

V.E.2 Highly Dispersed Alloy Catalyst for Durability

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Objectives

- Develop structurally and compositionally advanced supported alloy catalyst system with loading ≤ 0.3 mg platinum group metal (PGM)/ cm^2 .
- Optimize catalyst performance and decay parameters through quantitative models.
- Demonstrate 5,000 cyclic hours below 80°C with less than 40% loss of electrochemical surface area and catalyst mass activity.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (section 3.4.4) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Durability
- (B) Cost
- (C) Performance

Technical Targets

TABLE 1. DOE 2010 Technical Targets for Electrocatalysts and the Current Status of this Project

Electrocatalyst Targets	Units	Current Status	DOE 2010 Target
Pt group metal (total content)	g/kW	0.50	0.3
Pt group metal (total loading)	mg/ cm^2	0.40 [†]	0.3
Mass activity @ 900 mV	A/mg _{PGM} at 900 mV (iR-free)	0.14 (in MEA) 0.30 (in liquid cell)	0.44
Specific activity	$\mu\text{A}/\text{cm}^2$ at 900 mV (iR-free)	500 (in MEA) 612 (in liquid cell)	720
Cyclic durability			
At T $\leq 80^\circ\text{C}$	h	TBD	5,000
At T $> 80^\circ\text{C}$	h	TBD	2,000
ECA Loss*	%, percent	30	< 40
Cost	\$/kW at \$51.55/g	~26 [†]	5
Electrocatalyst Support mV after 400 hours @ 1.2 V	mV	~12	< 30

ECA = electrochemical area; TBD = to be determined; MEA = membrane electrode assembly, T = temperature

* Durability data measured after 30,000 cycles under UTC Power-defined accelerated test protocol.

[†] Based on current scaled-up 30% Pt₂IrCr MEA; anode/cathode loading – 0.1/0.3 mg/ cm^2 (PGM).

[†] Five year average PGM price \$51.55/g (Pt = \$1234.33/troy oz; Ir = \$369.06/troy oz); costs not projected to high volume production.

Accomplishments

- Down-selected a carbon (C4) that exceeds DOE's corrosion targets and verified a 30% Pt/C4 and a more active PtIrCo/C4 alloy catalyst in a subscale fuel cell which showed that PtIrM/C4 are more active and durable compared to the Pt/C4. Scale up of a 30% Pt₂IrCr alloy on C4 is in progress.
- Completed the scale up of both down-selected dispersed catalysts PtIrCr and PtIrCo for MEA optimization. Currently testing performance and durability of first trial full size MEA of 30% Pt₂IrCr/C.
- Modeling results show that Ir in the dispersed PtIrM (M=Co or Cr) ternary alloy catalysts imparts stability to the surface Pt atoms. The benefit of Ir in PtIrM alloy catalysts was evaluated and compared to PtM alloys.

- Sub-scale MEA catalyst layer optimization was completed to improve the ternary alloy MEA performance in H₂/air at high current densities with total PGM loading of 0.3 mg/cm².
- Correlation between segregation energies, activity and stability of core-shell catalysts based on their composition and surface characterization during potential cycling explains differences in the surface activity during core metal dissolution and the durability of core-shell catalysts.
- Activity and stability of Pt_{ML}/Pd₃Co core-shell catalysts prepared using scalable chemistries were evaluated using both rotating disk electrode (RDE) and sub-scale fuel cell tests.



Introduction

It is well known that, in order for the proton exchange membrane fuel cell (PEMFC) technology to become commercially viable, the production cost of the components in a fuel cell must be reduced and, more importantly, the durability of the MEA must be improved. This project focuses on two distinct approaches to the DOE 2010 durability and performance targets. The first approach is the development of somewhat conventional but high performance highly dispersed Pt alloy catalyst on a carbon support. The second system utilizes a novel “Pt monolayer (ML) core-shell” approach capable of achieving very high Pt mass activities [1-3]. Under this latter concept, the main objectives are to improve the durability of the cathode catalyst by further optimizing the core material selection, shell thickness of the ML, and the particle size of the cores and to develop scalable fabrication methods.

