

# V.F.20 Semi-Automated MEA Fabrication with Ultra-Low Total PGM Loadings

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- Demonstrate the potential of the proposed advanced strategy for preparation of gas diffusion electrodes (GDEs) and fabrication of large MEAs with performance that meet and/or exceed the DOE targets for activity and durability

## Technical Barriers

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

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

## Technical Targets

At BNL we have designed and developed a semiautomated system for electrodeposition of advanced Pt<sub>ML</sub>/Pd/WNi electrocatalysts with ultra-low PGM loading directly on GDLs. This innovative strategy allows fast and facile preparation of GDEs starting from raw materials (chemicals and GDL) and fabrication of MEAs in less than an hour. The project's technical targets are compared to the DOE 2020 targets in Table 1. The total PGM loading currently attained in 5 cm<sup>2</sup>, 25 cm<sup>2</sup>, and 50 cm<sup>2</sup> MEAs is 0.120 mg<sub>PGM</sub>/cm<sup>2</sup> with a projection of achieving less than 0.1 mg<sub>PGM</sub>/cm<sup>2</sup> by the end of the project. The mass activity target of 0.44 A/mg is achieved on 5 cm<sup>2</sup> MEAs and is approached closely on 50 cm<sup>2</sup> MEAs. Excellent durability performance after 34,000 accelerated stress test (AST) voltage cycles is observed in the MEAs. The loss in the mass activity is 20%, and the voltage loss at 0.8 A/cm<sup>2</sup> is only 19 mV.

**TABLE 1.** Progress towards Meeting the Technical Targets for Electrocatalysts for Transportation Applications

Characteristic	Units	DOE 2020 Targets	BNL 2015 Status	Project's Targets
PGM total loading (both electrodes)	mg/cm <sup>2</sup>	<0.125	0.120	<0.1
Loss in catalytic (mass) activity after 30,000 AST voltage cycles	% loss	<40	20	<30
Loss in performance at 0.8 A/cm <sup>2</sup>	mV	30	19	<25
Mass activity @ 900 mV <sub>IR-free</sub>	A/mg	0.44	0.46; 0.41*	>0.44

\*Measured on 50 cm<sup>2</sup> MEA

## Overall Objectives

- Design, develop, and demonstrate an innovative methodology for fast and facile electrodeposition of Pt monolayer (ML) shell on non-noble refractory metal core electrocatalysts for the oxygen reduction reaction, directly on gas diffusion layers (GDLs)
- Demonstrate the feasibility of developed electrodeposition strategy for scaling up and fabrication of electrodes and membrane electrode assemblies (MEAs) with ultra-low platinum group metal (PGM) loadings and performance that meet or exceed the DOE 2020 technical targets

## Fiscal Year (FY) 2015 Objectives

- Develop a semi-automated system for nanoengineering of Pt ML on Pd interlayer on refractory metal alloy (WNi) core catalysts directly on GDLs
- Optimize the composition, structure, and morphology of electrodeposited refractory metal alloy cores and the protocols for deposition of Pt ML shell for fast fabrication of highly active and durable cathodes for cost effective MEAs
- Explore the impact of the structure, morphology, and hydrophobicity of the GDLs from different commercial suppliers on the deposition of the catalysts layer, and optimize the pretreatment protocols to maximize the MEA performance

## FY 2015 Accomplishments

The accomplishments for the nine-month period since the beginning of the project are as follows.

- Designed and developed a semiautomated software controlled system for facile fabrication of large GDEs and MEAs with ultra-low total PGM loading, complete Pt utilization, and improved activity and performance stability
- Nanoengineered complex Pt ML shell on Pd interlayer on refractory metal alloy (W<sub>Ni</sub>) core electrocatalysts directly on the GDLs in a single electrochemical cell that allows reproducible fabrication of GDEs with geometrical size of up to 300 cm<sup>2</sup>
- Optimized electrochemical protocols and electrolyte compositions for in situ precise control of the catalyst layer structure, thickness, morphology, and composition for improved MEA performance
- The impact of the structure and the surface modification procedure of the GDLs from different suppliers on the catalyst layer structure and utilization was studied, and the best GDL was identified
- Optimized conditions for fabrication of MEAs with geometric areas of up to 50 cm<sup>2</sup>, and demonstrated potential for meeting the DOE 2020 targets for activity and durability with ultra-low total PGM loadings



## INTRODUCTION

It has recently been reported [1] that the Pt<sub>ML</sub> core-shell electrocatalysts (Pt<sub>ML</sub>Pd/C and Pt<sub>ML</sub>Pd<sub>0.9</sub>Au<sub>0.1</sub>/C) are among the most promising candidates that possess a potential to meet the DOE 2020 targets. However, reduction of the PGM loading in the cores, development of scaling up methods for reproducible synthesis, and improving the catalysts' durability are important unresolved challenges that will further reduce the catalysts' cost and improve their performance and durability.

