2013 DOE Hydrogen and Fuel Cells Program Review

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: Sep 2013(Phase I)

(No-cost Extension Apr-Sep 2013)

: March 2015 (Phase II)

- Percent complete: 65%

Budget

- Total project funding
  - **DOE share: $ 4,400,000**
    - ✓ Phase-I: $2,750,000
    - ✓ Phase-II: $1,650,000
  - **Contractor share: $1,100,000**
    - ✓ Phase-I: $687,500
    - ✓ Phase-II: $412,500
  - Funding Received till March 2013: $1,896,403
  - Expected Funding for Phase-I: $853,597 (Until 09/30/2013)

Partners

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

Barriers

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

DOE Technical Targets

Electrocatalyst/MEA	2017 Targets
PGM Loading (mg/cm^2)	0.125
PGM Total Content (g/kW)	0.18
Mass Activity (A/mg$_{Pt}$)	0.44
ECSA Loss after 30 k 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.

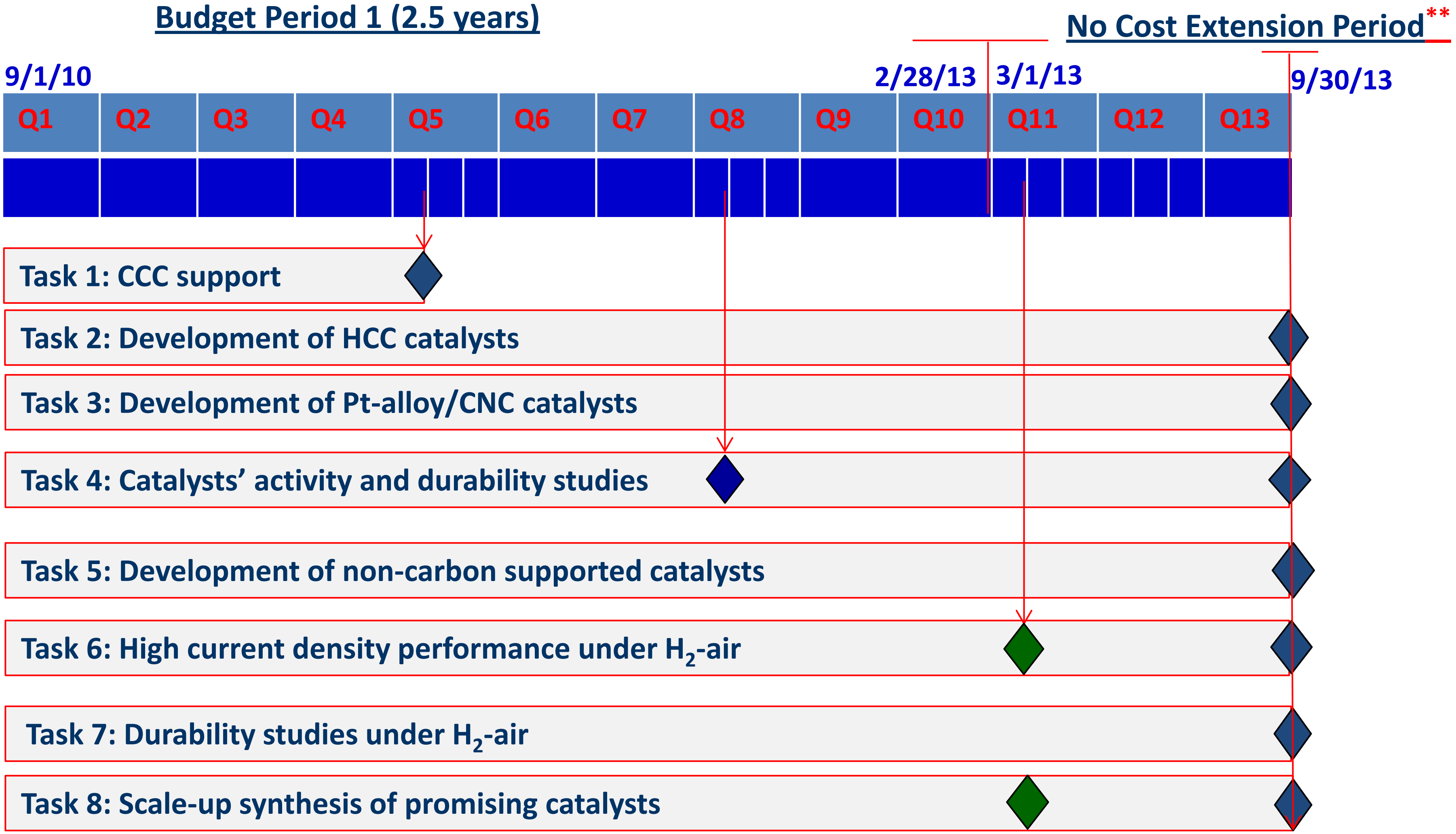
Approach:

- Optimization studies of **carbon composite catalyst** (**CCC**) support. (USC)
- Development of a process for the in-house synthesis of **carbon nanocage (CNC)** (USC and YU)
- 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). (USC & YU)
- Development of high volume procedures for the synthesis of promising catalyst. (USC & YU)

Primary Focus for Past Year:

- Performance evaluation of second generation CCC support. (USC)
  - Structural and physical characterization
  - Catalytic activity of CCC_{250} and CCC_{380} CCC supports
- Performance evaluation of USC Pt/CCC catalysts.
  - 40% Pt/CCC_{380} and 35% Pt/CCC_{250} catalysts
- Evaluation of different strategies for the optimization of **second generation hybrid cathode catalyst** (**HCC, HCC = PtCo/CCC_x, X=250 or 380 m^2/g**) with total loadings of 0.2 mg_{Pt} /cm^2 /MEA. (USC) (CCC supports having BET surface area between 250 and 380 m^2/g)
  - Initial and durability of kinetic mass activities.
  - Initial and durability of high current density performance in H_2-air.
    - ✓ HCC_{250} and HCC_{380} catalysts
  - Study the mass activity, durability and power density as a function of catalyst composition
- Performance evaluation of **Pt-alloy/CNC catalyst** activity and durability with total loadings of ~0.2 mg_{Pt} /cm^2 /MEA. (YU)

Project Timeline and Milestones*



◆ **End of task.**

◆ **Go-No-Go decision for the selection of 2 promising catalysts with high power density, mass activity and durability.**

◆ **Go-No-Go decision for the selection of 2 promising catalysts for further evaluation studies.**

*Milestones are explained in slides 5& 6

**No-cost extension (6 months) requested to complete Task 7

Technical Accomplishments
Milestone Progress (Apr '12 – Mar '13)

- 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. Milestone 1.

Characteristic	Units	2017 Targets	Status
Mass activity (80 ^{o}C, 100% RH, 150 kPa$_{abs}$.)	A/mg$_{Pt}$ @ 0.9 V$_{iR\text{-}free}$	0.44	0.43 (USC Pt$_2$Ni$_1$/CCC$_{<600}$) 0.38 (USC HCC$_{250}$) 0.37 (USC HCCC$_{380}$) 0.44 (YU Pt$_2$Ni$_1$/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 mV	47% (mass activity) & 15% (ECSA) for USC HCC$_{250}$ 53 mV loss at 0.8A/cm^2 under H_2-air for USC HCC$_{250}$ 46% (mass activity) & 19% (ECSA) for USC HCC$_{380}$ 53% (mass activity) & 27.8% (ECSA) for USC Pt$_2$Ni$_1$/CCC$_{<600}$) 31.8% (mass activity) & 26.3% (ECSA) for YU Pt$_2$Ni$_1$/CNC (Milestone 3)
Support durability (1.2 V for 400 h at 80 ^{o}C, H_2-$N_{2,\ 150}$ kPa$_{abs.}$ 100% RH)	% Mass activity loss % ECSA loss mV loss @ 0.8 A/cm^2	≤40% ≤40% ≤ 30 mV	50% mass activity loss and 42% ECSA loss for USC HCC$_{250}$ 29 mV loss at 0.8 A/cm^2 under H_2-air for USC HCC$_{250}$ 47% mass activity loss and 64% ECSA loss for the USC Pt/CCC$_{250}$ 118 mV loss at 0.8 A/cm^2 under H_2-air for the USC Pt/CCC$_{250}$ 47.7% mass activity loss and 42.7% ECSA loss For YU Pt$_2$Ni$_1$/CNC (NL) (Milestone 3)
PGM total loading	mg$_{Pt}$/cm^2	0.125	0.15-0.2 mg$_{catalyst}$/cm^2 with USC Pt/CCC$_{250}$, HCC$_{250}$, Pt$_2$Ni$_1$/CCC$_{<600}$, Pt$_1$Co$_1$/CCC$_{380}$ and 0.19 mg$_{catalyst}$/cm^2 with YU Pt$_2$Ni$_1$/CNC
PGM total content	g$_{Pt}$/kW (rated)	0.18	0.39 (33% Pt$_1$Co$_1$/CCC$_{380}$) – USC 0.36 (35% Pt/CCC$_{250}$ and HCC$_{250}$) – USC 0.34 (46% Pt$_2$Ni/CCC$_{<600}$) - USC 0.37 (50% Pt$_2$Ni/CNC-NL) – YU

Technical Accomplishments
Milestone Progress (Apr '12 – Mar '13)

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

Status: Achieved 1.25 and 1.04 A/cm^2 at 0.58 $V_{iR\text{-}free}$ for the Pt/CCC_{250} and HCC_{380} catalysts, respectively.

➢**Milestone 5: Sep 2013: 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. The catalyst durability studies under high current region in H_2-air for USC HCC and Pt_2Ni/CNC catalysts started in March 2012.

