<1^{(-)}$/ring

50% methoxylated
(0% is polygalacturonic acid)

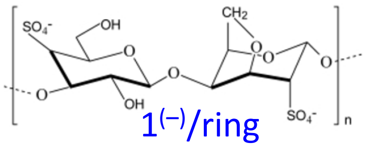






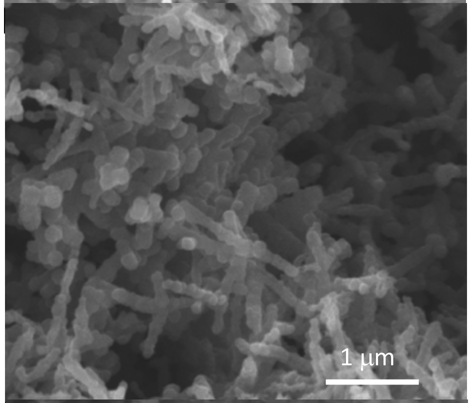
$0^{(-)}$/ring

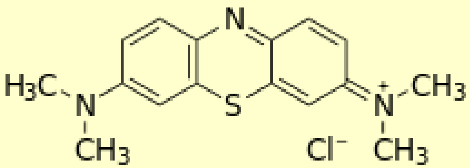
Starch



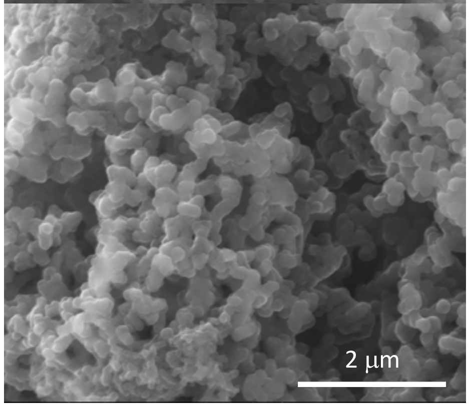
$1^{(-)}$/ring

ι-Carrageenan
(food grade)

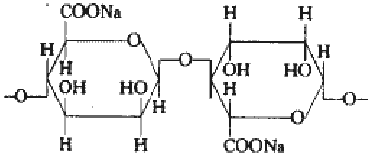




Methylene Blue

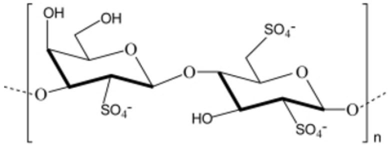


Na^+ Alginate
(food grade)

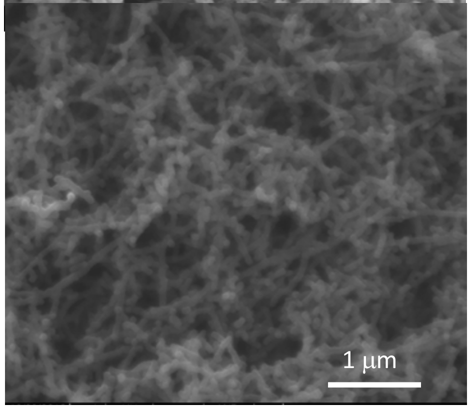


$1^{(-)}$/ring

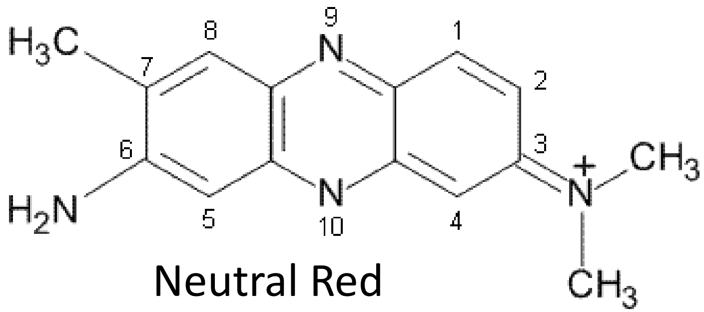
λ-Carrageenan
(food grade)



