Semi-automated MEA Fabrication with Ultra- Low Total PGM Loadings

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U.S. DEPARTMENT OF ENERGY | Office of Science

Project ID # FC126

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Overview

Timeline

- Project Start Date: 11/01/14
- Project End Date: 10/31/15*
- Percent complete: 50 %

* Project continuation and direction determined annually by DOE

Barriers

- **Performance:**

  Catalyst activity; ≥ 0.44 A/mg_{PGM}

- **Cost:**

  PGM loading; ≤ 0.125 mg_{PGM}/cm^2

- **Durability:**

  < 40% loss in activity under potential cycling

Budget

- FY15 Planned DOE Funding: $320 k
- Total DOE Funds Received to Date: $ 320 k

Partners

- **Chemistry Department at BNL**

  M. Vukmirovic, and R. Adzic

- **General Motors**

  A. Kongkanand

Relevance

Objectives

- Develop a semi-automated system for fast and facile electrodeposition of Pt monolayer (ML) shell on non-noble refractory metal core electrocatalysts with ultra-low PGM loadings and near 100% Pt utilization, directly on GDLs.
- Demonstrate the feasibility of proposed electrodeposition strategy for scaling-up and fabrication of MEAs with performance exceeding the DOE 2020 technical targets.

	Units	DOE 2020 Target	Projects' Target
Platinum group metal (PGM) total content (both electrodes)	g/kW	<0.125	**<0.1**
PGM total loading (both electrodes)	mg/cm^2	<0.125	**<0.1**
Loss in catalytic (mass) activity	% loss	<40	**<30**
Loss in performance at 0.8 A/cm^2	mV	30	**<25**
Loss in performance at 1.5 A/cm^2	mV	30	**<25**
Mass activity @ 900 $mV_{iR\text{-}free}$	A/mg_{PGM}	0.44	**>0.44**

- ✓ This project supports near-term commercialization through innovative market-relevant R&D that lowers the cost, raises the efficiency, and improves the durability of MEAs to greater than 30,000 voltage cycles with ultra-low PGM loadings and complete Pt utilization.

Approach: Electrodeposition of Pt ML catalyst directly on GDL

- Design and develop an automated system for electrodeposition of Pt ML shell on refractory metal core electrocatalysts, directly on GDLs. Achieve lower fabrication costs, higher catalyst activity, and better durability of the PEM fuel cell electrodes.

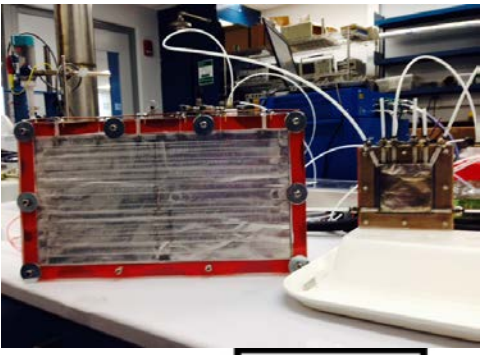
Technical approach	Uniqueness	Challenges to address
I. Electrodeposition of refractory metals or their alloys directly on GDLs – WNi/GDL.	Induced co-deposition of W with Iron group metals allows one to electrodeposit W!	**Reduce the cost** - less PGM loading **Improve the durability** - refractory metals in the core
II. Displacement of Ni with Pd and forming thin Pd shell - Pd/WNi.	Pd is the best support for Pt ML electrocatalysts!	**Increase the activity**
III. Deposition of Pt ML on the Pd surface by displacement of Cu ML pre-deposited at underpotentials – Pt_{ML}/Pd/WNi.	Precise control at sub-monolayer level for Pt deposition. Complete Pt utilization!	**Increase the activity** **Improve the durability** **Decrease the cost**

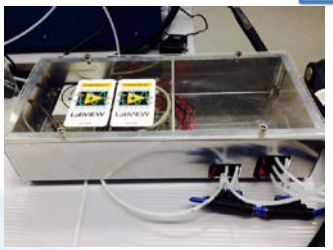
Approach: Milestones, Deliverables and Go/No-Go decisions

Qtr	Due date	Milestones, deliverables	Go/No-Go decisions	Accomplishment
Q1	01/31/15	Set up of semi-automated system for direct electro-deposition of Pt ML shells on Pd/WNi cores	Better than 98% Pt utilization in MEA tests	100 % Go/No-go decision met
Q2	04/30/15	Comparative testing of carbon cloths from three different suppliers for use as GDLs	Pt < 0.125 g/kW at rated power	80%
Q3	07/31/15	Measure cyclic losses from initial catalytic activity and scale up system for fabricating 300 cm^2 MEAs	Loss less than 40% after 30,000 voltage cycles	On schedule
Q4	10/31/15	Develop industrial partnerships and licensing agreements	Record of Invention	On schedule

Accomplishments and Progress

Semi-automated system for electrodeposition of Pt ML core-shell fuel cell electrocatalysts on GDL -*schematic*