Phase-II

- **Task 1-4. Optimization studies of selected catalysts (HCC and Pt-alloy/CNC).**
  - **a) Initial and durability of mass activity**
  - **b) Support durability**
  - **c) Initial and durability of high current performance under H_2-air.**

- **Task 8. Optimization of scale-up synthesis procedure.**

- **Task 9. Short-stack testing**
  - **a) Construction of short-stack (up to 10 cells, 50 cm^2) using two selected catalysts**
  - **b) Durability of high current performance under H_2-air**
  - **c) Catalyst down selection**

  Criteria: Durability under cycling transportation conditions at 80 °C for 5000 hours.

Deliverable: Fuel cell and short stack will be constructed using the most promising catalyst and supplied to a DOE designated site.

Technical Accomplishments (I. Support Development)
Progress in the Synthesis of CCC Supports (Apr '12 – Mar '13)

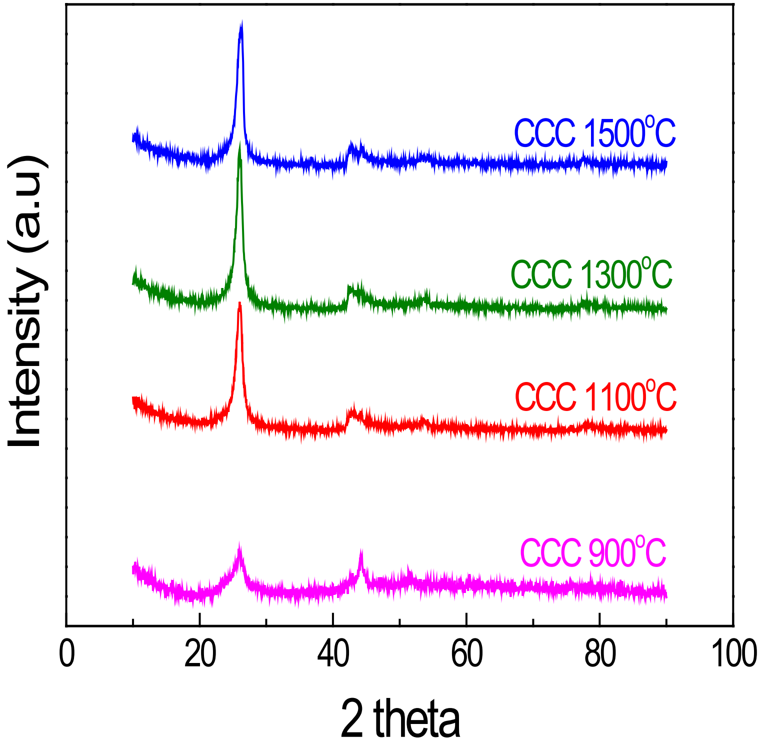
- **Surface modification** of carbon black with:
  - (i) **O**-containing group
  - (ii) **N**-containing group
- **Pyrolysis**

→

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

CCC,25°C → 5 °C/min → CCC,400°C, 1h → 5 °C/min → Pyrolysis (900-1500 °C)

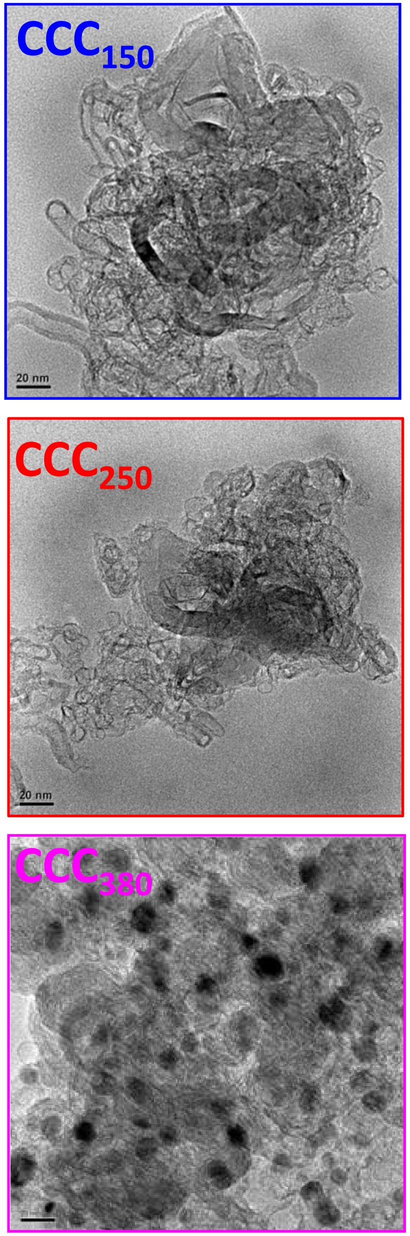
XRD



Pyrolysis Temp. (°C)	BET surface area (m^2/g)	Co % (ICP)
900	380	-
1100	250	0.66
1500	160	1.02

HIGHLIGHT:
XRD: The degree of graphitization increases with the increase in the pyrolysis temperature. Presence of Co particles are confirmed.
BET: The BET surface area decreases with the increase in the pyrolysis temperature.
HRTEM: Graphitic carbon containing carbon nano fibers/tubes are formed during pyrolysis between 1100 and 1500 °C in the presence of cobalt. **Milestone 1**

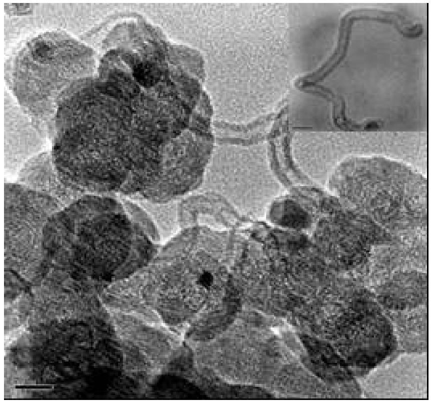
HRTEM



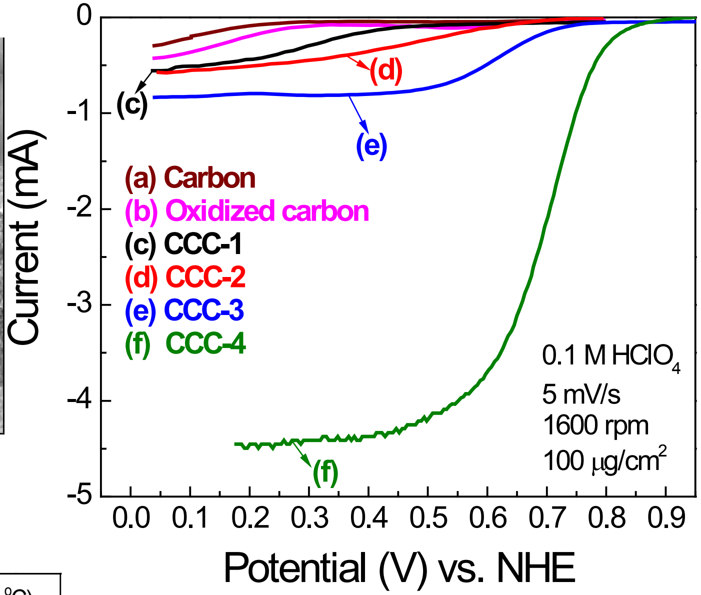
Scale bar 20 nm

Technical Accomplishments (I. Support Development)
Progress in Electrochemical Performance of CCC Supports (RRDE Studies) (Apr ’12 – Mar ’13)

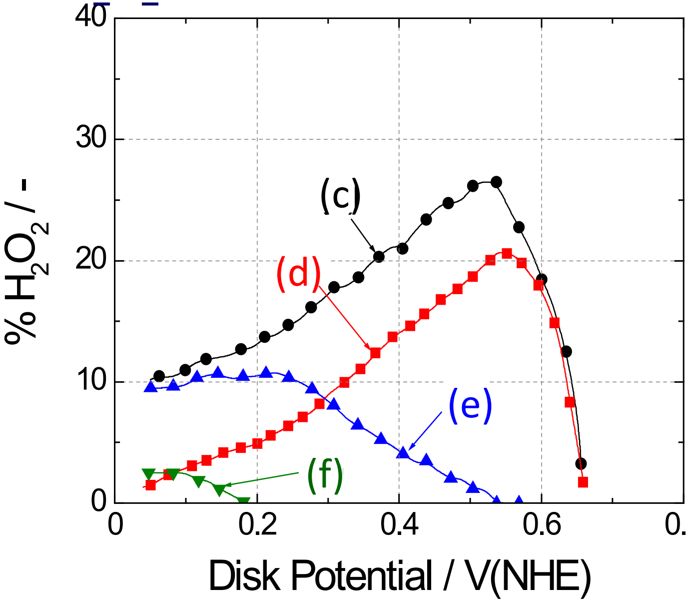
HRTEM



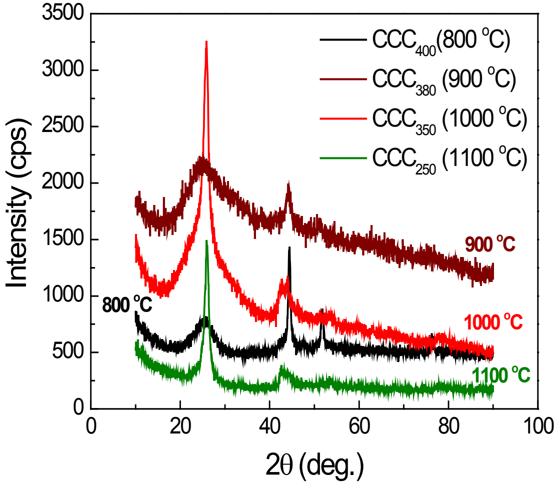
ORR – RRDE Studies



H_2O_2 production – RRDE Studies



XRD



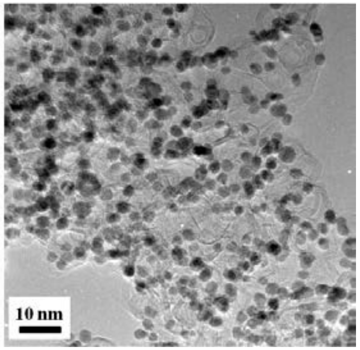
HIGHLIGHT:

