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

P. I.: Branko N. Popov
Center for Electrochemical Engineering
University of South Carolina
Columbia SC 29208.

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Overview

Timeline

- Start date: June 2010
- End date: Feb 2013 (Phase I)
  : May 2014 (Phase II)
- Percent complete: 15%

Budget

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

Partners

- Hyundai Motor Company (HMC), S. Korea
- Yonsei University (YU), S. Korea

Barriers

- Catalyst cost
- Catalyst performance
- Catalyst durability

Targets

- PGM loading of 0.1 mg/cm^2
- Mass activity of 0.44 A/mg$_{Pt}$ at 0.9 V (Year 2015).
- Specific activity of 720 μA/cm^2 at 0.9 V (Year 2015).
- Electrochemical surface area loss <40%
- Cycling performance for 5000 h at ≤ 80 ^{o}C and 5000 h at > 80 ^{o}C

Project Lead

- University of South Carolina (USC)

Relevance

- **Objectives:**
  - To develop low cost and durable hybrid cathode catalyst (HCC) consisting of Non-Pt carbon composite catalyst (CCC) and low PGM for ORR.
  - To develop Pt_3M/activated graphitic carbon (AGC) catalysts.
- **Specific objectives:**
  - Achieve kinetic mass activity in H_2/O_2 fuel cell higher than DOE target of 0.44 A mg_{PGM}^{-1} and demonstrate durability of the kinetic activity per DOE cycling protocol between 0.6 and 1.0 V.
  - Demonstrate high current density performance and durability in H_2/air fuel cell to meet 2015 DOE targets.
  - Define the parameters which control the number of non-metallic catalytic sites on CCC and optimize the procedure for the formation of more active leached Pt-alloy HCC.
  - Define the parameters that control the activity of leached Pt-alloy catalyst deposited on activated graphitic carbon (AGC) support.
  - Develop corrosion resistant hybrid supports such as TiO_2-CCC and AGC.
  - Develop facile scale-up synthesis procedure for the developed catalysts (at least 100g).
  - Construct short-stack (50 cm^2, up to 10 cells) and evaluate the performance under simulated automotive conditions.

Approach

- **Currently used approach is to decrease the platinum loading of cathode electrodes is based on optimization of electrode structures and implementation of more active Pt alloy catalyst. New approach is suggested in this project which consists of:**

- **Strategy 1:** Development of Hybrid Catalyst: **For the first time, a non-platinum carbon based composite catalyst (CCC) with active catalytic sites for ORR will be used to synthesize a hybrid catalyst (HCC) combining the contribution of the active sites from (CCC) when used as a support and low loading of Pt-alloy catalyst. [*B. N. Popov et. al., J Power Sources, 195 (2010) 445.*]**
  - The synergetic effect present in HCC results from contribution of the active sites present in CCC which improves the catalyst performance at low potentials.
  - Implementation of Pt or leached Pt-alloy active sites will increase the mass activity at high potentials.
  - Optimization of the electrode structure will increase the performance at low potentials.
- **Strategy 2: Development of Activated Graphitic Carbon Supported Pt-alloy catalyst.**
  - Evaluation of the effects which control the activity of leached Pt_3M catalyst deposited on AGC. [***H. Kim et. al., J. Power Sources, 183(2) (2008) 600.***]
- **Facile scale-up synthesis procedures for the promising catalysts (at least 100 g).**

- **Strategy 3: Development of Corrosion Resistant Catalyst Support : Synthesis of corrosion-resistant hybrid TiO_2-CCC [*B. N. Popov et. al., J. Am. Chem. Soc., 131 (2009) 13898.*] and activated graphitic carbon supports [*H. Kim et.al., Electrochem. Commun., 10 (2008) 1048.*] to overcome the drawbacks associated with carbon corrosion under automotive operating conditions**.

Milestones and GO/NO-GO (Phase – I)

- **Milestone 1**:

Sep 2011: Preparation of carbon composite catalyst (Support)

Status: Achieved onset potential for oxygen reduction reaction close to 0.9 V and < 2.5% H_2O_2 production. (needs durability optimization).

- **Milestone 2**:

Sep 2011: Initial mass activity > 0.44 A mg_{Pt}^{-1} in H_2/O_2 for the hybrid cathode catalysts.

Status: Accomplished 0.42 A mg_{Pt}^{-1},0.40 A mg_{Pt}^{-1} and 0.41 A mg_{Pt}^{-1} in two laboratories for HCC-1, HCC-2, and Pt_3M/AGC catalysts, respectively. (Need further increase and durability optimization.)

- **Milestone 3**:

Jun 2012: Durability of kinetic mass activity of HCC (Pt/CCC, Pt-M/CCC, Pt-M/TiO_2-CCC and Pt_3M/AGC). At least 0.24 A mg_{Pt}^{-1} after 30 K cycles tested according to DOE protocol (0.6-1.0 V).

Status: Achieved 0.27 A mg_{Pt}^{-1} after 30 K cycles for Pt_3M/AGC catalyst in 25 cm^2 cell. (Need similar or higher performance for HCC catalysts and to be confirmed in a 50 cm^2 cell in at least two laboratories.)

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

Goal: to maintain high activity and achieve $\leq$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).

Milestones and GO/NO-GO (Phase – I)

- **Milestone 4**:

Feb 2013: Initial high current density performance in H_2-air (80 ^oC, 100% / 40% RH, 150 $kPa_{abs.}$ outlet pressure, 1.5/1.8 stoic.)

Status: Achieved 1.2, 1.25 and 1.45 A cm^{-2} (@ 0.56 V) at 0.1 mg_{Pt} cm^{-2} for the HCC-1, HCC-2 and Pt_3M/AGC in 25 cm^2 cell. (Need improvements and to be performed in 50 cm^2 cell in at least two laboratories.)

- **Milestone 5:**

Feb 2013: Scale-up synthesis and durability of promising catalysts with optimum high current density performance in H_2/air.

Status: Not started.

Feb 2013: 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 0.56 V at 1.5 A cm^2 under H_2/air (1.5/1.8 stoic.), 80 ^oC, 40% RH, 150 $kPa_{abs.}$ outlet pressure.

Milestones and GO/NO-GO (Phase – II)

- **Milestone 6:**

Aug 2014 (end of project): The most promising catalysts will be selected for scale up synthesis. Short-stack (up to 10 cells, 50 cm^2) durability at high current density performance of at least 0.56 V at 1.5 A cm^2 in H_2/air (1.5/1.8 stoic.), 80 ^oC, 40% RH, 150 $kPa_{abs.}$ Outlet pressure. Individual performance evaluation at DOE site.

Status: Not started.

Technical Accomplishments: Synthesis of HCC

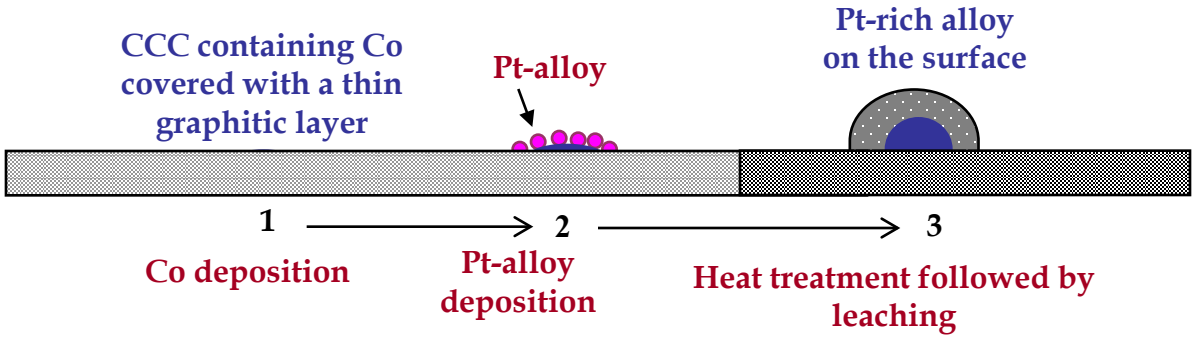
Strategy 1: Combine the catalytic activity of Pt/Pt-alloy at high potentials with that of carbon composite catalyst (CCC) at low potentials thus forming a hybrid cathode catalyst (HCC) having ultra-low Pt loading.

Carbon modification → **Carbon composite Catalyst** → **Hybrid cathode catalysts (HCC)**

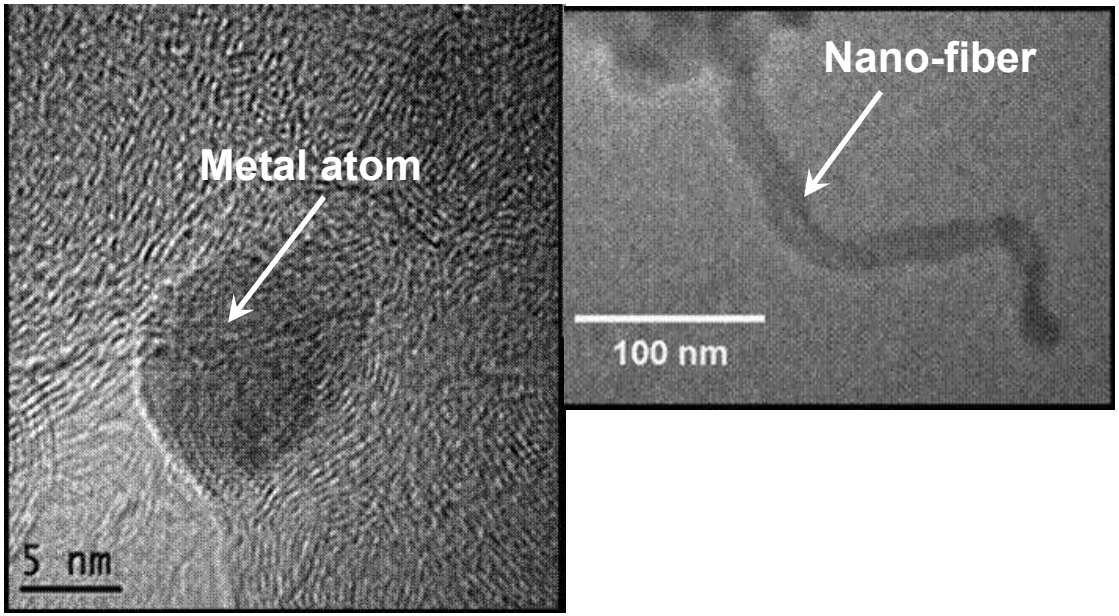
- Surface modification of carbon black with:
  - (i) O-containing group
  - (ii) N-containing group
- Pyrolysis