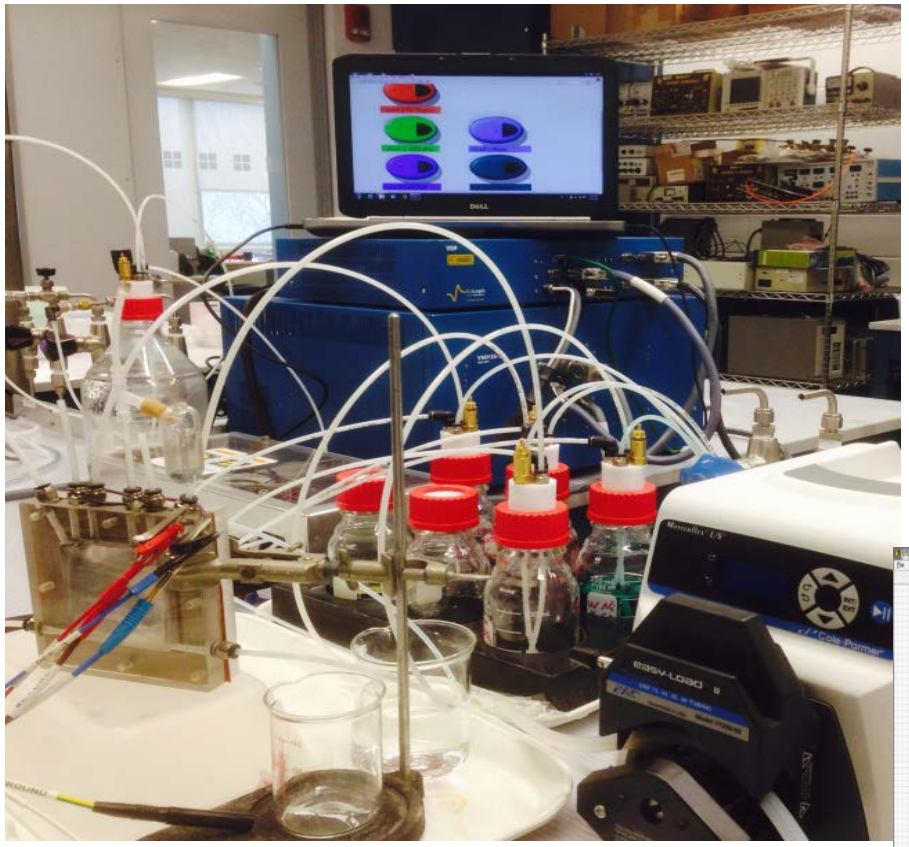


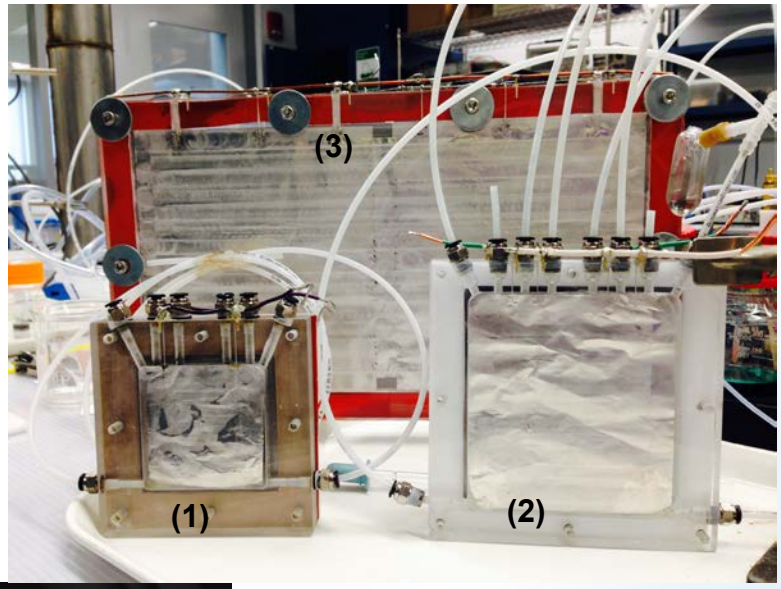


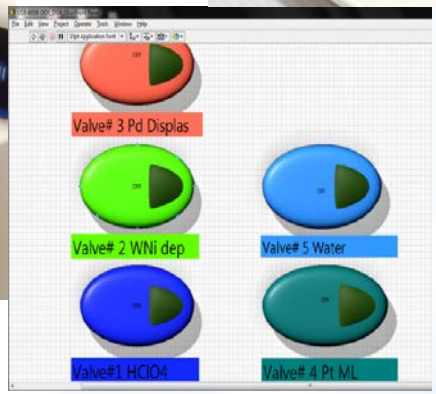
- ✓ The system executes a sequence of techniques (1.electrodeposition; 2. displacement; 3. UPD deposition of Cu ML and its displacement by Pt ML) and assures software controlled exchange of the respective electrolyte solutions into the cell!
- ✓ The strategy allows fast and facile fabrication of electrodes and MEAs – couple hours starting with chemicals and GDL

Accomplishments and Progress

Pictures of the semi-automated system







Electrochemical cells that allow to prepare electrodes with geometric areas of 5- 500 cm^2

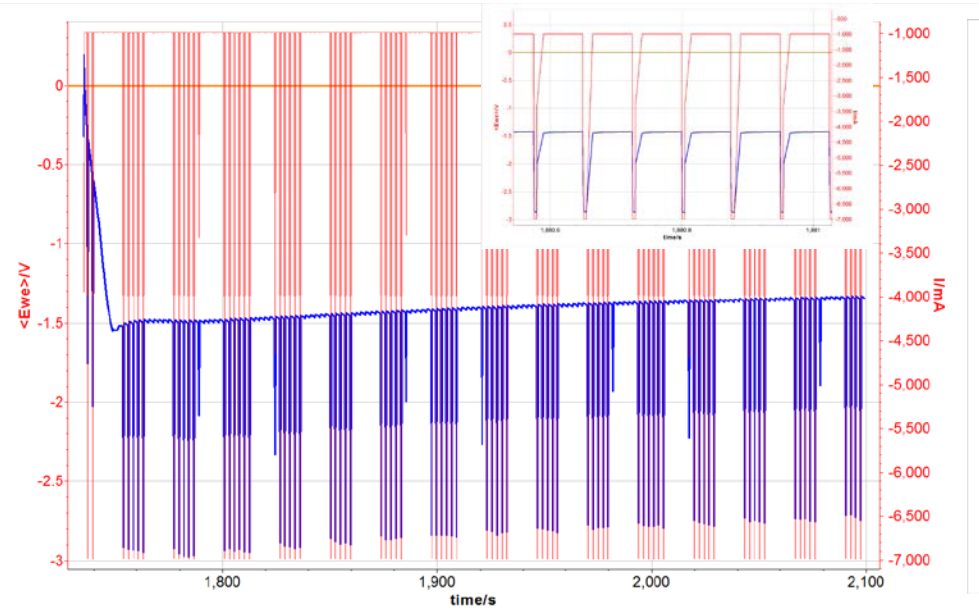
(1) 5- 25 cm^2
(2) 50- 100 cm^2
(3) 100 – 500 cm^2

Picture of the semi-automated system for electrodeposition of electrocatalysts with ultra-low total PGM loading, directly on the GDL.

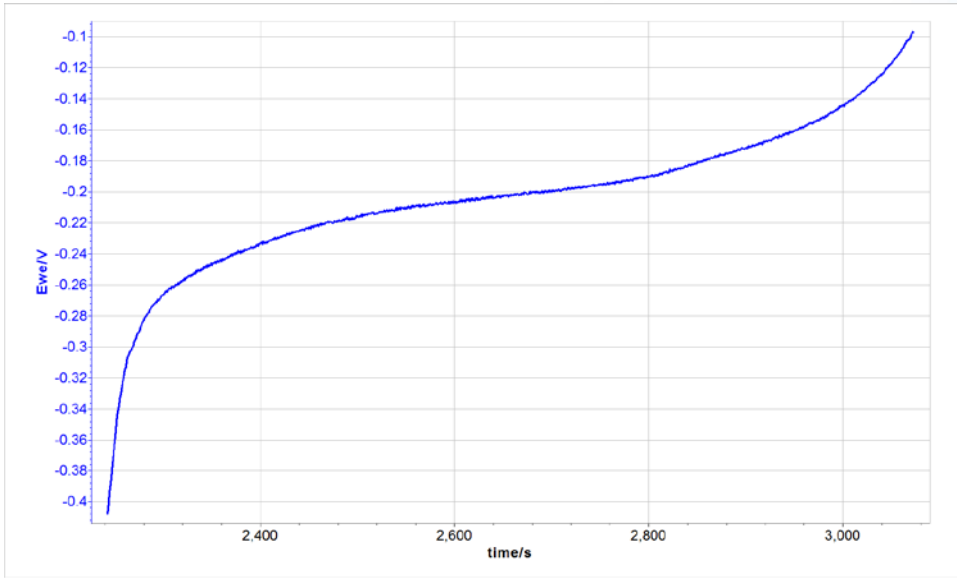
Front panel of the LabView software, that controls the exchange of the solutions into the electrochemical cell.

Sequential steps in the electrodes' fabrication

I. Induced pulse co-deposition of nanostructured WNi cores directly on 70 cm^2 GDL.



II. Galvanic displacement of part of Ni by Pd.



The electrodeposition protocol assures:

1). Precise quantitative control of the refractory alloys – **reduces the total PGM loading, and improves the durability of the catalysts;**

2). Fine tuning of the composition, shape and size of the nanostructures of interest – **maximizes the mass activity and stability of the catalysts;**

3). Homogeneous distribution of the catalysts exactly at the three-phase boundary – **maximizes the catalysts' accessibility, reduces the Ohmic and transport resistances, and improves the MEA performance.**

The displacement step accounts for:

