

Development of Ultra-low Platinum Alloy Cathode Catalyst for PEM Fuel Cells

2010 DOE Hydrogen Program Fuel Cell Project Kick-Off

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Overview

Timeline

- Start date: June 01 2010
- End date: Nov 30 2012 (Phase I)
: May 31 2014 (Phase II)

Budget

- Total project funding
 - DOE share: \$ 4,400,000
 - Contractor share: \$1,100,000
- Incremental funding received in FY10: \$750,000
- Funding for FY11: \$1,100,000

Barriers

- Catalyst cost
- Catalyst performance
- Catalyst Durability

Targets

- PGM loading of 0.2 mg/cm²
- Mass activity of 0.44 A/mg_{Pt} at 0.9 V (Year 2015).
- Specific activity of 720 μA/cm² at 0.9 V (Year 2015).
- Electrochemical surface area loss <40%
- Cycling performance for 5000 h at ≤ 80 °C and 5000 h at > 80 °C

Partners

- Hyundai Motor Company, S. Korea
- Yonsei University, S. Korea

Problem Definition – In Developing Low Loading Platinum Catalysts

- Catalyst Performance
 - Platinum and catalyst support ratio
 - Catalyst agglomeration during alloying process
 - Pt dissolution and agglomeration
 - Increase of inter-particle resistance and dis-bonding of catalyst particles during the leaching process
 - Loss of electrochemical surface area
 - Alloying metal dissolution and incorporation in to the membrane
 - Catalyst-ionomer interaction
 - Catalyst layer properties – thickness, porosity and pore-size distribution and hydrophilic/hydrophobic properties.
- Catalyst Support Stability
 - Water content.
 - Low pH (< 1).
 - High temperature (50 – 90 °C).
 - High oxygen concentration.
 - Carbon corrosion at high potentials (Increases between 1.2 and 1.5 V during start-up and shut-down cycles in automotive application)
 - ✓ $C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^-$ $E^0 = 0.118 \text{ V vs. RHE at } 25^\circ\text{C}$
- Carbon oxidation results in:
 - Increase in the hydrophilic properties and affects the water removal leading to increased mass transport losses.
 - Decreases the thickness of the catalyst layers which increases the cell resistance.
 - Pt catalyst accelerates the rate of carbon corrosion.

Project Objectives

- Ultra-low loading Pt catalysts for oxygen reduction reaction with high activity and good stability will be developed through:
 - Synthesis of hybrid cathode catalyst (HCC) consisting of carbon composite catalyst (CCC) developed at USC as support and activated platinum with high electrochemical surface area.
 - ✓ Platinum catalyst activation will be performed using USC developed leaching procedure for Pt-Co, Pt-Ni and Pt-Cu alloys.
 - Synthesis of activated low loading platinum catalysts with high electrochemical surface area using:
 - ✓ Stable conductive TiO_2 based supports synthesized by template assisted procedure developed at USC.
 - ✓ Stable and electrochemically active CCC- TiO_2 hybrid support with pyridinic active sites for ORR.
 - Synthesis of leached Pt-Ni alloy catalysts with high electrochemical surface area Pt deposited on activated graphitic carbon developed at HMC.
 - Synthesis of leached Pt-Cu catalysts with high electrochemical surface area Pt deposited on activated carbon developed at Yonsei University.
 - ❖ **Facile scale-up synthesis procedure for the production of all the suggested catalysts.**
 - Elimination of Pt-alloy particle agglomeration during annealing process at high temperature using a procedure developed at Yonsei University.
 - Decreasing the inter-particle resistance and prevent the catalyst particle detachment from the support through:
 - ✓ Introduction of a thin interlayer of Pt or Pd between the support and the catalyst
 - ✓ Optimization of Pt and alloying metal composition.

Project Objectives

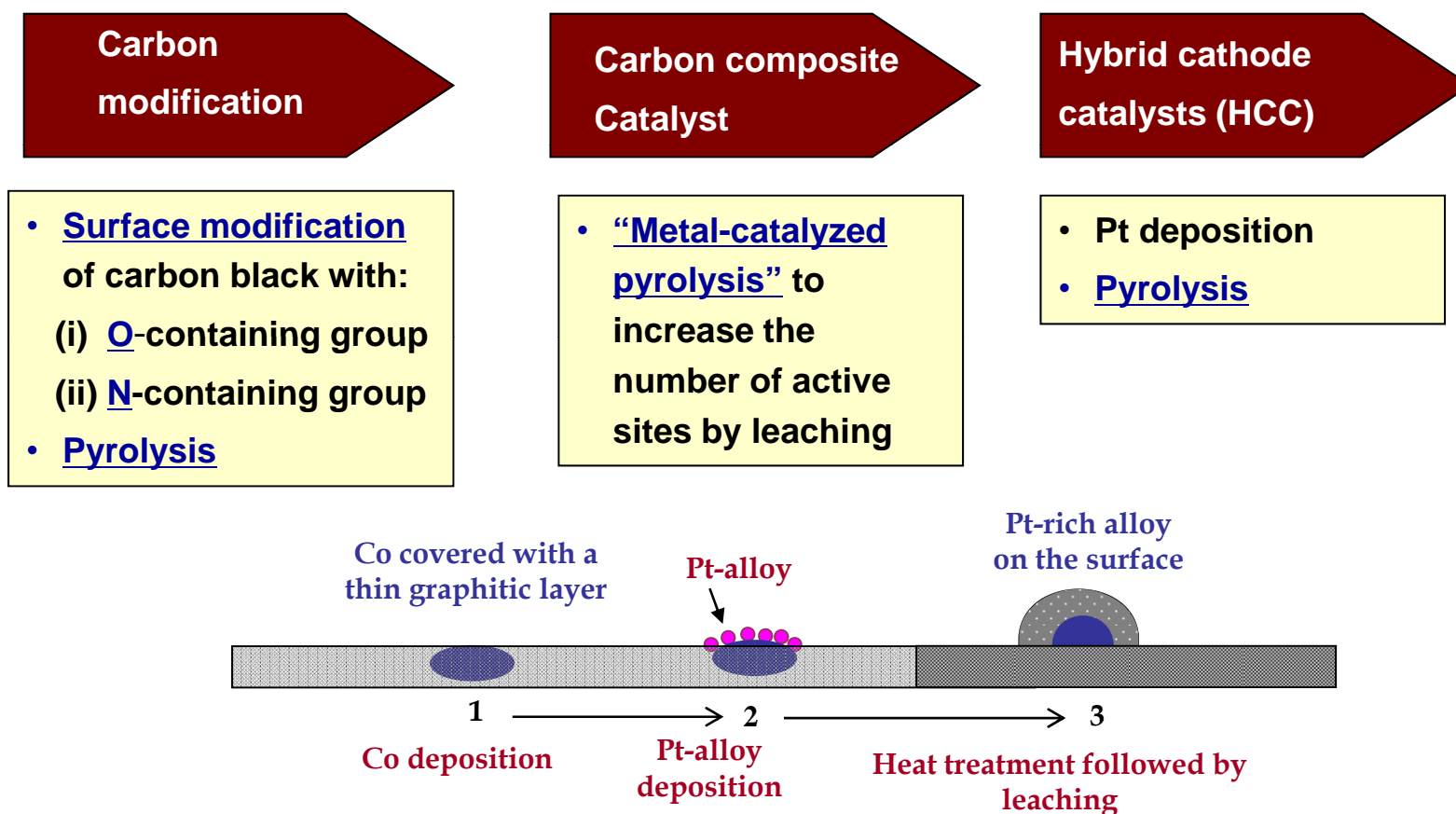
- Synthesis of high distribution of Pt with high initial loading over carbon support without Pt loss. Initial results (HR-TEM) at Yonsei University indicated that the Pt particle size of 70 wt.% Pt/C is smaller than the commercial 40 wt.% Pt/C catalyst.
- Engineer membrane electrode assembly (MEA) with
 - ✓ thin catalyst layer
 - ✓ optimize the catalyst-catalyst support ratio
- Study the activity and durability of different low loading Pt catalysts in single cell (50 cm²) test conditions.
- Construct short-stack (50 cm², up to 10 cells) containing ultra-low Pt loading catalyst and evaluate the performance under simulated automotive operating conditions.

Previous Accomplishments at University of South Carolina

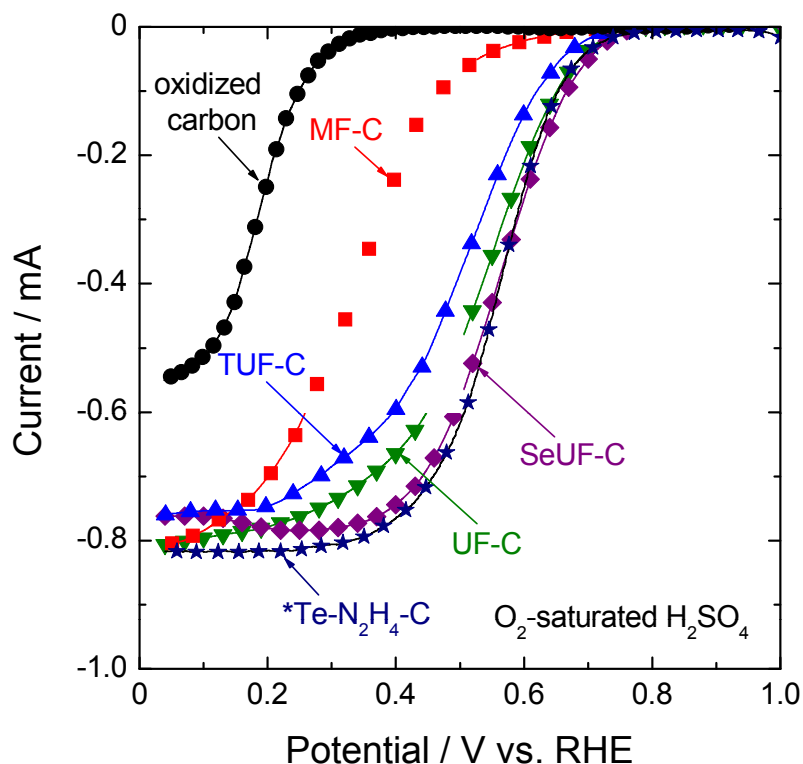
Development of Metal Free Catalyst

USC Strategy: HCC Catalyst

Strategy: Combine the catalytic activity of Pt at high potentials with that of carbon composite catalyst (CCC) at low potentials forming a hybrid cathode catalysts (HCC) having ultra-low Pt loading.



Metal-Free Catalyst: Catalytic Activity and Selectivity



Nitrogen-modified carbon-based catalyst	% H ₂ O ₂ at 0.5 V
MF-C	28
TUF-C	17
UF-C	3
SeUF-C	1
Te-N ₂ H ₄ -C	1

***Synthesis of Te-N₂H₄-C**
 (1) Adsorption of telluric acid on carbon black
 (2) Reduction by hydrazine
 (3) Pyrolysis at 1000 °C

HIGHLIGHT

- The nitrogen-containing polymer modification methodology increases the onset potential for oxygen reduction by ca. 400 mV, as compared with carbon black.
- The nitrogen modified carbon-based catalyst catalyzes oxygen reduction to water with low H₂O₂ production.

