Mo_2C – Pt System for Fuel Cell Applications

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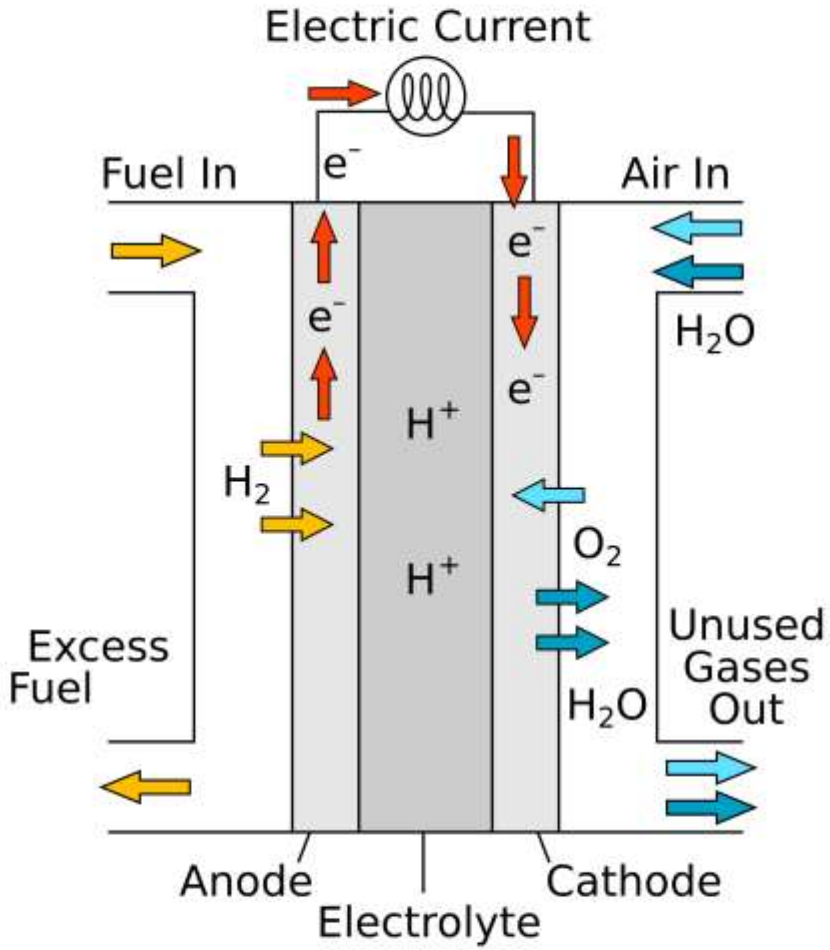
Proton Exchange Membrane Fuel Cell (PEMFC)



Fuel Cell

Advantages:

- Water as the oxidized byproduct
- More efficient than traditional combustion oxidations (less energy lose thru heat)

Challenges:

- High cost
  - Precious metal catalyst (Pt on carbon black) at high loadings for desired performance
- Low durability
  - Low catalyst loading decreases performance due to amalgamation (unstable/reactive system)
  - Fuel crossover degrades membrane

Motivation

- This project takes advantage of the current, and rapidly increasing nanofabrication techniques to synthesize phase-pure molybdenum carbide (Mo_2C) nanotubes

- Study and understand the synergy between Pt and phase-pure Mo_2C nanotubes
  - Allow further Pt loading reduction without compromising desirable catalytic activity
  - Increase the longevity and performance of the cell
  - Reduce the cost per unit made

Catalyst Synthesis – Mo_2C nanotubes

<u>Synthesis via a salt flux reaction</u>

- Raw materials and amounts: 0.13 g of sodium chloride, 0.37 g of sodium fluoride, 0.05 g of multi-walled carbon nanotubes, and 0.20 g of molybdenum powder

- Grind in a mortar for homogeneous result

- Place mixture in a crucible boat and move to a tube furnace

Catalyst Synthesis – Mo_2C nanotubes

<u>Synthesis via a salt flux reaction</u>

- Ramp the furnace temperature to 975°C over 9.75 hours and hold at 975°C for 14 hours in an argon environment
- After the furnace temperature reaches room temperature, the powder is removed and excessive salts are washed away by boiling and rinsing the mixture in deionized water
- Dry the Mo_2C nanotubes powder in a vacuum oven at 50°C for 3 hours