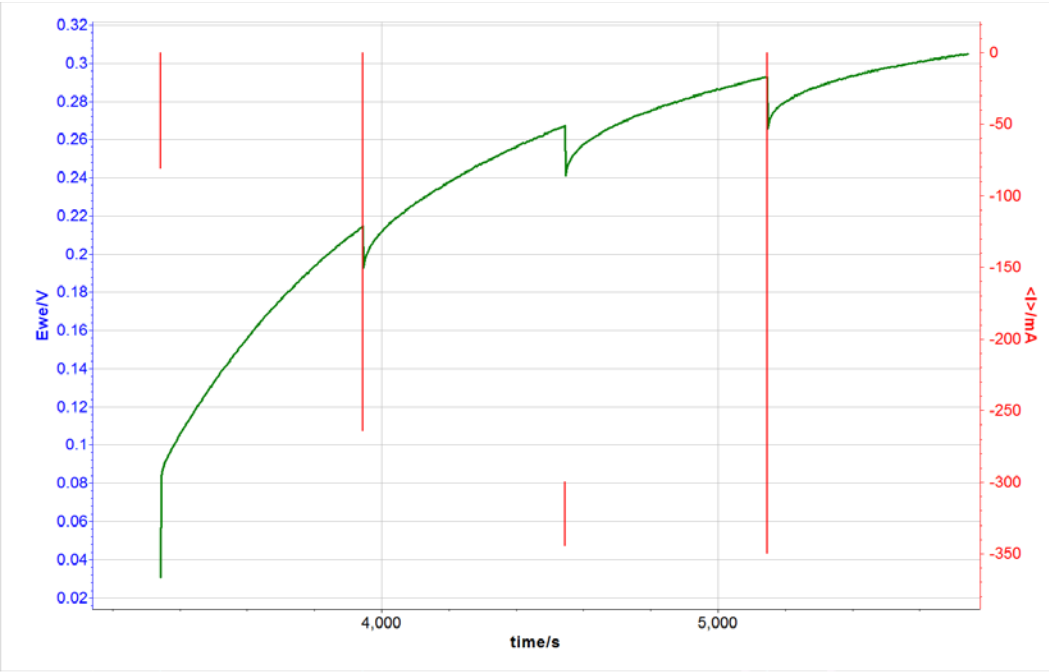
1). Formation of thin Pd shell (2-3 MLs) on the WNi core – **reduces the PGM loading;**

2). Pd is the best support for the Pt ML – **maximizes the catalysts' activity;**

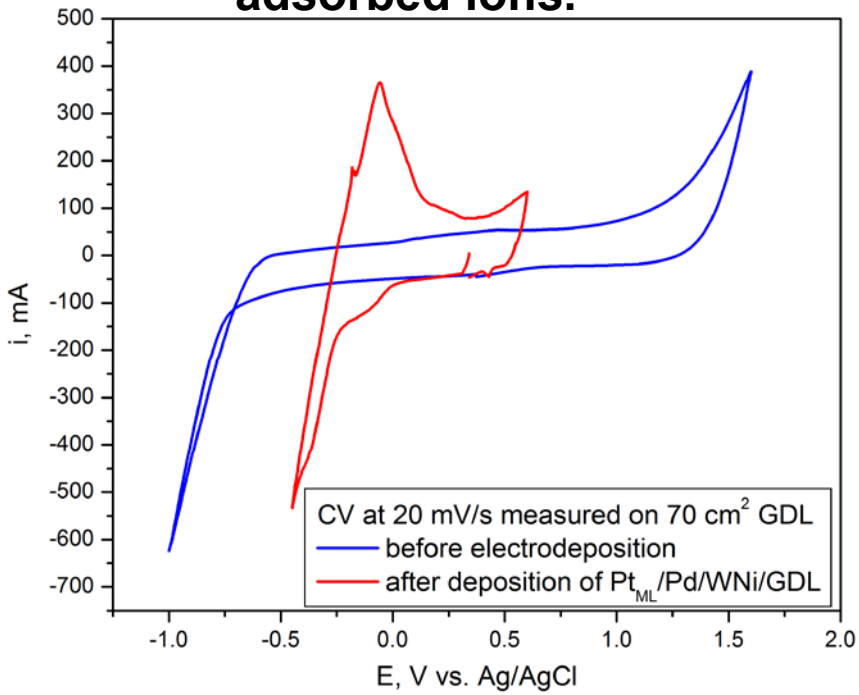
3). *In situ* control of the amount of Pd and the quality of the formed shell – **fine tuning of the electronic interaction between the core-shell structure that results in improving the catalysts' stability.**

Sequential steps in the electrodes' fabrication

III. Pt ML deposition on pre-deposited Pd/WNi nanostructures.



IV. Washing the electrode and cleaning its surface from adsorbed ions.



UPD deposition of Cu ML and its displacement by Pt in one-pot configuration:

1). Both ions (Cu^{2+} and Pt^{2+}) are present in the electrolyte, but the Pt concentration is 2 orders of magnitude lower than that of Cu.

2). Short pulses are applied to form a Cu UPD ML followed by OCP time, when the Cu ML is displaced by Pt ML.

3). The strategy allows for sub-monolayer control of deposited Pt. Increasing the number of pulses increases the Pt content – **precise control of the Pt loading, and 100 % Pt utilization.**

Rinsing with nano-pure water and running CVs in 0.1 M perchloric solution :

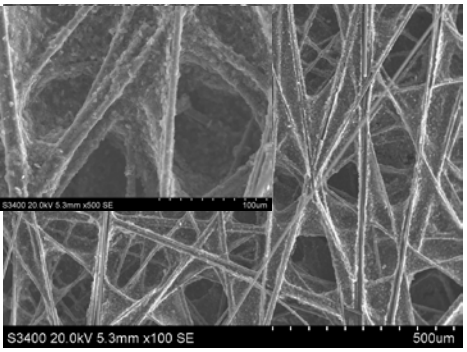
1). The electrode is rinsed 3 times.

2). The CVs at 20 mV/s before and after deposition of the catalyst are compared in the figure above.