$1.5^{(-)}$/ring



Dye Templating Functionality



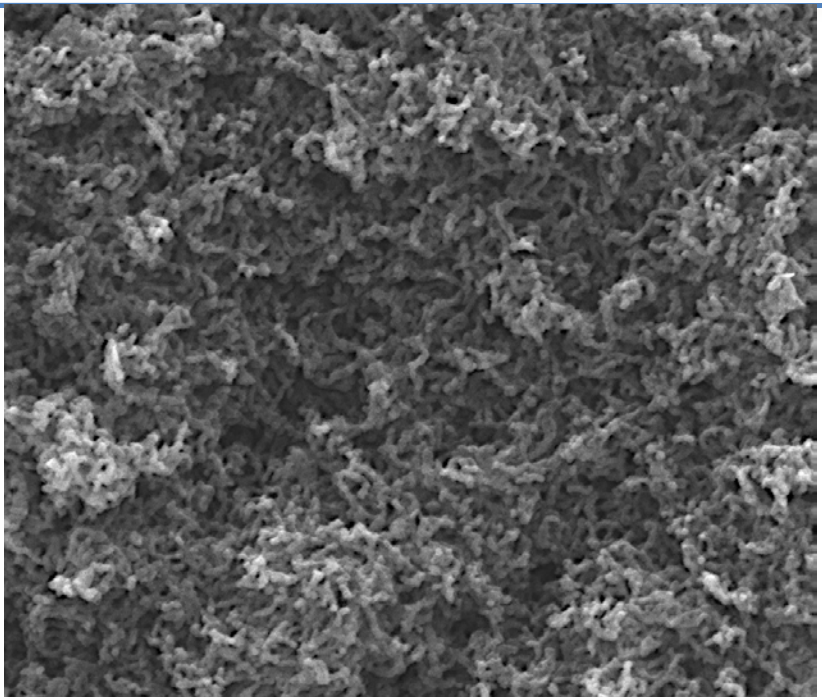
Neutral Red

Dye	Position on anthracene molecule					Result
	3	6	7	9	10	
Methylene Blue	$–N(CH_3)_2$	$–N(CH_3)_2$	C	N	S	Fibers
Neutral Red	$–N(CH_3)_2$	$–NH_2$	$–CH_3$	N	N	Globules
Basic Blue 3	$–N(CH_2CH_3)_2$	$–N(CH_2CH_3)_2$	C	N	O	Globules
Pyronin Y	$–N(CH_3)_2$	$–N(CH_3)_2$	C	C	O	Globules*
Toluidine Blue O	$–N(CH_3)_2$	$–NH_2$	$–CH_3$	N	S	Fibers
Azure C	$–NHCH_3$	$–NH_2$	C	N	S	Fibers

*Fine, fibers obtained when used in combination with pectin

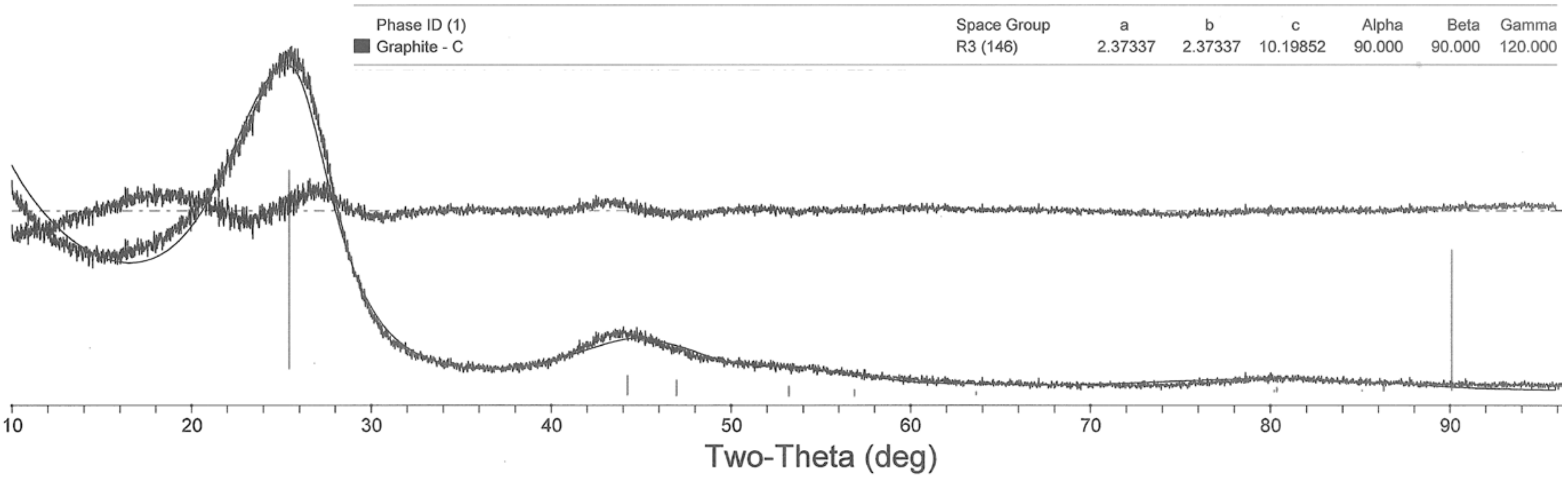
<u>Key functionality</u> for templating wires: sulfur heteroatom at position 10