Catalyst Characterization – Pt on Mo_2C nanotubes

<u>Synthesis via vapor phase atomic layer deposition (ALD)</u>

- Selective X-ray diffraction (XRD) is performed in Mo_2C nanotubes powder to identify impurities

- Pure Mo_2C nanotubes are shipped to our collaborators in Boulder, CO for ALD cycling:
  - 15 cycles
  - 30 cycles
  - 75 cycles

Catalyst Characterization – Pt on Mo_2C nanotubes

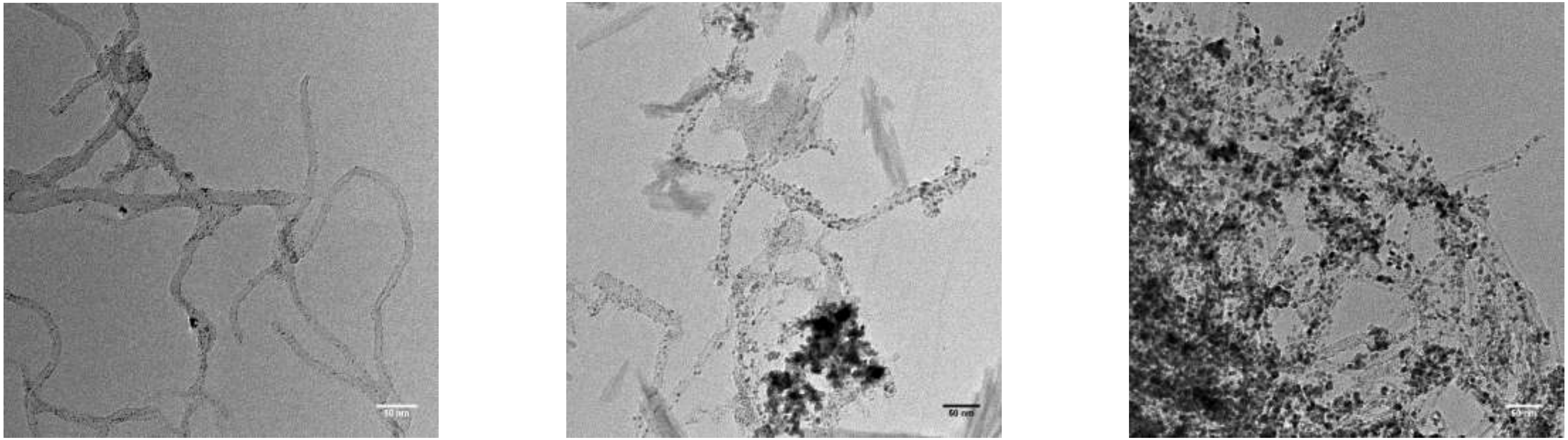
- Amount and distribution of Pt in Mo_2C – Pt system are tested for every ALD cycling via atomic absorption spectroscopy (AAS) and high-resolution transmission electron microscopy (HRTEM) respectively

AAS Results

Table 1 – Pt quantification for different ALD cycles

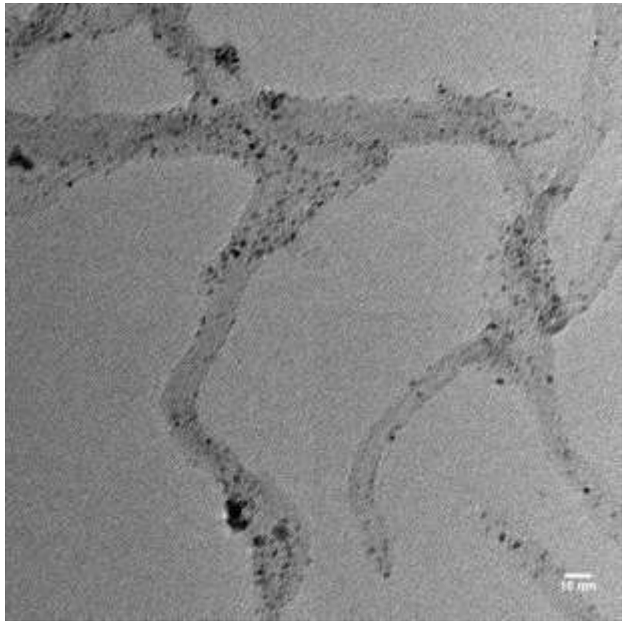
Sample	Pt wt% by AAS
75 ALD cycle Pt/Mo_2C	4.78%
30 ALD cycle Pt/Mo_2C	2.19%
15 ALD cycle Pt/Mo_2C	0.77%