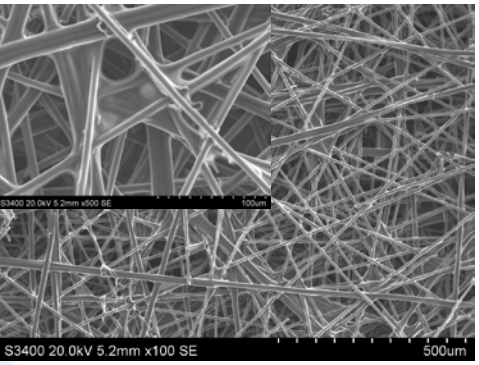
Accomplishments and Progress

Performance evaluation on three different GDLs

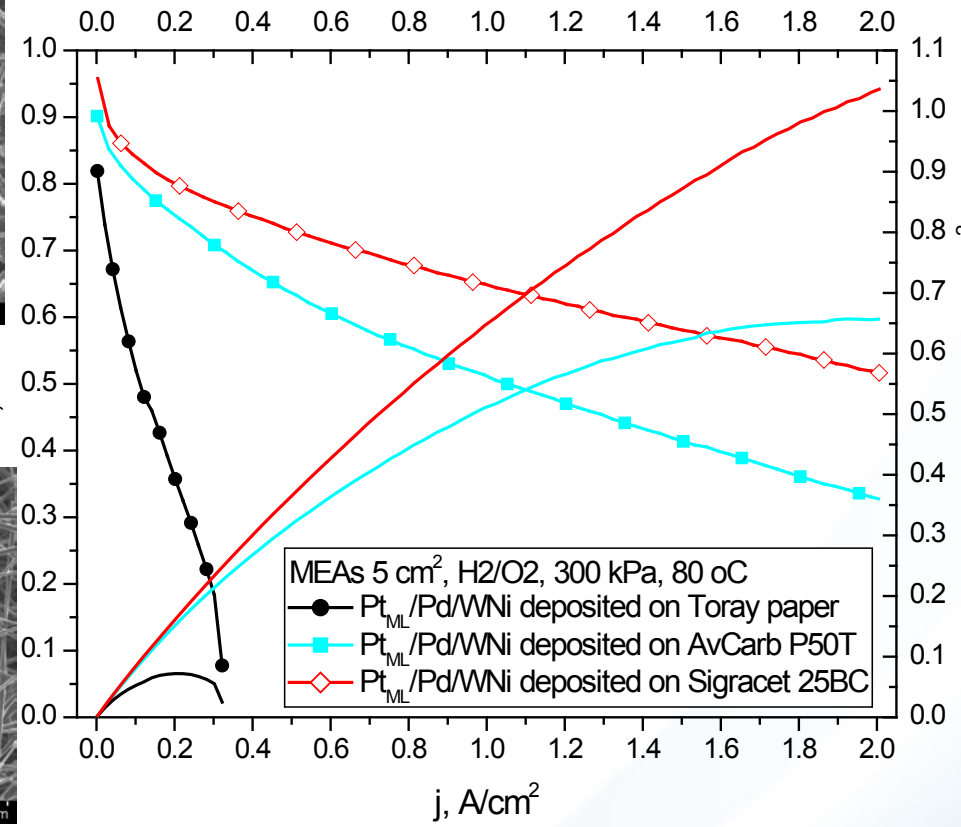
GDL-Sigracet® 25 BC

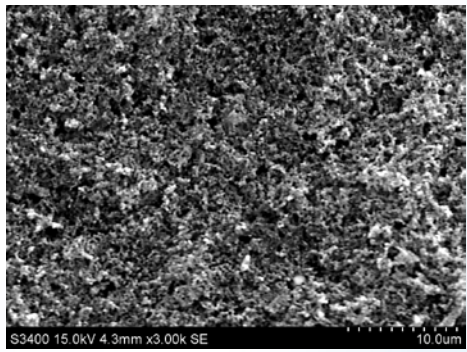


GDL- AvCarb® P50T

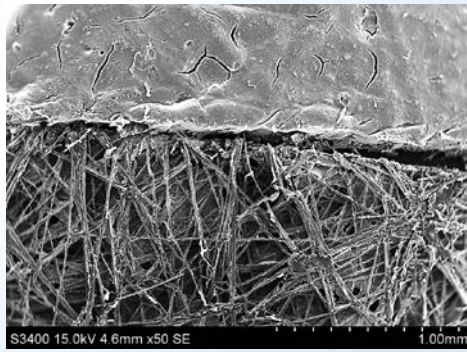


GDL - Toray 90





Microporous Layer
Front side

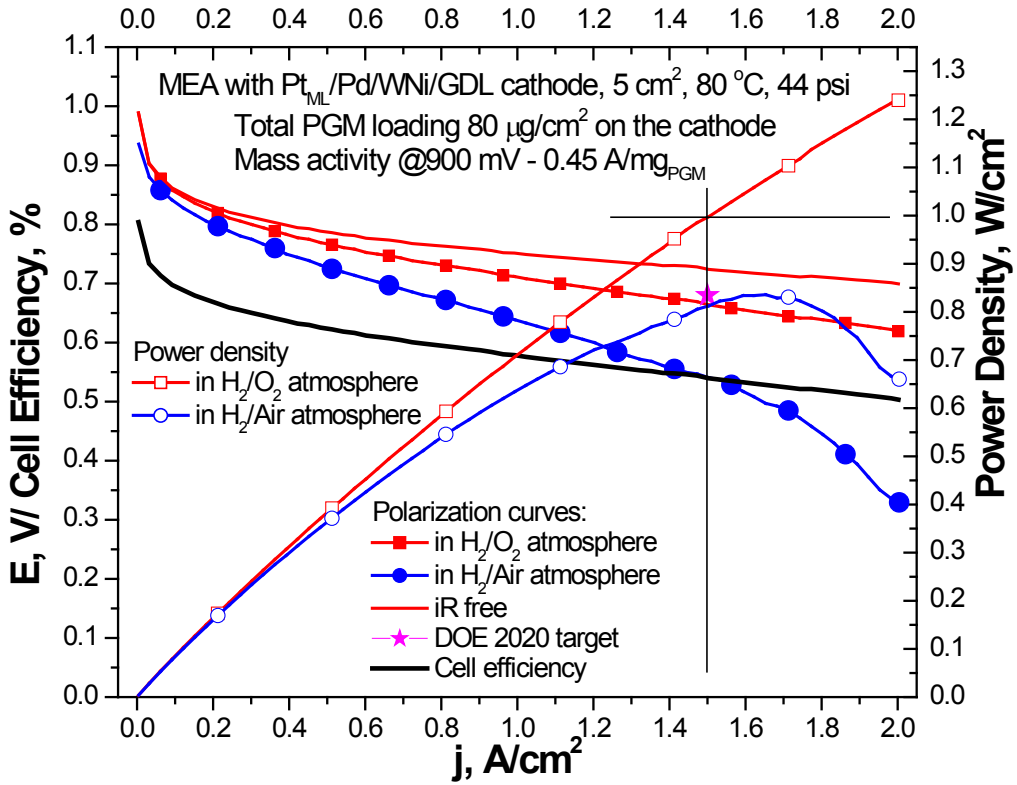


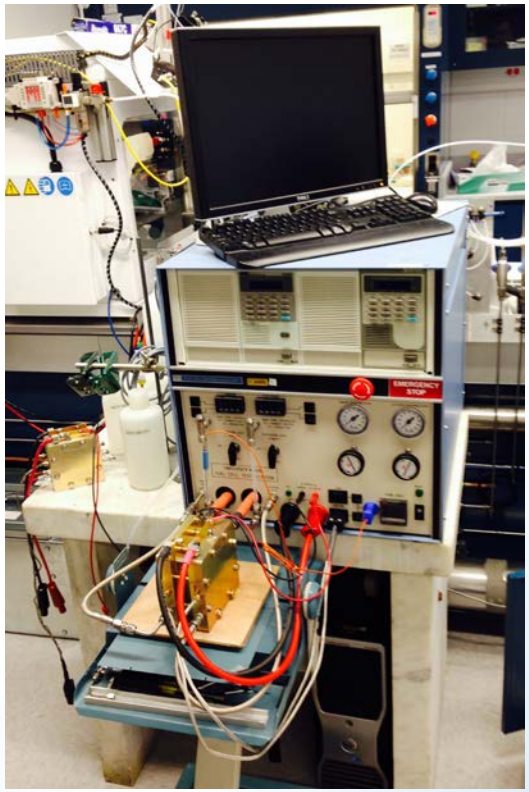
Back side

- ✓ **Sigracet 25BC is the best GDL for direct electrodeposition of Pt_{ML}/Pd/WNi electrocatalysts**
- ✓ **Presence of microporous layer is of crucial importance**

