Project ID: FC_19_Wang

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

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Overview

Timeline

- Project start date: Jan 2007
- Project end date: Dec 2010
- Percent complete: 55%

Budget

- Total project funding
  - DOE share: $4,234K
  - Contractor share: $255K
- Funding received in FY07
  - $1,241K (federal, requested)
  - $820K (federal, approved)
  - $72K (cost share)
- Funding received in FY08
  - $1,300K (federal, requested)
  - $1,400K (federal, approved)
  - $72K (cost share)
- Funding in FY09
  - $1,095K (federal, requested)

Barriers

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

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
2007	▶ Provide fundamental understanding of Pt/support model systems ▶ Synthesize high surface area durable cathode supports ▶ Select a potential support with better stability than commercial carbon black support
2008	▶ Identify lead cathode compositions with better durability than carbon black supported Pt cathode
2009	▶ Identify compositions with 2X better stability than carbon black supported catalyst for cell demonstration.
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	
1	Better stability of model Pt/WC	09/30/07	09/30/07	9/30/07	100%	completed
2	High surface area WC and CMO	09/30/07	12/31/07	12/31/07	100%	completed
2	Down select carbon supports	09/30/07	12/31/07	1/31/09	100%	completed[1]
2&3	Identify lead compositions	09/30/08	12/31/08	1/31/09	100%	completed
2&3	Identify compositions for cell test	09/30/09	12/31/09		30%	On track
3	Demonstrate target durability	09/30/10	12/31/10		20%	On track

[1] delayed due to both the reduced budget in FY07 and a longer time to develop an appropriate test protocol

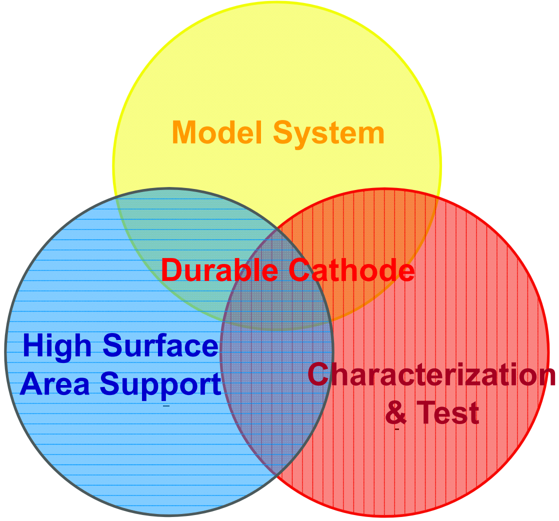
Go/no-go decisions:
Year 1: Decided to use mesoporous carbon as both scaffold and as template for CMO synthesis
Year 2: Continue effort if stable compositions can be identified
Year 3: Move forward with cell test if durable supported catalyst can be identified

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)
  - Oxycarbides
  - Conductive metal oxides (ITO)
  - SnO_2
  - TiO_2
- Enhance Pt dispersion and stability on these new classes of cathode supports

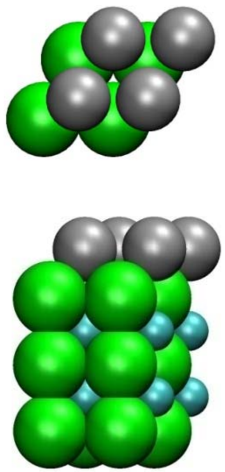
Approach – Specific Tasks

- 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.

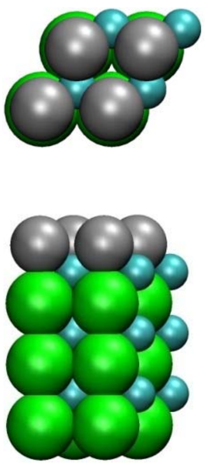


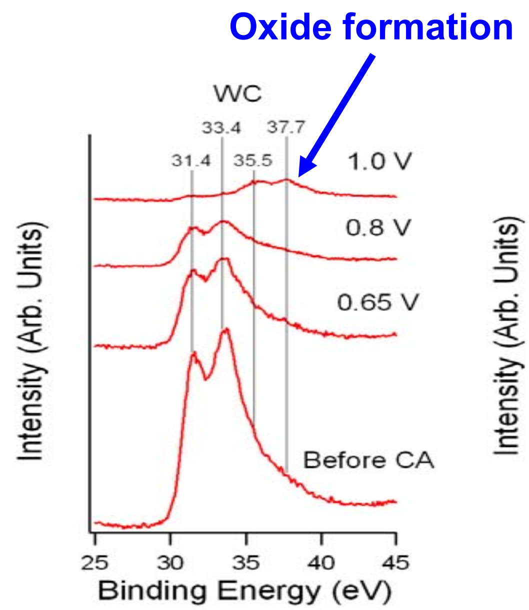
Technical Accomplishment: Model System
Guidance from DFT Modeling and Experimental Studies

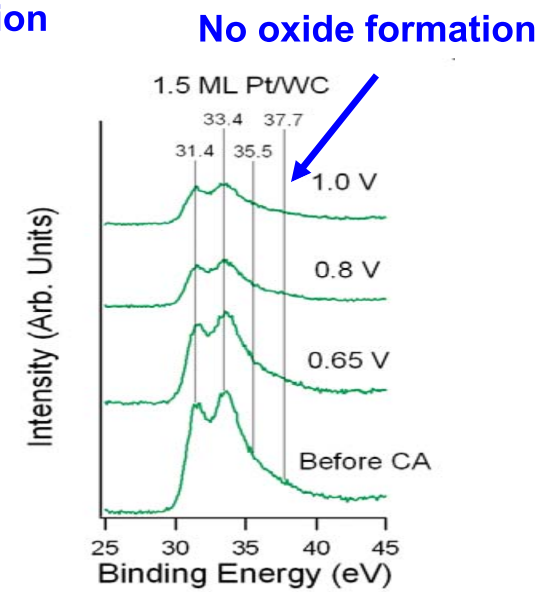
Pt-WC(0001)



Pt-CWC(0001)





