Project FC141

Platinum Monolayer Electrocatalysts

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Brookhaven National Laboratory

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Office of Science
U.S. DEPARTMENT OF ENERGY

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Overview

Timeline

Start: July 2009
End: Project continuation and direction determined annually by DOE % completed N/A

Barriers

Catalysts' Performance:
Catalyst activity; ≥ 0.44 A/mg_{PGM}
Catalysts' Cost:
PGM loading; ≤ 0.125 mg PGM /cm^2
Catalysts' Durability:
< 40% loss in activity under potential cycling

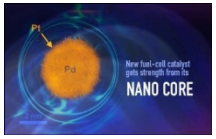
Budget

Funding received in
FY2016: $900,000 (includes partner)
Funds planned for FY2017: 900,000 (includes partner)
Funds received in FY2017: 700,000

Partners

Los Alamos National Laboratory
PI: Piotr Zelenay
Coworker: Ulises Martinez

Relevance



Project objectives:

Synthesizing high performance Pt monolayer (ML) electrocatalysts for the oxygen reduction reaction (ORR) consisting of a Pt ML shell on stable, inexpensive metal, alloy, metal oxide, nitride or carbide nanoparticle cores.

This reporting period:

Further improvement of performance of Pt monolayer catalysts while reducing their PGM contents by the following studies and strategies:

- **MEA testing of Pt ML catalysts with high RDE performance**
- **Modifying non-noble metal core components by nitriding, alloying, doping**
- **Modifying Pt ML shell by doping by very small amount of Au**
- **Metal aerogels as support**
- **Doping carbon by oxide for stabilization**
- **Improving catalyst response at high current densities**

Two projects were selected for support by Technology Commercialization Fund (TCF)

Relevant results from other studies:

Elucidating different kinetics of HOR and HER in acid and base

Elucidating a 4e ORR on Au(100)(more active than Pt in a limited potential region) and identifying role of adsorbed water.

Approach

MEA testing of high performance catalysts with new non-noble metal cores

- Developing catalysts with non-noble metal core components stabilized by nitriding.
- Developing catalysts with cores having a refractory metal inner core and noble metal thin outer cores.
- Nitriding at high pressure and high temperature of non-noble metal core components

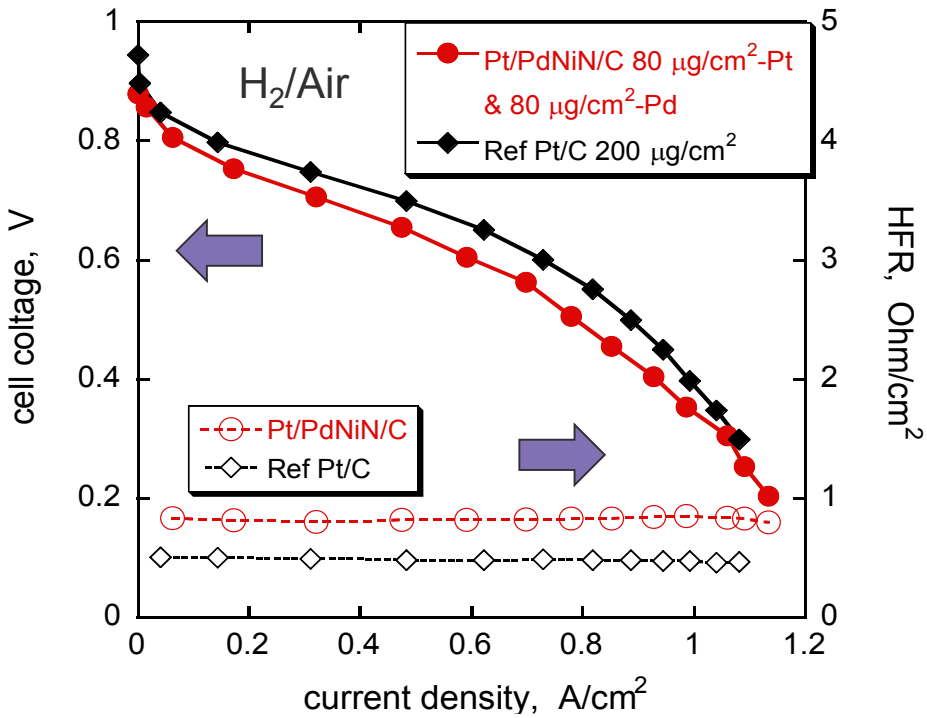
Milestone 1: Develop Pt ML catalysts with cores consisting predominantly of non-noble metals that meet the 2020 targets