In order to address these challenges, we have developed a semiautomated system for electrodeposition of Pt<sub>ML</sub> shell on electrodeposited PdW<sub>Ni</sub> nanoparticles core directly on the GDL. In this approach we substitute most of Pd in the core by refractory metal alloy (W<sub>Ni</sub>) and limit the thickness of the Pd interlayer to two to three MLs. This results in reducing the PGM loading and improving the stability of the core. The proposed innovative strategy is not only an alternative to the existing methodology for synthesis of Pt ML core-shell catalysts, but outlines a novel pathway for fast preparation of GDEs, and hence facile fabrication of MEAs with geometric size of industrial significance. As-prepared electrodes are

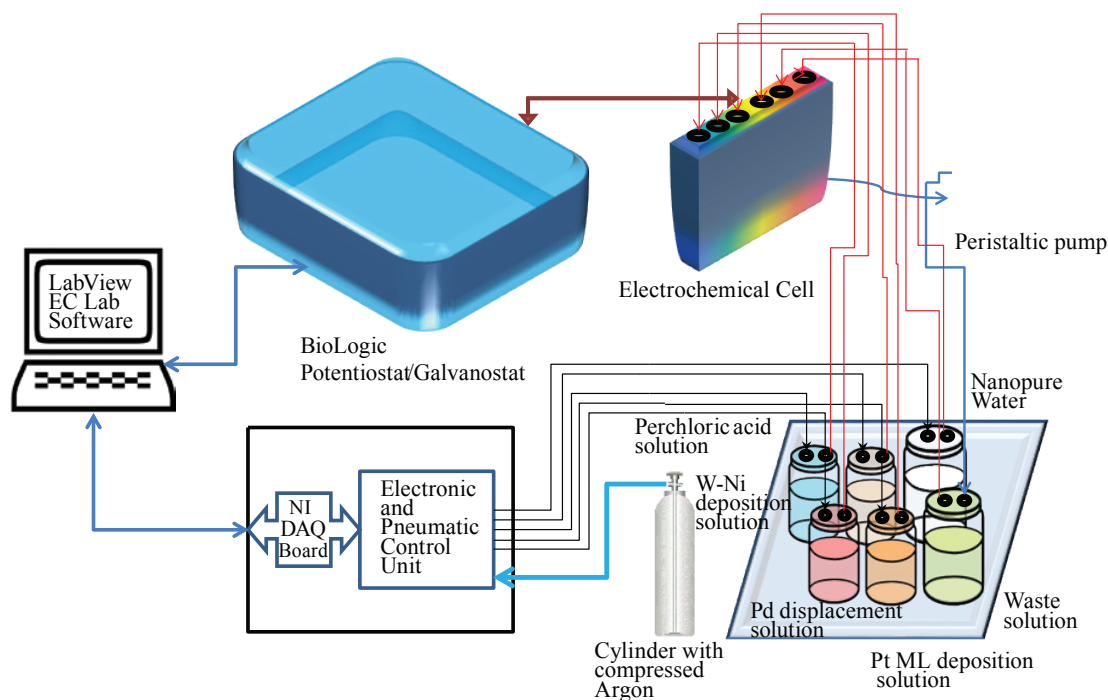
with ultra-low PGM loading and complete Pt utilization. The strategy allows in situ precise control of the structure, composition, thickness, and morphology of the catalyst layer directly on the GDL for fine tuning of the electrode's performance, which is advantageous over the conventional ink spraying methodology.

