Development of Alternative and Durable High Performance Cathode Supports for PEM Fuel Cells

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Project ID: FC003

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Overview

Timeline

- Project start date: Jan 2007
- Project end date: Dec 2010
- Percent complete: 80%

Barriers

- A. Durability of cathode catalyst supports
- C. Performance of cathode supported catalyst

Budget

- Total project funding
  - DOE share: $4,120K
  - Contractor share: $255K
- Funding in FY09
  - $1,430K
- Funding in FY10
  - $950K

Partners

- AFCC– guidance on fuel cell testing
- Oak Ridge National Laboratory – mesoporous carbon supports
- University of Delaware and University of Connecticut – Model materials
- Pacific Northwest National Laboratory
  - Synthesis and test of cathode/fuel cell
  - Project management

Objectives

Overall	▶ **Develop and evaluate new classes of alternative and durable high-performance cathode supports**
2010	▶ **Demonstrate durability under accelerated test protocols that meet DOE lifetime criteria**

Milestones, Schedule and Go/no-go Decisions

Task Number	Project Milestones	Task Completion Date				Progress Notes
		Original Planned	Revised Plan	Actual	Percent Complete	
2&3	Identify compositions for cell test	09/30/09	07/31/10[1]		80%	On track
3	Demonstrate target durability	09/30/10	12/31/10		65%	On track

[1] delayed due to late arrival of FY09 funding

Go/no-go decisions:

Year 3: Move forward with cell test if durable supported catalyst can be identified

Outline

- DFT modeling to determine stable and active supports
- Screening using rotating disc electrode (RDE) to downselect lead supported catalysts
- Activity and durability results
  - Carbon supports - XC72, CNT, graphene, graphitic mesoporous carbon (GMC)
  - Conductive metal oxide (CMO) modified carbon supports
  - Optimum CMO/carbon support ratio for maximum activity/durability
  - Non-carbon supports - CMOs, nitrides, carbides
- DFT modeling to predict Pt-CMO-carbon support interaction

Relevance

- Overall objective: develop stable support with 2X stability over conventional carbon supports with equivalent performance
  - Novel carbon supports
  - Conductive oxide mediated carbon supports
  - Non-carbon support
- The barriers addressed are poor durability of cathode catalyst supports and cathode performance
- Novel supports developed in this project show higher durability than XC72
- Metal oxide modified graphene show significantly higher durability and activity compared to XC72 – stability results predicted by DFT model
- Lessons learned from graphene model system can be easily transferred to other carbon supports
- Non-carbon supports show lower activity, but higher durability than XC72
  - Improving performance trend for non-carbon support has been demonstrated
- Pathway has been established towards carbon-free supports and supports with less emphasis on carbon

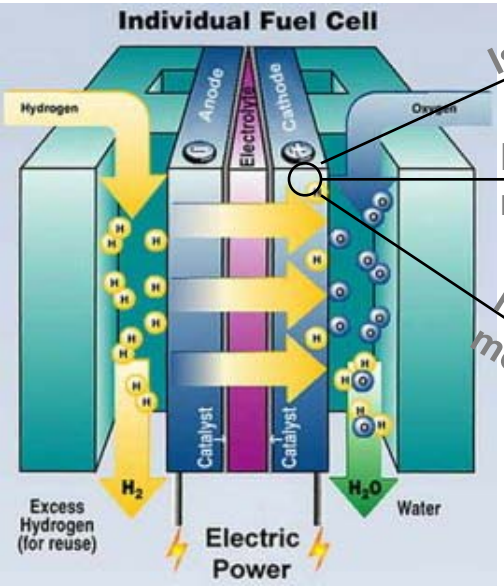
Major Accomplishments

- Demonstrated 2X durability for Pt/GMC over baseline Vulcan carbon (VC or XC72) at equivalent activity
- Demonstrated 3X durability for CNT over baseline Vulcan carbon at 80% of baseline activity (in-situ test)
- Demonstrated improved activity (1.5X) and durability (1.7X) over baseline for ITO/graphene support .
  - Obtained optimum ITO content in ITO/graphene to maximize activity and stability
- Demonstrated 50% of baseline activity and 3X baseline durability for non-carbon support (Pt/ITO)
  - Doubled activity with modified synthesis approach, and established pathway for further increasing activity
  - Established pathway for non-carbon supports and CMO mediated carbon supports

Approach - Overall

- Develop and evaluate new classes of alternative and durable cathode supports using graphitized carbons as scaffolds and protect carbon surface with
  - Tungsten carbide (WC)
  - Conductive metal oxides (ITO)
  - SnO_2
  - TiO_2
  - Nitrides
- Develop non-carbon supports using conductive metal oxides, carbides and nitrides
- Enhance Pt dispersion and stability on these new classes of cathode supports

Development of Alternative and Durable High Performance Cathode Supports for PEM Fuel Cells



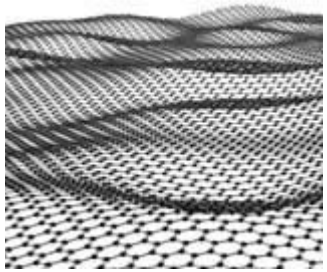
Issues

poor durability at high pH, high potential

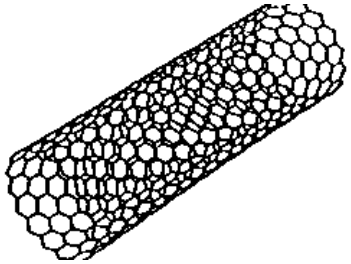
New carbon materials

With and w/o metal oxide modification

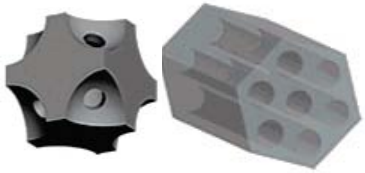
Graphene

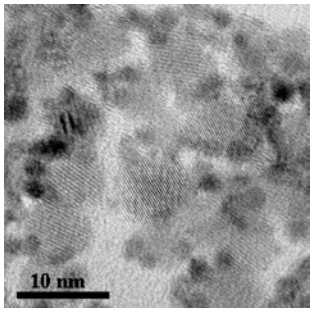


CNT

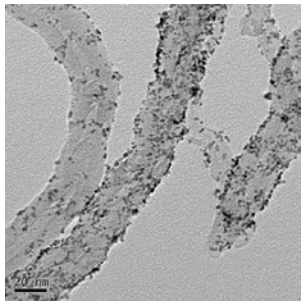


Mesoporous carbon

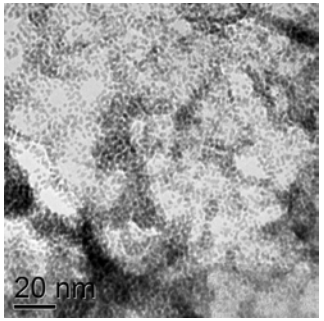




Pt on ITO modified graphene



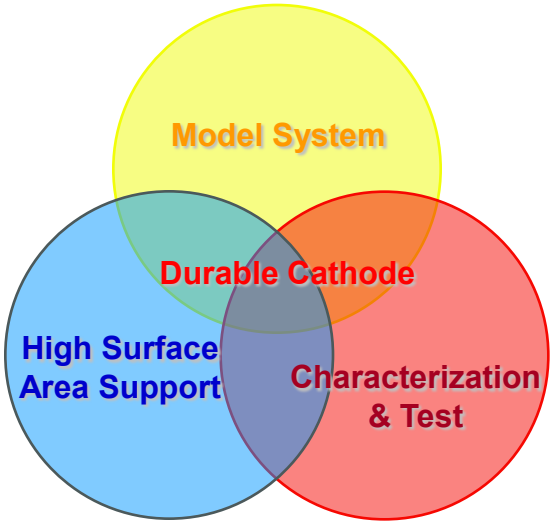
Pt on CNT



Pt on graphitized mesoporous carbon (GMC)

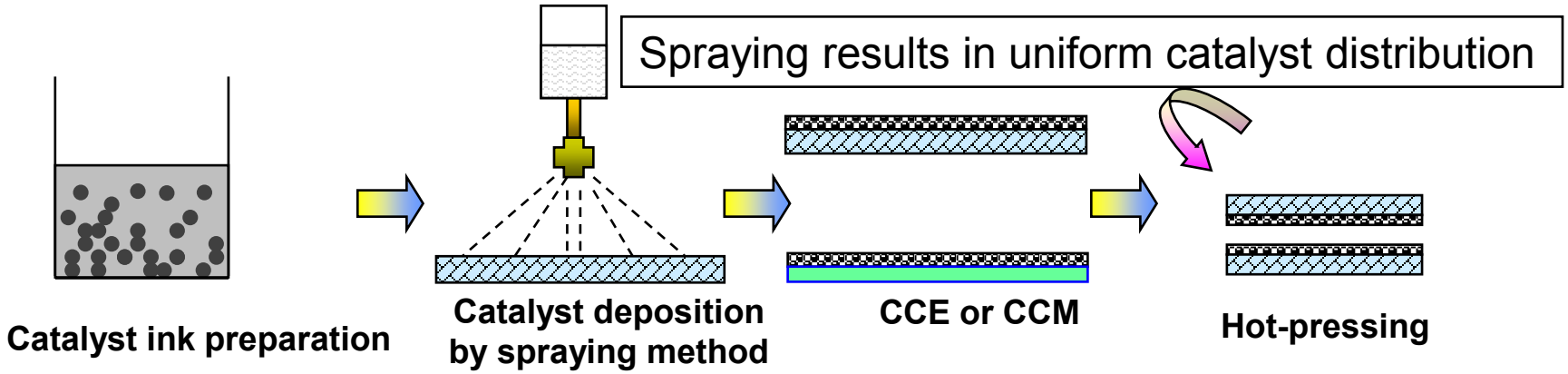
Approach – Specific Tasks

- Fundamental understanding of model systems with well defined structures and compositions to guide the design of advanced and durable cathode materials.
- Synthesis of high surface area cathode supports with improved durability using carbon scaffolds.
- Characterization and electrochemical evaluation of improved cathode supports.



Electrochemical Test - Fast Screening with RDE

- Rotating disc electrode (RDE) test protocol
  - Potential step between 0.85V (30 sec) to 1.4V (150 sec) Vs. NHE
  - Test for 44hrs
  - Cyclic voltammograms and ORR curves
  - Comparison of the catalyst
    - Original ESA and ORR activity @0.9V
    - The percentage of the remaining ESA and ORR activity @0.9V
- MEA test protocol (old within brackets)
  - Hold fuel cell for 20h at 1.2V using H_2/N_2 at 7.4 psig (0 psig), 80°C, 100% RH for 20 hours
  - Flow H_2/air (H2/O2) stoichiometry 3/3 (1.2/2) 7.4 psig (0 psig) 80°C, 100% RH for polarization curves and activity at 0.9V

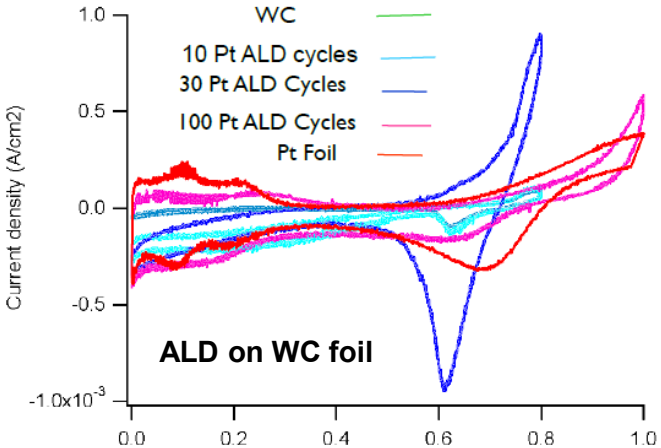


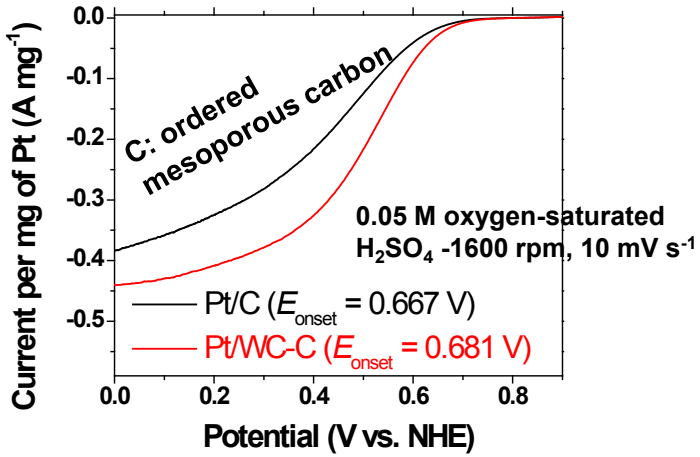
Y Shao, R Kou, J Wang, VV Viswanathan, JH Kwak, J Liu, Y Wang, and Y Lin., Journal of Power Sources 185(1):280-286, 2008
Y Shao, R Kou, J Wang, JH Kwak, VV Viswanathan, Y Wang, J Liu, and Y Lin., In Proton Exchange Membrane Fuel Cells 8. ECS Transactions, vol. 16, no. 2, ed. T. Fuller, et al, pp. 361-366. The Electrochemical Society, 2008.