Approach

To achieve the objectives on this project, UTC Power (UTCP) has teamed with Brookhaven National Laboratory (BNL), Texas A&M University (TAMU) and Johnson Matthey Fuel Cells (JMFC). The research focus and the role of all partners were reported previously [4]. BNL's role on the project focuses on the development of Pt ML “core-shell” systems on various cores including ideal surfaces such as single crystals. In addition, BNL leads our efforts to understand the effect of electronic properties, crystal structure and particle size on activity and durability of this class of electrocatalysts. TAMU focuses on development of computational atomistic models to study parameters that influence the activity and durability of core shell and dispersed catalyst systems. The overall scope of JMFC activities in the project encompasses development of (i) dispersed Pt alloy catalysts including scale up on conventional

and advanced carbon supports, (ii) novel synthesis methodologies to scale up Pt ML core-shell catalysts and (iii) MEA optimization and fabrication. Apart from overall project management, UTCP primarily focuses on the development of advanced dispersed Pt-based binary and ternary alloy catalysts. UTCP activities also include modeling support for MEA optimization, carbon support corrosion studies, fuel cell testing on single-cell level and fabrication and test of a 20-cell short stack for verification.

Results

Molecular Modeling

The main topic that was studied this year was calculation of activity and stability of PtIrM ternary alloys based on surface segregation, Bader charge, d-band center analysis of Pt and potential shifts in the dissolution potential for Pt in these alloys. It was previously reported that, in Pt₃M binary alloys, electronically the Pt atoms on skin surfaces differ little from those on the non-segregated alloy surface [4]. In contrast, incorporating Ir into the bimetallic alloy increases the tendency of Pt-skin formation and enhances the stability of the alloy systems. Since Ir has a smaller atomic volume and higher surface energy than Pt, a much stronger Pt segregation trend is expected in the ternary PtIrM alloy system. The calculated segregation energies (in vacuum) of -2.90 eV for Pt₂IrCo, -2.10 eV for Pt₄IrCo₃, and -1.60 eV for Pt₆IrCo₇, suggests that the presence of Ir reduces the lattice mismatch between Pt-Co and favors the formation of a Pt monolayer skin surface. However, the trend to form Pt-skin in PtIrCr alloys is lower compared with the corresponding PtIrCo alloy surfaces. Bader charge analysis (shown in Table 2) on the Pt-skin surfaces, indicates that Pt surface atoms have an excess of electrons in their valence shell and a deficit of electron charge on the subsurface atoms (Ir, Co and Cr), which suggests a higher oxygen reduction reaction (ORR)

TABLE 2. Average valence charge for surface and subsurface atoms of Pt_xIr_yM_z systems.

Geometry	Charge surface Pt atoms	Charge subsurface Co/Cr atoms
pure Pt(111)	-0.05	
Pt ₂ IrCr (Pt-skin)	-0.25	1.22
Pt ₄ IrCr ₃ (Pt-skin)	-0.25	1.11
Pt ₆ IrCr ₇ (Pt-skin)	-0.40	0.77
Pt ₂ IrCo (Pt-skin)	-0.14	0.57
Pt ₄ IrCo ₃ (Pt-skin)	-0.25	0.43
Pt ₆ IrCo ₇ (Pt-skin)	-0.24	0.37

activity for these alloy catalysts compared to a pure Pt (111).

Ir also induces a larger average *d*-band center shift for the Pt-skin surfaces on PtIrM compared to Pt₃M. For comparison, the average *d*-band center shift for Pt-skin on Pt₂IrCo and Pt₃Co is -2.23 eV and -2.18 eV respectively. This negative shift is due to the presence of Ir in the subsurface and thereby modifying the electronic structure of the surface Pt atoms. A *d*-band center shift to more negative values indicates that the Pt-skin surface is less reactive and hence, certain repulsion towards oxygenated species is expected due to the negative charges located on the surface atoms. The calculated *d*-band centers relative to the Fermi level also show a shift towards lower energies in the alloys as a function of the amount of Ir in the alloy as shown in Figure 1 for PtIrCo alloys.