## APPROACH

BNL's unique approach allows facile fabrication of large fuel cell electrodes with ultra-low PGM loadings, starting from raw materials, in less than an hour. The strategy employs two phenomena: (i) induced co-electrodeposition of refractory W<sub>Ni</sub> alloys and (ii) displacement of under-potential deposited (UPD) Cu monolayer by Pt. The as-developed semiautomated system assures software controlled exchange of the solution in the electrochemical cell, where the deposition and displacement processes are taking place under controlled conditions. The catalysts' synthesis is realized in three sequential steps. First, W<sub>Ni</sub> refractory alloy nanoparticles are co-electrodeposited from citrate solution of both metals of interest, and then after exchanging the solution in the cell with Pd<sup>2+</sup> containing electrolyte, Pd partially displaces the Ni and forms a Pd interlayer over the W<sub>Ni</sub> core. The displacement step is monitored in situ by measuring the open circuit potential, and the amount of the Pd is controlled precisely. In the last step, the solution is exchanged with an electrolyte containing both Pt<sup>2+</sup> and Cu<sup>2+</sup> ions, in which the Cu<sup>2+</sup> concentration is two orders of magnitude higher than that of Pt<sup>2+</sup>. Pt<sub>ML</sub> is deposited on top of the Pd interlayer by applying a short pulse in the Cu UPD range to form a Cu ML on Pd. Then after releasing the potential control, the more noble Pt ions displace the Cu atoms. After rinsing the cell with plenty of nanopure water, the electrode is dried and an appropriate amount of liquid Nafion<sup>®</sup> (5%) ionomer is sprayed over the catalyst layer. The electrode is then dried again. Finally, the electrode is assembled with a Nafion<sup>®</sup> membrane and an anode, prepared by spraying of commercial Pt catalyst ink onto a GDL, by hot pressing together at 130°C for 1 min. The as-prepared MEA is mounted in a single cell hardware, activated, and its performance is evaluated at real fuel cell operating conditions.

## RESULTS

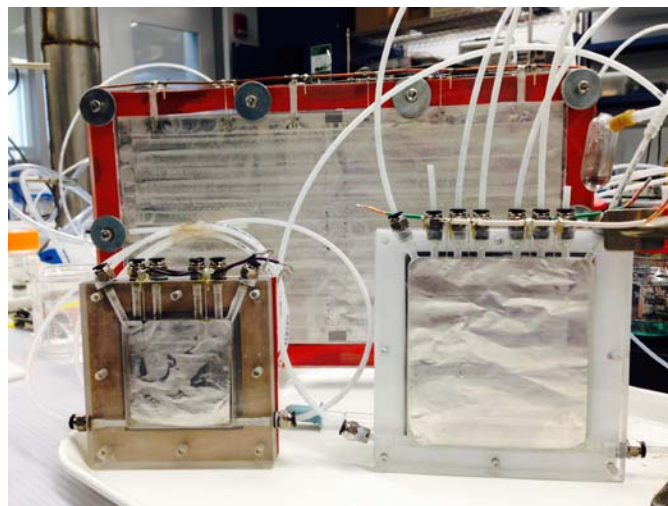
In the first quarter of the project we designed and developed a semiautomated system for electrodeposition of Pt ML core-shell fuel cell electrocatalysts with ultra-low PGM loading (<0.07 mg<sub>PGM</sub>/cm<sup>2</sup>) and complete Pt utilization, directly on GDLs. The system is software controlled and allows fabrication of highly active and durable fuel cell cathodes starting from raw materials (chemical salts and commercial GDLs). A schematic of the system is shown in Figure 1. The system consists of (i) an electrochemical cell that allows fabrication of electrodes with size of up



**FIGURE 1.** Schematic of the semiautomated system for electrodeposition of core-shell ( $Pt_{ML}/Pd/WNi$ ) fuel cell electrocatalysts, directly on GDL

to  $300\text{ cm}^2$ ; (ii) a pneumatic control unit with respective electronics that controls the flow of different electrolyte solutions from the deaerated (purged with Ar) stock solutions (WNi plating solution, Pd displacement solution, Pt ML deposition solution, perchloric acid solution, and water) to the cell in a particular order; (iii) an electronic data acquisition board from National Instruments that allows the LabVIEW software to control all the processes step by step; and (iv) a BioLogic potentiostat galvanostat that controls the WNi electrodeposition, Pd displacement, and Cu UPD and Pt ML deposition processes.