Milestone: Catalyst Scaleup for Ballard



Catalyst for Ballard:

- A total of 1.2 g sent
- High nanowire surface area, 20-30 nm width
- Highly graphitic C + 10% N content XRD:
    - *a*=0.24nm, *c*= 1.02nm,high amplitude for in plane peaks
    - Order parameter ~ 1.3 nm
    - ~ 90 m^2/g
- 14wt% Pt catalyst
    - Modified polyol process
    - High Pt Dispersion
        - ~ 2 nm-3 nm particles



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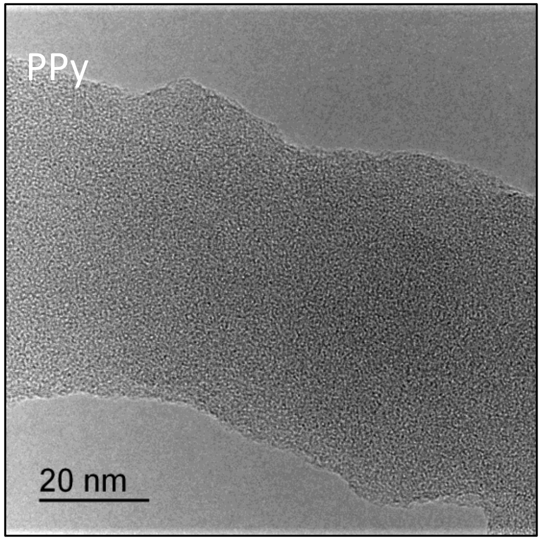
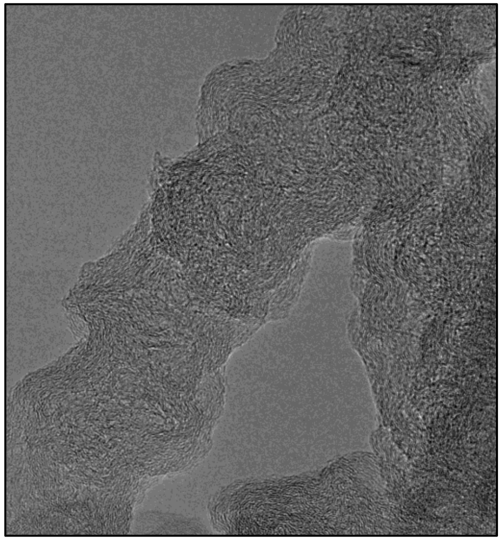
PPy to Pt-PPPy Nanowire Catalysts Scale Up

- 1.2 g of high quality catalyst been sent to Ballard for FC testing
- The pyrolyzed polypyrrole, $C_x N_y$ nanowires formed using the low cost, two-part carrageenan plus methylene blue soft template
- Surface area is 90 m^2/g, about 25% higher than previously reported, fiber diameter of about 25 nm.