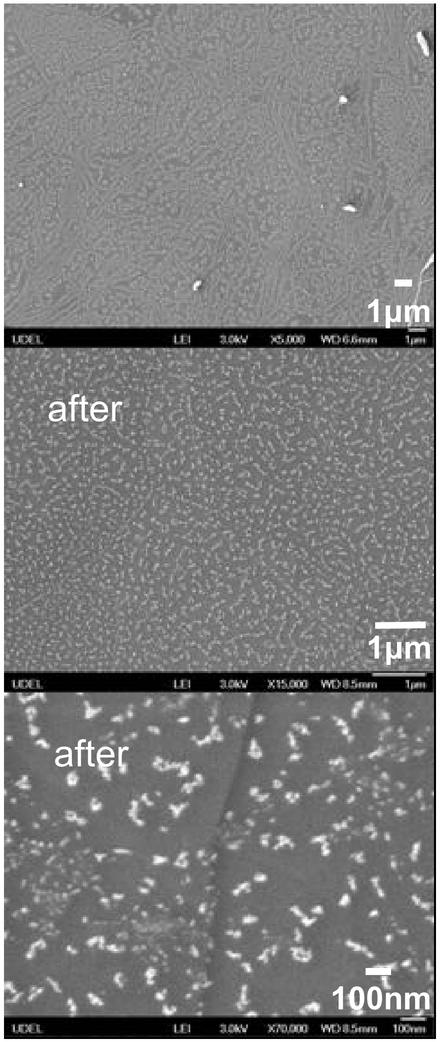


WC and VC are potential supports

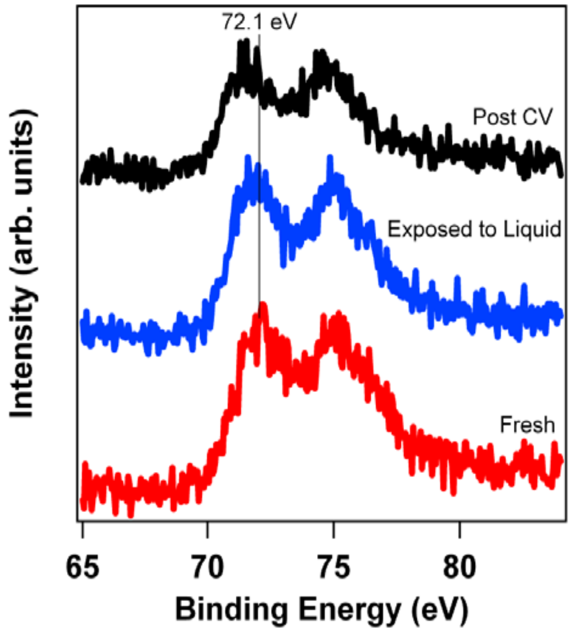
- Pt-WC(0001) and Pt-VC(111) should have better ORR activity than Pt/C.
- Pt/WC(0001) and Pt/VC(111) are predicted to be stable in oxygen environment
- XPS studies showed that the deposition of Pt on WC improves the stability of WC at high potential limit

Technical Accomplishment: Model System
Characterization Using SEM, XPS, STM, & CV Cycling

SEM micrographs of Pt/C agglomeration 9 hrs CV 0-1.0V

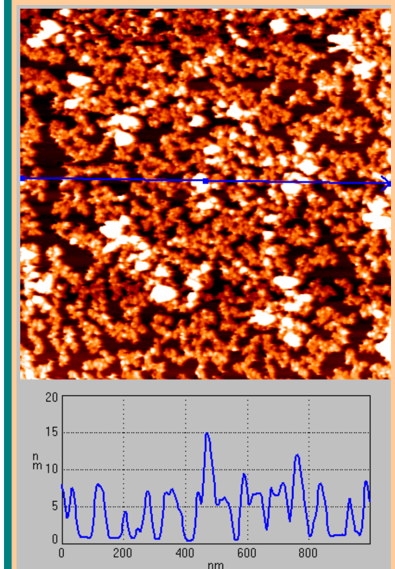


In situ Pt 4f XPS data for fresh Pt/HOPG, exposed to H_2SO_4, after 180 CV cycles

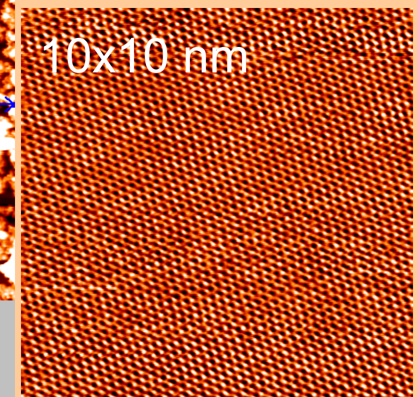


STM micrographs

Pt/C after CV cycling



C surface after CV cycling



Accomplishments

- Pt agglomeration by CV cycling as confirmed by SEM and *in situ* XPS.
- No change in carbon support at 1.0 V as confirmed by STM.
- Pt agglomeration separated from carbon support corrosion.

Future Work

- Study C degradation under more severe and representative conditions.
- Understand the mechanisms of Pt particle growth under CV cycling.
- Evaluate the effects of WC, VC, and functionalized/roughed C surfaces

High Surface Area Cathode Materials

- **Development of novel carbon supports**
  - Ordered mesoporous carbon (OMC)
  - Graphene
- **Dispersion and activation of Pt**
  - Substrates: XC-72, carbon nanotubes (CNT), graphene and OMC
  - Loading method : incipient wetness approach
  - Activation
    - Reduction in H_2 at 300°C,500°C, or
    - Reduction with ethylene glycol
- **Metal oxide modification of XC-72**
  - SnO_2,In_2O_3,TiO_2 etc.
- **Synthesis of high surface area ITO and WC substrates**

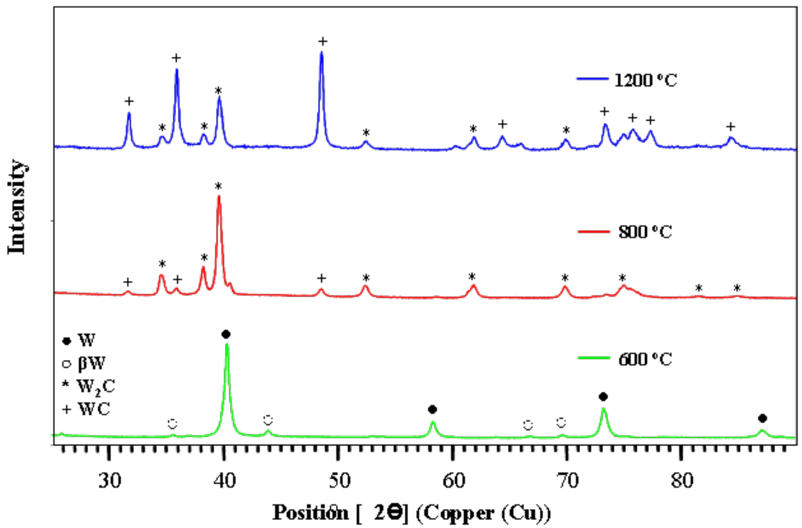
Summary of Samples and Support Modifications