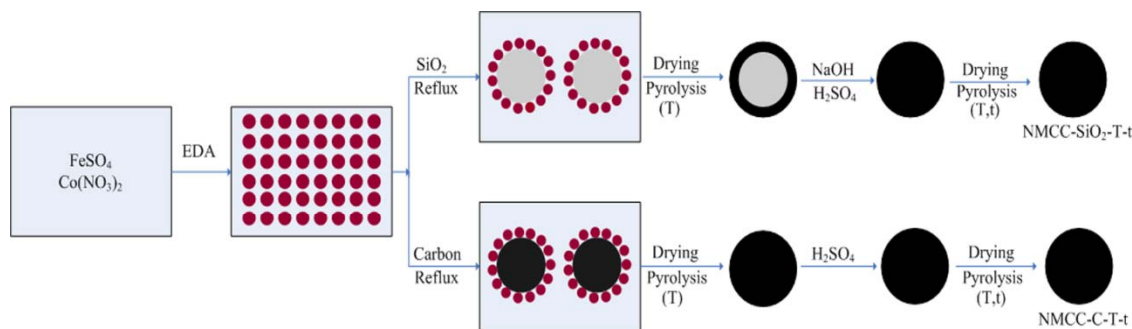
Popov et.al., *J. Power Sources*, 182 (2008) 18-23.

Center for Electrochemical Engineering, University of South Carolina

Previous Accomplishments at University of South Carolina

Development of Carbon Composite Catalyst

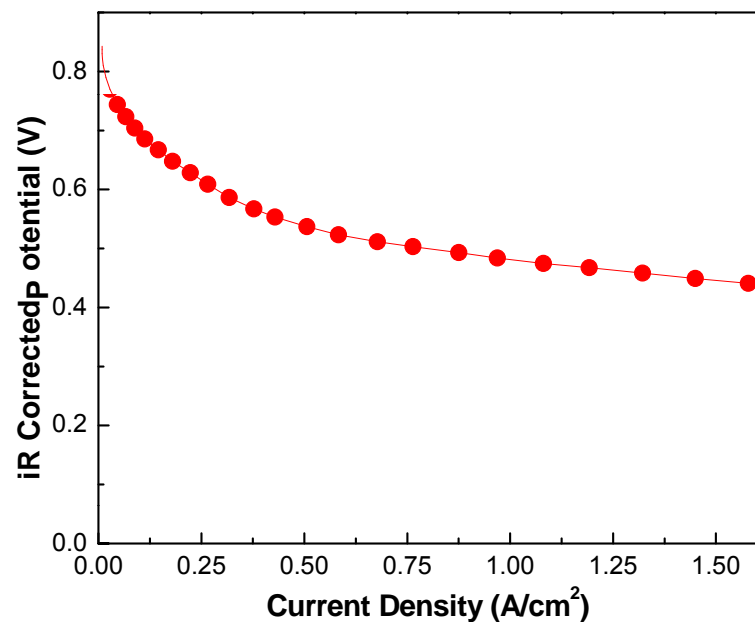
Synthesis of Carbon Composite Catalyst



HIGHLIGHT

The exclusion of carbon black in the catalyst synthesis can increase nitrogen content in the resulting catalysts, hence, increases the density of ORR active sites.

Popov et.al., *Electrochim. Acta.* 55 (2010) 2853-2858.

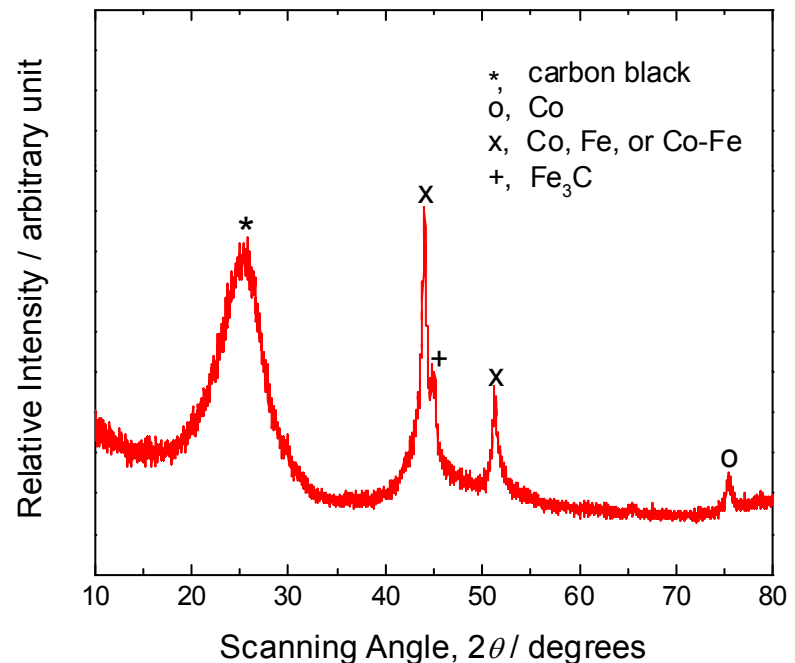
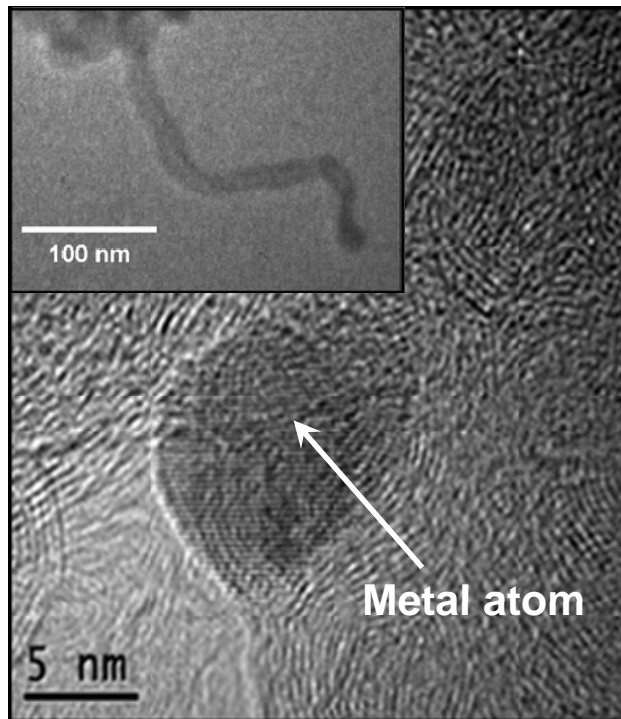


HIGHLIGHT

Iron has the ability to alloy with carbon and nitrogen and at 800 °C the saturation of iron particles relieves by the precipitation of carbon and nitrogen. (S. Maldonado and K. J. Stevenson, *J. Phys. Chem. B*, 109 (2005) 4707).

- **Anode:** E-TEK 20% Pt/C (0.4 mg cm⁻² Pt)
- **Cathode:** 2 mg cm⁻² of carbon composite catalyst
- **Membrane:** Nafion™ 112
- **Operating temperature:** 77 °C (H₂); 75 °C (O₂); 75 °C (cell)

Active Sites: TEM and XPS



HIGHLIGHT

- Metal atoms are covered with several graphitic layers.
- Nanostructured fiber of graphitic carbon was formed as a result of metal-catalyzed pyrolysis.
- No metal traces were detected on the surface of carbon-based composite catalyst.

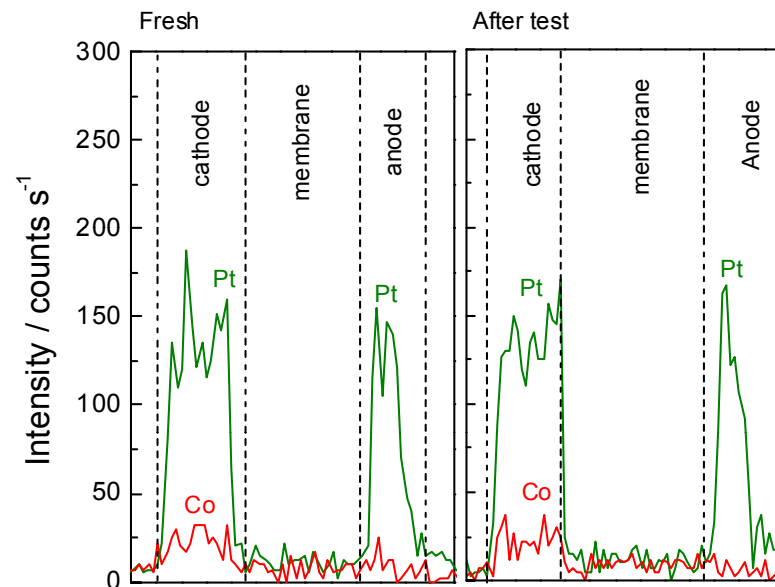
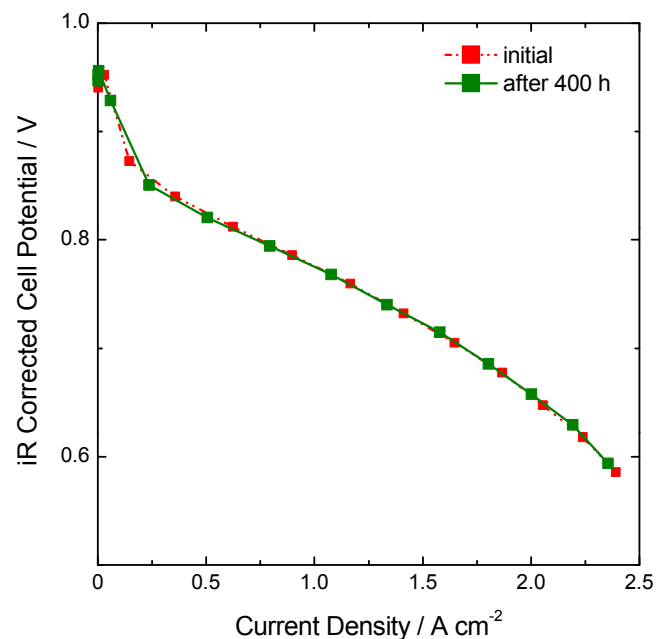
HIGHLIGHT

- In carbon composite catalyst, metals and cementite (Fe_3C) species are present inside the carbon particles.
- No metallic element on the surface was detected by XPS.