Figure 2 presents a picture of the electrochemical cells that have been developed for fabrication of electrodes with geometric area of up to  $300\text{ cm}^2$ . We have developed the capabilities to fabricate large electrodes, but, unfortunately, our current fuel cell test station allows us to evaluate the performance of MEAs with a maximum geometric area of  $50\text{ cm}^2$ . Larger electrodes and MEAs will be fabricated and tested upon availability of additional funding for purchasing a 2 kW fuel cell test station. The uniform and homogeneous deposition of the catalysts of interest over the entire electrode surface area is defined by the distribution of the electric field in the cell, and as well as from the hydrodynamic flow of the electrolyte in the cell. Both factors strongly depend on the geometry and the volume of the cell, which were optimized. Homogeneous distribution of the electrocatalyst over the electrode area was confirmed for up to  $50\text{ cm}^2$  electrodes. The reproducibility of the catalyst deposition is governed by the repeatability of each step in the multi-step sequence that



**FIGURE 2.** Picture of the electrochemical cells designed for fabrication of GDEs with geometric areas of up to  $300\text{ cm}^2$

is programmed in the software controlling the potentiostat. Thus, the software assures exact repeating of each step, and that the reproducibility in the composition, structure, and morphology for the fabricated electrodes exceeds 98%.

The optimization of the electrodeposition protocols, as well as the catalyst layer structure, composition, morphology, and thickness, was first performed on  $5\text{ cm}^2$  electrodes and MEAs, respectively; then,  $50\text{ cm}^2$  MEAs



were fabricated and their performance was evaluated. In addition, GDLs from different commercial suppliers were examined, and Sigracet® 25BC was identified as the best support for the electrodeposited Pt<sub>ML</sub>/Pd/WNi catalyst layer. The polarization curves measured on 5 cm<sup>2</sup> MEA in H<sub>2</sub>/O<sub>2</sub> atmosphere, 80°C and 150 kPa backpressure after different numbers of AST voltage cycles, are presented in Figure 3. The initial mass activity is 0.46 A/mg<sub>PGM</sub>, and only 20% loss is observed after 34,000 AST voltage cycles. The voltage loss at 0.8 A/cm<sup>2</sup> is only 19 mV after 34,000 cycles. The polarization curves measured on 50 cm<sup>2</sup> MEAs, at the same conditions, but at two different backpressures, are presented in Figure 4. The mass activity at 900 mV (iR-free) is 0.41 A/mg<sub>PGM</sub>, which is very close to the targeted value of 0.44 A/mg<sub>PGM</sub>. The results obtained render a developed strategy for direct electrodeposition of Pt ML shell on PdWNi core electrocatalysts on the GDL as a viable methodology for fast and facile fabrication of MEAs that possess the potential to meet and even to exceed the DOE 2020 targets for cost, durability, and performance.

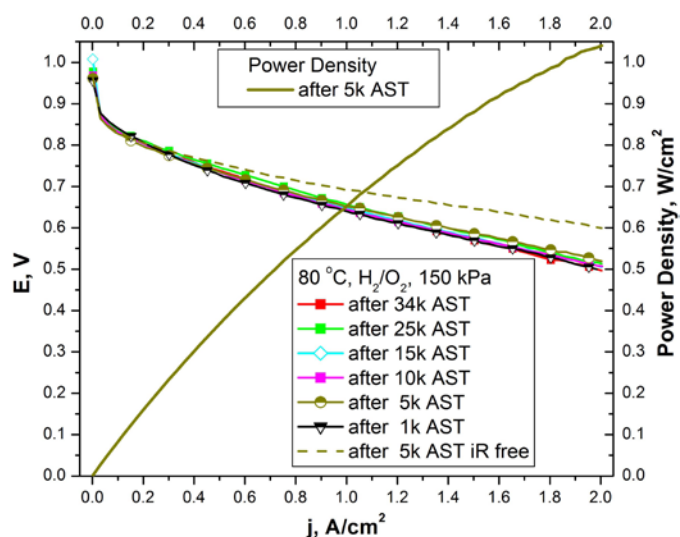
## CONCLUSIONS AND FUTURE DIRECTIONS

Conclusions derived from the work in FY 2015 include the following.

