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

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Project ID # FC088

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Overview

Timeline

- Start date: June 2010
- End date: Dec 2012 (Phase I)
  : May 2014 (Phase II)
- Percent complete: 50%

Budget

- Total project funding
  - DOE share: $ 4,400,000
  - Contractor share: $1,100,000
- Funding received FY 11: $750,000
- Planned Funding FY 12: $1,000,000

Partners

- Yonsei University (YU), S. Korea
- Hyundai Motor Company (HMC), S. Korea (Funding ended in Dec 2011; will resume in Dec 2012)

Barriers

- Catalyst performance
- Catalyst durability
- Scale-up synthesis procedures

DOE Technical Targets

Electrocatalyst/MEA	2017 Targets
PGM Loading (mg/cm^2)	0.125
Mass Activity (A/mg_{Pt})	0.44
ECSA Loss after 30K Cycles (Catalyst Stability) (%)	≤ 40
ECSA Loss after 400 h (Support Stability) (%)	≤ 40

Project Lead

- University of South Carolina (USC)

Additional Interactions

- Rudiger Laufhutte (Univ. Illinois)
- Dr. JoAn Hudson (Clemson University)

Relevance and Approach

Objectives: Development of high performance, low cost and durable cathode catalyst and support able to meet the 2017 DOE targets.

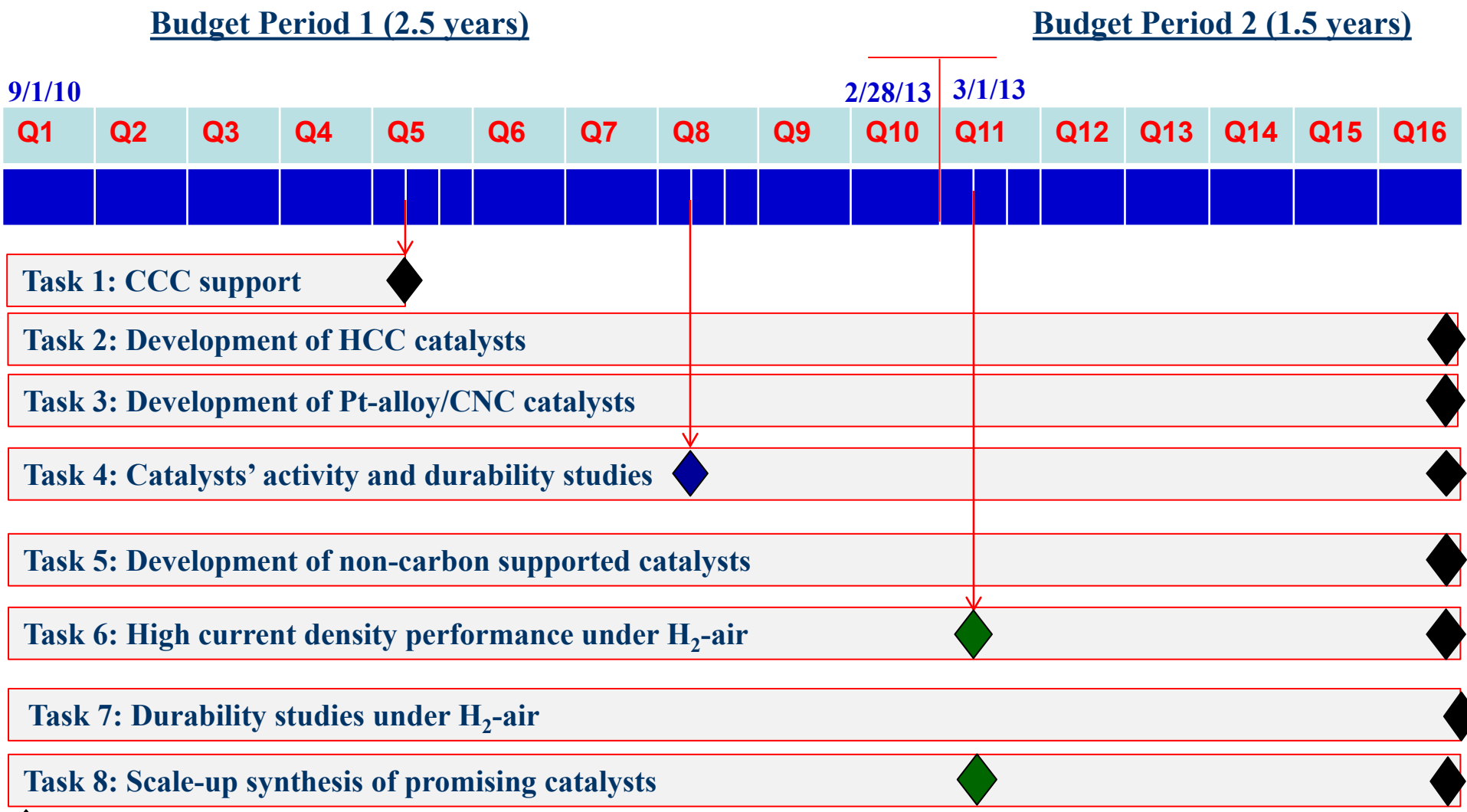
Approach:

- Optimization studies of **carbon composite catalyst** (**CCC**) support. (USC)
- Development of advanced hybrid catalyst based on CCC support and Pt [low Pt-alloy loading catalyst]. (USC)
- Development of **carbon nanocage** (**CNC**) supported Pt-alloy catalyst (Pt-alloy/CNC). (YU)
- Synthesis of corrosion resistant hybrid TiO_2–CCC support (USC)
- Development of high volume procedures for the synthesis of promising catalyst. (USC & YU)

Primary Focus for Past Year:

- Performance evaluation of USC Pt/C catalyst.
- Performance evaluation of CCC support. (USC)
- Evaluation of different strategies for the optimization of **hybrid cathode catalyst** (**HCC**) with total loadings of 0.2 mg_{Pt} /cm^2 /MEA. (USC)
  - Initial and durability of kinetic mass activities.
  - Initial high current density performance in H_2-air.
- Performance evaluation of Pt-alloy/CNC catalyst activity and durability with total loadings of 0.2 mg_{Pt} /cm^2 /MEA. (YU)
  - Initial and durability of kinetic mass activities.
  - Initial high current density performance in H_2-air.

Project Timeline and Milestones*



End of task.

Go-No-Go decision for the selection of 2 promising catalysts with high mass activity, specific activity and durability.

Go-No-Go decision for the selection of 2 promising catalysts to be tested under short-stack conditions.

*Milestones are explained in slides 5 & 6

Milestones

- **Milestone 1**: **Sep 2011**: **Preparation of carbon composite catalyst (support) (Task 1)**

  Status: Achieved onset potential for oxygen reduction reaction close to 0.9 V and < 2.5% H_2O_2 production. The CCC support is stable after 10 k cycles (0.6-1.0 V) under RRDE.

- **Milestone 2**: **Sep 2011**: **Initial mass activity and specific activity (Tasks 2, 3 and 4)**

  Status: (i) Accomplished initial mass activity of 0.45 A/mg_{Pt} and specific activity of 1036 $\mu A\ cm^{-2}$ for the **USC** Pt_2Ni_1/C catalyst.

  (ii) Accomplished initial 0.44 A/mg_{Pt} and specific activity of 1023 $\mu A\ cm^{-2}$ for **YU** Pt_2Ni_1/CNC catalyst.

  (iii) The initial mass activity values for **USC** Pt_2Ni_1/C catalyst and **YU** Pt_2Ni_1/CNC satisfy the 2017 DOE mass activity target of 0.44 A/mg_{Pt}

- **Milestone 3**: **Jun 2012**: **Durability of kinetic mass activity at least 0.24 A mg_{Pt}^{-1} after 30 k cycles tested according to DOE protocol (0.6-1.0 V). (Task 4)**

  Status: Achieved 0.3 A mg_{Pt}^{-1} after 30 k cycles for Pt_2Ni_1/CNC (**YU**) catalyst in 25 cm^2 cell. Need similar or higher performance for USC HCC catalysts and to be confirmed in a 50 cm^2 cell in at least two laboratories.

  The durability of mass activity and support stability for USC catalysts are planned to be accomplished in June 2012 and will be reported in July 2012 quarterly report.

Jun 2012: GO/NO-GO decision for Milestones 2 and 3

Selection of HCC and Pt-M/CNC catalysts. The goal is to maintain high activity and achieve ≤40% loss of initial catalytic activity after 30 k cycles.

Possible solution: Development of corrosion resistant supports such as TiO_2-CCC and activated graphitic carbon (AGC). **(Task 5)**

Milestones

- **Milestone 4**: **Dec 2012**: **Initial high current density performance in H_2-air (80 ^oC, 100% / 40% RH, 150 $kPa_{abs.}$ outlet pressure, 1.5/1.8 stoic.). (Task 6 and 7)**

  Status: (i) Achieved 1.25 A cm^{-2} @ 0.58 $V_{iR\text{-}free}$ in 25 cm^2 cell at PGM loading of 0.125 mg_{Pt} cm^{-2} for **USC** Pt_2Ni_1/C catalyst.

  (ii) Achieved 1.03 A/cm^2 @ 0.7 $V_{iR\text{-}free}$ in 25 cm^2 cell at PGM loading of 0.1 mg_{Pt} cm^{-2} for **Yonsei University** Pt_2Ni_1/CNC catalyst. (Need improvements and to be performed in 50 cm^2 cell in at least two laboratories.)

- **Milestone 5: Dec 2012: Scale-up synthesis and durability of promising catalysts with optimum high current density performance in H_2/air. (Task 8)**

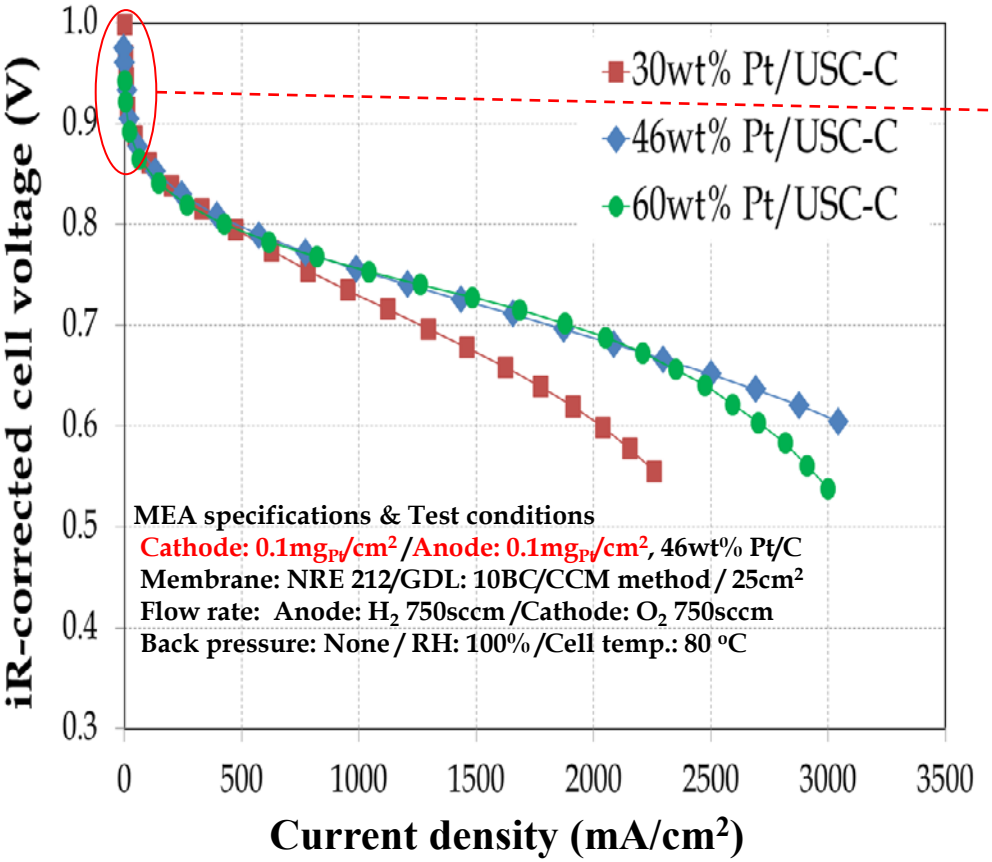
  Status: Scale-up synthesis of HCC and Pt_2Ni/CNC: On going catalyst durability under high current region in H_2-air for USC Pt_2Ni/C and Pt_2Ni/CNC catalysts: Started in March 2012.