- **Nanostructured fibers of graphitic carbon was formed as a result of metal-catalyzed pyrolysis (HRTEM).**
- **The degree of graphitization increases as the pyrolysis temperature increased (XRD)**
- **The onset potential for ORR increases when the as received carbon is subjected to various surface modifications.**
- **The carbon composite catalyst (curve f) showed an onset potential of 0.9 V_{RHE} and well-defined kinetic and mass transfer regions.**
- **The CCC-4 exhibits oxygen reduction to water via four-electron transfer with <2% H_2O_2 production (above 0.2 V vs. NHE). Milestone 1**

Technical Accomplishments (II. Catalyst Development)

Progress in the Synthesis of Pt/CCC and HCC Catalysts (Apr ’12 – Mar ’13)

Pt/CCC



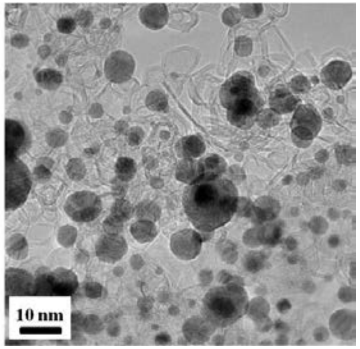
Transition metal salt impregnation

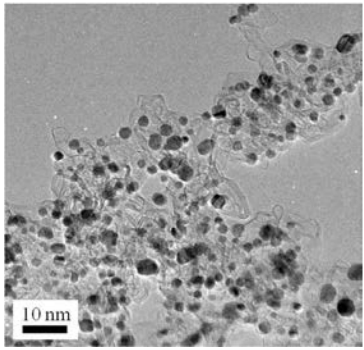
900℃ normal heat –treatment

Transition metal salt impregnation

900℃ modified heat –treatment

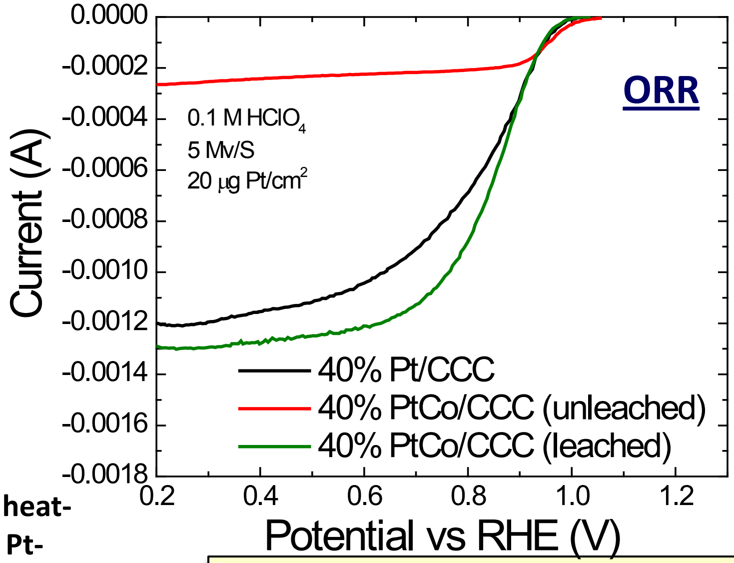
Normal heat-treatment Pt-alloy/CCC (HCC)

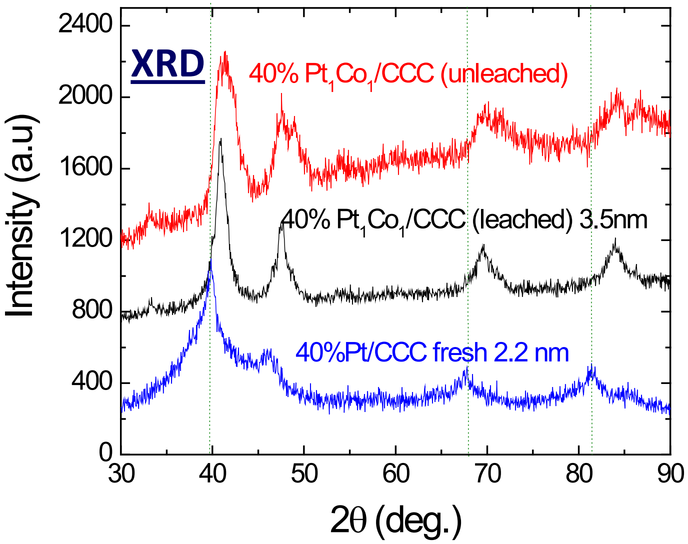


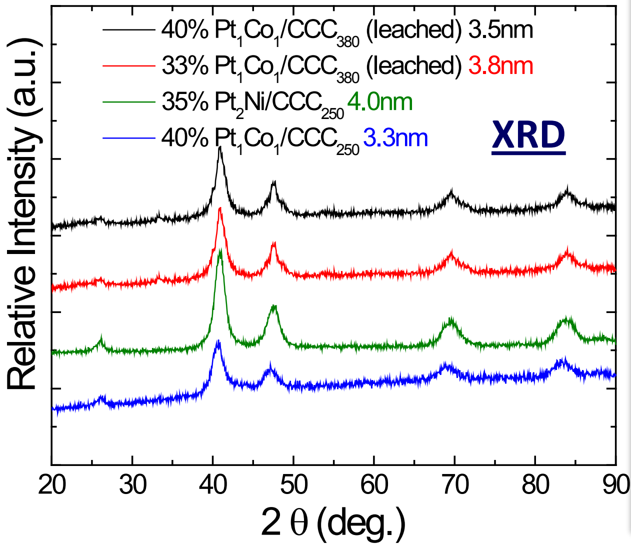


Modified heat-treated Pt-alloy/CCC (HCC)

HCC = Different Pt alloy catalysts





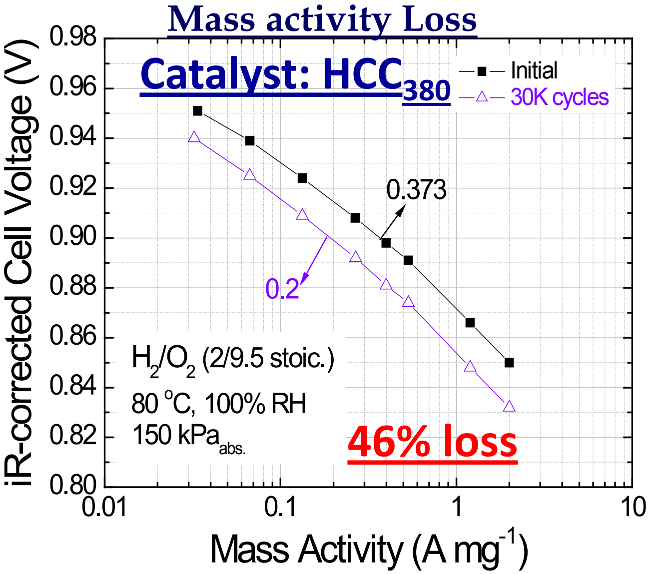


HIGHLIGHT:

- **Normal heat-treatment results in 8-10 nm particles. The new process yields in uniform particle size distribution with ~3.4 nm Pt-alloy particles.**
- **The alloy formation is confirmed from the shift in the Pt (220) peak and the particle size is ~3.5 nm.**
- **The ORR activity of the un-leached catalyst (0.2 mA) is drastically increased after leaching (1.2 mA). The onset potential for ORR is 1.0 V for the Pt_1Co_1/CCC_{250} (leached) catalyst.**
- **Current research is focused on the control of Pt/Co ratio and heat-treatment temperature which will result in highly active catalyst without the leaching step.**

Technical Accomplishments (III. Catalyst Durability)
Progress in Catalyst Durability Studies (0.6-0.925 V Cycling) Apr '12 – Mar '13