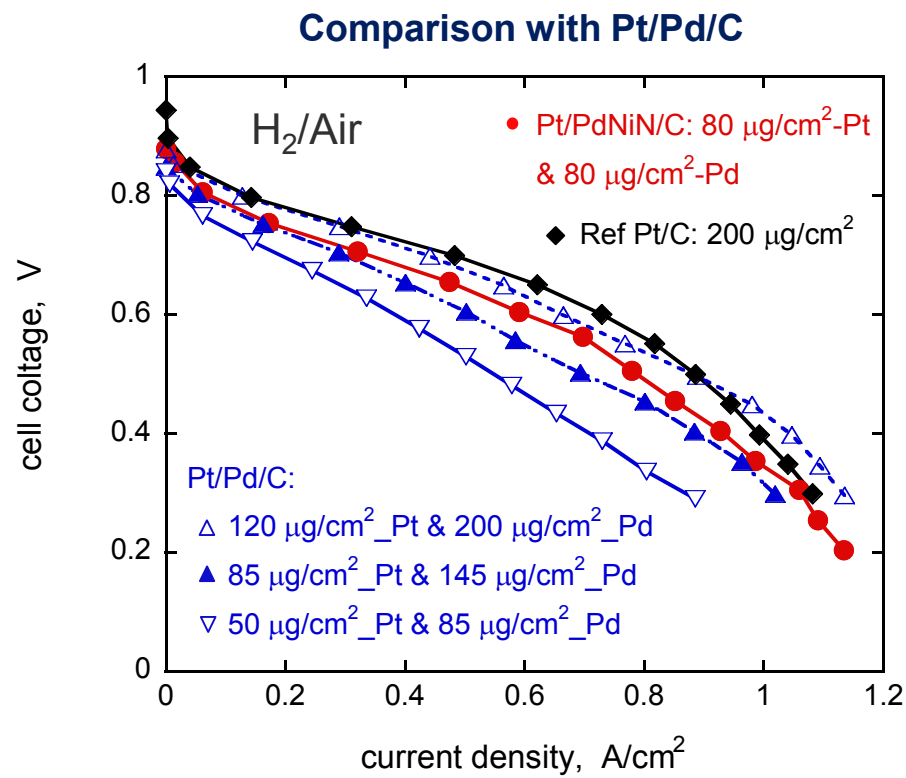
Doping Pt ML shell and carbon supports to increase catalysts stability and activity

- Modifying Pt ML shell by doping by very small amount of Au; doping core by Ir
- Improving stability of the Pt/C catalysts by doping C by NbO_2
- Metal aerogels as support
- Improving catalyst response at high current densities by better proton penetration into the catalyst layer, achieving high ECSA and aerogels.

Milestone 2: Improve catalyst response at high current density by 80% from 1.1A/cm^2 to 2 A/cm^2.

Accomplishments and Progress: MEA tests of nitride-stabilized Pt/PdNiN/C





The result of the scale-up sample (0.5 g batch):

- ○ The MEA performance lower than expected
- ✓ High HFR → Double membranes used for PtPdNiN test

- ❑ Pt ML catalyst activity lower than Pt/C
- ❑ The performance of Pt/PdNiN/C comparable to Pt/Pd/C

The performance would be better with a single membrane to be used next.

Cathode: PtPdNiN/C 80 $\mu g_{Pt} cm^{-2}$, 80 $\mu g_{Pd} cm^{-2}$, air, 1.0 bar air
Anode: TKK Pt/C (47 wt.%) ca. 60 $\mu g_{Pt} cm^{-2}$, H_2, 1.0 bar H_2
Membrane: double Nafion®,211 for Pt/PdNiN; Cell: 80°C
Reference Fuel Cell: 0.1 mg cm^{-2} anode; 0.2 mg cm^{-2} cathode; 47 wt.% Pt/C (TKK).