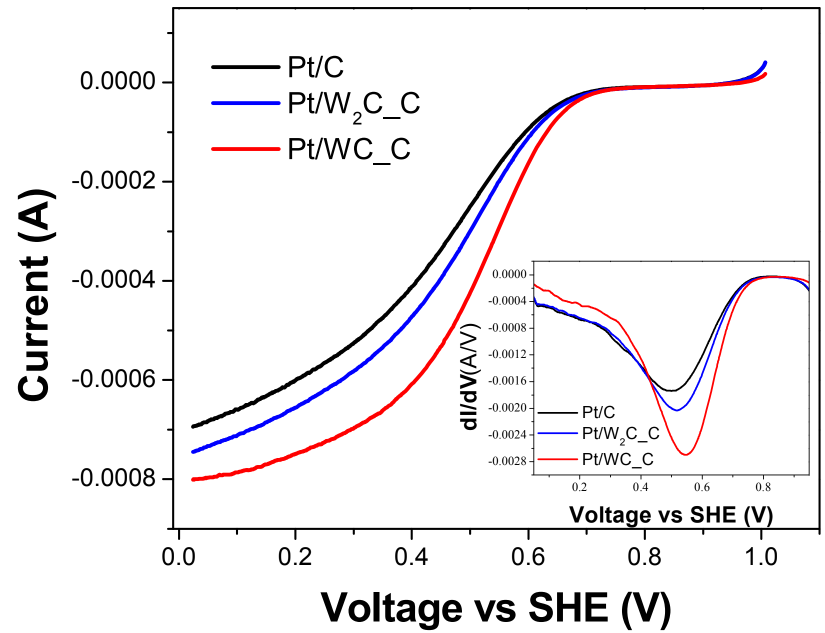
Modification \ Support	Vulcan X72	CNT	Meso-porous carbon	Graphene
none	RDE test complete; MEA test complete	RDE test complete; MEA test complete	RDE test complete	RDE test complete; MEA test complete
TiO_2	RDE test complete; MEA test complete			RDE test complete; MEA test complete
SnO_2	RDE test complete; MEA test complete			
ITO	RDE test complete; MEA test complete			RDE test in progress
WC				
SiO_2	RDE test in progress			RDE test complete

Legend:
- ● (red) RDE test complete
- ● (teal) RDE test in progress
- ▲ MEA test complete

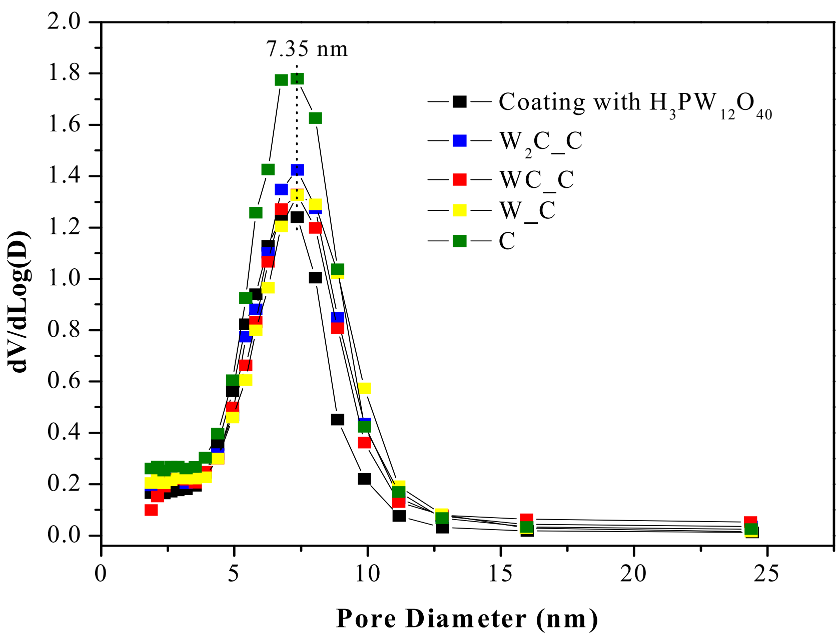
RDE test: **initial screening for activity and stability**
MEA test: **detailed durability testing including CO_2 evolutions and charge during potential hold**

Technical Accomplishment
WC Supported on Mesoporous Carbon





0.05 M oxygen-saturated H_2SO_4 -1600 rpm, 10 mV/s.



Accomplishments

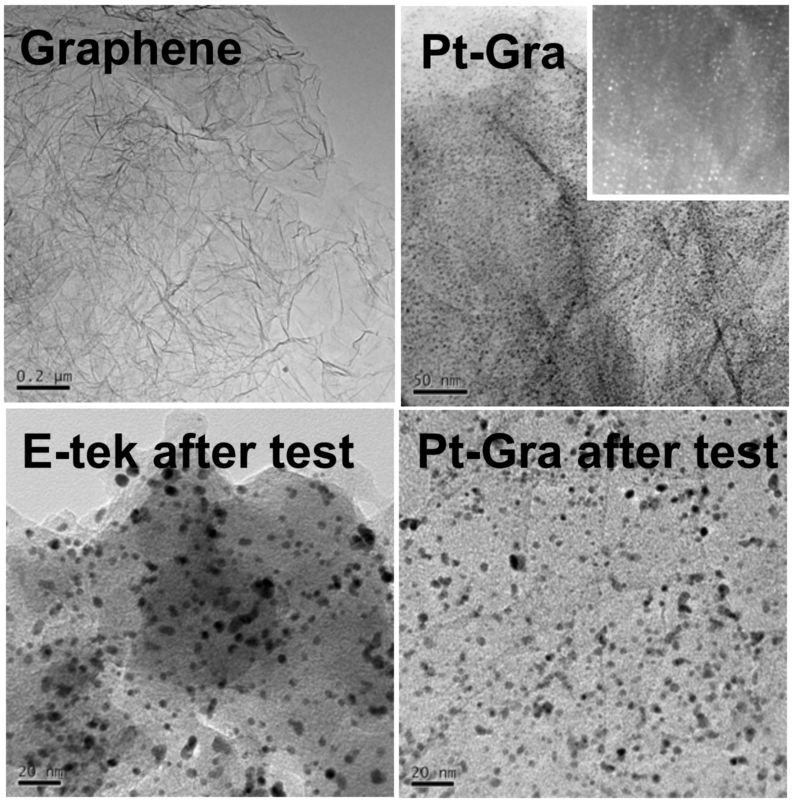
- XRD confirmed the formation of WC
- Mesopores are retained after forming WC
- ORR tests showed that WC modification of mesoporous carbon surfaces enhances the Pt activity