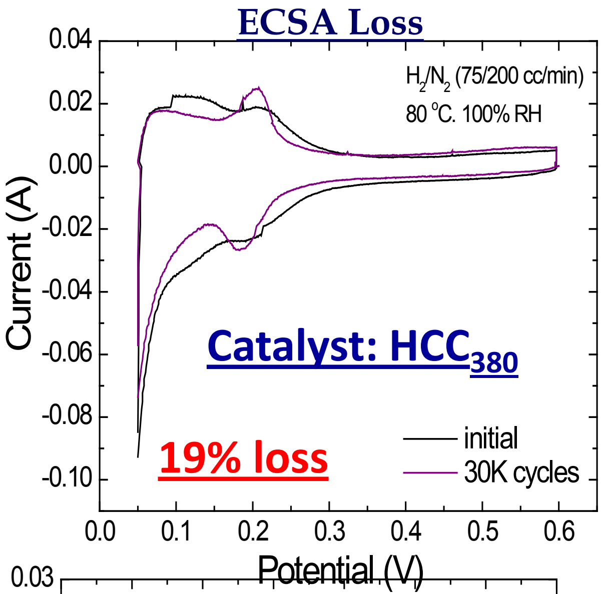
Mass activity Loss

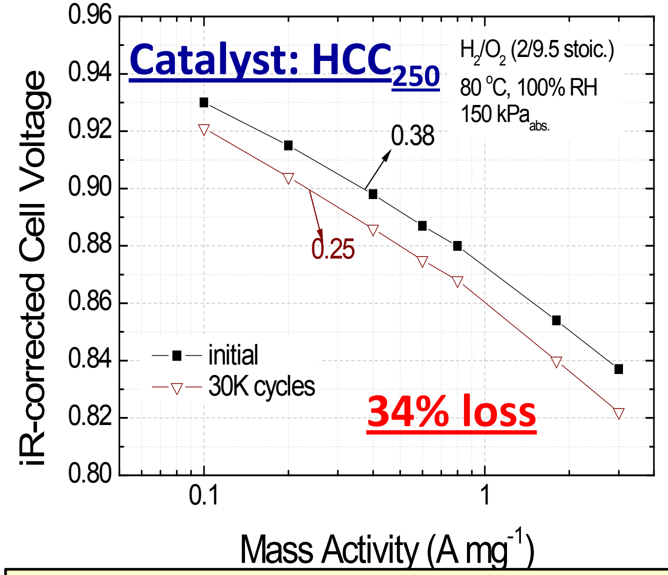


HCC_{380}	Mass Activity@0.9V (A/mg)	Loss (%)
Initial	0.37	-
30 k cycles	0.2	46%

HCC_{380}	ECSA (m^2/g)	Loss (%)
Initial	21.4	-
30 k cycles	17.4	19%

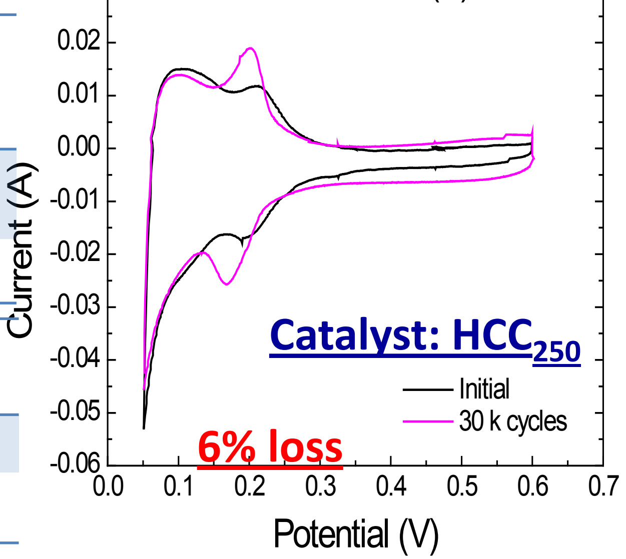
ECSA Loss





HCC_{250}	Mass Activity@0.9V (A/mg_{Pt})	Loss (%)
Initial	0.38	-
30K cycles	0.25	34

HCC_{250}	ECSA (m^2/g_{Pt})	Loss (%)
Initial	22.6	-
30K cycles	21.24	6



DOE Accelerated Stress Test Protocol

0.6 ~ 0.925 V, 50mV/s, 30,000 cycle, H_2/N_2 (200/75 sccm), 80°C, 100 % RH, single cell 25cm²

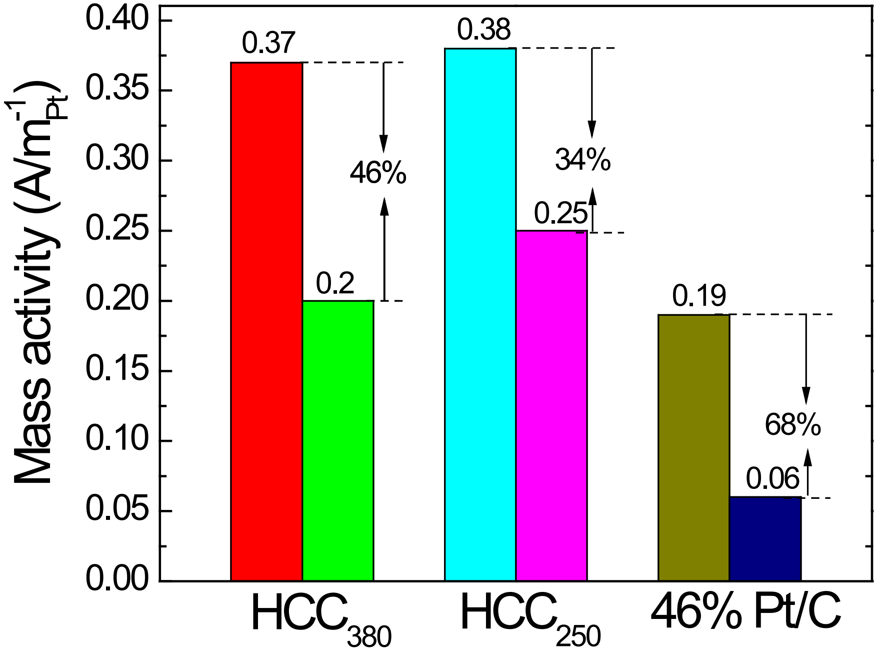
Pt mass activity : H_2/O_2, 2.0/9.5 stoic, 100% RH, 80°C, 150 kPa

HIGHLIGHT: (Status against 2017 DOE targets)

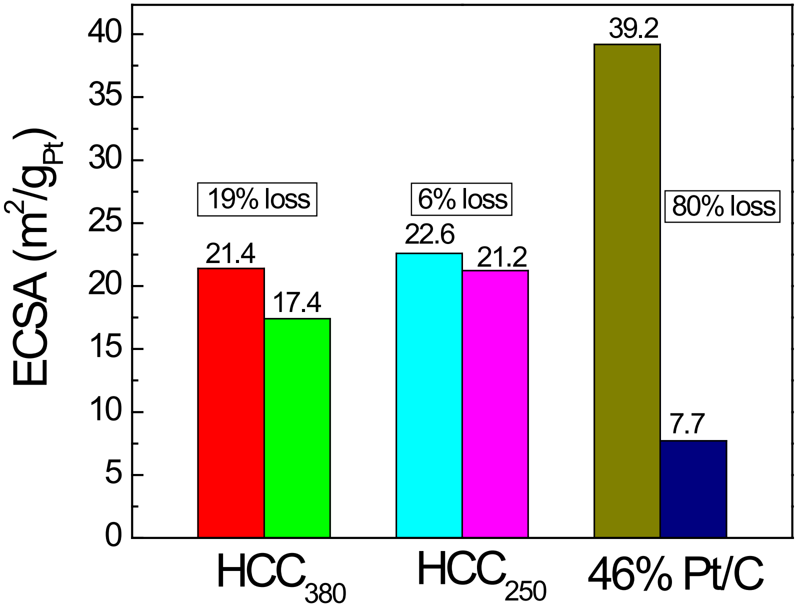
- **HCC_{250} satisfies the 2017 DOE target of ≤40% mass activity and ECSA loss after 30 k cycles (0.6-0.925 V). (Milestone 3)**

Technical Accomplishments (III. Catalyst Durability)
Progress in Catalyst Durability Studies (0.6-0.925 V Cycling) Apr '12 – Mar '13

Comparison Mass activity loss of HCC Catalysts



Comparison of ECSA loss of HCC Catalysts



Catalysts	Support BET (m^2/g)	Particle size (nm)	Initial mass activity (A/mg$_{Pt}$)	Mass activity loss (%)
46% Pt/C	-	2.2	0.19	68.0
HCC$_{380}$	380	3.5	0.37	46.0
HCC$_{250}$	250	4.0	0.38	34.0

HIGHLIGHT:

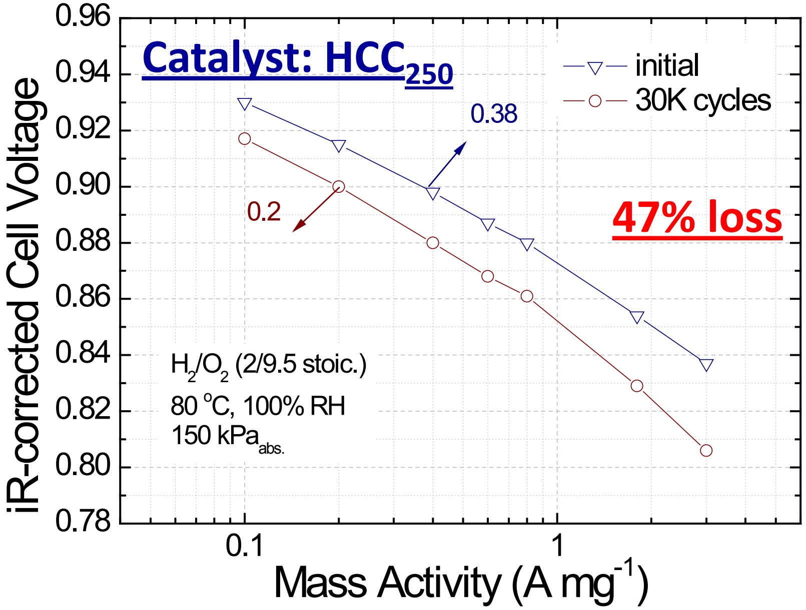
- HCC$_{250}$ satisfies the 2017 DOE target of ≤40% mass activity and ECSA loss after 30 k cycles (0.6-0.925 V). (Milestone 3)

HIGHLIGHT: (Status against 2017 DOE targets)

- HCC$_{250}$ and HCC$_{380}$ catalysts show mass activity loss of 34 and 46%, respectively. 46% Pt/C shows 68% mass activity loss. The 2017 DOE target is ≤40% loss after 30 k cycles. (Milestone 3)
- HCC$_{250}$ and HCC$_{380}$ catalysts show ECSA loss of 6 and 19%, respectively. The 46% Pt/C shows 80% ECSA loss.
- USC HCC catalysts satisfy the 2017 DOE target of ≤40% ECSA loss after 30 k cycles. (Milestone 3)