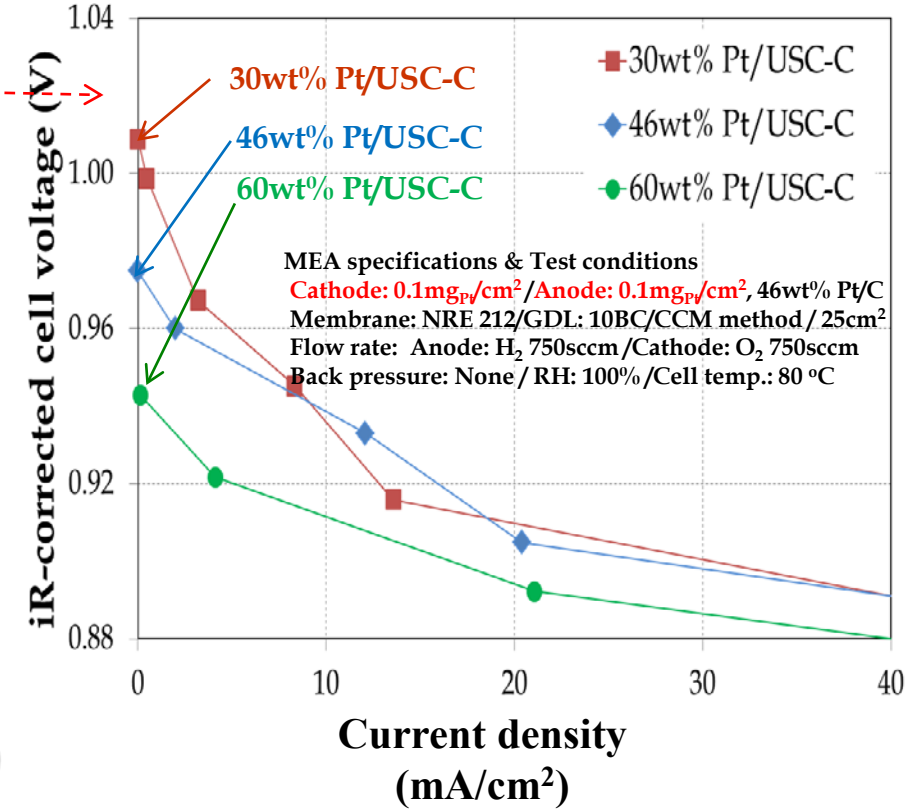
Dec 2012: GO/NO-GO decision for Milestones 4 and 5

Criteria: Selection of two most promising catalysts with (i) high kinetic mass activity, (ii) $\leq$40% loss of initial catalytic activity after 30 k cycles, (iii) initial high current density performance of at least 1.5 A cm^2 at 0.58 $V_{iR\text{-}free}$ under H_2/air (1.5/1.8 stoic.), 80 ^oC, 40% RH, 150 $kPa_{abs.}$ outlet pressure.

MEA Optimization Studies (Effect of Initial Pt Loading)

Effect of initial Pt loading on polarization performance and OCP in H_2-O_2



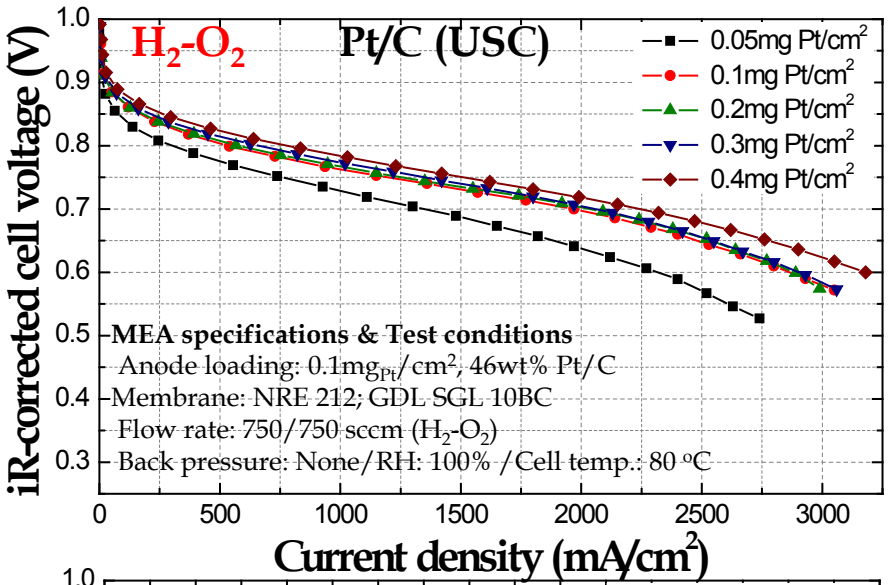


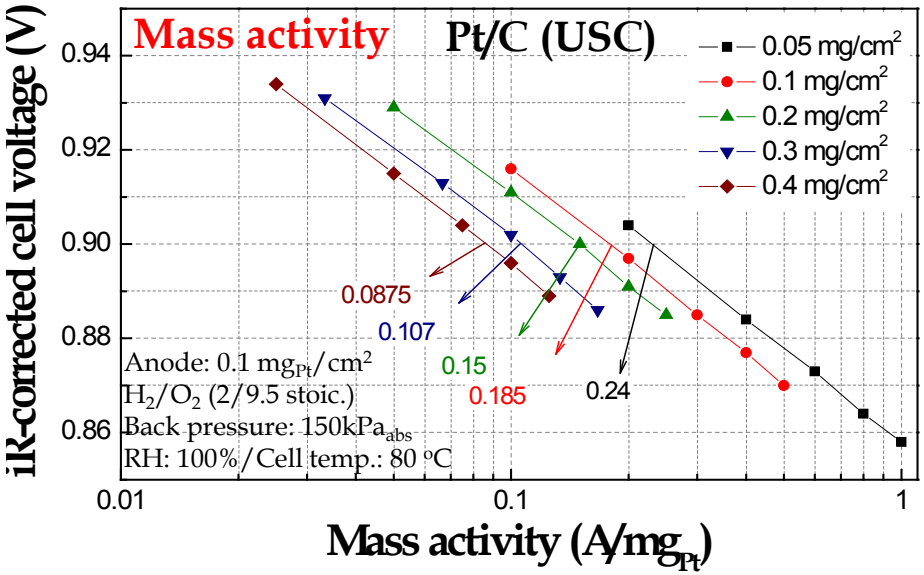
Highlight

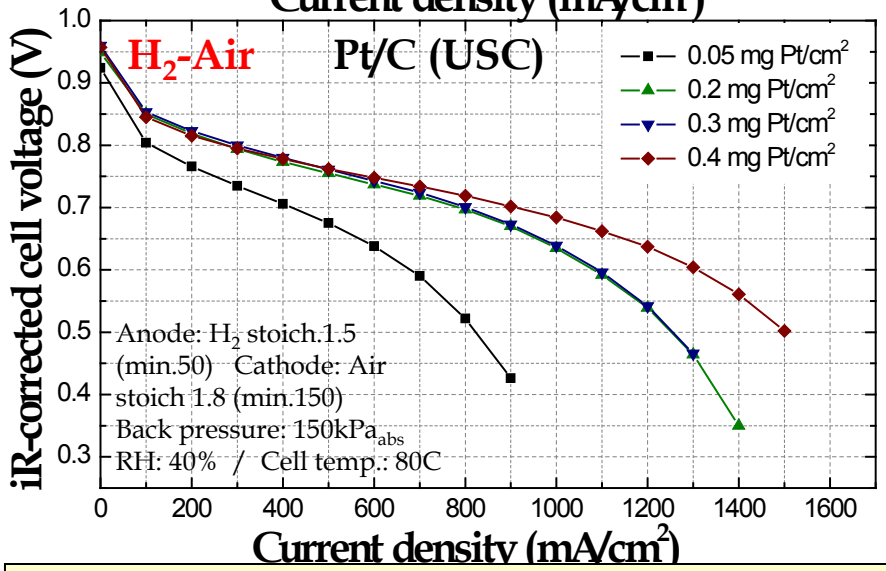
OCV decreases from 1.009 V to 0.943 V as the initial Pt loading increases from 30 wt% to 60 wt%.

Pt initial loading (wt%)	OCV (V)
30	1.009
46	0.975
60	0.943

Effect of Pt Loading on the Mass Activity of 46% USC Pt/C Catalyst







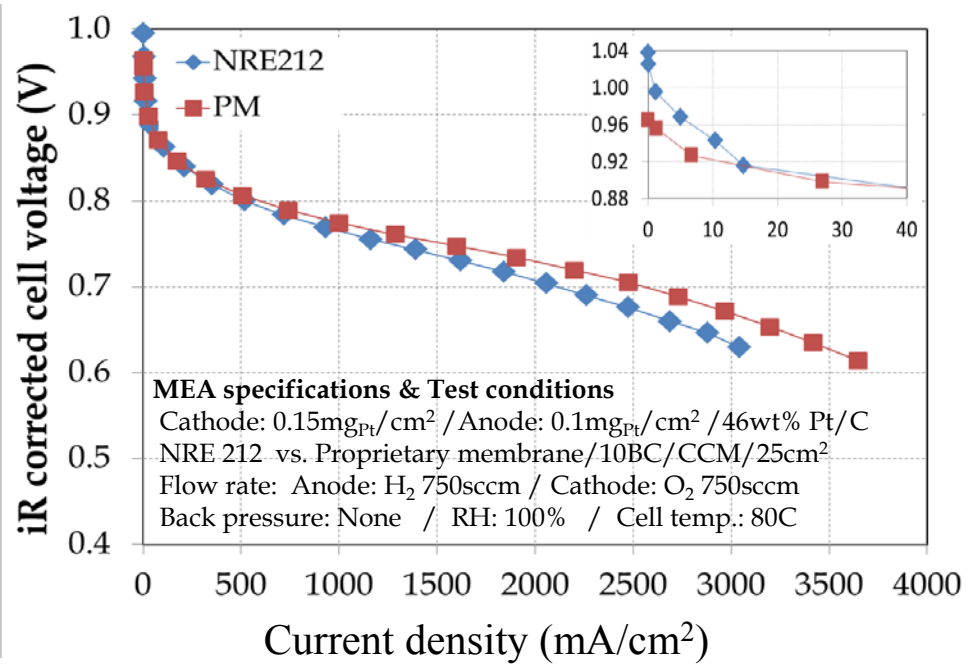
- **At 0.6$V_{iR\text{-}free}$, the current density increases from 700mA/cm² to 1300mA/cm² as the Pt loading increases from 0.05mg_{Pt}/cm² to 0.4mg_{Pt}/cm².**

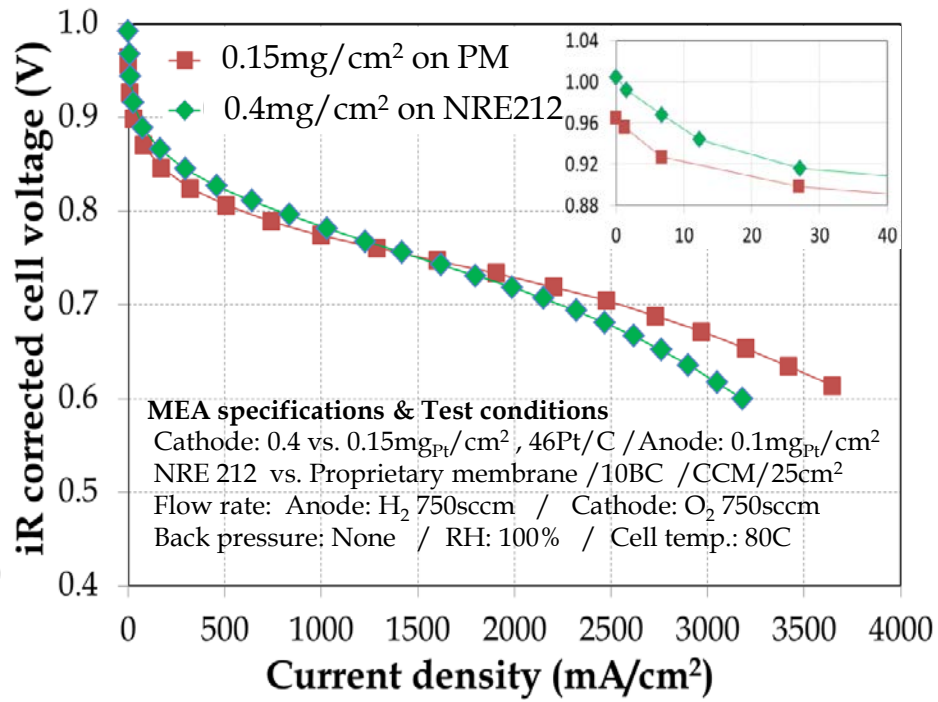
- **The catalyst mass activity increases as the Pt loading decreases.**
- **Pt utilization increases as the Pt loading decreases.**

Pt loading (mg/cm²)	Current Density @0.9V (A/cm²)	Mass Activity (A/mg)	ECSA Fuel Cell /RDE (m²/g)	Utilization (%)
0.05	0.012	0.24	70.18/85.00	82.56
0.1	0.0185	0.185	67.86/85.00	79.83
0.2	0.03	0.15	49.45/85.00	58.18
0.3	0.0321	0.107	47.63/85.00	56.04
0.4	0.035	0.0875	41.08/85.00	48.33

MEA Optimization Studies (Effect of Membrane)

Membrane optimization studies to increase the OCP and MEA performance at high current density was studied using NRE212 membrane and proprietary membrane(PM).





Highlight

- PM increases the current density by 450mA/cm² at 0.7V while OCV decreases.

