Development of Ultra-low Doped-Pt Cathode Catalysts for PEM Fuel Cells (PHASE II)

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

Washington DC
June 09, 2015

UNIVERSITY OF SOUTH CAROLINA

Project ID # FC088

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

Timeline

- Start date: June 2010
- End date: December 2015 (No-cost Extension June-Dec 2015)
- Percent complete: 95%

Budget

- DOE Share: $3,800,000
- USC Cost Share : $950,000
- **Total Project Cost: $4,750,000**
- **Total DOE Funds Spent*: $3,192,283**

***as of 03/31/15**

Barriers

A. Durability

- Retain kinetic activity and high current density performance in H_2/air after potential holding (support durability) and potential cycling (catalyst durability) experiments.

B. Cost

- Decrease in PGM content
- Cost effective synthesis procedures

C. Performance

- Obtain high current density performance in H_2/air and maintain the power density.

DOE Technical Targets

Electrocatalyst/MEA	2017 Targets
PGM loading	0.125 mg/cm^2
Initial mass activity	≥0.44 A/mg$_{PGM}$
Mass activity and ECSA loss after 30k cycles **(0.6-1.0V) (Catalyst durability)**	≤ 40%
Potential loss after 30k cycles **(0.6-1.0V) (Catalyst durability)**	≤30 mV
Mass activity and ECSA loss after 400 h **(1.2 V) (Support stability)**	≤30 mV
Potential loss after 400 h **(1.2 V) (Support stability)**	≤30 mV
Mass activity and ECSA loss after 5k cycles **(1.0-1.5 V) (Support stability)**	≤ 40%
Potential loss after 5k cycles **(1.0-1.5 V) (Support stability)**	≤30 mV

Project Lead

- University of South Carolina (USC)

Subcontractor

- National Renewable Energy Laboratory (NREL)

Additional Interactions

- Rudiger Laufhutte (Univ. Illinois, Urbana Champaign)
- Dr. Lax Saraf (Clemson University)
- Dr. Alan Nicholls (Univ. Illinois, Chicago)
- Electron Microscopy Center, USC

Relevance

- Develop unique hybrid cathode catalyst (HCC) through interaction of **highly active and stable Pt and compressive Pt-lattice catalyst (Pt*)** with catalytically active and highly stable **carbon composite catalyst support (CCCS)** and **activated carbon composite support (A-CCS)**.
- Enhance the activity of HCC by increasing the synergistic effect of catalytic active sites present in the supports and those in Pt or Pt* catalyst.
- The specific objectives are to:
  - Perform optimization studies to develop two catalyst supports (CCCS and A-CCS) with high kinetic activity and stability.
  - Estimate the role of BET surface area, porosity, pore-size, pore-size distribution and hydrophilic/hydrophobic properties on the support stability.
- Synthesize low-PGM cathode catalyst for automotive application by decreasing the PGM loading while simultaneously increasing the catalytic activity and stability of CCCS and A-CCS and the activity of Pt* .
- Develop low cost procedure to synthesize the following hybrid cathode catalysts:
  - Pt/CCCS
  - Pt*/CCCS
  - Pt/A-CCS
  - Pt*/A-CCS

Develop a low cost catalyst with optimized mass activity, stability of mass activity, initial high current performance under H_2/air (power density), catalyst and support stability able to meet 2017 DOE targets.

Pt* = Compressive Pt Lattice Catalyst

Approach

- The technology is based on a two-step USC-patented process to synthesize highly active and stable ultra-low PGM **hybrid cathode catalyst (HCC)**.

Step I - Synthesis of CCCS and A-CCS supports

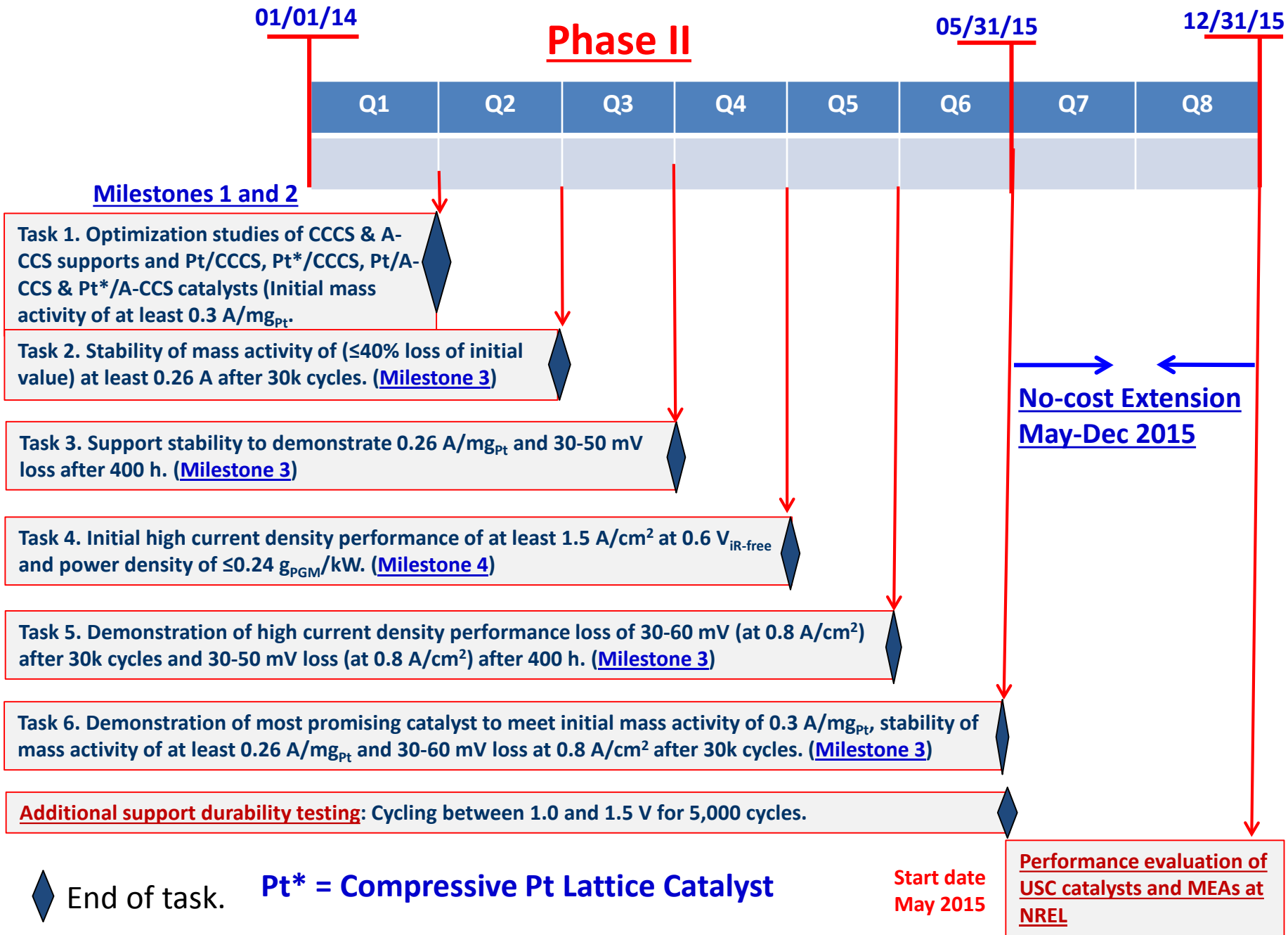
- The following major constraints were addressed when developing cathode catalyst supports for PEMFC for automotive applications:
  - Chemically and electrochemically stable at low pH and high temperature.
  - An onset potential and kinetic activity for ORR similar to that of the platinum catalyst.
- To accomplish these requirements CCCS and A-CCS were synthesized with optimized:
  - BET surface area, porosity, pore size and pore size distribution
  - Hydrophilic/hydrophobic ratio
  - Structural properties (amorphous/crystalline ratio).
  - Number of catalytic active sites through metal catalyzed pyrolysis.
  - Pt-support interaction by inclusion of active surface functional groups
  - Transition metal necessary for the formation of Pt* is encapsulated in the graphitic carbon structure.

Step II - Synthesis of compressive Pt-lattice catalyst

- Pt-lattice catalyst was synthesized through:
  - USC heating procedure that controls the particle size during pyrolysis.
  - Monolayers of Pt* were formed by diffusing Co atoms into Pt.
- Mathematical model was used to optimize:
  - The Co diffusion time
  - The pyrolysis temperature
  - Pt/Co stoichiometric ratio

Pt* = Compressive Pt Lattice Catalyst

Project Timeline (As per Revised SOPO Dated 01/23/2014)



Technical Accomplishments

Development of CCC Support

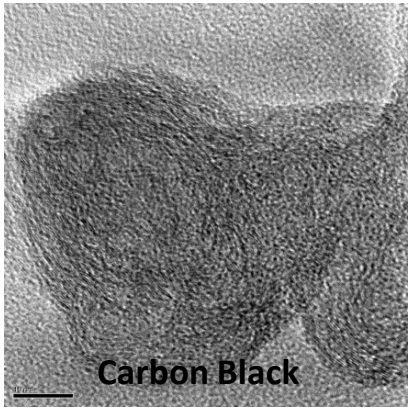
- Metal-catalyzed pyrolysis
- BET surface area, porosity, and pore-size optimization
- Optimization of hydrophilic/hydrophobic properties
- Evaluation of onset potential for oxygen reduction reaction and hydrogen peroxide formation.

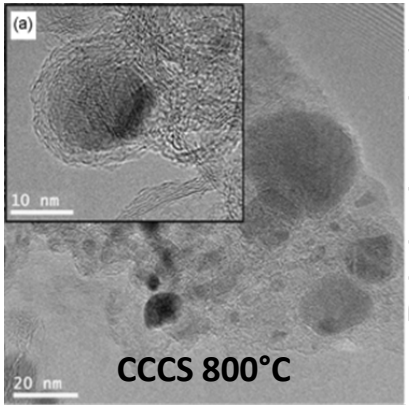
Carbon Black → (Pyrolysis at 800°C w/ metal-nitrogen chelate compounds) → Metal-enriched Intermediate → (Leaching at 80°C w/ 0.5 M H_2SO_4) → Carbon composite catalyst support (CCCS)

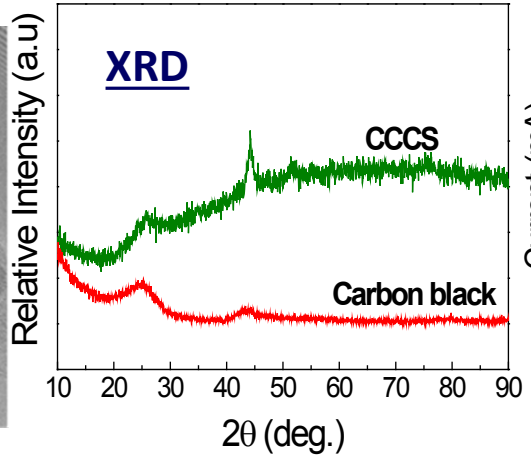
- Surface modification:
  (i) O-containing group
  (ii) N-containing group

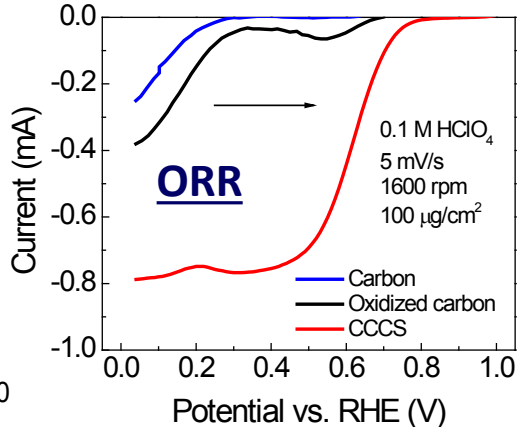
→

- "Metal-catalyzed pyrolysis" to increase the number of active sites by leaching









HIGHLIGHT:

CCCS - High surface area support

XRD: The degree of graphitization increases with the increase in the pyrolysis temperature. Presence of metal particles are confirmed.

BET: The BET surface area decreases with the increase of pyrolysis temperature.

HRTEM: Graphitic carbon containing carbon nano fibers/tubes are formed during pyrolysis in the presence of cobalt.

ORR: The CCCS showed an onset potential of *0.85 V vs. RHE* and well-defined kinetic and mass transfer regions. The peroxide formation is <2%.

Popov et al. J. Power Sources, 273, (2015) 761-774.