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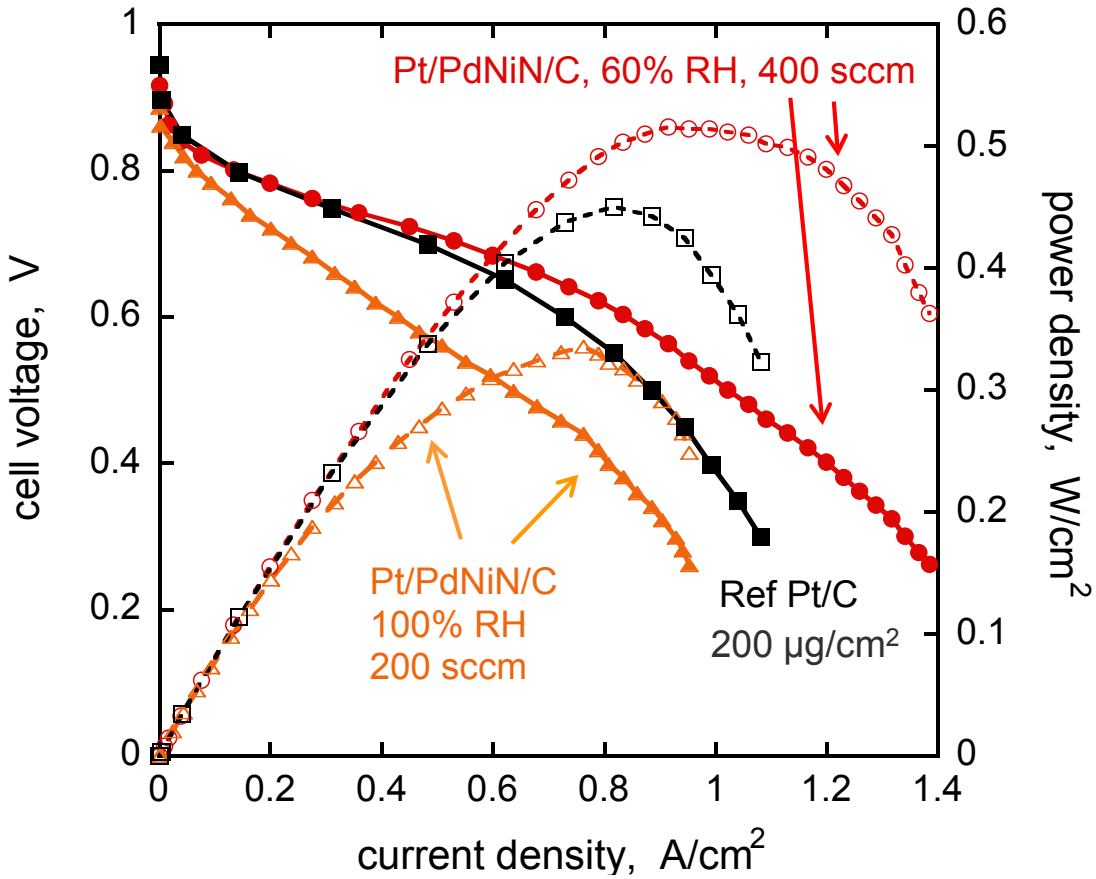
Accomplishments and Progress: Improvement of MEA performance of nitride-stabilized Pt/PdNiN/C

- MEA tests of Pt/PdNiN/C & Ref Pt/C with higher I/C ratio (1:1) at 100% RH, 200 sccm air, 1 bar pressure
- Hysteresis was observed at low voltage due to possible flooding. Decreased RH from 100% to 60% and increased air flow from 200 to 400 sccm, caused significant performance increase.



Cathode: Pt/PdNiN/C 120 $\mu g_{Pt} cm^{-2}$, 70 $\mu g_{Pd} cm^{-2}$, air, 1.0 bar air partial pressure
Anode: commercial Pt/C GDE 200 $\mu g_{Pt} cm^{-2}$, H_2, 200 sccm; 1.0 bar H_2 partial pressure
Membrane: double Nafion®,211; Cell: 80°C
Reference Fuel Cell: : 200 $\mu g_{Pt} cm^{-2}$ anode/cathode commercial GDEs

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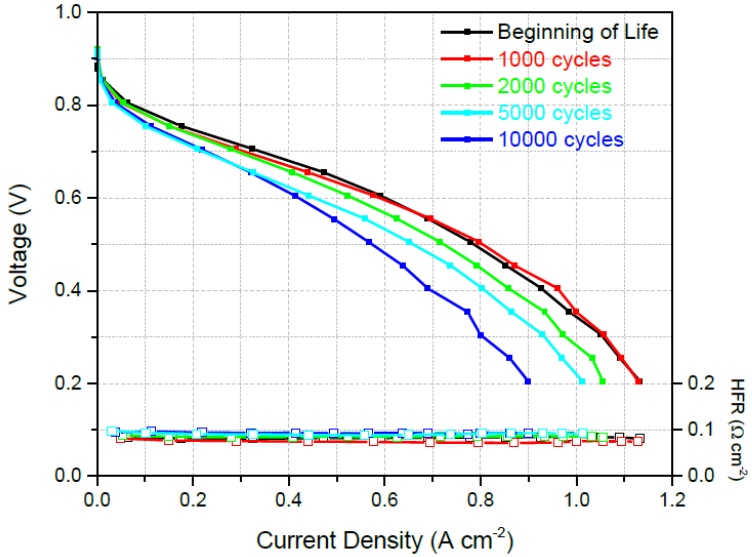
Accomplishments and Progress: Stability tests of Pt/PdNiN/C