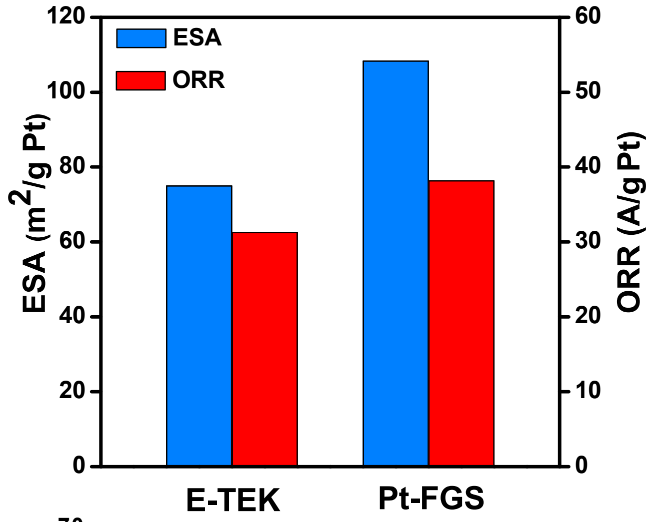
Future Work

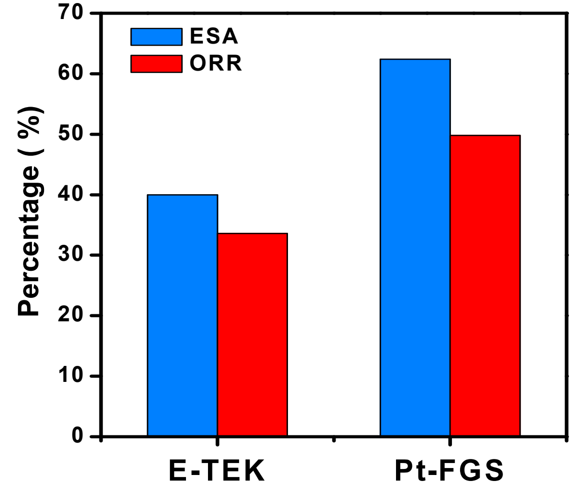
- Durability test in MEA, enhance the activity
- Synthesize metal oxide modified OMC support

Technical Accomplishments:
Pt on Graphene

Advantages of graphene: **bridging to the model system, high surface area (600~900 m2/g), high conductivity, unique graphitized basal plane structure, amenable to large scale production.**

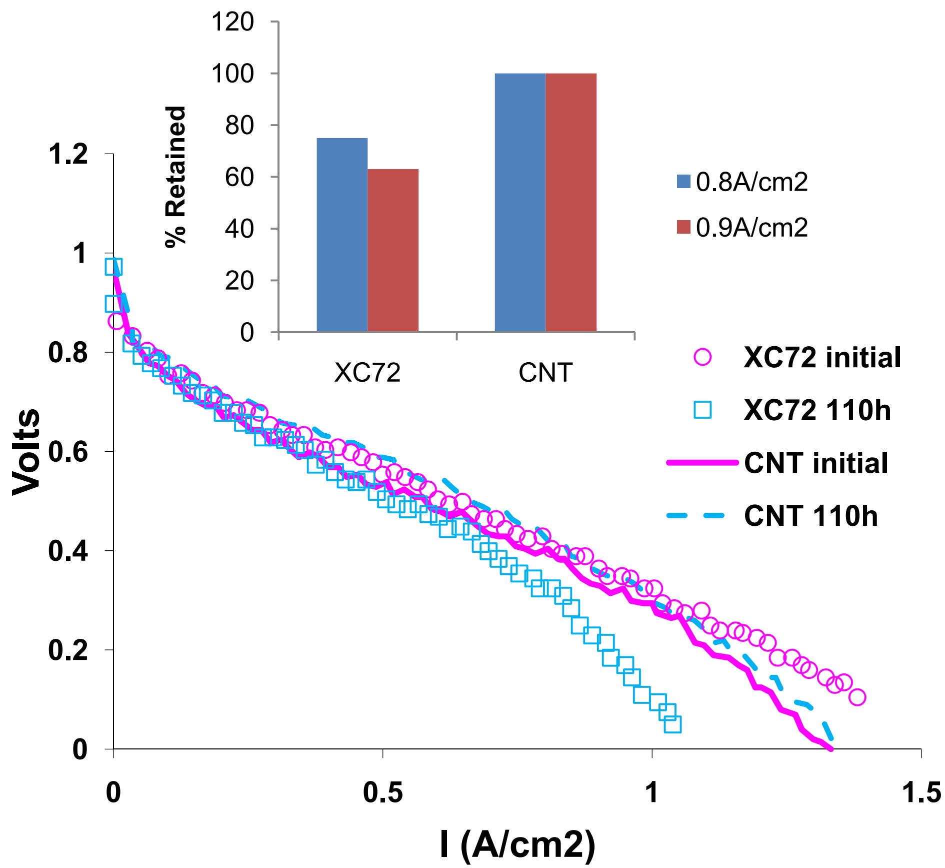


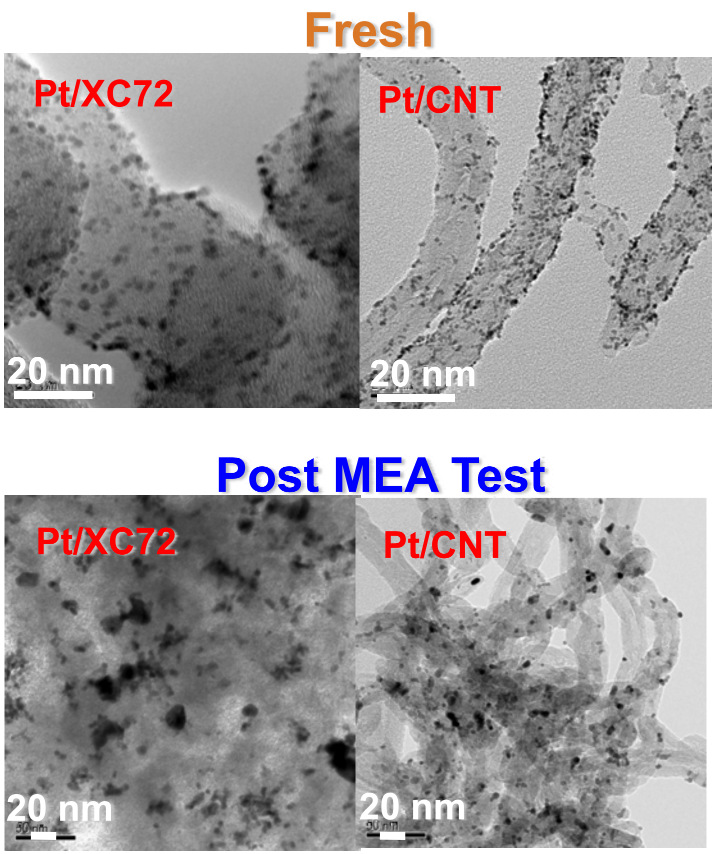




- **Small Pt nanoparticles uniformly loaded on graphene; size of Pt on graphene is smaller than on E-tek after test, indicating less agglomeration.**
- **Pt on graphene shows higher activity and durability - 5000 CV(0.6-1.1V)**