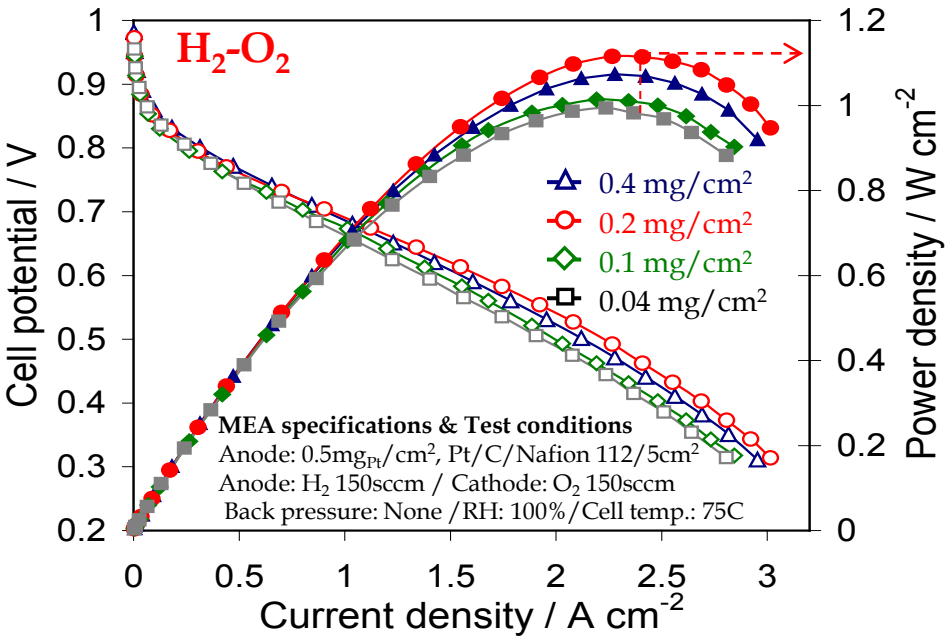
Membrane	Current density at 0.7V (mA/cm²)	OCV (V)
Nafion® NRE 212	2050	1.038
Proprietary membrane	2500	0.965

Highlight

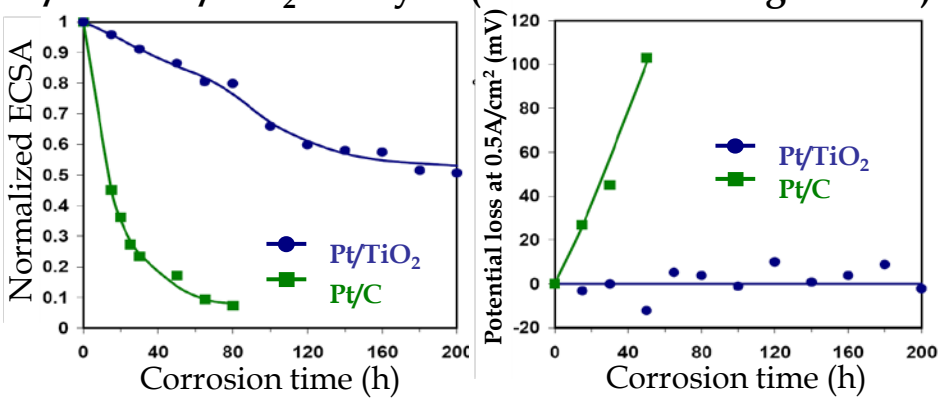
- At 0.6V$_{iR\text{-}free}$, 0.15mg$_{Pt}$/cm² on PM shows 500mA/cm² higher current density when compared with 0.4mg$_{Pt}$/cm² on NRE212 membrane.

MEA Optimization Studies (Effect of non-carbon Support)

H_2-O_2 polarization performance of Pt/TiO_2



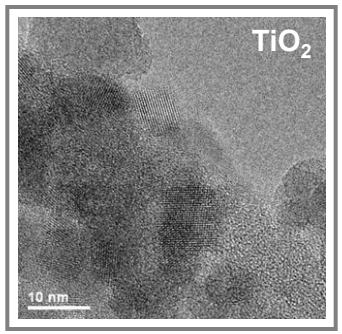
Comparison of Accelerated Corrosion Test Results of Pt/C and Pt/TiO_2 Catalysts (Potential Holding at 1.2 V)

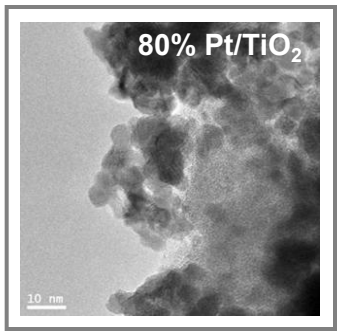


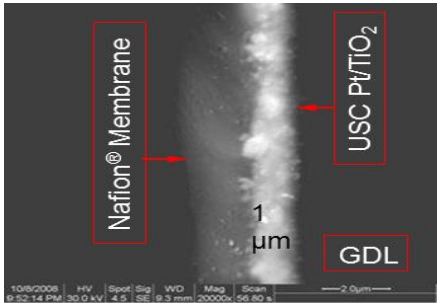
- Pt/C shows 93% loss in ECSA at T_c = 80h.
- Pt/TiO_2 shows ~20% loss in ECSA at T_c = 80h.
- Potential loss of 100mV was observed for Pt/C after 40hrs.
- No Potential loss is observed for Pt/TiO_2.

Highlights

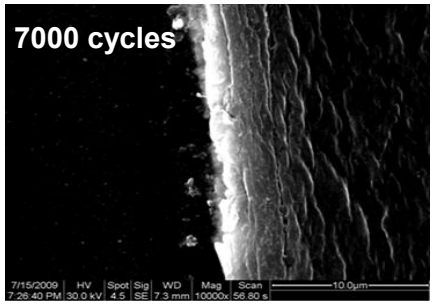
- Pt/TiO_2 shows low mass transport loss.
- Pt/TiO_2 shows OCV close to 1.0V.
- Pt/TiO_2 shows power density 1.15W/cm².







Initial state



After test

- Pt/TiO_2 electrode retained a similar morphology and catalyst layer thickness (1µm) before and after accelerated durability test.

Synthesis of HCC

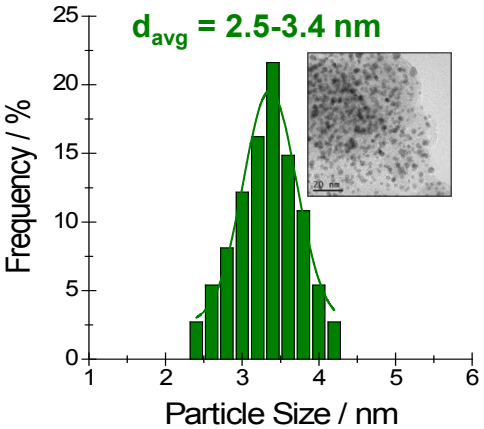
Objective: Combine the catalytic activity of Pt/Pt-alloy with that of carbon composite catalyst (CCC) thus forming a hybrid cathode catalyst (HCC) having ultra-low Pt loading.

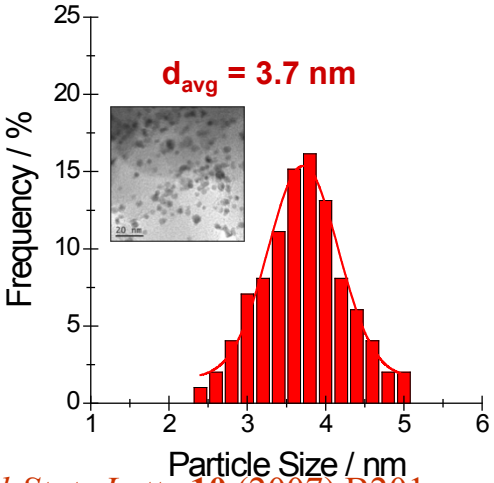
Carbon modification (Step 1) → **Carbon composite Catalyst (Step 2)** → **Hybrid cathode catalysts (HCC) (Step 3)**

- **Surface modification of carbon black with:**
  - **(i) O-containing group**
  - **(ii) N-containing group**
- **Pyrolysis**

- **"Metal-catalyzed pyrolysis" (Fe or Co) to increase the number of active sites by leaching**

- **Pt deposition**
- **Pyrolysis**





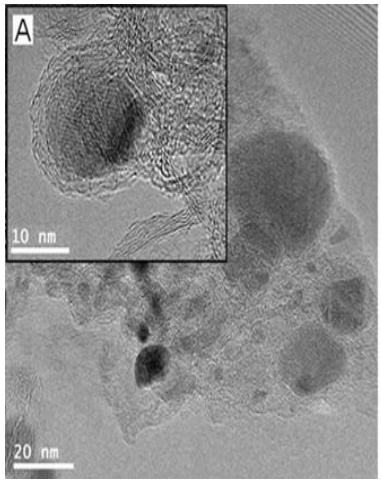
The advantages of this approach are:

- **(i) no leaching step is necessary in order to remove the un-reacted transition metal.**
- **(ii) no increase of Pt particle size in step 3.**
- **(iii) avoids destruction of Pt-alloy catalyst/carbon support interaction.**
- **(iv) easy to scale-up.**

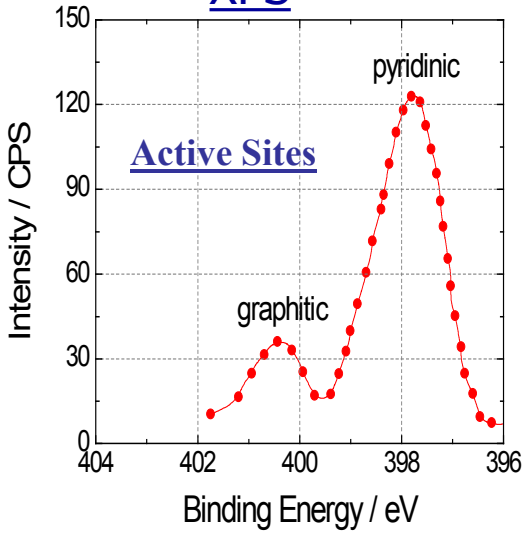
B. N. Popov et. al., Electrochem. Solid-State Lett., **10** (2007) B201.

Performance Evaluation of Carbon Composite Support

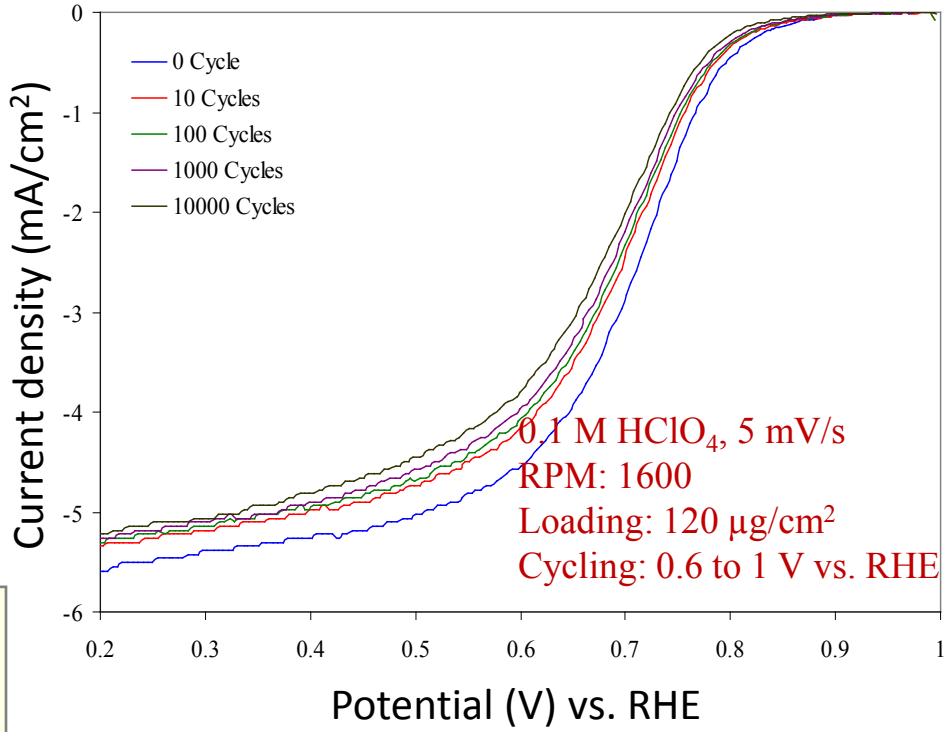
TEM



XPS



RRDE Stability Test for CCC



HIGHLIGHT:

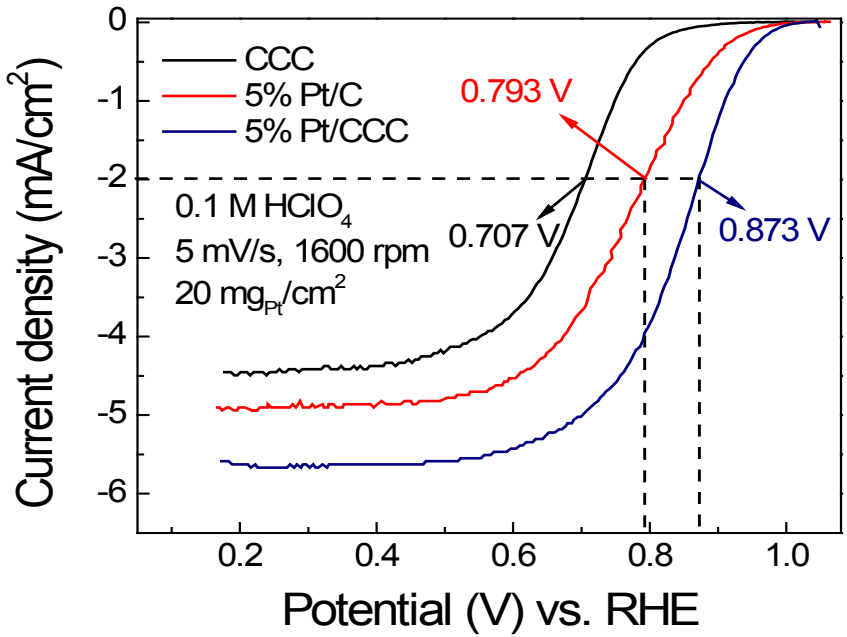
- **Metal atoms are covered with several graphitic layers.**
- **Nanostructured fibers of graphitic carbon was formed as a result of metal-catalyzed pyrolysis.**
- **XPS indicated that the high-temperature pyrolysis increased the Lewis basicity due to the increased concentration of pyridinic–type nitrogen.**

HIGHLIGHT:

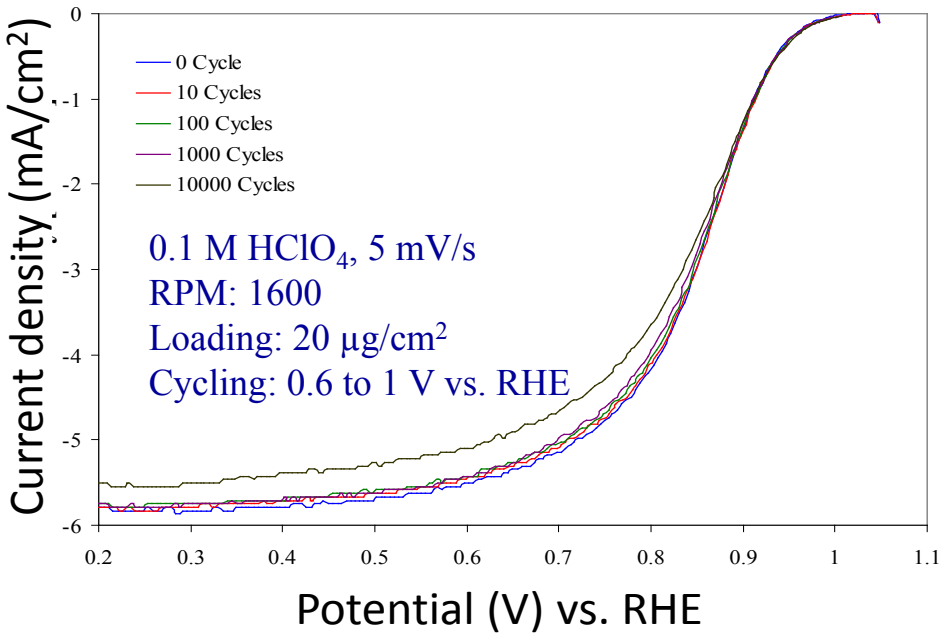
- **CCC support showed onset potential of 0.9 V vs. RHE for ORR.**
- **The support is stable after 10K potential cycles between 0.6 and 1.0 V vs. RHE.**

RRDE Comparison Studies of CCC, 5% Pt/C and 5% Pt/CCC Catalysts

RRDE Comparison



RRDE Stability Test for 5% Pt/CCC



HIGHLIGHT:

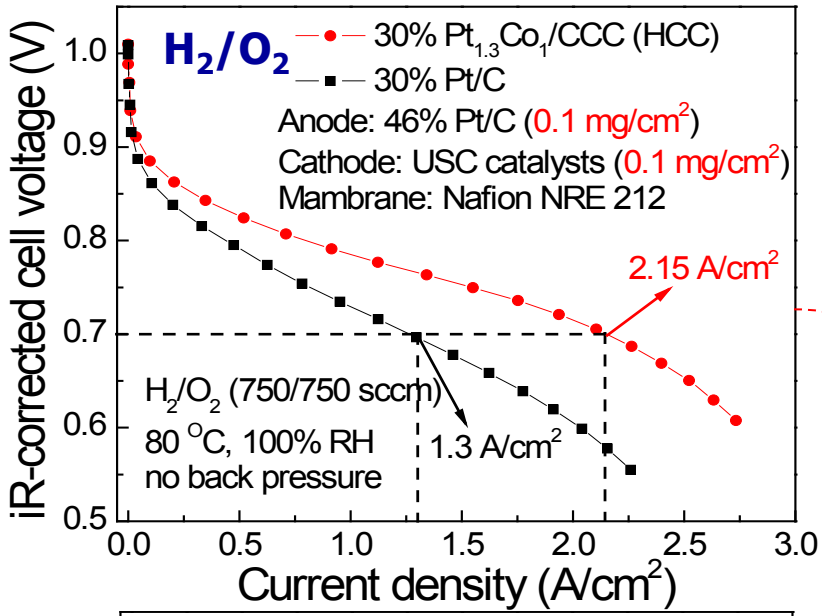
- **CCC, 5% Pt/C and 5% Pt/CCC show onset potential of 0.9, 0.985 and 1.0 V vs. RHE, respectively, for ORR.**
- **The potential at 2 mA/cm^2 is 0.707, 0.793 and 0.873 V for CCC, 5% Pt/C and 5% Pt/CCC, respectively.**

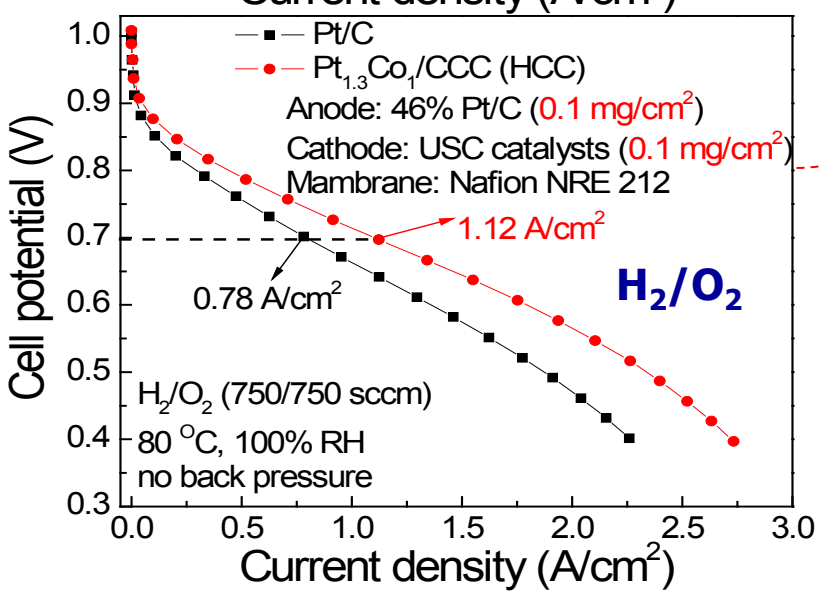
HIGHLIGHT:

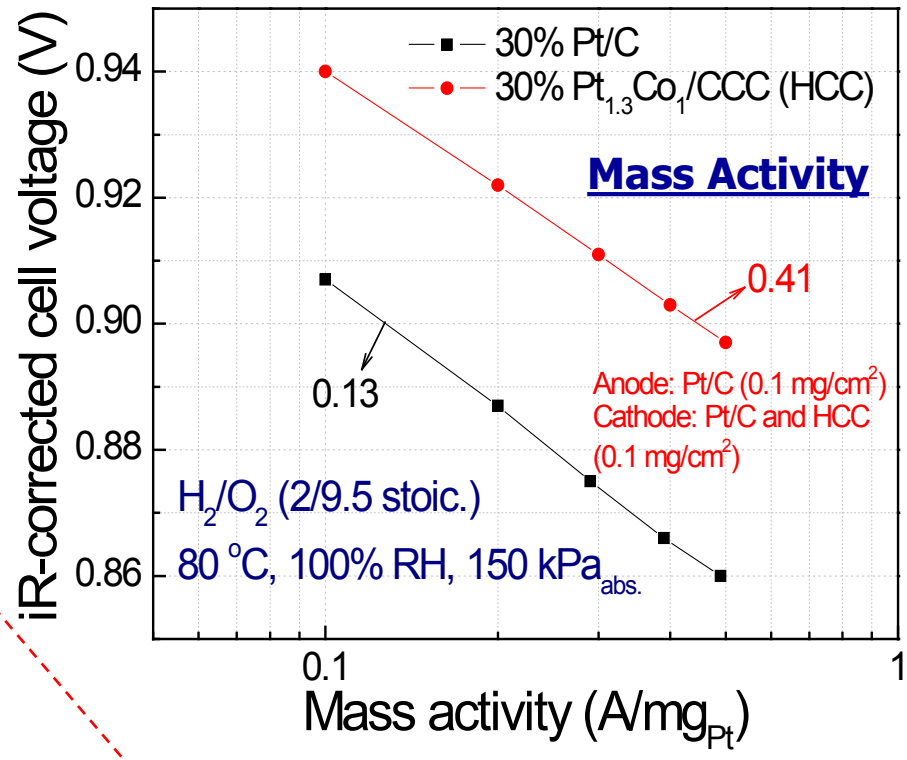
- **5% Pt/ CCC showed onset potential of 1.0 V vs. RHE for ORR.**
- **The catalyst is stable after 10K potential cycles between 0.6 and 1.0 V vs. RHE. The current density at 0.9 V remains constant (1.4 mA/cm^2) and the ECSA decreased only by 18% after 10K cycles.**

	Initial	10 Cycles	100 Cycles	10000 Cycles
ECSA [m^2/g]	67.2 (100 %)	67.2 (100%)	61.8 (92 %)	55.1 (82 %)

Comparison of 30% Pt/C and 30% Pt/CCC Catalysts (Effect of Catalytically Active CCC Support)







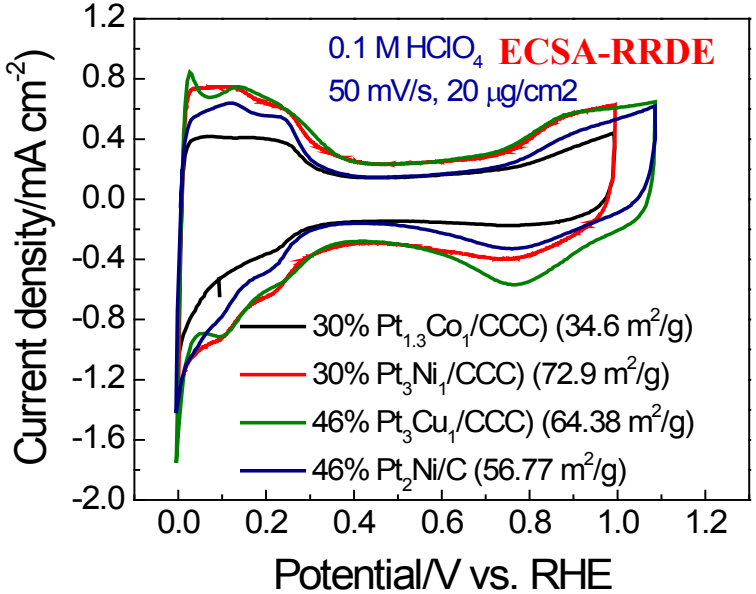
HIGHLIGHT :

The 30% $Pt_{1.3}Co_1$/CCC (HCC) catalyst shows 30% current density increase at 0.7 V and 40% current density increase at 0.7 $V_{iR\text{-}free}$ when compared to the 30% Pt/C catalyst.

HIGHLIGHT :

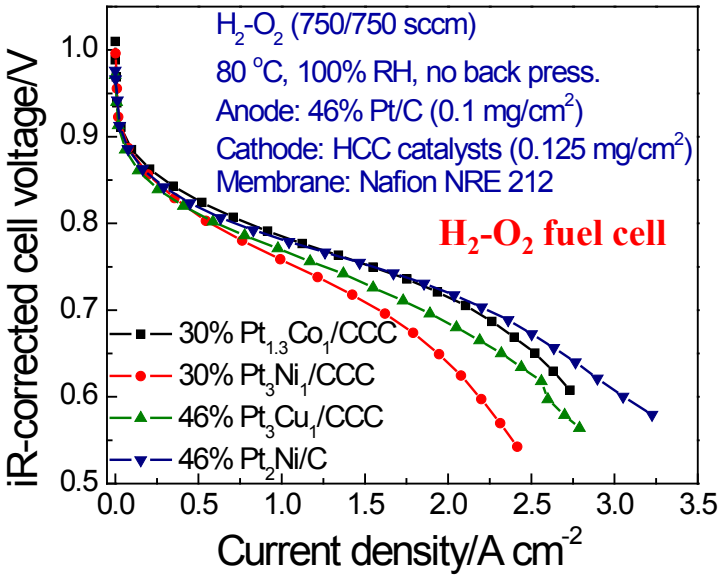
The mass activity of 30% $Pt_{1.3}Co_1$/CCC (HCC) increased >3 times when compared to 30% Pt/C.

