

V.C.3 Highly Dispersed Alloy Cathode Catalyst for Durability

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- Johnson-Matthey Fuel Cells, Sonning Commons, UK
- Texas A&M University, College Station, TX
- Brookhaven National Laboratory, Upton, NY

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Project End Date: April 25, 2010

Objectives

- Optimize catalyst performance and decay parameters through quantitative models.
- Design a high-performance supported alloy catalyst system with loading ≤ 0.3 platinum group metal (PGM)/cm².
- Demonstrate 5,000 cyclic hours below 80°C with less than 40% loss of electrochemical surface area.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure 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 progress on this project towards meeting them.

Characteristic	This project achievement as of 6/1/2008	DOE 2010 Target	Units
PGM Total Content	TBD	0.3	g/kW rated
PGM Total Loading	TBD	0.3	mg PGM/cm ²
Durability with cycling <80°C; >80°C	TBD	5,000; 2,000	h; h
Electrochemical Area Loss	TBD	<40	%, Percent
Mass Activity at 900 mV _{RHE} (IR-Free)	0.28 (Pt ₂ IrCo) 1.01 (Pt ML on Pd ₃ Co)	0.44	A/mg Pt
Specific Activity at 900 mV _{RHE} (IR-Free)	519 (Pt ₂ IrCo) 417 (Pt ML on Pd ₃ Co)	720	μA/cm ²
Cost	TBD	5	\$/kW

PGM - Platinum group metal
TBD - to be determined

Summary of Progress

- Modeling of the segregation behavior of dispersed binary alloys shows that most transition metals will segregate to the surface in the presence of less than a monolayer (ML) of O on the surface.
- Chemical potential calculations of the Pt dissolution reaction show that a Pt ML on Pd₃Co and Pd cores exhibit improved cyclic durability. These calculations are guiding the selection of core materials for core-shell catalysts.
- Dispersed catalysts with different Pt mass fractions in the Pt₂IrCo alloy system were synthesized and characterized. The 30 wt% Pt catalyst was found to be the optimum within the range explored. The PtIrCo system is being further investigated with respect to variables such as composition, type of carbon support, etc.
- Pt ML catalysts on Pd₃Co and Ir cores were synthesized and characterized for mass activity. When normalized to Pt content, the two catalyst systems exhibited mass activities of 1.01 and 0.57 A/mg, respectively. These values exceed the DOE 2010 target of 0.44 A/mg.

- The scale-up of the Pt ML catalysts is challenging and is currently being investigated on the project.



Introduction

On this project, we are working toward achieving the 2010 DOE Catalyst Technical Targets by focusing on two distinct systems. The first is a conventional dispersed Pt alloy system on a carbon support. The second system is the Pt ML approach on novel cores (core-shell approach). Under in this concept, we are working to optimize the thickness of the ML, core material selection and the particle size of the cores.

Approach

Details of the approach and the role of the partners are described in Figure 1. 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). BNL's role on the project is to synthesize a Pt ML on various cores and to test for stability and performance. BNL will also probe, using advanced X-ray techniques, the correlation between electronic properties, crystal structure and particle size on activity and durability. Dr. Perla Balbuena's group at TAMU will use computational atomistic modeling methods to study parameters that influence the activity and durability of core shell and dispersed catalyst systems. For example, TAMU's modeling studies will focus on quantifying metal catalyst stability against dissolution as a function of nanoparticle size, overall composition, exposed surface structure, etc. The overall scope of JMFC activities in the project will encompass development of novel dispersed Pt alloy catalysts,