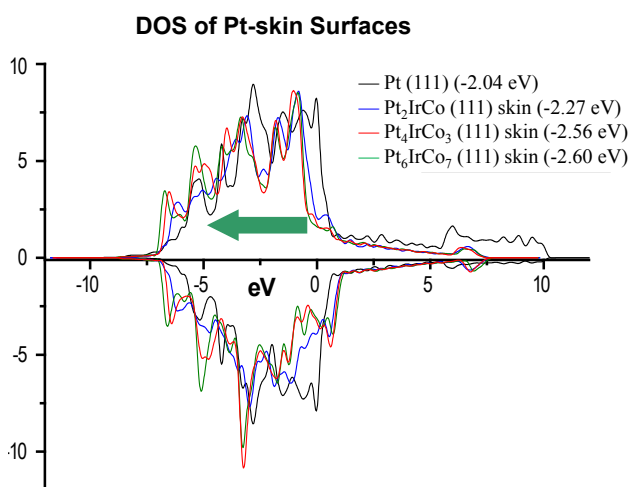


FIGURE 1. Calculated *d*-band centers relative to the Fermi level for the various Pt-skin/PtIrCo alloy surfaces as a function of the amount of Ir in the alloy.

TABLE 3. Electrochemical stability of Pt atoms on Pt-skin/PtIrM (M=Co or Cr) alloy surfaces relative to Pt (111) surfaces on surfaces covered with 1/8 ML of O.

System	μ_{Pt} (eV)	$\Delta\mu$ (eV)	ΔU (V) (under 1/8 ML O)
Pt(111)	-6.64	0	0
Pt/Pt ₂ IrCo(111)	-7.00	-0.36	0.18
Pt/Pt ₄ IrCo ₃ (111)	-7.04	-0.40	0.20
Pt/Pt ₆ IrCo ₇ (111)	-6.91	-0.27	0.14
Pt/Pt ₂ IrCr(111)	-7.63	-0.99	0.5
Pt/Pt ₄ IrCr ₃ (111)	-7.21	-0.57	0.29
Pt/Pt ₆ IrCr ₇ (111)	-7.67	-1.03	0.52

The electrochemical stability of Pt atoms shown in Table 3 indicates that the Pt atoms are more stable on the alloy surfaces than on pure Pt (111) surfaces as shown by the positive shift in potentials on surfaces covered with 1/8 ML of O. The maximum values found for an intermediate amount of Ir suggests that further lowering the amounts of Ir in the alloy compositions may result in less stable surfaces due to the large lattice mismatch between Pt and transition metal atoms [5].

In the core-shell catalyst concept, the activity and stability trends of Pt ML on various Pd-containing metal cores such as Pd₃Co, Pd₃Cr and Pd₃Ti were investigated. Adsorption energies of OH, O and H₂O suggest that both Pt/Pd₃Co and Pt/Pd₃Cr are more active than a pure Pt although the Pt/Pd₃Co shows the weakest adsorption energies. The electrochemical stability investigation of Pd, Co and Cr in these core-shell catalysts shows that Pd, Co and Cr are more stable in the alloy cores than in their pure state and their stability towards leaching follows the order Pd > Co > Cr. Based on these activity and stability results, Pt_{ML}/Pd₃Co is estimated to be a more favorable core-shell system for ORR compared to Pt/Pd₃Cr.