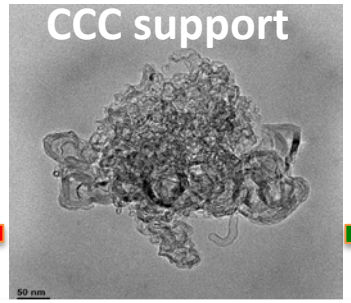
Technical Accomplishments

Pt/CCCS and Pt*/CCCS Catalyst Development

Platinum Deposition (Pt/CCCS)

CCCS - High surface area support

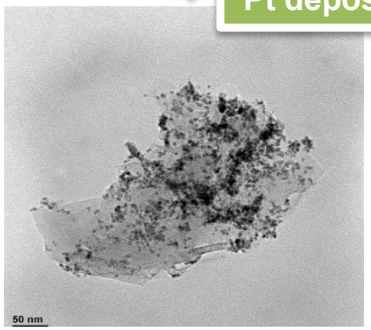
Heat-treatment (Pt*/CCCS)



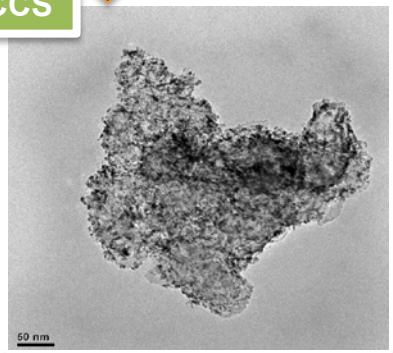
No Surface Modification

With Surface Modification

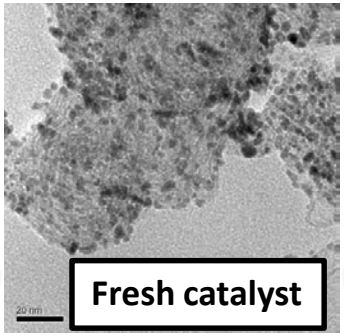
Pt deposited on CCCS



Non-uniform Pt deposition



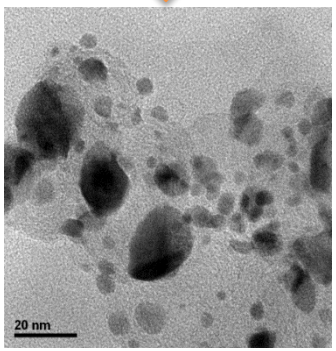
Uniform Pt deposition



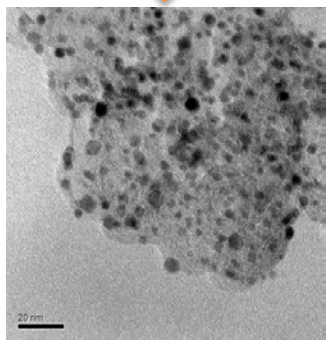
Fresh catalyst

Conventional Pyrolysis (800°C/0.5h)

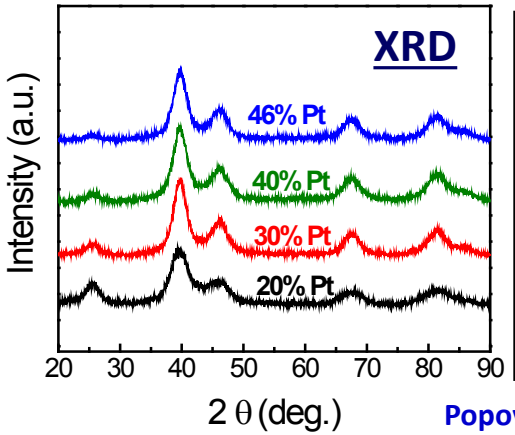
Modified Pyrolysis (800°C/1h)



10-20 nm Particles

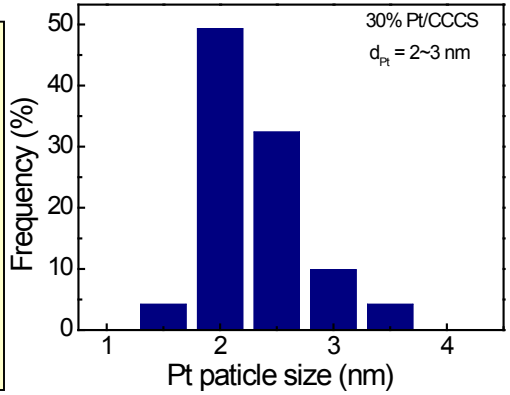


3~3.5 nm Particles



HIGHLIGHT:

- Pt deposition: Uniform particle distribution with an average particle size of 2-3 nm is achieved with the USC developed modified polyol process.
- Heat-treatment: Normal heat-treatment results in 10 to 20 nm particles.
- USC-developed process yields uniform particle size distribution with ~3.4 nm Pt* catalyst particles.



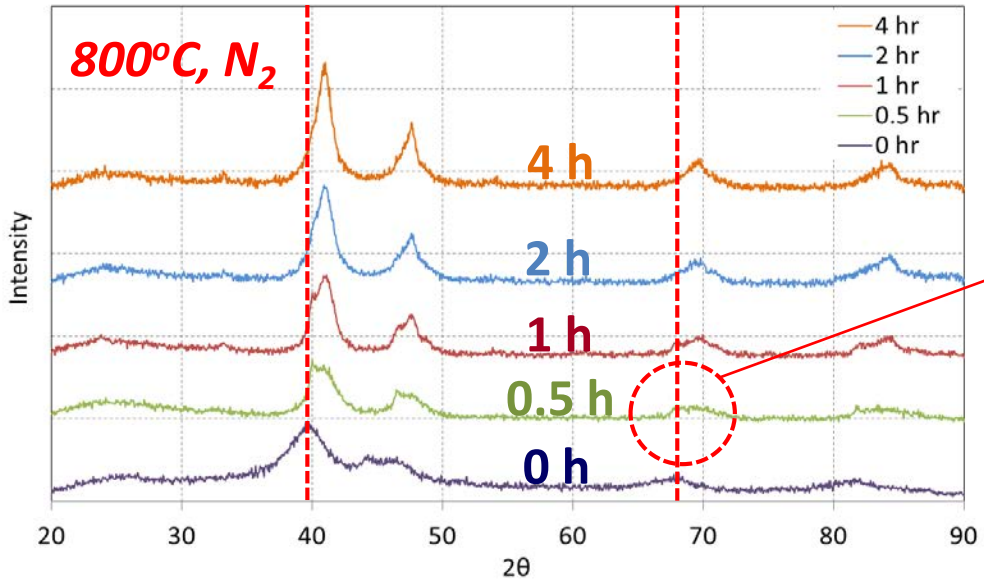
Popov et al. J. Electrochem. Soc. 161 (2014) F1489.

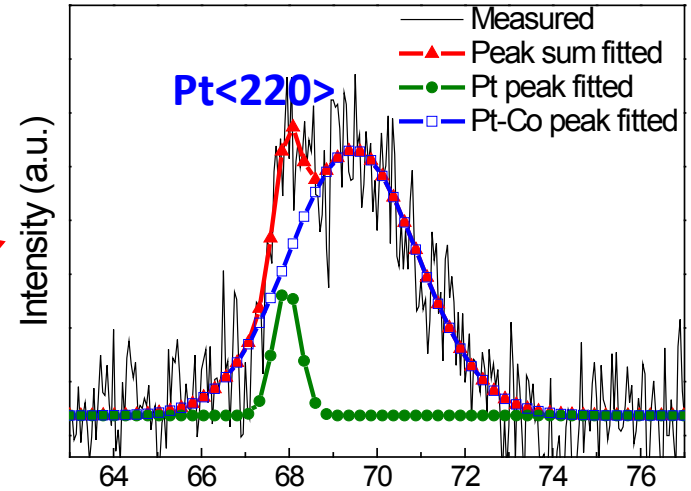
Pt* = Compressive Pt Lattice Catalyst

Technical Accomplishments: Catalyst Development

Pt*/CCCS Catalyst Synthesis: Effect of Heat-treatment

CCCS - High surface area support



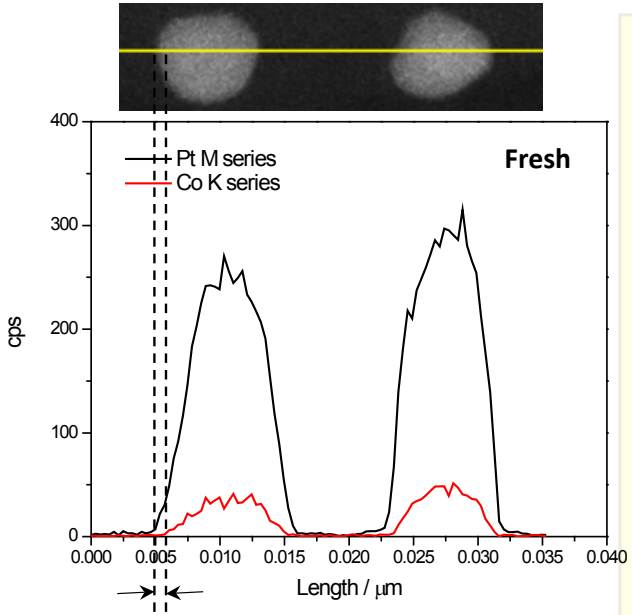


Mathematical model was used to optimize the Co diffusion time, pyrolysis temp., and Pt/Co ratio.

Heat treatment time (h)	Pt peak (deg.)	PtCo peak (deg.)	Particle size (nm)
0	67.3	--	2.5
0.5	67.9	69.4	2.8
1	67.8	69.5	3.9
2	--	69.4	3.9
4	--	69.5	4.5

Pt* = Compressive Pt Lattice Catalyst

Popov et al. Electrochim. Acta, 167 (2015) 1-12.



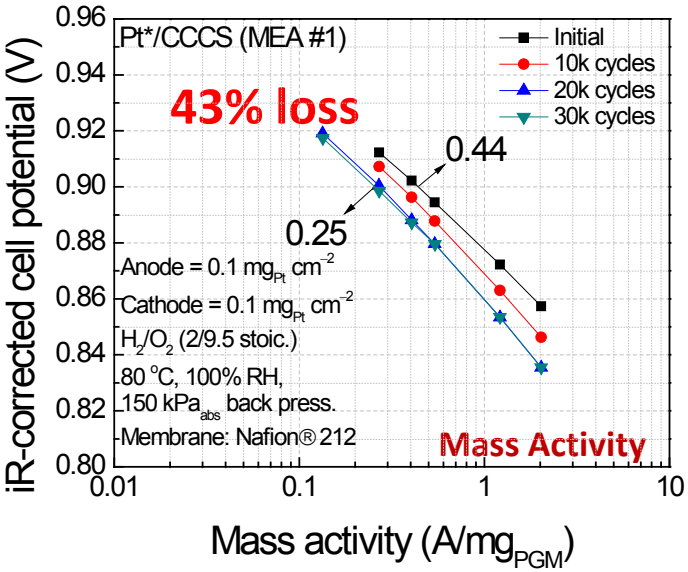
Pt shell thickness: 0.75 nm

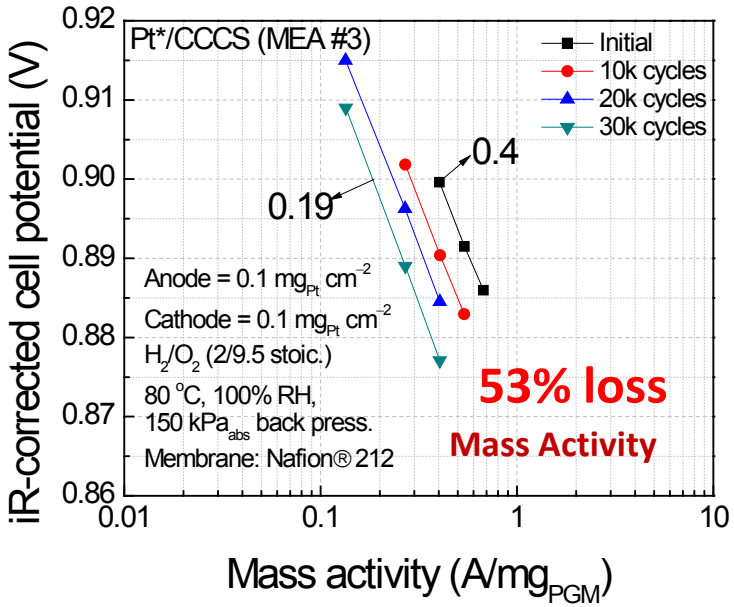
HIGHLIGHT:

- **XRD shows the presence of Pt and PtCo phases after 0.5 h heat treatment.**
- **Single-phase Pt* is formed after 2 h.**
- **The shift in 2θ can be varied by adjusting the heat treatment time.**
- **Line scan confirms the existence of Co in the core and a Pt-shell thickness of 0.5-0.8nm (Core-shell structure).**

Technical Accomplishments: 30% Pt*/CCCS Catalyst Development

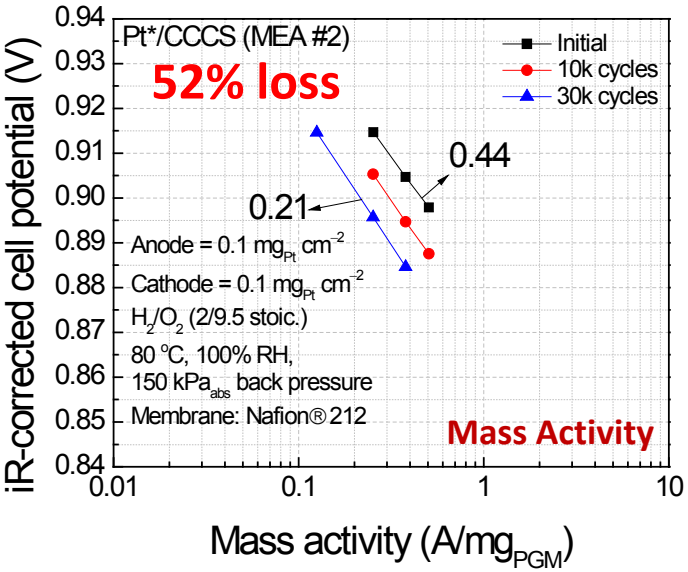
Reproducibility of Stability of Mass Activity under 0.6-1.0 V Cycling





DOE Accelerated Stress Test (AST) Protocol
0.6 ~ 1.0 V, 50mV/s, 30k cycles, H_2/N_2, 80°C, 100 % RH, single cell 25cm^2
Pt mass activity : H_2/O_2, (2/9.5 stoic.), 100% RH, 150 kPa$_{abs.}$

CCCS - High surface area support



HIGHLIGHT:

- All three MEAs of the Pt*/CCCS catalyst show very high mass activity (0.4~0.44 A/mg$_{Pt}$) at 0.9 V$_{iR\text{-free}}$.
- **43~53% loss in mass activity** for Pt*/CCCS catalyst (in three 25 cm^2 MEAs) with final mass activities of **0.19~0.25 A/mg$_{Pt}$ after 30k cycles (0.6-1.0 V).**

- *Popov et al. Electrochim. Acta*, 121 (2014) 116-127.
- *Popov et al. J. Electrochem. Soc.*, 160 (2013) F406-F412.
- *Popov et al. J. Power Sources*, 243 (2013) 958-963.