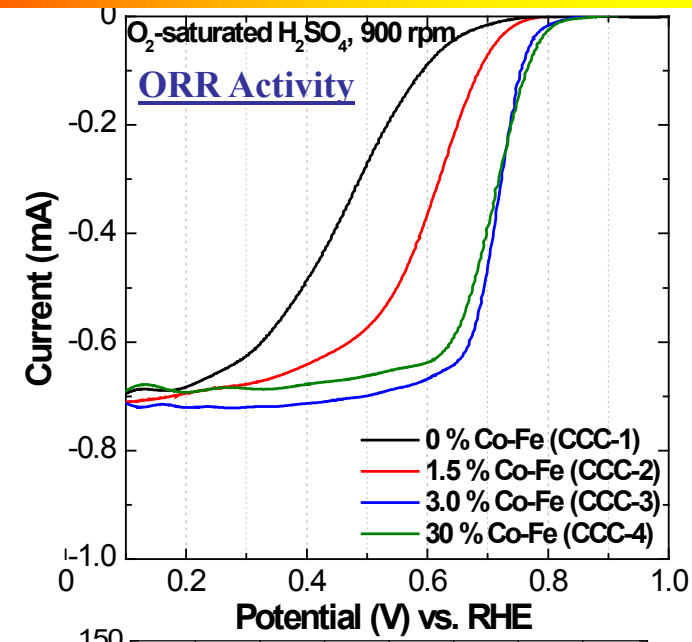
- "Metal-catalyzed pyrolysis" (Fe or Co) to increase the number of active sites by leaching

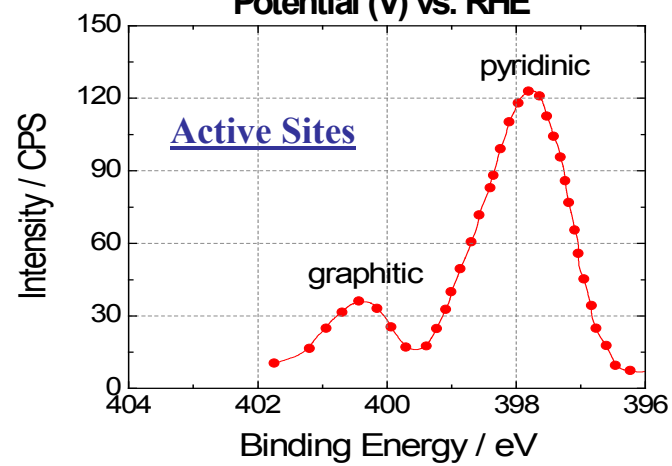
- Pt deposition
- Pyrolysis



Technical Accomplishments – Properties of Carbon Composite Catalyst (CCC) Support







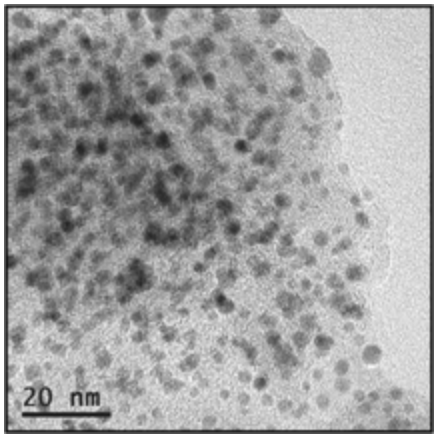
HIGHLIGHT

- **Metal atoms are covered with several graphitic layers.**
- **Nanostructured fiber 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.**

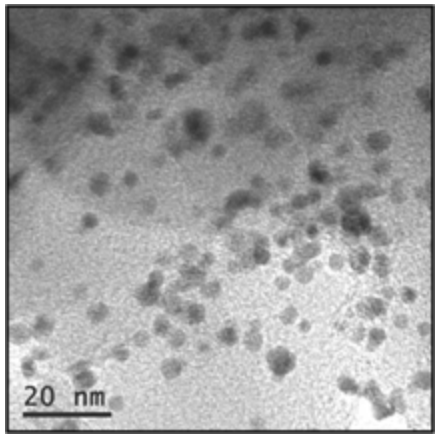
Potential	Current density (A cm^{-2})		
0.7 V	0	0.03 (~15% H_2O_2)	0.05 (~1.5% H_2O_2)
0.4 V	0.3 (~ 37% H_2O_2)	0.7 (~ 10% H_2O_2)	0.9 (~1.5% H_2O_2)

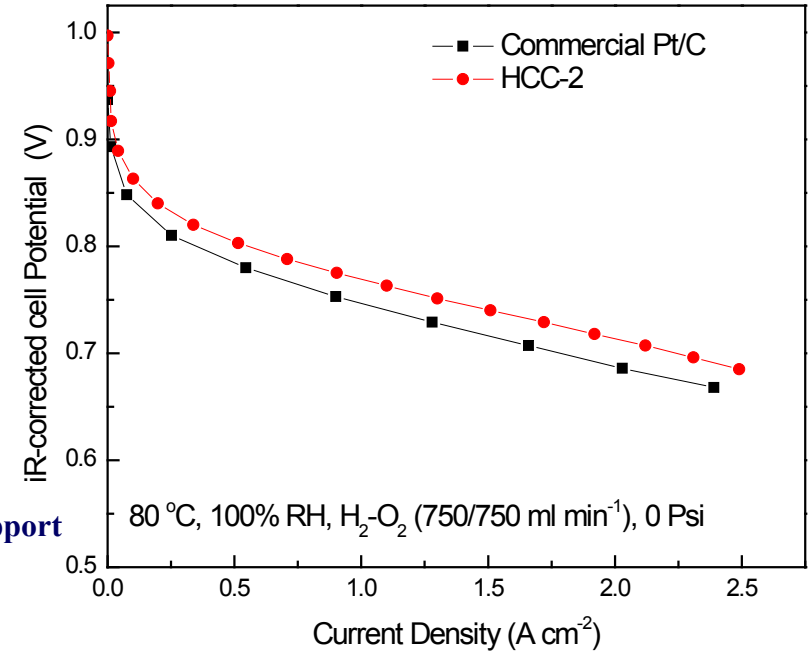
Technical Accomplishments – Properties of Hybrid Cathode Catalyst (HCC)

Pt-Co/CCC (HCC)

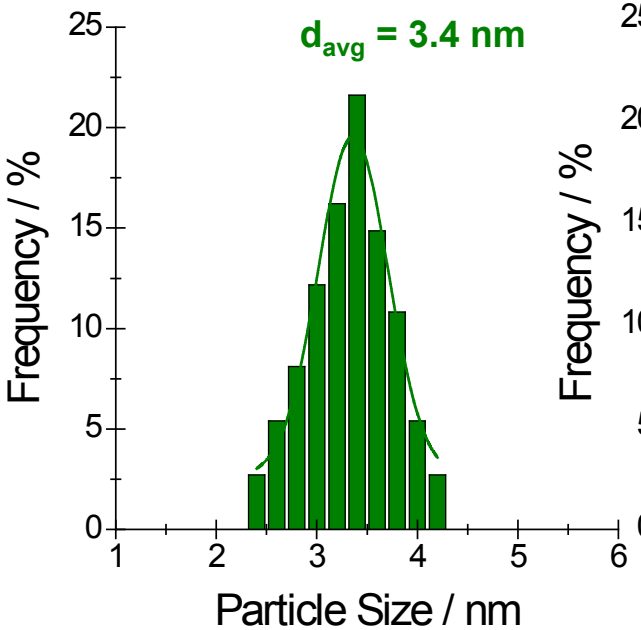


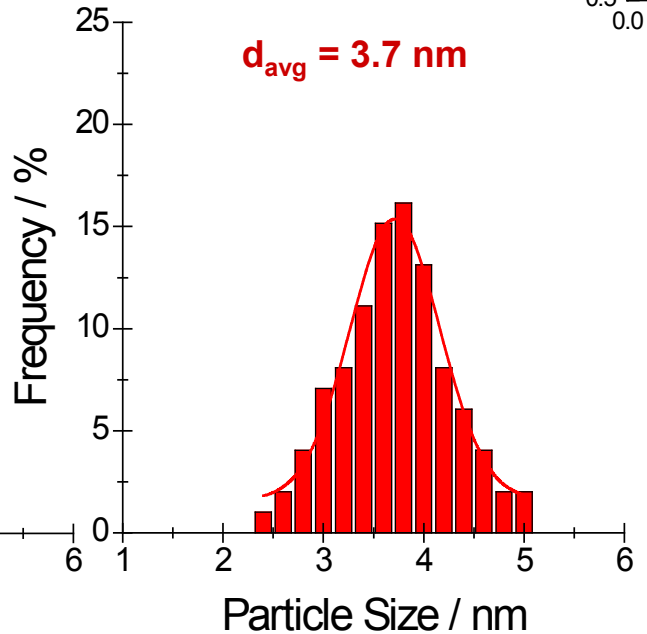
Conventional Pt-Co/C





- **HCC catalyst shows more uniform dispersion of particles over the CCC support**