Technical Accomplishment:

ORR Activity Estimation Based on Oxygen Binding Energy and Consistency with Experimental Results

Surface	O Binding E (kcal/mol)
Pt(111)	-39
Pt-Ni-Pt(111)	-19
Ni-Pt-Pt(111)	-118
Pt-WC(0001)	-24
W-Pt-WC(0001)	-202
Pt-CWC(0001)	-74
W-Pt-CWC(0001)	-156
VC(111)	-193
Pt-VC(111)	-15
V-Pt-VC(111)	-237



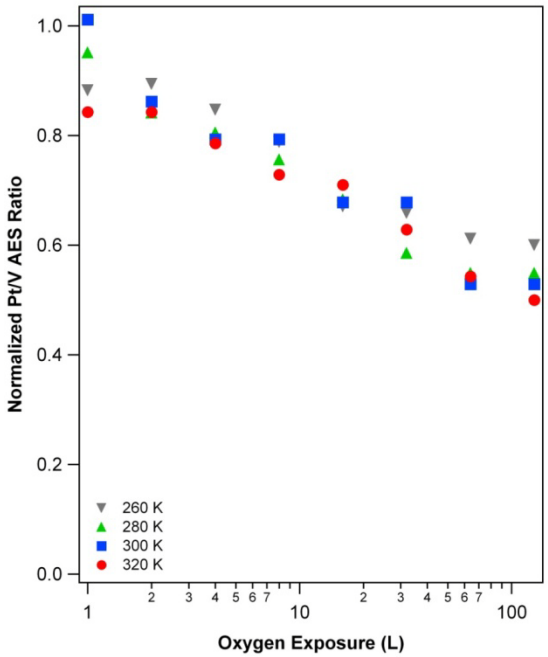


- Based on values of oxygen binding energy, the Pt-WC(0001) and Pt-VC(111) should have comparable ORR activity as the Pt-Ni-Pt(111) (Pt-skin) catalyst
- Pt-WC shown to have higher activity than Pt with and without carbon support

Technical Accomplishment:
Stability Estimation in Oxygen Environment and Consistency with Measured Results

Alloy	ΔE_{Vacuum} (kcal/mol)	$\Delta E_{0.5\ ML\ O}$ (kcal/mol)
Pt-Ni-Pt(111)	13	-12
Pt-Ni-CWC(0001)	25	6
Pt-Ni-WC(0001)	4	-18
Pt-WC(0001)	64	20
Pt-CWC(0001)	46	25
Pt-V(110)	20	-36
Pt-VC(111)	86	30
Pt-VN(111)	N/A	
Pt-VP(0001)	34	
Pt-VB2(0001)	70	

AES: Pt/V(110) exposed to 3000L O_2 at 300ºK

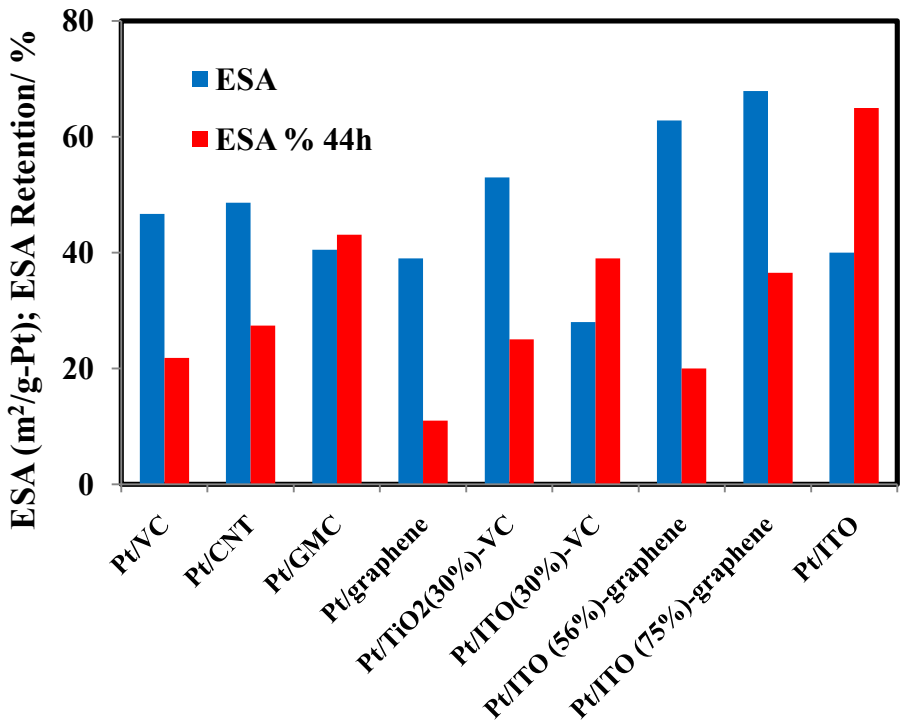


- Decrease of Pt/V ratio indicates oxygen is pulling V to the surface concomitant with a large oxygen uptake
- Much smaller decrease found for Pt/VC

- Positive value of $\Delta E_{0.5\ ML\ O}$ indicates that the surface structure is stable in the presence of oxygen. Both Pt-WC(0001) and Pt-VC(111) should have higher stability than the Pt-Ni-Pt(111) (Pt-skin) catalyst
- Predicted higher stability of Pt-VC verified by AES

Technical Accomplishment:
Lead Supported Catalysts Identified by RDE

RDE: Potential step between 0.85V (30 sec) to 1.4V (150 sec) vs. NHE



- Pt/GMC has higher performance and durability than baseline Pt/VC
- Pt/CNT has higher durability than baseline
- ITO modified VC and graphene improves durability
- ITO addition improves activity for graphene based support by 2-3X over Pt/graphene
- Non-carbon support provides 3X durability over baseline at equivalent ESA and 50% activity
- Selected Pt/GMC, Pt/CNT, Pt/graphene Pt/ITO/graphene and Pt/ITO for in-situ MEA testing

Accomplishments

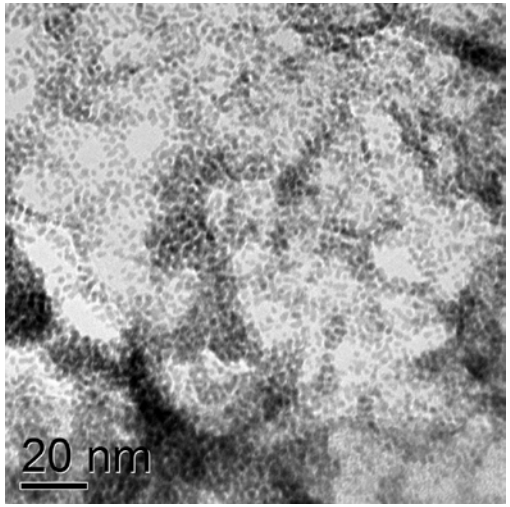
- Demonstrated 2X durability improvement over baseline using novel carbon supports, conductive metal oxide mediated supports, and non-carbon supports

Future Work

- Optimize CMO properties to improve activity for non-carbon support

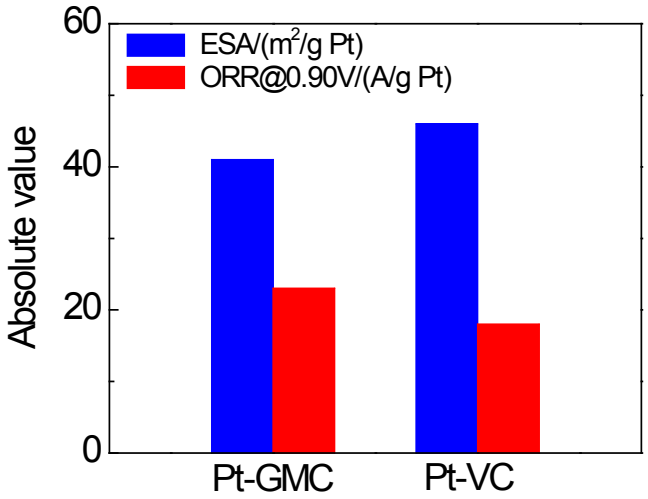
Technical Accomplishment:
Pt on Graphitized Mesoporous Carbon (GMC) RDE

Pt on GMC

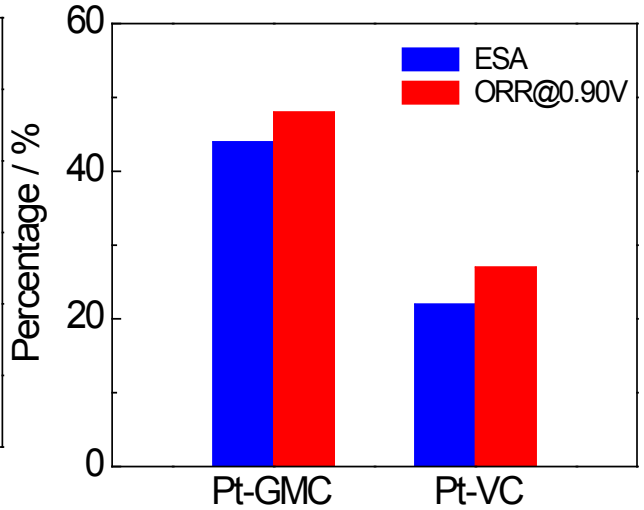


RDE: Potential step between 0.85V (30 sec) to 1.4V (150 sec) vs. NHE

Initial activity



Durability 44h



Accomplishments

- **Obtained durability 2X of Pt/XC-72, with equivalent activity**
- **Improvements are likely due to better stability of graphitized mesoporous carbon (GMC), stronger Pt-GMC interaction.**

Future Work

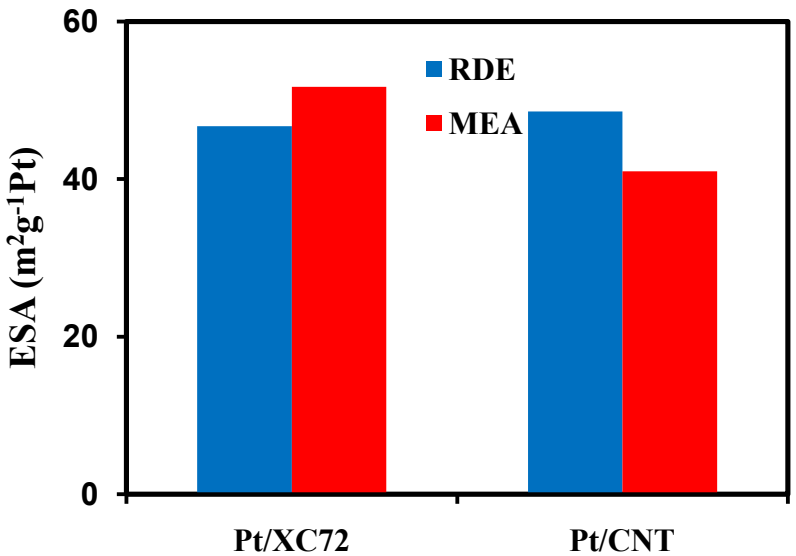
- Perform MEA tests

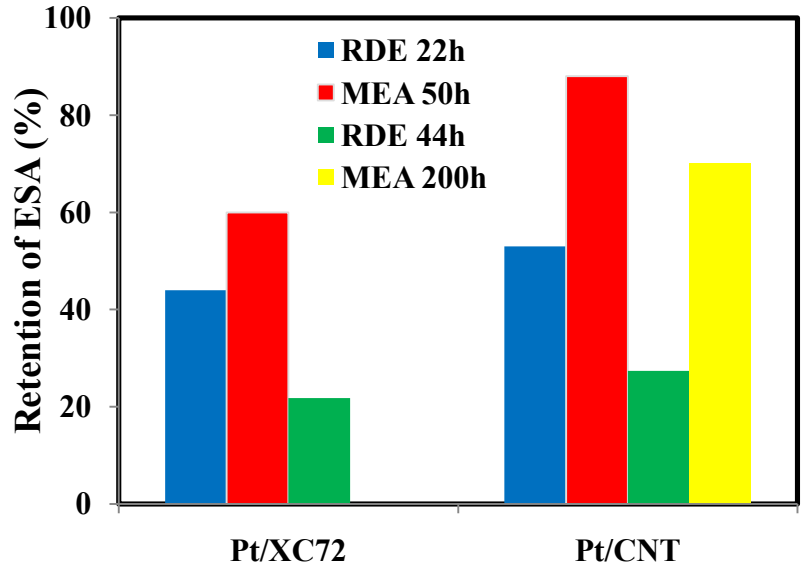
Y Shao, S Zhang, R Kou, X Wang, C Wang, S Dai, V Viswanathan, J Liu, Y Wang, Y Lin, submitted