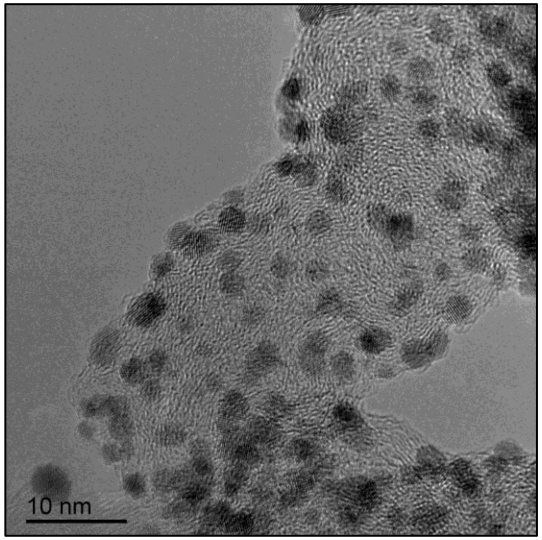
- EDX & CHNO analysis results indicate a N content of 6-12% despite the relatively high pyrolysis temperature of 1000˚C.
- XRD & TEM (ORNL) indicates 2-3 nm Pt particle size



Molecular Template Dye/carbohydrate polymerization of PPy
Metal-free ammonium persulfate oxidative polymerization forms nanowires



Pyrolysis: 1000˚C, 1h
~ 50% wt loss
~ 90% C- 10% N
Highly graphitic structure
No sulfur detected



Platinization: polyol process
13.5 wt% Pt: surface loading~ 3x 20%Pt/C
2.6 nm particles (TEM)

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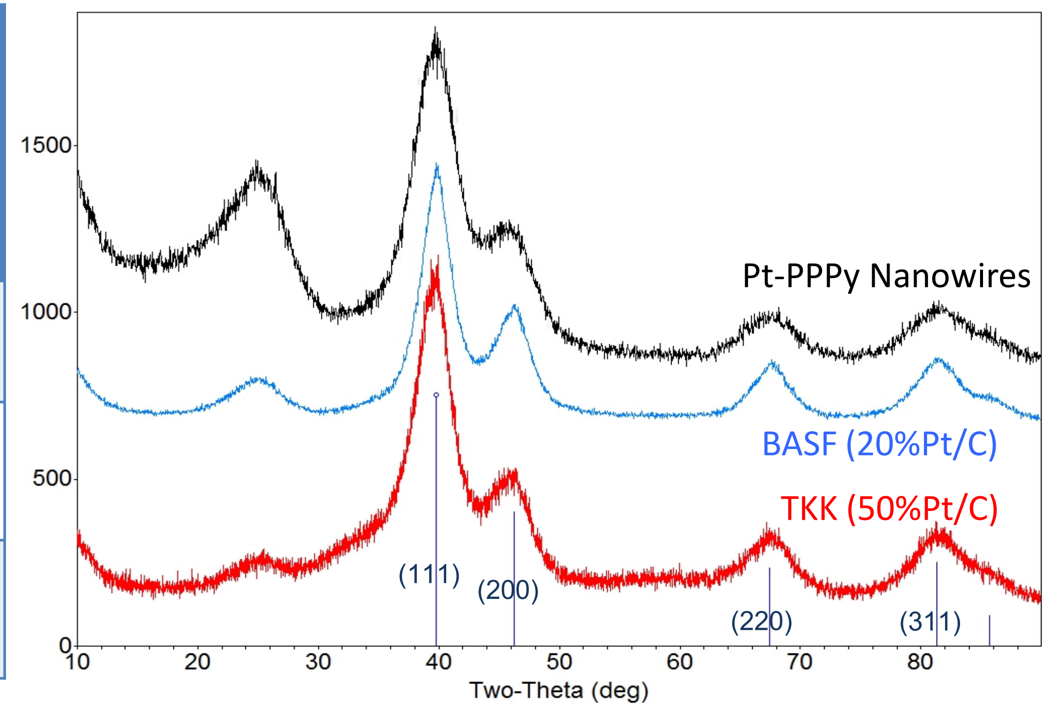
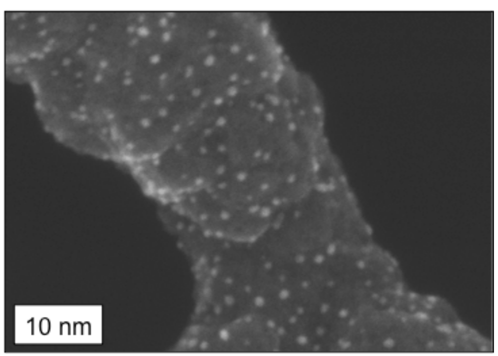
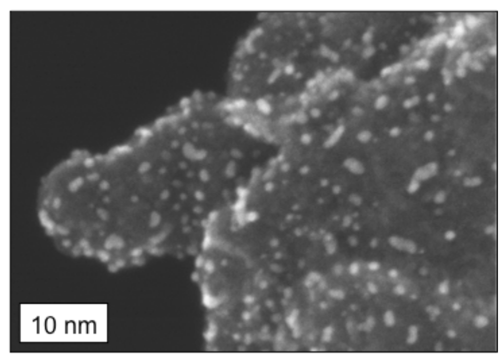
Support Loadings: Comparisons with Commercial Catalysts