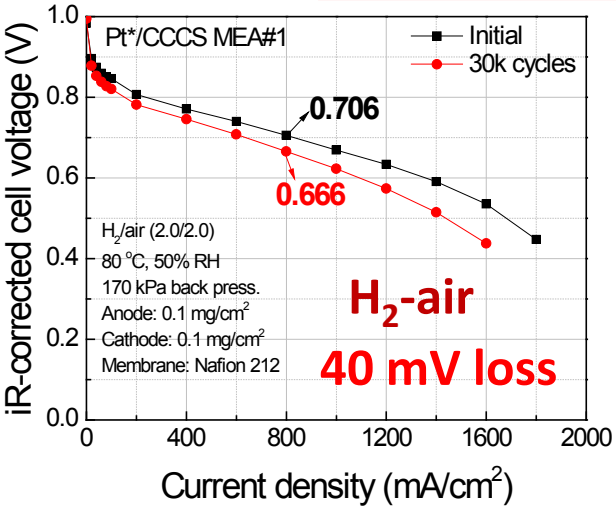
Pt* = Compressive Pt Lattice Catalyst

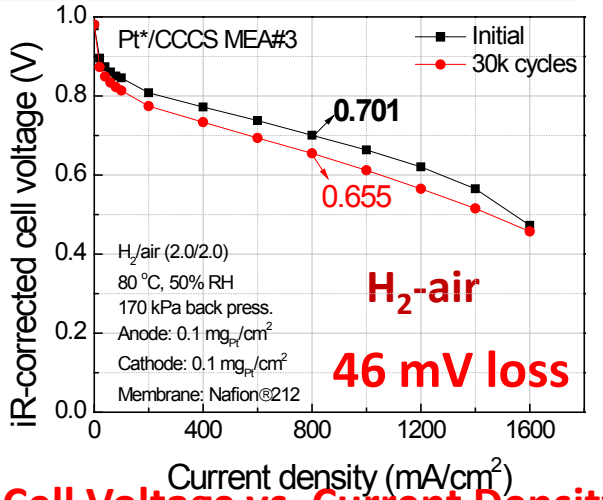
Technical Accomplishments: 30% Pt*/CCCS Catalyst Development

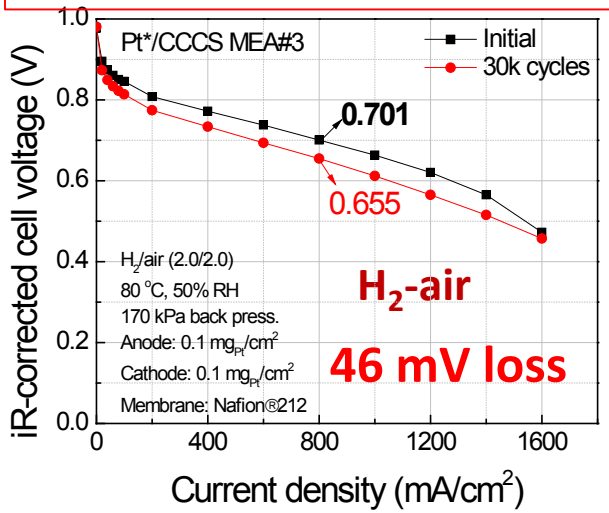
Reproducibility of H_2-air performance under 0.6-1.0 V Cycling

iR-Corrected Cell Voltage vs. Current Density

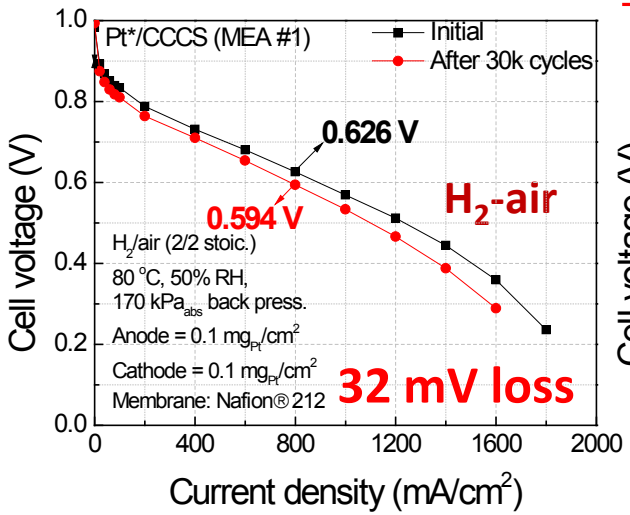
CCCS - High surface area support

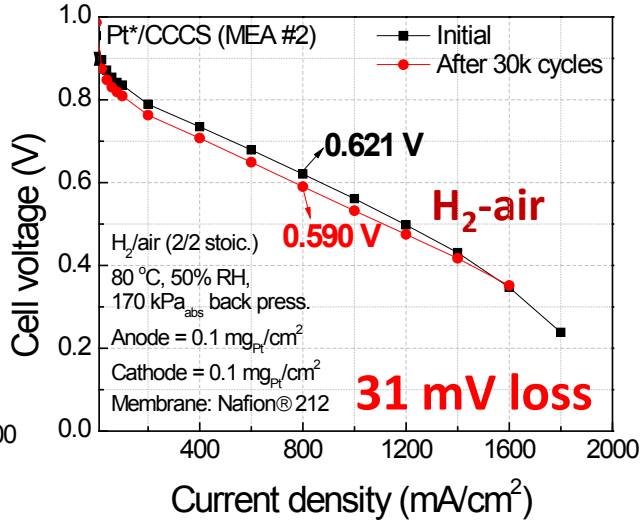


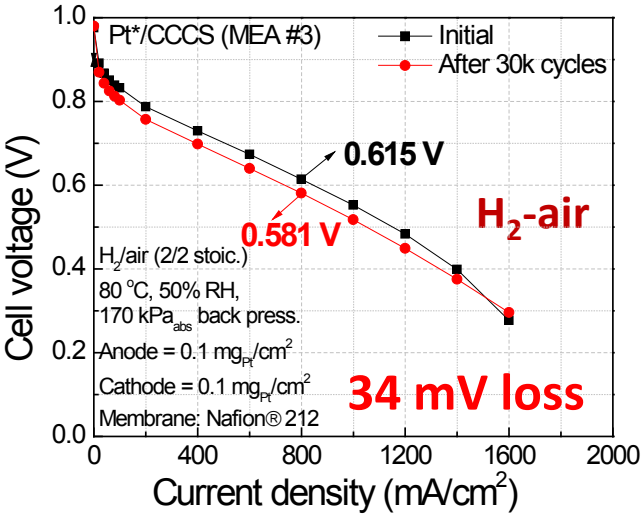




Cell Voltage vs. Current Density







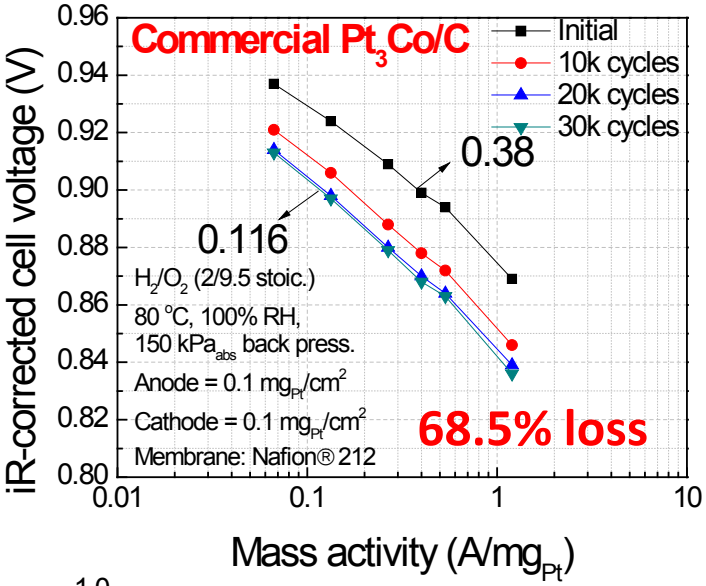
HIGHLIGHT:

- The Pt*/CCCS catalyst tested in **three 25 cm² MEAs** showed stable H_2-air fuel cell performance with only **40~46 mV (iR-free) and 31~34 mV (cell voltage) loss at 800 mA/cm²** after 30,000 cycles (0.6 and 1.0 V). **Pt* = Compressive Pt Lattice Catalyst**

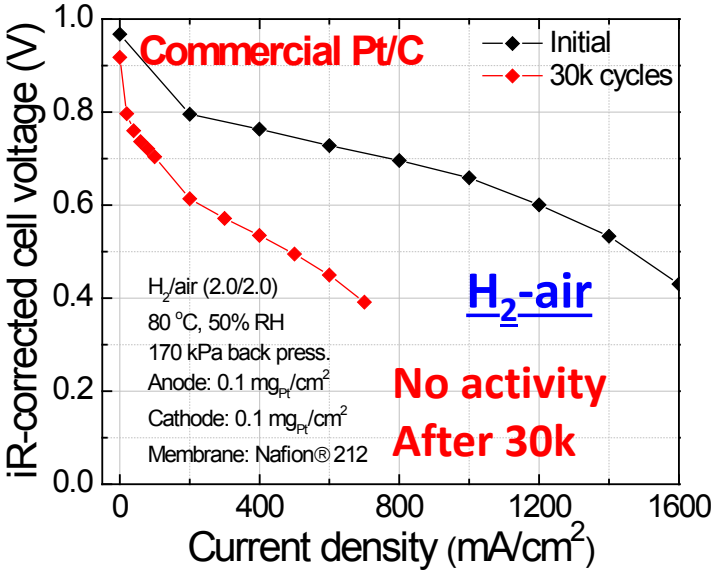
Technical Accomplishments

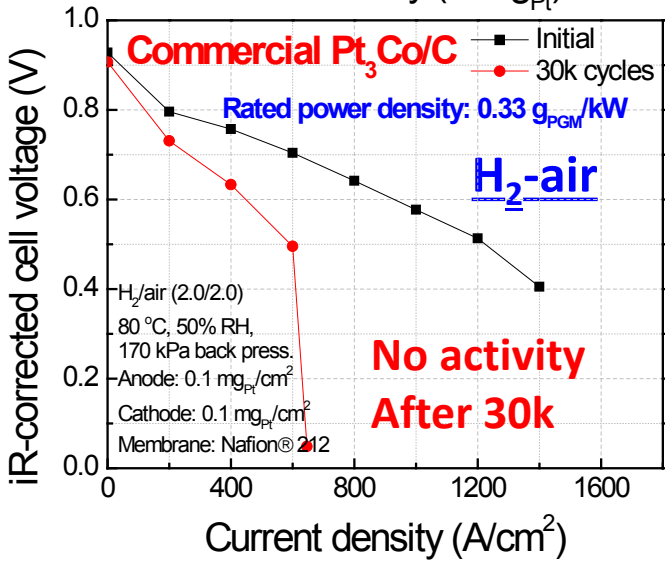
Catalyst Durability of Commercial Pt/C and Pt_3Co/C Catalysts

Mass Activity



DOE Accelerated Stress Test (AST) Protocol
0.6 ~ 1.0 V, 50mV/s, 30k cycles, H_2/N_2, 80°C, 100 % RH, single cell 25cm²
Pt mass activity : H_2/O_2, (2/9.5 stoic.), 100% RH, 150 kPa_{abs}.
H_2/air: 2.0/2.0 stoic, 50% RH, 80°C, 170 kPa backpressure





HIGHLIGHT:

Commercial Pt_3Co/C catalyst

- ❖ Showed 68.5% loss of mass activity after 30k cycles.
- ❖ No activity at 0.8 A/cm² after 30k potential cycles between 0.6 and 1.0 V.

Commercial Pt/C catalyst

- ❖ Showed 67% loss of mass activity (not shown here).
- ❖ No activity at 0.8 A/cm² after 30k potential cycles between 0.6 and 1.0 V.