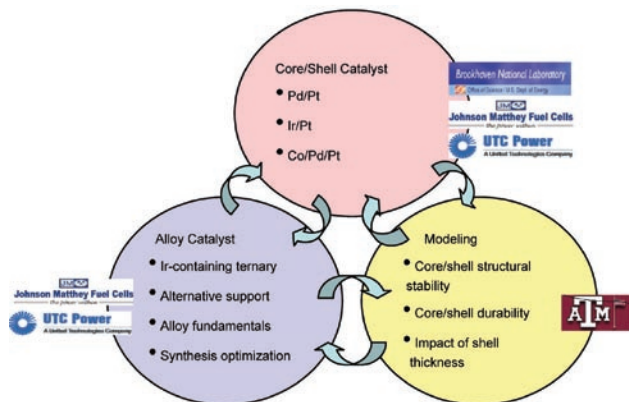


FIGURE 1. The UTC Power Catalyst Project Approach and Partners (The arrows represent the relationship between the different tasks and partners.)

scale-up of Pt ML core-shell catalysts and membrane electrode assembly (MEA) fabrication. In addition to Program Management, UTC Power will focus on the development of advanced dispersed Pt-based binary and ternary catalysts. UTC Power will also fabricate and test a 20-cell short stack for verification of performance and stability of catalyst that meets DOE's 2010 targets.

Results

Molecular Modeling

There were two topics studied this year. The first dealt with quantifying segregation energies to study the stability of dispersed Pt alloys. For various binary Pt alloys, the Vienna Ab-Initio Simulation Package (VASP) was used to calculate the thermodynamic favorability for Pt to remain on the surface of the alloy. The simulations were carried out under assumed conditions of vacuum and in the presence of a ML of oxygen on the surface. In vacuum, it was observed that Pt remained on the surface for most transition metals [1]. In contrast, with as little as a quarter ML of oxygen on the surface, the transition metal segregated to the surface in most cases. These data are shown in Table 2 which contains segregation energies in eV for the vacuum and O ML case for four different alloys. Note that negative segregation energy signifies stable Pt on the surface. From Table 2, it is seen that only in the presence of a non-transition metal like Ir, Pt exhibits stability against segregating to the interior of the particle. Even in the case of Ir, the relatively low energies signify a borderline stability.

TABLE 2. Segregation Energies in Vacuum and in the Presence of 0.25 ML of O on the Surface

	Pt ₃ Ir(111)	Pt ₃ Co(111)	Pt ₃ Fe(111)	Pt ₃ Ni(111)
Under 0.25 ML of O	-0.04	0.14	0.45	0.2
Vacuum	-0.54	-0.61	-0.41	-0.38

The modeling results with Ni, Co and Fe agree with published low energy electron diffraction data measured [2,3].

For core-shell structures, VASP was used to study the chemical potentials for the Pt dissolution reaction. This data is presented in Figure 2.

The delta potential presented in Figure 2 represents the difference in the equilibrium potential for Pt dissolution between the core shell structure and pure Pt. A negative potential difference indicates reduced stability with respect to the baseline pure Pt. As seen from the Figure 2, a Pt ML on Pd₃Co and Pd show improved stability with and without oxygen adsorption. These calculations are informing our core shell synthesis

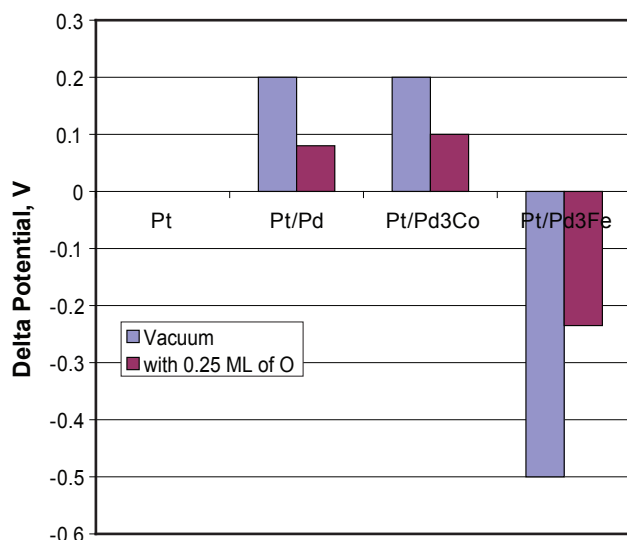


FIGURE 2. Difference in Equilibrium Potential for Pt Dissolution on bare Pt and different Core-Shell Pt ML Catalysts (A negative delta potential signifies a less stable catalyst compared to pure Pt.)

and characterization work. Results on the activity will be presented in a later section. Durability data for the core shell catalysts is available elsewhere [1].