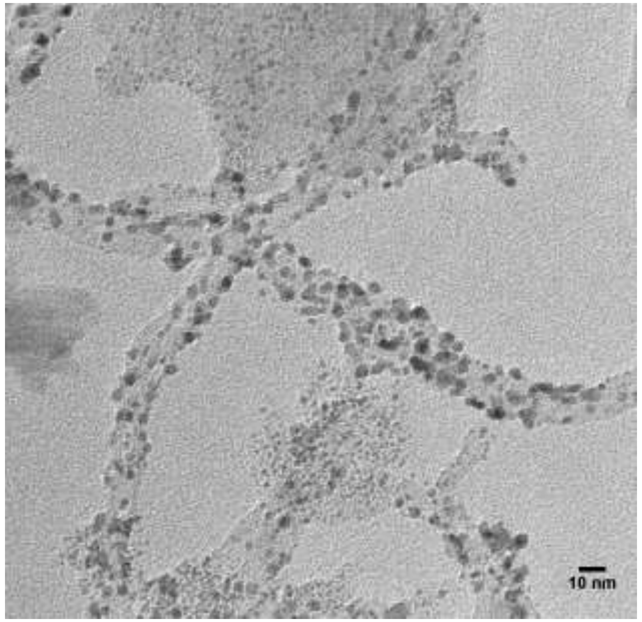
HRTEM Results – 50 nm

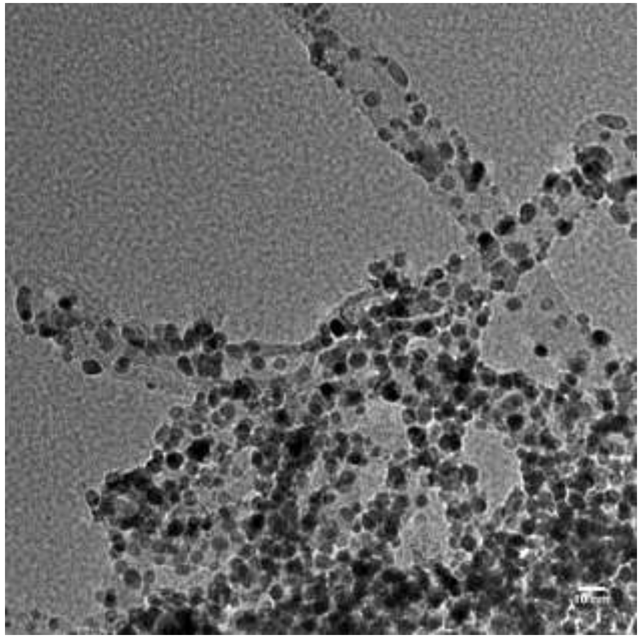


From left to right: 15, 30, and 75 ALD cycles Pt/Mo_2C

HRTEM Results – 10 nm







From left to right: 15, 30, and 75 ALD cycles Pt/Mo_2C

Catalyst Preparation – Electrochemical Performance

<u>Empirically determined</u>

- 2.5 mg Pt/Mo_2C
- 375 μL solution:
  - 75% Nafion of total solids (171.6 μL)
  - 203.4 μL of 18.2 MΩ distilled water
- Sonicate for 10 minutes
- Deposit 10 μL with pipet in glassy carbon electrode
- Vacuum dry for 10 minutes