Popov et al. Electrochim. Acta, 167 (2015) 1-12.

Pt* = Compressive Pt Lattice Catalyst

Technical Accomplishments

Development of A-CCS Support, Pt/A-CCS and Pt*/A-CCS Catalysts

Porous carbon support is susceptible to corrosion under PEMFC fuel cell operating conditions:

- High water content; Low pH (<1); High temperature (70-80°C); High oxygen concentration
- Very high potential (1.2~1.5 V vs. RHE) at the cathode interface during start-up/shutdown cycles and fuel starvation.

❖ Carbon oxidation occurs according to:

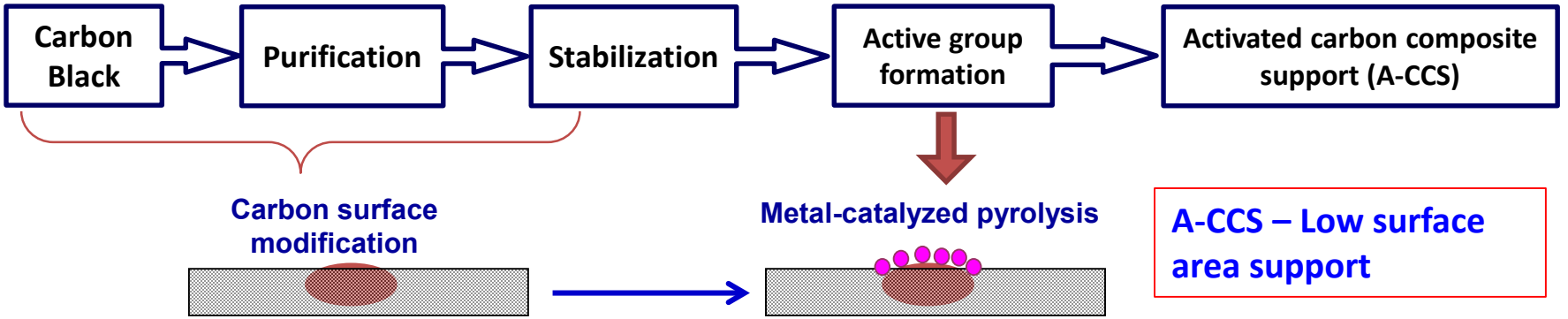
$$C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^-$$ (E^o = 0.207 V vs. NHE at 25 °C)

❖ Carbon oxidation results in:

- Increase in hydrophilicity – affects water removal (increased mass transport losses)
- Decrease in catalyst layer thickness (increase in cell resistance)

Pt catalyst accelerates the carbon corrosion rate

❖ Porosity and pore-size distribution
❖ Hydrophobic/hydrophilic property
❖ Surface functional group to enhance Pt-support interaction



A-CCS – Low surface area support

- **Carbon black**
  - (i) Removal of amorphous carbon
  - (ii) Increase of hydrophobicity
- **This methodology results in enhancement of support stability**

→ **Surface modification** →

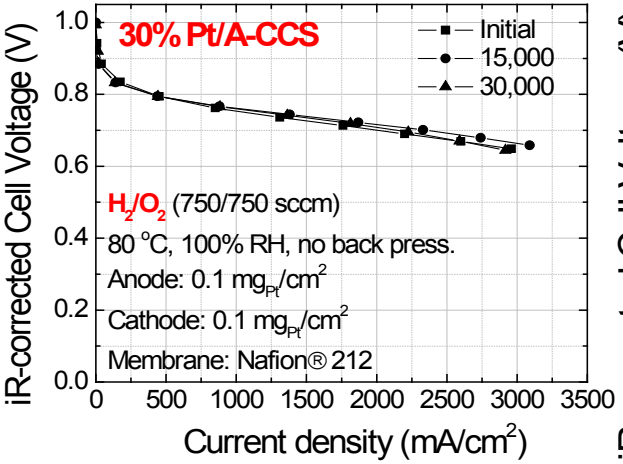
- **Metal-catalyzed pyrolysis** to increase the number of active sites

Pt* = Compressive Pt Lattice Catalyst

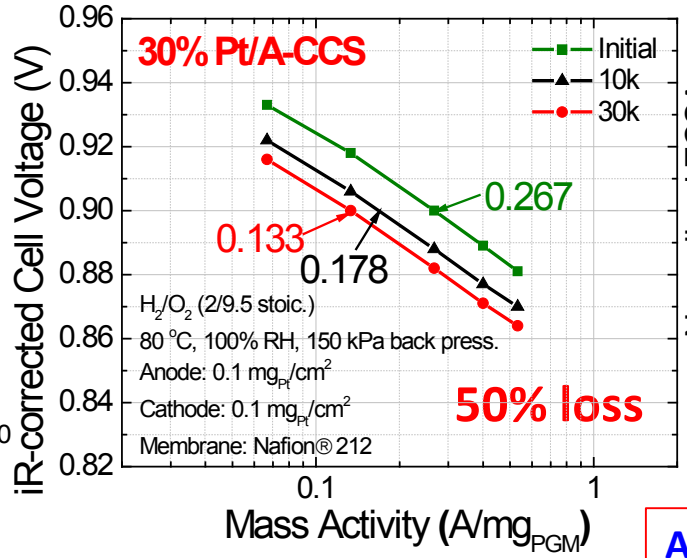
Technical Accomplishments: 30% Pt/A-CCS Catalyst Development

Catalyst Durability (0.6-1.0 V Cycling)

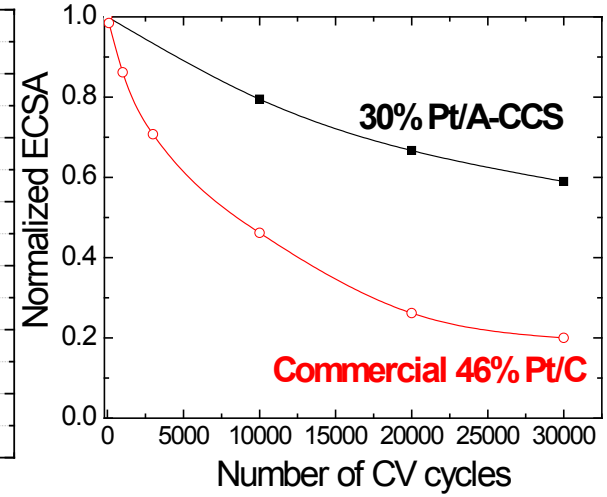
H_2-O_2 polarization curves of Pt/A-CCS and commercial Pt/C catalysts

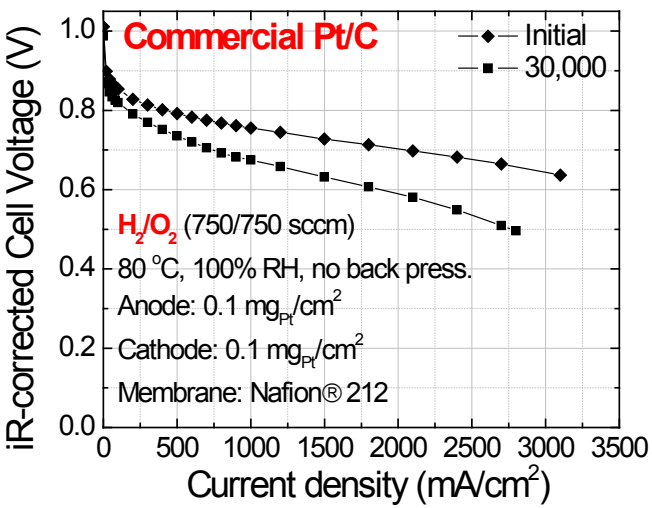


Mass activity of Pt/A-CCS



Normalized ECSA for Pt/A-CCS and Pt/C





A-CCS – Low surface area support

HIGHLIGHT:

- When the cathode reactant is sufficiently supplied for ORR at 100% RH, the Pt/A-CCS catalyst maintains its initial activity after 30k cycles. However, the performance loss of the commercial Pt/C catalyst is much more significant during the AST.
- The better stability is due to (i) strong π-bond act as anchoring sites; (ii) larger particle size between 3 to 4nm compared to that of ~2 nm for Pt/C; (iii) surface nitrogen group to enhance better Pt to carbon interaction.
- After 30k cycles, the mass activity of Pt/A-CCS decreases from 0.267 to 0.133 A/mg_{PGM}, which is 50% loss, while the final mass activity of Pt/C is 0.08 A/mg_{Pt} after 30k cycles (67% loss).
- The ECSA of commercial catalyst experienced significant loss from 65 to 13 m^2/g while that of Pt/A-CCS is much more stable during the cycling test with only 41% loss (from 39 to 23 m^2/g[1]).

DOE Accelerated Stress Test Protocol

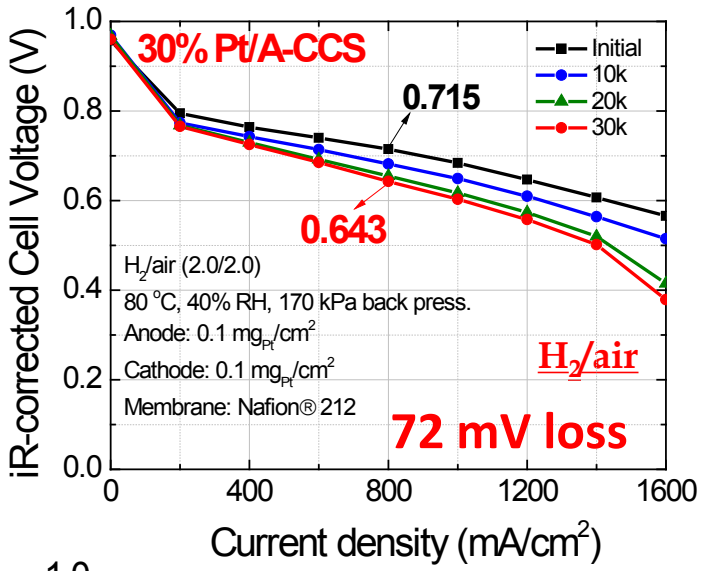
0.6 ~ 1.0 V, 50mV/s, 30k cycles, H_2/N_2, 80°C, 100 % RH, single cell 25cm²

Popov et al. J. Electrochem. Soc. 161 (2014) F1489.

Technical Accomplishments: 30% Pt/A-CCS Catalyst Development

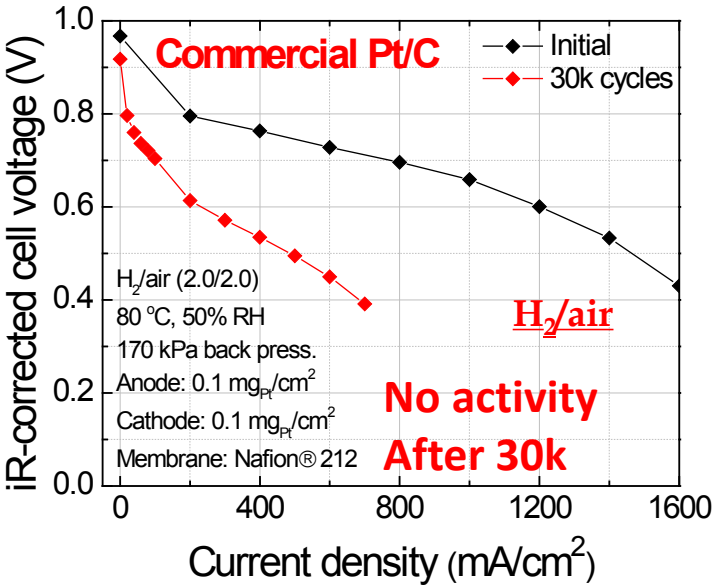
Catalyst Durability (0.6-1.0 V Cycling)

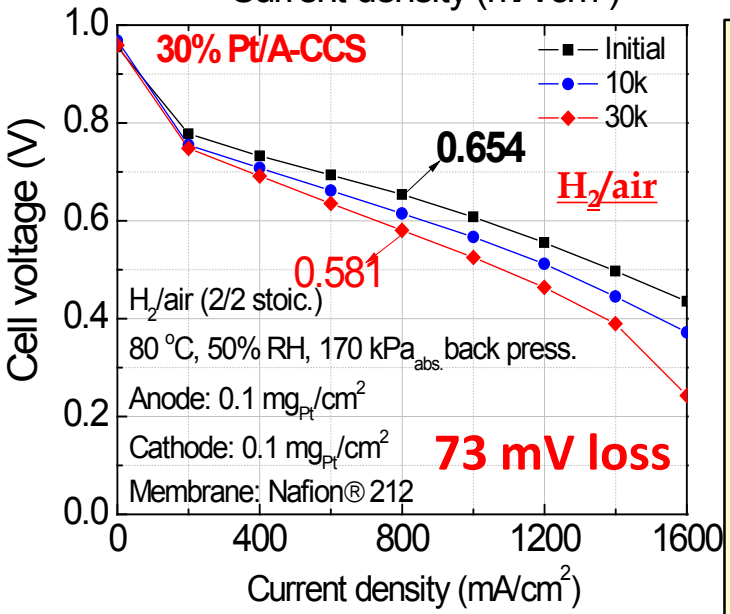
Comparison of H_2-air polarization curves of Pt/A-CCS and commercial Pt/C