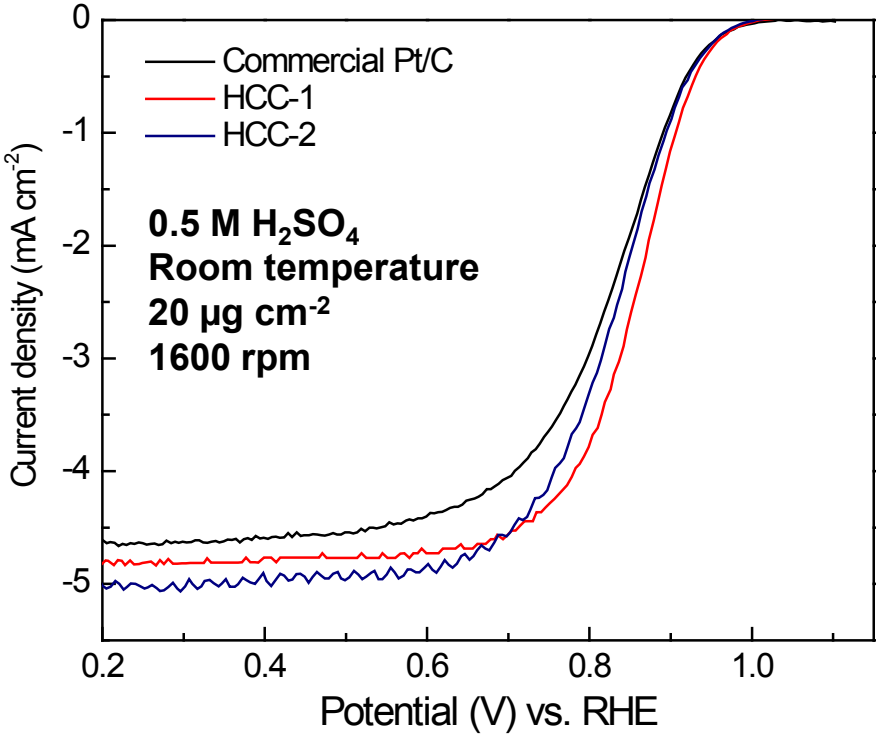


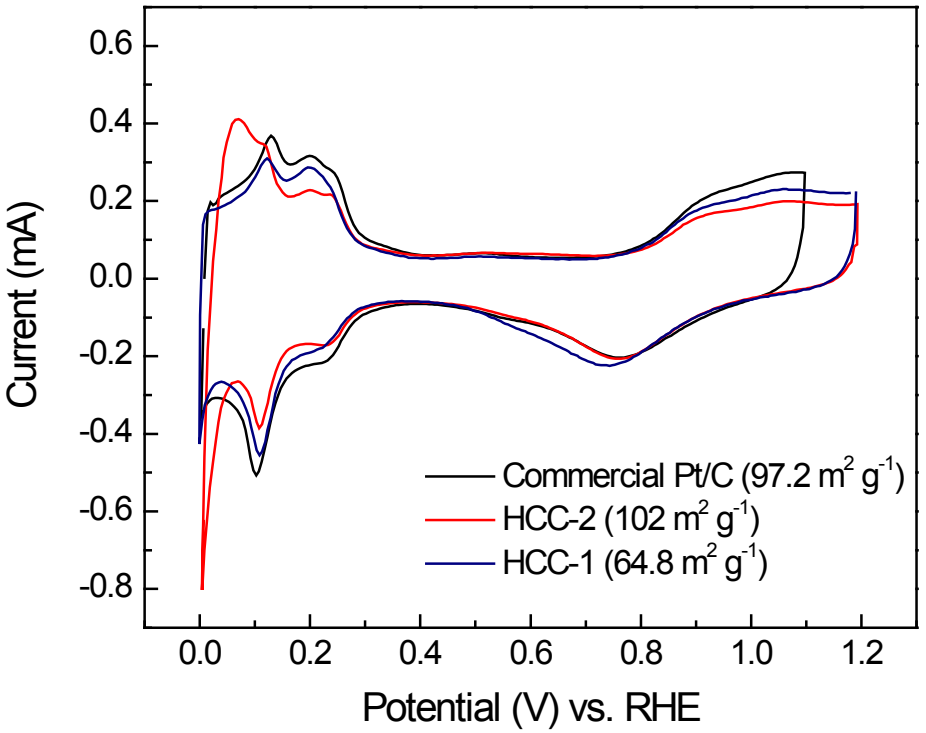


Anode: Commercial Pt/C (0.1 mg_{Pt} cm^{-2})
Cathode: HCC-1 and commercial Pt/C (0.1 mg_{Pt} cm^{-2})
Membrane: NRE 212

- **HCC catalyst shows smaller mean particle size and narrower distribution.**

Technical Accomplishments – Comparison of RRDE of HCC Catalysts

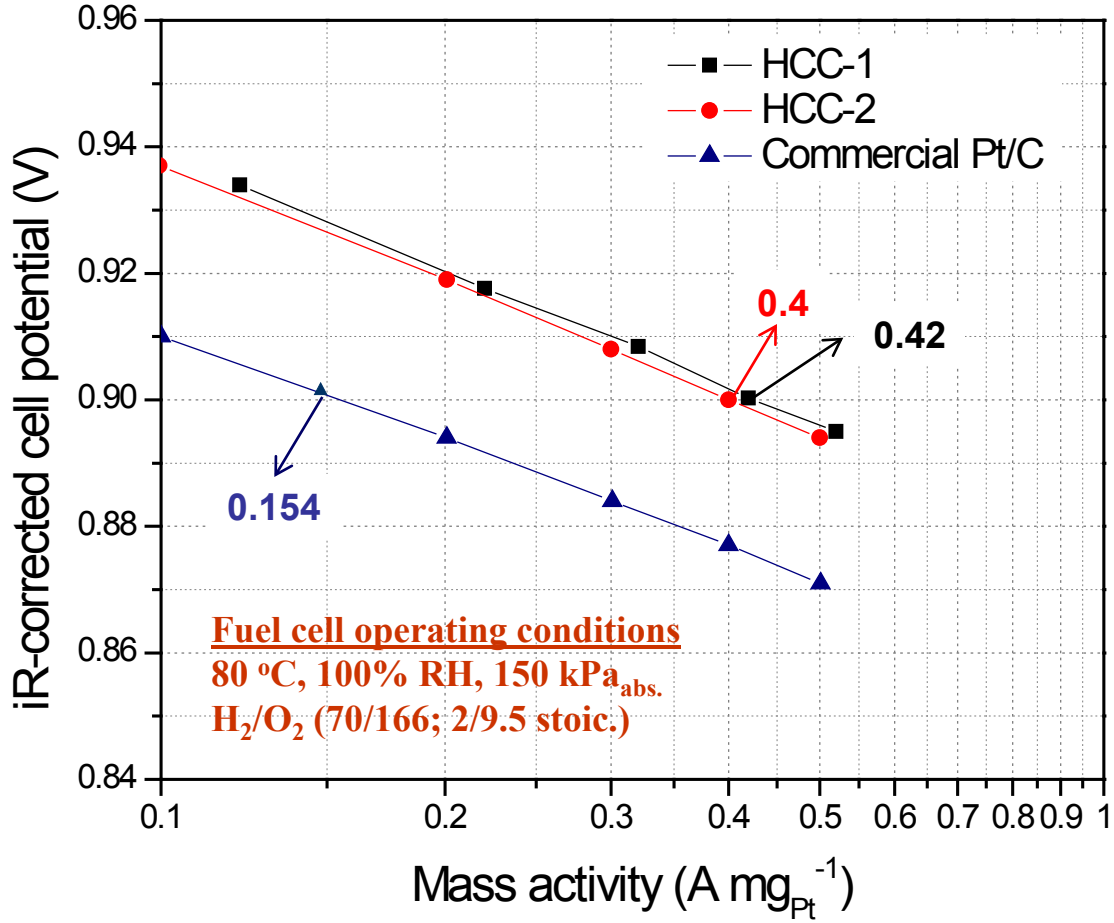




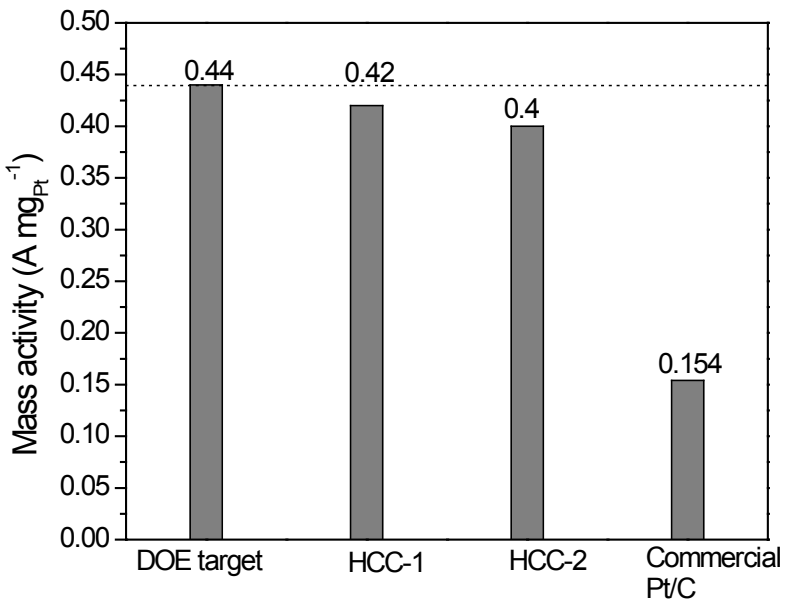
HIGHLIGHT

- **The activity of HCC catalysts are higher than that of commercial Pt/C.**
- **The HCC-2 catalyst shows higher ECSA than commercial Pt/C.**

Technical Accomplishments – Comparison of Initial Mass Activities of HCC Catalysts in H_2/O_2



Anode: Commercial Pt/C (0.1 mg_{Pt} cm^{-2})
Cathode: HCC-1 and HCC-2 (0.1 mgPt cm^{-2})
Membrane: NRE 212