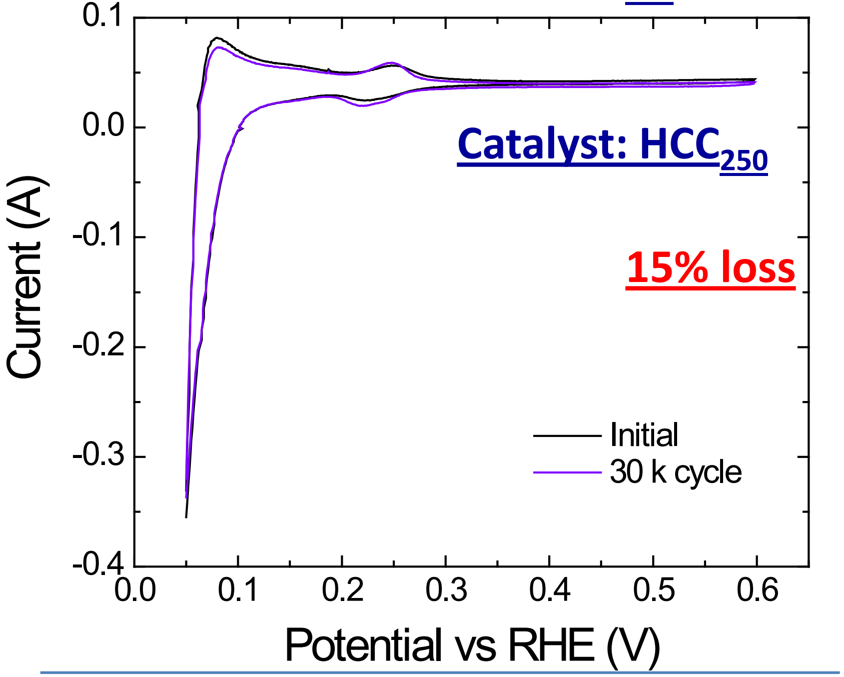
Technical Accomplishments (III. Catalyst Durability)
Progress in Catalyst Durability Studies (0.6-1.0 V Cycling) Apr ’12 – Mar ‘13

Mass activity loss of HCC_{250}



	Mass Activity@0.9V (A/mg)	Loss (%)
Initial	0.38	-
30K cycles	0.20	47%

ECSA loss of HCC_{250}



	ECSA (m^2/g_{Pt})	Loss (%)
Initial	23.2	-
30K cycles	19.8	15

DOE Accelerated Stress Test Protocol
0.6 ~ 1.0 V, 50mV/s, 30,000 cycle, H_2/N_2
80°C, 100 % RH, single cell 25cm²
Catalyst : HCC_{250}
Pt mass activity : H_2/O_2, 2.0/9.5 stoic, 100% RH, 80°C, 150 kPa

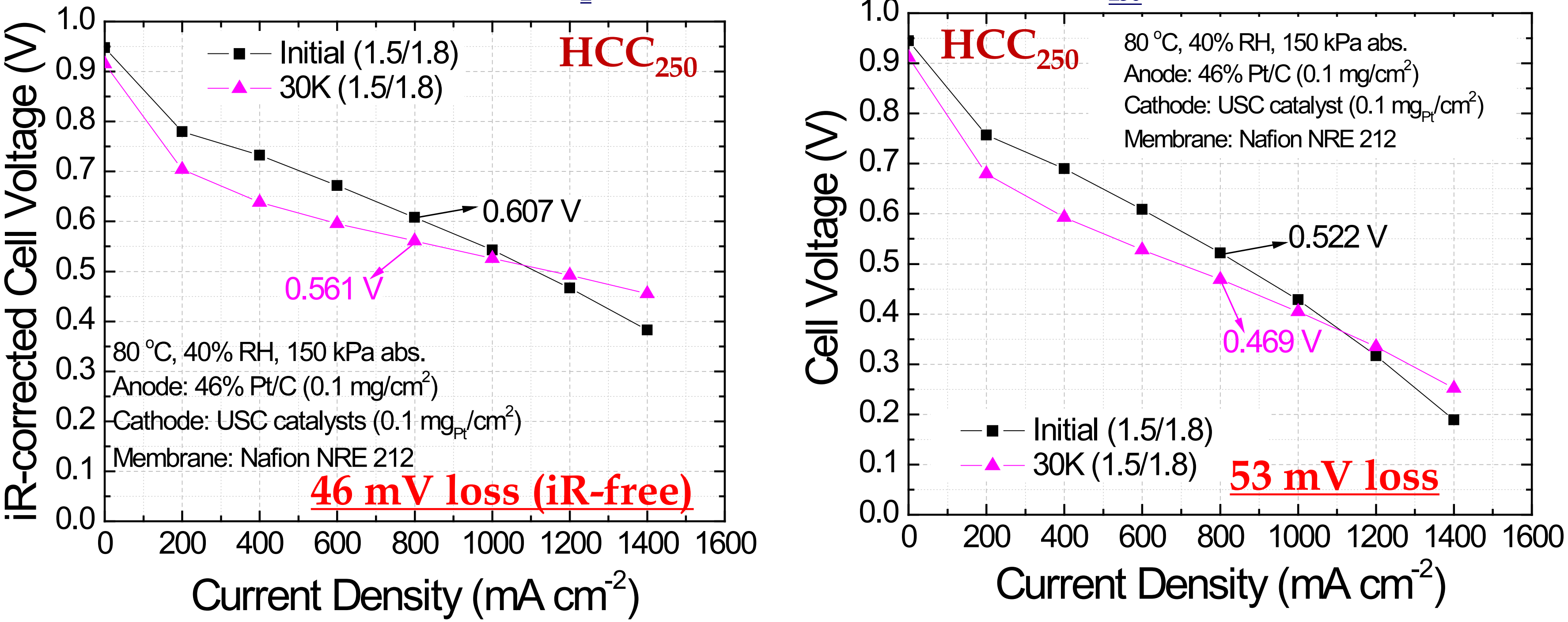
HIGHLIGHT: Status against 2017 DOE targets

- **USC HCC_{250} catalyst shows 47% mass activity loss (2017 DOE target is ≤40%) and 15% ECSA loss (2017 DOE target is ≤40%) after 30 k cycles between 0.6 and 1.0 V. (Milestone 3)**

Technical Accomplishments (III. Catalyst Durability)

Progress in Catalyst Durability Studies: HCC_{250} (0.6-1.0 V Cycling) Apr ’12 – Mar ‘13

H_2-air Fuel Cell Performance of HCC_{250}



80 °C, 40% RH, 150 kPa abs.
Anode: 46% Pt/C (0.1 mg/cm²)
Cathode: USC catalysts (0.1 mg_{Pt}/cm²)
Membrane: Nafion NRE 212

46 mV loss (iR-free)

80 °C, 40% RH, 150 kPa abs.
Anode: 46% Pt/C (0.1 mg/cm²)
Cathode: USC catalyst (0.1 mg_{Pt}/cm²)
Membrane: Nafion NRE 212

53 mV loss

DOE Accelerated Stress Test Protocol
0.6 ~ 1.0 V, 50mV/s, 30,000 cycle, H_2/N_2, 80°C, 100 % RH, single cell 25cm²
Catalyst : HCC_{250}
Polarization : H_2/air, 1.5/1.8 stoic, 40% RH, 59°C, 150 kPa

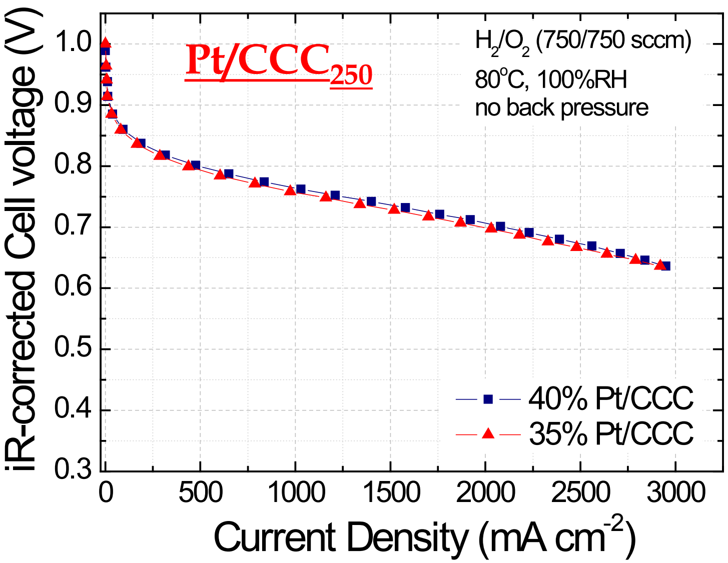
Catalysts	Cell voltage loss after cycling (mV)
HCC_{250}	53 (30 k)
46% Pt/C	237 (20 k) (Not shown)

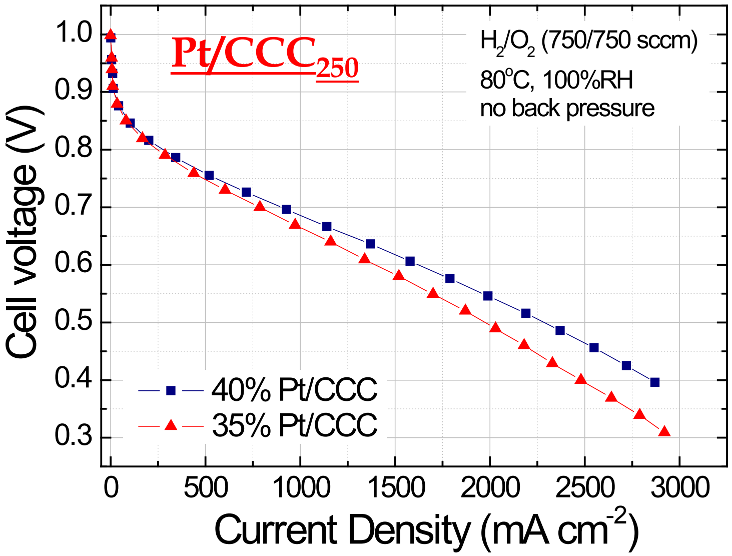
HIGHLIGHT: (Status against 2017 DOE targets)

- **The iR-corrected cell voltage loss at 800 mA/cm² (1.5/1.8 stoic.) is 46mV (from 607mV to 561mV).**
- **The cell voltage loss at 800 mA/cm² (1.5/1.8 stoic.) is 53 mV (from 522 mV to 469 mV) against the 2017 DOE target of 30 mV loss after 30 k cycles.**
- **The 46% Pt/C shows 237 mV loss after 20 k cycles at 0.8 A/cm². (Milestone 3)**