P. V.Shanahan, L.B. Xu, C.D. Liang, M. Waje, S.Dai, Y.S.Yan, J. Power Sources 2008, 185, 423-427

Technical Accomplishment:
Pt on Carbon Nanotubes (CNT)

RDE: Potential step between 0.85V (30 sec) to 1.4V (150 sec) vs. NHE
MEA: Hold fuel cell for 20h at 1.2V using H_2/N_2 at 7.4 psig, 80°C, 100% RH





- Durability of Pt/CNT 25% higher than baseline for RDE and 50% over baseline for MEA after 50 hours
- Pt/CNT durability for MEA after 200 hours 12% higher than baseline after 50 hours

Accomplishments

- Pt/CNT durability > 2X of baseline with equivalent ESA

Future Work

- Optimize MEA ink formulation for better performance
- Modify CNT with conductive metal oxide

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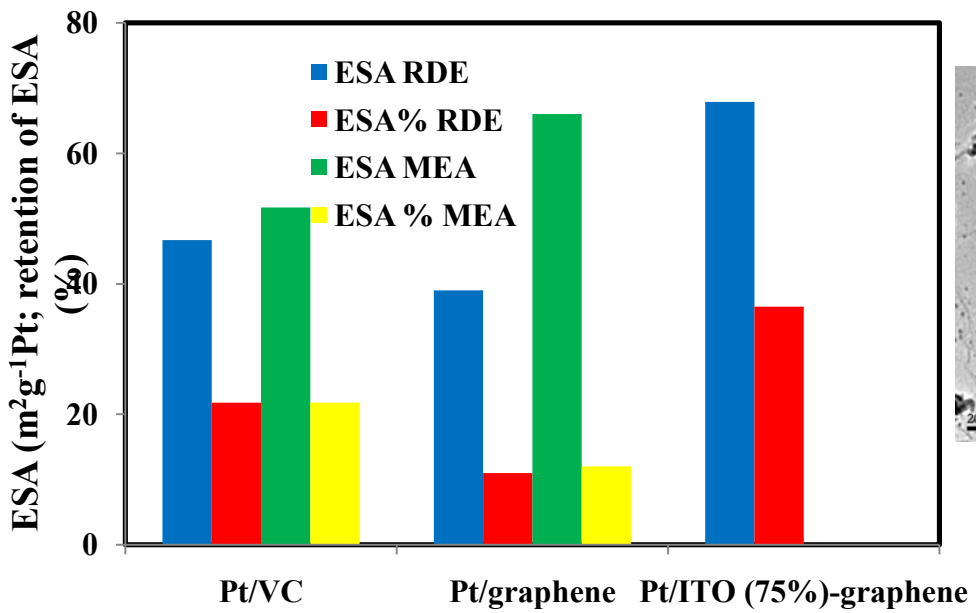
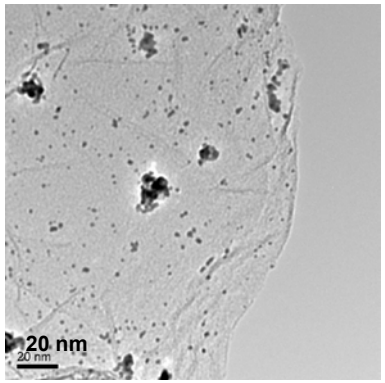
Technical Accomplishment:
Pt on Graphene with and without CMO Modification

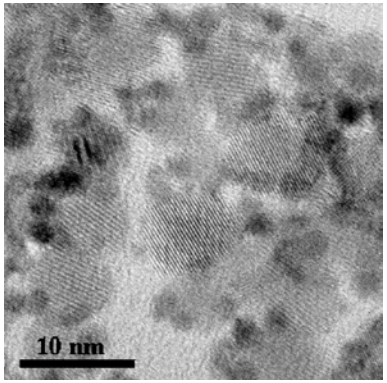
RDE: Potential step between 0.85V (30 sec) to 1.4V (150 sec) vs. NHE
MEA: Hold fuel cell for 20h at 1.2V using H_2/N_2 at 7.4 psig, 80°C, 100% RH



Pt/graphene



Pt/ITO/graphene



Pt agglomerates without ITO
ITO helps to disperse Pt nanoparticles

- Graphene is the building block of all graphitic materials, with potential for low cost production
- Poor durability for Pt/graphene
- Activity nearly doubled and durability increased 3-fold over Pt/graphene with ITO modified graphene for RDE

Accomplishments

- Increased activity and durability of ITO modified graphene by 50% and 65% over baseline

Future Work

- MEA testing in progress

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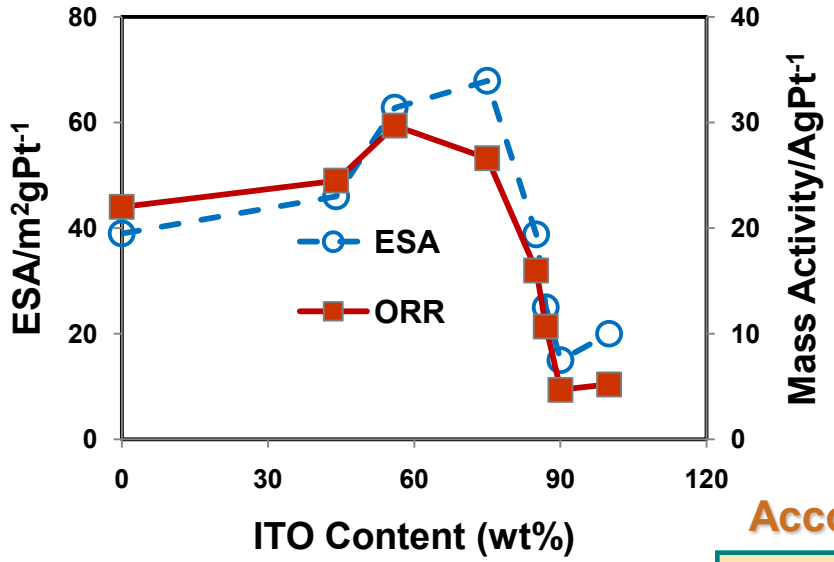
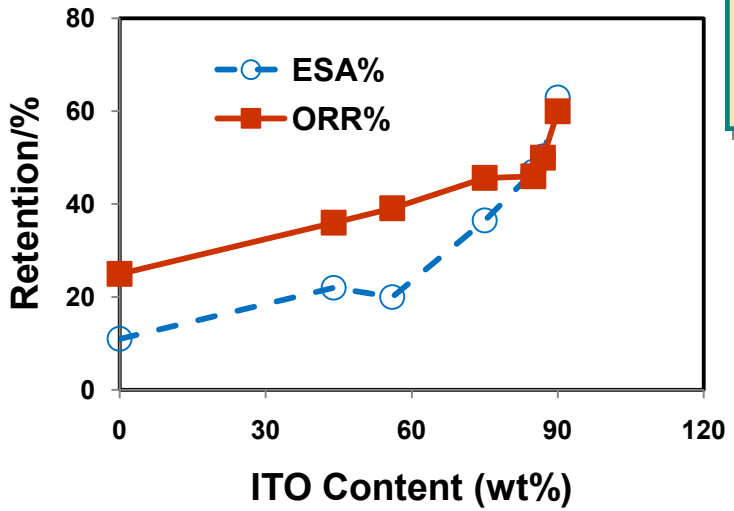
Technical Accomplishment:
Optimization of ITO Content in Graphene

RDE: Potential step between 0.85V (30 sec) to 1.4V (150 sec) vs. NHE



- Investigated effect of ITO content on activity and durability of supported catalyst
- Determined optimum ITO/graphene ratio for maximum activity and durability
- Activity (ESA and ORR) goes through maximum at 60-75% ITO content (1.5X Pt/graphene)
- Durability increases with ITO content, and tops off at 2.5X graphene (and 2X Vulcan carbon)
- Data supported by findings of DFT model



Accomplishments

- Established pathway to improve activity and durability of graphene supported catalyst by optimizing CMO content
- Concept can be applied across variety of carbon supports

Future Work

- Optimize MEA formulation to demonstrate this effect in a fuel cell
- Transfer lessons learned from ITO/graphene model system to other carbon supports to surpass DOE targets for activity and stability

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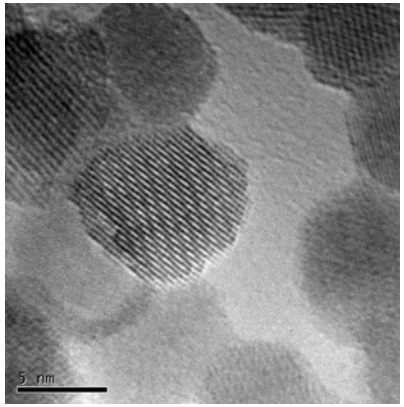
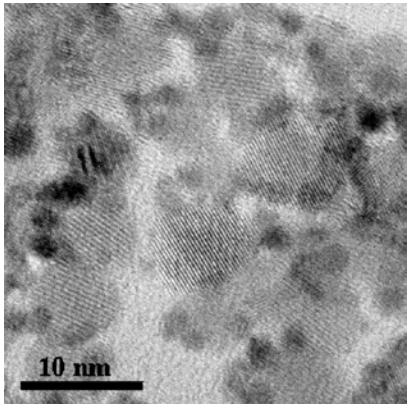
Technical Accomplishment:
Model Pt-ITO-graphene System

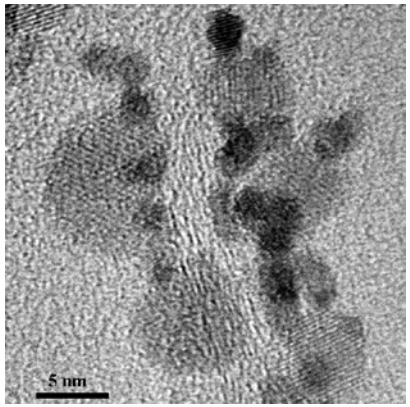
ITO nanoparticles on graphene

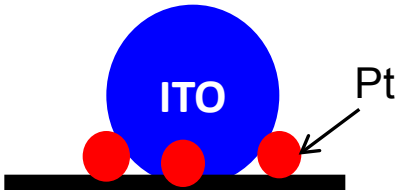


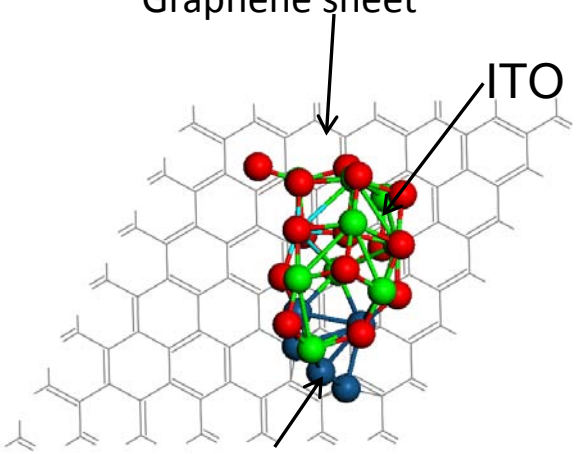
Pt loaded on ITO/graphene



Cross section of Pt/ITO/graphene







- ITO nanoparticles 10-15 nm
- Pt appears to be deposited at interface of ITO/graphene
- Schematic shows Pt location on ITO/graphene
- DFT model shows Pt located in ITO/graphene interface
- Good correlation between TEM and DFT model