Catalyst Testing – Electrochemical Performance

<u>Empirically determined</u>

- Rotating disk electrode (RDE) instead of static method

- 2500 rpm

- H^+ source, 0.1 M $HClO_4$

Catalyst Performance and Durability

Hydrogen evolution reaction (HER) activity

- Linear sweep voltammetry (LSV) in N_2 environment
  - 10 replicates from -0.4 to 0 V
- Constant potential electrolysis (CPE) in N_2 environment
  - 48 hours at -0.2 V
- Potential cycling (CV) in N_2 environment
  - 3000 cycles from -0.4 to 0.6 V

Oxygen reduction reaction (ORR) activity

- Linear sweep voltammetry (LSV) in O_2 environment
  - 5 replicates from -0.3 to 0.7 V
- Potential cycling (CV) in N_2 environment
  - 7200 cycles from -0.3 to 1.2 V

HER Results

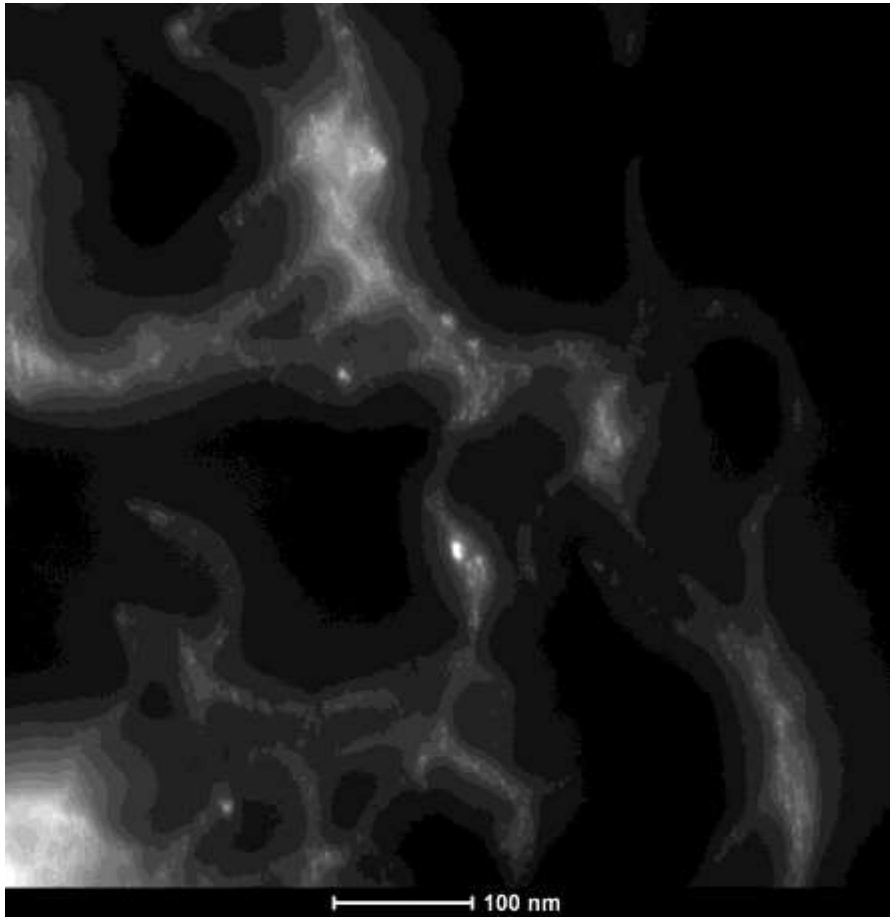
Table 2 – LSV results of 15 ALD cycle Pt/Mo2C						
	Highest (most "-")			Lowest (most "+")		
	mA/cm^2	mA/mg Pt	$mA/cm^2 \cdot$ mg Pt	mA/cm^2	mA/mg Pt	$mA/cm^2 \cdot$ mg Pt
Initial	-6.57	-2512.99	-12798.54	-5.96	-2279.22	-11607.98
After 1 CPE	-7.38	-2824.68	-14385.95	-6.72	-2571.43	-13096.18
After 2 CPE	-8.25	-3155.84	-16072.58	-7.54	-2883.12	-14683.59
After 3 CPE	-9.93	-3798.70	-19346.63	-8.91	-3409.09	-17362.36
After 3000 cycles	-10.19	-3896.10	-19842.69	-8.86	-3389.61	-17263.14