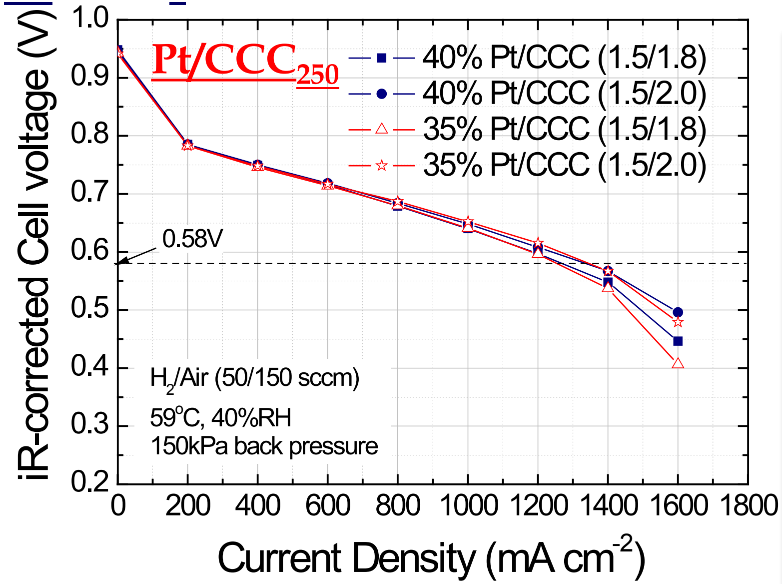
Technical Accomplishments
Progress in Initial Performance Evaluation of Pt/CCC$_{250}$ Catalysts (Apr ’12 – Mar ’13)

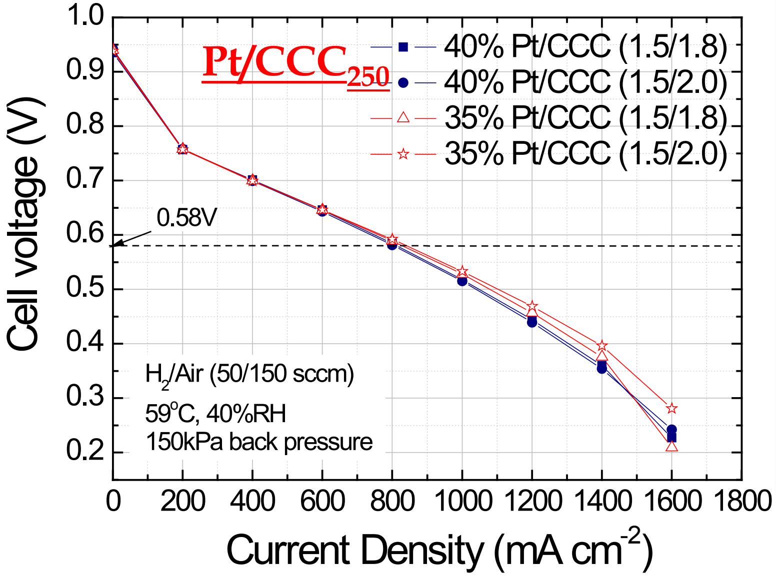
H_2-O_2 Fuel Cell Performance Pt/CCC$_{250}$





H_2-air Fuel Cell Performance of Pt/CCC$_{250}$





HIGHLIGHT:

- **The Pt/CCC$_{250}$ catalysts show 1.25 and 1.3 A/cm^2 current density at 0.58 V$_{iR\text{-}free}$ at cathodic stoics of 1.8 and 2, respectively.**
- **The better fuel cell performance is due to the support purification process developed at USC to remove the amorphous carbon to obtain purified graphitic carbon support.**

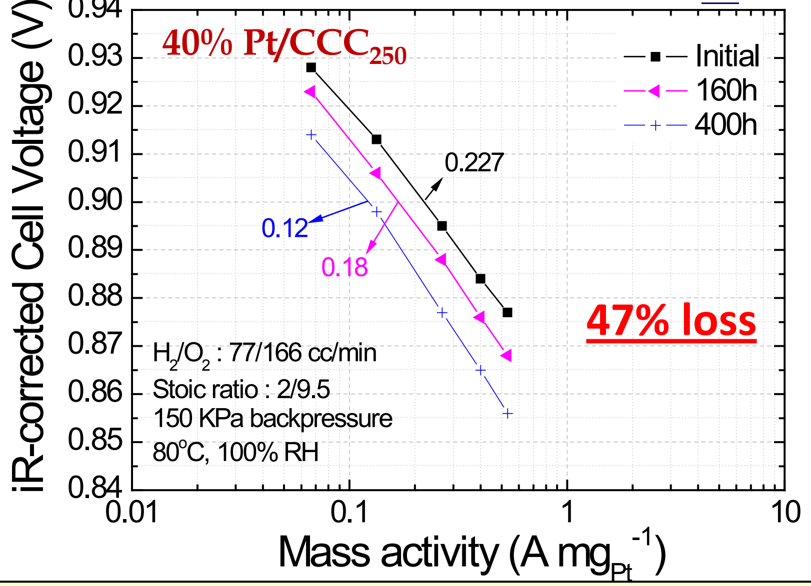
Milestone 4 (Initial high current performance under H_2/air)

Technical Accomplishments (IV. Support Durability)

Progress in Support Stability Studies at 1.2 V Potential Holding (Apr ’12 – Mar ’13)

1. Support Stability Studies of 40% Pt/CCC_{250}

Mass Activity Loss of Pt/CCC_{250}



HIGHLIGHT: (Status against 2017 DOE targets)

•The mass activity decreases from 0.227 to 0.12 A/mg (47.1% mass activity loss) after 400 h.

•At 800 mA/cm², the iR-cell voltage loss is 130 mV (from 673mV to 543mV) after 400 h potential holding at 1.2 V.

• At 800 mA/cm², the cell voltage loss is 118 mV (from 584 mV to 466 mV) after 400 h potential holding at 1.2 V. (Milestone 3)

DOE Test Protocol

Hold at 1.2V for 24 h, H_2/N_2

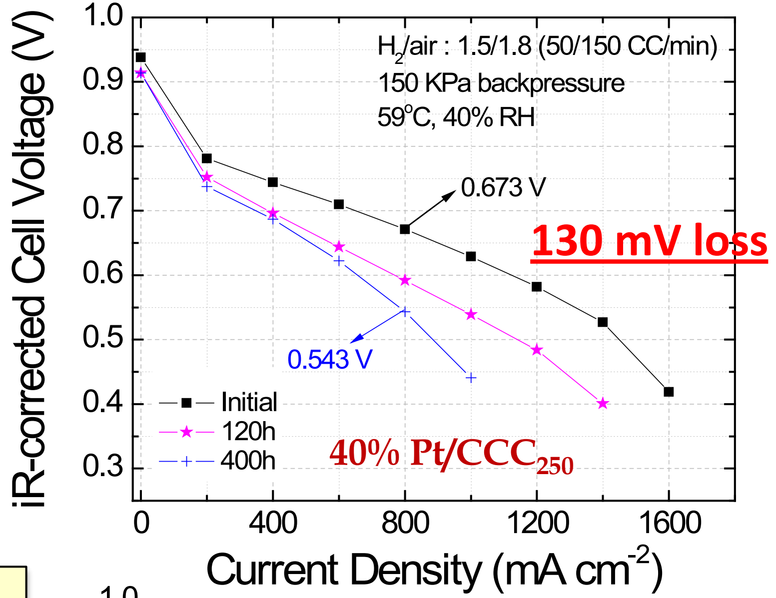
80°C, 150 kPa, 100 % RH, single cell 25cm²