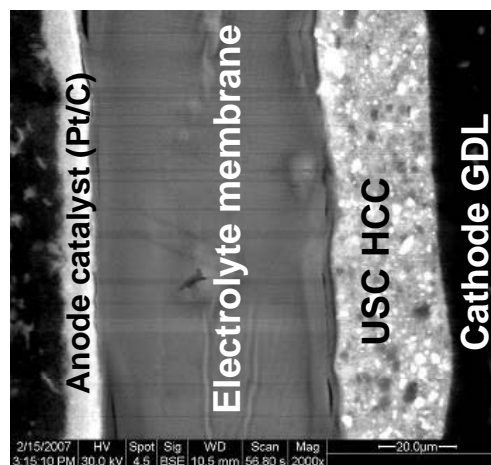
Previous Accomplishments at University of South Carolina

Development of Low Pt Loading Cathode Catalyst

Stability of USC HCC in Fuel Cell

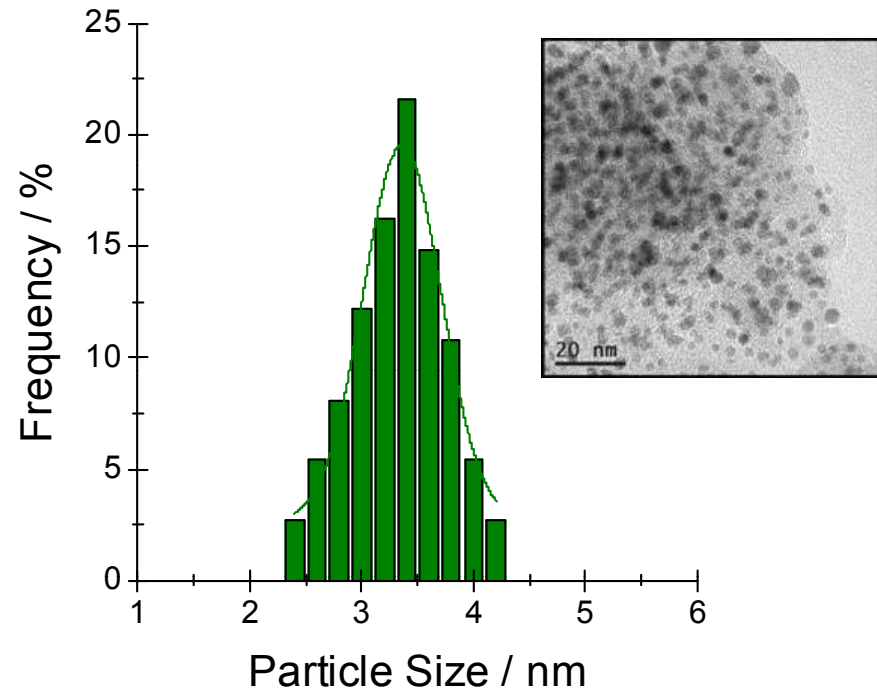
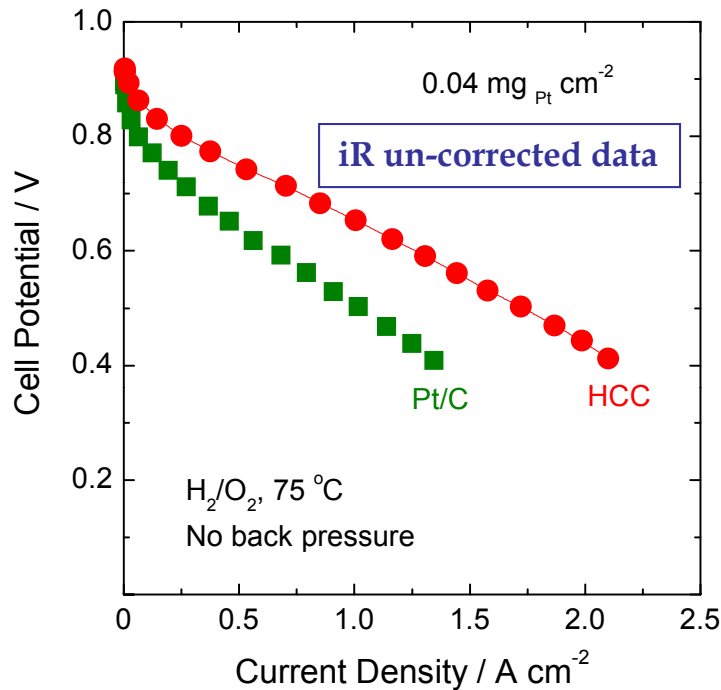


- **Cathode:** 0.4 mg cm⁻² Pt-Co
- **Anode:** 0.5 mg cm⁻² ETEK Pt
- **Membrane:** Nafion 112
- **Operating conditions:**
 - (i) H₂/O₂
 - (ii) no back pressure
 - (iii) 77/75 °C



No dissolution of Co from the catalyst and diffusion into the membrane after 400 h of continuous operation.

Comparison of Catalytic Activity: Fuel Cell Studies

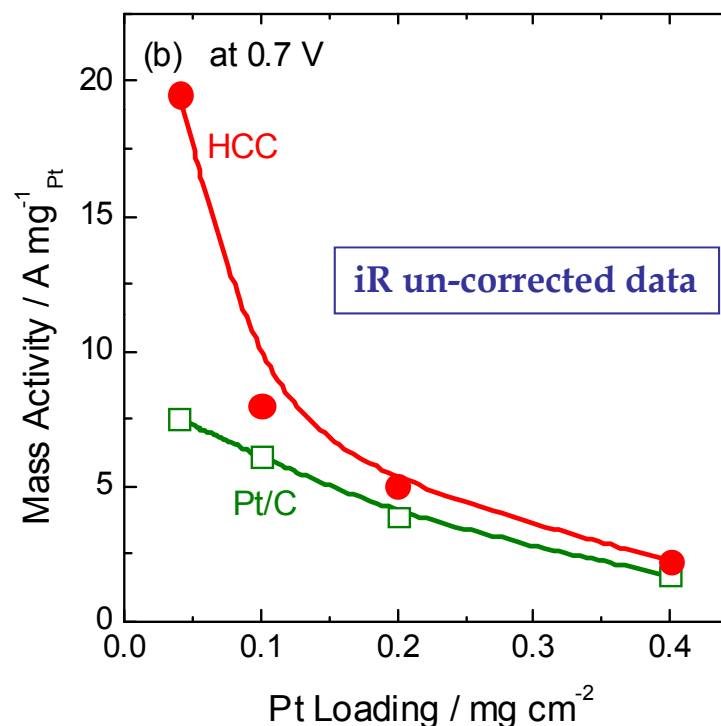
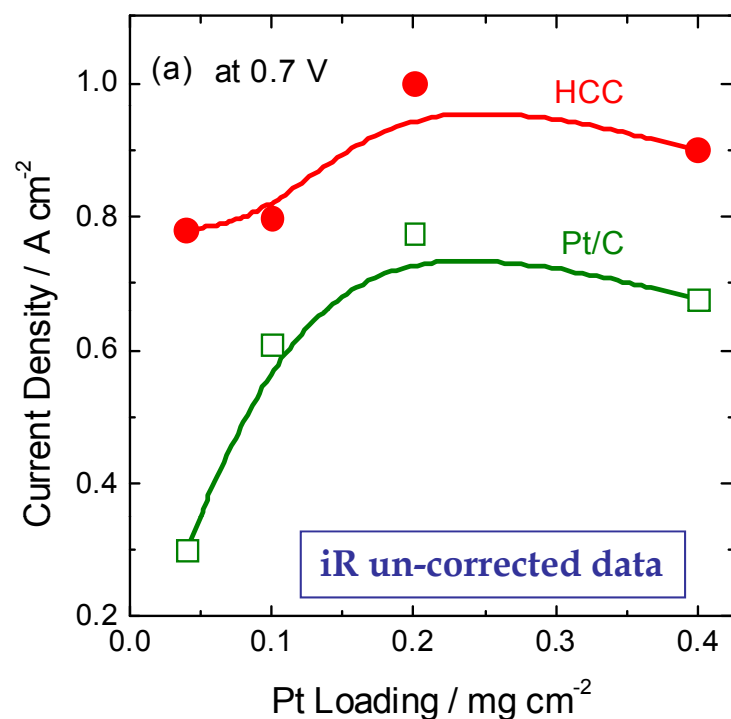


HIGHLIGHT

- CCC is highly active for oxygen reduction, while carbon black is inactive.
- The catalytic performance of HCC is higher than Pt/C according to both RDE and fuel cell test.

TEM: The USC HCC catalyst shows more uniform dispersion of particles over the active support with small average particle size and narrower distribution.

Effect of Pt Loading on Catalytic Activity: Fuel Cell Study



HIGHLIGHT

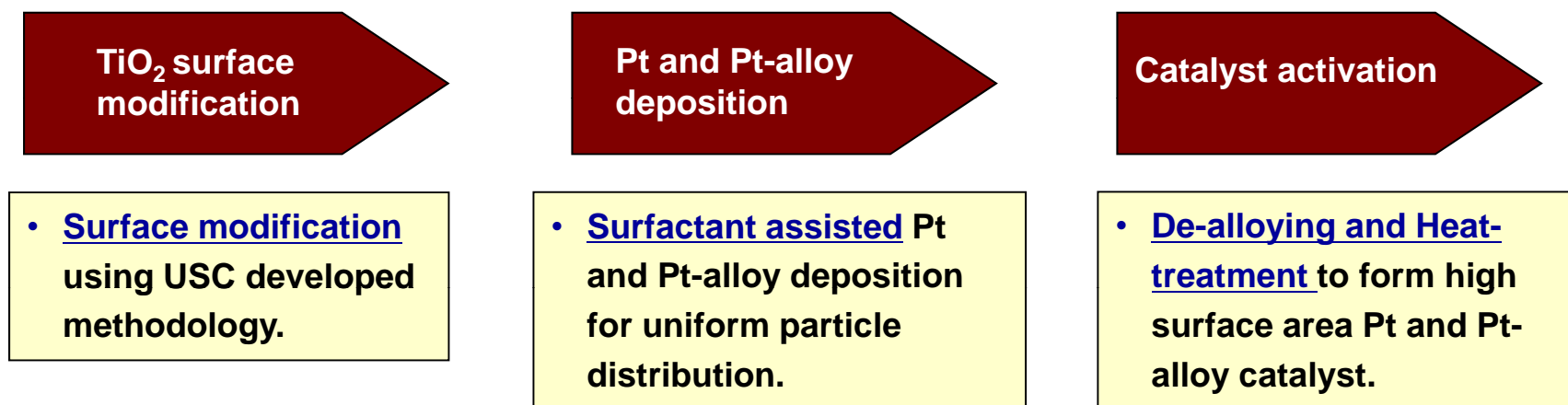
- The mass activity of HCC shows a 150% enhancement when Pt loading is decreased from 0.1 to 0.04 mg cm⁻² due to the contribution from the support at ultra-low Pt loading.