Table 3 – LSV results of 30 ALD cycle Pt/Mo2C						
	Highest (most "-")			Lowest (most "+")		
	mA/cm^2	mA/mg Pt	$mA/cm^2 \cdot$ mg Pt	mA/cm^2	mA/mg Pt	$mA/cm^2 \cdot$ mg Pt
Initial	-7.03	-945.21	-4813.89	-6.06	-815.07	-4151.11
After 1 CPE	-8.30	-1116.44	-5685.97	-7.18	-965.75	-4918.54
After 2 CPE	-9.12	-1226.03	-6244.11	-7.49	-1006.85	-5127.84
After 3000 cycles	-8.30	-1116.44	-5685.97	-7.03	-945.21	-4813.89

Table 4 – LSV results of 75 ALD cycle Pt/Mo2C						
	Highest (most "-")			Lowest (most "+")		
	mA/cm^2	mA/mg Pt	$mA/cm^2 \cdot$ mg Pt	mA/cm^2	mA/mg Pt	$mA/cm^2 \cdot$ mg Pt
Initial	-2.89	-177.93	-906.18	-2.62	-161.30	-821.48
After 1 CPE	-2.87	-176.67	-899.79	-2.24	-138.08	-703.21

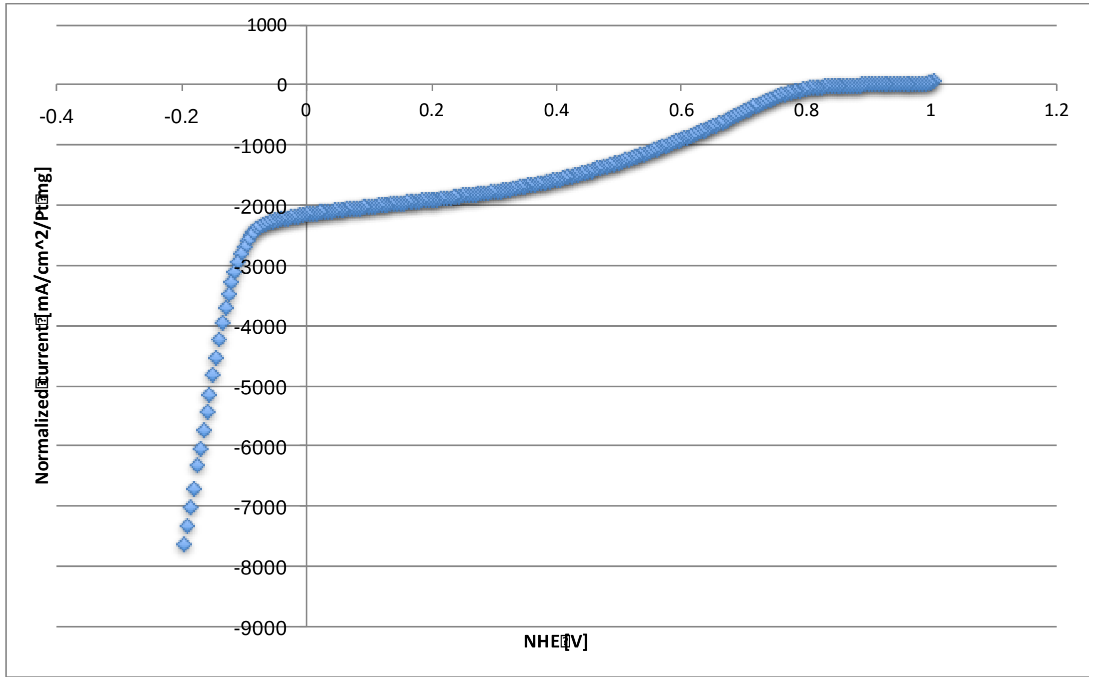
Why current density improves?