Accomplishments and Progress

Performance assessment of 5 cm^2 MEA





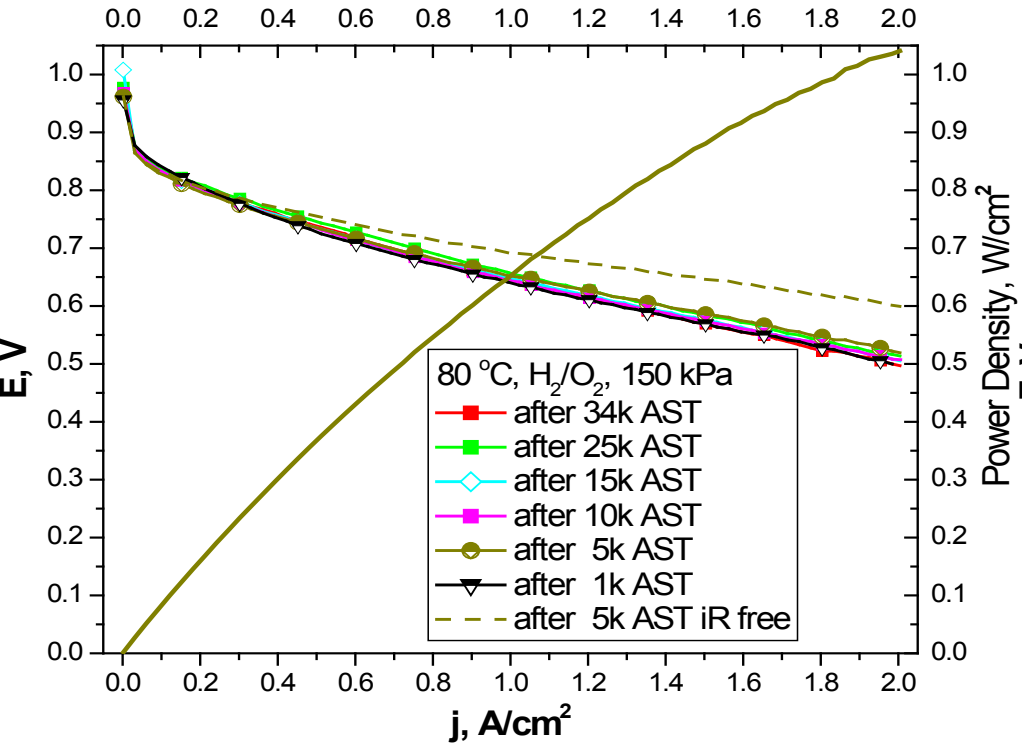
Polarization curves measured on a 5 cm^2 MEA with Pt_{ML}/Pd/WNi/GDL catalyst on the cathode, standard E-TEK Pt catalysts on the anode, and Nafion® XL membrane.

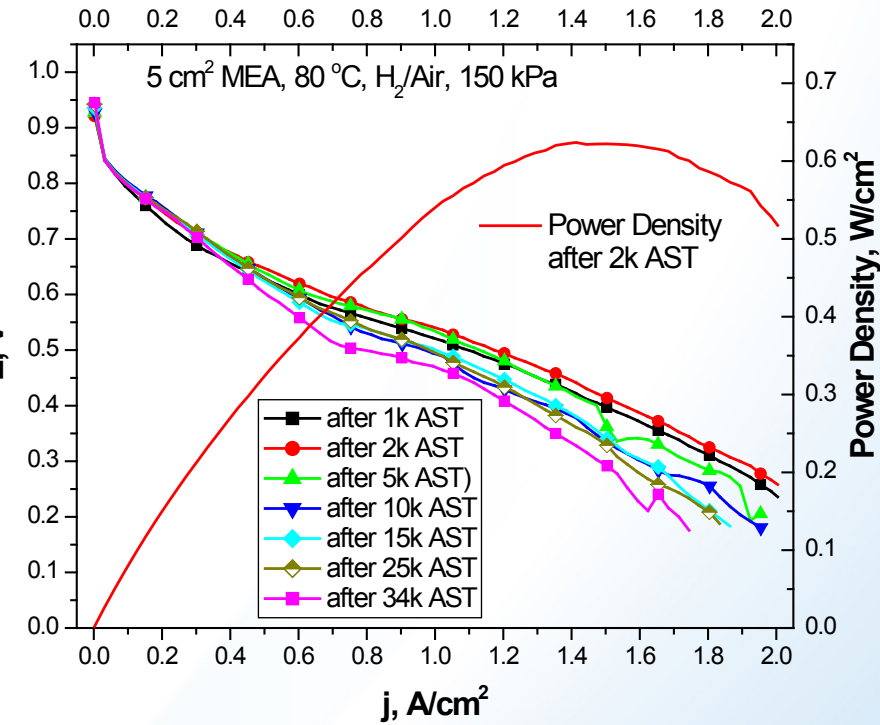
	Cell Power Density, W/cm^2	Voltage at 1.5 A/cm^2	Current density at 0.8 V	LHV electrical efficiency	Mass activity @900 $mV_{iR\ free,}$
DOE target	1 W/cm^2	0.68 V	0.31 A/cm^2	55 %	>0.44 A/mg_{PGM}
Current project	**1 W/cm^2**	**0.67 V**	**0.31 A/cm^2**	**54%**	**0.45 A/mg_{PGM}**