Accomplishments

- Model predicts stable Pt/ITO/graphene configuration
- Obtained consistency with better stability for Pt/ITO/graphene from RDE results

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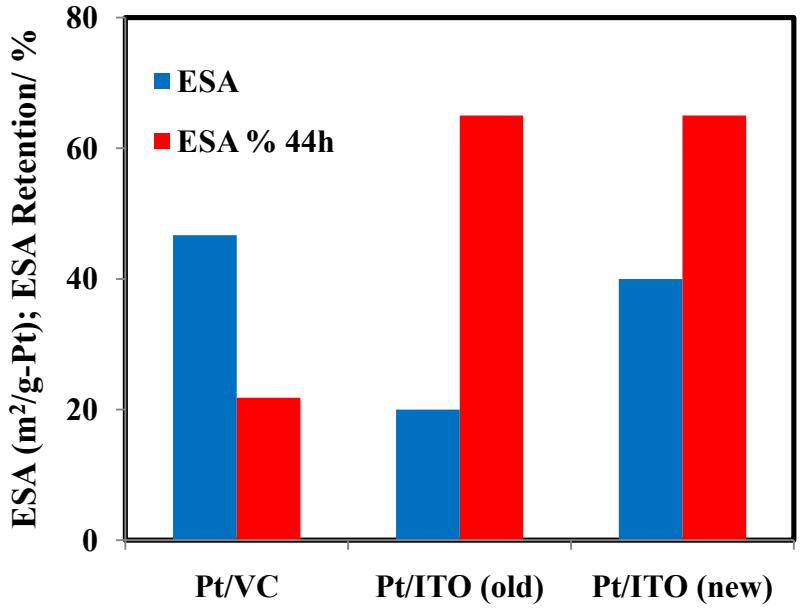
Technical accomplishments:

Non-carbon Support - ITO

RDE: Potential step between 0.85V (30 sec) to 1.4V (150 sec) vs. NHE



- Significant improvement in activity and ESA obtained by optimizing synthesis for Pt/ITO (ORR activity is 50% of Pt/XC72)
- Room for improvement in activity by increasing ITO conductivity and improving Pt dispersion

Accomplishments

- Obtained 3X improvement in durability for Pt/ITO over baseline
- Doubled ESA and activity by modification of Pt/ITO synthesis

Future Work

- Increase performance by improving Pt dispersion on ITO and increasing ITO conductivity

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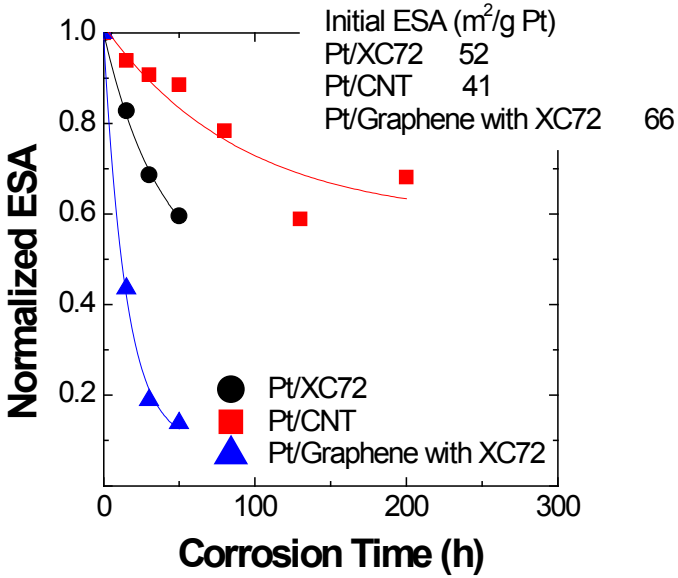
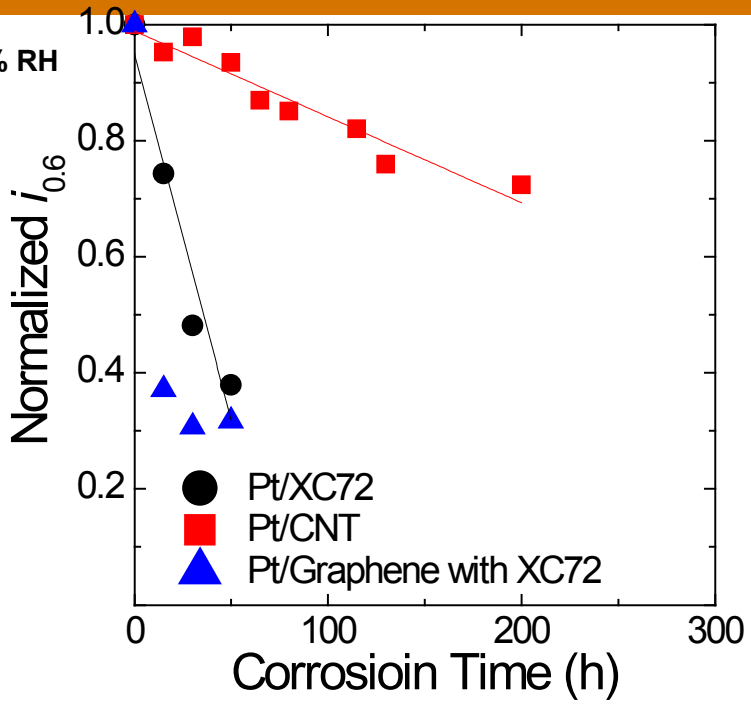
Technical Accomplishment:
Comparison of activity and durability for MEAs

Hold fuel cell for 20h at 1.2V using H_2/N_2 at 7.4 psig, 80°C, 100% RH





- Activity (not shown) and ECSA for Pt/XC72, Pt/CNT and Pt/graphene nearly equivalent
- CNT supported catalyst after 200h more durable than XC72 supported catalyst after 50h
- ESA for Pt/graphene degrades faster than baseline, but stability at 0.6V equivalent to baseline
- Charge transfer resistance (not shown) increased rapidly for Pt/graphene
- Durability for Pt/graphene is poorer than Pt/XC72

Accomplishments

- Demonstrated > 2X durability for Pt/CNT over baseline
- Showed similar trend for Pt/graphene as RDE results

Future Work

- Optimize MEA ink formulation for Pt/CNT and Pt/graphene/ITO
- Perform MEA durability test on ITO modified graphene using optimum ITO content determined from RDE

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Technical Accomplishments and Future Work

Accomplishments

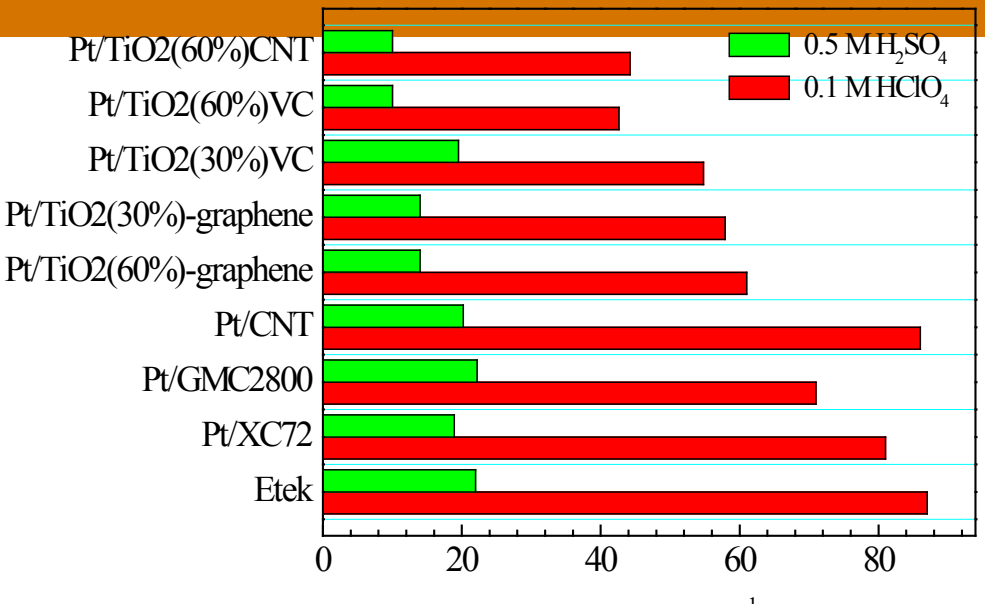
- Optimum ITO content in graphene found to maximize activity and durability
  - Activity and durability are 1.5X and 1.7X of baseline
  - Pt distributed uniformly at ITO/graphene interface as predicted by DFT model
- Demonstrated Pt/CNT stability of >2X over Pt/XC72
- Demonstrated 2X activity and durability of Pt/GMC over Pt/XC72
- Demonstrated 3X durability of Pt/ITO non-carbon support over baseline
- Obtained consistency between RDE and MEA test results
- Obtained promising preliminary results for other non-carbon supports such as WC, W2N

Future Work

- Optimize ITO properties to further improve performance for Pt/ITO/graphene and Pt/ITO
- Improve Pt dispersion on ITO
- Perform MEA tests for ITO modified graphene supports and Pt/GMC
- Demonstrate >2X stability over XC72 support by modifying CNT, GMC and graphene with CMO, WC and W_2N identified in this work, using lessons learned from the ITO/graphene system.

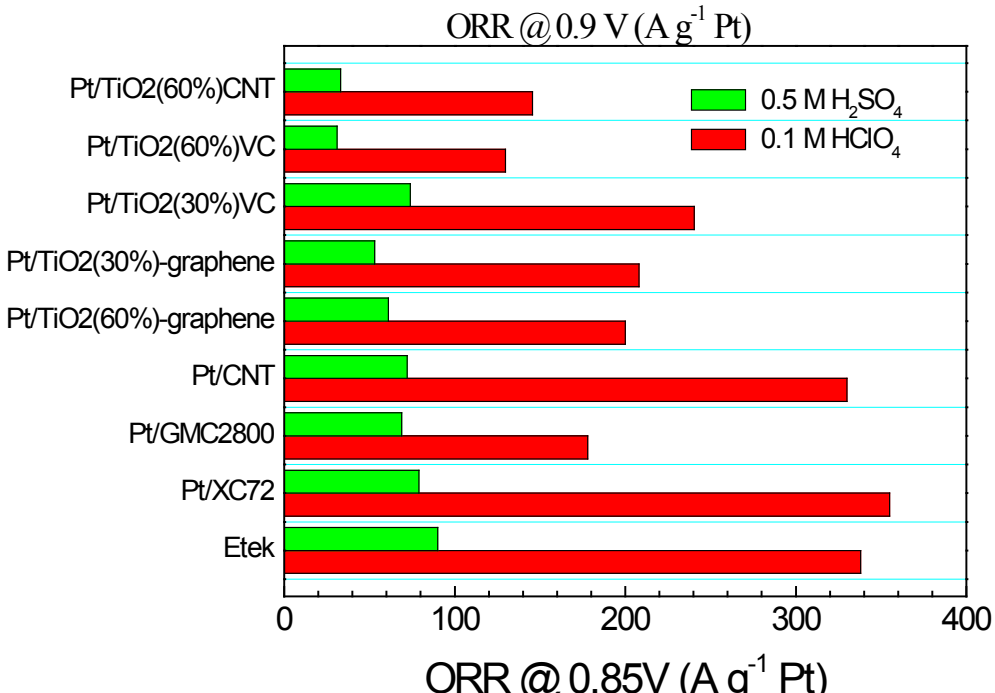
Supplemental Slides

Effect of Electrolyte on Mass Activity for RDE



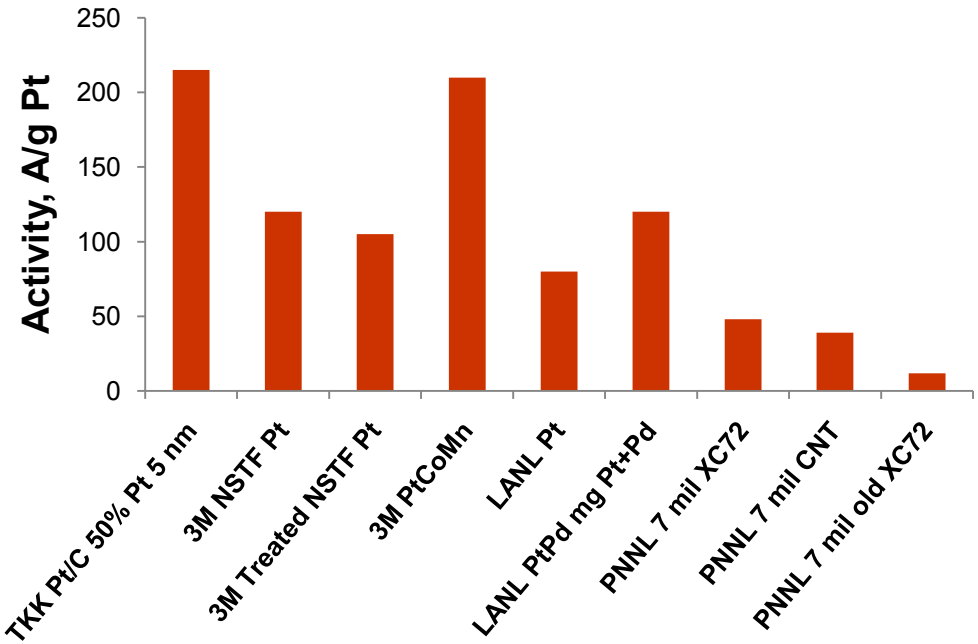
0.1 M HClO4: 5 mV/s, 1600 rpm
0.5 M H2SO4: 10 mV/s, 1600 rpm