Previous Accomplishments at University of South Carolina

Development of TiO_2 Supported Pt Catalyst

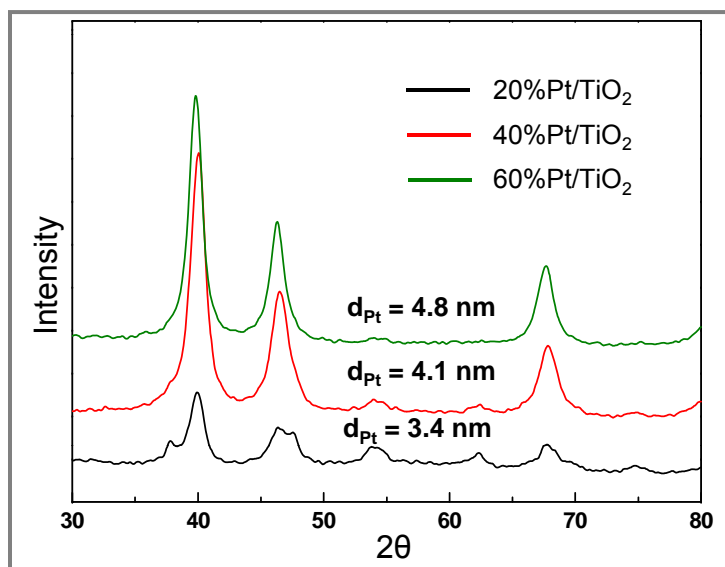
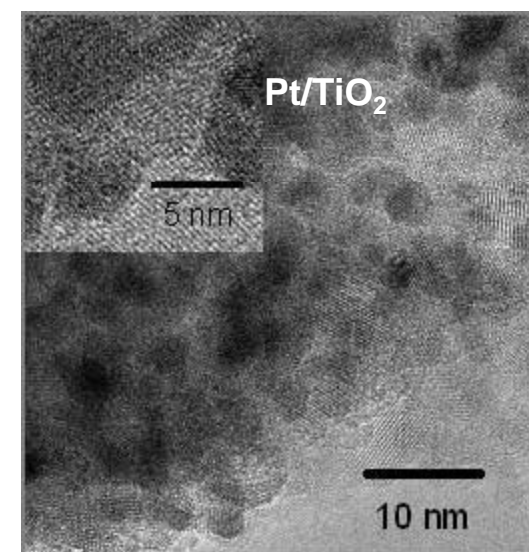
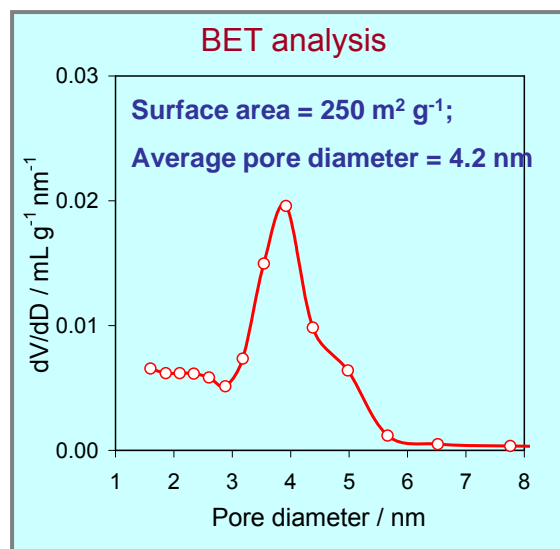
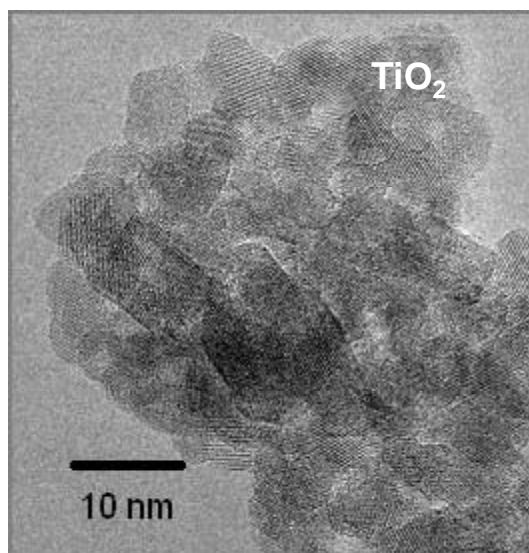
USC Strategy: Pt/TiO₂ Catalyst

Strategy: Modification of titanium dioxide support for the facile deposition of Pt and Pt-alloy catalysts.



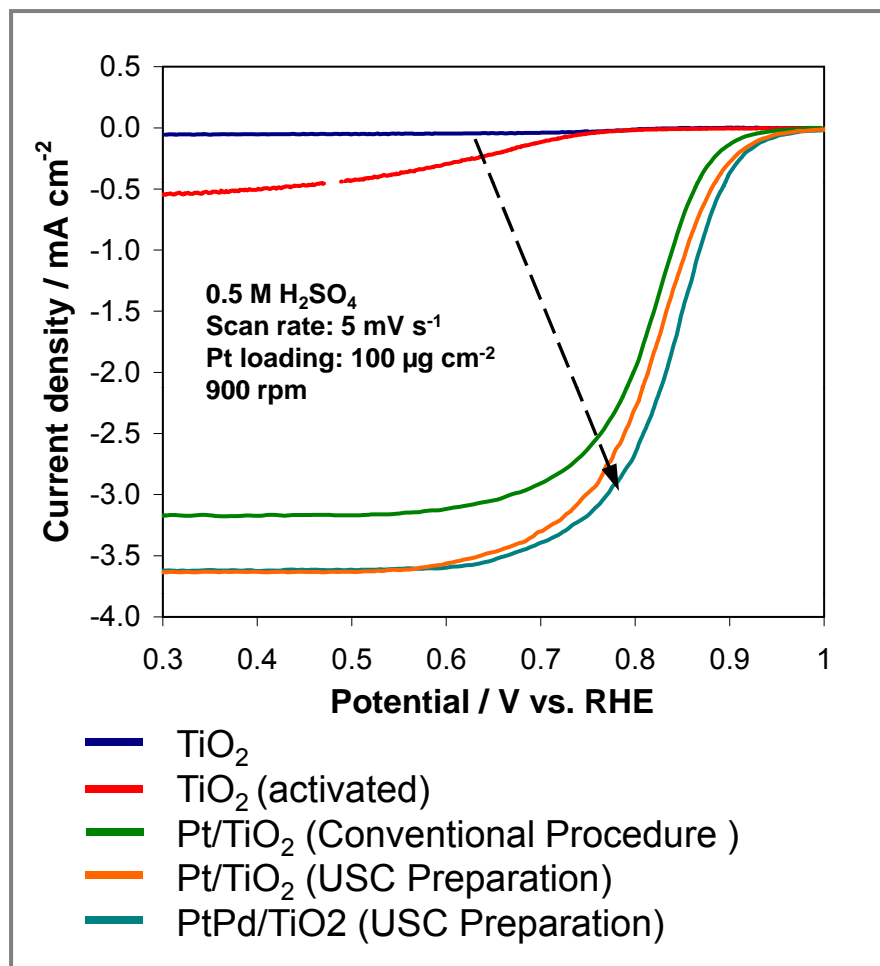
Popov et.al., *J. Am. Chem. Soc.*, 131 (2009) 13898-13899
Popov et.al., *Appl. Catal. B: Environmental*, 96 (2010) 224-231

Characterization – TiO₂ and Pt/TiO₂



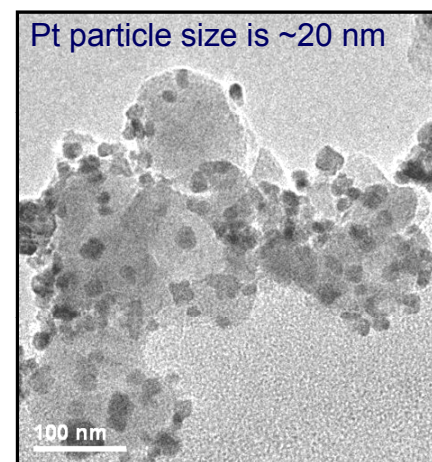
- Surface area of TiO₂ = 250 m² g⁻¹.
- Pt particles with d_{Pt} = 3-5 nm were deposited on TiO₂.
- Pt particle size can be optimized by controlling the nucleation rate.

Optimization Studies on Pt/TiO₂ Catalysts: LSV

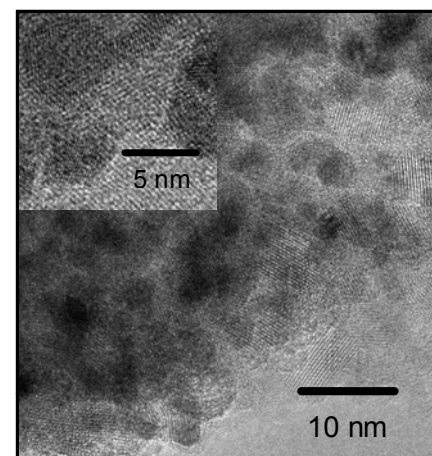


Pt and PtPd nanoparticles (3-6 nm) can be deposited on to TiO₂ supports using USC developed procedure.

Conventional procedure for Pt deposition

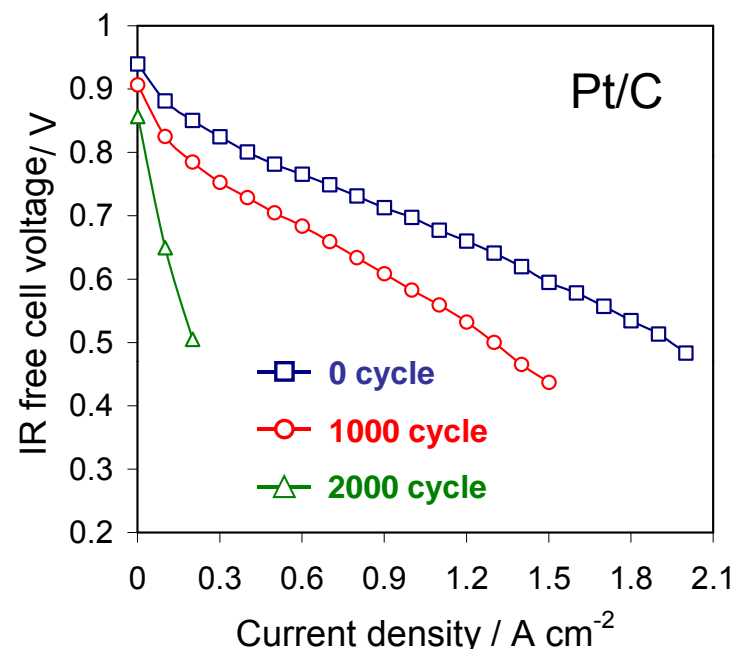
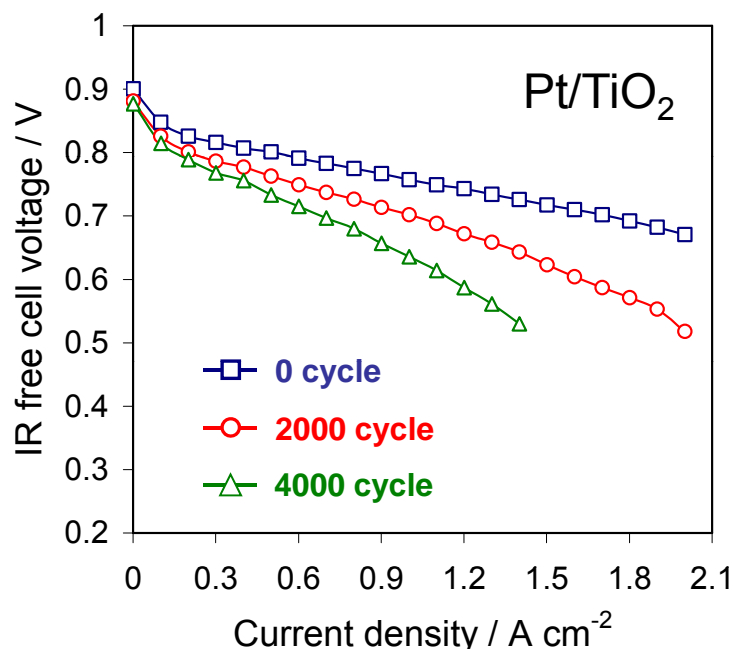


USC deposition procedure



Pt particle size is 3 – 6 nm

Accelerated Durability Test of Different Catalysts – CV Cycling between 0.6 and 1.4 V (Fuel Cell)



IV curves were obtained after CV cycles.