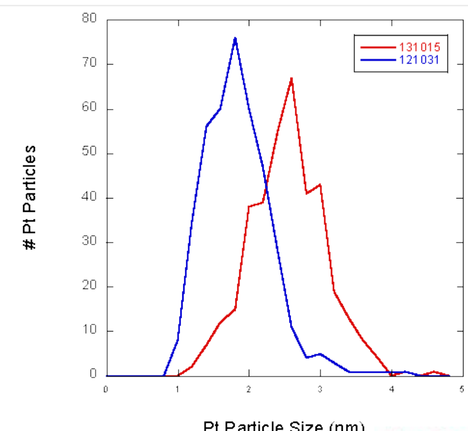
Catalyst	Pt (wt%)	Support SA (m^2/g)	Support Loading ($mgPt/m^2$)*	Pt particle size (nm)
Pt-PPPy	14	90	1.81	2.4
BASF 20%Pt/ XC72	20	250	1.00	3.
TKK-TEC10E 50E	50	800	1.25	2.8



support loading = 1000(wt%Pt)/(wt%Support*SupportSA)







Mass Activity and Specific Activity of Pt/PPPy

Sample	Mass Activity (mA/g)	Specific Activity (mA/cm^2)	ECSA (m^2/g)	Estimated Pt diameter (nm)
Pt/PPPy (100 µg/cm^2)	**0.15 (0.23)**	**0.19 (0.29)**	**82**	**3.4**
Pt/PPPy (500 µg/cm^2)	**0.067 (0.20)**	**0.069 (0.25)**	**84**	**3.3**
Pt/Graphitized C (100 µg/cm^2)	**0.072 (0.16)**	**0.20 (0.40)**	**40**	**6.5**
LANL's data*	**0.078**	**0.085**	**91**	**3.1**

(Mass transport corrected values)

- As expected, the mass transport corrected activities are much higher vs. the uncorrected values.
- The Pt/PPPy sample has a slightly higher mass activity, but lower specific activity vs. the Pt/Graphitized C catalyst.
- LANL's data performed in H_2SO_4.

[1] **Applied Catalysis B: Environmental, 56, 9 (2005)**

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MEA Composition and AST Conditions

MEA Composition

	Cathode Pt Loading (mg/cm^2)	Anode Pt Loading (mg/cm^2)
Baseline MEA	0.055	0.1
LANL Pt/PPPy MEA	0.075	0.1

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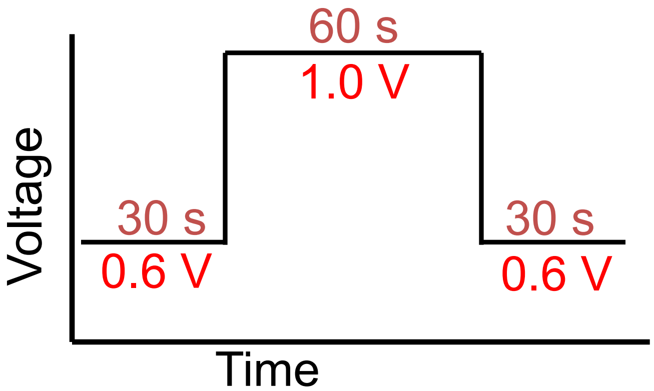
AST Conditions