Activity decreases with potential cycling, but no PGM loss is observed

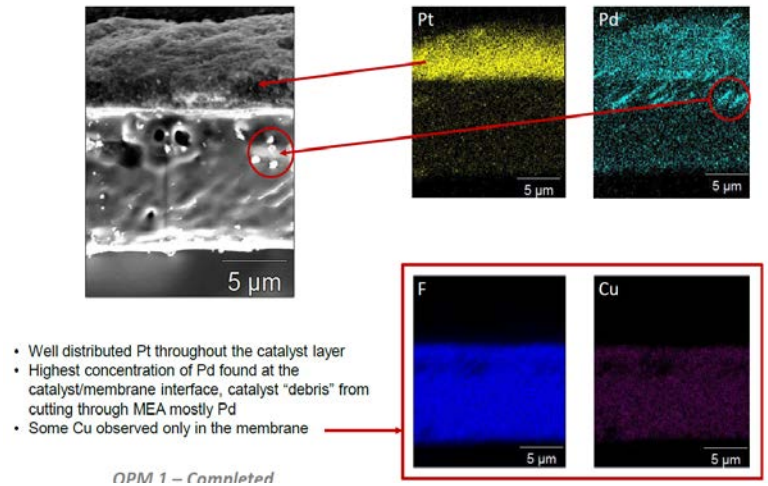


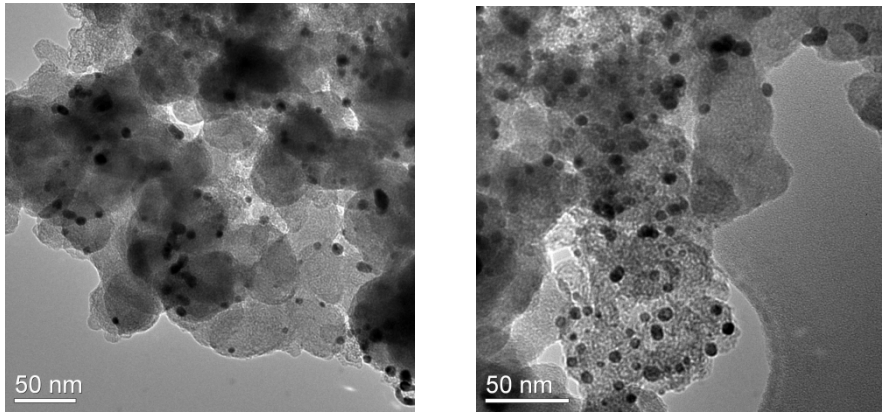
The stability test result

- ❑ Lower than expected
- ❑ 150 mV decrease at 1.0 A/cm^2 after 5k cycles

Possible causes of low stability
Broad distribution of particle size → decrease of ECSA due to Ostwald ripening – no loss of PGM

EDS mapping of Pt_{ML}/PdNiN/C MEA after 10,000 cycles





TEM images of catalyst after 10.000 cycles

Sample obtained by improved synthesis procedure is being checked

Cathode: PtPdNiN/C ca. 80 $\mu g_{Pt} cm^{-2}$, 80 $\mu g_{Pd} cm^{-2}$, air, 200 sccm, 1.0 bar air
Anode: TKK Pt/C (47 wt.%) ca. 60 $\mu g_{Pt} cm^{-2}$, H_2, 200 sccm; 1.0 bar H_2
Membrane: double Nafion®,211; Cell: 80°C;
Cathode Durability Cycling: 0.6-1.0 V, 0-10000 cycles, N_2.

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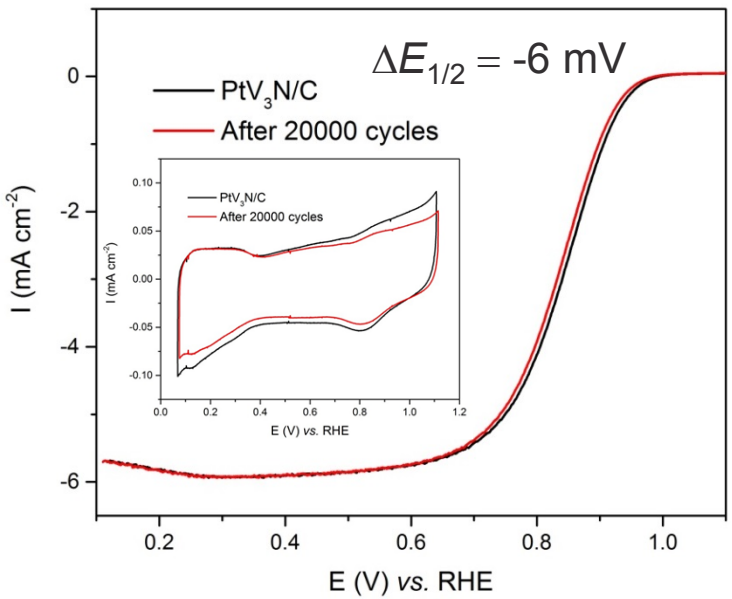
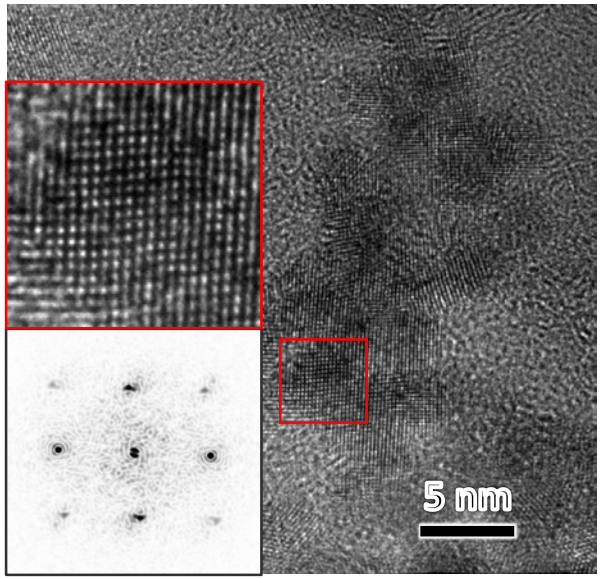
Accomplishments and Progress: PtV_3N by High-Pressure Nitriding