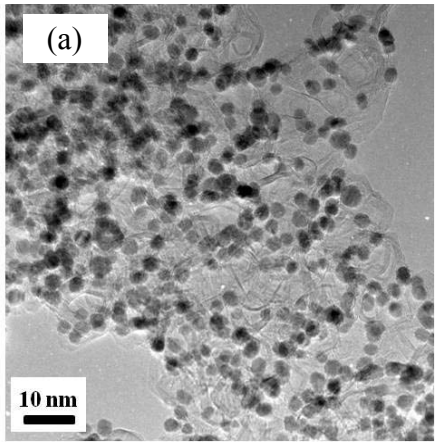


HIGHLIGHT

- **Both HCC-1 and HCC-2 catalysts show mass activities very close to that of DOE 2015 target.**
- **The Tafel slopes of both the HCC catalysts are 62.5 mV decade^{-1} and that of commercial Pt/C is 56.8 mV decade^{-1}.**

Technical Accomplishments: Synthesis of Pt_3M/AGC Catalyst (Strategy 2)

Pt/AGC

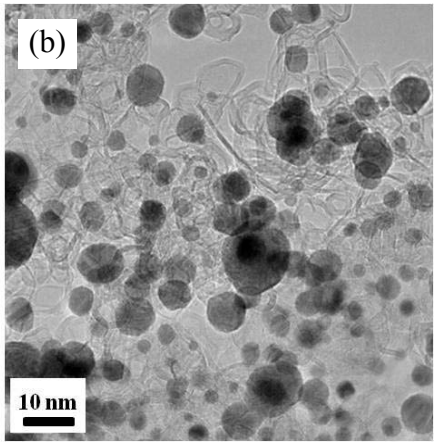


Transition metal salt impregnation

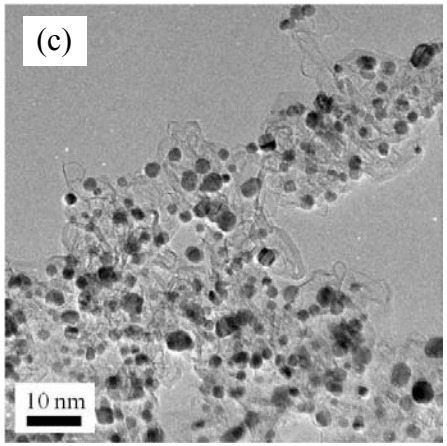
900°C normal heat –treatment

Transition metal salt impregnation

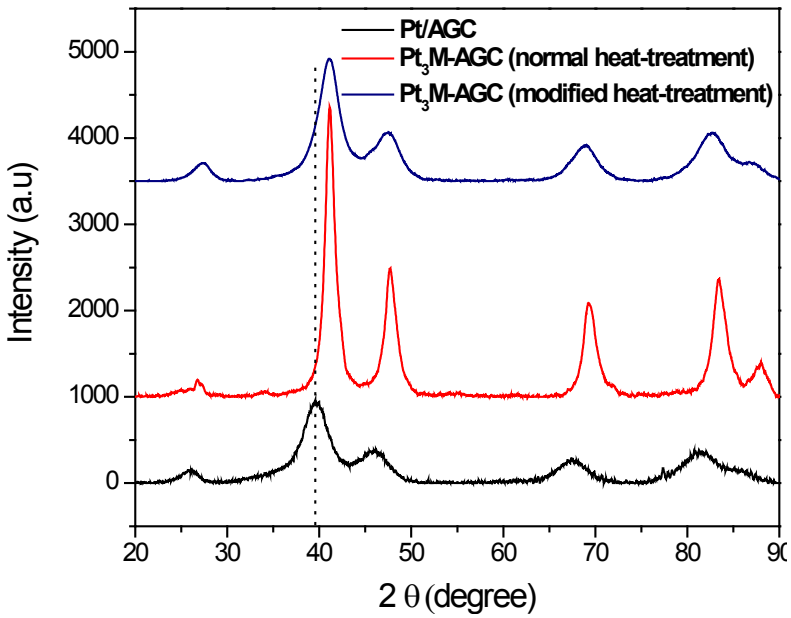
900°C modified heat –treatment



Normal heat-treatment Pt_3M/AGC



Modified heat-treated Pt_3M/AGC

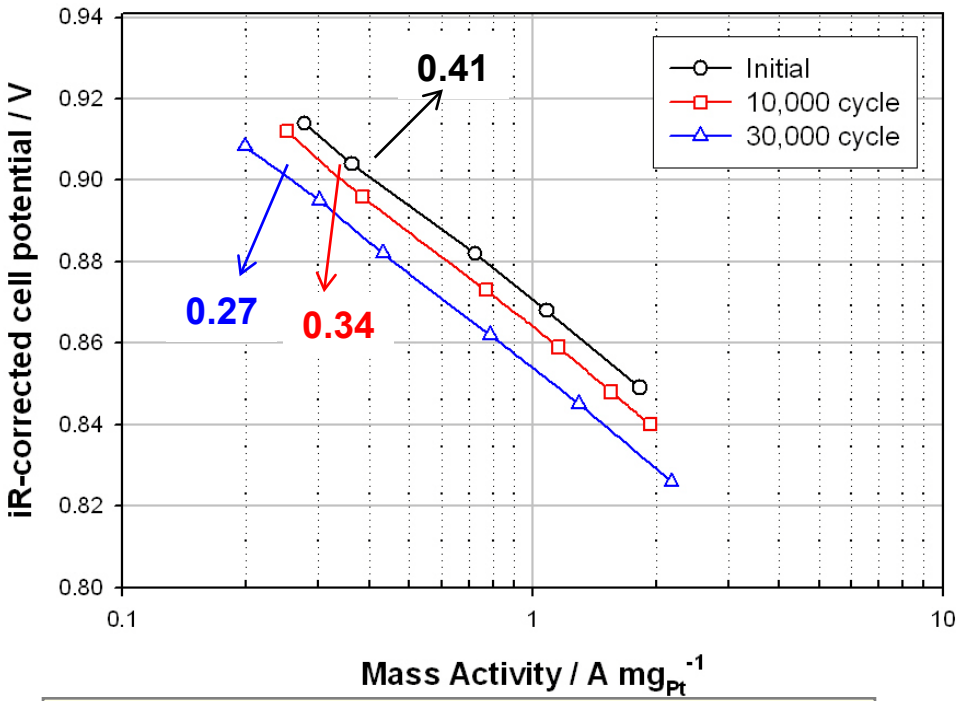


Sample	Pt (111)	Particle size (nm)
Pt/AGC	39.47 (0.0)	2.8
Normal heat-treatment Pt_3M/AGC	40.90 (+ 1.43)	10.8
Pt_3M/AGC Modified heat-treatment	40.90 (+ 1.43)	3.4

HIGHLIGHT

- **Pt_3M/AGC catalyst exhibits $d_{ave.}$=3.4 nm using a modified heat-treatment procedure.**

Technical Accomplishments – Durability of Mass Activity (Pt_3M/AGC)

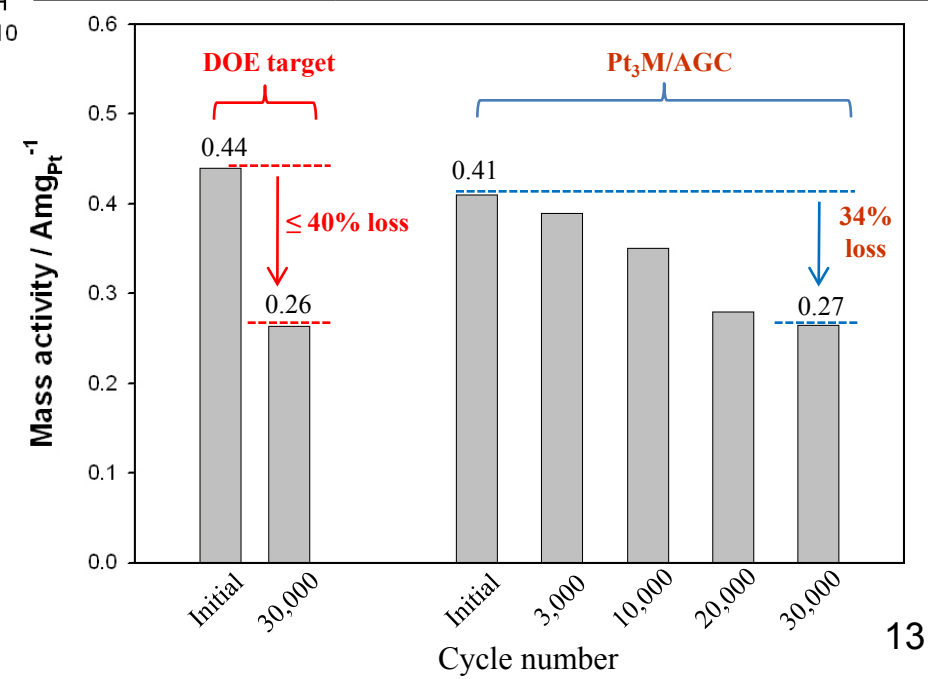


DOE Protocol
0.6 ~ 1.0 V, 50mV/s, 30,000 cycle, H_2/N_2
80 °C, 100 % RH, single cell 25cm^2
Catalyst : Pt_3M/AGC (0.1mg cm^{-2})
Pt mass activity : H_2/O_2, 2/9.5 stoic, 100% RH, 80 °C, 150 kPa