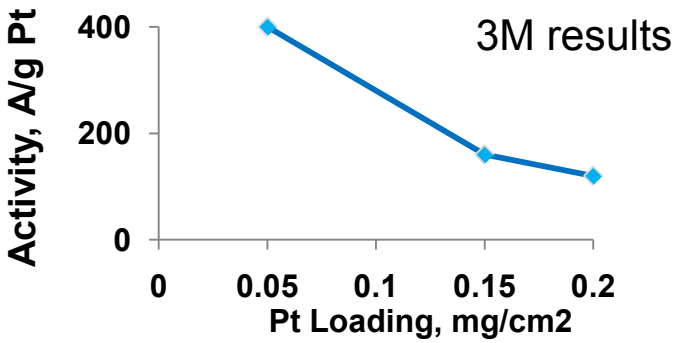
Ratio of activity in 0.5MH2SO4/ activity in 0.1M *HClO4* ~ 4



- Determined activity for select electrodes in 0.1M *HClO4*
- Activity of 85 A/g at 0.9V and 350 A/g at 0.85V in line with literature values

MEA Activity and comparison with literature





Activity increases with decrease in loading

- Compared MEA activity with literature values
- Activity within a factor of 1.5-2 of literature values
- Higher Pt loading (0.2 mg Pt/cm^2) probable cause for lower activity

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Summary of Samples and Support Modifications

Modification \ Support	Vulcan X72	CNT	Meso-porous carbon	Graphene	Carbon-free
none	● ▲	● ▲	● ▲	● ▲	
TiO_2	● ▲	●		● ▲	
SnO_2	● ▲				
ITO	● ▲			● △	○ △
WC			●		

● RDE test complete
▲ MEA test complete
○ RDE test in-progress
△ MEA test in-progress
▲ MEA test planned

RDE test: **initial screening for activity and stability**
MEA test: **detailed durability testing**

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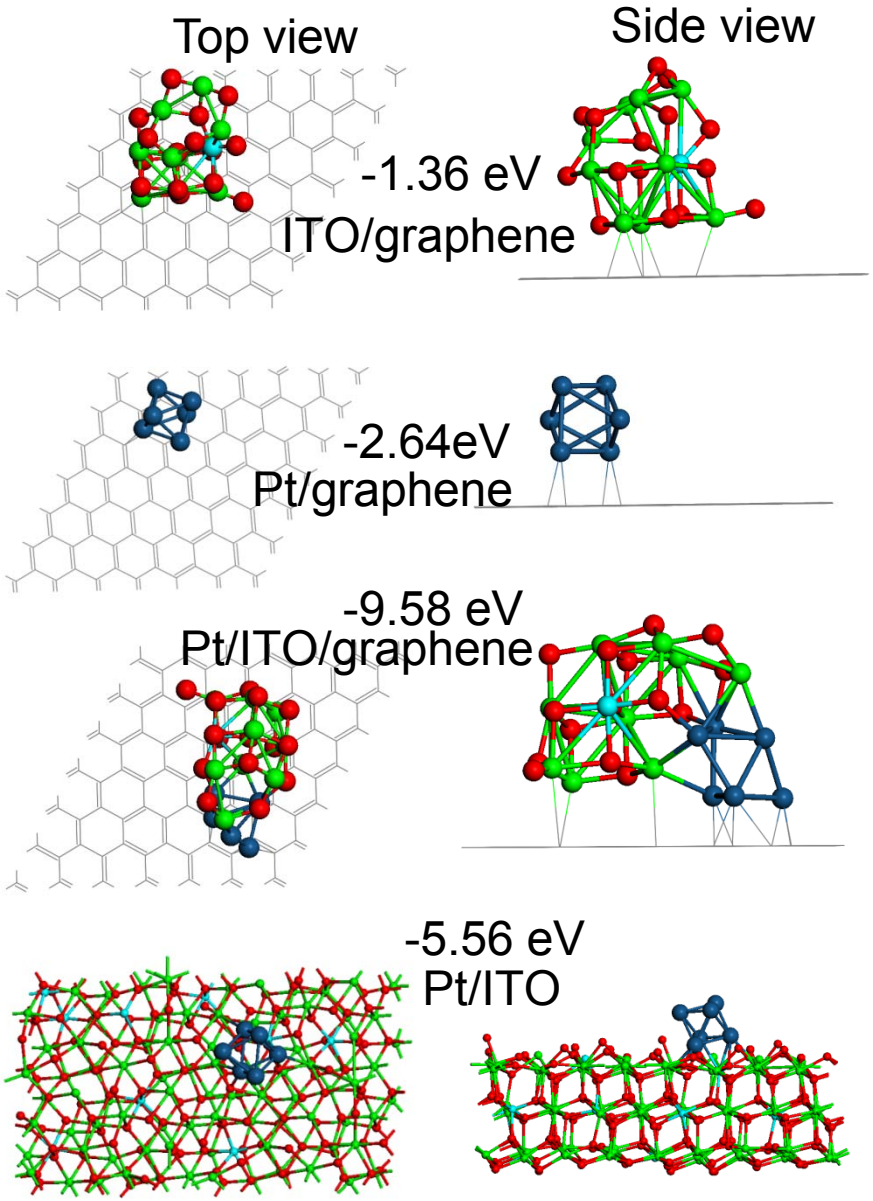
Technical Accomplishment:
DFT calculations to compute stability of Pt-ITO-graphene



- Graphene substrate modeled as single sheet
- ITO described on basis of bixbyite structure of In_2O_3

$$E_{\text{int}} = E_{cluster+substrate} - \left(E_{cluster} + E_{substrate}\right)$$

- Pronounced enhancement of Pt_6-graphene found when Pt_6 cluster also binds with ITO cluster
- The interaction energy of Pt-ITO cluster on graphene much stronger than total interaction energy when each binds to graphene separately
- When ITO content too low, there could be some Pt just bound to graphene
- When ITO content too high, there may not be enough exposed graphene. Pt bound to ITO without contact to graphene. This has high stability, but activity expected to be low due to poor ITO conductivity – verified by data

- Predicts stable Pt/ITO/graphene configuration

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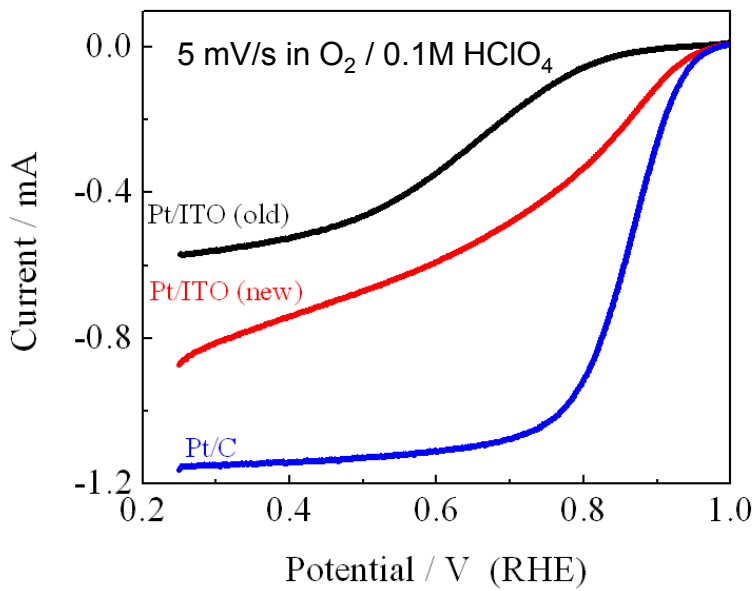
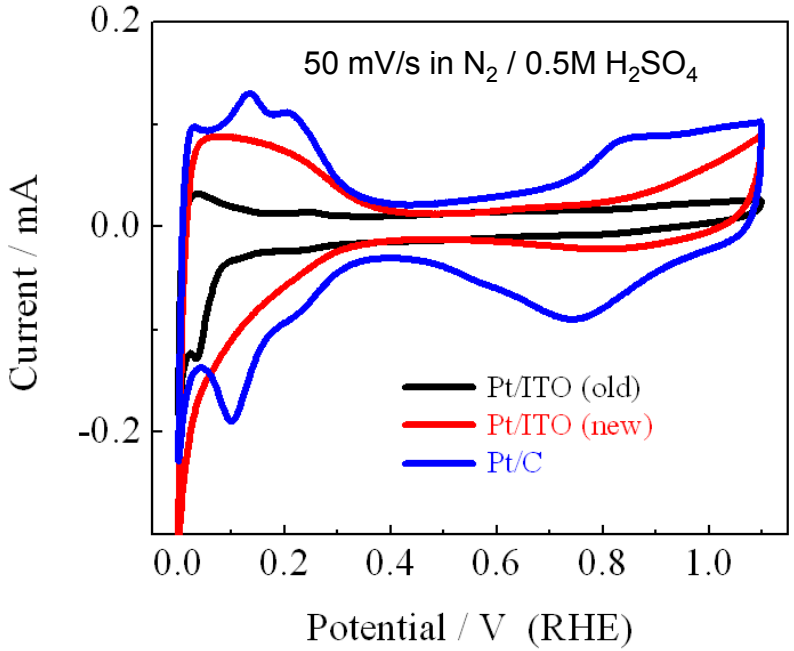
Activity and ESA improvement for Non-carbon ITO support

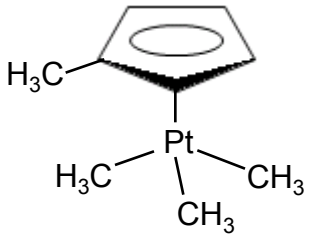




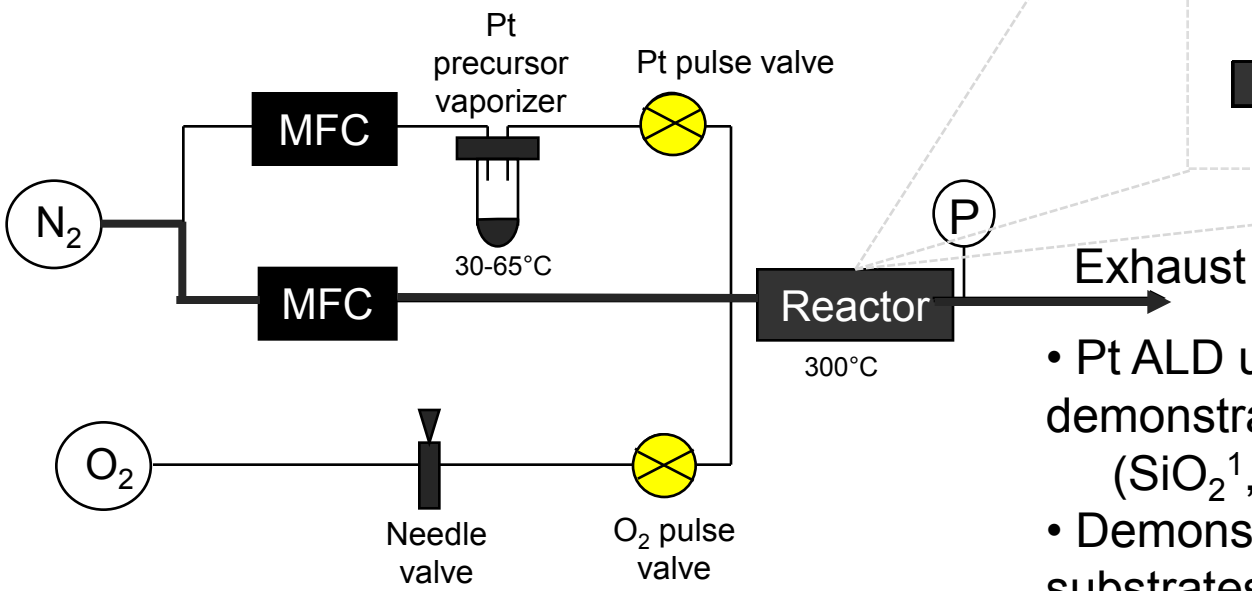
Significant improvement in activity and ESA obtained by optimizing synthesis for Pt/ITO (ORR activity much lower than for Pt/XC72)