Membrane: Nafion® 112; Cell area: 25 cm² cell.

Anode: 0.5 mg Pt cm⁻² (E-TEK); Cathode: 0.4 mg Pt cm⁻².

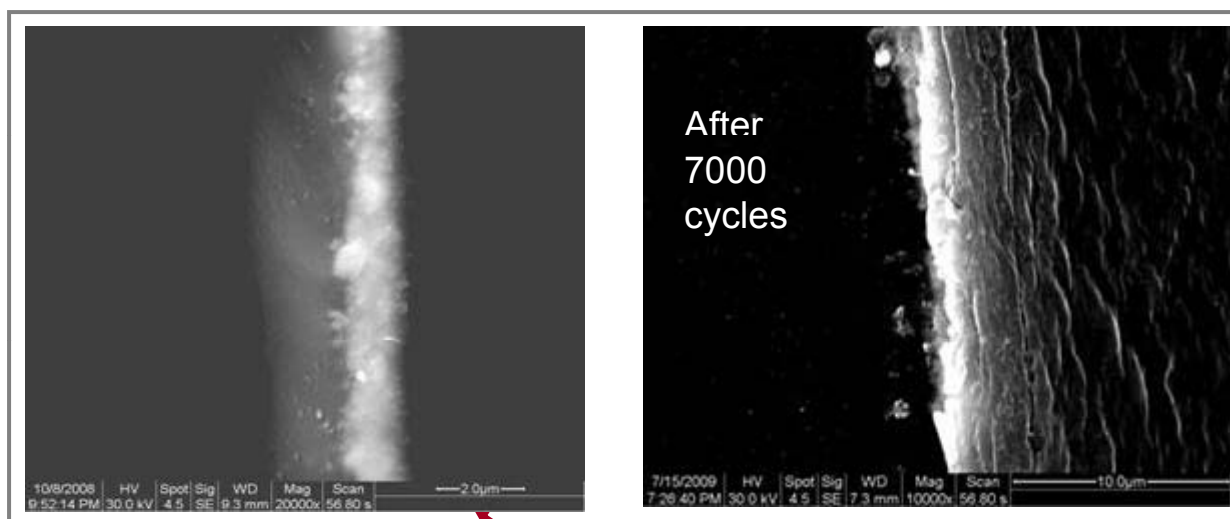
Operating conditions: (i) H₂/air; (ii) 25/25 psi; (iii) 80 °C.

Flow rate H₂/air: 1.2/2 Stoich; Humidity: 100% RH.

- Slight decrease in cell voltage (0.09 V) at 0.8 A cm⁻² was observed after 4000 cycles for Pt/TiO₂.
- Pt/C exhibited a large voltage drop after 2000 cycles due to carbon corrosion and detachment and agglomeration of catalyst particles.

Cross-section Analysis of MEA with Pt/TiO₂ and Pt/C Cathodes

Pt/TiO₂ cathode

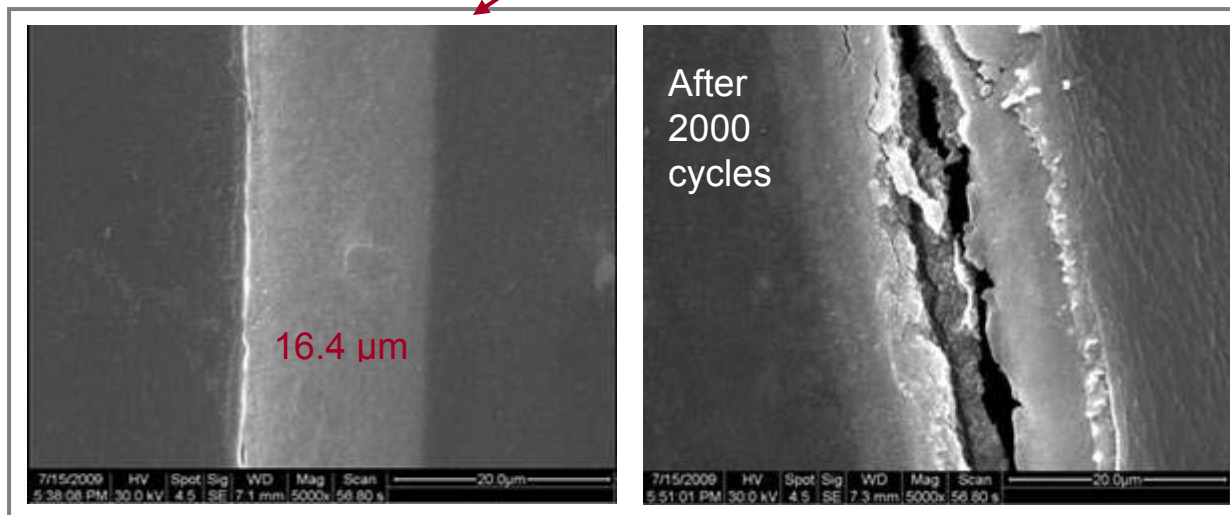


- Pt/TiO₂ electrode retained a similar morphology and catalyst layer thickness (1 μm) before and after ADT.

Pt/C cathode

Initial state

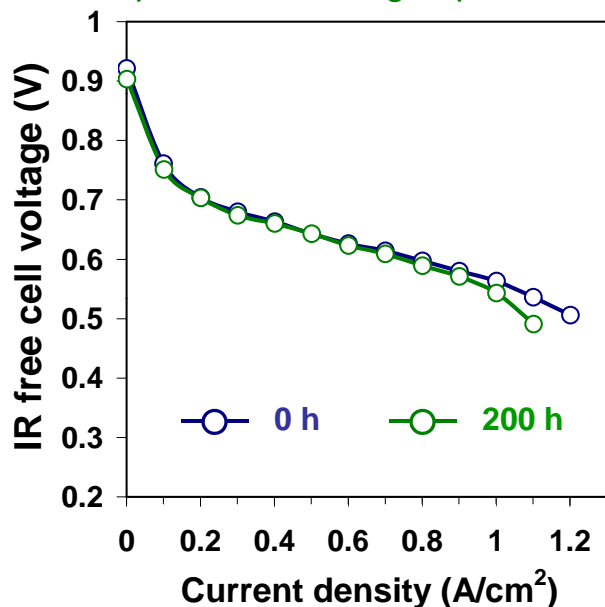
After test



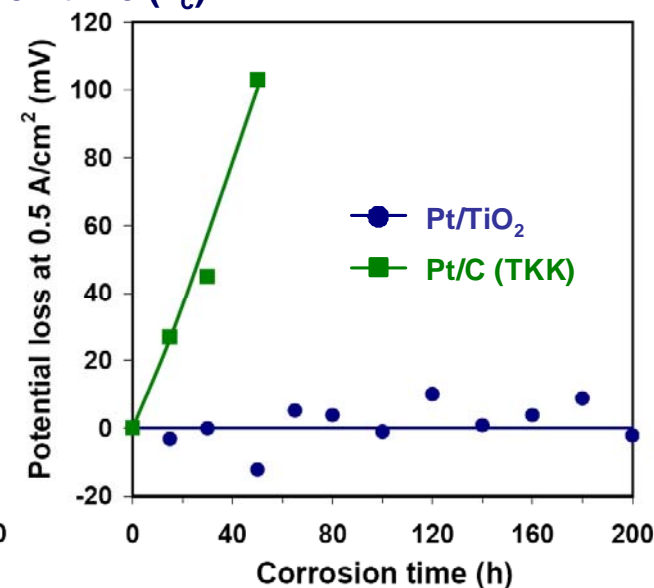
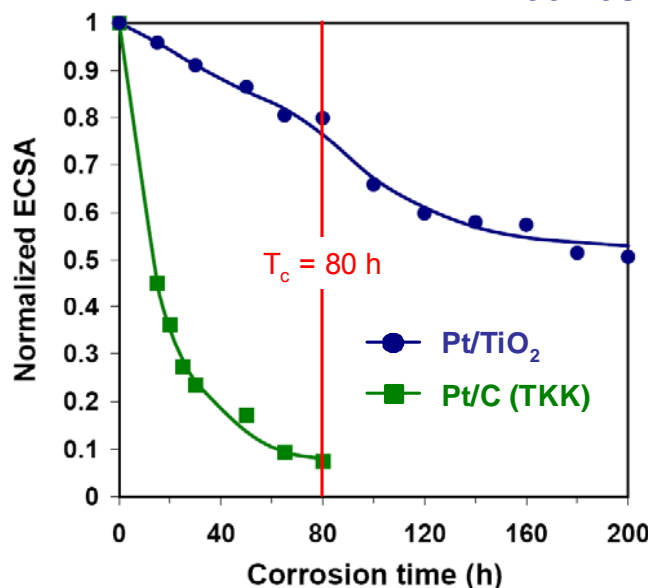
- Cracks were observed in the Pt/C cathode after ADT due to disintegration of the catalyst layer.

Accelerated Corrosion Test of Pt/TiO₂ and Pt/C Catalysts - Effect of Potential Holding at 1.2 V on Fuel Cell Performance

IV curves were obtained after potential holding experiment.