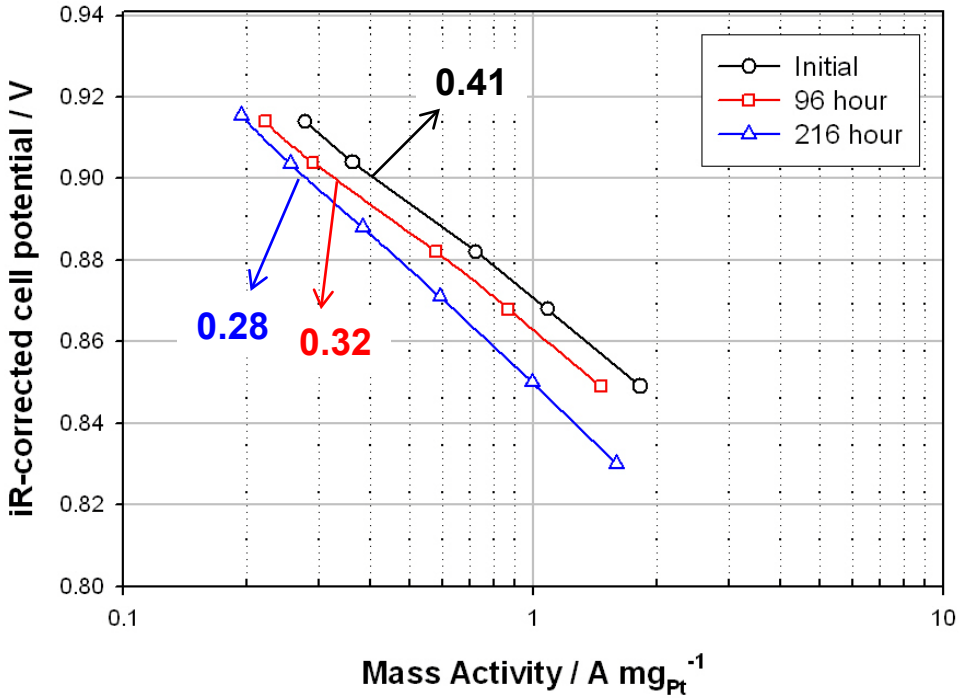
	After 30,000 cycles	
	Mass activity at 0.9V	ECSA in MEA
DOE target	≤ 40% loss	≤ 40% loss
Pt_3M/AGC	34 % loss	30 % loss

HIGHLIGHT

- The Pt_3M/AGC catalyst shows a mass activity of 0.41 A mg$_{Pt}^{-1}$ and 34% loss after 30 K cycles.
- The slopes did not change during cycling (78.7 mV decade^{-1}).
- The ECSA loss is only 30% (decreased from 29.5 to 20.8 m^2 g^{-1}) after 30 K cycles.
- DOE target is ≤40% of the initial activity.



Technical Accomplishments – Catalyst Support Durability (Pt_3M/AGC)



DOE Protocol

Hold at 1.2V for 24 h, H_2/N_2

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

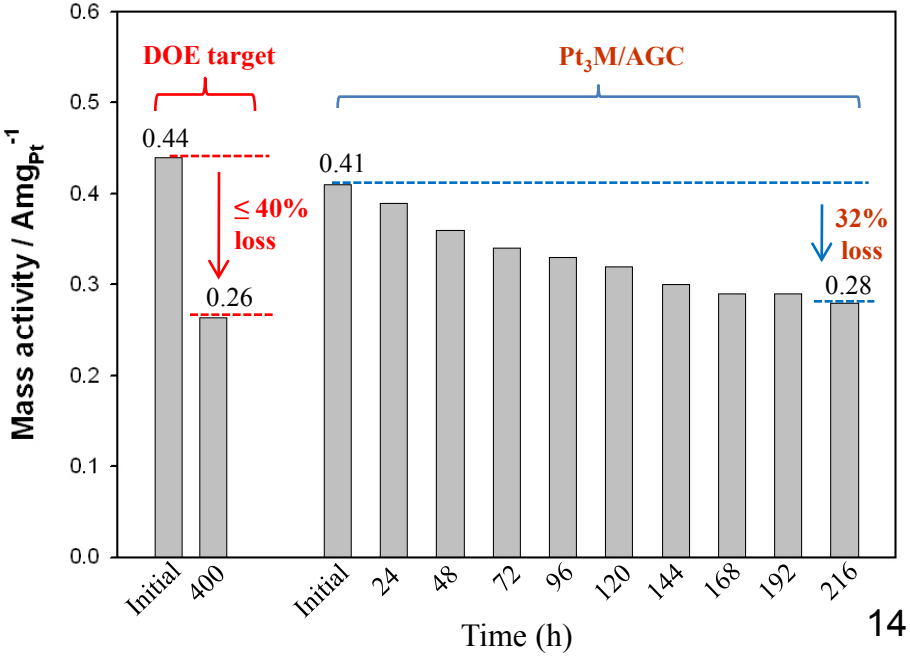
Catalyst : Pt_3M/AGC (0.1mg cm^{-2})

Pt mass activity : H_2/O_2, 2/9.5 stoic, 100% RH, 80°C, 150 kPa

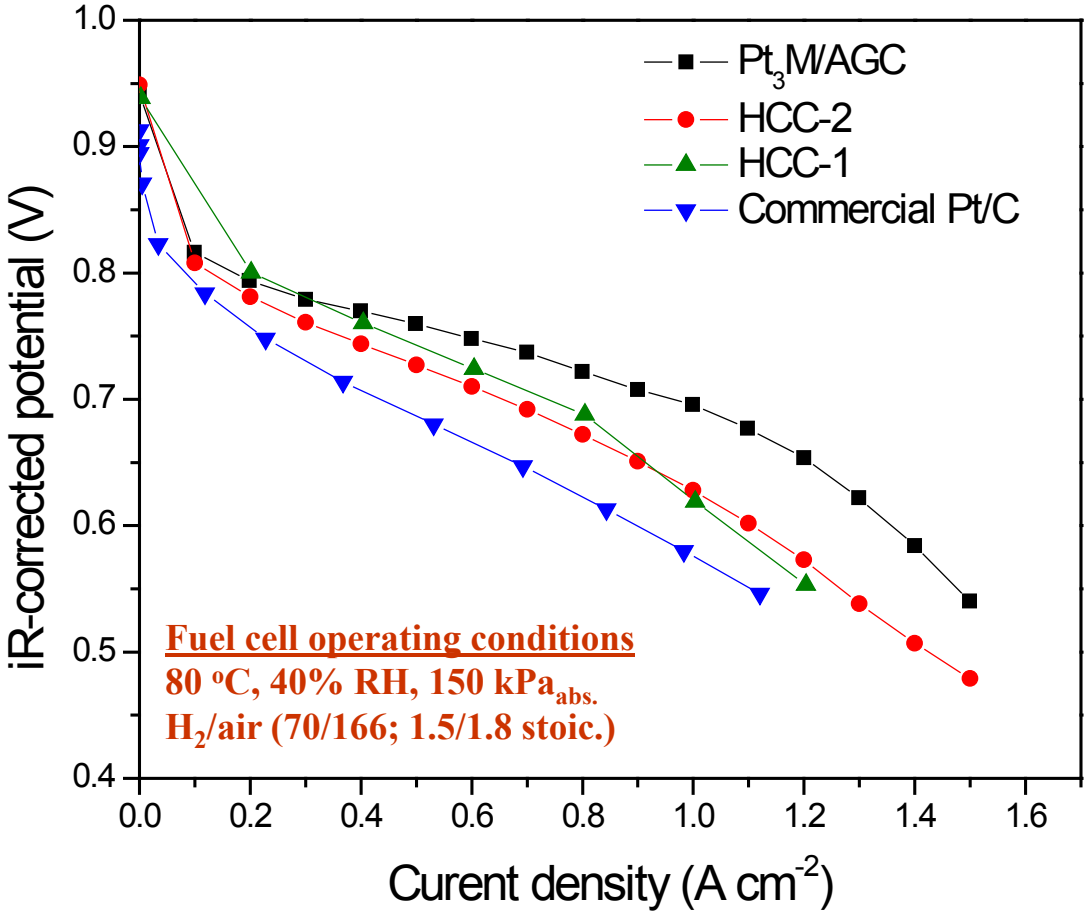
	Mass activity at 0.9 V	ECSA in MEA
DOE target (400h)	≤ 40% loss	≤ 40% loss
Pt_3M/AGC (216 h)	32 % loss	25 % loss

HIGHLIGHT

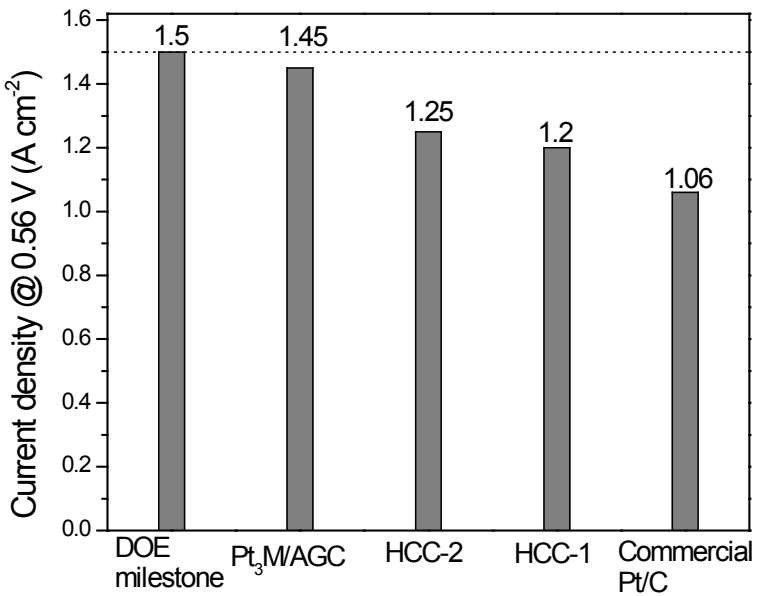
- The Pt_3M/AGC catalyst shows a mass activity of 0.41 A mg$_{Pt}^{-1}$ and 32% loss after 216 h.
- The slope remains the same up to 96 h (82.5 mV decade^{-1}) and increases to 90.5 mV decade^{-1} after 216 h.
- The ECSA loss is only 32% (decreases from 29.5 to 22.1 m^2 g^{-1}) after 30 K cycles.
- DOE target is ≤40% loss of initial ECSA



Technical Accomplishments –Comparison of Initial High Current Density Performance in H_2/air (HCC and Pt_3M/AGC Catalysts)