Intermetallic PtV_3N

HRTEM image indicates intermetallic structure (red square)
(by L. Wu, BNL)

Catalyst Loading (μg/cm²)		MA (A/mg$_{PGM}$)	SA (mA/cm²)
PtV_3N	**6.12**	**0.22**	**3.4**
Pt/C (TKK)	9.7	0.22	0.25

- MA of PtV_3N is comparable to Pt/C
- SA is much higher
- Stability is significant

- The preliminary results indicate that the high-pressure nitriding can generate a unique atomic structure and enhanced durability

- Continue the synthesis of new nitride cores from other refractory metals (W, Nb, Ta) using the reactor

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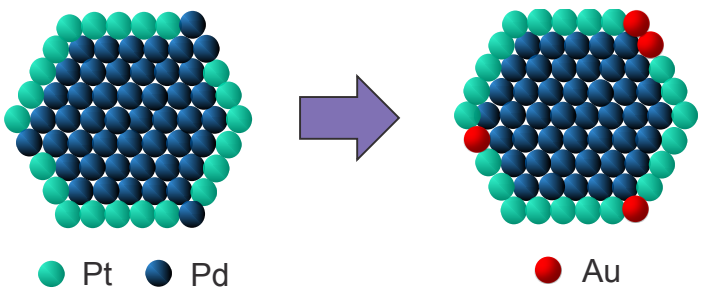
Accomplishments and Progress: Au-doped Pt_{ML}/Pd/C

The Au content is very small, difficult to observe



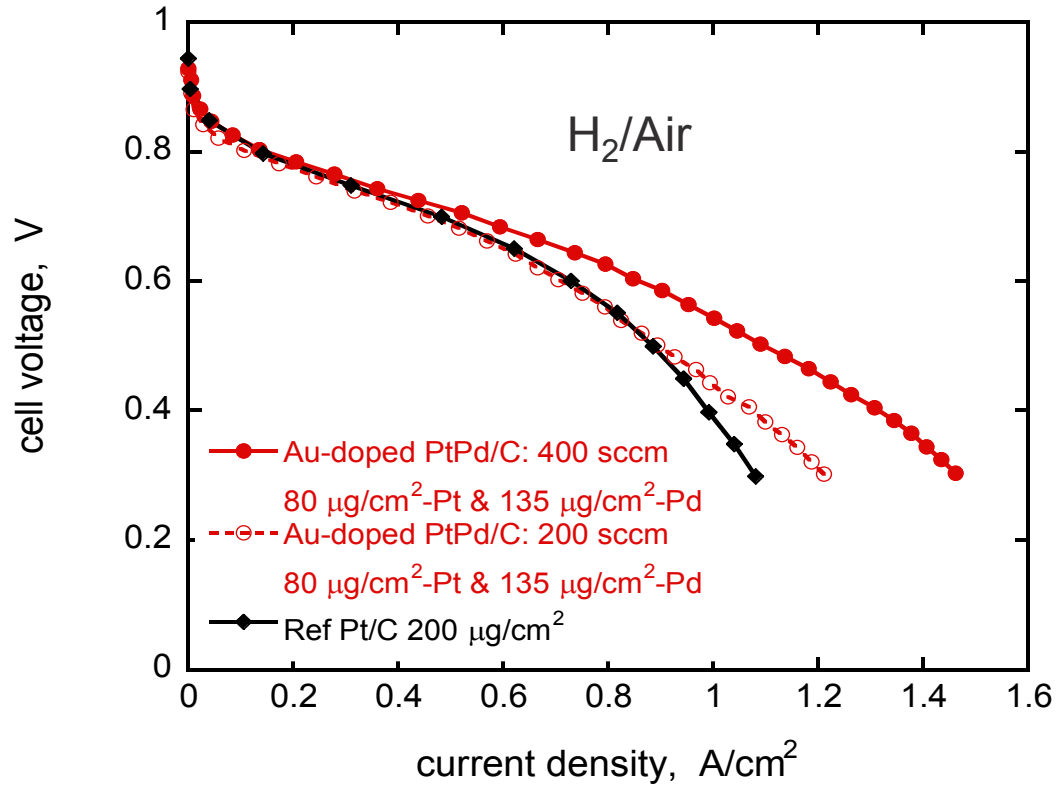
Cathode: BNL Au-doped Pt/Pd/C, air 200/400 sccm, 1.0 bar partial pressure 80 μg/cm²-Pt, 135 μg/cm²-Pd