MEA Testing - Comparison of Long-term Stability of 20% Pt on XC72 and CNT Supports (1.2V hold)





- XC72 support has loss especially at high current density
- CNT support very stable, likely due to different structures and surface properties

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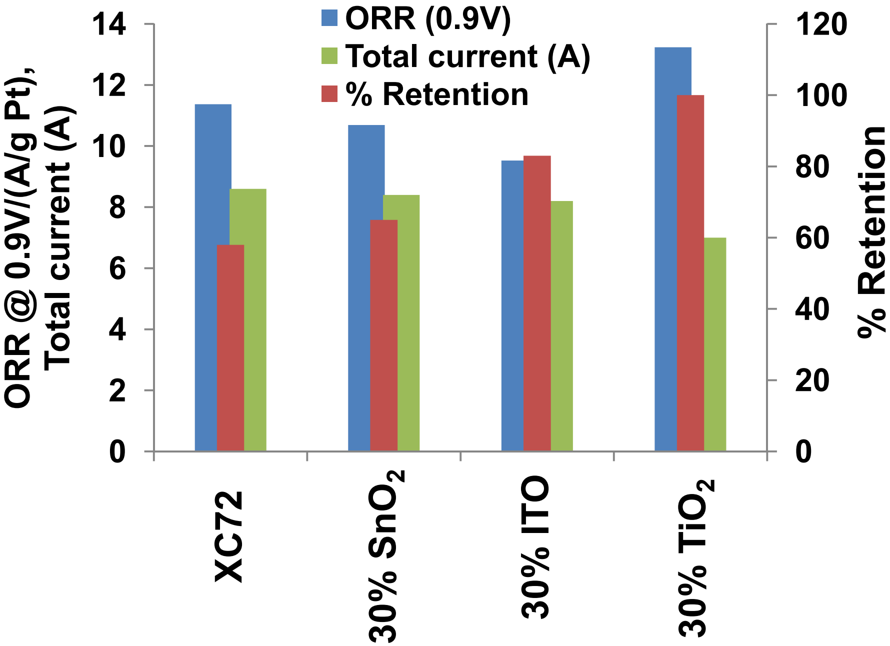
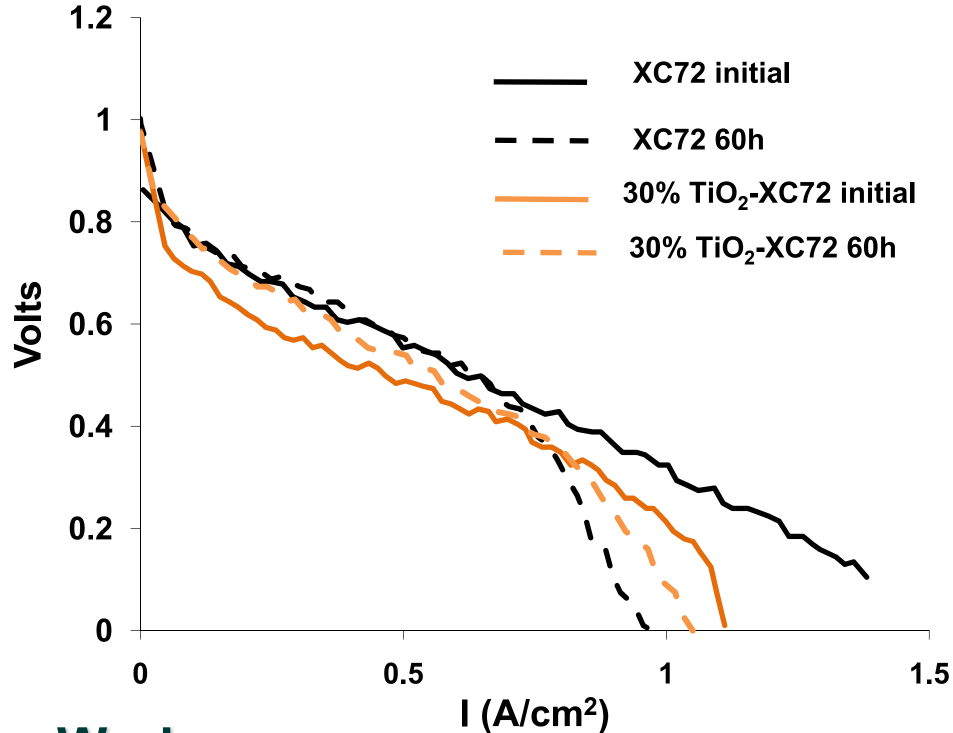
MEA Testing – Activity and Stability of 20% Pt on MOx Modified XC72 (1.2V Hold)





Accomplishments

- Similar ORR with metal oxide modification
- Lower degradation for SnO_2 and ITO
- No degradation for TiO_2

Future Work

- Modify protocol to hold MEA at 1.4V in order to accelerate testing
- Test metal oxide modified CNT and OMC supports with potential for 2X stability over XC72 support

Technical Accomplishments and Future Work

Accomplishments

- Model system studies demonstrated stable carbon surface at 1.0 V, and separated Pt agglomeration from carbon corrosion.
- DFT calculations guide the selection of materials with better durability and activity, e.g., WC and VC.
- Modification of ordered mesoporous carbon (OMC) with WC increased activity.
- Carbon nanotubes (CNT) showed higher stability and activity than XC72.
- Modification of carbon supports with metal oxides, e.g., graphene and XC72 with TiO_2, showed improved stability.

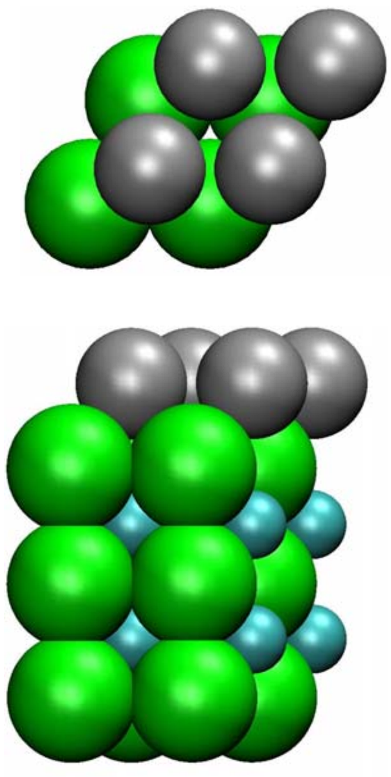
Future Work

- Study C degradation and evaluate and Pt-support interactions of model systems under more severe and representative conditions (1.2 and 1.4 V).
- Accelerate MEA testing by modifying the protocol, e.g., holding at 1.4V.
- Demonstrate 2X stability over XC72 support, e.g., modifying CNT with metal oxides.