Dispersed Pt Alloy Catalyst

Many factors such as structure, particles dispersion, particle size, type of carbon support used etc., influence the electro-catalytic activity of Pt and Pt alloy nanoparticles. Previously, within this project a 30 wt% Pt₂IrCo and a 30% Pt₄IrCo₃ exhibited an activity almost two times higher than pure Pt based on RDE and MEA testing. The Ir containing ternary alloy catalysts also showed more durability in both their ECA and mass activity (MA) under potential cycling which show much lower loss (~30% ECA and MA) compared to the standard Gore Pt/C which showed ~50% loss. Based on these results the PtIrM ternary alloys were down-selected for further development [4]. In the past year, a significant amount of effort was focused towards scale up of a large size batch (200 g) of the down-selected ternary alloys 30% Pt₄IrCo₃ and 30% Pt₂IrCr, development and optimization of the cathode catalyst layer in an MEA of PtIrM (M= Co, Cr) alloy catalysts to improve the catalyst utilization in an MEA keeping low PGM loading and enabling good performance at high current densities. This involved MEA iterations to identify key parameters such as catalyst ink formulations and ionomer content, to achieve optimum cathode catalyst layer capable of achieving good fuel cell performance operating on not only H₂/O₂ but also on H₂/Air at high current densities.

Figure 2a shows the fuel cell performance curves in H₂/Air for an optimized and un-optimized 30% Pt₂IrCr/C MEA in a sub-scale size (25 cm²) solid plate fuel cell operating at 80°C, 100% relative humidity (RH) and 50 kPa backpressure compared to a commercial Gore 5710 Pt/C MEA. It should be noted that the Pt

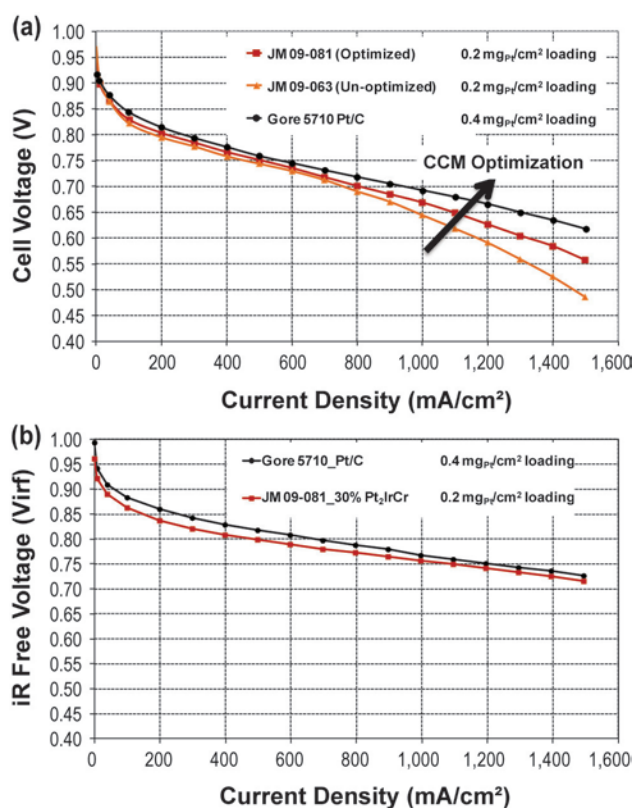


FIGURE 2. Fuel cell polarization curves in (a) H₂/air at 80°C in a solid plate fuel cell at 100% RH and 150 kPa backpressure for an optimized and un-optimized Pt₂IrCr ternary alloy catalyst MEA compared to a state-of-art Pt/C MEA and (b) H₂/O₂ at 65°C in a WTP cell at 100% RH and 100 kPa backpressure, for an un-optimized Pt₂IrCr ternary alloy catalyst MEA compared to a state-of-art Pt/C MEA.