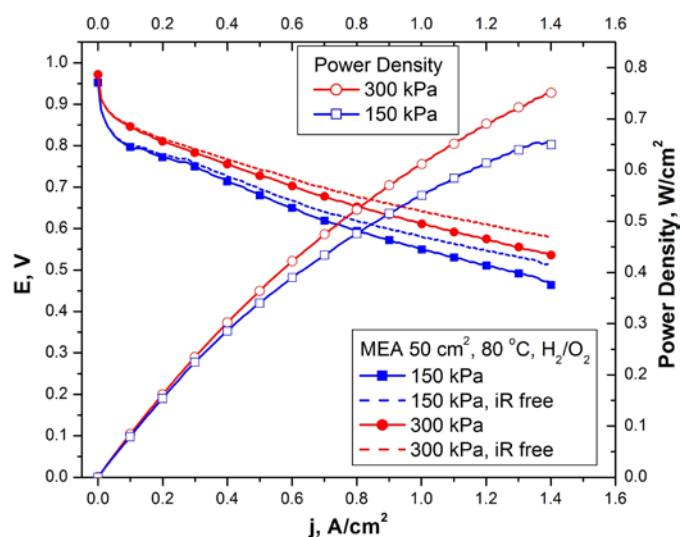
- A semiautomated system for fabrication of fuel cell electrodes and MEAs with ultra-low PGM loading has been developed.
- The proposed electrodeposition strategy allows fast and facile preparation of electrodes with a geometric area of up to 300 cm<sup>2</sup>.
- Different GDLs were tested, and Sigracet® 25BC GDL was identified as the best support for the Pt<sub>ML</sub>/Pd/WNi electrocatalysts.
- The performance of the MEAs, with geometric areas of 5 cm<sup>2</sup>, 25 cm<sup>2</sup>, and 50 cm<sup>2</sup>, was examined.
- The mass activity and durability performance of the MEAs of interest meet and in some cases exceed the DOE 2020 targets.

Future directions include the following.

- Explore different electrodeposition protocols to determine the impact of the size and shape of the refractory cores on the activity and durability of 300 cm<sup>2</sup> MEAs
- Reduce MEA fabrication time to less than 30 min by optimizing each step
- Develop a protocol for electrodeposition of anode catalysts with ultra-low Pt loading (less than 30 μg/cm<sup>2</sup>), and thus reduce the total PGM loadings to less than 0.1 mg<sub>PGM</sub>/cm<sup>2</sup> for both electrodes



**FIGURE 3.** Polarization curves measured on 5 cm<sup>2</sup> MEA in H<sub>2</sub>/O<sub>2</sub> at backpressure of 150 kPa. The PGM loading on the Pt<sub>ML</sub>/Pd/WNi/GDL cathode is 0.07 mg<sub>PGM</sub>/cm<sup>2</sup>, and the Pt loading on the anode is 0.05 mg<sub>Pt</sub>/cm<sup>2</sup> (TKK Pt catalysts). The MEA is assembled with a Nafion® HP membrane



**FIGURE 4.** Polarization curves measured on 50 cm<sup>2</sup> MEA in H<sub>2</sub>/O<sub>2</sub> at backpressures of 150 kPa and 300 kPa. The MEA is assembled with Pt<sub>ML</sub>/Pd/WNi/GDL cathode (0.09 mg<sub>PGM</sub>/cm<sup>2</sup>), standard Pt/C (TKK Pt catalyst, 0.05 mg<sub>Pt</sub>/cm<sup>2</sup>) anode, and Nafion® XL membrane

- Improve the MEA performance at high power densities and in H<sub>2</sub>/air atmosphere
- Conceptualize an automated/low cost roll-to-roll 100% Pt utilization MEA fabrication process in support of fuel cell manufacturing needs, and reduce the time for electrode and MEA fabrication to less than 15 min

## FY 2015 PUBLICATIONS/PRESENTATIONS

1. R. Adzic, S. Bliznakov, and M. Vukmirovic, US Patent: Core-Shell Fuel Cell Electrodes, **US2015/0017565 A1**, Jan. 15, 2015.
2. S. Bliznakov, M. Vukmirovic, R. Adzic, Electrochemical Atomic-level Controlled Synthesis of Electrocatalysts for the Oxygen Reduction Reaction, *Atomically-Precise Methods for Synthesis of Solid Catalysts*, S. Hermans and T. Visart de Bocarme, Editors, Chapter 6, p. 144, *The Royal Society of Chemistry*, RCS Catalysis Series No. **22**, (2015).

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1. K. Sasaki, H. Naohara, Y. Choi, Y. Cai, W.-F. Chen, P. Liu, and R.R. Adzic, “Highly Stable Pt Monolayer on PdAu Nanoparticle Electrocatalysts for the Oxygen Reduction Reaction,” *Nature Communications*, **3**, 1115 (2012).