Anode: Commercial Pt/C (0.1 mg_{Pt} cm^{-2})
Cathode: HCC-1 and HCC-2 (0.1 mgPt cm^{-2})
Membrane: NRE 212



HIGHLIGHT

- **The Pt_3M/AGC shows high current density performance of 1.45 A cm^{-2} at 0.56 V.**
- **The high current density performance of both the HCC needs improvements in terms of electrode structure optimization.**

Technical Accomplishments – Comparison of Electrochemical Properties of Different Catalysts

Catalyst	ECSA ($m^2\ g^{-1}$) RRDE	ECSA ($m^2\ g^{-1}$) Fuel cell	Pt utilization (%)	Mass activity* ($A\ mg_{Pt}^{-1}$)	Specific activity ($\mu A\ cm^{-2}$)	Current density @ 0.56 V ($A\ cm^{-2}$)**
HCC-1	49	25	51	0.42	1680	1.20
HCC-2	102	76.4	74.9	0.4	524	1.25
Pt_3M/AGC	33.5	29.5	88	0.41	1135	1.45
Commercial Pt/C	70.8	37.9	56	0.154	641	1.06

* 80 °C, 100% RH, H_2/O_2, 70/166, (2/9.5 stoic.), 150 $kPa_{abs.}$ outlet pressure. 25 cm^2 single cell.
** 80 °C, 40% RH, H_2/air, 70/166 (1.5/1.8 stoic.), 150 $kPa_{abs.}$ outlet pressure, 25 cm^2 single cell.

Collaborations/Sub-contractors

USC Research Activities

- The research activities are a continuation of the previous work supported by DOE, NASA and NSF.
- Performance optimization of HCC (Pt/CCC and Pt-M/CCC) and meet DOE 2015 targets.
- Development and scale-up synthesis (50-100 g) of HCC and corrosion-resistant supports such as CCC and TiO_2-CCC hybrid.
- Overall technical coordination and project administration.
- Catalyst selection for evaluation by HMC, YU and DOE designated site.

YU Research Activities

- Optimization studies and scale-up synthesis of Pt-M/AGC catalyst (50-100 g).
  - Effect of graphitic carbon activation procedure on catalyst activity and durability.
  - Optimization of post catalyst synthesis treatments to eliminate Pt particle agglomeration.
  - Implementation of more active Pt-alloy catalyst deposited on AGC support.
- Catalyst support corrosion studies using *in-situ* GC-MS.
- Select catalyst to be evaluated by USC, HMC, and DOE designated site.

HMC Research Activities

- Provide testing and unique techniques for catalyst electrode optimization under automotive cycling conditions.
- Manufacture of MEAs and fuel cell testing (50 cm^2) of the catalysts supplied by USC and YU.
- Electrode optimization for good performance at high current density under H_2/air.
- Select materials to be evaluated by USC, YU, and DOE designated site.

Common Research Activities

- Catalyst performance evaluation using RRDE and physical characterization such as HR-TEM, XPS, and SEM-EPMA (USC & YU).
- Manufacture and testing of MEAs in 25 and 50 cm^2 fuel cells (USC, HMC & YU).
  - Kinetic mass activity in H_2/O_2 at 0.9 V.
  - High current density performance and durability in H_2/air.
- Performance evaluation in short-stack (USC & HMC).
- Short-stack construction for evaluation at DOE designated site (USC & HMC).

Proposed Future Work

FY 2011 (Milestones 1 & 2):

- Accomplish initial mass activities above DOE 2015 target of 0.44 A mg_{Pt} cm^{-2} for HCC and Pt-alloy/AGC catalysts.
  - USC will synthesize HCC with increased activity for ORR and durability.
    - ✓ Increase the number of non-Pt catalytic sites of CCC ORR.
    - ✓ Implementation of more active Pt-alloy catalyst on CCC.
    - ✓ Increase the Pt utilization by decreasing the Pt agglomeration during post-synthesis treatments.
    - ✓ Develop large scale process for the activation/leaching procedure.
  - YU will synthesize Pt-alloy/AGC with increased ORR activity and durability.
    - ✓ Optimization of post catalyst synthesis treatment to eliminate Pt particle agglomeration.
    - ✓ Optimize the Pt distribution on the activated graphitic carbon support.
- USC and YU will develop procedures for scale-up synthesis for HCC and Pt-alloy/AGC (50-100 g level).
- USC, YU and HMC will perform structure-catalyst property studies using RRDE, HR-TEM, XRD, XPS, SEM, techniques.
- YU will perform *in-situ* corrosion studies using GC-MS.
- USC, HMC and YU will evaluate initial ORR activities in 50 cm^2 single cell using galvanostatic/potentiostatic techniques.

Proposed Future Work

FY 2012 (Milestone 3):

- Accomplish durability of kinetic mass activity for HCC and Pt-alloy/AGC catalysts at least 0.24 A mg_{Pt} cm^{-2} after 30 K cycles tested according to DOE protocol (0.6-1.0 V cycling).
  - Implementation of more durable Pt-alloy catalyst.
  - USC and YU will optimize the Pt-alloy distribution on the supports by increasing the Pt-alloy nucleation rate while decreasing its crystallization rate.
  - USC and YU will optimize the post catalyst synthesis treatment to eliminate Pt particle agglomeration.
  - Increase the support durability through synthesis of TiO_2-CCC hybrid and post treatment of AGC support.
  - USC, YU, and HMC will evaluate the durability of kinetic mass activity in 50 cm^2 cells.

FY 2012 (Milestone 4):

- Accomplish initial high current density performance in H_2/air (80 ^oC, 100% / 40% RH, 150 $kPa_{abs.}$ Outlet pressure & 1.5/1.8 stoic.).
  - USC, HMC, and YU will address the drawbacks of mass transfer limitations due to low Pt loaded catalyst and low O_2 content by:
    - ✓ Optimizing the catalyst layer thickness by tailoring the Pt-alloy/support ratio.
    - ✓ Varying the Nafion® content to achieve optimum hydrophilic/hydrophobic property.
    - ✓ Decreasing the thickness of gas diffusion layer (GDL).
    - ✓ Decreasing the water flooding by tailoring GDL hydrophilic/hydrophobic properties.
- USC, HMC and YU will evaluate the initial high current density performance in 50 cm^2 cells.

Summary

Relevance: Develop low cost (reduce the loading of platinum) and synthesize durable cathode catalyst.

Approach: Synthesis of highly active catalyst for ORR and development of corrosion resistant supports.

Technical Accomplishments and Progress: Required initial kinetic activity and durability has been demonstrated for one of the catalysts.

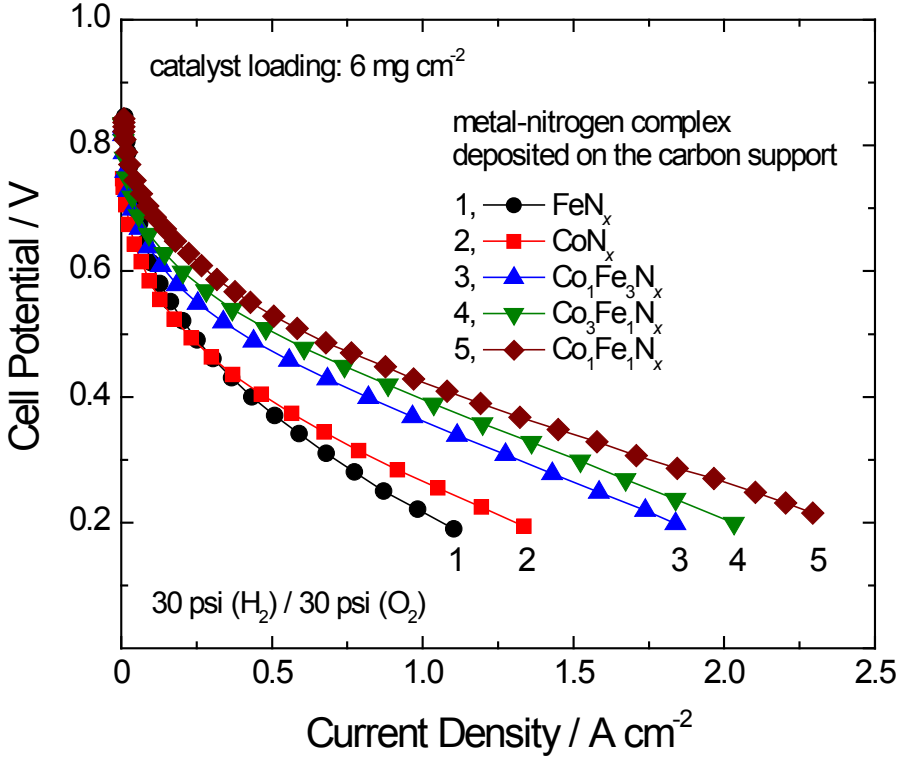
- Initial kinetic mass activity of HCC-1, HCC-2 and Pt_3M/AGC catalysts were determined in H_2/O_2 fuel cells.
- Durability and high current density performance in air has been demonstrated for 216 hours for one of the catalysts.