✓ **The MEA meets the DOE targets for mass activity**

Accomplishments and Progress

Durability assessment – DOE H_2/N_2 AST protocol



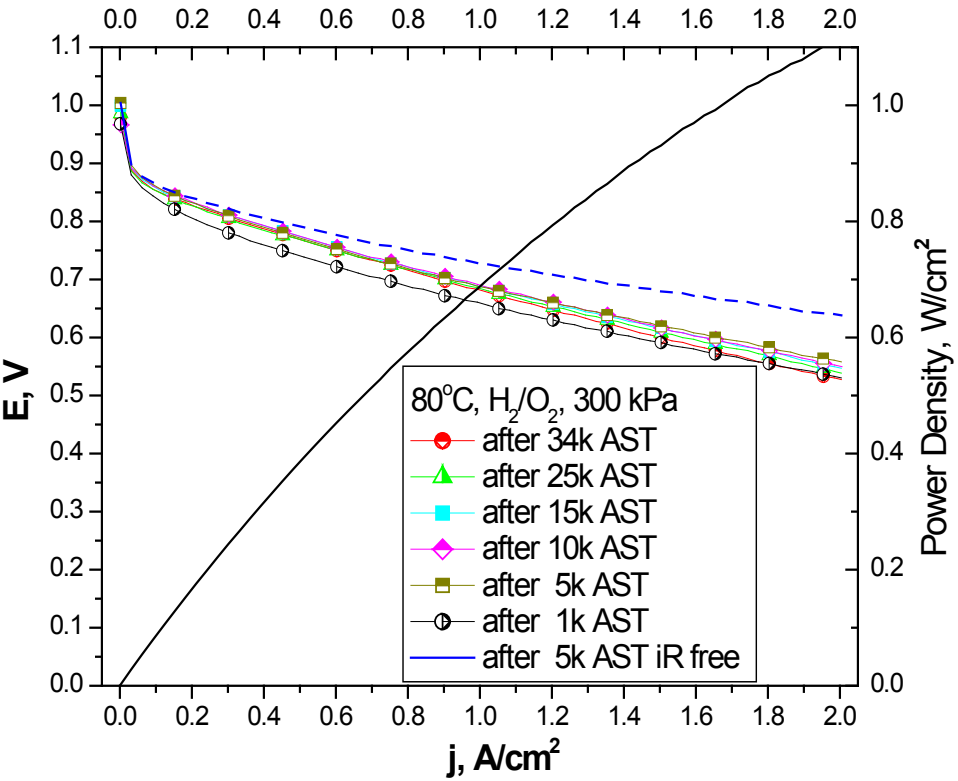


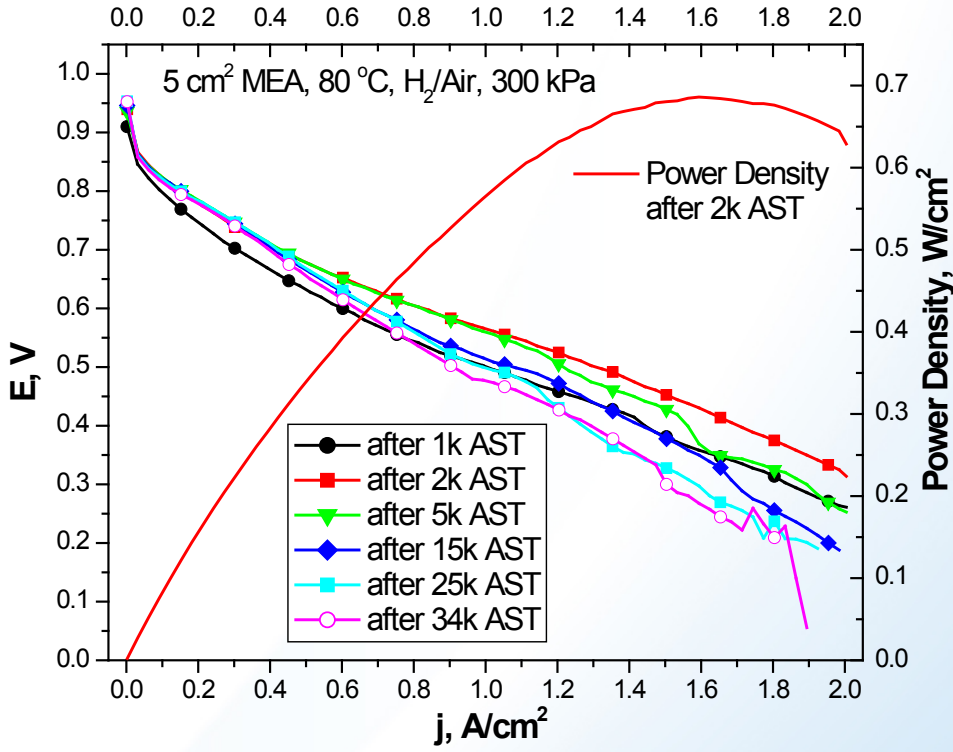
Polarization curves measured on 5 cm^2 MEA in H_2/O_2 and H_2/Air at backpressure of 150 kPa. The PGM loading on the Pt_{ML}/Pd/WNi/GDL cathode is 0.07 mg_{PGM}/cm^2, and the Pt loading on the anode is 0.05 mg_{Pt}/cm^2 (TKK Pt catalysts). The MEA is assembled with a Nafion® HP membrane

- ✓ The mass activity is 0.37 A/mg_{PGM}
- ✓ The loss in the performance at 1.5 A/cm^2 is only 22 mV after 34 000 AST
- ✓ The performance in Air needs to be improved

Accomplishments and Progress

Durability assessment – DOE H_2/N_2 AST protocol





Polarization curves measured on 5 cm^2 MEA in H_2/O_2 and H_2/Air at backpressure of 300 kPa. The PGM loading on the Pt_{ML}/Pd/WNi/GDL cathode is 0.07 mg_{PGM}/cm^2, and the Pt loading on the anode is 0.05 mg_{Pt}/cm^2 (TKK Pt catalysts). The MEA is assembled with a Nafion® HP membrane

- ✓ The mass activity is 0.46 A/mg_{PGM}
- ✓ The loss in the performance at 1.5 A/cm^2 is only 19 mV after 34 000 AST
- ✓ The performance in Air needs to be improved

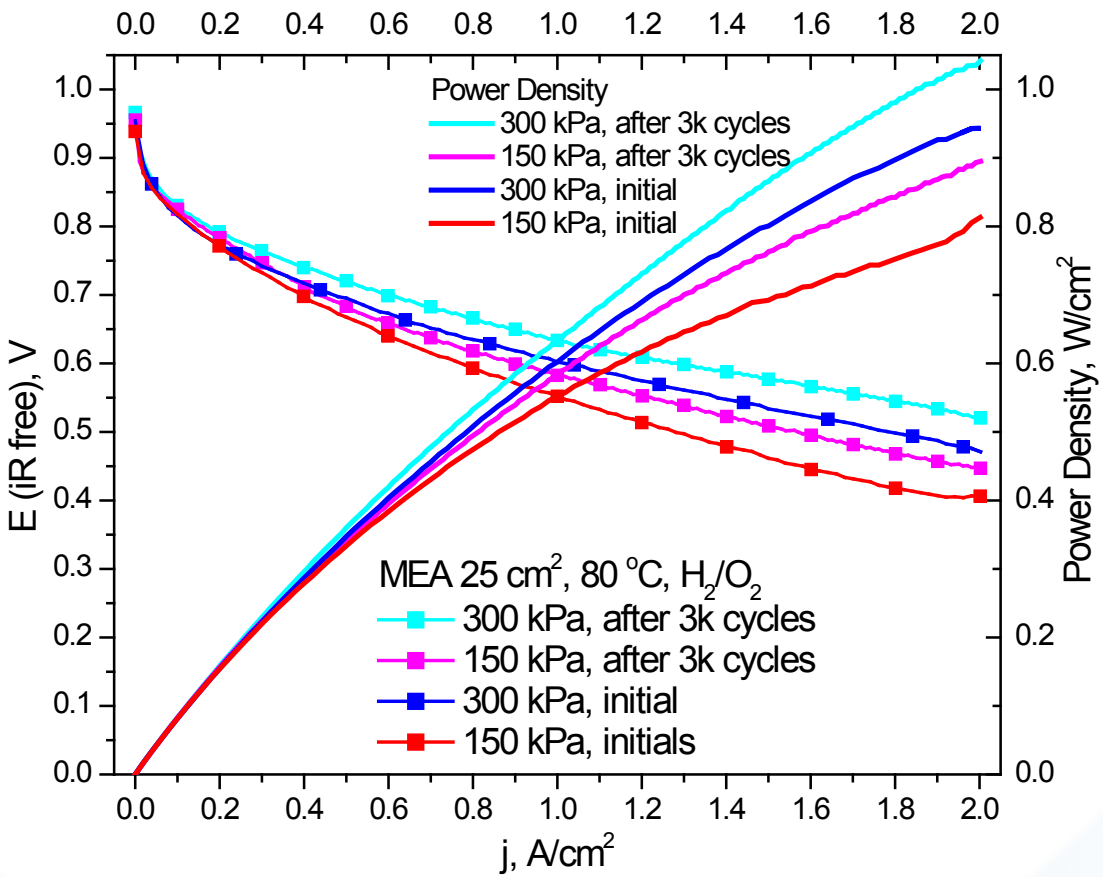
Durability assessment - summary

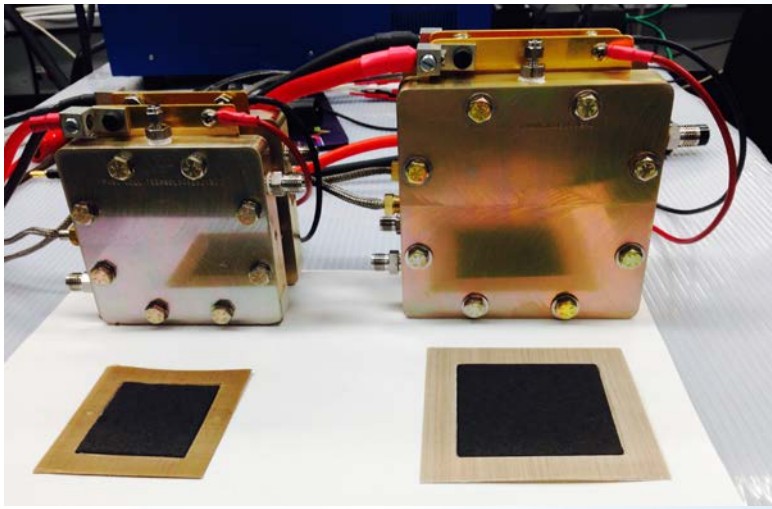
	DOE 2020 targets	Pt_{ML}/Pd/WNi/GDL 80°C, H_2/O_2, 150 kPa	Pt_{ML}/Pd/WNi/GDL 80°C, H_2/O_2, 300 kPa
PGM total loading, mg_{PGM}/cm^2	< 0.125	0.07 mg_{PGM} /cm^2 at the cathode	0.07 mg_{PGM} /cm^2 at the cathode
Loss in performance at 0.8 A/cm^2	< 30 mV	19 mV after 34000 AST	7 mV after 34000 AST
Loss in performance at 1.5 A/cm^2	< 30 mV	22 mV after 34000 AST	19 mV after 34000 AST
Mass activity @900 $mV_{iR\ free,}$ A/mg_{PGM}	>0.44	0.37	0.46