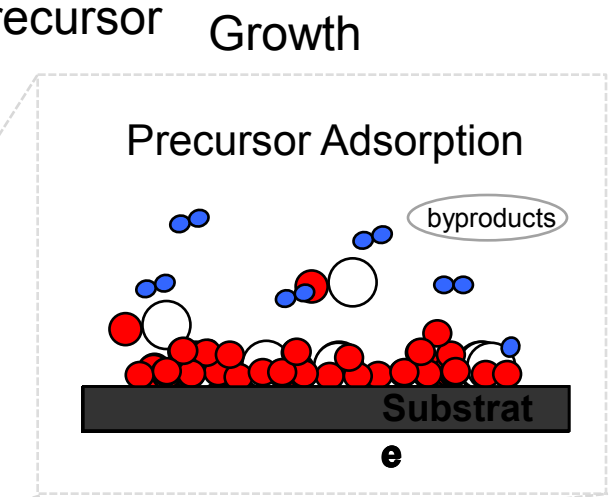
Pt ALD – Reactor

Precursor: $MeCpPtMe_3$



- Very commonly used Pt precursor (heavily studied)
- Thermally stable
- High vapor pressure
- Sensitive in air





- Pt ALD using this precursor mostly demonstrated on oxide surfaces (SiO_2[1], Al_2O_3[1], TiO_2[2], $SrTiO_3$[3]).
- Demonstrated on carbon substrates; higher temperature and longer pulse times usually required.[4]

[1]T. Aaltonen, M. Ritala, *et. al.* Chem. Mater., **2003**, 15 (9), 1924-1928. [2]S. Takakusagi, K. Fukui, *et al.* Phys. Rev. Lett. , **2003**, 91 (6), 066102.
[3]S. Christensen, J. Slam, *et al.* Chem. Mater., **2009**, 21 (3), 516-521. [4]J. King, A. Wittstock, *et al.* Nano Lett., **2008**, 8 (8), 2405-2409.

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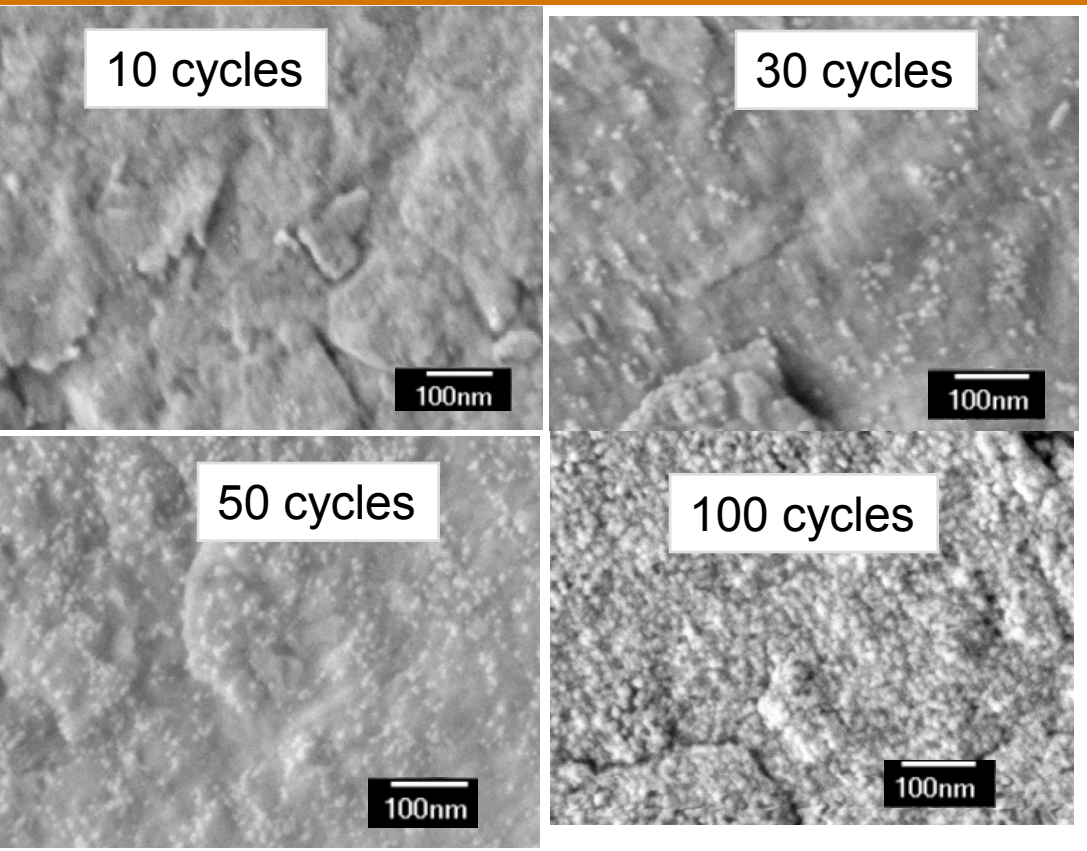
Technical Accomplishment:
ALD Pt on WC – Characterization (non-carbon support)



- Explore the use of ALD to make Pt-WC catalysts.
  - Pt reduction necessary for commercial viability.
  - WC has shown Pt-like activity for some reactions.
  - Synergistic effects between Pt and WC have been observed.

- $MeCpPtMe_3$ precursor
- Non-linear Pt growth due to slow nucleation
- Existing Pt provides sites for precursor absorption
- Pt particle size measured to be ~10 nm.

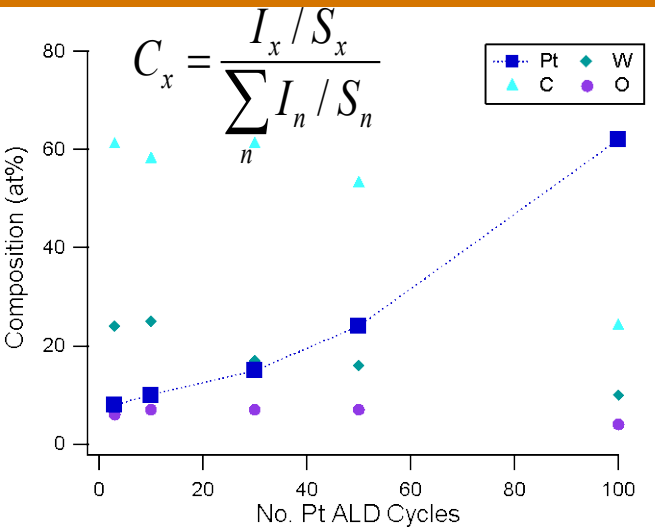
Accomplishments

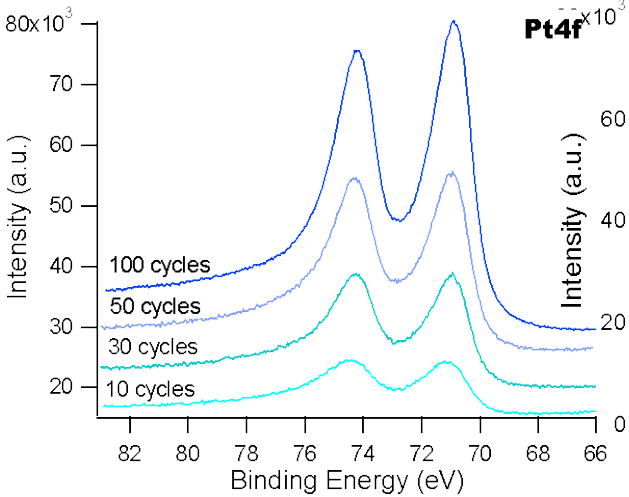
- Demonstrated Pt ALD on WC substrates

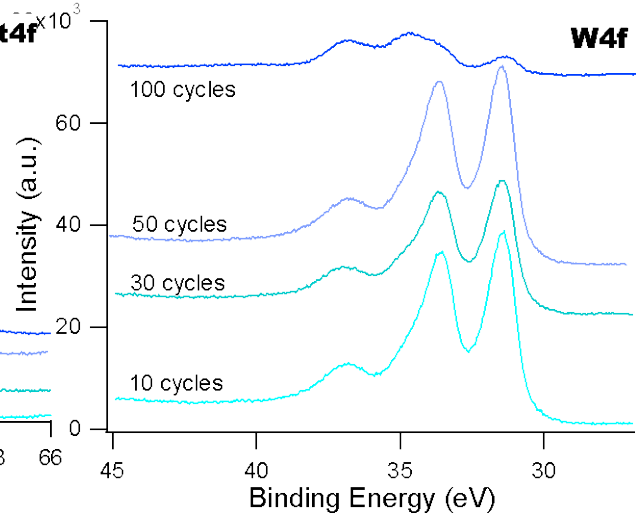
Future Work

- Functionalize WC surface with oxygenated species to better adsorb Pt precursor
- Vary deposition temperature

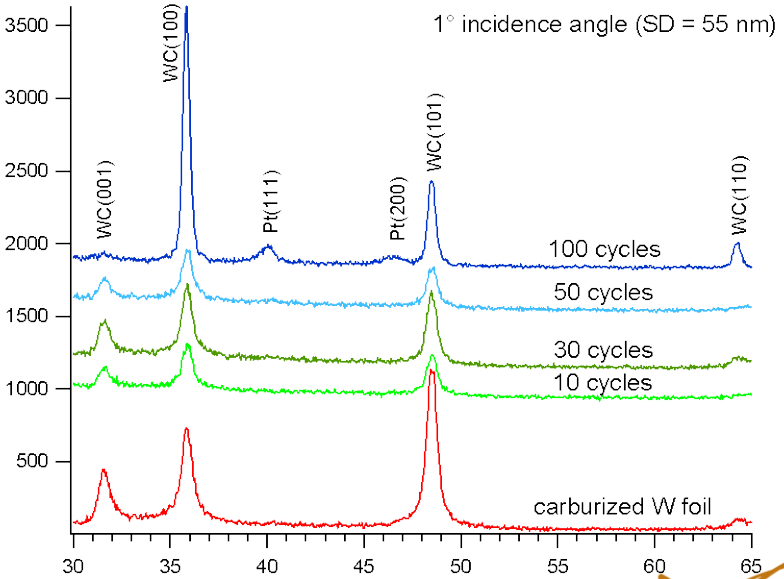
ALD Pt on WC – Characterization







- Non-linear Pt growth due to slow nucleation
- Existing Pt provides sites for precursor adsorption
- WC surface may be getting oxidized, providing nucleation sites for Pt as ALD progresses
- XPS (10 nm sampling depth) shows Pt peaks for all cycles, but Pt peaks present only for 100 cycles in XRD (55 nm sampling depth)