loading in the commercial MEA is about two times of that of the alloy MEAs used in this project. The internal resistance for the PtIrCr MEA is also higher than the Gore 5710 MEA resistances which arise from differences in the membrane thickness and the catalyst layer fabrication process. The initial MA obtained for the alloy catalyst in the optimized and un-optimized MEA were 0.14 and 0.156 A/mg_{PGM}, respectively compared to a MA of 0.17 A/mg PGM observed for the commercial Pt/C MEA. This observed low activity is attributed to the low utilization of the catalyst in the MEA as seen by their low ECA of ~30 m²/g. However, a clear evidence of improvement for high current density performance in H₂/Air in a solid plate fuel cell is observed from these catalyst layer optimization steps. The 30% Pt₂IrCr ternary alloy MEA optimized for solid-plate fuel cell performance was also verified in a full-size UTC Water Transport Plate (WTP) fuel cell operating at 65°C, 100% RH and 0 kPa backpressure. Figure 2b shows the internal resistance (iR) corrected fuel cell polarization curves obtained in H₂/O₂ for the 30% Pt₂IrCr in the WTP fuel cell. Our results shows clear

evidence that lower catalyst loading of 0.2 mgPt/cm² in MEAs can achieve high initial performances, although lower than a commercial Pt/C which has 0.4 mg Pt/cm² in the cathode, in both solid plate and a WTP fuel cell. Our preliminary investigation into MEA fabrication process suggests that different ink formulations can significantly increase both mass transport properties and kinetic performance of alloy catalysts. Further optimization steps are currently being pursued to improve the MEA fabrication process and utilization of the catalyst in the MEA.

Core-Shell Pt Catalysts

The primary focus of core-shell development was (a) to synthesize Pt ML catalysts on Pd₃Co and Ir cores using scalable chemistries without compromising the intrinsic activity of the catalyst as demonstrated by BNL and (b) to incorporate these advanced catalyst concepts in an MEA. Previously, a large batch (30 g) of Pd₃Co and Ir cores and 5g batch Pt ML core-shell catalyst were synthesized successfully by JMFC via a chemical method.

Figure 3 shows the MA based on PGM loading for a scaled-up Pt_{ML}/Pd₃Co core-shell catalyst prepared via chemical methods and a pure Pt/C catalyst obtained from RDE and MEA testing. Although the mass activity obtained on the pure Pt/C in an MEA is slightly lower than that obtained from RDE measurements, the Pt_{ML}/Pd₃Co core-shell catalyst shows a significant lower activity in an MEA (0.044 A/mg PGM) than from RDE measurements (0.254 A/mg PGM). This is mainly attributed to (a) instability of Pt_{ML}/Pd₃Co at 80°C under MEA test conditions and (b) to the incomplete or non-uniform coverage of Pt on the core Pd₃Co particles. Detailed studies of the Pt_{ML}/Pd₃Co core-shell catalysts in 1M H₂SO₄ solution at 80°C using electrochemical and physical characterization using inductively coupled plasma shows substantial loss of Co and Pd on exposure to the acid which indicates incomplete coverage of Pt. Efforts are on currently to improve the Pt monolayer coverage by optimizing the catalyst preparation methods.

Durable Carbon Support

The main focus of this task was to explore alternate durable carbons capable of withstanding high voltage spikes relevant for automotive applications. In the past year, several carbon supports from a number of vendors available both commercially and under developmental proprietary agreements were investigated. Based on the ex situ testing of each of these carbon supports at a constant potential hold of 1.4 V in 0.5 M H₂SO₄ at 80°C for 5 hours and further testing in a fuel cell under the DOE 2008 carbon corrosion protocol, an alternate carbon C4 was down-selected for incorporation of PtIrM ternary alloys into MEAs and demonstration in

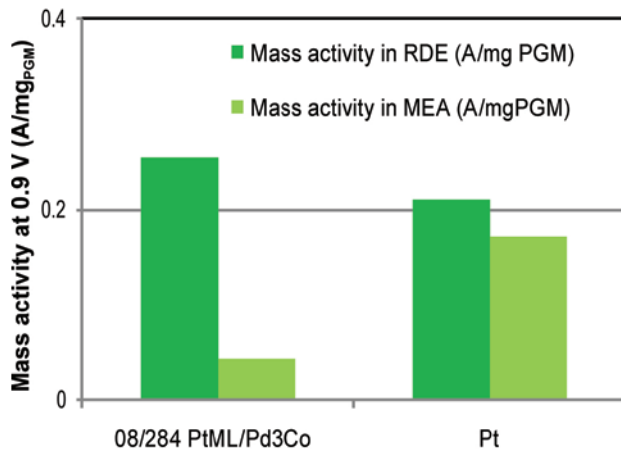


FIGURE 3. Comparison of PGM MA of Pt_{ML}/Pd₃Co and a Pt/C obtained from RDE and MEA testing.