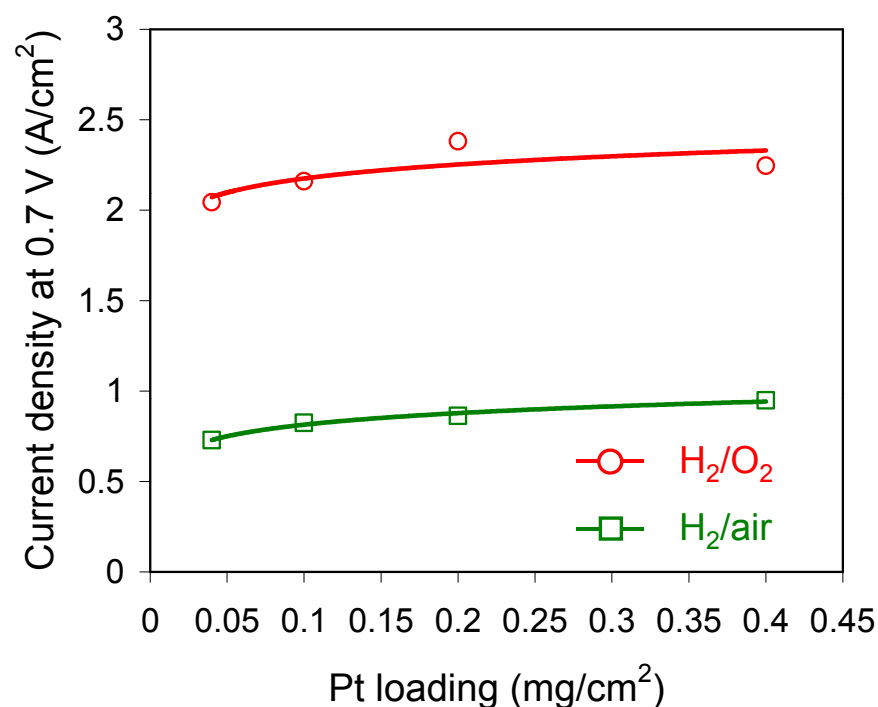
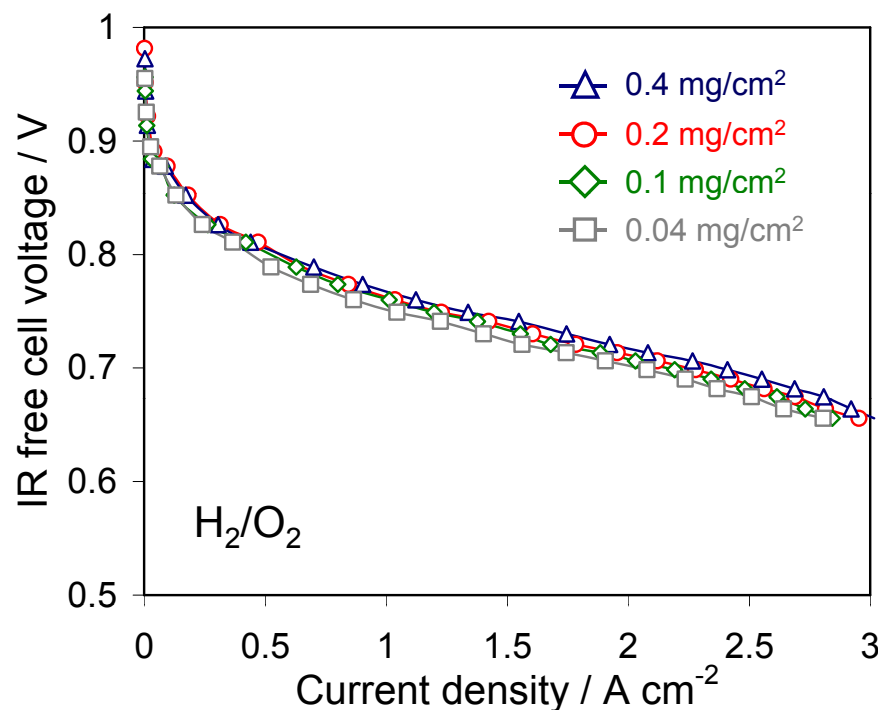
Normalized ECSA and potential loss at 0.5 A cm⁻² as a function of corrosion time (T_c)



Membrane: Nafion® 112.
 Anode: 0.5 mg Pt cm⁻² (Pt/C, E TEK).
 Cathode: 0.4 mg cm⁻² Pt catalysts.
 Operating conditions: (i) H₂/air;
 (ii) 150 kPa; (iii) 80 °C;
 (iv) 25 cm² cell;
 (v) flow rate H₂/air: 3/3;
 (vi) humidity: 50% RH.

- Pt/C electrocatalyst showed a rapid decay (93%) in ECSA at T_c = 80 h.
- For Pt/TiO₂, total loss of ECSA is ~20% after T_c = 80 h.
- No decrease in catalytic activity up to 200 h when compared to Pt/C (45%, TKK) at 0.5 A cm⁻² when polarized at 1.2 V.

Fuel Cell Performance of Pt/TiO₂ Cathode Catalyst: Effect of Pt loading



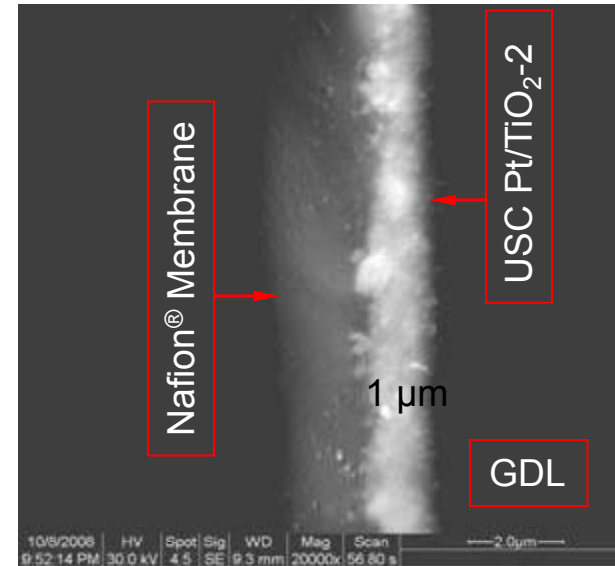
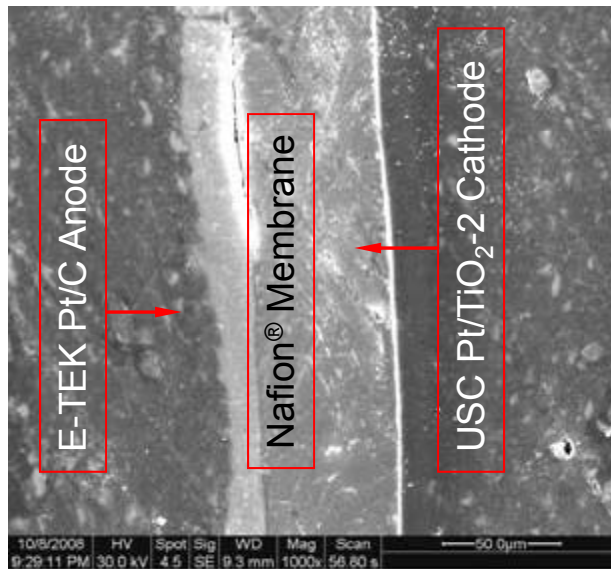
Membrane: Nafion[®] 112; Cell area: 5 cm² cell.

Anode: 0.5 mg Pt cm⁻² (Pt/C, E-TEK); Cathode: Pt/TiO₂ catalyst.

Operating conditions: (i) H₂/O₂ or air; (ii) no back pressure; (iii) 77/75 °C; (iv) 5 cm² cell; (v) Flow rate H₂/O₂/air: 150/150/300 ccm; (vi) Humidity: 100% RH.

- Current density at 0.7 V is 2.25, 2.38, 2.16, and 2.04 A/cm² for 0.4, 0.2, 0.1, and 0.04 mg_{Pt}/cm².

Cross-section Analysis of MEA with Pt/TiO₂ Cathode



- Very thin cathode catalyst layer (~1 μm) can be made using USC developed methodology.
- USC developed methodology enables to load Pt (3-5 nm) up to 60% uniformly on the TiO₂ support.

Summary (Previous Accomplishments)

USC HCC Catalyst

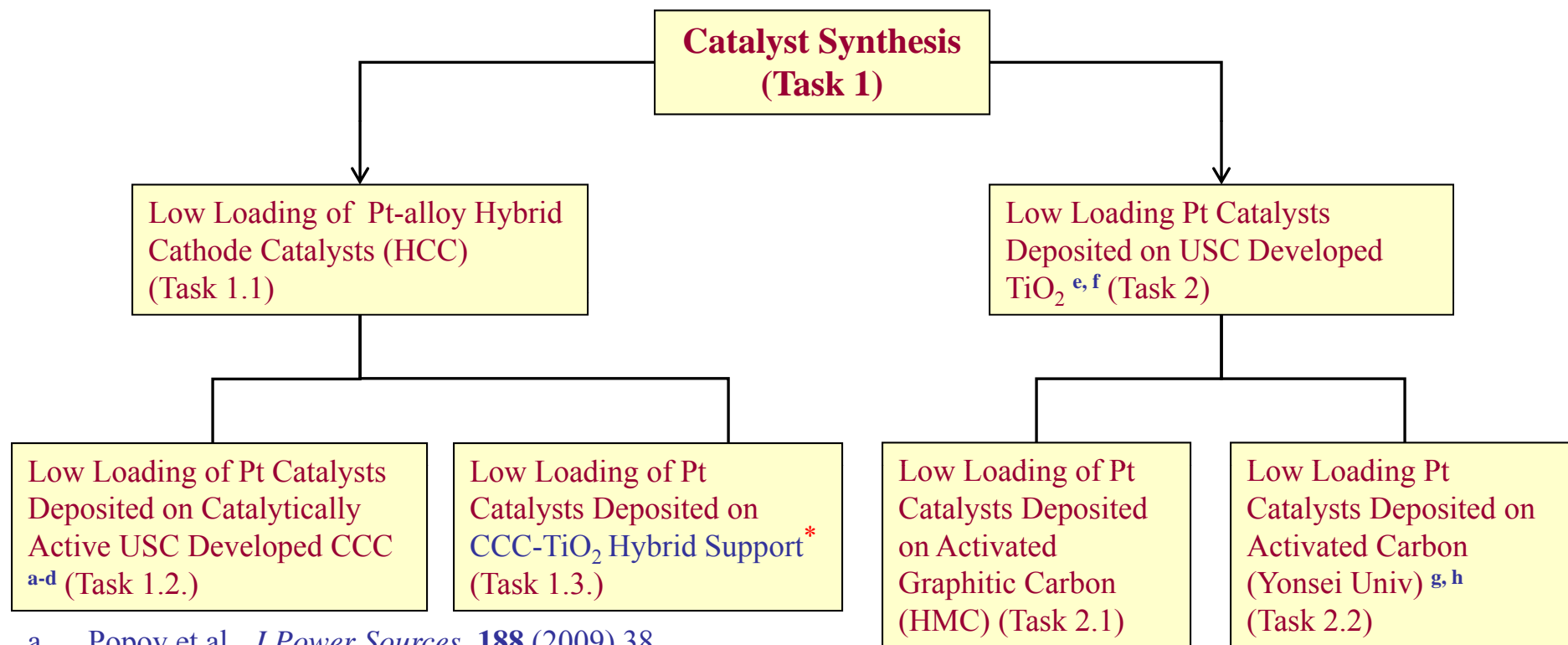
- ❖ USC HCC catalyst shows higher performance than Pt/C at all loadings between 0.04 and 0.4 mg cm⁻².
- ❖ The mass activity of HCC shows a 150% enhancement when Pt loading is decreased from 0.1 to 0.04 mg cm⁻² due to the contribution from the support (CCC) at ultra-low Pt loading.

Low Loading Leached Pt Catalyst (USC Developed TiO₂ Support)

USC Pt/TiO₂ Catalyst

- ❖ Slight decrease in cell voltage (0.09 V) at 0.8 A cm⁻² was observed after 4000 cycles (cycling between 0.6 and 1.4 V) for Pt/TiO₂. Pt/C exhibited a large voltage drop after 2000 cycles due to carbon corrosion and detachment and agglomeration of catalyst particles.
- ❖ Pt/TiO₂ do not show any decrease of fuel cell performance after 200 h DOE accelerated corrosion test. Pt/C electrocatalyst showed a rapid decay (93%) in ECSA after 80 h.