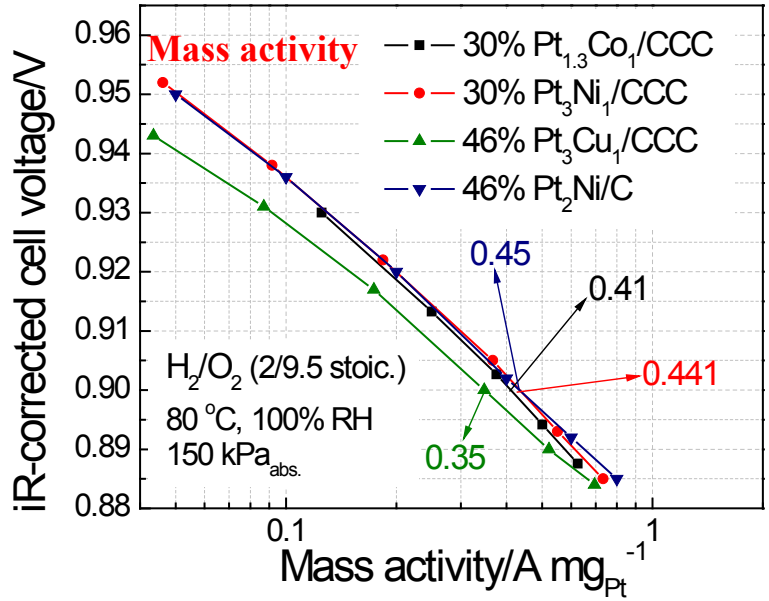
Comparison of Electrochemical Properties of Different HCC Catalysts



HIGHLIGHT:

USC catalysts show ECSA in the range from 34.6 – 72.9 m^2/g.





HIGHLIGHT:

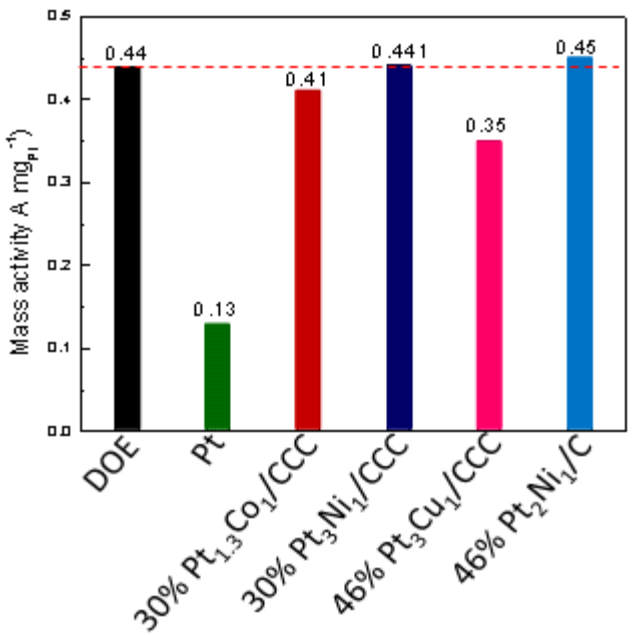
USC catalysts show mass activities in the range from 0.35 to 0.45 A mg_{Pt}^{-1}.

Catalyst	OCV (V)
30% $Pt_{1.3}Co_1$/CCC	1.010
30% Pt_3Ni_1/CCC	0.995
46% Pt_3Cu_1/CCC	0.976
46% Pt_2Ni_1/C	0.971
46% Pt/C	0.975

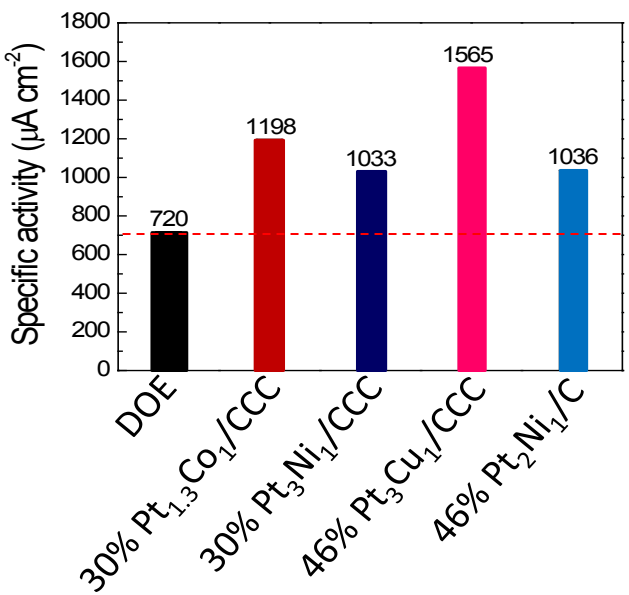
Comparison of Electrochemical Properties of HCC Catalysts

Catalyst	Particle size (nm)	Mass activity (A/mg_{Pt})	Specific Activity ($\mu A/cm^2$)	ECSA in RDE (m^2/g)	ECSA in MEA (m^2/g)	Utilization (%)	Current density @ 0.7 V (A/cm^2) H_2/O_2 (750/750 sccm)
30% $Pt_{1.3}Co_1$/CCC	3.6	0.41	1198	34.55	33.14	95.90	2.15
30% Pt_3Ni_1/CCC	2.9	0.441	1033	58.90	42.6	72.30	1.58
46% Pt_3Cu_1/CCC	3.3	0.35	1565	64.38	22.36	34.73	1.83
46% Pt_2Ni_1/C	3.5	0.45	1036	56.77	43.43	76.52	2.25

Comparison of Mass Activity



Comparison of Specific Activity

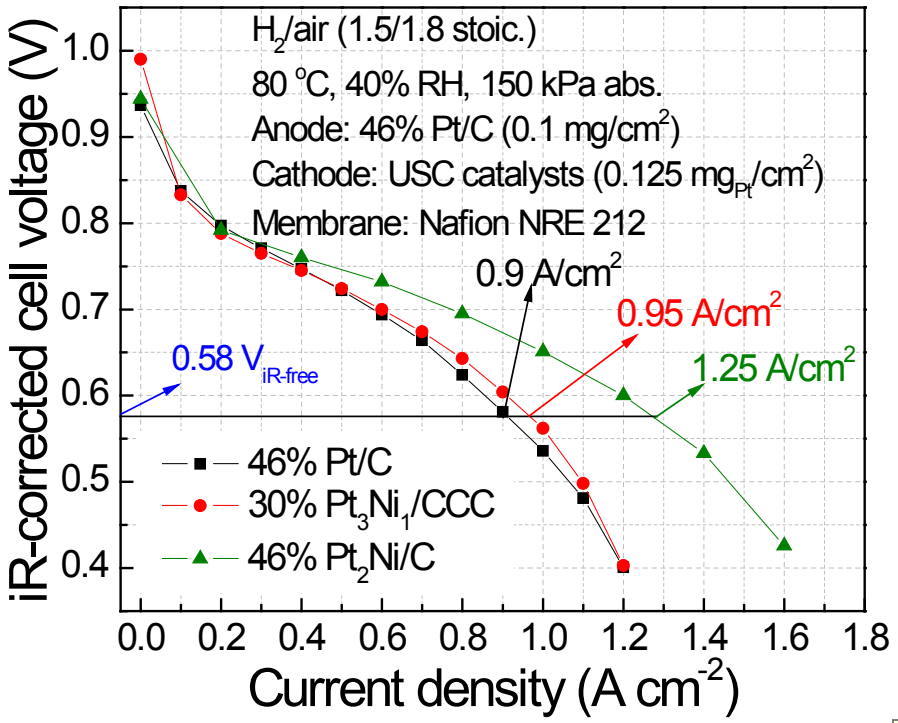


HIGHLIGHT:

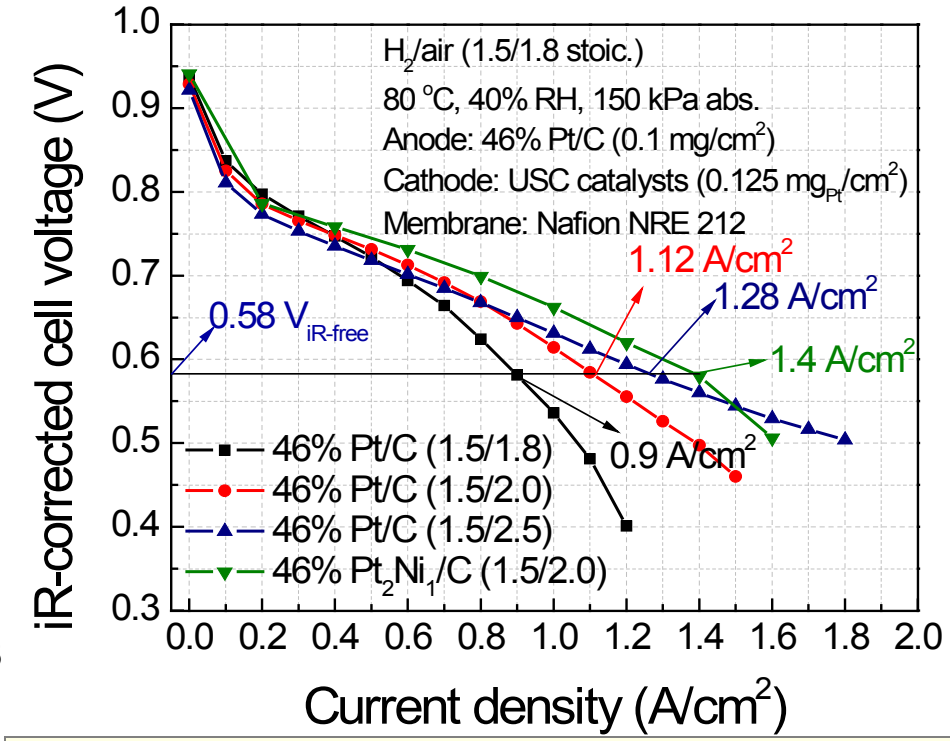
- **30% and 46% USC catalysts show particle sizes in the range between 2.9 and 3.6 nm.**
- **The ECSA ranges from 34.6 – 72.9 m^2/g and mass activities in the range from 0.35 to 0.45 A mg_{Pt}^{-1}.**
- **The open circuit potential depends on the initial catalyst loading. 30% USC catalysts showed OCP of ~1 V and 46% USC catalysts showed OCP of ~ 0.97 V.**

Comparison of H_2-Air Fuel Cell Performance

H_2-air fuel cell performance (DOE)



Effect of Cathode Stoic.



HIGHLIGHT:

- **30% Pt_3Ni_1/CCC USC catalyst shows ~1.0 V OCP under H_2-air operating conditions.**
- **USC Pt_2Ni_1/C shows 1.25 A/cm^2 at 0.58 $V_{iR\text{-}free}$.**

HIGHLIGHT:

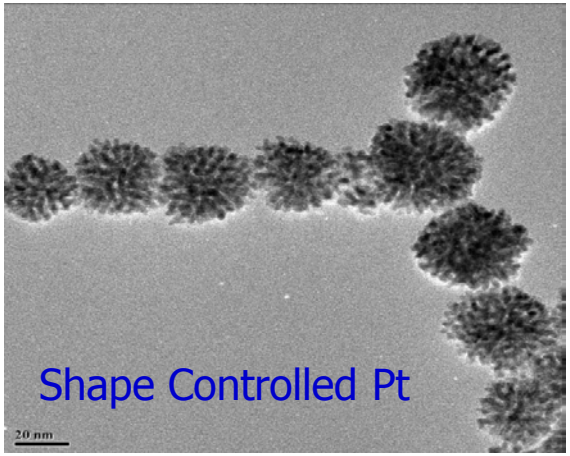
- **The cathode stoic. significantly increases the H_2-air fuel cell performance and USC Pt_2Ni_1/C catalyst shows 1.4 A at 0.58 $V_{iR\text{-}free}$ 1.5/2.0 stoic is used.**
- **Currently the catalyst layer structure is being optimized to achieve high current density performance under DOE suggested H_2-air operating conditions.**

Synthesis and Characterization of Pt_2Ni_1/CNC Alloy Catalyst

Objective: Develop Pt and Pt-alloy catalysts deposited on carbon nano cage (CNC)

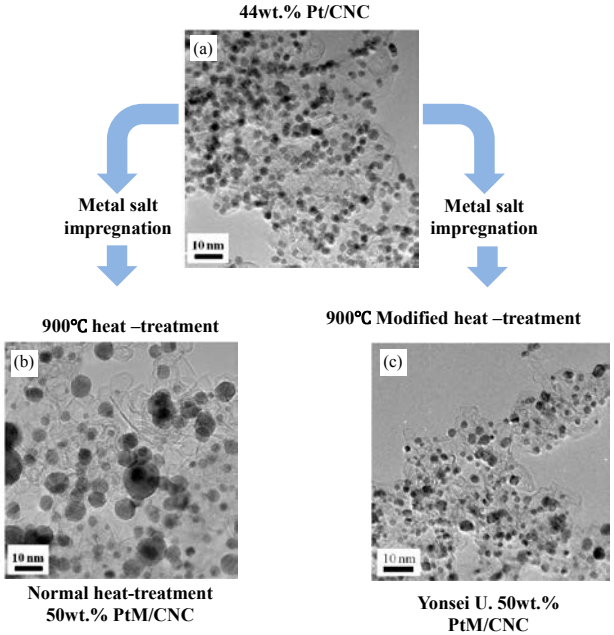
Graphitic Carbon Modification

- Surface modification of graphitic carbon with a non-covalent π-π interaction using (i) Pyrenyl and (ii) Carboxylic acid groups
- Process optimization