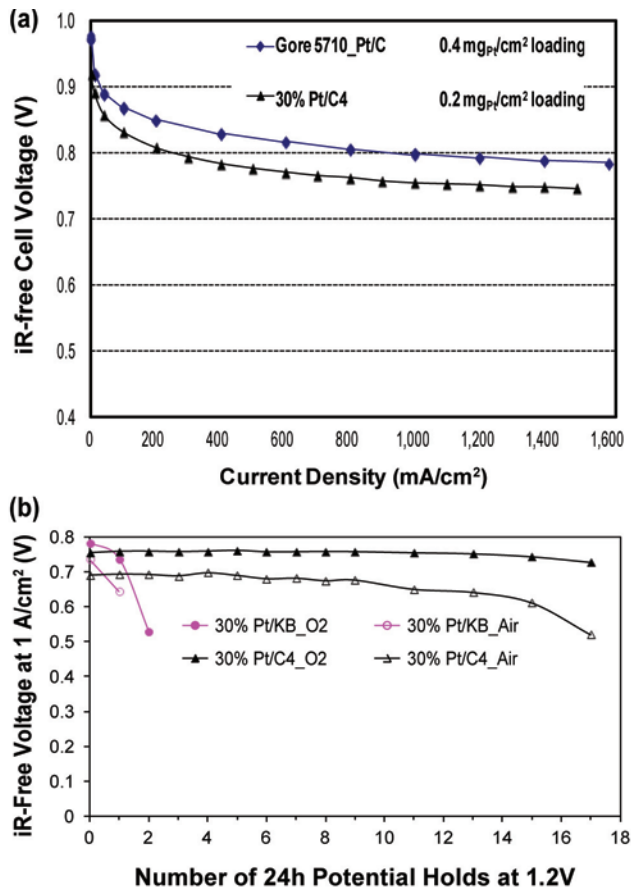


FIGURE 4. (a) iR corrected fuel cell performance curves at beginning of life for a 30% Pt/C4 compared to a standard 0.4 mgPt/cm² Gore 5710 Pt/C MEA obtained from WTP sub-scale fuel cell testing at 80°C, 100% RH under H₂/O₂ at zero backpressure and (b) performance loss at 1 A/cm² after 400 hours at 1.2 V potential hold in H₂/N₂ at 80°C, 100% RH under H₂/O₂ and H₂/air at zero backpressure.

a fuel cell. Figure 4a shows the iR-free performance curves at BOL for a 30% Pt/C4 compared to a standard 0.4 mgPt/cm² Gore 5710 Pt/C MEA obtained from 25 cm² WTP fuel cell testing at 80°C, 100% RH under H₂/O₂ at zero backpressure. Although the beginning of life performance for the 0.2 mg_{Pt}/cm² Pt/C4 low surface area carbon shows lower performance than that of a standard Gore Pt/C, its performance after the 1.2 V potential hold tests show considerable differences as shown in Figure 4b. The 30% Pt/C4 showed 59 mV loss after the fuel cell corrosion test of a total of 17 potential holds of 24 h each at 1.2 V at 80°C, 100% RH under H₂/O₂ at zero backpressure. All other carbons tested under this test protocol showed significant losses in performance after only 3-5 potential holds. Further, our preliminary sub-scale MEA testing of a 30% Pt₈IrCo₂/C4 under the 2008 DOE carbon corrosion protocol in a WTP cell at 80°C shows higher initial performance corresponding to 2x in MA compared to the Pt/C4. Figure 5 shows the performance curves for the 30% Pt₈IrCo₂/C4 and a 30% Pt/C4 in H₂/O₂ before and after 400 hours of potential hold at 1.2 V which shows that the PtIrCo/C4 is more stable than the Pt/C4 as it shows only ~12 mV loss at 1.5 A/cm² in O₂ after 1.2 V potential holds with negligible iR losses. Efforts to scale up and understand the stability of a 30% Pt₂IrCr alloy on C4 and mechanism for high current density performance loss is currently ongoing.