DOE Accelerated Stress Test Protocol
0.6 ~ 1.0 V, 50mV/s, 30k cycles, H_2/N_2, 80°C, 100 % RH, single cell 25cm²

A-CCS – Low surface area support





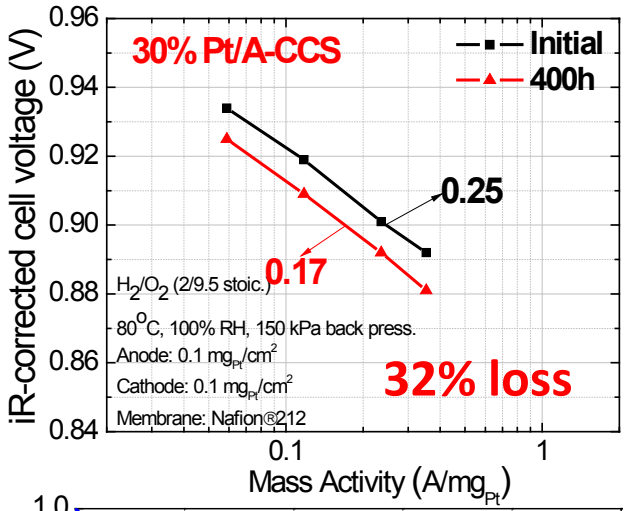
HIGHLIGHT:

- **The Pt/A-CCS catalyst exhibits potential loss of 72 mV at 0.8 A/cm² after 30k cycles**
- **The maximum power density loss is 26% (from 944 to 703 mW/cm²).**
- **Commercial Pt/C showed no activity at 0.8 A/cm² and the maximum power density drops from 746 to 274 mW/cm² (63% loss) due to Pt dissolution and agglomeration during cycling.**
- **Surface nitrogen group enhances better Pt to carbon interaction in Pt/A-CCS.**
- **Higher loss (>50 mV) in open circuit potential is observed for commercial Pt/C when compared with Pt/A-CCS (7 mV) after 30k cycles.**

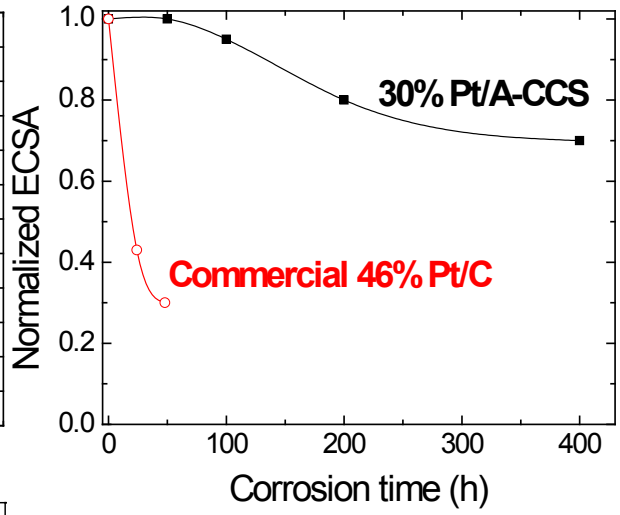
Technical Accomplishments: 30% Pt/A-CCS Catalyst Development

Support Stability (1.2 V potential holding)

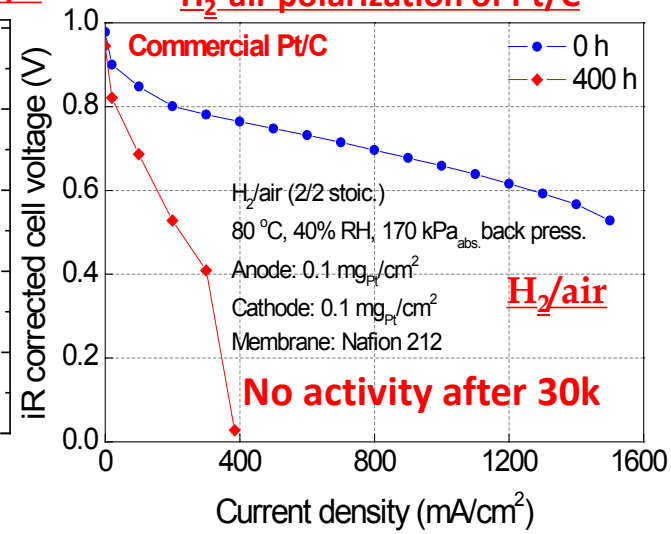
Mass activity of 30% Pt/A-CCS

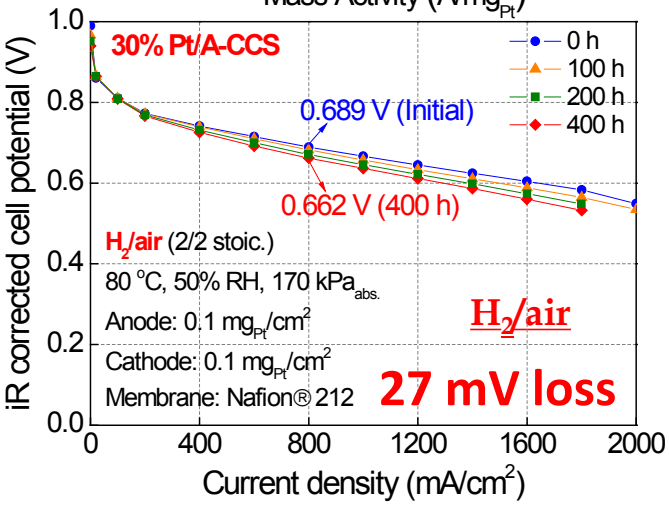


Normalized ECSA for Pt/A-CCS and Pt/C



H_2-air polarization of Pt/C





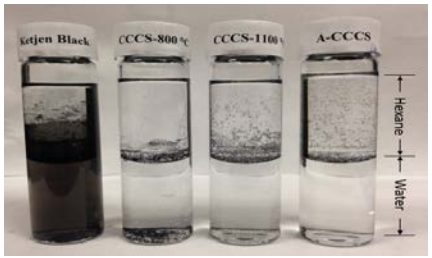
HIGHLIGHT:

- After 400h holding, the **mass activity** decreases from 0.25 to 0.17 A/mg_{Pt} (32% loss) while the commercial Pt/C shows 72% loss.
- Pt/A-CCS maintained about 70% of its initial **ECSA** after 400 h and the commercial Pt/C catalyst showed 70% ECSA loss after 48 h.
- **The results clearly indicates that Pt is safe on the A-CCS support, but not on the commercial carbon. The amorphous property as well as the high surface area and hydrophilicity of commercial carbon increases the corrosion rate at high potential.**
- **27 mV loss was observed on the Pt/A CCS catalyst at 0.8 A/cm^2** after 400h while the commercial 46% Pt/C catalyst which uses high surface area carbon as support showed no activity after 48 h.
- **The hydrophobicity (shown in the photograph) also exhibits large difference between commercial ketjen black® (extreme left) and A-CCS (extreme right). Better water removal not only increases the maximum power density at mass transfer region, but also slow down the carbon corrosion.**

A-CCS – Low surface area support

DOE AST Protocol

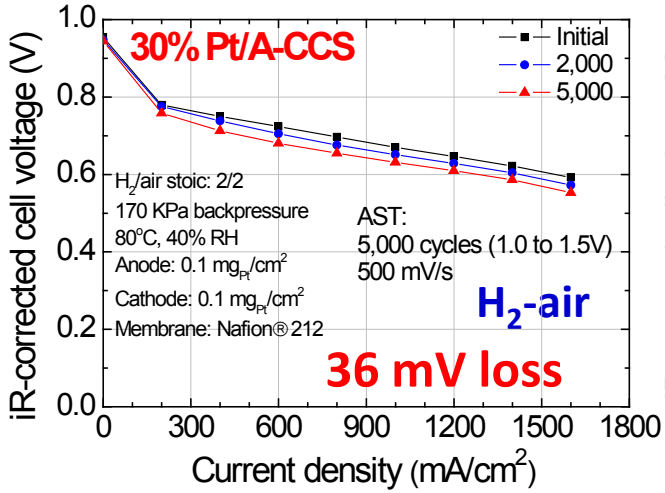
1.2 V holding for 400 hours, H_2/N_2, 80°C, 100 % RH, 150 kPa, single cell 25cm^2

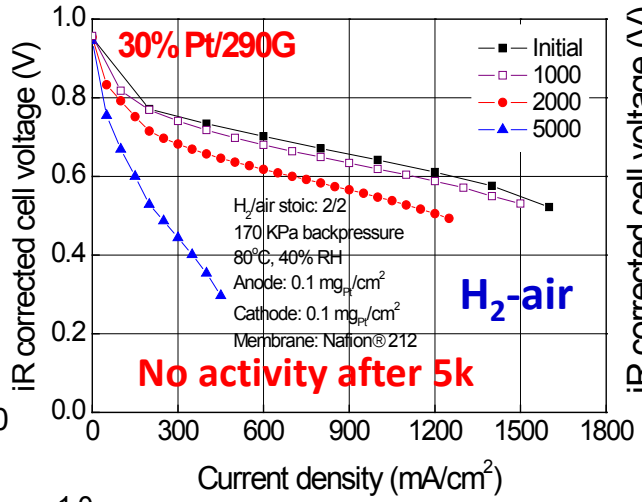


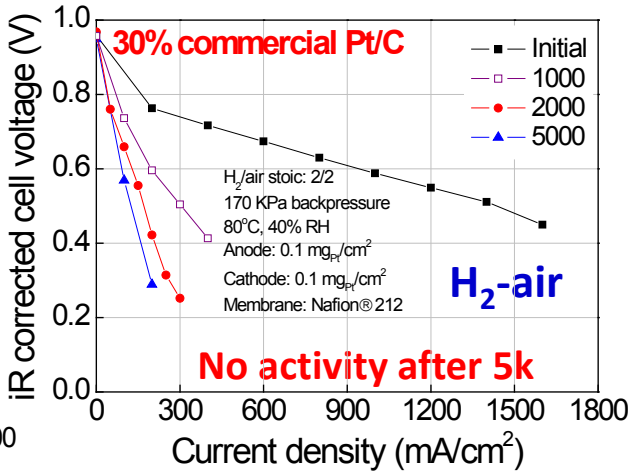
Technical Accomplishments: Support Stability (1.0 to 1.5 V potential cycling)

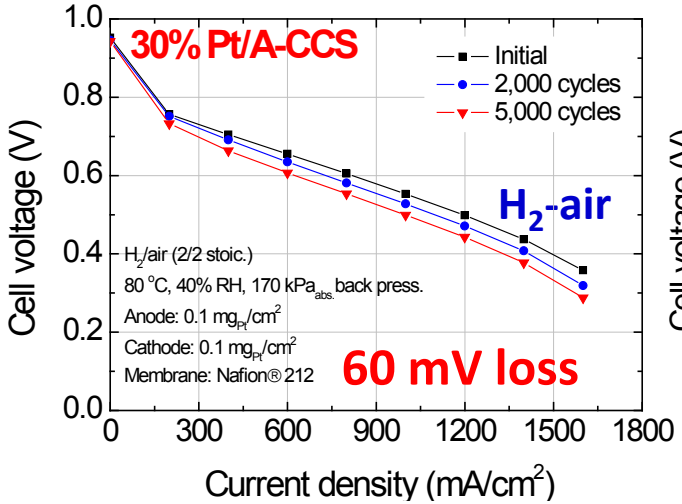
Comparison of H_2-air polarization curves of Pt/A-CCS, Pt/290G, and commercial Pt/C Catalysts

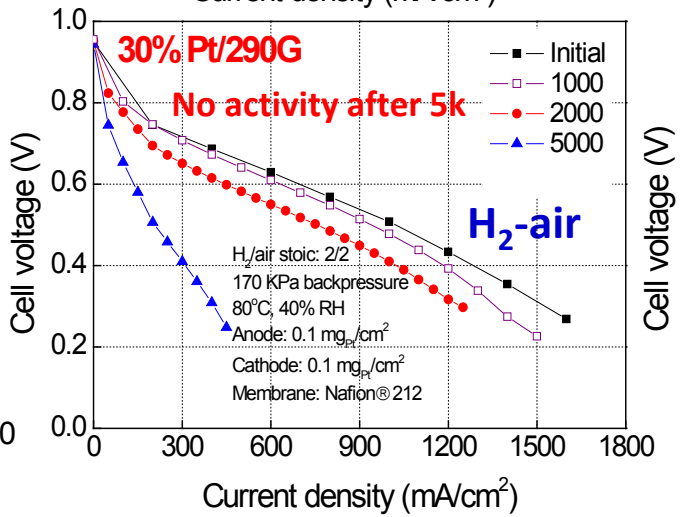
(290G – Commercial carbon support)