- Consider the presence of an oxide layer at the beginning of the experiment
- As negative potential is applied MoO_3 reduces and gets activated as Mo_2C

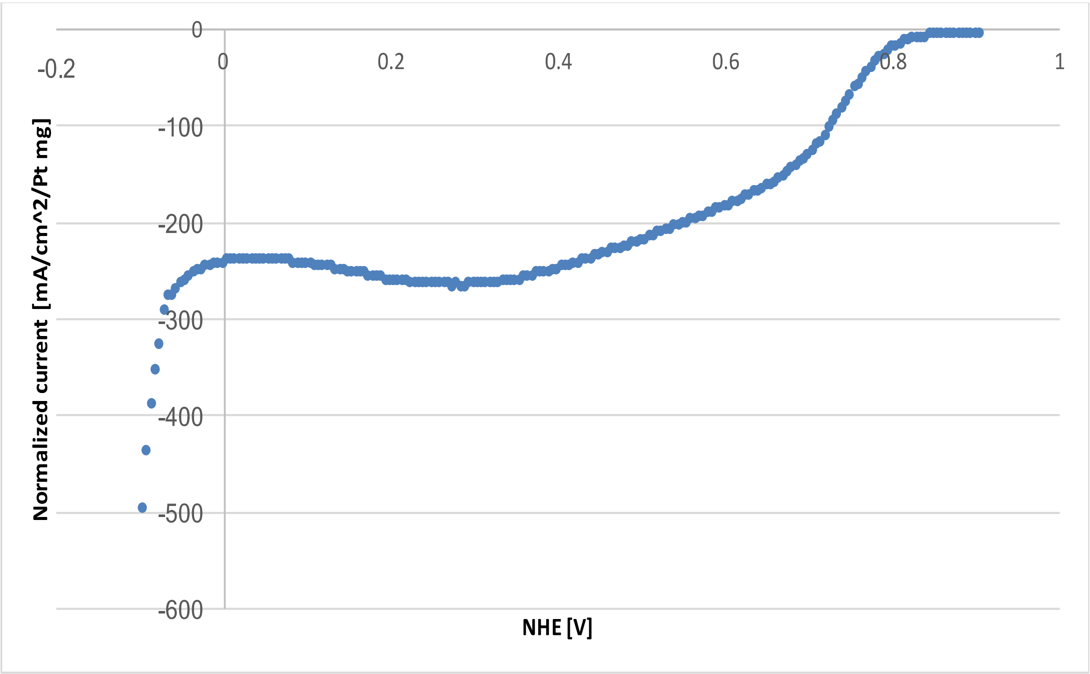


ORR Results

15 ALD cycle Pt/Mo_2C

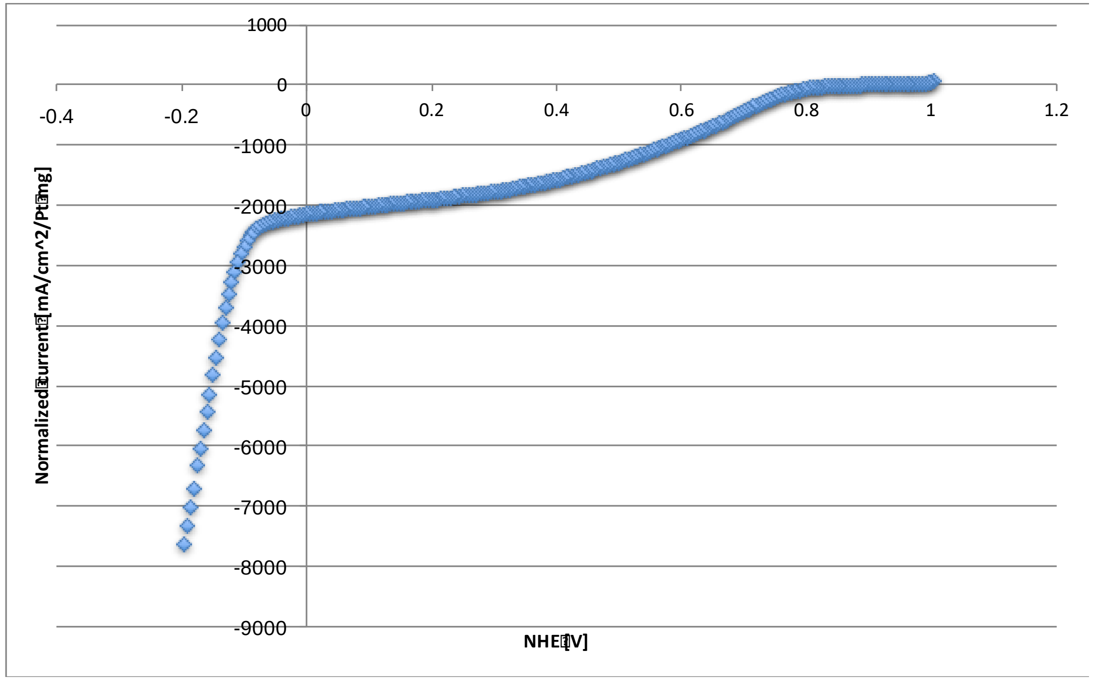


30 ALD cycle Pt/Mo_2C

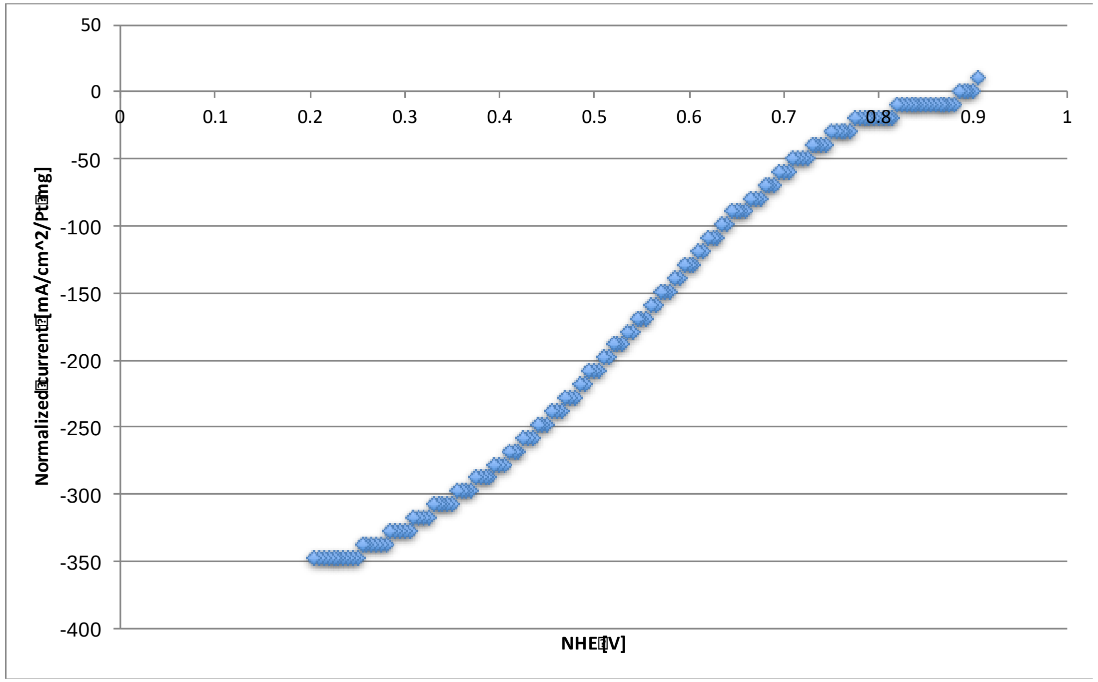


ORR Results

15 ALD cycle Pt/Mo_2C



15 ALD cycle Pt/Mo_2C after cycling



Future Work

- Perform X-ray photoelectron spectroscopy (XPS) in Mo_2C – Pt system for every ALD cycling

- Understand durability differences between HER and ORR

- Assemble and test a fuel cell with the promising 15 ALD cycle Pt/Mo_2C catalyst

Acknowledgements

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