Anode: Commercial GDE *ca*. 0.2 mg/cm²-Pt H_2, 200 sccm, 1.0 bar partial pressure

Membrane: Nafion 211, Cell Temp 80ºC

Reference: 0.2 mg/cm², anode/cathode, commercial GDEs, 20 wt-% Pt/C

MEA test of Au-doped Pt_{ML}/Pd/C



Large increase of the response at high current density, 1.1 to 1.5 A/cm²

Au atoms in a Pt ML, by its size, can cause some contraction in the surrounding Pt atoms and increase activity and stability

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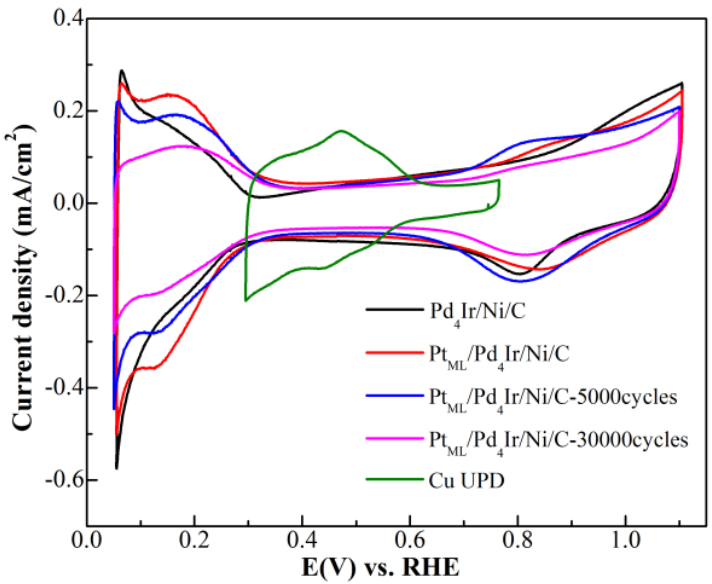
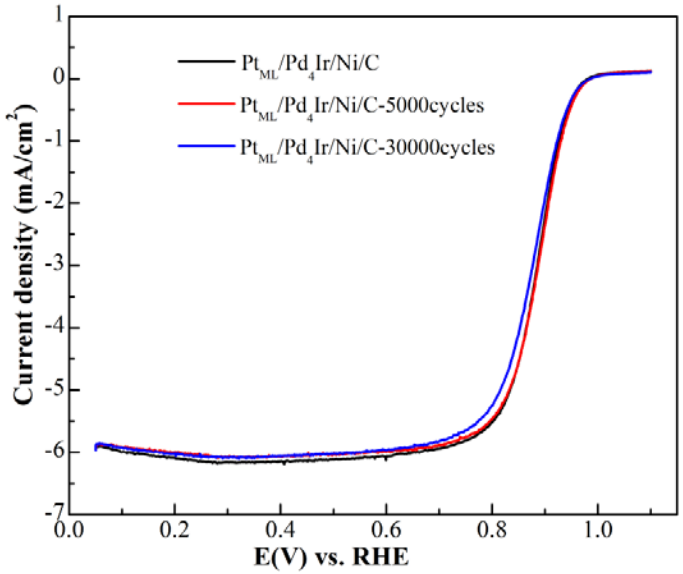
Accomplishments and Progress: Ir-doped $Pt_{ML}/Pd_4Ni/C$

Preliminary data on the effect of small addition of Ir to Pd containing core show a remarkable stability of the catalyst





	0 cycled	5000 cycles	10000 cycles(?)	20000 cycles	30000 cycles
Mass activity (A/mg_{Pt})	1.67	1.68	0.346	1.4	1.35
Mass activity (A/mg_{PGM})	0.155	0.156	0.032	0.130	0.126
Half-wave potential (mV)	884	884	829	878	876

Element	*Wt %*	*At %*
C K	71.22	95.79
PdL	18.85	02.86
NiK	02.67	00.73
IrL	07.26	00.61

Accomplishments and Progress: New Nb Nitride Cores/Substrates

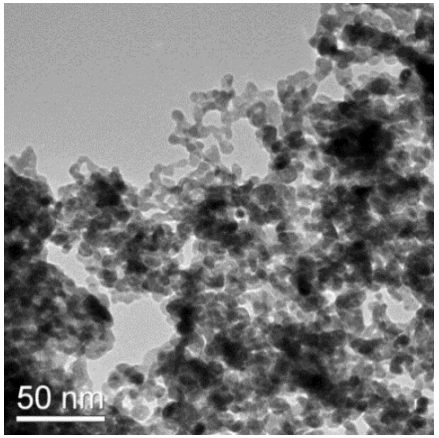
Synthesis of NbN/C (86 wt-%NbN, 14 wt-% C) by ammonolysis and nitridation