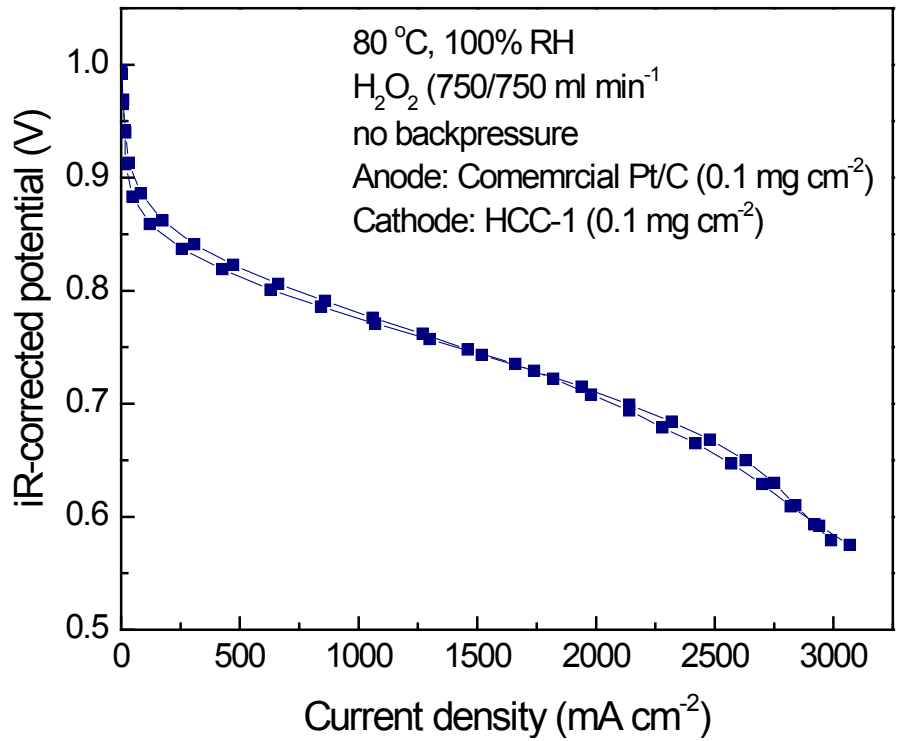
Proposed Future Work: Future research was identified to satisfy the DOE targets for catalyst initial kinetic activity, durability and high current density performance in air.

Technology Transfer/Collaborations: Two are universities (developers of fuel cell catalysts), one is industrial fuel cell developer.

Technical Back-Up Slides

Fuel Cell Performance of Different Carbon Composite Catalysts and HCC-1 Catalyst

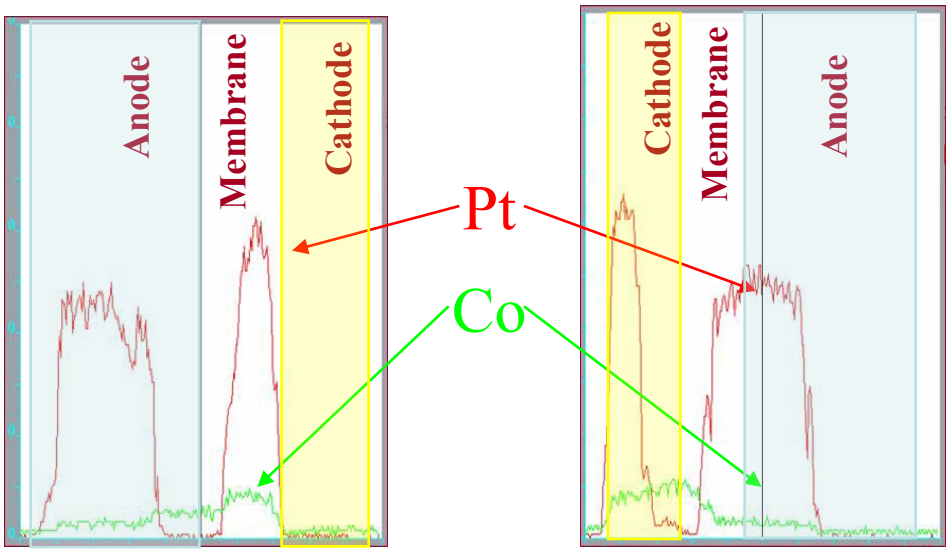




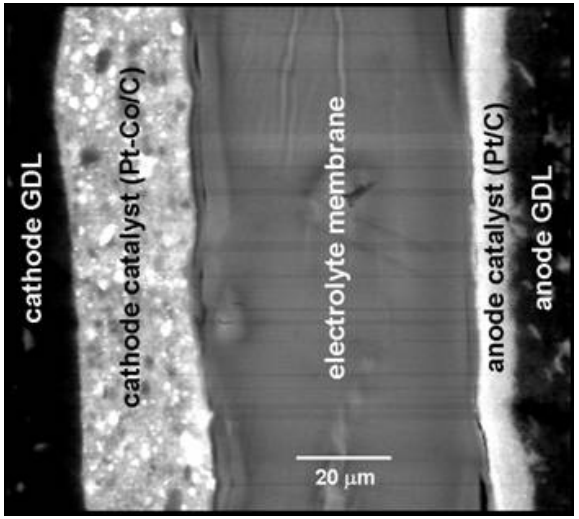
- ***Anode:** 2 mg cm^{-2} of E-TEK 20% Pt/C (0.4 mg cm^{-2} Pt)*
- ***Cathode:** 6 mg cm^{-2} of carbon composite catalyst*
- ***Membrane:** Nafion® 112*
- ***Operating temperature:** 77 °C (H_2); 75 °C (O_2); 75 °C (cell)*

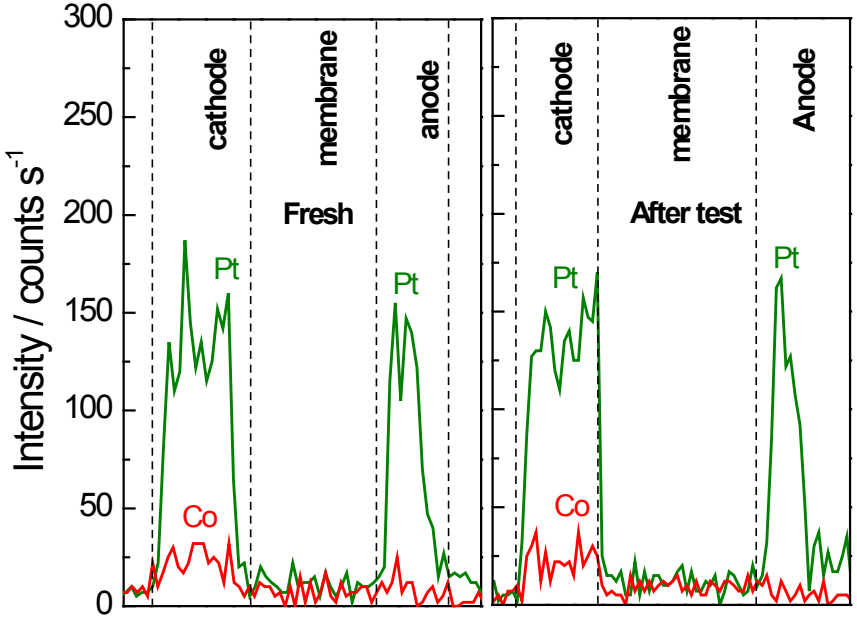
Technical Accomplishments – Post-fuel cell test Analysis of HCC-1 Catalyst

Conventional Pt-Co/C



HCC

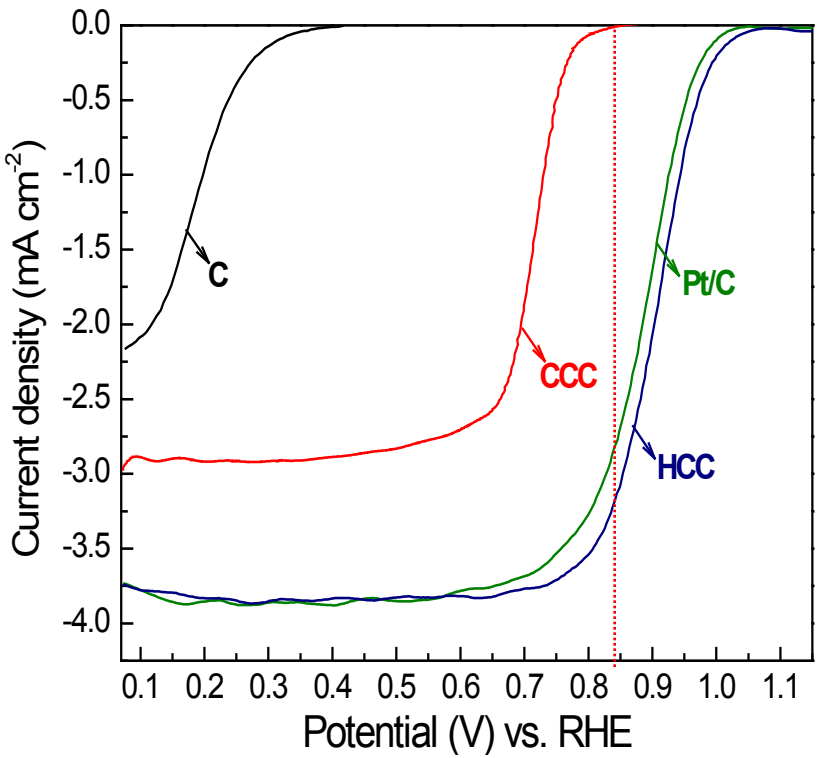


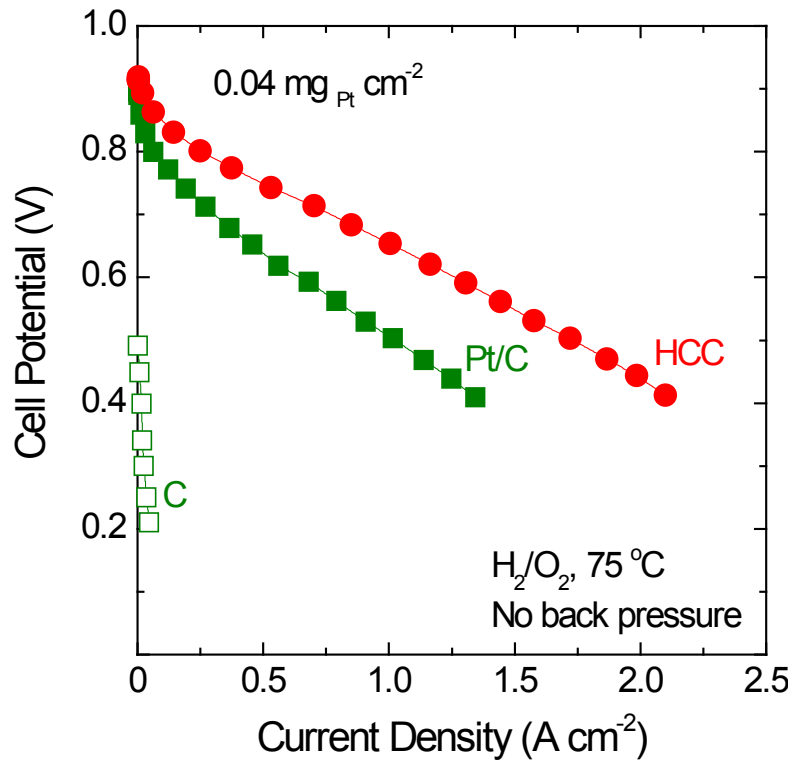


HIGHLIGHT

- **EPMA analysis indicates the Co dissolution from the cathode catalyst layer followed by diffusion into the membrane.**
- **No dissolution of Co from the catalyst and diffusion into the membrane after 400 h of continuous operation.**