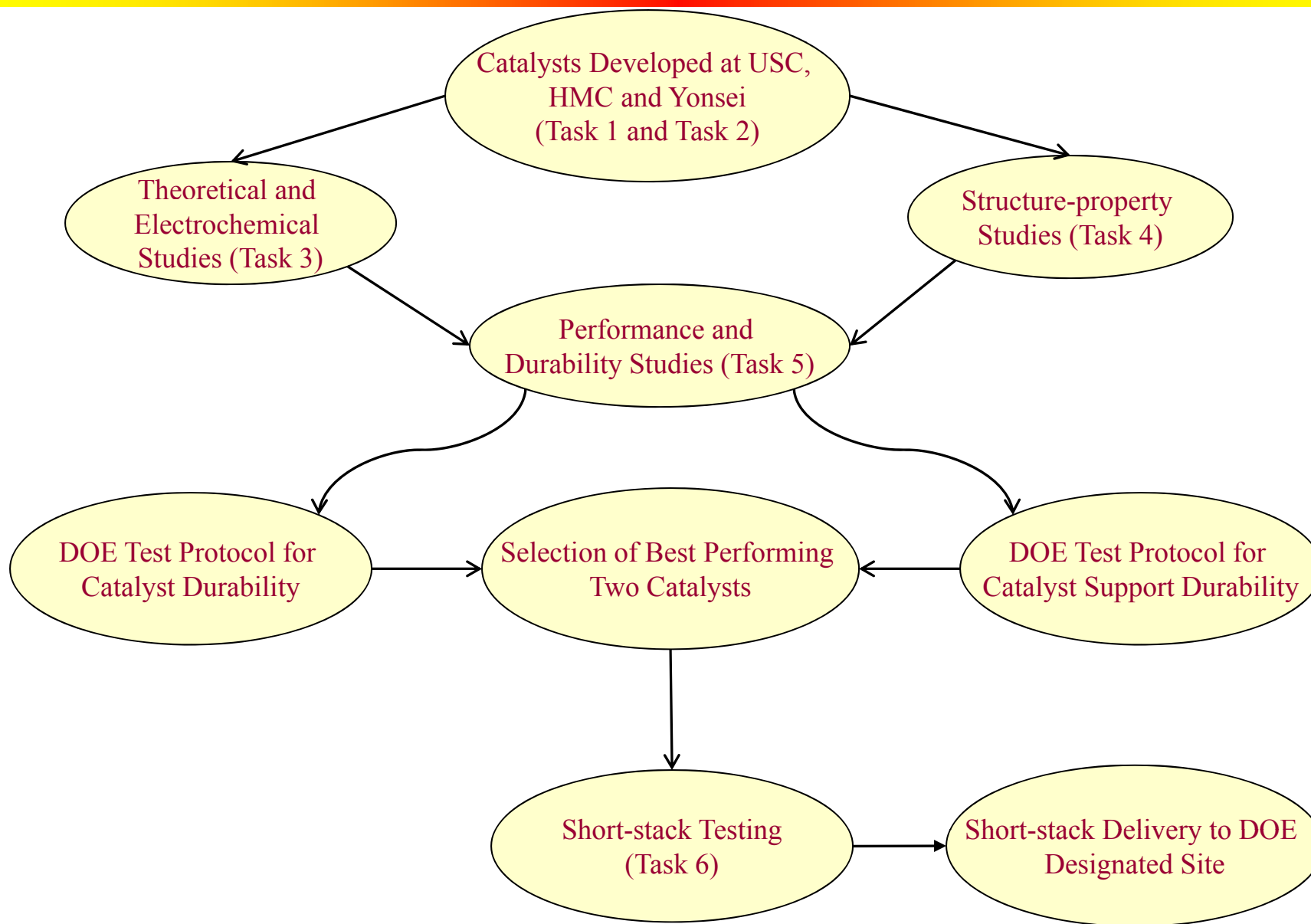
USC Approach and Future Work (Catalyst Synthesis Based on Leached Pt-alloy Catalysts Deposited on CCC, TiO₂, Activated Graphitic Carbon Supports)



- a. Popov et.al., *J Power Sources*, **188** (2009) 38.
- b. Popov et.al., *Appl. Catal. B: Environmental*, **93** (2009) 156.
- c. Popov et.al., *J Power Sources*, **183** (2008) 34.
- d. Popov et.al. *J. Power Sources*, **157** (2006) 56.
- e. Popov et.al., *Appl. Catal. B: Environmental*, **96** (2010) 224.
- f. Popov et.al., *J. Am. Chem. Soc.*, **131** (2009) 13898.
- g. Kim et.al., *Electrochem. Commun.*, 11 (2009) 1131.
- h. Kim et.al., *Electrochim. Acta*, 54 (2009) 6515.

* Hybrid support made of carbon composite catalyst and metal oxide (TiO₂)

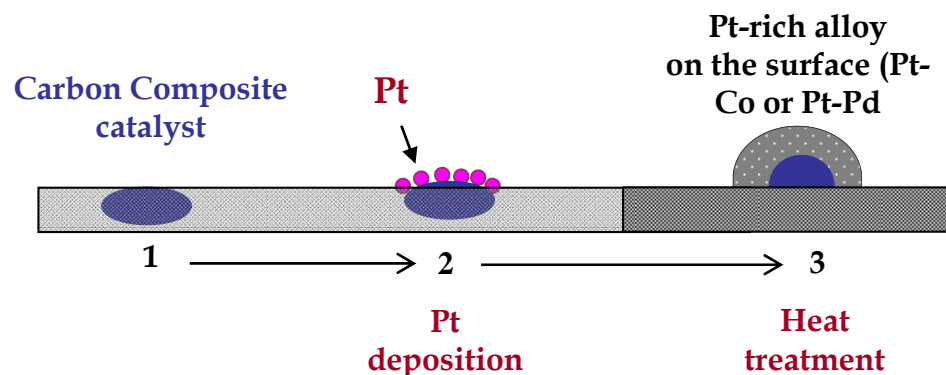
USC Approach and Future Work (Catalyst Performance Evaluation)



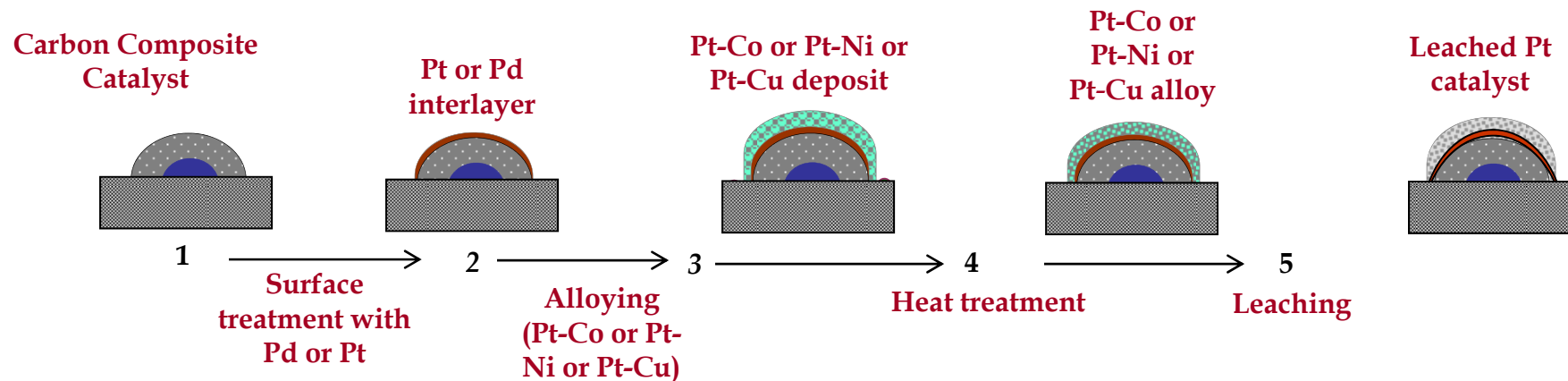
Proposed Future Work

- **Objectives:** To synthesize low cost, high stability leached Pt catalysts with high performance using different catalyst supports.