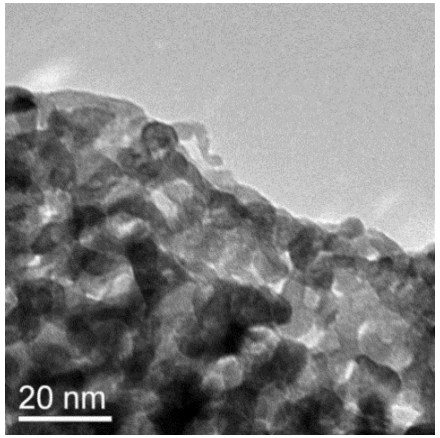
- $NbCl_5$ mix in chloroform with XC72R in Ar
- Flow a NH_3 gas over the solution for 10 h
- Evaporate the solvent at 100ºC under NH_3
- Anneal in NH_3 at 600ºC for 8h (nitridation)

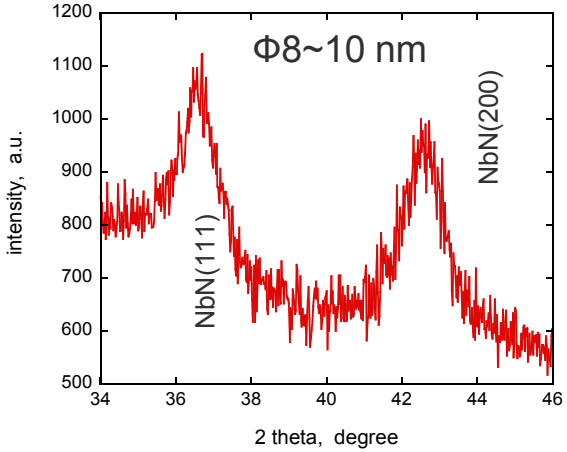
J. Am. Ceram. Soc., **2011**, 94, 2371-2378

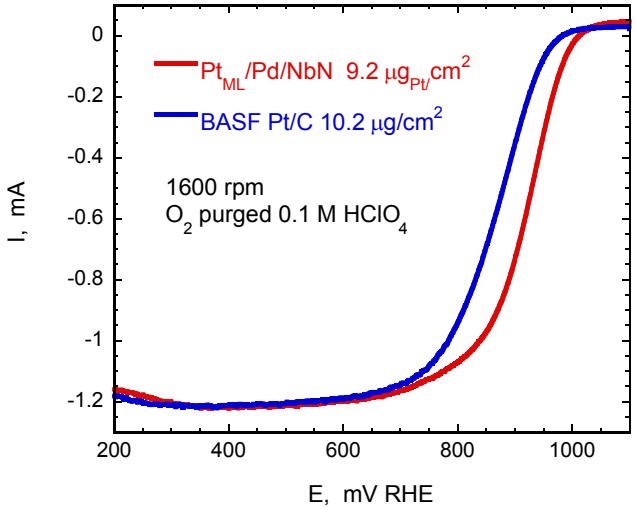
NbN nanoparticles – High conductivity & corrosion resistance

❖ NbN nano-frameworks with high surface area (63.5 m^2/g)









Catalysts	MA (A/mgPGM M_{Pt})	**SA (mA/cm^2)**
Pt/Pd/NbN/C	**1.18**	**0.48**
Pt/C	0.22	0.24