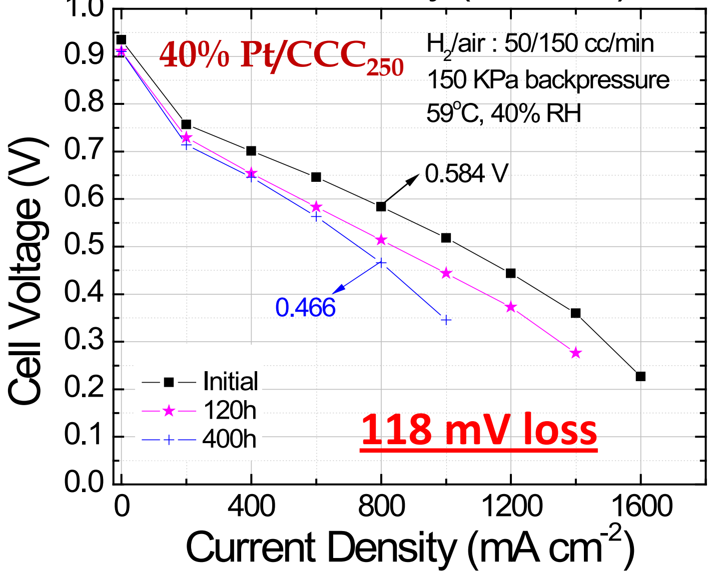
Catalyst : USC Pt/CCC_{250}

Polarization : H_2/air, 1.5/1.8 stoic, 40% RH, 59°C, 150 kPa

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

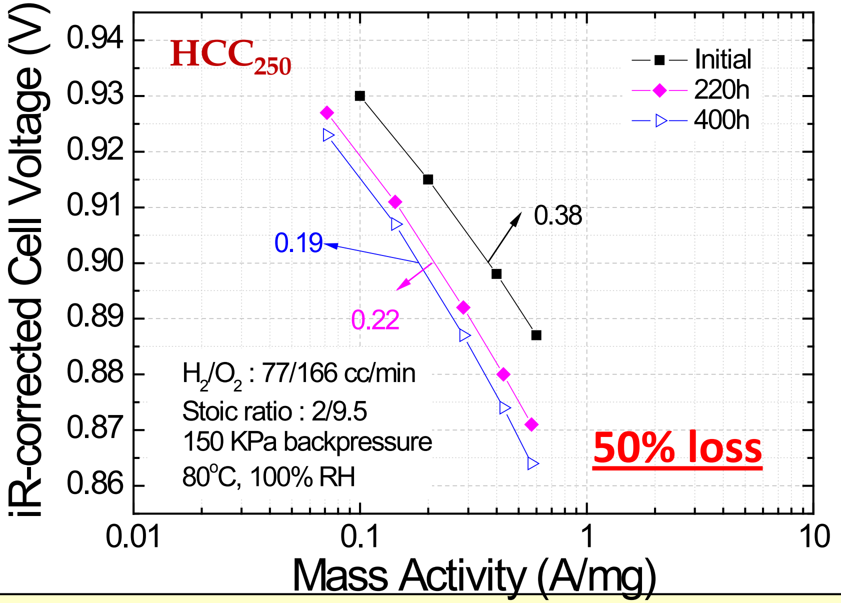
H_2-air Performance of Pt/CCC_{250}



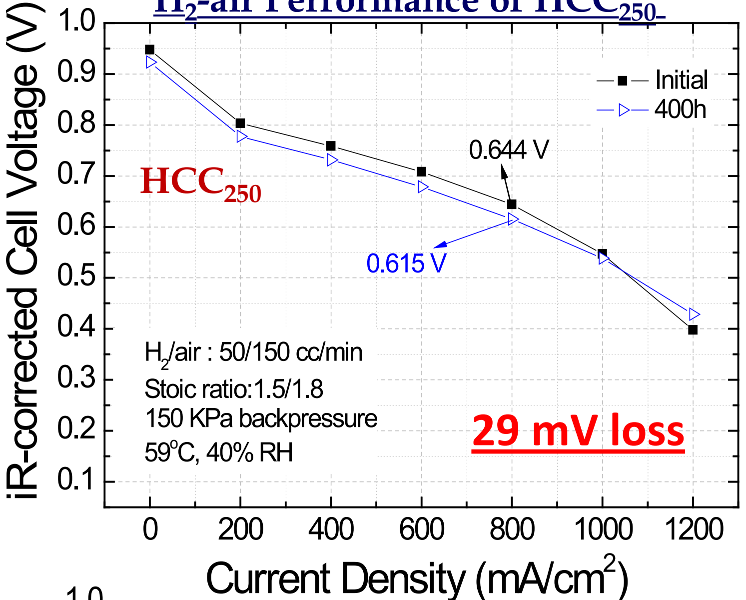


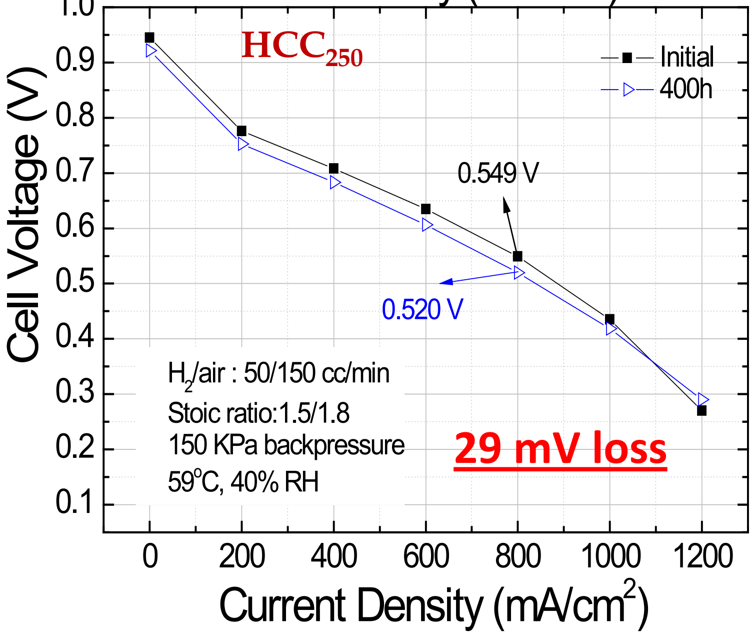
Technical Accomplishments (IV. Support Durability)
Progress in Support Stability Studies at 1.2 V Potential Holding (Apr ’12 – Mar ’13)
2. Support Stability Studies of HCC_{250}

Mass Activity Loss of HCC_{250}



H_2-air Performance of HCC_{250}





HIGHLIGHT: (Status against 2017 DOE targets)

- **The mass activity decreases from 0.38 to 0.19 A/mg after 400 h potential holding at 1.2 V (50% mass activity loss).**
- **The potential loss is 29 mV (iR-corrected) after 400 h potential holding.**
- **The cell potential loss is 29 mV after 400 h potential holding against the 2017 DOE target of 30 mV loss after 400 h. (Milestone 3)**

DOE Test Protocol
Hold at 1.2V for 24 h, H_2/N_2
80°C, 150 kPa, 100 % RH, single cell 25cm²
Catalyst : USC HCC_{250}
Polarization : H_2/air, 1.5/1.8 stoic, 40% RH, 59°C, 150 kPa
Pt mass activity : H_2/O_2, 2.0/9.5 stoic, 100% RH, 80°C, 150 kPa

Technical Accomplishments (IV. Support Durability)
Progress Against DOE 2017 Targets for Pt/CCC$_{250}$ and HCC$_{250}$ Catalysts

Catalyst Durability Test (Potential Cycling between 0.6 and1.0 V) (Milestone 3)

Catalyst	Particle size (nm)	Mass activity (A/mg$_{Pt}$)		ECSA (m^2/g)		Cell voltage loss at 800 MA/cm^2 (mV)	
		Initial	30 k	Initial	30 k	Cell voltage	Cell voltage (iR-free)
HCC$_{250}$	4.0	0.38	0.2 (47% loss)	23.2	19.8 (15% loss)	53 mV	46 mV

Support Stability Test (Potential Holding at 1.2 V) (Milestone 3)

Catalyst	Particle size (nm)	Mass activity (A/mg$_{Pt}$)		ECSA (m^2/g)		Cell voltage loss at 800 MA/cm^2 (mV)	
		Initial	400 h	Initial	400 h	Cell voltage	Cell voltage (iR-free)
HCC$_{250}$	4.0	0.38	0.19 (50% loss)	21.3	16.2 (42% loss)	29 mV	29 mV
Pt/CCC$_{250}$	2.5	0.227	0.12 (47% loss)	59.4	21.3 (64% loss)	118 mV	130 mV

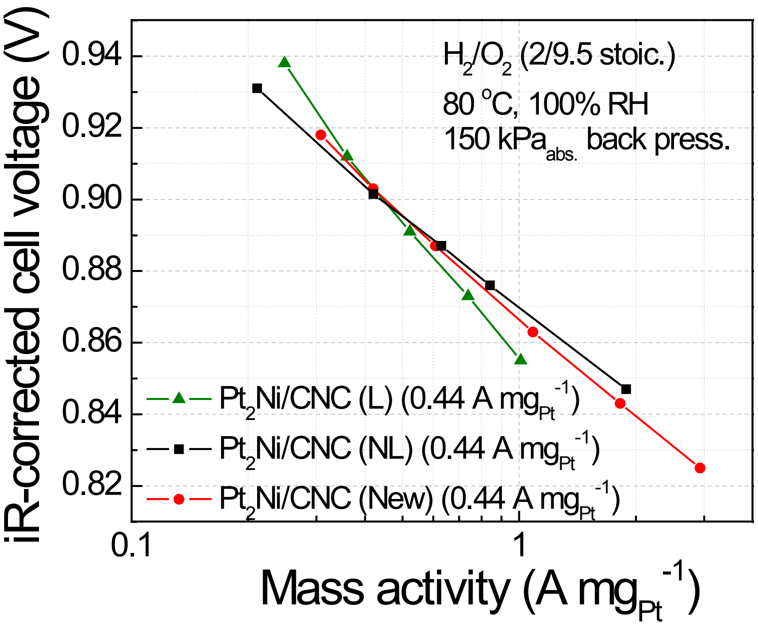
HIGHLIGHT: (Status against 2017 DOE targets)

- **HCC$_{250}$ catalyst shows 47% mass activity loss and 15% ECSA loss after 30 k cycles between 0.6 and 1.0 V. The 2017 DOE target is ≤40% loss of mass activity and ECSA after 30 k cycles. The potential loss at 800 mA/cm^2 (1.5/1.8 stoic.) is 53 mV for the HCC$_{250}$ against 2017 DOE target of 30 mV after 30 k cycles.**
- **The mass activity loss is 50% and the potential loss at 800 mA/cm^2 is 29 mV after 400 h potential holding at 1.2 V for the HCC$_{250}$ catalyst. The 2017 DOE targets are ≤40% mass activity loss and 30 mV potential loss after 400 h.**

Sep 2013: GO/NO-GO decision for Milestones 3, 4 and 5

Criteria: Selection of two most promising catalysts with (i) high kinetic mass activity, (ii) ≤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 ^{o}C, 40% RH, 150 kPa$_{abs.}$ outlet pressure.

Technical Accomplishments
Progress in Catalyst Stability Studies of Pt-alloy/CNC Catalysts (YU) (0.6-1.0 V Cycling)



HIGHLIGHT: (Milestone 2)

• YU catalysts show mass activities of 0.44 for Pt_2Ni/CNC (L), Pt_2Ni/CNC (NL) and Pt_2Ni/CNC(New) catalysts.