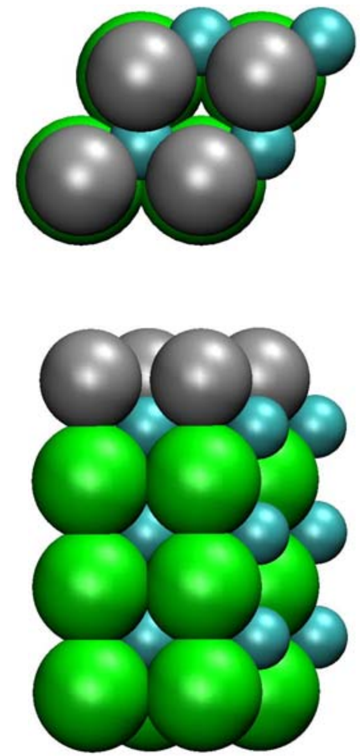
Additional Slides

DFT Structures of Carbide Supported Pt

Pt-WC(0001)



Pt-CWC(0001)



Calculation Methods:
Vienna Ab-intio Simulations Package (VASP)
3x3x1 MP K-point mesh
2x2 unit cell

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ORR Activity Predicted Based on Oxygen Binding Energy on Pt-WC(0001), Pt/VC(111) and Pt-Ni-Pt(111)

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

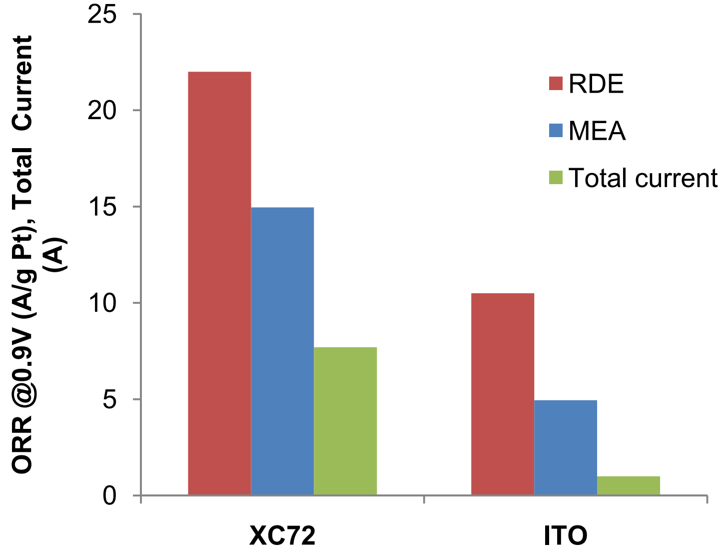
Based on values of oxygen binding energy, the Pt-WC(0001) and Pt-VC(111) should have comparable ORR activity as the Pt-Ni-Pt(111) (Pt-skin) catalyst

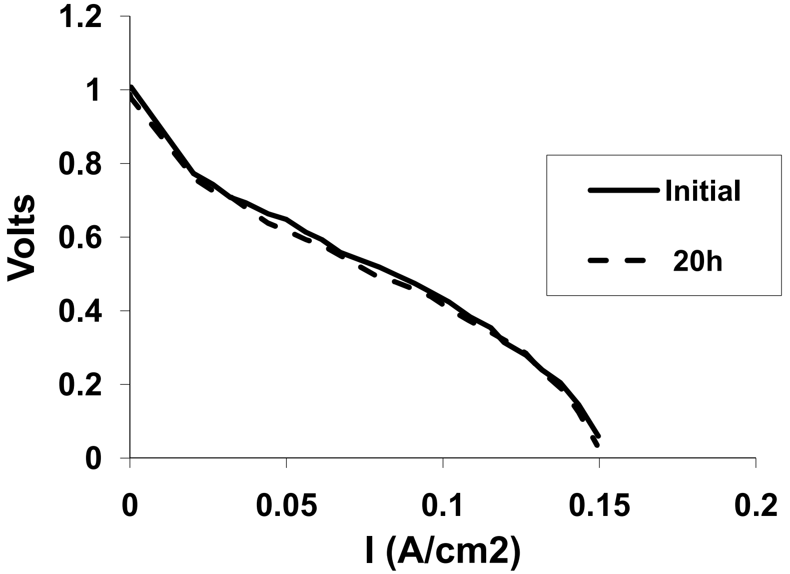
Pt/WC(0001) and Pt/VC(111) Predicted to Be Stable in Oxygen Environment

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	

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

Carbon Free Support - 20% Pt on ITO





- Carbon free ITO support shows reasonable activity with no degradation after 20 hours. This provides the potential of controlling ITO/carbon ratio to optimize conductivity, activity, performance and durability.
- Low activity was due to low surface area of ITO, justifying the needs of modifying C with metal oxides.

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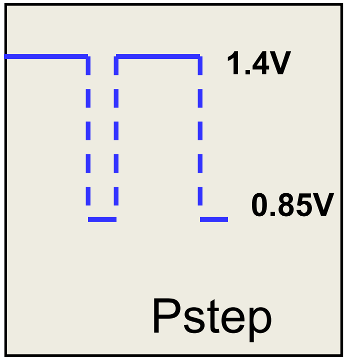
RDE and MEA Tests: Protocol

- RDE test: fast screening
  - To separate Pt nanoparticle dissolution/redeposition from carbon support corrosion
    - focus on carbon support corrosion.
  - Potential step accelerated degradation test (1.4V-0.85V).