USC methodology 1 – Development of hybrid cathode catalyst

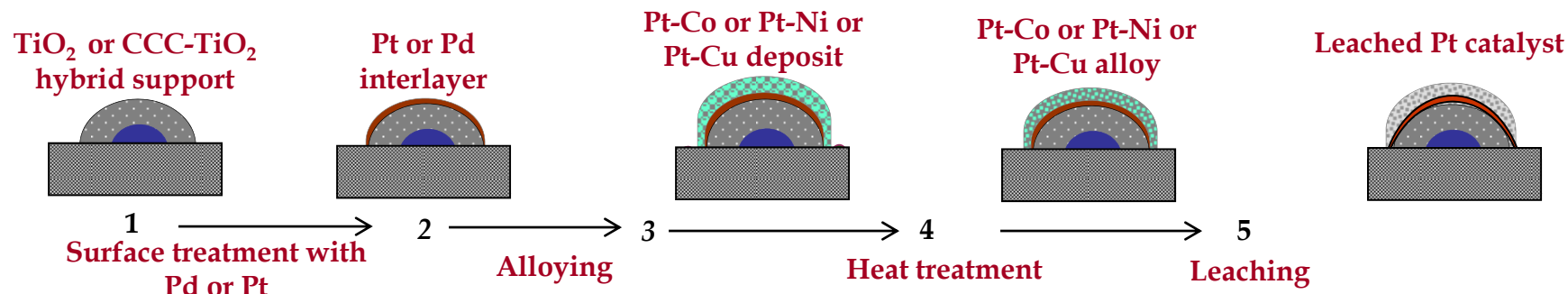


USC methodology 2 – Development of leached hybrid catalysts

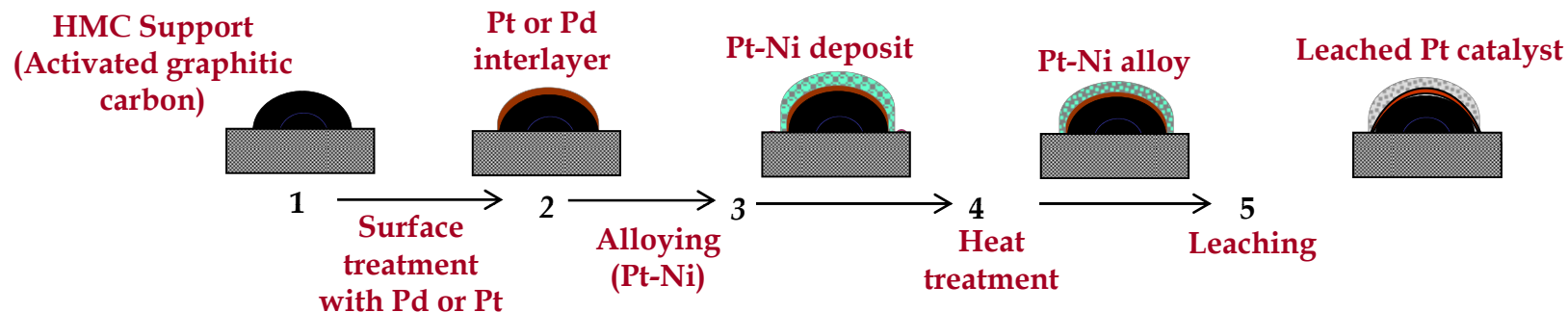


Proposed Future Work

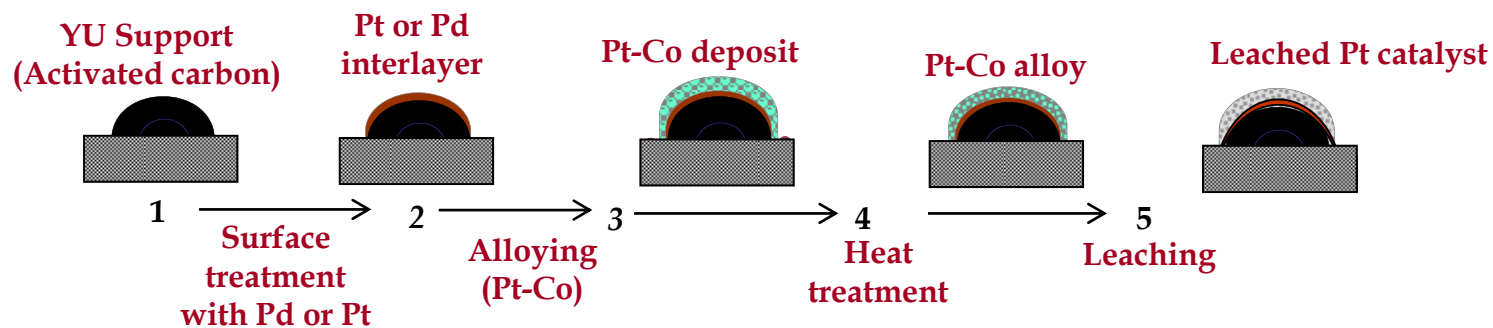
USC methodology 3 – Development of Pt leached hybrid catalysts



HMC methodology – Development of Pt leached catalysts

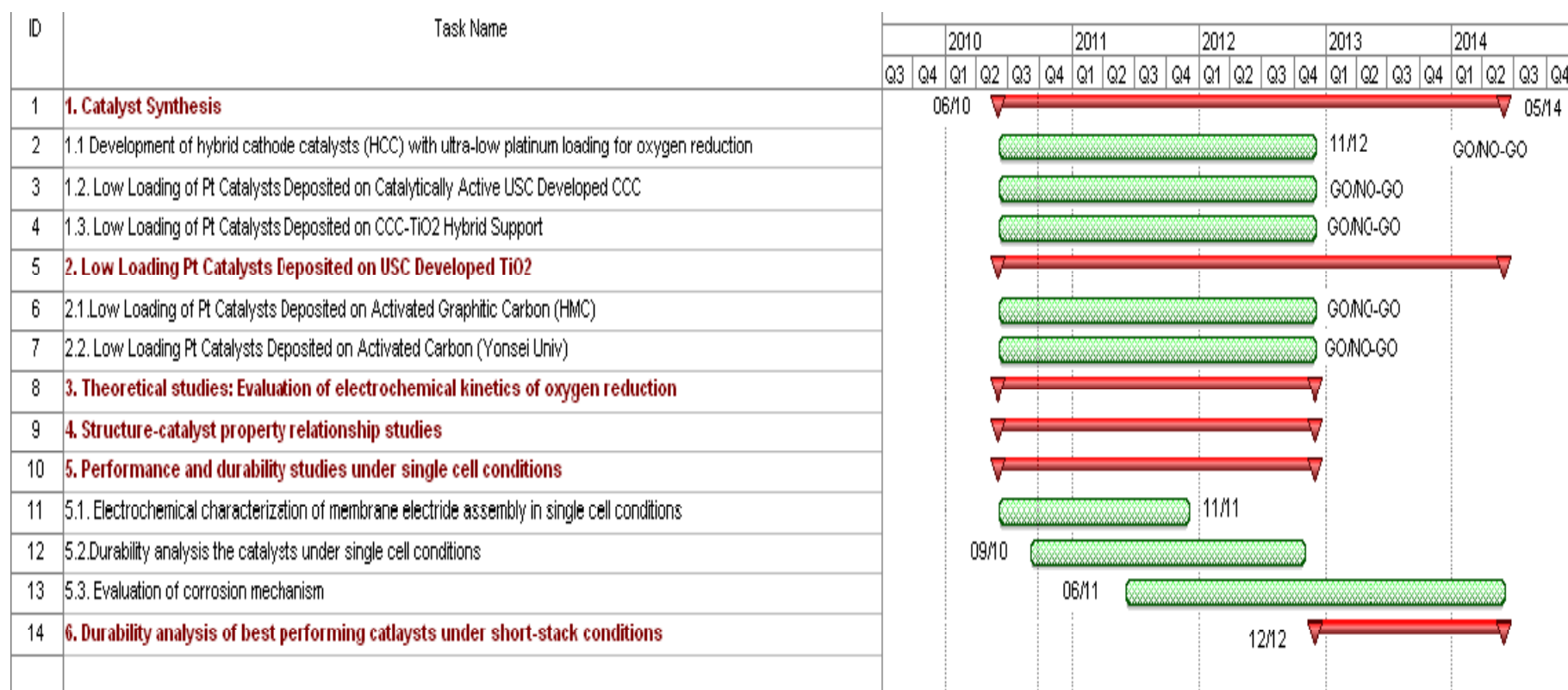


Yonsei University methodology – Development of Pt leached catalysts



Project Timeline

Catalyst Synthesis Based on Leached Pt-alloy Catalysts Deposited on CCC, TiO_2 , Activated Graphitic Carbon Supports



Task Duration

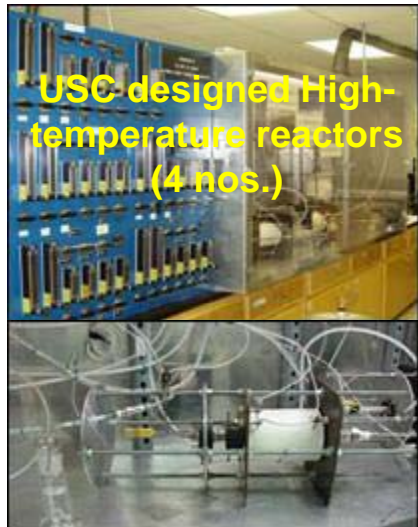


Subtask Duration

Milestone Schedule

	Tasks	Milestone or Go/No-Go Decision
Phase I	<ol style="list-style-type: none"> 1. Catalyst synthesis Go/No-Go decision: Leached Pt-Co/CCC, Pt-Ni/CCC, Pt-Cu/CCC 2. Low Loading Pt Catalysts Deposited on USC Developed TiO₂ Go/No-Go decision: Pt/TiO₂, leached Pt-Co/TiO₂, Pt-Cu/TiO₂, Pt-Co/CCC-TiO₂, Pt-Cu/CCC-TiO₂, Pt-Ni/HMCS, Pt-Co/YUS 3. Theoretical/Electrochemical studies 4. Structure-property studies 5. Performance and durability studies under single cell conditions 	
Phase I Milestone		<ul style="list-style-type: none"> • Low peroxide formation (<1% H₂O₂) • Uniform Pt catalyst distribution with 3-4 nm size particle size • Pt loading < 0.2 mg/cm²; 0.2 g/kW • Electrochemical surface area >50 cm² • Catalyst stability (≤30 mV loss at 0.8 A/cm² and support stability (DOE AST for catalysts and supports) • Durability > 2000 h at ≥80 °C • Construction of single cell with optimized catalyst
Phase II	6.	Durability analysis of selected catalysts under short-stack conditions
Phase II Milestone		<ul style="list-style-type: none"> • Durability analysis of best performing catalyst under short-stack conditions • Ultra-low Pt loading of 0.2 mg/cm² at power density of 0.2 gPt/kW • Delivery of short-stack (up to 10 cells) to DOE designated site.

Facilities at USC



USC designed High-temperature reactors (4 nos.)



BET surface area analyzer



JEOL HR-TEM



Automatic coater



FISCHER X-ray Fluorescence



Micromeritics Hg Porosimeter



Zeiss Ultra Plus HR-SEM



Fuel cell technologies Dual fuel cell test station (2 nos.)



RRDE - PINE (2 nos.)



FEI Quanta ESEM



Scribner fuel cell test station (2 nos.)

Facilities at Eco-Technology Research Center (HMC)



100 kW Stack Test Station



Environmental Chamber



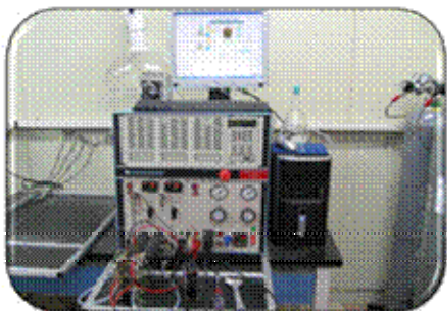
100W-1kW Test Stations



Multi Channel Test Station

Facilities at Yonsei University

No.	Facility	Qunatity	Purpose
1	Fuel cell test station	5	Single cell performance test
2	RRDE (Rotating Ring Disk Electrode)	1	Electrochemical characterization
3	Multi-Potentiostat / Impedance	6	Electrochemical characterization
4	Mass spectrometry	1	Qualitative and quantitative analysis of gas
5	ICP (Inductively Coupled Plasma)	1	Quantitative analysis of element
6	XRD (X-Ray Diffractometer)	1	Structural characterization
7	TGA (Thermogravimetric Analyzer)	1	Evaluation of thermal stability
8	BET	1	Measurement of the specific surface area
9	HR-TEM (High Resolution - Transmission Electron Microscope)	1	Fine structure analysis
10	AFM (Atomic force microscopy)	1	Surface morphology analysis



Fuel cell test station



ICP



TGA

Summary

- Ultra-low loading Pt catalysts for oxygen reduction reaction with high activity (high electrochemical surface area) and good stability will be developed through:
 - Synthesis of hybrid cathode catalyst (HCC).
 - Synthesis of activated low loading platinum catalysts with high electrochemical surface area deposited on conductive TiO_2 and active CCC- TiO_2 hybrid supports.
 - Synthesis of leached Pt-Ni alloy catalysts with high electrochemical surface area Pt deposited on activated graphitic carbon developed at HMC.
 - Synthesis of leached Pt-Cu catalysts with high electrochemical surface area Pt deposited on activated carbon developed at Yonsei University.
 - ❖ **Facile scale-up synthesis procedure for the production of all the suggested catalysts.**
 - Pt-alloy particle agglomeration during annealing process at high temperature will be eliminated using a procedure developed at Yonsei University.
 - The inter-particle resistance and the catalyst particle detachment from the support will be minimized by:
 - ✓ the introduction of a thin interlayer of Pt or Pd between the support and optimization
 - ✓ optimization of Pt and alloying metal composition.
 - Synthesis of high distribution of Pt with high initial loading over carbon support without Pt loss.
 - Engineer membrane electrode assembly (MEA) with thin catalyst layer and optimize the catalyst-catalyst support ratio

Team Members who contributed to this presentation

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