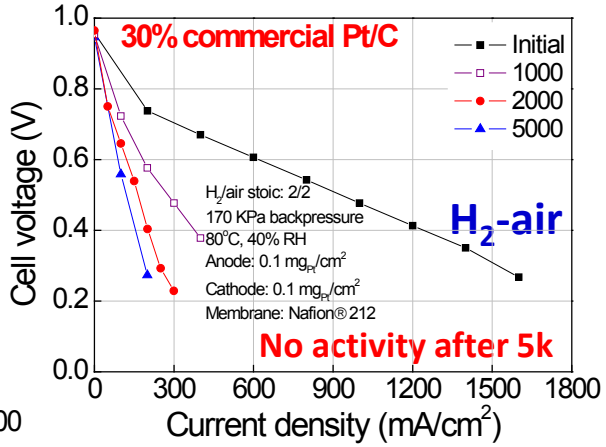












HIGHLIGHT: **A-CCS – Low surface area support**

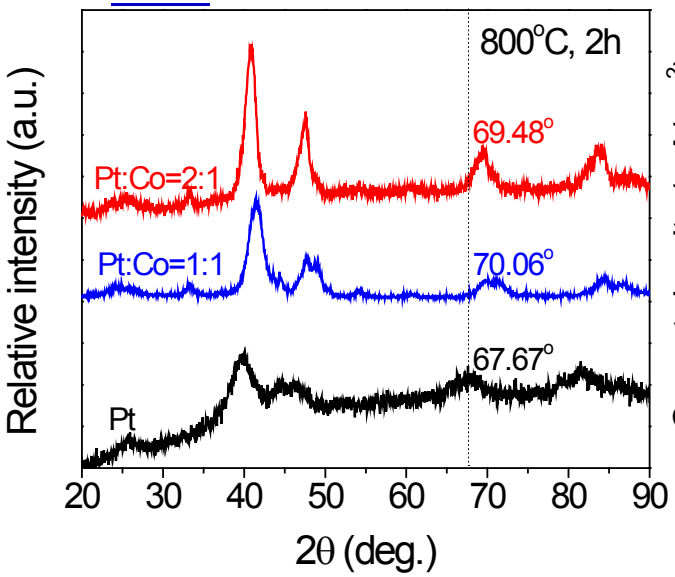
- **30% Pt/A-CCS catalyst shows excellent support stability (only 36 mV loss after 5k cycles)**
- **30% Pt/290G keeps support stability until 2000 cycles but shows rapid decay between 2k ~ 5k cycles.**
- **30% commercial Pt/C shows very poor support stability only after 1000 cycles.**

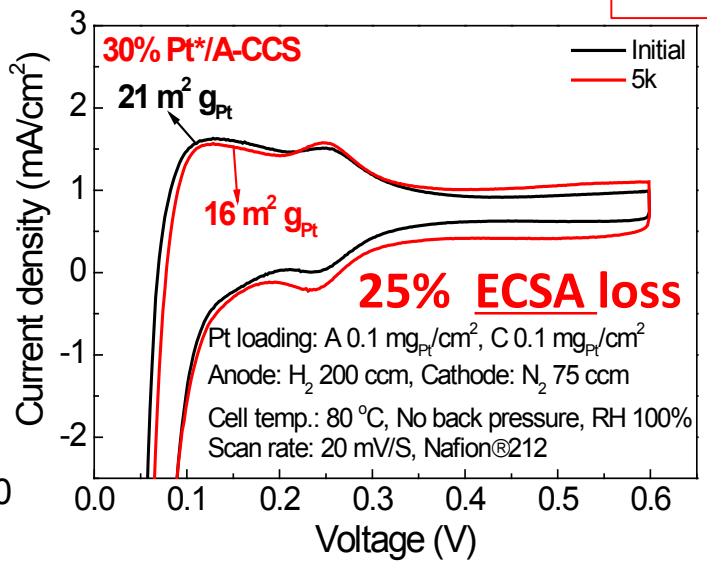
DOE AST Protocol
1.0~ 1.5 V, 500mV/s, 5k cycles, H_2/N_2, 80°C, 100 % RH, single cell 25cm²

Technical Accomplishments: 30% Pt*/A-CCS Catalyst Development (Support Stability 1.0 to 1.5 V potential cycling)

A-CCS – Low surface area support

XRD : Effect of Pt to Co ratio

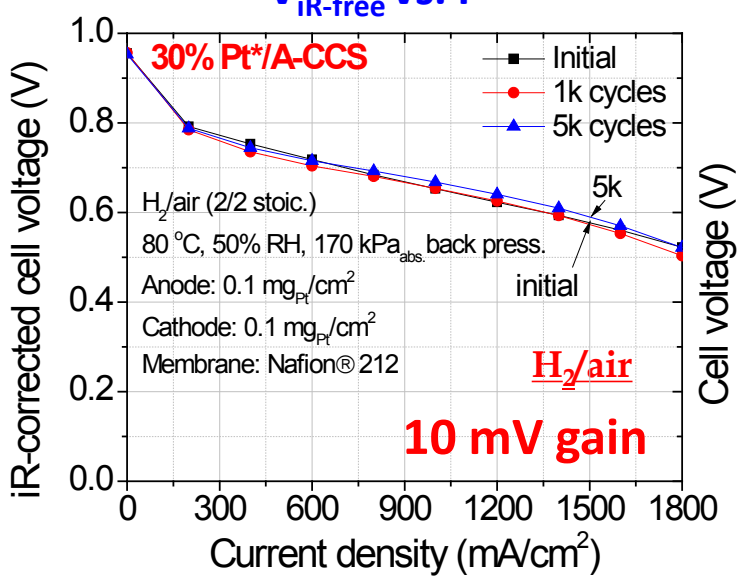




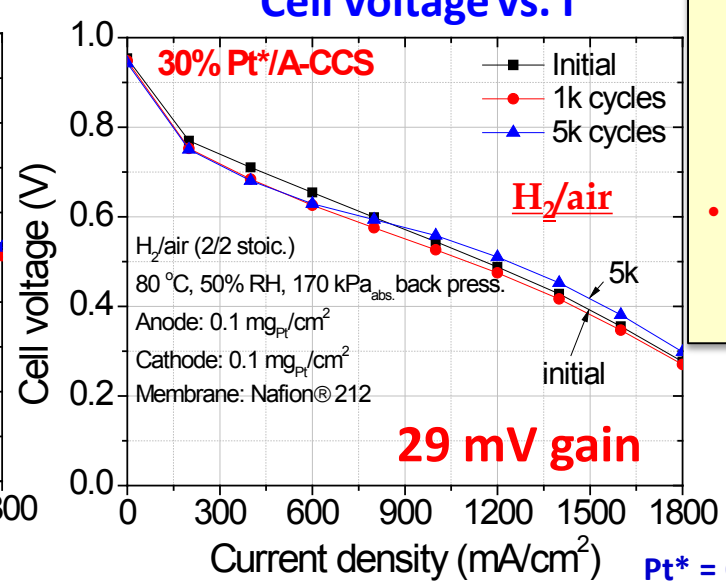
HIGHLIGHT:

- **XRD:** The Pt(111) peak shift is higher for Pt:Co =1:1.
- The catalyst showed initial mass activity of 0.41 A/mg_{PGM} and 0.192 A/mg_{PGM} after 5k cycles (53% loss).
- **H_2-air:** The initial current density at 0.6 $V_{iR\text{-}free}$ is 1.4 A/cm^2. After 5k cycles, the current density increased to 1.45 A/cm^2.
- **H_2-air:** The catalyst showed an increase of ~10 mV (iR-free) and 29 mV (cell voltage) at 1500 mA/cm^2 after 5k cycles
- **ECSA:** The ECSA loss is 25% after 5k cycles (decreased from 21 to 16 m^2/g_{Pt}).

$V_{iR\text{-}free}$ vs. I



Cell voltage vs. I



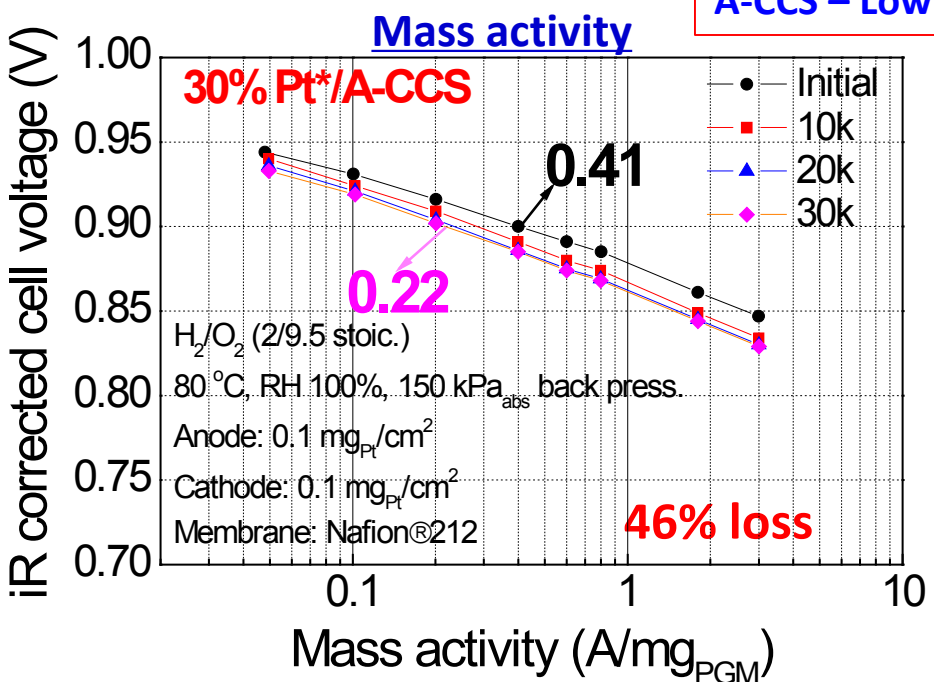
DOE AST Protocol
1.0 ~ 1.5 V, 500mV/s, 5k cycles, H_2/N_2, 80°C, 100 % RH, single cell 25cm²

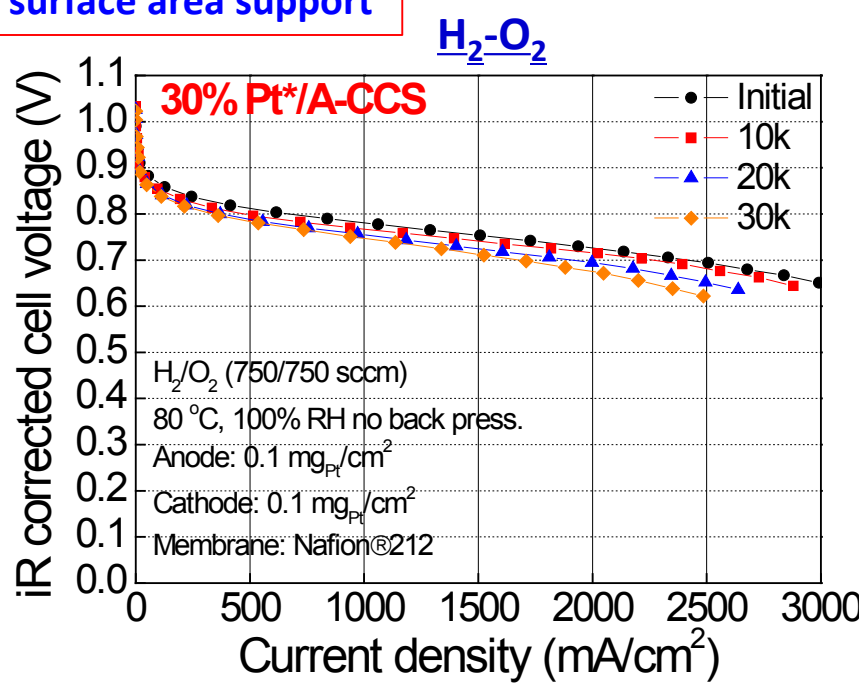
Pt* = Compressive Pt Lattice Catalyst

Technical Accomplishments 30% Pt*/A-CCS Catalyst Development

Catalyst Durability (0.6-1.0 V Cycling)

A-CCS – Low surface area support





HIGHLIGHT:

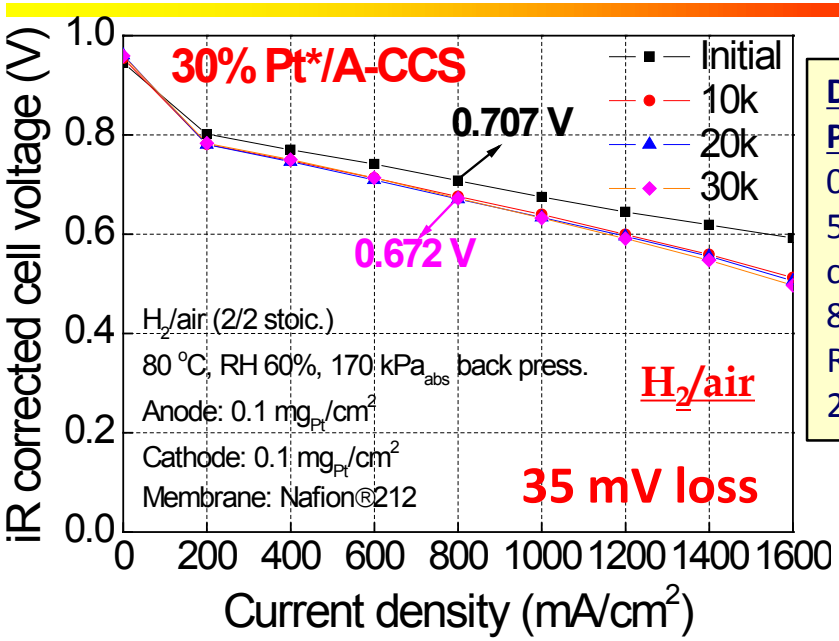
- **Mass activity**: The 30% Pt*/A-CCS catalyst showed initial mass activity of 0.41 A/mg_{Pt} and 46% loss after 30k cycles.
- **H_2-O_2:** The 30% Pt*/A-CCS catalyst showed initial current density of 2.5 A/cm^2 at 0.7 $V_{iR\text{-}free}$.