Dispersed Pt Alloy Catalyst

The activity and durability of the dispersed alloy catalyst depends on many factors including composition of alloy, particle size, particle dispersion uniformity, type of carbon used, etc. In a previous project, UTCP showed that the durability of PtIrCo ternary alloys was “best in class” [4]. To further improve the mass activity of this ternary alloy, the impact of Pt mass fraction on electrochemical activity was investigated. Various samples of Pt₂IrCo with mass fraction of Pt between 20 to 40 percent were investigated using the rotating disk electrode (RDE) method. Physical characterization data including X-Ray diffraction and transmission electron microscopy thus far have shown that lowering the Pt mass fraction lead to smaller particles and less agglomeration. Electrochemical RDE testing has yielded higher electrochemical surface area (ECA) and higher mass activity. An optimum loading of 30 wt% of Pt in Pt₂IrCo exhibited an activity almost two times higher than 20 and 40 weight percent samples (0.28 A/mg_{Pt} compared to 0.15 A/mg_{Pt}). These data are shown in Figure 3. The 30 weight percent catalyst is currently being used to fabricate MEAs to quantify performance and durability in a subscale cell. The synthesis method and the impact of the composition of Pt, Ir and Co and other transitional metals instead of Co are currently being investigated to further improve mass activity.

To further improve the durability of the Pt alloys being synthesized on this project, deposition of Au

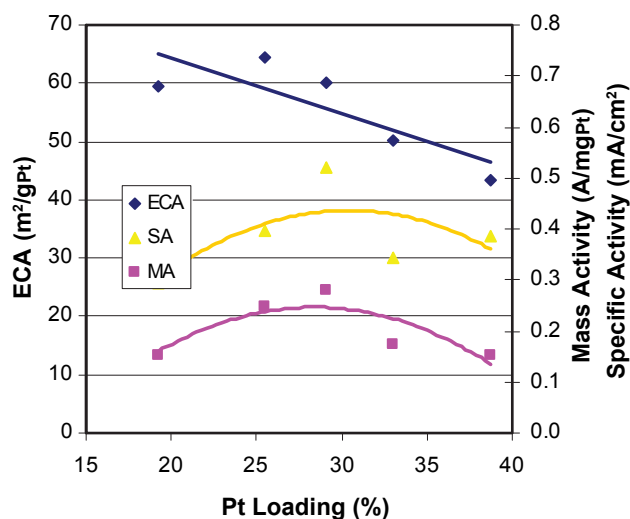


FIGURE 3. ECA, Mass Activity and Specific Activity Dependence as a Function of Pt Mass Fraction for Pt₂IrCo Cathode Catalyst (The support for all the samples was Ketjen Black.)

clusters is being investigated. Sasaki et al. showed using X-ray absorption spectroscopy that the Au clusters improve cycling stability by raising the potential for oxide formation on the surface of the Pt [5]. As a potential method to improve the durability of alloys being synthesized on this project, the effect of the deposition of Au on carbon supported large Pt particles was studied. JMFC synthesized 8 nm diameter Pt particles on Ketjen Black which were subsequently treated with 0.6 ML of Au by BNL. The Pt catalyst with and without Au were tested for electrochemical activity and durability by potential cycling in an RDE experiment. In the cycling experiment, the potential varied from 0.95-0.7 V in a square wave format with 30 second holds at each of the voltages. For both the electrodes, with and without Au deposited, the electrochemical surface area and the catalyst activity decreased with increasing cycle number. However, the loss of catalytic activity was suppressed in the Au deposited electrode. The activity of the catalyst decreased by approximately 20 mV in 30,000 cycles and 37 mV in 10,000 cycles for the cases with and without Au deposition, respectively.