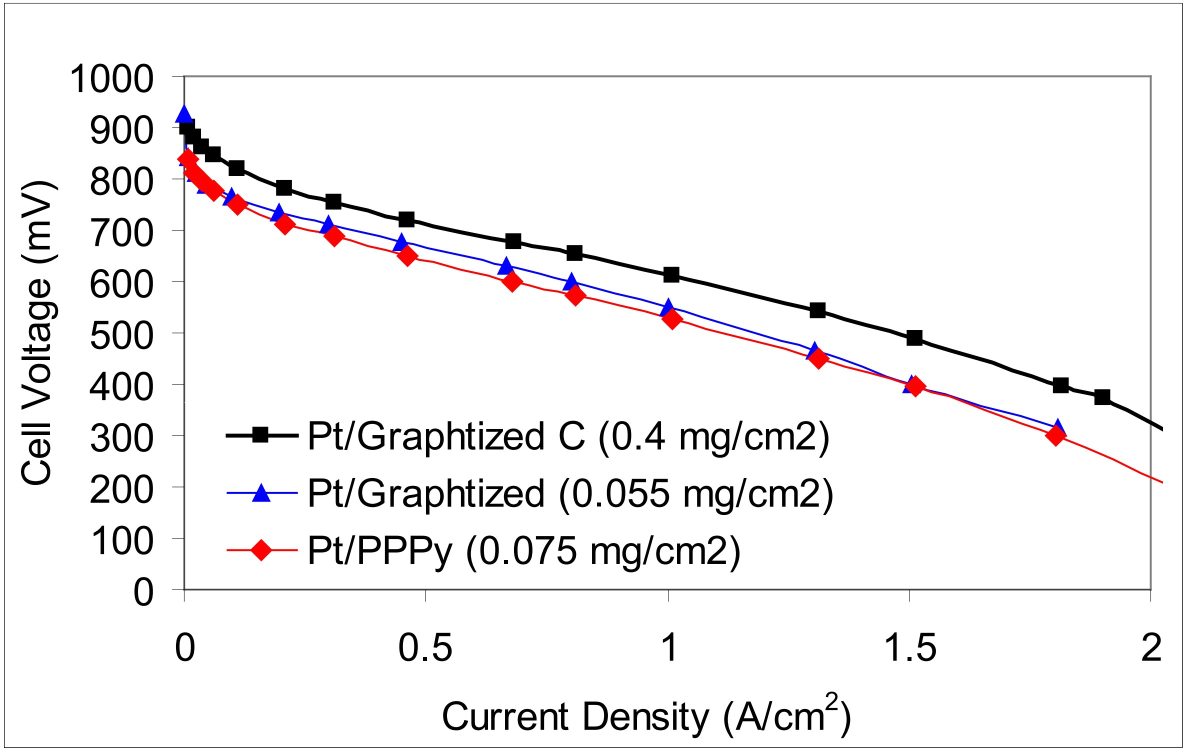
Temperature: 80 ^{o}C

Anode/Cathode Pressure: 5 psig

Anode/Cathode Humidity: 100 %

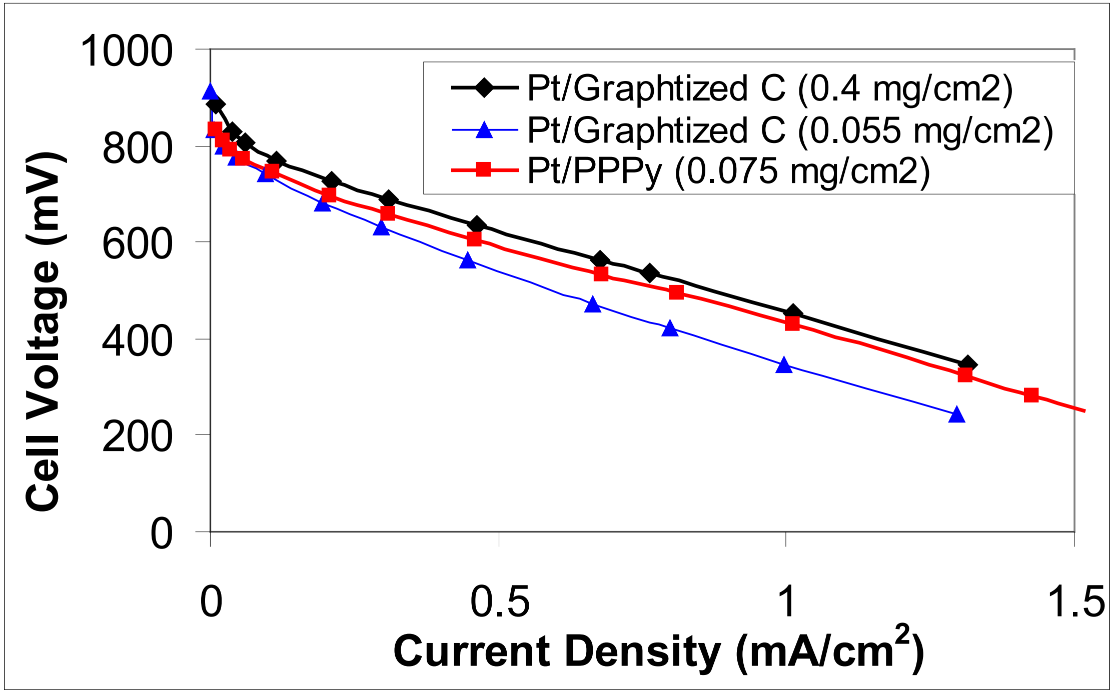
Diagnostics at: BOL, 700, 1400, 2100, 4700 cycles

MEA Performance of Pt/PPPy vs. Pt/C Baseline at 100% RH