Technical Accomplishments: Comparison of Catalytic Activity of CCC, HCC, and Commercial Pt/C Catalysts (RDE and Fuel Cell)

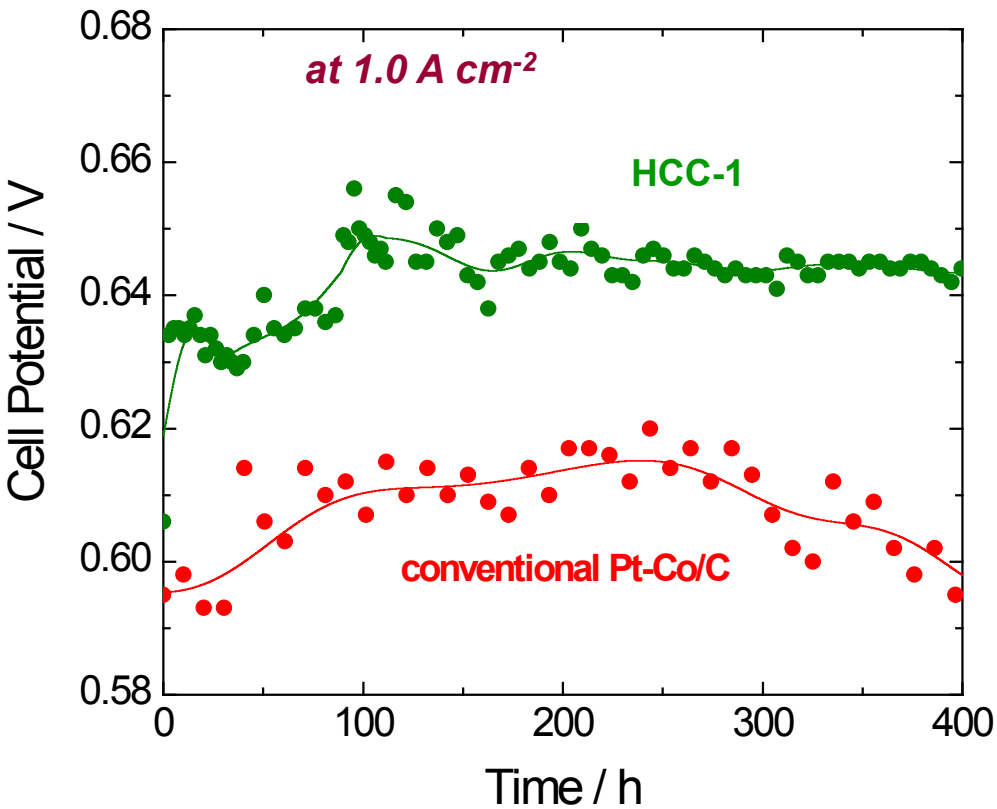


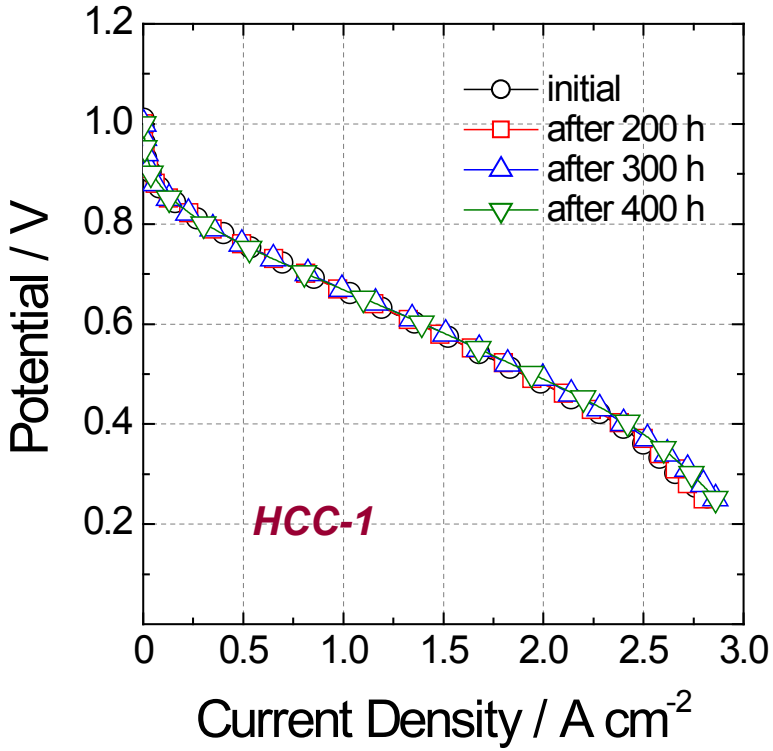


HIGHLIGHT

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

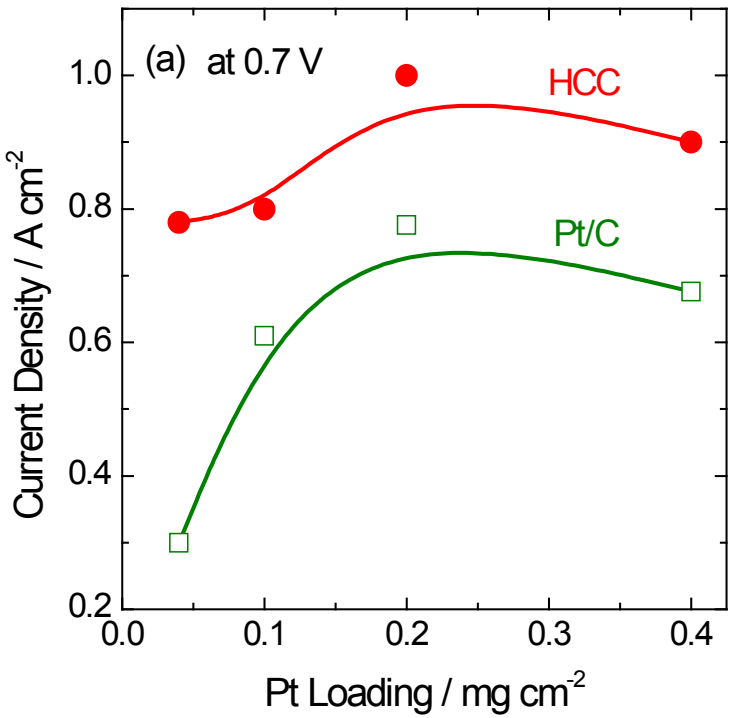
Stability of HCC-1 Catalyst in H_2/O_2 Fuel Cell

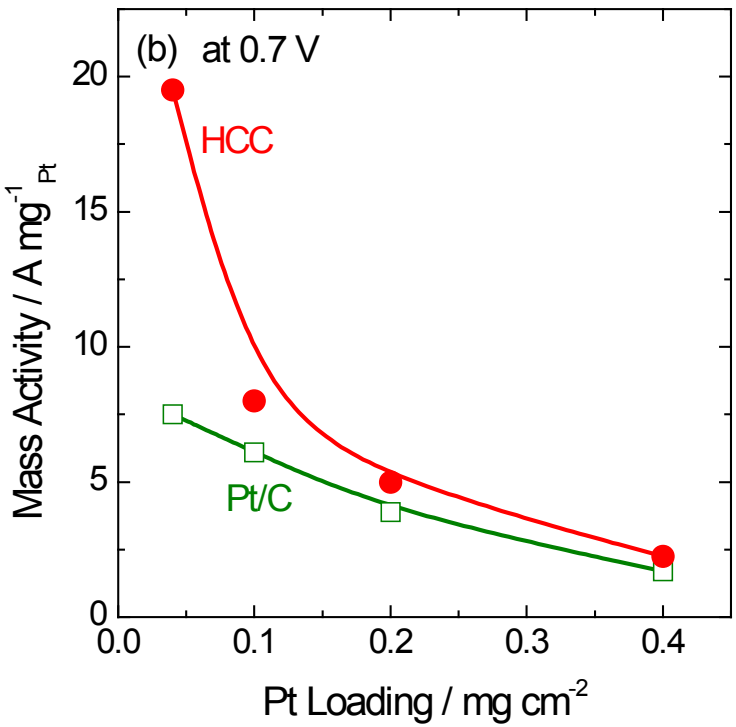




- *Cathode: 0.4 mg cm^{-2} Pt-Co* • *Anode: 0.5 mg cm^{-2} E-TEK Pt* • *Membrane: Nafion® 112*
- *Operating conditions: (i) H_2/O_2; (ii) no back pressure; (iii) 77/75 ^{o}C*

Technical Accomplishments – Effect of Loading on Catalytic Activity of HCC-1 (Initial Fuel Cell Performance in H_2/O_2)





- *Cathode: HCC* • *Anode: 0.5 mg cm^{-2} Pt/C*
- *Membrane: Nafion® NRE 212*
- *Operating conditions: (i) H_2/O_2; (ii) no back pressure; (iii) 77/75 ^oC*

HIGHLIGHT

- **The mass activity of HCC shows 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.**