- MEA test
  - Hold fuel cell for 20h at 1.2V/80°C under 100% RH H_2/N_2
  - Determine polarization curves and activity at 0.9V
  - Determine amount of CO_2 evolved for selected experiments using mass spectrometer
  - Relate degradation to CO_2 evolved and charge passed during potential hold

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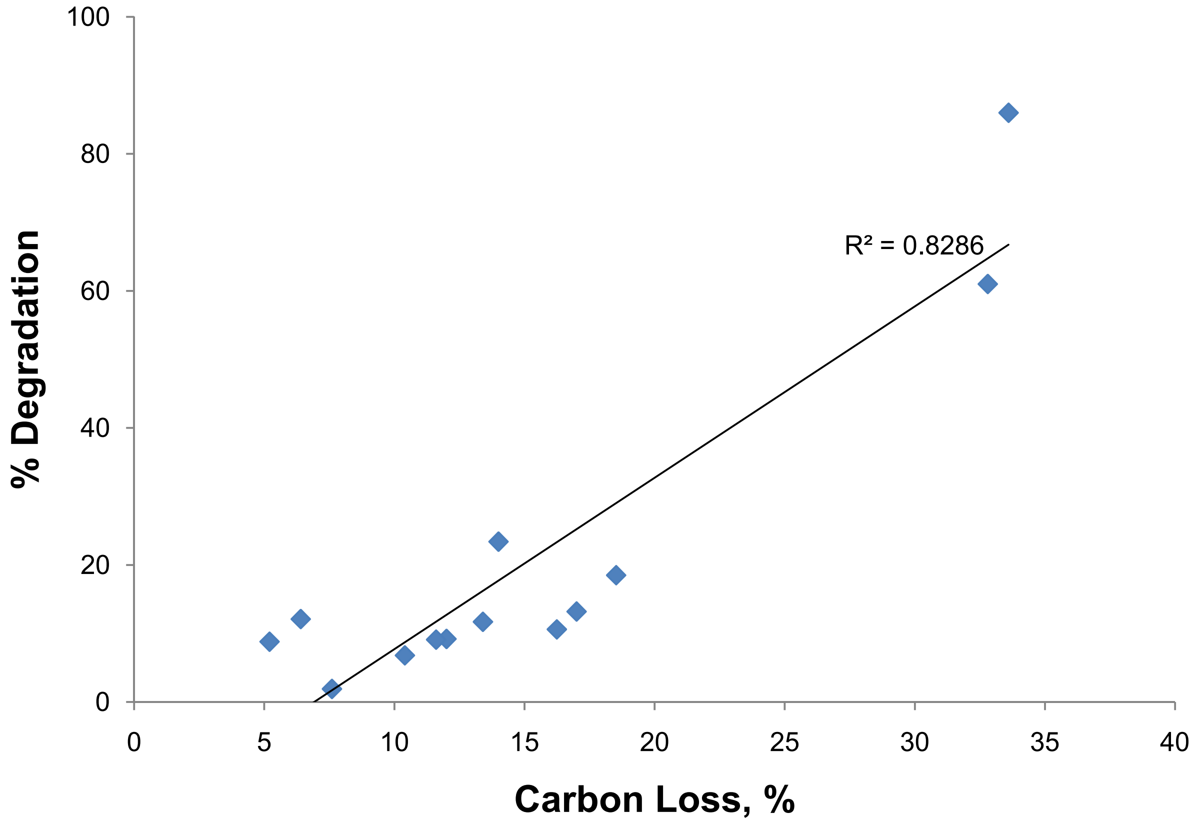
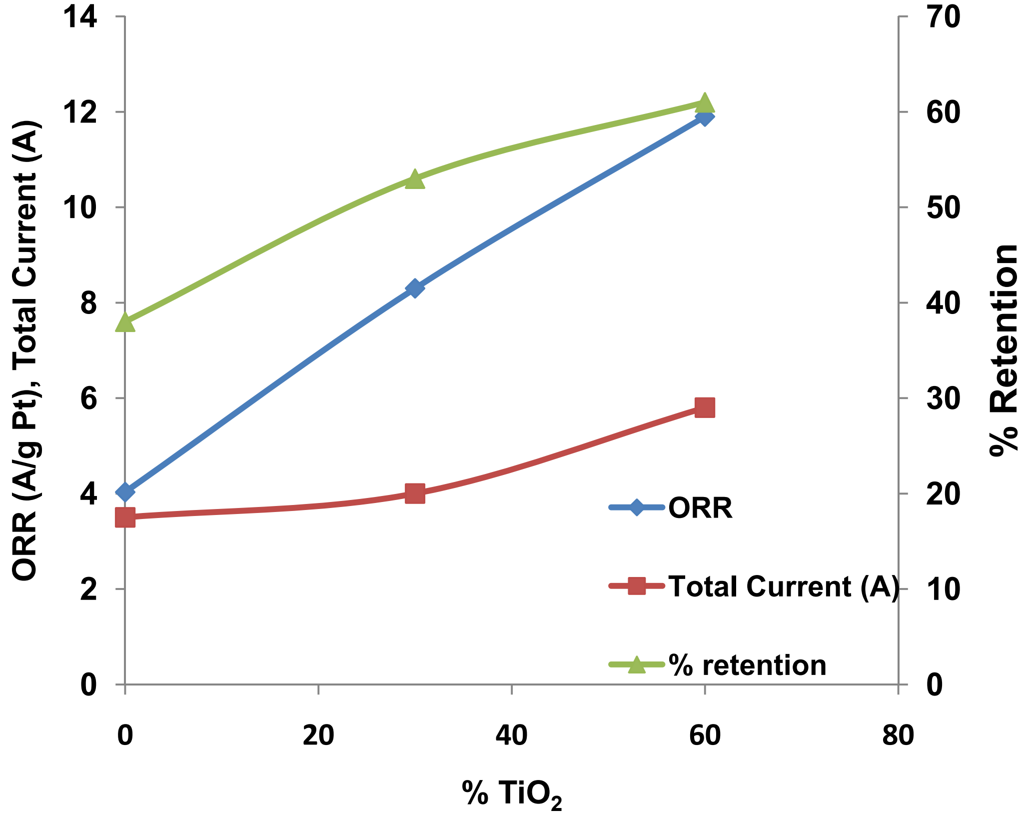
MEA Testing – Correlation of Degradation with CO_2 Evolution During 1.2V hold



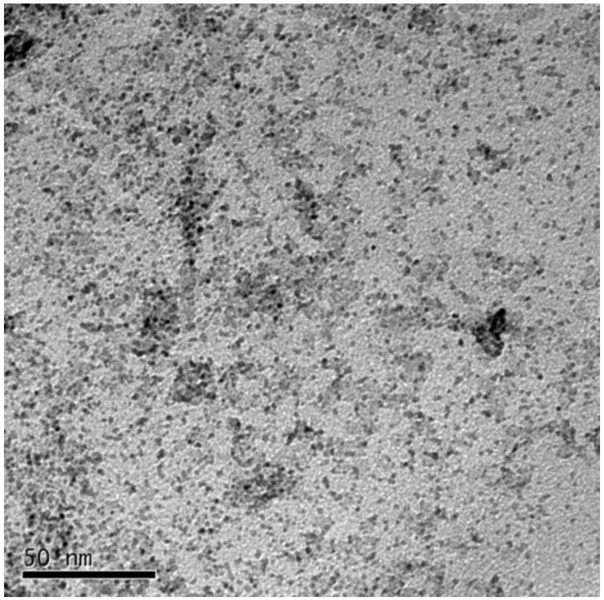
- Degradation increases with carbon loss - threshold for carbon loss > 20% for significant degradation