- ✓ Achieved lower PGM loading and high Pt utilization
- ✓ Surpassed the DOE targets for mass activity and loss in performance at higher back pressure
- ✓ The performance in Air needs to be further improved

Accomplishments and Progress

Performance assessment of 25 cm^2 MEA





25 cm^2 MEA

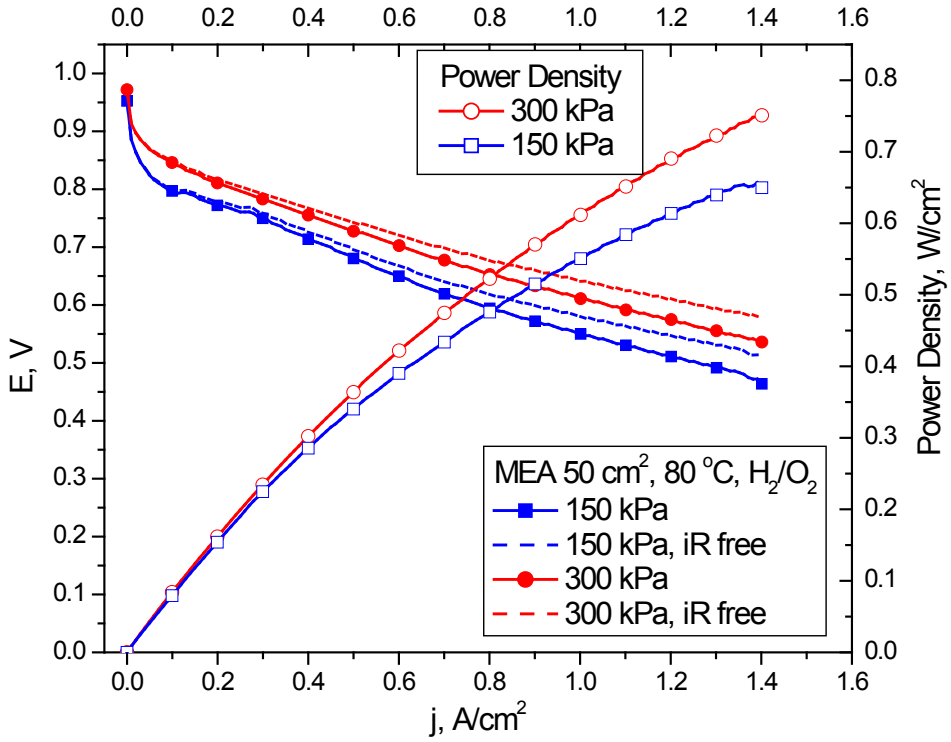
50 cm^2 MEA

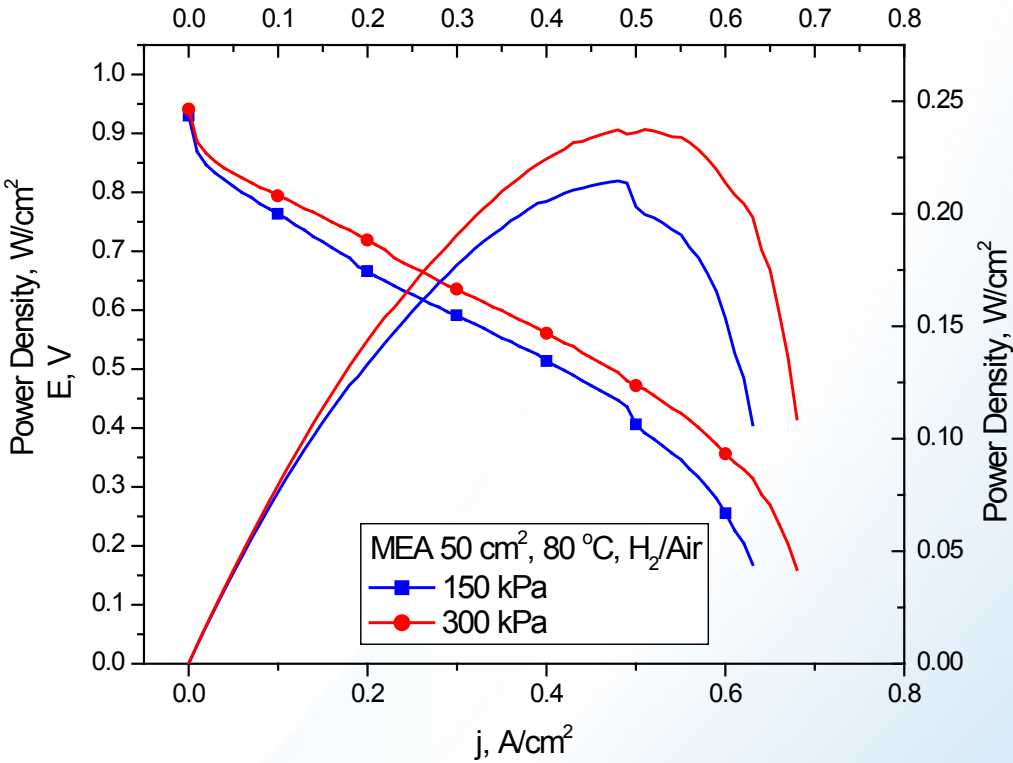
Polarization curves of 25 cm^2 MEA, assembled with Pt_{ML}/Pd/WNi/GDL cathode, standard Pt/C (TKK 46 %) anode, and Nafion® HP membrane.

- ✓ Mass activity @ 900 mV, iR-free – 0.4 A/mg$_{PGM}$

Accomplishments and Progress

Performance assessment of 50 cm^2 MEA



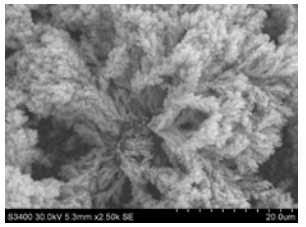


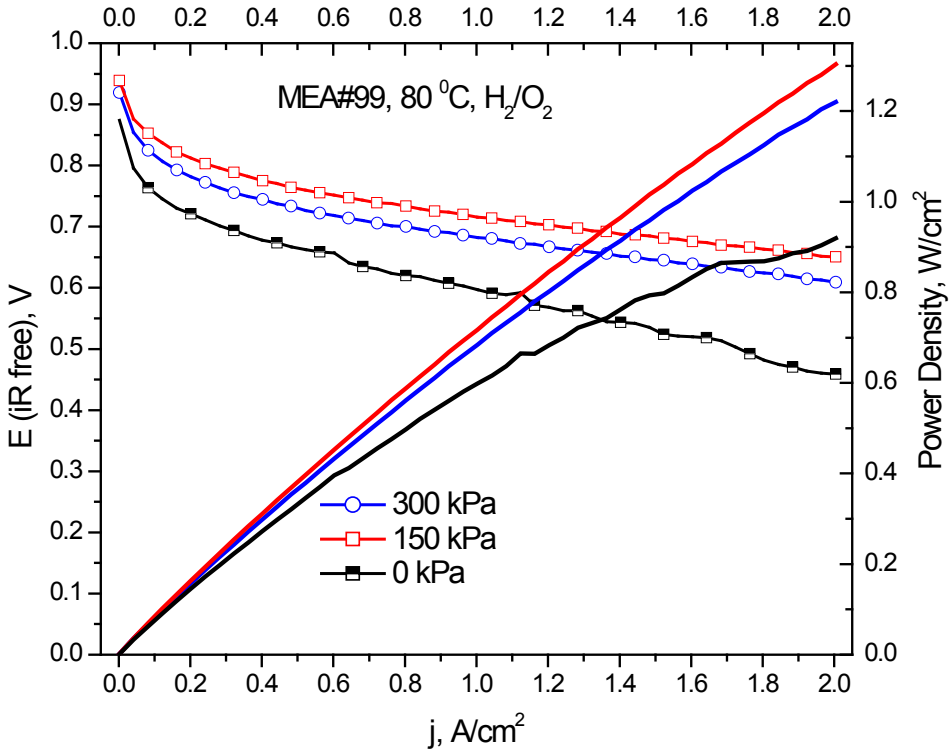
Polarization curves of 50 cm^2 MEA, assembled with Pt_{ML}/Pd/WNi/GDL cathode, standard Pt/C (TKK 46%) anode, and Nafion® XL membrane.