Synthesis of Pt/CNC Catalyst

- Deposition of Pt on functionalized CNC using in-house deposition process
- Control of Pt particle size and Pt dispersion on surface modified CNF



Synthesis of Pt-alloy on Surface Modified CNC

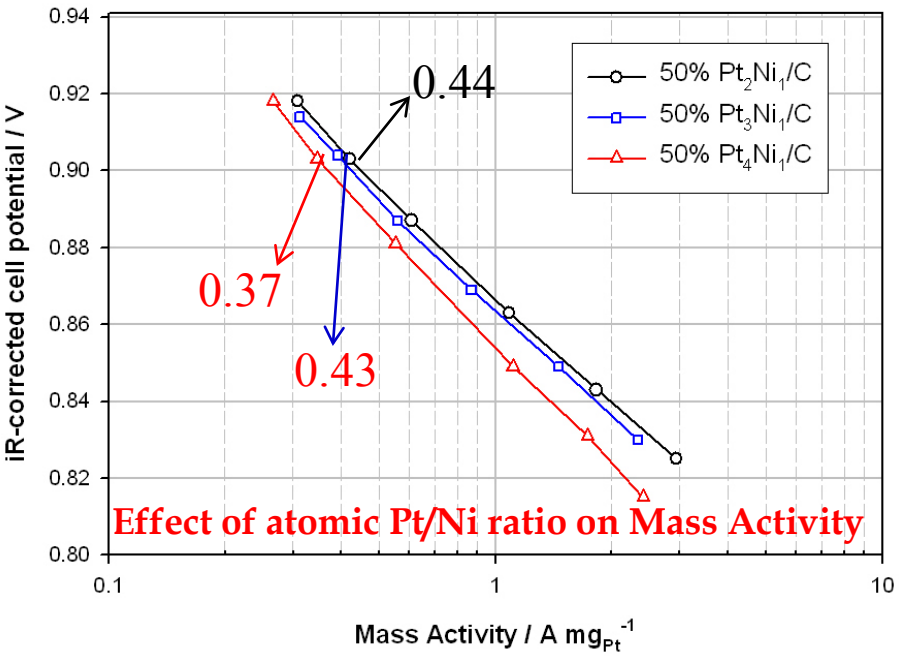
- Inhibition of Pt sintering at alloying temperature using in-house developed heat-treatment procedure.
- Impregnation of transition metal precursor.
- Leaching of the catalyst to remove non-alloyed transition metal.

Technical Accomplishments and Progress

Electrochemical Performance Evaluation* of Pt_2Ni_1/CNC Catalyst (Effect of atomic Pt/Ni ratio)

Effect of atomic Pt/Ni ratio

Sample	Particle size in XRD (nm)	Mass activity (A/mg_{Pt})	ECSA (m^2g^{-1})		Utilization (%)
			Three electrode system	MEA	
Yonsei U. 50wt% Pt_2Ni_1/CNC	3.4	0.44	33.2	24.6	74
Yonsei U. 50wt% Pt_3Ni_1/CNC	3.3	0.43	34.5	26.3	76
Yonsei U. 50wt% Pt_4Ni_1/CNC	3.3	0.37	33.7	25.9	77



HIGHLIGHT:

- **YU Pt_xNi_y/CNC catalysts show particle sizes of ~3.3 nm.**
- **The mass activity of Pt_xNi_y/CNC catalysts increases with the increase in the Ni content.**
- **The catalyst utilization for the Pt_xNi_y/CNC catalysts are between 74 and 77%.**

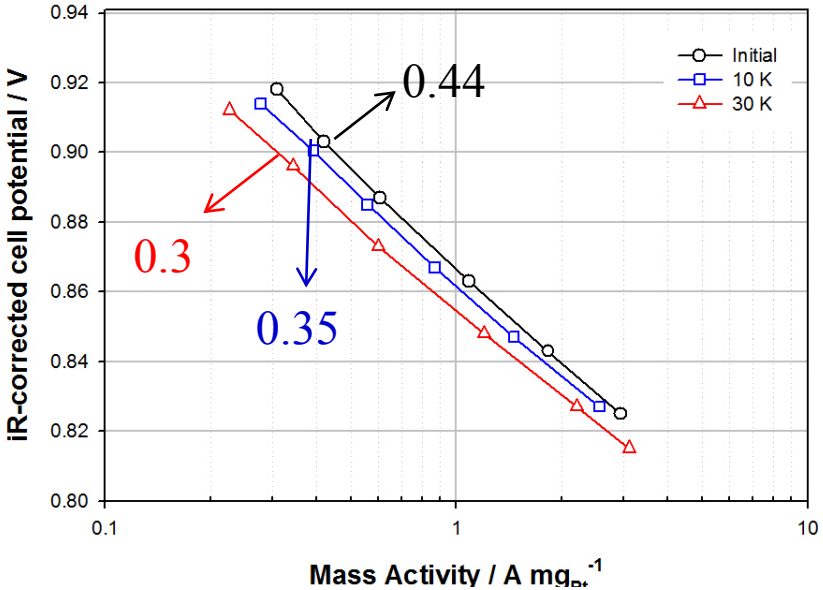
Condition : 150kPa, 80°C, 100 % RH, H_2/air 2/9.5 stoic, 25 cm^2, 0.1mg_{metal}/cm^2

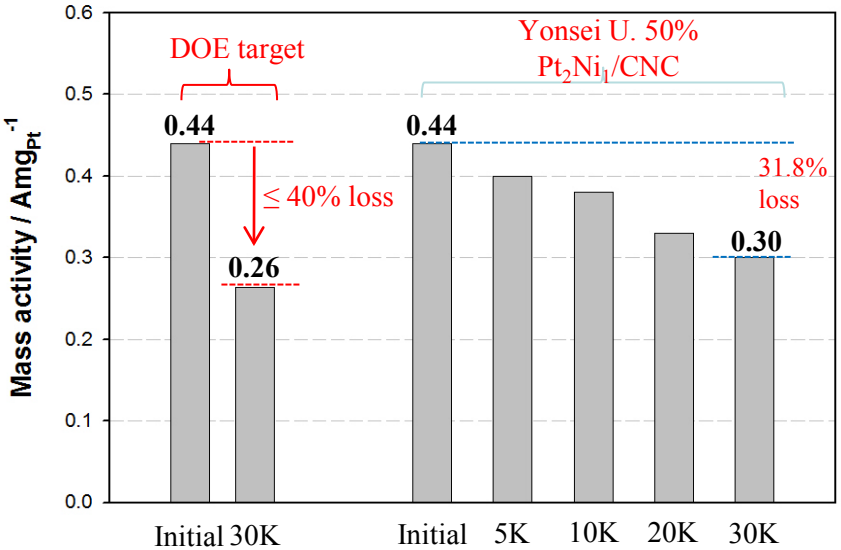
Catalyst : Yonsei U. Pt_2Ni_1/CNC, TKK 46 Pt/C

***Catalyst performance evaluation is under progress at USC**

Technical Accomplishments and Progress
Pt_2Ni_1/CNC Catalyst Durability Studies*

Effect of Potential Cycling on the Mass Activity





Effect of Potential Cycling

	After 30,000 cycles	
	Mass activity at 0.9V	ECSA in MEA
DOE target	≤ 40% loss	≤ 40% loss
Yonsei U. 50wt% Pt_2Ni_1/CNC	31.8 % loss	26.3 % loss

HIGHLIGHT:

- **YU Pt_2Ni_1/CNC catalyst shows 31.8% mass activity loss and 26.3% ECSA loss after 30k cycles.**
- **The catalyst durability satisfies the DOE target of ≤ 40% after 30K cycles.**

DOE Accelerated Protocol

0.6 ~ 1.0 V, 50mV/s, 30,000 cycle, H_2/N_2

80°C, 100 % RH, single cell 25cm^2

Catalyst : Yonsei U. Pt_2Ni_1/CNC, 0.1mg$_{metal}$/cm^2

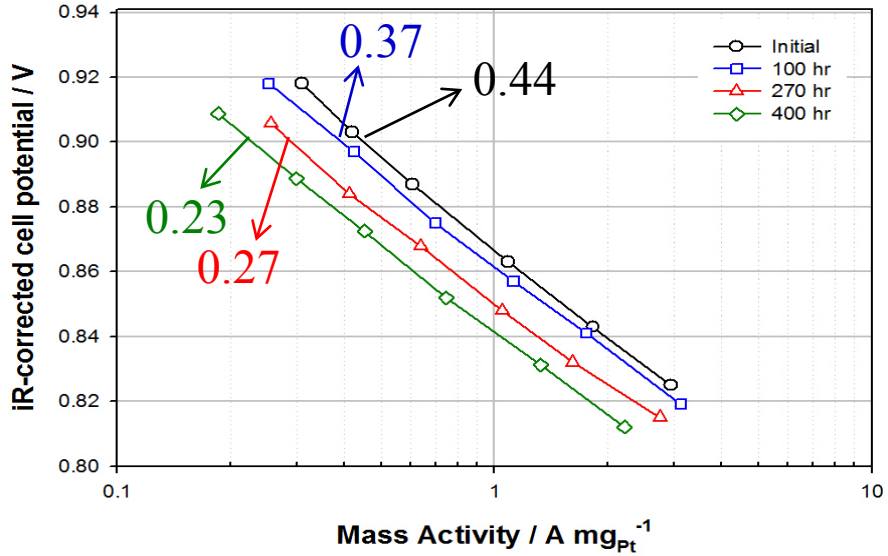
Pt mass activity : H_2/O_2, 2.0/9.5 stoic, 100% RH, 80°C, 150 kPa

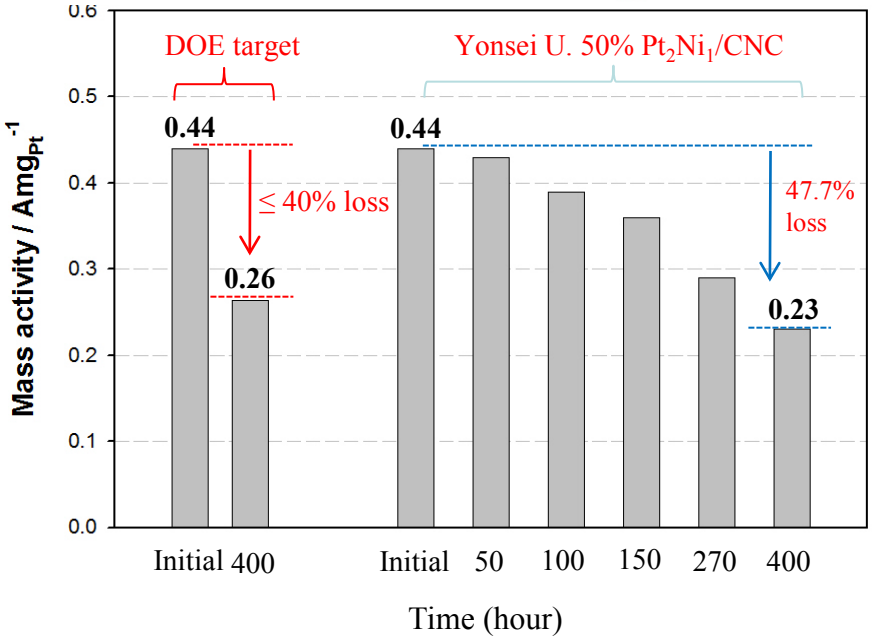
***Catalyst cycling performance evaluation is under progress at USC**

Technical Accomplishments and Progress

Pt_2Ni_1/CNC Support Durability Studies (Potential hold at 1.2 V)

Effect of 1.2 V Potential Hold on the Mass Activity





Effect of 1.2 V Potential Holding

	Mass activity at 0.9V	ECSA in MEA
DOE target (400h)	≤ 40% loss	≤ 40% loss
Yonsei U. 50wt% Pt_2Ni_1/CNC (400h)	47.7 % loss	42.4 % loss

HIGHLIGHT:

- **YU Pt_2Ni_1/CNC catalyst shows 47.7% mass activity loss and 42.7% ECSA loss after 400 h potential holding.**
- **The support durability of YU Pt_2Ni_1/CNC does not satisfy the DOE target of ≤ 40% after 400 h.**