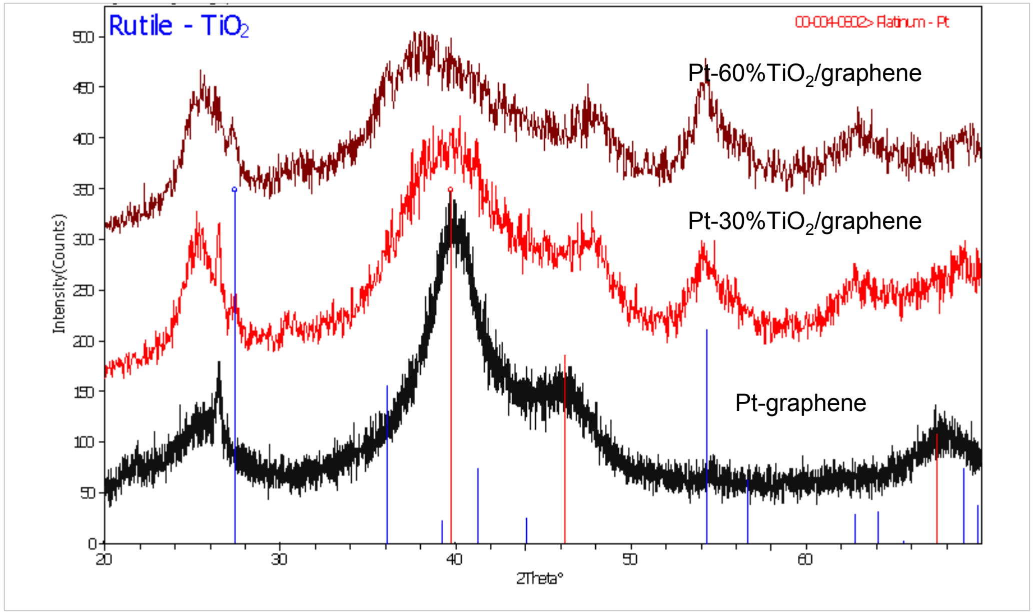
MEA Testing – Activity and Stability of 20% Pt on Graphene Support with Different Amount of TiO_2 Modification



- Activity and stability increased with TiO_2 content
- Promise for use of higher TiO_2 loading

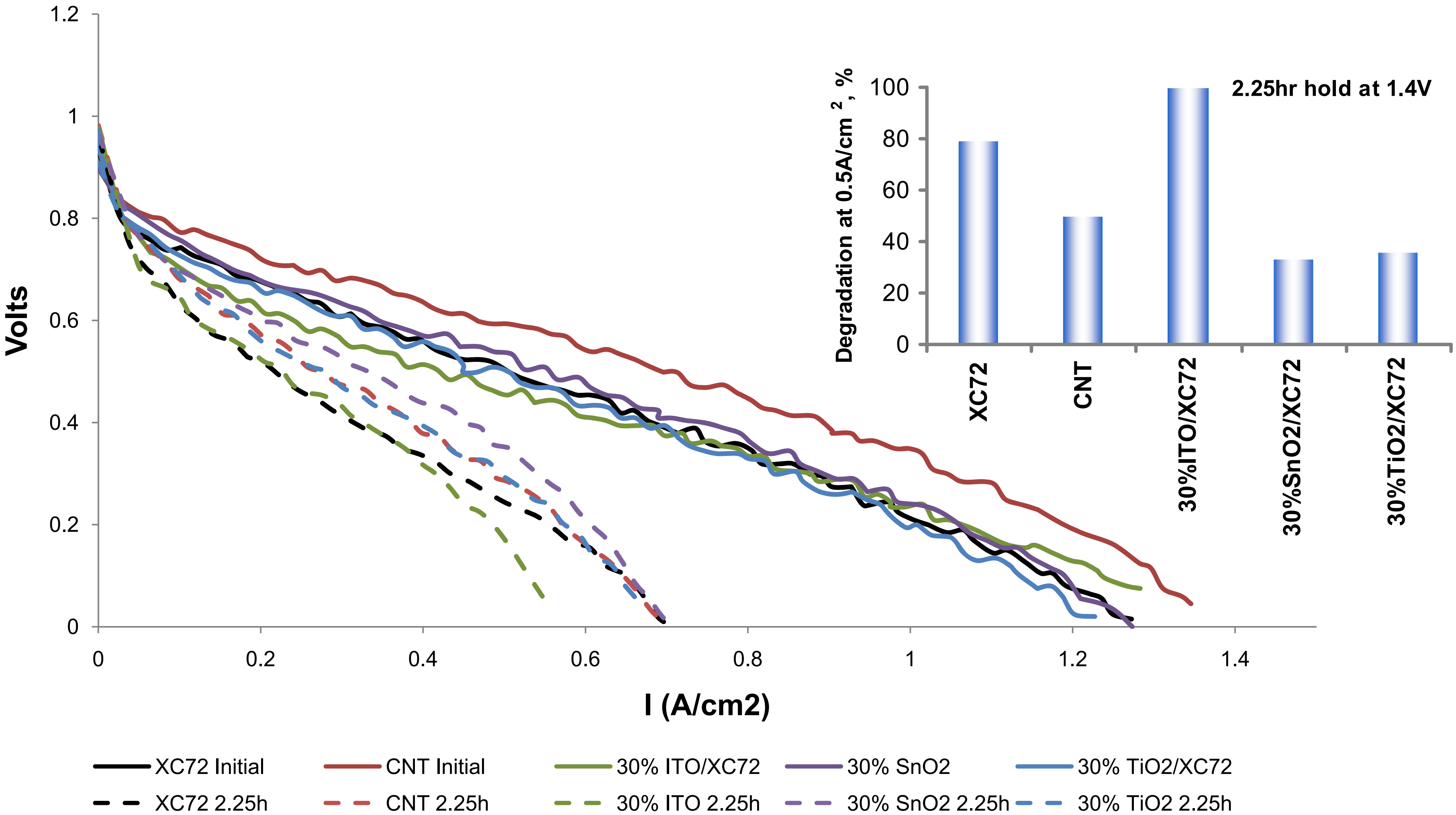
Addition of TiO_2 on Graphene





- **TEM image shows a uniform dispersion of Pt nanoparticles on the substrate of 60%TiO_2/40%graphene.**
- **XRD spectra shows the size of Pt nanoparticles decreased on the TiO_2 modified graphene substrates.**

MEA Testing – Activity and Stability of 20% Pt on CNT and MO_x Modified XC72 at 1.4V Hold



- **The 1.4V degradation data at 3A for 2.25hr shows 2X stability improvement for 30%TiO_2/XC72 and 30%SnO_2/XC72 over XC72**

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