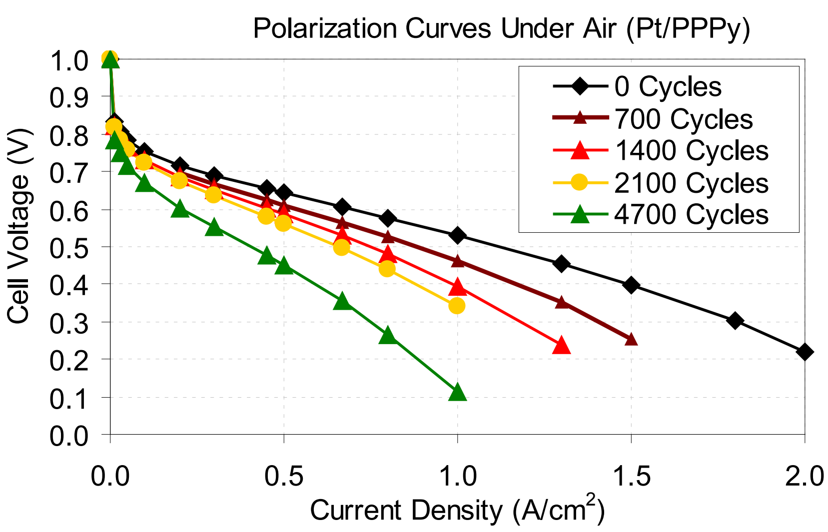
- At 100%RH, the preliminary data suggest that the Pt/PPPy showed similar performance to the Pt/Graphitized C catalysts with similar loading.
- As expected, the low Pt loaded MEAs showed lower performance than the MEA with 0.4 mg/cm^2 Pt at the cathode.