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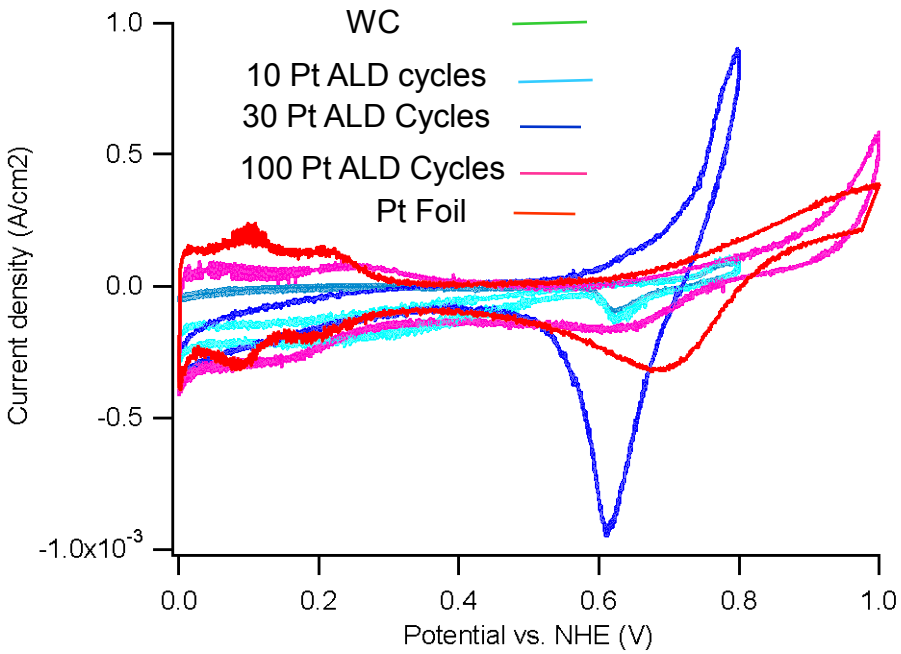
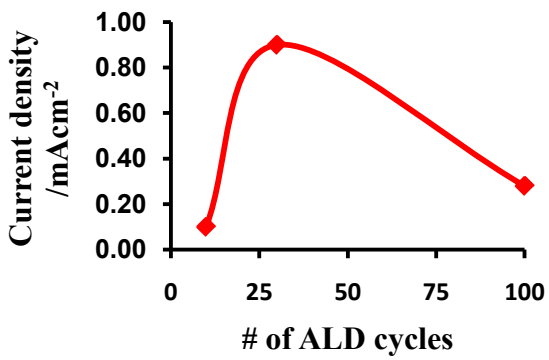
Non-carbon support: ALD Pt-WC oxygen reduction current

50 mV/s in O_2-saturated 0.5 M H_2SO_4





- Determined activity for Pt-WLC synthesized by ALD with various Pt contents
- WC not very active for ORR
- Small amounts of Pt has poor ORR activity
- Very large amounts of Pt on WC – CV looks more Pt-like, but ORR activity is small.
- 30-cycle sample more active than Pt
- There appears to be an optimum Pt content for which activity is maximized

Accomplishments

- **CV show promising ORR activity for 30-cycle ALD sample**

Future Work

- **Perform RDE studies**
- **Synthesize supported catalysts using ALD**

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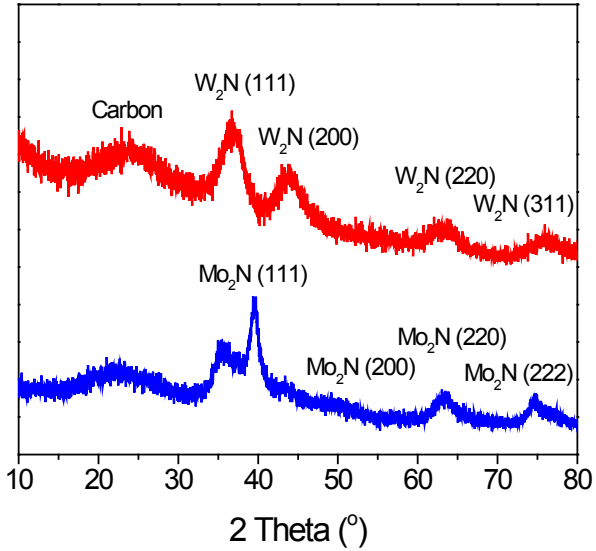
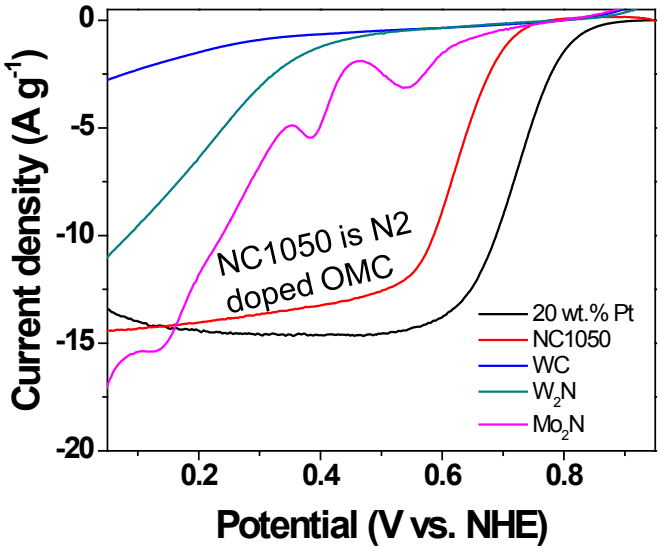
Technical Accomplishment:
Non-carbon support :WC and W_2N oxygen reduction current





0.05 M oxygen-saturated H_2SO_4 -1600 rpm, 10 mV s^{-1}.

- Develop alternate non-carbon nitride supports for Pt catalyst
- Determine if these supports are active towards ORR

Accomplishments

- XRD confirmed the formation of W_2N and Mo_2N
- ORR tests showed that W_2N and Mo_2N exhibit a higher ORR activity than WC

Future Work

- Incorporate Pt on W_2N
- Determine activity and durability of Pt/W_2N
- Synthesize W_2N/OMC with and without nitrogen doping of OMC, incorporate Pt and determine activity and durability

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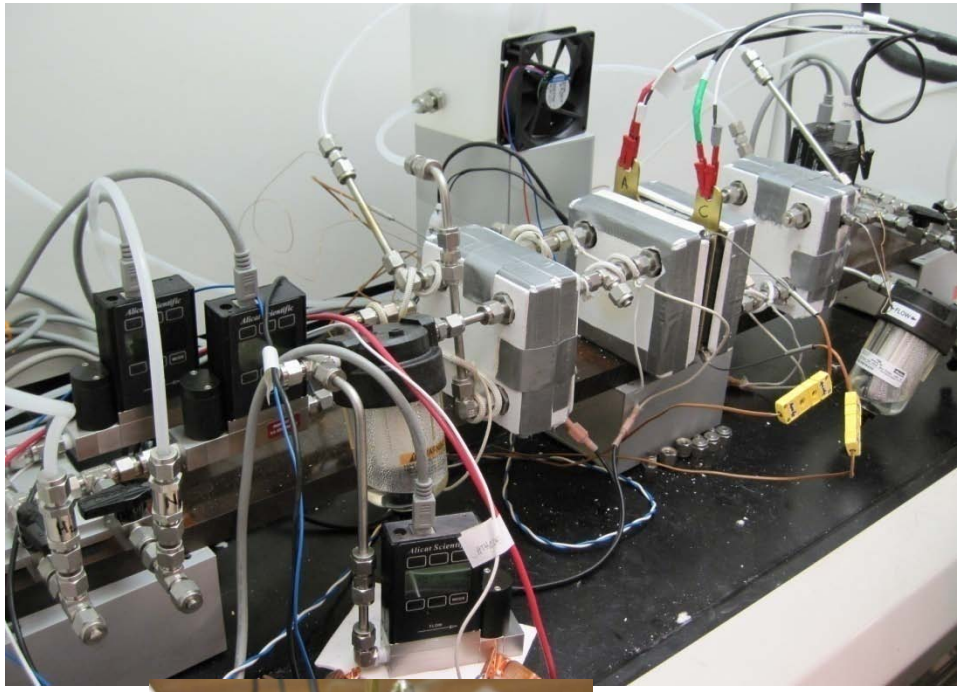
In-house built fuel cell test station



Cell & Heat Exchangers

- Mass controlled flow of gases into system
  - Automatic or manual control of gas flow
  - Automatic flow based on selected stoichiometry of cell current
- Back Pressure control up to at least 25 PSI
- Programmable scanning of potential or current
- Programmable PID control of temperature for humidifiers, cell and gas lines
- Data Logging of potential, current, power, gas flow, backpressure and temperature

Test stand design, assemblyand shake-down testing by Peter Rieke And Silas Towne

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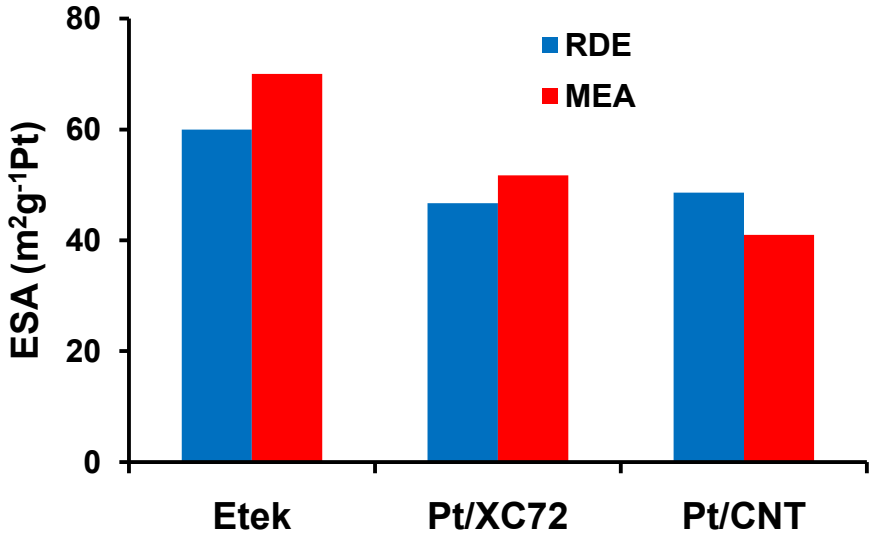
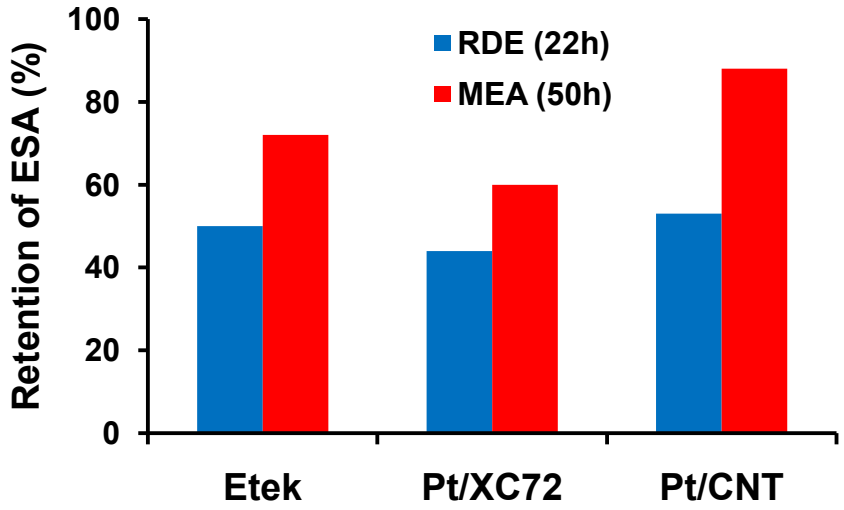
Technical Accomplishment
Comparison of RDE and MEA performance & durability

RDE: Potential step between 0.85V (30 sec) to 1.4V (150 sec) vs. NHE
Hold fuel cell for 20h at 1.2V using H_2/N_2 at 7.4 psig, 80°C, 100% RH





- Determine consistency between RDE and MEA results

Accomplishments

- Consistent results obtained for Etek, XC72 and CNT
- 200h test done for CNT. The retention of ECSA was 68%

Future Work

- Improve MEA formulation for non-vulcan carbon supports
- Test MEA with non-carbon support