DOE Accelerated Protocol

Hold at 1.2V for 24 h, H_2/N_2

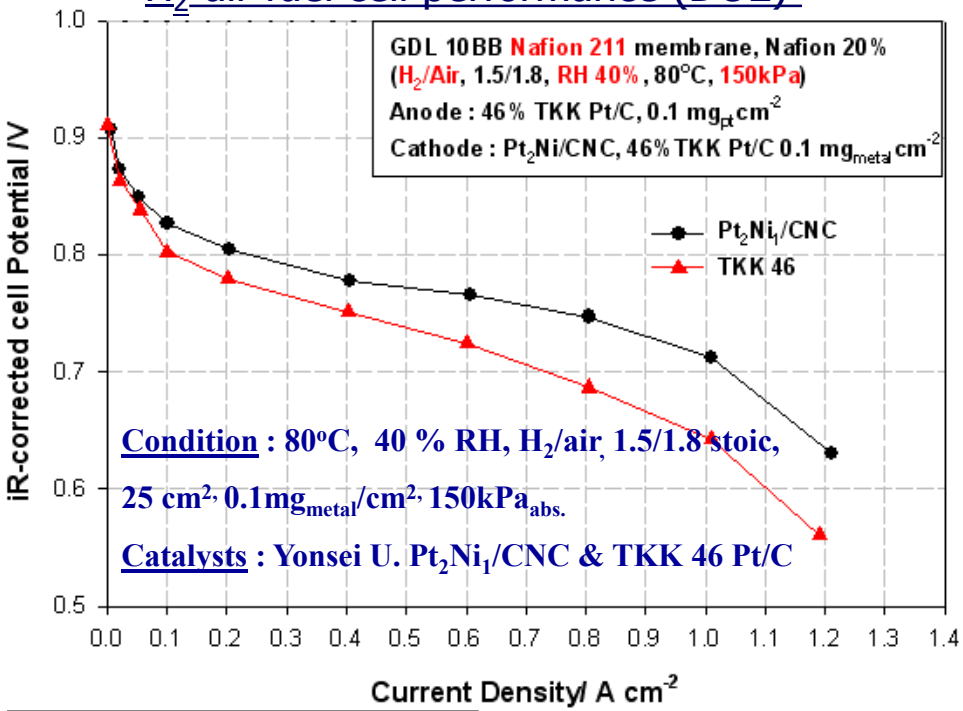
80°C, 150 kPa, 100 % RH, single cell 25cm^2

Catalyst : Yonsei U. Pt_2Ni_1/C, 0.1mg$_{metal}$/cm^2

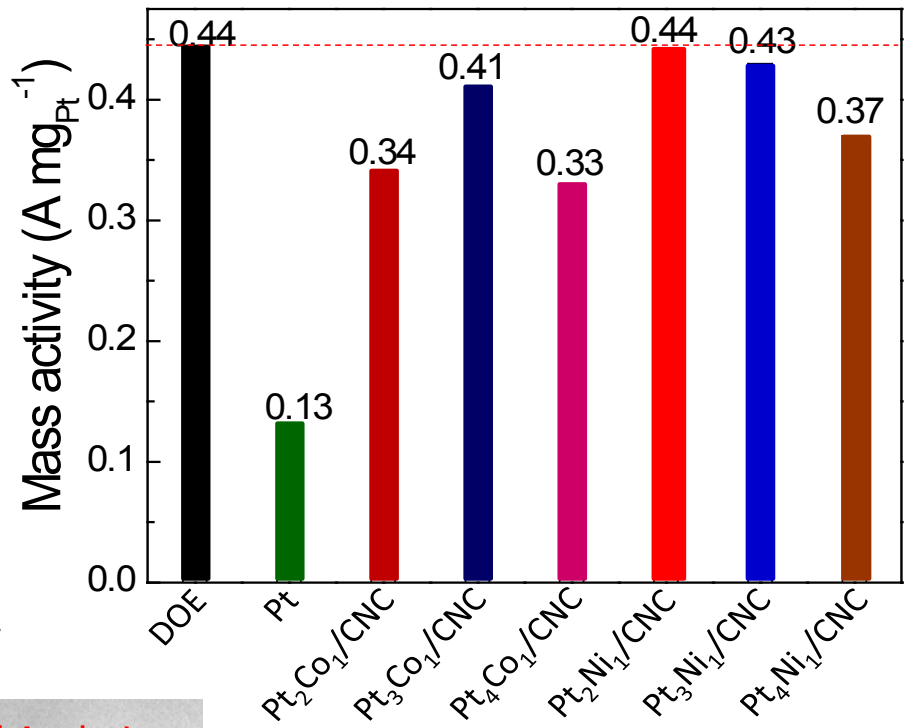
Pt mass activity : H_2/O_2, 2.0/9.5 stoic, 100% RH, 80°C, 150 kPa

H_2-Air Fuel Cell Performance and Mass Activity Comparison

H_2-air fuel cell performance (DOE)

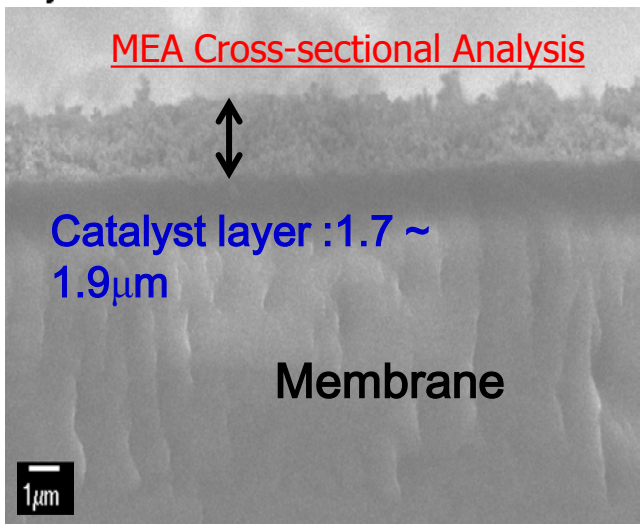


Mass Activity Comparison of YU Catalysts



HIGHLIGHT:

- **YU Pt_2Ni_1/CNC catalyst shows 1.03 A/cm^2 at 0.7 $V_{iR\text{-}free}$.**
- **Very thin (~2 µm) uniform catalyst layer can be deposited directly on the membrane**



HIGHLIGHT:

YU Pt_xCo_y/CNC Pt_xNi_y/CNC catalysts show mass activities in the range between 0.33 and 0.44 A/mg_{Pt}.

Collaborations

Subcontractors:

- **Yonsei University**
  - Activation procedure to deposit Pt on graphitic carbon support.
  - Pt-alloy/CNC catalyst development with high mass activity, specific activity and durability.
  - Process to control the particle size at high temperature treatment.
  - Evaluation of high current density performance under H_2-air.
  - Support corrosion mechanism studies.
- **Hyundai Motor Company** (Funding ended Dec. 2011 and will resume in Feb 2013)
  - Pt-Pd catalyst development and performance evaluation.
  - Flow-field design optimization.
  - Short-stack design and construction.
  - Performance evaluation of Pt/C catalyst under short-stack conditions.
  - Construction and delivery of short-stack (10 cells, 50 cm^2) to University of South Carolina. HMC delivered a short-stack (50 cm^2) in Nov 2011.

Additional Interactions:

- Rudiger Laufhutte (University of Illinois, Urbana Champagne): ICP analysis of Pt-alloy catalysts.
- JoAn Hudson & Haijun Qian (Clemson University): Transmission Electron Microscopy analysis.
- Soumitra Goshroy (EM Center, USC): HR-TEM analysis
- Scribner Associates: Design and construction of fuel cell test station according to USC requirements.
- Fuel Cell Technologies: Design and construction of 25 and 50 cm^2 single cells according to USC specifications.

Future Work

USC:

Milestone 3: June 2012

- Develop support which will increase the catalyst utilization and eliminate the loss of electrochemical surface area through performance optimization of carbon composite support (CCS).
- Accomplish durability of kinetic mass activity of at least 0.24 A mg_{Pt}^{-1} after 30 K cycles tested according to DOE protocol (cycling between 0.6-1.0 V) or less than 40% loss of mass activity at 0.9 V and ECSA loss less than 40%.
- Accomplish durability of catalyst support according to DOE target: hold at 1.2 V (400h) with less than 40 % loss of mass activity at 0.9 V and less than 40% loss of ECSA.

Milestone 4 & 5: December 2012

- Accomplish high current density performance and durability in H_2/air fuel cells (80 ^oC, 100% / 40% RH, 150 $kP_{abs.}$ outlet pressure, 1.5/1.8 stoic) to meet the DOE targets.
- Demonstrate facile scale-up synthesis of the catalyst.

Yonsei University

Specific Objectives to Accomplish Milestone 3 and Milestone 4

- Support durability optimization studies of Pt_2Ni_1/CNC catalyst.
- Modification of protecting coating method to improve the durability of Pt-Ni catalyst.
- Modification of synthesis method to reduce particle size of Pt/CNC-S catalyst.
- Durability test for Pt/CNC-S catalyst.
- Additional research for physical characterization of Pt/CNC-S catalyst.

Summary: Status Against DOE Targets (As of March 2012)

- Carbon composite support was synthesized with onset potential for oxygen reduction closer to 0.9 V vs. SHE and less than 2.5% H_2O_2 production . **Project Milestone 1**.

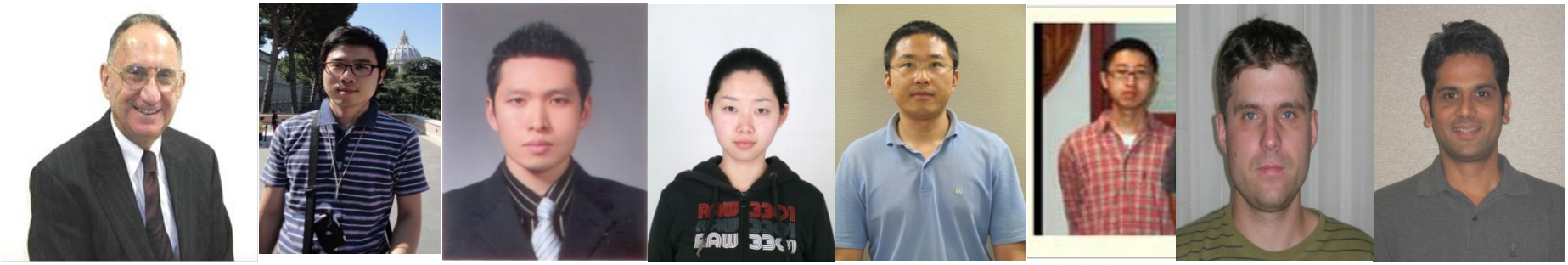
Characteristic	Units	2017 Targets	Status
PGM total loading	mg_{Pt}/cm^2	0.125	0.1-0.15 $mg_{catalyst}/cm^2$ with **USC** Pt_2Ni_1/C and 0.1 $mg_{catalyst}/cm^2$ with **YU** Pt_2Ni_1/CNC
Mass activity (80 °C, 100% RH, 150 kPa_{abs}.)	A/mg_{Pt} @ 0.9 $V_{iR\text{-}free}$	0.44	0.45 A/mg_{Pt} with **USC** Pt_2Ni_1/C and 0.44 A/mg_{Pt} **YU** Pt_2Ni_1/CNC **(Milestone 2)**
Catalyst durability (30,000 cycles 0.6-1.0 V, 50 mV/s, 80/80/80, 100 kPa_{abs}., H_2/N_2)	% Mass activity loss % ECSA loss mV loss @ 0.8 A/cm^2	≤40% ≤40% ≤ 30	31.8% mass activity loss 26.3% ECSA loss For **YU** Pt_2Ni_1/CNC **(Milestone 3)**
Support durability (1.2 V for 400 h at 80 °C, H_2-$N_{2,\ 150}$ $kPa_{abs.}$ 100% RH)	% Mass activity loss % ECSA loss	≤40% ≤40% ≤ 30 mV @ 0.8 A/cm^2	47.7% mass activity loss 42.7% ECSA loss For **YU** Pt_2Ni_1/CNC

- Corrosion resistant Pt/TiO_2 catalyst was developed with Pt particle size d_{Pt}= 3-6 nm which showed high stability under potential holding at 1.2 V.

Team Members who contributed to this presentation

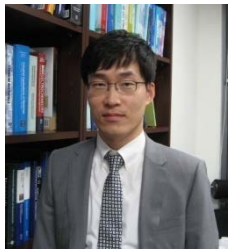
University of South Carolina

Branko N. Popov, Tae-keun Kim, Won-suk Jung, Xie Tianyuan, Xuguang Li, Gang Liu, Akos Kriston and Prabhu Ganesan



Yonsei University (S. Korea)

Hansung Kim



Acknowledgement

U.S. Department of Energy

Technical Backup Slides

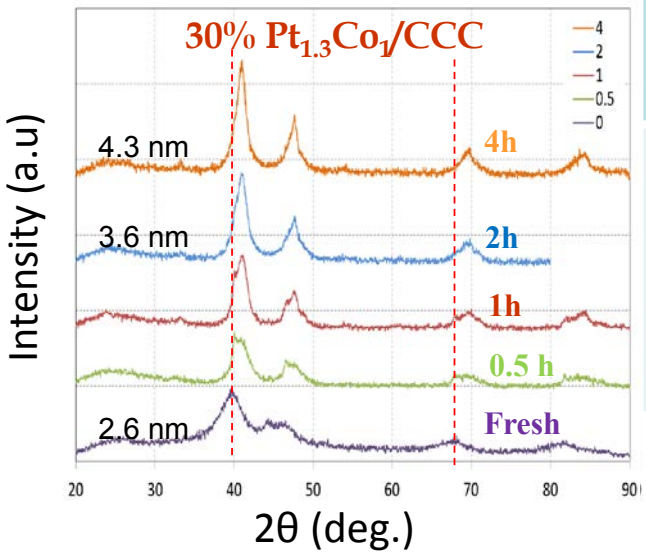
Major Technical Accomplishments since Last Review (06/10/11)

- Developed methodologies to increase the open circuit potential (OCP) and mass activities of catalysts synthesized at USC. For e.g. a gain of 66 mV (from 0.943 to 1.009 V) can be achieved for the USC catalyst by optimizing the catalyst particle size, surface area and porosity of the catalyst support.
- Polarization curves obtained at different Pt loadings in H_2-O_2 indicated that the mass activity depends up on the utilized Pt surface area (ECSA).
- The ECSA is found to depend on the Pt loading. The ECSA increased from 41.08 m^2/g (Pt loading = 0.4 mg/cm^2) to 70.18 m^2/g (Pt loading = 0.05 mg/cm^2).
- An increase in mass activity up to 0.24 A/mg_{Pt} (for USC Pt/C catalyst) was observed for a Pt loading of 0.05 mg/cm^2 compared to 0.0875 A/mg_{Pt} for 0.4 mg_{Pt}/cm^2. The observed increase is due to the increase of Pt utilization from 48.33% (Pt loading = 0.4 mg/cm^2) to 82.56% (Pt loading = 0.05 mg/cm^2).
- The current density under H_2-air measured at 0.6 $V_{iR\text{-}free}$ increased from 700 mA/cm^2 to 1300 mA/cm^2 as the Pt loading increased from 0.05 to 0.4 mg/cm^2.
- Identified and optimized an appropriate membrane to increase the high current density performance under H_2-air. The optimized proprietary membrane (PM) increased the current density of the MEA containing 0.15 mg_{Pt}/cm^2 by 500 mA/cm^2 at 0.7 $V_{iR\text{-}free}$ when compared to the Nafion® NRE 212 having 0.4 mg_{Pt}/cm^2 under H_2-O_2.