Conclusions and Future Directions

MAs of ~0.15 A/mg_{PGM} in sub-scale MEA testing have been reproduced and verified for a scaled-up 30% Pt₂IrCr and has been down-selected as the dispersed alloy catalyst system for full-scale fuel cell demonstration. The Pt₂IrCr alloy was chosen, over the PtIrCo alloy, based on the higher durability of Cr over Co in the alloy catalysts under the MEA fabrication process. Key barriers to overcome for the incorporation of the 30% Pt₂IrCr in an MEA are the low catalyst utilization in an MEA and the cathode catalyst layer optimization for high current density performance in a WTP fuel cell and are currently the main focus under this project. A key challenge for the core-shell catalysts is their poor durability in an MEA under operating fuel cell conditions and is an ongoing investigation in the project. All modeling activities under this project are complete and have clearly shown the benefit of Ir and the stability it imparts to the surface Pt atoms in the ternary PtIrM alloys. Also, our computational calculations played a significant role in identifying core materials and shell thickness and in understanding the activity and stability benefits of core-shell catalysts. A carbon support C4 with significant resistance to corrosion (<30 mV loss at 1.5 A/cm², 80°C in H₂/O₂) has been down-selected for further scale up of a 30% Pt₂IrCr alloy catalyst, MEA optimization and durability evaluation in a sub-scale fuel cell.

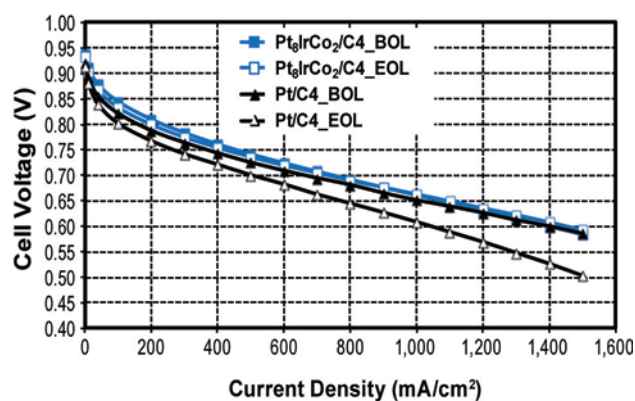


FIGURE 5. Fuel cell performance curves at 65°C in a WTP cell at 100% RH and 100 kPa backpressure for a 30% Pt₈IrCo₂/C₄ and a 30% Pt/C₄ in H₂/O₂ before and after 400 hours of potential hold at 1.2 V.

Future Directions

Our future objective is to demonstrate the durability of a highly active Pt₂IrCr alloy catalyst in an MEA with a durable carbon support capable of withstanding high voltage spikes relevant for automotive applications. Some of the tasks undertaken to achieve these goals are listed below.

- Optimization of dispersed alloy catalyst systems in MEAs is in progress aiming to approach high mass activity and more importantly high current density performance in an operating fuel cell. This is being resolved by investigating:
 - MEA fabrication process to understand the gap between MEA and RDE data.
 - Electrode structure optimization for water-transport-plate cells.
- The fundamental benefit of PtIrM ternary alloys on C₄ for activity and durability compared to Pt/C₄ is being further investigated based on their particle size, particles dispersion and electronic properties.
- In the case of the core-shell catalysts, preventing dissolution of the core material from the bulk phase of nanoparticles is a major challenge that is being addressed by the development of various scalable methods specifically geared towards achieving uniform Pt coating.

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