New = CNC under development at YU

NL – Not Leached
L - Leached

Catalyst Durability Test (Potential Cycling between 0.6 and1.0 V)

Catalyst	$MA_{Initial}$ (A mg_{Pt}^{-1})	MA_{30k} (A mg_{Pt}^{-1})	$ECSA_{Initial}$ (%)	$ECSA_{30k}$ (%)
Pt_2Ni/CNC (L)	0.44	0.28 (36% loss)	24.6	16.9 (31% loss)
Pt_2Ni/CNC (NL)	0.44	0.30 (31.8% loss)	24.3	17.9 (26.3% loss)

HIGHLIGHT: (Status against 2017 DOE targets)

- **Pt_2Ni/CNC (L) catalyst shows mass activity loss of 36% and ECSA loss of 31% after 30 k cycles. This catalyst satisfies the 2017 DOE target of ≤40% loss of mass activity and ECSA after 30 k cycles. (Milestone 3)**
- **Pt_2Ni/CNC (NL) catalyst shows mass activity loss of 31.8% and ECSA loss of 26.3% after 30 k cycles. This catalyst satisfies the 2017 DOE target of ≤40% loss of mass activity and ECSA after 30 k cycles. (Milestone 3)**

DOE Accelerated Protocol

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

80°C, 100 % RH, single cell 25cm²

Catalysts : Yonsei U. Pt-alloy/CNC, 0.1mg_{metal}/cm²

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

Technical Accomplishments
Progress in Support Durability Studies of Pt-alloy/CNC Catalysts (YU) (1.2 V Potential Holding)

Support Stability Test (Potential Holding at 1.2 V)

Catalyst	$MA_{Initial}$ ($A\ mg_{Pt}^{-1}$)	MA_{400h} ($A\ mg_{Pt}^{-1}$)	$ECSA_{Initial}$ m^2/g_{Pt}	$ECSA_{400h}$ m^2/g_{Pt}
Pt_2Ni/CNC (L)	0.44	0.2 (54% loss)	24.6	12.5 (49% loss)
Pt_2Ni/CNC (NL)	0.44	0.23 (47.7% loss)	24.3	14.0 (42.4% loss)

HIGHLIGHT: (Status against 2017 DOE targets)

- **YU catalysts show mass activities of 0.44 and 0.44 for Pt_2Ni/CNC (L) and Pt_2Ni/CNC (NL) catalysts, respectively.**
- **Pt_2Ni/CNC (L) catalyst shows mass activity loss of 54% and ECSA loss of 12.5% after 400 h.**
- **Pt_2Ni/CNC (NL) catalyst shows mass activity loss of 47.7% and ECSA loss of 14.0% after 400 h.**
- **The 2017 DOE target is ≤40% loss of mass activity and ECSA after 400 h potential holding at 1.2 V. (Milestone 3)**

NL – Not Leached; L - Leached

DOE Accelerated Protocol

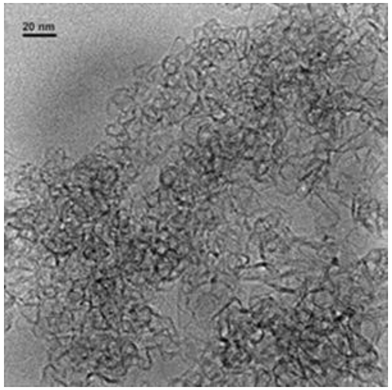
Hold at 1.2V for 24 h, H_2/N_2

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

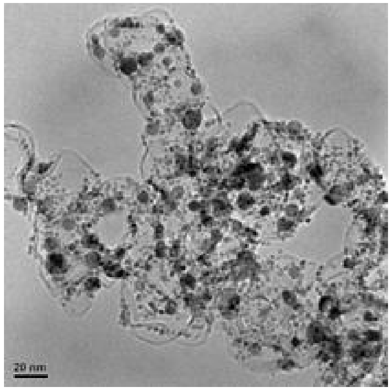
Catalyst : Yonsei U. Pt_2Ni_1/C, $0.1mg_{metal}/cm^2$

Pt mass activity : H_2/O_2, 2.0/9.5 stoic, 100% RH,

80°C, 150 kPa



CNC



Pt_2Ni/CNC(L)

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 Phase II)
  - 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

In the future work during the no-cost extension period (April 01, 2013 – September 30, 2013), we plan to continue with the progress made so far with the HCC catalysts and further research will be focused on the following tasks:

Task 1: Transition metal content optimization studies and synthesis of Pt-alloy/CCC_{250} catalysts containing low transition metal content (<8 wt.%) in the alloy using the procedure developed at USC.

Task 2: Transition metal content optimization studies and synthesis of Pt-alloy/CNC catalysts containing low transition metal content (<8 wt.%) in the alloy.

Task 3: Synthesis of highly stable graphitized CCC and CNC supports. These supports will be synthesized by using two different methods which require (i) preparation of carbon composite support synthesized at 900 ^{o}C and (ii) removal of amorphous carbon from the CCC and CNC support by chemical oxidation at elevated temperature in the presence of oxygen. The CCC and CNC supports will also be synthesized using transition metal containing precursors at elevated temperatures (between 700 and 1500 ^{o}C). The goal is to obtain CCC and CNC supports with BET surface area of 150 m^2/g only by heating and/or removal of any amorphous carbon present by means of chemical oxidation. Our preliminary studies indicated that the percentage of amorphous carbon decreases due to the high temperature annealing procedure.

Subtask 3.1: Optimizing the procedures to purify the high temperature treated carbon composite supports to remove transition metals and amorphous carbon.

Task 4: Deposition of Pt-alloy catalysts on 140-180 m^2/g highly graphitized carbon composite supports which are completely purified to remove both amorphous carbon and traces of transition metals.

The goal is to select a best performing catalysts which satisfy the 2017 DOE requirements of ≤40% loss of mass activity, ≤40% loss of ECSA and <30 mV loss at 0.8 A/cm^2 under H_2-air after 30 k potential cycling (between 0.6 and 1.0 V) and potential holding (at 1.2 V for 400 h) experiments.

Summary: Status Against 2017 DOE Targets (As of March 2013)

Characteristic	Units	2017 Targets	Status
PGM total loading	mg_{Pt}/cm^2	0.125	0.15-0.2 $mg_{catalyst}/cm^2$ with USC Pt/CCC_{250}, HCC_{250}, $Pt_2Ni_1/CCC_{<600}$, Pt_1Co_1/CCC_{380} and 0.19 $mg_{catalyst}/cm^2$ with YU Pt_2Ni_1/CNC
PGM total content	g_{Pt}/kW (rated)	0.18	0.39 (33% Pt_1Co_1/CCC_{380}) – USC 0.36 (35% Pt/CCC_{250} and HCC_{250}) – USC 0.34 (46% $Pt_2Ni/CCC_{<600}$) - USC 0.37 (50% Pt_2Ni/CNC-NL) – YU
Mass activity (80 °C, 100% RH, 150 kPa_{abs}.)	A/mg_{Pt} @ 0.9 $V_{iR\text{-}free}$	0.44	0.43 (USC $Pt_2Ni_1/CCC_{<600}$) 0.38 (USC HCC_{250}) 0.37 (USC $HCCC_{380}$) 0.44 (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 mV	47% (mass activity) & 15% (ECSA) for USC HCC_{250} 53 mV loss at 0.8A/cm^2 under H_2-air for USC HCC_{250} 46% (mass activity) & 19% (ECSA) for USC HCC_{380} 53% (mass activity) & 27.8% (ECSA) for USC $Pt_2Ni_1/CCC_{<600}$) 31.8% (mass activity) & 26.3% (ECSA) 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 mV loss @ 0.8 A/cm^2	≤40% ≤40% ≤ 30 mV	50% mass activity loss and 42% ECSA loss for USC HCC_{250} 29 mV loss at 0.8 A/cm^2 under H_2-air for USC HCC_{250} 47% mass activity loss and 64% ECSA loss for the USC Pt/CCC_{250} 118 mV loss at 0.8 A/cm^2 under H_2-air for the USC Pt/CCC_{250} 47.7% mass activity loss and 42.7% ECSA loss For YU Pt_2Ni_1/CNC (NL) (Milestone 3)

Team Members who contributed to this presentation

University of South Carolina

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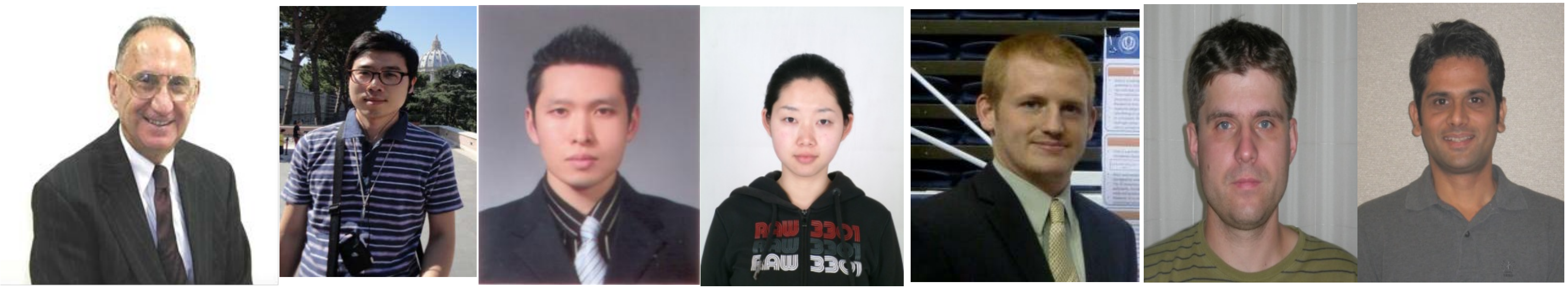
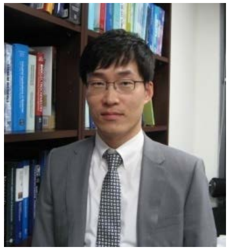
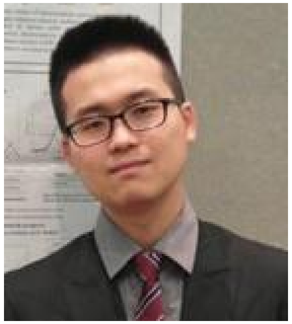


Yonsei University (S. Korea)

Hansung Kim Hyun-suk Oh Woong Hee Lee





Acknowledgement

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