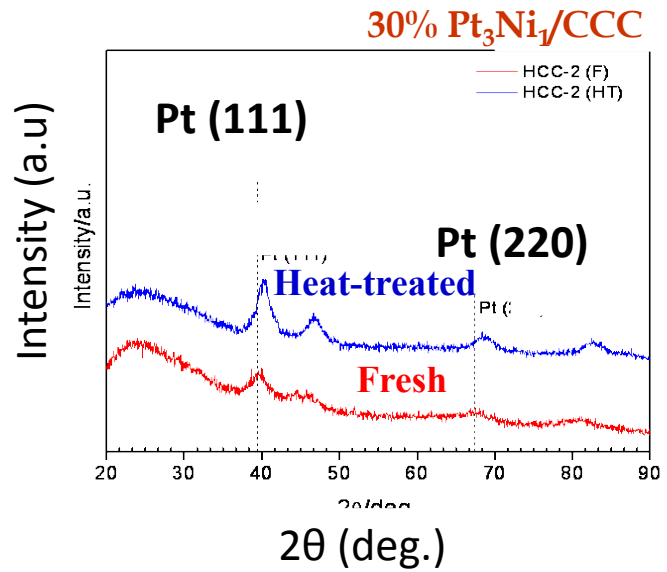
Major Technical Accomplishments since Last Review (06/10/11)

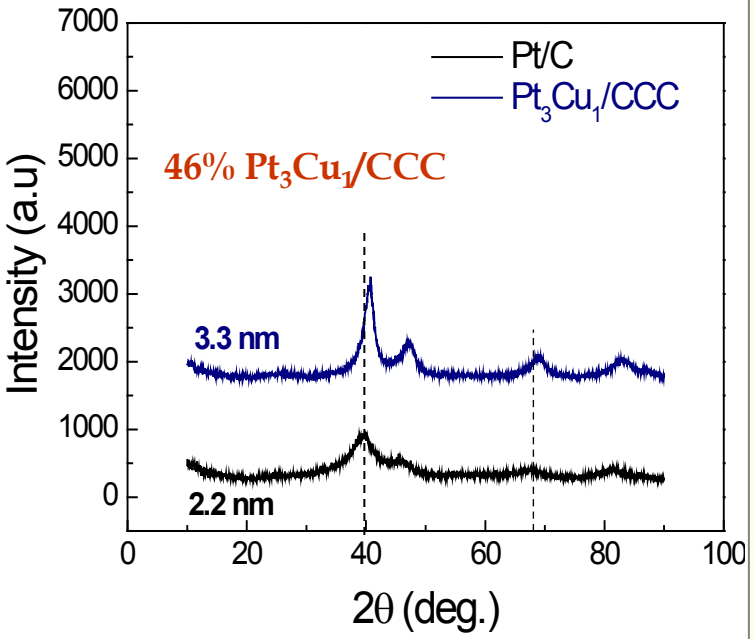
- Developed TiO_2-based non-carbon support which showed OCP close to 1.0 V and low mass transfer loss.
- Corrosion studies on Pt/TiO_2 indicated only 20% ECSA loss compared to 93% ECSA loss for conventional Pt/C catalyst. No potential loss was observed at 0.5 A/cm^2 after 200 h support corrosion test whereas, Pt/C showed 100 mV loss after 40 h.
- Validated a new process for the synthesis of Pt-alloy catalysts which does not increase the particles size after heat treatment.
- The BET surface area of the catalyst support has an important role on the stability of the catalysts. Low surface area supports drastically increased the catalyst stability.
- New methodology was developed at USC to decrease the BET surface area and partial graphitization of different carbon supports from 800 m^2/g up to 100-150 m^2/g using low heat treatment temperatures.
- Novel technique was developed to increase the hydrophilic character of the graphitic carbon which enabled uniform Pt deposition having particles sizes between 2 and 3.5 nm.
- New process was developed to synthesize Pt-rich alloy having particles size ~3.5 nm by interacting Pt nanoparticles and transition metals, which were previously embedded in the bulk of the carbon, at high temperature.
- Studies performed on 30% Pt/C and 30% HCC indicated that the OCP depends on the reactants' partial pressure, H_2 crossover, and the porosity of the catalyst layer.
- The lower OCP results from the presence of trace amounts of mixed oxides of Pt and alloying metals formed during high temperature treatment.

Synthesis of HCC Catalysts



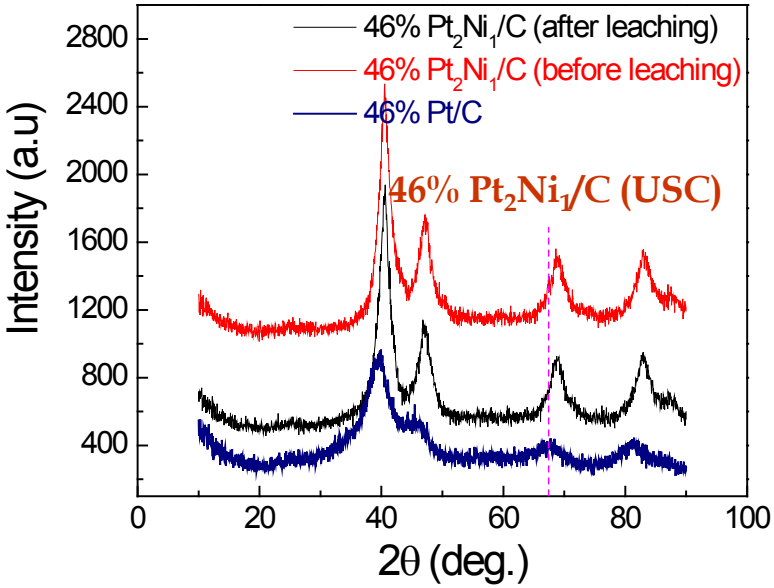
Catalysts	Particle size (nm)
30% $Pt_{1.3}Co_1$/CCC	3.6
30% Pt_3Ni_1/CCC	2.9
46% Pt_3Cu_1/CCC	3.3
46% Pt_2Ni_1/C (USC)	3.5



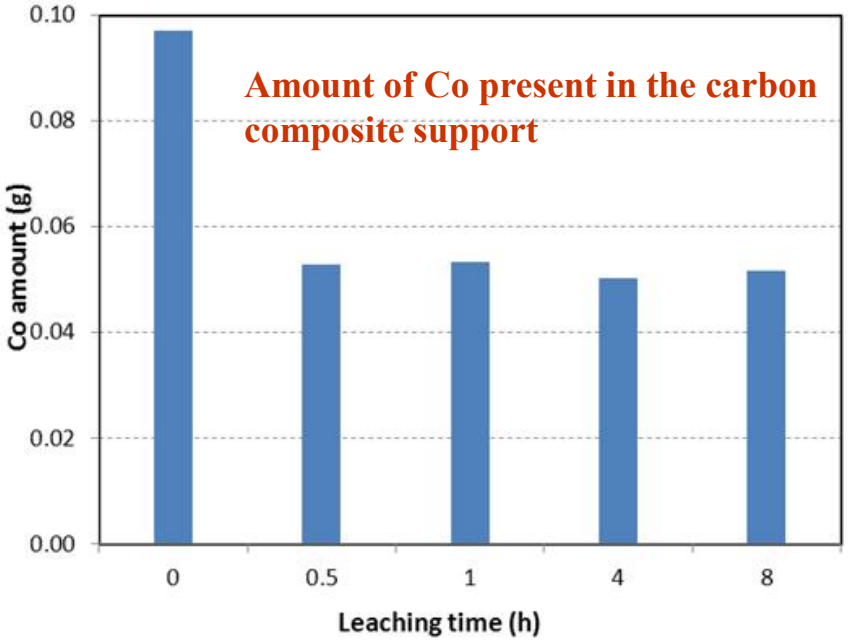


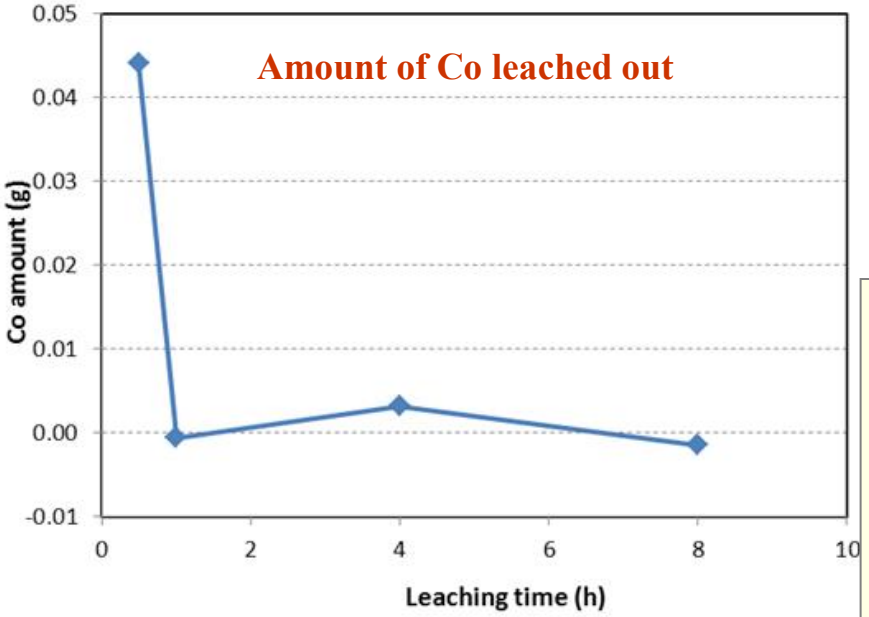
HIGHLIGHT:

- **Alloy formation is confirmed by the shift in the 2θ values of all the USC catalysts thus decreasing the Pt-Pt interatomic distance.**
- **Complete alloying process since no peaks corresponding to the alloying metals are observed.**
- **The particle size can be controlled with in the range between 3 and 4 nm using the proprietary coating and heating procedures developed at USC.**



Mass Balance of HCC Catalyst

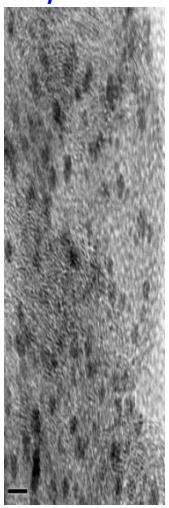




Sample Calculation for the Final HCC Catalyst Composition

Co amount in the CCC (g)	0.0516
Co amount in the CCC (wt%)	10.32%
Pt amount (wt%)	30
Support(C+Co) amount (%)	70
Carbon amount (wt%)	62.776
Cobalt amount (wt%)	7.224
Pt MW (g/mol)	195.084
Co MW (g/mol)	58.933
Pt amount (mol ratio)	0.154
Co amount (mol ratio)	0.123
Pt/Co mol ratio	**1.3**
Final catalyst composition (assuming that all the cobalt were formed Pt-Co alloy)	**$Pt_{1.3}Co_1/C$**

Pt/CCC



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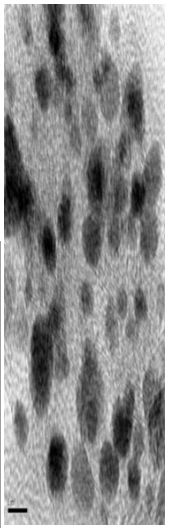

HIGHLIGHT:

- **New method was developed to synthesize Pt-alloy catalysts by interacting Pt and transition metal previously embedded in the bulk of the carbon support at high temperature**
- **The Co content stabilizes after 30 minutes leaching in 0.5 M H_2SO_4**