DOE AST Protocol
0.6 ~ 1.0 V, 50mV/s, 30k cycles, H_2/N_2, 80°C, 100 % RH, single cell 25cm^2

Pt* = Compressive Pt Lattice Catalyst

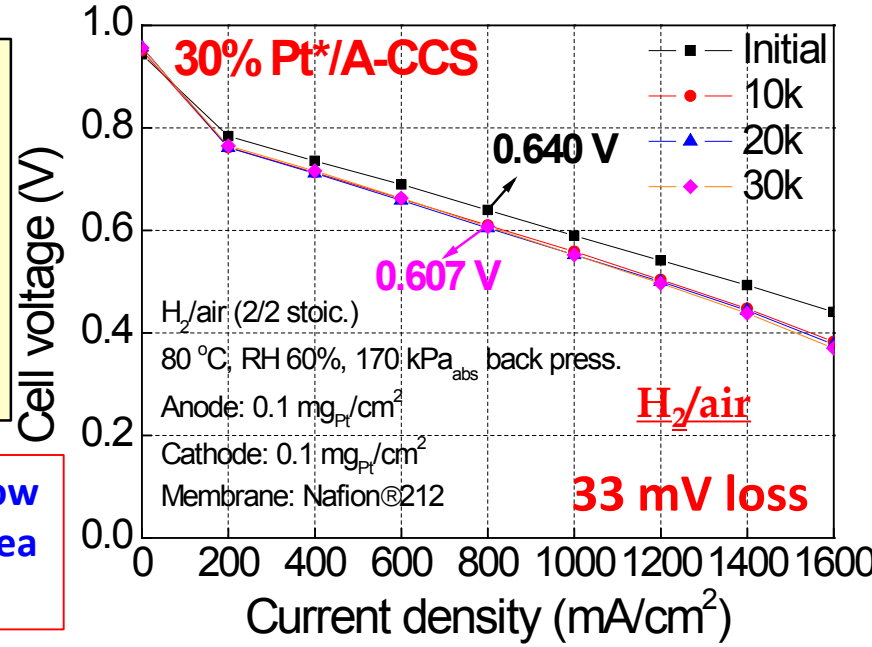
Technical Accomplishments 30% Pt*/A-CCS Catalyst Development

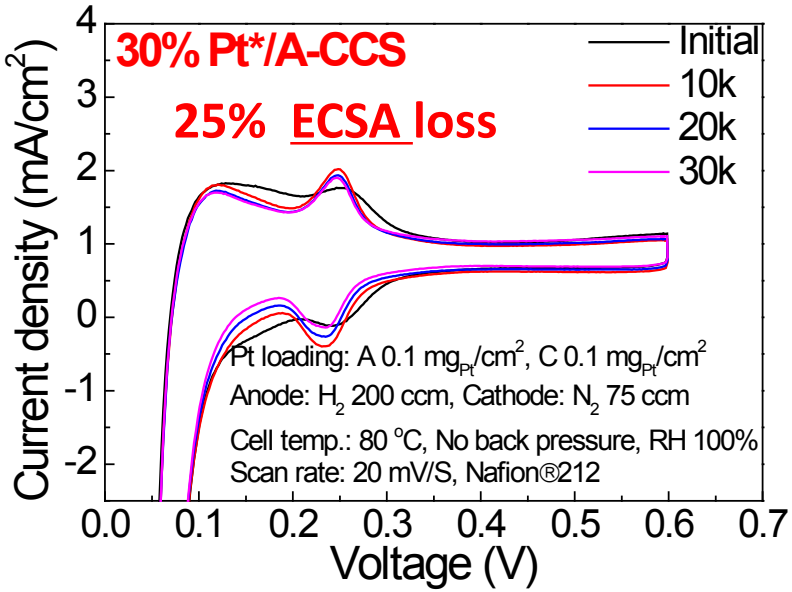
Catalyst Durability (0.6-1.0 V Cycling)



DOE AST Protocol
0.6 ~ 1.0 V, 50mV/s, 30k cycles, H_2/N_2, 80°C, 100 % RH, single cell 25cm²

A-CCS – Low surface area support





HIGHLIGHT:

- **H_2-air:** The 30% Pt*/A-CCS catalyst showed an initial current density of 1.5 A/cm² at 0.6 $V_{iR\text{-}free}$.
- The catalyst showed **35 mV (iR-free) loss and 33 mV (cell voltage) loss at 0.8 A/cm²** after 30k cycles (0.6 and 1.0 V).
- The **rated power density is 0.19 g_{PGM}/kW**.
- **ECSA:** The **ECSA loss is 25%** (decreased from 24.1 m^2/g_{Pt} to 18 m^2/g_{Pt})

Pt* = Compressive Pt Lattice Catalyst

Summary

30% Pt*/CCCS Catalyst

- For the first time, at USC, we have achieved **initial mass activity of 0.44 A/mg$_{PGM}$** and **loss of mass activity of 43% after 30k cycles** (0.6-1.0 V) (2017 DOE target is ≥40%).
- Accomplished potential loss of 40 mV after 30k cycles (0.6-1.0 V) at 0.8 A/cm^2.
- Accomplished **32% ECSA loss** after 30k cycles (0.6-1.0 V).
- Accomplished (rated) initial power density of 0.23 g$_{PGM}$/kW.

30% Pt/A-CCS Catalyst

- Accomplished initial mass activity of 0.26 A/mg$_{PGM}$ and loss of mass activity of 50% after 30k cycles (0.6-1.0 V).
- Accomplished potential loss of 72 mV at 0.8 A/cm^2 after 30k cycles (0.6-1.0 V).
- Accomplished **40% ECSA** loss after 30k cycles (0.6-1.0 V) .
- For the first time, we have achieved only **27 mV (at 0.8 A/cm^2) loss after 400 h holding at 1.2 V**. At more severe conditions, such as potential cycling between 1.0-1.5 V (5,000 cycles), the Pt/A-CCS catalyst maintained its activity in H_2/air and showed **36 mV loss (at 1.5 A/cm^2) after 5k cycles (1.0-1.5 V).**
- Accomplished **41% mass activity loss** and **45% ECSA loss** after 5k cycles (1.0-1.5 V).
- Accomplished (rated) initial power density of 0.18 g$_{PGM}$/kW.

30% Pt*/A-CCS Catalyst

- Accomplished initial mass activity of 0.41 A/mg$_{PGM}$ and loss of mass activity of 46% after 30k cycles (0.6-1.0 V).
- Accomplished potential **loss of 35 mV (iR-free) and 33 mV (cell voltage) loss at 0.8 A/cm^2 after 30k cycles** (0.6 and 1.0 V).
- Accomplished **25% ECSA loss** after 30k cycles (0.6 and 1.0 V).
- The catalyst showed a **gain of ~10 mV cell potential at 1500 mA/cm^2 after 5k cycles** (1.0-1.5 V).
- Accomplished **53% mass activity loss** and **25% ECSA loss** after 5k cycles (1.0-1.5 V).
- Accomplished (rated) initial power density of 0.19 g$_{PGM}$/kW.

Pt* = Compressive Pt Lattice Catalyst

Future Work (May-Dec 2015)

- We synthesized Pt*/A-CCS catalysts with optimized Pt-Co structures which showed high initial mass activity (0.41 A/mg_{PGM}), stability of mass activity (46% loss after 30k cycles), high H_2-air performance (1.5 A/cm^2 at 0.6 $V_{iR\text{-}free}$), and high rated power density (0.19 g_{PGM}/kW).
- Our studies showed formation of ordered tetragonal Pt-Co phase, while the disorder to ordered Pt-Co phase increased with the increase in pyrolysis temperature. The catalyst performance was found to depend on the disordered/ordered Pt-Co structures (Pt*/A-CCS).
  - Detailed studies will be carried out to optimize the performance of Pt*/A-CCS with the structural properties of Co-doped Pt.
  - Structure-property performance will be evaluated for different Pt-Co ratios which result in structures with different degree of formation of compressive Pt-lattice structure.
  - Mathematical model developed at USC and European Commission will be used to optimize the ratio of ordered and disordered Pt-Co phases.
- Further studies will be carried out to increase the H_2-air fuel cell performance of Pt/A-CCS and Pt*/A-CCS catalysts by controlling the hydrophilic/hydrophobic property of A-CCS.
  - The goal is to eliminate the eventual flooding of the support under 1.0-1.5 V cycling.
- Selection of a best performing catalyst to achieve 2017 DOE technical targets for electrocatalyst and catalyst support.

Future Work (May-Dec 2015)

- Reproducibility studies of selected catalyst in 25 and 50 cm^2 MEAs.
- High-volume production:
  - Optimization of high volume production procedures for A-CCS support and Pt/A-CCS and Pt*/A-CCS catalysts.
- Cost-reduction:
  - Further decrease of PGM loading
  - Cost-effective synthesis procedures by eliminating the chemical leaching process during Pt*/A-CCS synthesis.

Deliverables

- **Supply of MEAs for independent evaluation at NREL (From May 2015 – Dec 2015).**

Summary of Accomplishment of 30% Pt*/CCCS Cathode Catalyst (Phase II)

Metric	Units	*Status April 30, 2015*	Commercial Pt/C	2017 DOE target
Initial Mass Activity (Milestone 2)				
Initial Mass activity	A/mg_{PGM} @ 900 $mV_{iR\text{-}free}$	***0.44***	0.18	≥0.44
Catalyst Stability (0.6-1.0 V cycling) (Milestone 3)				
Loss in catalyst activity	% loss after 30k cycles	***43 %*** ***(0.25 A/mg_{PGM})***	68%	≤40%
Loss in ECSA	% loss after 30k cycles	***32%*** ***(75 → 64 m^2/g_{Pt})***	80%	≤40%
Potential loss @ 800 mA/cm^2	mV loss after 30k cycles	***40 mV***	No Activity	≤30 mV
PGM Content and PGM Loading (Milestone 4)				
PGM total content (Power Density)	g_{PGM}/kW (rated)	***0.23***	0.3	≤0.125
PGM total loading	mg_{PGM}/cm^2_{geo}	***0.2***	0.2	≤0.125

Met the 2017 DOE Targets

Pt* = Compressive Pt Lattice Catalyst

Summary of Accomplishment of 30% Pt/A-CCS Cathode Catalyst (Phase II)

Metric	Units	*Status April 30, 2015*	Commercial Pt/C	2017 DOE target
Initial Mass Activity (Milestone 2)				
Initial Mass activity	A/mg_{PGM} @ 900 $mV_{iR\text{-}free}$	***0.26***	0.18	≥0.44
Catalyst Stability (0.6-1.0 V cycling) (Milestone 3)				
Loss in catalyst activity	% loss after 30k cycles	***50% (0.13 A/mg_{PGM})***	68%	≤40%
Loss in ECSA	% loss after 30k cycles	***40% (39→23 m^2/g_{Pt})***	80%	≤40%
Potential loss @ 800 mA/cm^2	mV loss after 30k cycles	***72 mV***	No Activity	≤30 mV
Support Stability (1.2 V holding) (Milestone 3)				
Loss in catalyst activity	% loss after 400 h	***32% (0.17 A/mg_{PGM})***	72%	≤40%
Loss in ECSA	% loss after 400 h	***6% (39→37 m^2/g_{Pt})***	71%	≤40%
Potential loss @ 800 mA/cm^2	mV loss after 400 h	***27 mV***	No Activity	≤30 mV
Support Stability (1.0-1.5 V cycling) (New Test Performed)				
Loss in catalyst activity	% loss after 5k cycles	***41% (0.15 A/mg_{PGM})***	*	≤40%
Loss in ECSA	% loss after 5k cycles	***45% (39→21 m^2/g_{Pt})***	92%	≤40%
Potential loss @ 1500 mA/cm^2	mV loss after 5k cycles	***36 mV***	No Activity	≤30 mV
PGM Content and PGM Loading (Milestone 4)				
PGM total content (Power Density)	g_{PGM}/kW (rated)	***0.18***	0.3	≤0.125
PGM total loading	mg_{PGM}/cm^2_{geo}	***0.2***	0.2	≤0.125

*Very low final mass activity – not comparable

Met the 2017 DOE Targets

Summary of Accomplishment of 30% Pt*/A-CCS Cathode Catalyst (Phase II)

Metric	Units	*Status April 30, 2015*	Commercial Pt/C	2017 DOE target
Initial Mass Activity (Milestone 2)				
Initial Mass activity	A/mg_{PGM} @ 900 $mV_{iR\text{-}free}$	***0.41***	0.18	≥0.44
Catalyst Stability (0.6-1.0 V cycling) (Milestone 3)				
Loss in catalyst activity	% loss after 30k cycles	***46% (0.22 A/mg_{PGM})***	68%	≤40%
Loss in ECSA	% loss after 30k cycles	***25% (24→18 m^2/g_{Pt})***	80%	≤40%
Potential loss @ 800 mA/cm^2	mV loss after 30k cycles	***35 mV***	No Activity	≤30 mV
Support Stability (1.0-1.5 V cycling) (New Test Performed)				
Loss in catalyst activity	% loss after 5k cycles	***53%* (0.19 A/mg_{PGM})***	**	≤40%
Loss in ECSA	% loss after 5k cycles	***25% (21→16 m^2/g_{Pt})***	92%	≤40%
Potential loss @ 1500 mA/cm^2	mV loss after 5k cycles	***No loss (10 mV gain)***	No Activity	≤30 mV
PGM Content and PGM Loading (Milestone 4)				
PGM total content (Power Density)	g_{PGM}/kW (rated)	***0.19***	0.3	≤0.125
PGM total loading	mg_{PGM}/cm^2_{geo}	***0.2***	0.2	≤0.125

Met the 2017 DOE Targets

*** The loss is due to high RH and support oxidation which caused water flooding under H_2/O_2 when subjected to 1.0-1.5 V cycling.**

****Very low final mass activity – not comparable**

Pt* = Compressive Pt Lattice Catalyst

Collaborations

European Commission (DG Joint Research Centre, Institute for Energy and Transport Cleaner Energy Unit): Mathematical model development for Co-diffusion and compressive Pt-lattice catalyst formation (**Dr. Akos Kriston**).