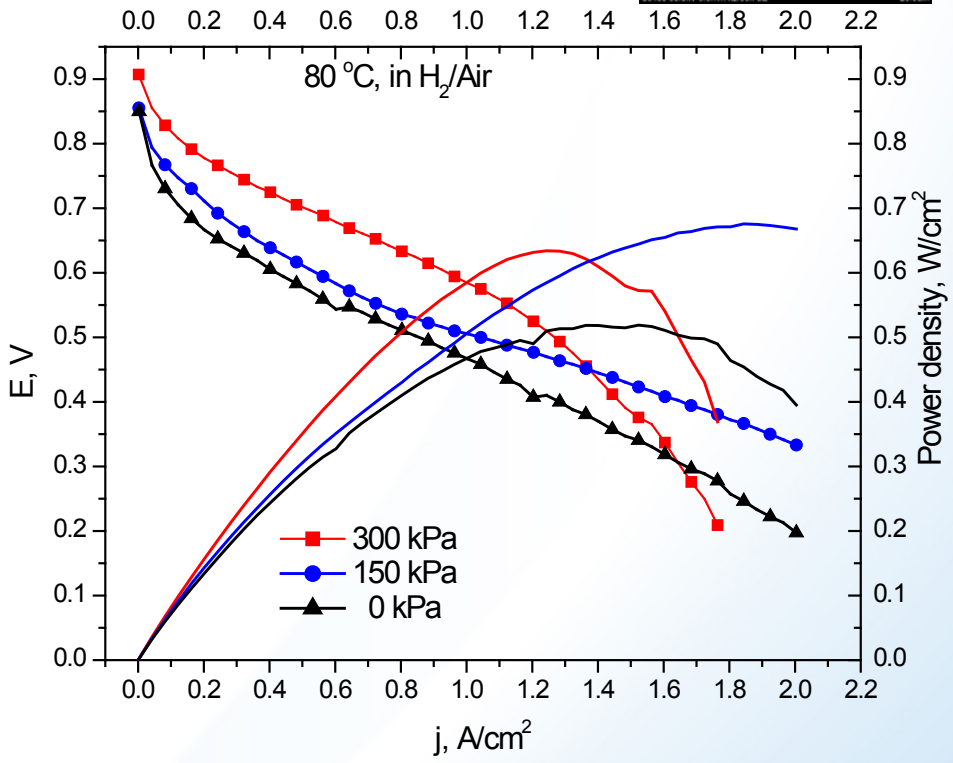
- ✓ Mass activity @ 900mV, iR-free – 0.41 A/mg_{PGM}
- ✓ The performance in Air needs to be improved

Accomplishments and Progress

Strategy for improving the MEA performance at lower pressures, higher current densities and in Air







Polarization curves of 5 cm^2 MEA, assembled with Pt_{ML}/Pd/GDL (dendritic Pd nanostructures) cathode, standard Pt/C (TKK 46%) anode, and Nafion® HP membrane

✓ Electrodeposition of dendritic nanostructured cores directly on the GDL surface, followed by deposition of Pt ML on their surface is a promising strategy for further improvement of the MEA's performance at lower or no back pressure, high current density, and in H_2/Air atmosphere.

Collaborations

- **Interdepartmental collaboration at BNL – Federal Laboratory**

  - **Sustainable Energy Technology Department**
    Designing, automation and software development
  - **Chemistry Department**
    Building of the semi-automated system
    Catalysts synthesis
    Electrodes fabrication
    Preparation and testing of MEAs with area of 5-50 cm^2
  - **Center for Functional Nanomaterials**
    Electrocatalyst characterization by state-of-the-art microscopic (TEM, SEM) and spectroscopic techniques.

- **General Motors - Industry**
  Fabrication and testing of MEAs with areas of up to 300 cm^2
  Fabrication and testing small stacks with power of up to 1 kW

Remaining Challenges and Barriers

- Validate the high **activity** and the **durability** on bigger MEAs (up to 300 cm^2).
- Improve the chemical and structural stability of the GDL - support.
- Improve the MEAs' performance at high current densities and in H_2/Air atmosphere.
- Reduce the time for electrodes fabrication to less than 30 minutes.
- Develop a roll-to-roll technology, based on the semi-automated system for MEAs fabrication with ultra low PGM loadings. Save time and reduce **the cost**.

Proposed Future Work

FY 2015

- Explore electrodeposition (constant current, constant potential or pulse deposition) protocols to determine the impact of size and shape of the refractory cores on the activity and durability of 300 cm^2 or larger MEAs.
- Reduce MEA fabrication time to less than 1 hour by optimizing each step.
- Develop a protocol for electrodeposition of anode catalysts with ultra-low Pt loading (less than 30 $\mu g/cm^2$), and thus reduce the total PGM loading to less than 0.1 mg_{PGM}/cm^2 for both electrodes.

FY 2016

- Improve the MEA performance at high power densities and in H_2/Air atmosphere.
- Develop novel GDLs, with a microporous layer of carbon nanotubes or conductive nanocrystalline diamond (boron or phosphorous doped) nanoparticles, and demonstrate higher chemical and structural stability and superior performance on MEAs with industrial significance.
- 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 electrodes and MEAs fabrication (less than 30 min).

Technology Transfer Activities

- Patents, licensing, or potential licensing information.
  - Adzic R., Bliznakov S., and Vukmirovic M. US Patent: Core-Shell Fuel Cell Electrodes,**US2015/0017565 A1**, Jan. 15, 2015.
  - Automated system for electrodeposition of fuel cell electrocatalysts with ultra-low PGM loading, directly on GDLs – Provisional Application (in preparation).

- Future funding from alternative sources
  - NYSERDA
  - ARPA-E
  - CRADA projects with GM and/or Toyota

- Future technology transfer to GM and/or Toyota

Summary

- A semi-automated system for fabrication of fuel cell electrodes and MEAs with ultra-low PGM loading (less then 125 μg/cm^2 for both electrodes) has been developed.
- The proposed electrodeposition strategy allows fast and facile preparation of the electrodes with a geometric area of up to 500 cm^2 (couple hours starting from chemicals and GDLs).
- Different GDLs are tested, and Sigracet 25BC GDL is identified as the best support for the Pt_{ML}/Pd/WNi electrocatalysts.
- The performance of the MEAs, with geometric areas of 5, 25, and 50 cm^2, is examined either in H_2/O_2 or H_2/Air atmosphere.
- The mass activity and durability performance of the MEAs of interest meet and in some cases exceed the DOE 2020 targets.
- The performance of the MEAs at high current densities needs further improvement.
- The performance of the MEAs in Air also needs to be improved.