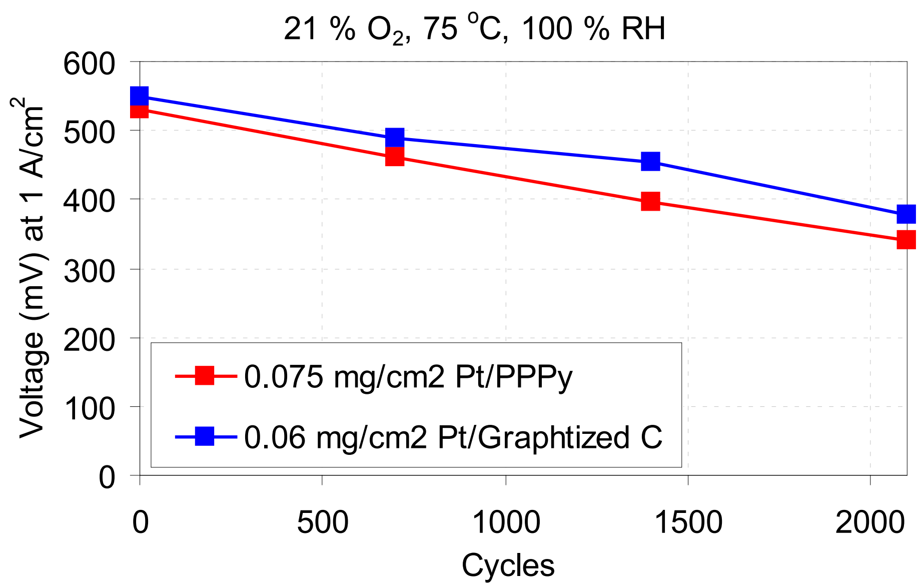
Performance at 60% RH



- At low (60%) RH, the PPPy-based catalyst shows higher performance than similarly loaded Pt/Graphitized C, and comparable performance to the 0.4 mg/cm^2 Pt-loaded MEA at high current densities.
- It is possible that the PPPy structure helps to manage water in the catalyst layer, but further work is required to verify this.

Results of AST Cycling (0.6-1.0 V)





- The performance loss of the Pt/PPPy catalyst was found to be similar to that of Pt/Graphitized C following a voltage cycling AST.

Milestones & No-Go Decisions

- **Milestones:**
  - Nov 2013
    - Accomplish large batch synthesis of novel nanowire PGM catalysts- LANL *completed*
    - Complete ceria nanoparticle migration study using APS synchrotron X-ray microprobe LANL & UNM *completed*
  - Feb 2014
    - Complete oxygen free radical decomposition studies for Pr, Gd and Zr doped Ceria – LANL *completed,*
    - Complete AST testing of MEAs incorporating ceria free-radical scavengers – LANL & Ballard *completed,*
  - March 2014
    - Complete characterization (XRF, SEM, HRTEM, XRD,) of LANL Catalyst materials delivered to Ballard–LANL & ORNL *completed*
    - Perform fuel cell testing using novel nanowire PGM catalysts to demonstrate 50 cm^2 single cell performances with << 0.1 mg Pt/cm^2 that equal or exceed conventional MEAs with 0.2 mg Pt/cm^2 – LANL & Ballard *achieved*

- **No-Go Decisions**
  - Ceria/carbon composite Pt supports – <~8 nm ceria counterproductive
  - Pt Pd nanoplatelet catalyst development-could not reduce particle size
  - Pt_3Sc & Pt_3Y catalysts - ORNL microanalysis indicated HSA materials were oxides

Summary

- Ceria free-radical scavengers
  - Identified particle size range that maximizes scavenging
  - Identified dopants that improve free radical elimination
  - Structurally characterized ceria and doped cerias
  - FC OCV testing results meet durability technical target
    - 2017 Durability Target: OCV hold 500 h
      - < 20 mA/cm^2 H_2 X-over (achieve < 5 mA/cm^2)
      - < 20 % OCV loss (achieve about 10%)
  - AST testing completed
  - Ce migration study completed
- Pt-PPPy nanowire catalysts
  - Successful scale up of low-cost soft-template PPy nanowire synthesis process
  - Achieved reproducible high Pt dispersions with high surface loadings on highly graphitic surfaces in repeated large batches
  - Completed fuel cell testing; low loading low humidity performance is enhanced compared to conventional carbons

- Conclusions: Low loading Pt supported on novel nanowire structured carbon catalyst show promise in improving performance in low PGM loading fuel cells thus lowering cost.
- Doped Ceria nanoparticle additives of the right size and composition improve lifetimes of low loading fuel cells

Proposed Future Work

- Ceria free-radical scavenger additives:
  - FC lifetime OCV testing and performance testing with Zr and Gd-doped cerias
  - Additions of doped ceria to Pt nanowire catalysts and performance testing
- Pyrolyzed PPy nanowire supports:
  - Synthesize finer nanowires
  - Optimization of pyrolysis process to maximize durability and Pt dispersion
  - Enhanced PPPy nanowire functionality via heteroatom doping
  - Catalyst layer composition and processing optimization
  - Comprehensive Fuel cell and full suite accelerated stress testing
  - Scale up catalyst production to stack testing quantities