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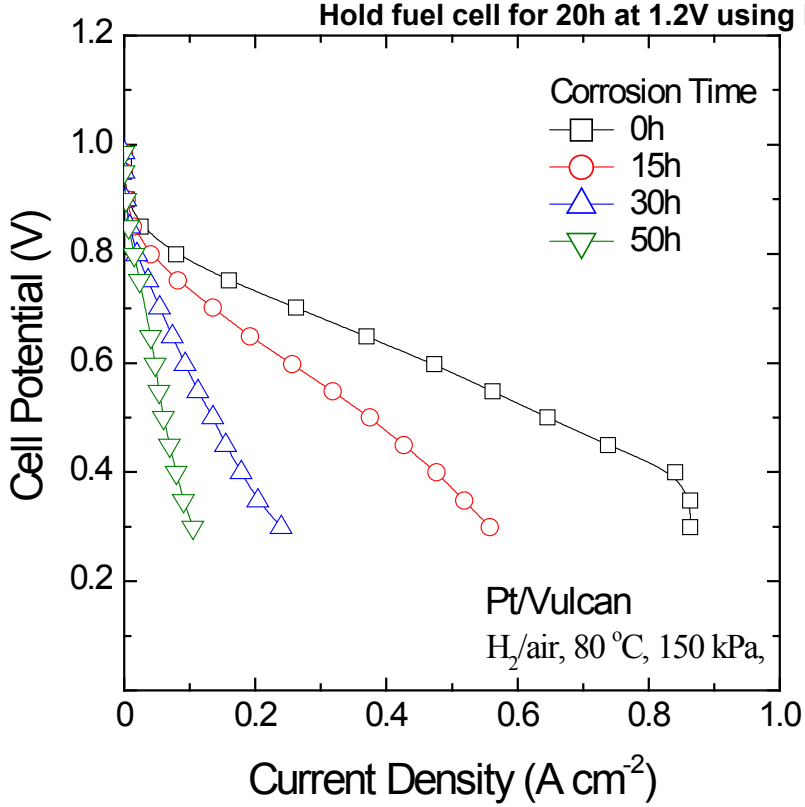
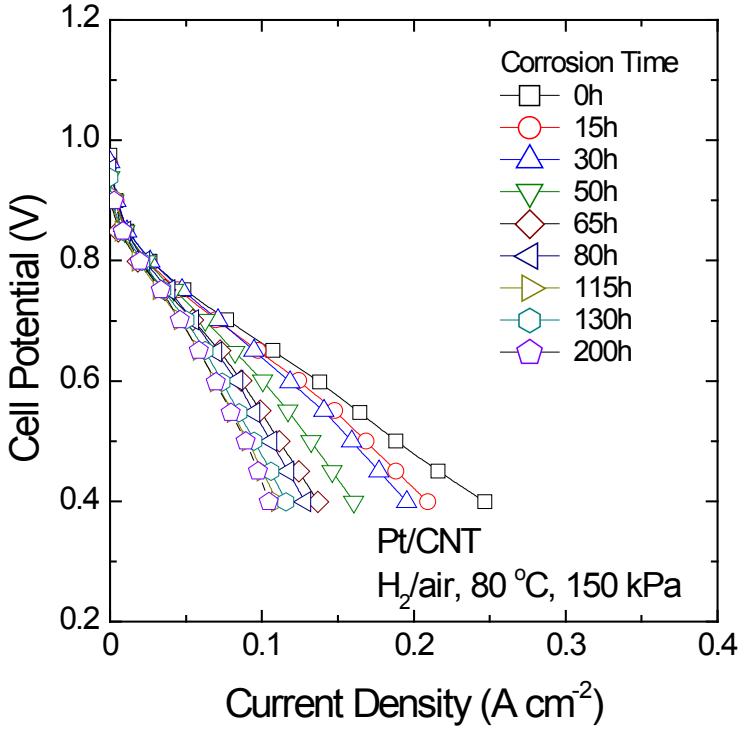
Polarization curves for Pt/XC72 and Pt/CNT

Hold fuel cell for 20h at 1.2V using H_2/N_2 at 7.4 psig, 80°C, 100% RH



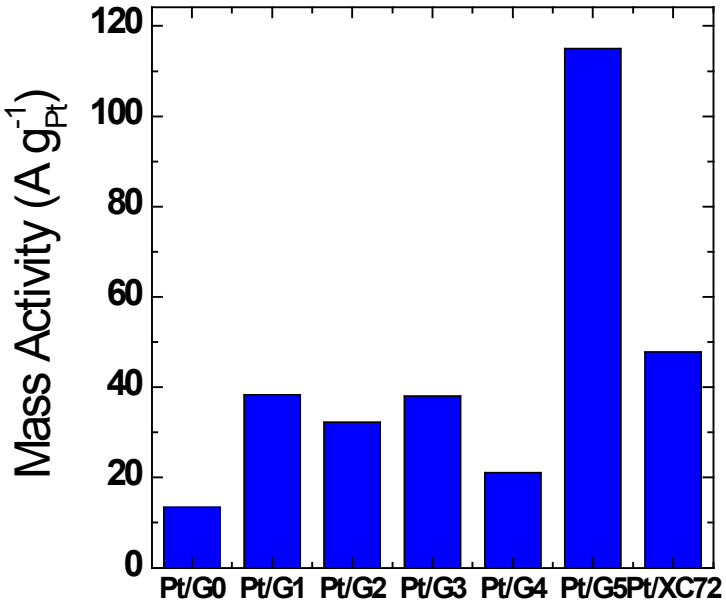


- Initial performance for CNT supported catalyst poorer than XC72
- After 50 hours, CNT supported catalyst much more durable than XC72 supported catalyst
- After 200 hours, Pt/CNT performance better than Pt/XC72 50 h performance by 2X

Future Work

➢ Improve Pt/CNT performance by better MEA ink formulation

Technical Accomplishment:
Optimization of MEA formulation for graphene based support



- More solvent needed to disperse catalyst compared to XC72 and CNT
- Lowering Pt loading to 0.03 mg_{Pt} cm^{-2} nearly tripled mass activity
- Adding XC72 to Pt/graphene increased mass activity
  - Optimum XC72 was 25 wt.%
  - Increased mass activity by 3X

Pt/G0 : 20 wt% Pt, 0.2 mg_{Pt} cm^{-2}
Pt/G1: 20 wt% Pt, 0.03 mg_{Pt} cm^{-2}
Pt/G2: 18 wt.% Pt in catalyst (90 wt.% Pt/graphene + 10 wt.% XC72), 0.2 mg_{Pt} cm^{-2}
Pt/G3: 15 wt% Pt (75 wt.% Pt/graphene +25 wt.% XC72), 0.2 mg_{Pt} cm^{-2}
Pt/G4: 10 wt.% Pt in catalyst (50 wt.% Pt/graphene + 50 wt.% XC72), 0.2 mg_{Pt} cm^{-2}
Pt/G5: 15 wt% Pt (75 wt.% Pt/graphene +25 wt.% XC72), 0.03 mg_{Pt} cm^{-2}

Accomplishments

- **Pt/graphene MEA activity was increased to 90% of Pt/XC72 by optimization of MEA formulation**

Future Work

- **Improve performance and durability with ITO modified graphene**

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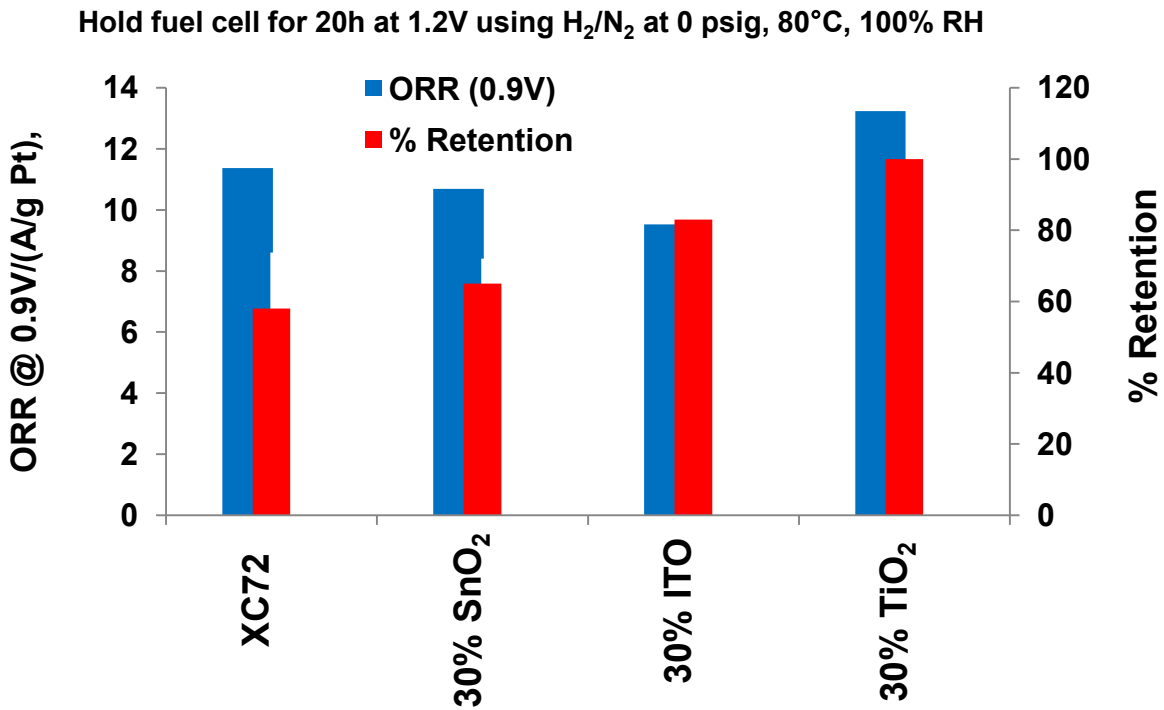
Technical Accomplishment:
Pt on Metal Oxides Modified XC72 (60hrs)



MEA test (Old)

- Similar ORR with metal oxide modification
- No degradation for TiO_2
- Lower degradation for SnO_2 and ITO
- The knowledge learned from Vulcan carbon benefits research on novel carbon materials, such as graphene and mesoporous carbon.

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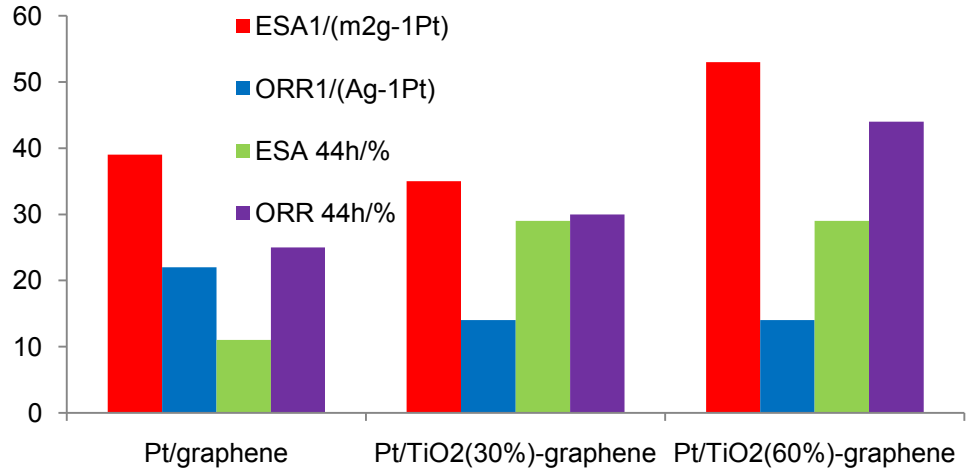
Technical Accomplishment:
Metal Oxides Modified Graphene Pt on TiO_2/Graphene Hybrid Substrate

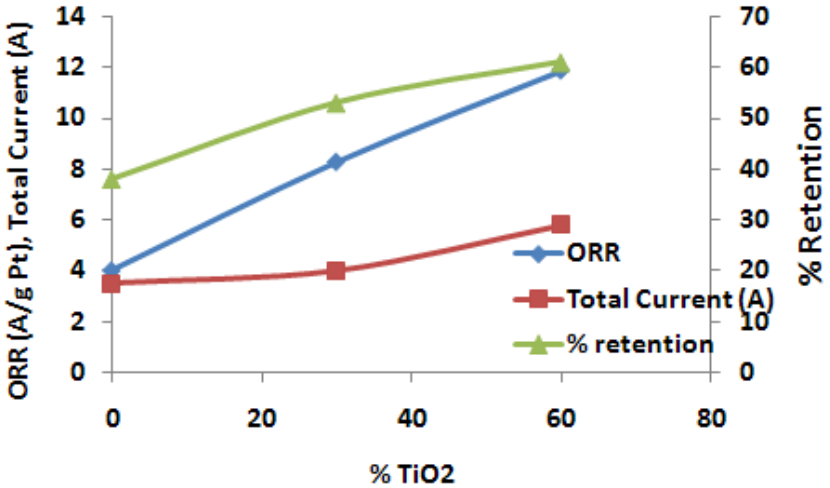
Potential step between 0.85V (30 sec) to 1.4V (150 sec) vs. NHE

RDE results



Hold fuel cell for 20h at 1.2V using H_2/N_2 at 0 psig, 80°C, 100% RH

MEA results (Old) (60hrs)



RDE and MEA tests confirmed

- **The durability was improved with the modification of TiO_2.**
- **The higher durability was observed with higher amount TiO_2 addition.**

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