Core-Shell Pt Catalysts

Zhang et al. showed the feasibility of Pt ML deposition on mixed PGM and transition metal cores to reduce the usage of Pt for the oxidation reduction reaction [6]. Modeling the impact of different cores and Pt ML shells is being carried out under this project at TAMU. This work is also being complemented with synthesis of core-shell structures. Pt ML on Ir and Pd₃Co cores were synthesized and evaluated for durability and electrochemical activity using the RDE technique. Ir cores were synthesized at UTCP and sent

to BNL for Pt ML deposition. The existing oxides on the Ir cores were first reduced by annealing at 500°C in a H₂ environment prior to the Pt deposition. The carbon-supported Ir and Pd₃Co cores were mixed with a Nafion® solution and deposited onto an RDE electrode as a film. Onto this film, a Pt ML was deposited by displacing Cu that was pre-deposited via the Cu under potential deposition method.

The mass activity data measured using the RDE technique for the two cores mentioned above are shown in Figure 4. The mass activity is presented normalized to the Pt and on the electrodes. The mass activity of the Pt baseline (TEC10E50E-HT, 50% TKK catalyst) is approximately 0.18 A/mg.

When only the mass of Pt is considered, the ML approach easily exceeds the DOE 2010 target of 0.44 A/mg (1.01 and 0.57 A/mg for the Pd₃Co and Ir cases, respectively, as shown in Figure 4). More cores have been synthesized including Ir, Ir_xCo_y, Co, Pd₃Co and Pd₃Fe. After the deposition of 1 or 2 ML of Pt, the catalysts will be evaluated for durability and activity.

A key challenge for the ML Pt catalysts is the scale-up beyond the use on an RDE. JMFC, BNL and UTCP are investigating various scale-up methods for the deposition of the Pt ML. Thus far methods looked at result in a decrease in the mass activity. An investigation into the loss in activity with scale-up is ongoing.

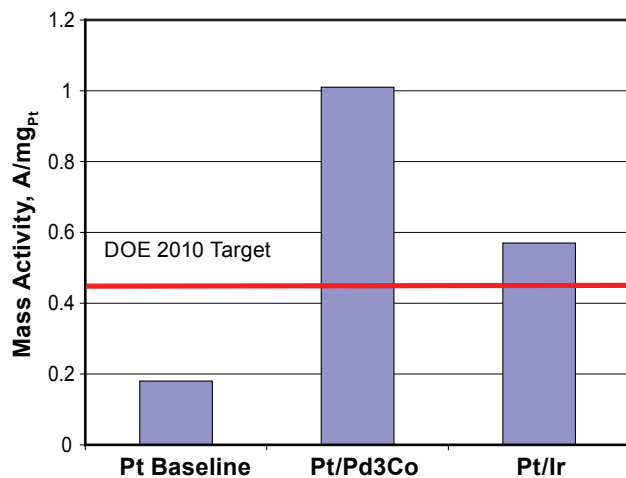


FIGURE 4. Mass Activities of 1 Pt ML on Pd₃Co and Ir Cores

Conclusions

The dispersed catalyst and Pt ML catalyst syntheses have been established at UTCP, JMFC and BNL and many samples have been synthesized and characterized. The atomistic modeling work is guiding the synthesis project by providing fundamental activity and durability controlling information. Preliminary samples synthesized on the project exceed the DOE 2010 targets for mass activity when normalized to mass of Pt.

Future Work

The dispersed and core-shell catalyst systems studied thus far will be further improved and the most promising catalyst systems capable of meeting the DOE targets will be selected in 2008. These catalysts will then be scaled-up by JMFC and UTC Power to produce adequate quantities for MEA fabrication. The scaled catalyst systems will be used to investigate optimal MEA characteristics for performance and durability in single cell testing. Performance and durability data will be used to select the MEA configuration for the short stack to be fabricated at the end of this project.

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