NREL (Subcontractor): Evaluation of catalyst durability and support stability of USC catalysts according to Fuel Cell Tech Committee Accelerated Stress Test Protocol (**May – Dec 2015**)

- **Rudiger Laufhutte** (University of Illinois, Urbana-Champaign): ICP analysis of Pt*/CCCS and Pt*/A-CCS catalysts.
- **Alan Nicholls** (University of Illinois, Chicago): HRTEM & XEDS mapping.
- **Lax Saraf & Haijun Qian** (Clemson University): Transmission Electron Microscopy analysis.
- **EM Center** (University of South Carolina): HR-TEM analysis
- **Scribner Associates**: Design and construction of fuel cell test stations according to USC requirements.
- **Fuel Cell Technologies**: Design and construction of single cells according to USC specifications.

Pt* = Compressive Pt Lattice Catalyst

Team Members who contributed to this presentation

University of South Carolina

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

Acknowledgement

U.S. Department of Energy

Publications

1. Wonsuk Jung, Tianyuan Xie, Taekeun Kim, Prabhu Ganesan, Branko N. Popov, Highly Active and Durable Co-Doped Pt/CCC Cathode Catalyst for Polymer Electrolyte Membrane Fuel Cells, *Electrochim. Acta*, **167** (2015) 1-12.
2. T. Kim, T. Xie, W.S. Jung, F. Gadala-Maria, P. Ganesan, B.N. Popov, Development of Catalytically Active and Highly Stable Catalyst Supports for Polymer Electrolyte Membrane Fuel Cells, *J. Power Sources*, **273**, (2015) 761-774.
3. T. Xie, W.S. Jung, T. Kim, P. Ganesan, B.N. Popov, Development of Highly Active and Durable Hybrid Cathode Catalysts for Polymer Electrolyte Membrane Fuel Cells, *J. Electrochem. Soc.*, **161** (2014) F1489-F1501.
4. Ákos Kriston, Tianyuan Xie and Branko N. Popov, Impact of Ultra-low Platinum loading on Mass Activity and Mass Transport in H_2-Oxygen and H_2-Air PEM Fuel Cells, *Electrochim. Acta*, **121** (2014) 116-127.
5. Akos Kriston, Tianyuan Xie, Prabhu Ganesan, Branko N. Popov, "Effect of Pt Loading on Mass and Specific Activity in PEM Fuel Cells" *J. Electrochem. Soc.*, **160** (2013) F406-F412.
6. Ákos Kriston, Tianyuan Xie, David Gamliel, Prabhu Ganesan, Branko N. Popov,, "Effect of Ultra-Low Pt Loading on Mass Activity of PEM Fuel Cells" *J. Power Sources*, **243** (2013) 958-963.
7. Branko N. Popov, Tianyuan Xie, Taekeun Kim, Won Suk Jung, and Prabhu Ganesan, "Development of Ultra-Low Loading Pt Alloy Cathode Catalyst for PEM Fuel Cells," *ECS Transactions*, 58 (2013) 761-778.
8. Akos Kriston, Tianyuan Xie, Taekeun Kim, Won Suk Jung, David Gamliel, Brian Murphy Prabhu Ganesan, Branko N. Popov, Analyzing the effect of Ultra-Low Pt Loading on Mass and Specific Activity of PEM Fuel Cells, *ECS Transactions*, **50**, (2013) 1427-1438.
9. Tianyuan Xie, Taekeun Kim, Won Suk Jung, Kriston Akos Prabhu Ganesan and Branko N. Popov, "Development of Highly Active Pt_2Ni/C Catalyst for PEM Fuel Cell", *ECS Transactions*, **50** (2) (2013) 1615-1626.
10. Taekeun Kim, Won Suk Jung, Tianyuan Xie, Akos Kriston, Prabhu Ganesan, David Gamliel, Brian Murphy and Branko N. Popov, "Development of Hybrid Cathode Catalyst for PEM Fuel Cells", *ECS Transactions*, **50** (2) (2013) 1875-1885.
11. Branko N. Popov, Tianyuan Xie, Taekeun Kim, Won-suk Jung, Akos Kriston Brian Murphy and Prabhu Ganesan, "Development of Ultra-Low Pt Alloy Cathode Catalyst for PEM Fuel Cells", *ECS Transactions*, **50** (2) (2013) 773-785.
12. Xuguang Li and Branko N. Popov, Development of Non-Precious Metal Catalysts for Oxygen Reduction Reaction in Fuel Cells with High Activity and Stability, *ECS Trans.* 2010, *33*, 2333-2339.
13. Xuguang Li, Gang Liu, Prabhu Ganesan, Hansung Kim, Bumwook Roh, and Inchul Hwang, Development of Ultra-Low Pt Alloy Cathode Catalyst for PEM Fuel Cells, Branko N. Popov, *ECS Transactions*, 2011, 41 (1), 955-969.
14. Xuguang Li, Sheng-Yang Huang, Branko Popov, "Development of Low Pt Loading Cathode Catalysts for Polymer Electrolyte Membrane Fuel Cells", *ECS Trans.* 2010, *33*, 239-246.

Presentations

1. Development of Ultra-Low Loading Pt Hybrid Catalyst for PEM Fuel Cells, Tianyuan Xie, Taekeun Kim, Won Suk Jung, Prabhu Ganesan, and Branko N. Popov, *224th ECS Meeting*, San Francisco, CA, October 27-November 01, 2013.
2. Development of Ultra-Low Loading Pt Alloy Cathode Catalyst for PEM Fuel Cells, Branko N. Popov, Tianyuan Xie, Taekeun Kim, Won Suk Jung, and Prabhu Ganesan, *224th ECS Meeting*, San Francisco, CA, October 27-November 01, 2013.
3. Development of Ultra-Low Loading Pt/AGC Catalyst for PEM Fuel Cells, Taekeun Kim, Won Suk Jung, and Prabhu Ganesan, Tianyuan Xie, and Branko N. Popov, *224th ECS Meeting*, San Francisco, CA, October 27-November 01, 2013.
4. Analyzing the effect of Ultra-Low Pt Loading on Mass and Specific Activity of PEM Fuel Cells, Akos Kriston, Tianyuan Xie, Taekeun Kim, Won Suk Jung, David Gamliel, Brian Murphy Prabhu Ganesan, Branko N. Popov, *222nd ECS Meeting*, Honolulu, HI, October 7-12, 2012.
5. Development of Ultra-Low Pt Alloy Cathode Catalyst for PEM Fuel Cells, Branko N. Popov, Tianyuan Xie, Taekeun Kim, Won-suk Jung, Akos Kriston Brian Murphy, David Gamliel and Prabhu Ganesan, *222nd ECS Meeting*, Honolulu, HI, October 7-12, 2012.
6. Development of Highly Active Pt_2Ni/CCC Catalyst for PEM Fuel Cell, Tianyuan Xie, Won Suk Jung, Taekeun Kim, Kriston Akos Prabhu Ganesan and Branko N. Popov, *222nd ECS Meeting*, Honolulu, HI, October 7-12, 2012.
7. Development of Hybrid Cathode Catalyst for PEM Fuel Cells, Taekeun Kim, Won Suk Jung, Tianyuan Xie, Akos Kriston, Prabhu Ganesan, David Gamliel, Brian Murphy and Branko N. Popov, *222nd ECS Meeting*, Honolulu, HI, October 7-12, 2012.
8. Development of ultra-low platinum alloy cathode catalyst for PEM fuel cells, Branko N. Popov, Tae-keun Kim, Xie Tianyuan, Prabhu Ganesan, and Hansung Kim, *220th ECS Meeting*, Boston, MA, October 9-14, 2011.
9. Titanium Dioxide-Supported Platinum Catalysts, S. Huang, P. Ganesan, and B. N. Popov, *220th ECS Meeting*, Boston, MA, October 9-14, 2011.
10. Development of Non-Precious Metal Catalysts for Oxygen Reduction Reaction in Fuel Cells with High Activity and Stability, X. Li, G. Liu, T. Kim, S. Ganesan, P. Ganesan, and B. N. Popov, *220th ECS Meeting*, Boston, MA, October 9-14, 2011.
11. Development of Low Platinum Loading Cathode Catalysts for Polymer Electrolyte Membrane Fuel Cells, X. Li, S. Huang, B.N. Popov, *218th Meeting of the Electrochem. Soc.*, Las Vegas, Nevada, October 13, 2010.
12. Recent Advances in Non-Precious Metal Catalyst for Oxygen Reduction Reaction in Fuel Cells," X. Li, B.N. Popov, T. Kawahara, H. Yanagi, *218th Meeting of the Electrochem. Soc.*, Nevada, October 13, 2010.

Response to Reviewers' Comments

Response to Reviewers' Comments

The accomplishments of this project are generally considered good, based on the performance data provided. The PI should address the following questions regarding the achievements:

Comment 1: Catalytic activity of the "support" measured by RDE was reported. The PI should have also included the "support" activity study measured in MEA at the single-cell level.

Response: The results of H_2-O_2 fuel cell performance of various CCCS are presented in Fig. 1

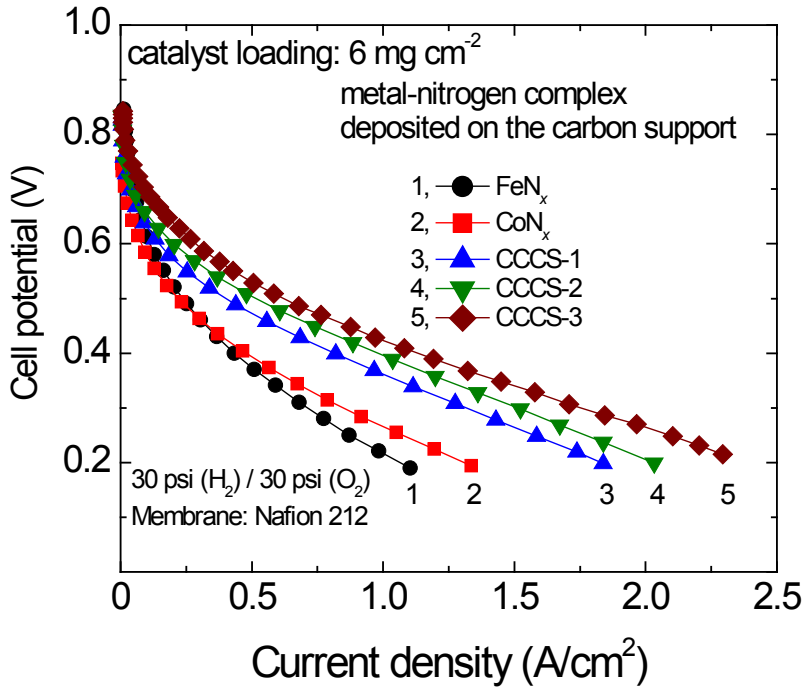


Fig. 1. H_2-O_2 polarization curves of various CCCS synthesized at USC.

Response to Reviewers' Comments

Comment 2: The PI demonstrated an excellent improvement in stability against commercial Pt/C material. Representative data of the commercial Pt/C catalyst/MEA should also be included in the presentation for comparison.

Response: As suggested by the reviewer, the H_2-air and H_2-O_2 polarization curves of commercial Pt/C and commercial Pt_3Co/graphitic carbon are included in this presentation. Please refer **slide number 11**.

Comment 3 : The catalyst demonstrated good stability under a relatively mild cycling condition (0.6–1 V). For the Pt-based catalyst, a more severe aging condition should have been used.

Response: A more severe aging conditions such as potential cycling between 1.0 and 1.5 V (5,000 cycles) and potential holding at 1.2 V (400 h) have been applied to the Pt/A-CCS and Pt*/A-CCS catalysts. Please refer **slide numbers 15-17**.