❖ RDE tests showed high ORR activity

❖ Pursue to develop deposition methods of thin Pd interlayers on NbN surfaces

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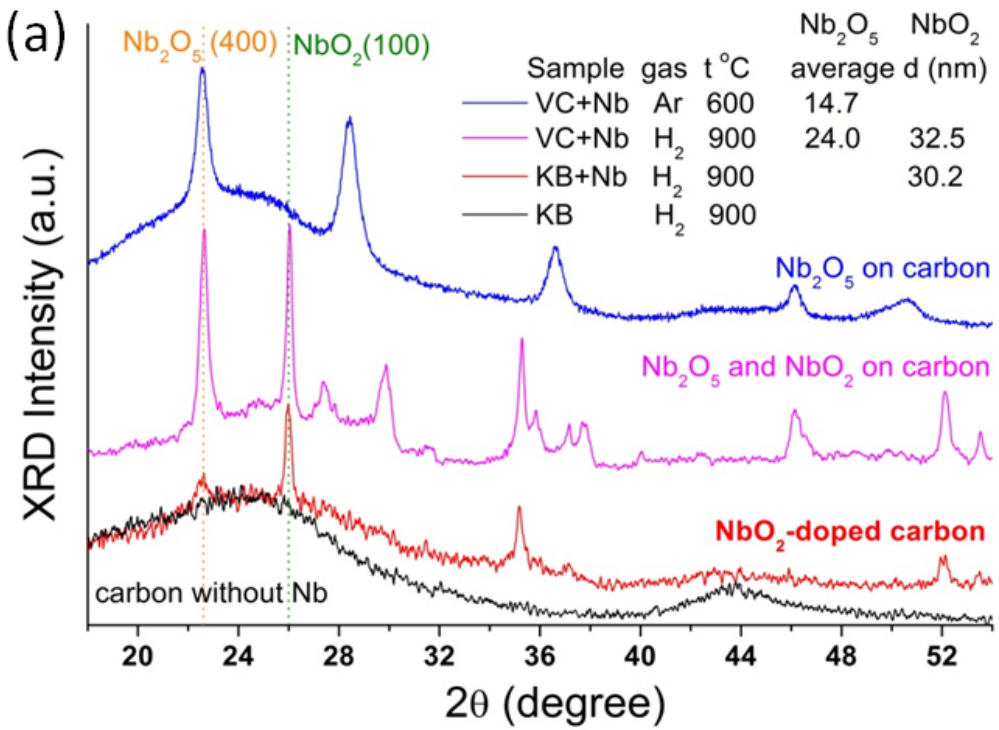
Accomplishments and Progress: NbO_2-doped carbon support for high activity and durability to 1.5 V

At transient potential of 1.5 V accelerated carbon corrosion results in agglomeration of Pt particles and performance degradation.

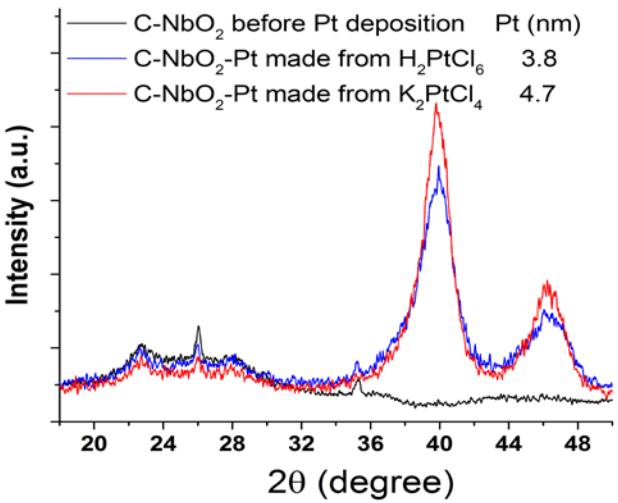
A new promising approach: prevent carbon corrosion, while retain the good catalyst activity by corrosion-resistant NbO_2-doped carbon black.

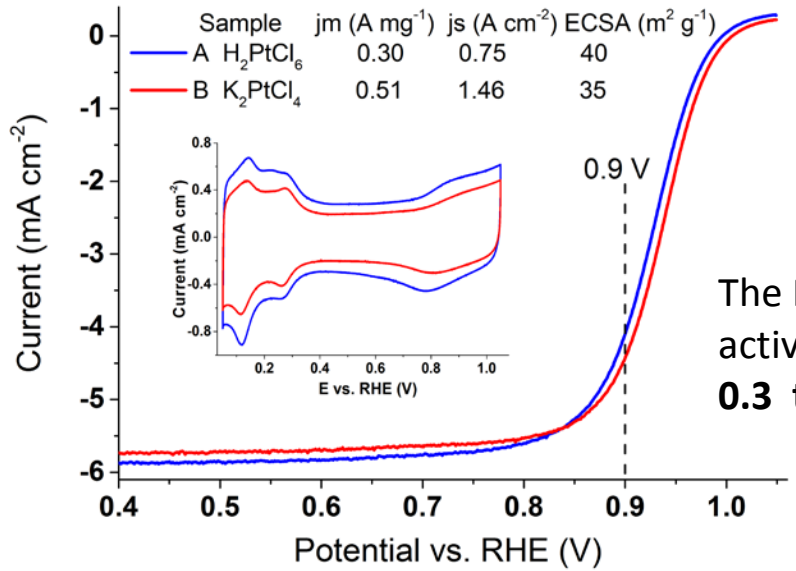


- NbO_2-doped carbon from $NbCl_5$ or Nb ethoxide and H_2 as the reducing agent.
- Nb_2O_5 (**blue**) in the absence of H_2.
- In H_2 at 650 and 900 °C, for Vulcan XC-R72 (VC) (**purple**) peaks for both oxides occur indicting incomplete reduction of Nb(V) to Nb(IV). The Nb_2O_5 peaks nearly vanished for Ketjenblack EC 600JD (KB) (**red**).
- Weakened XRD is due to a large portion of Nb being inside the < 4 nm pores, a small portion is at the KB surface reduced to NbO_2.

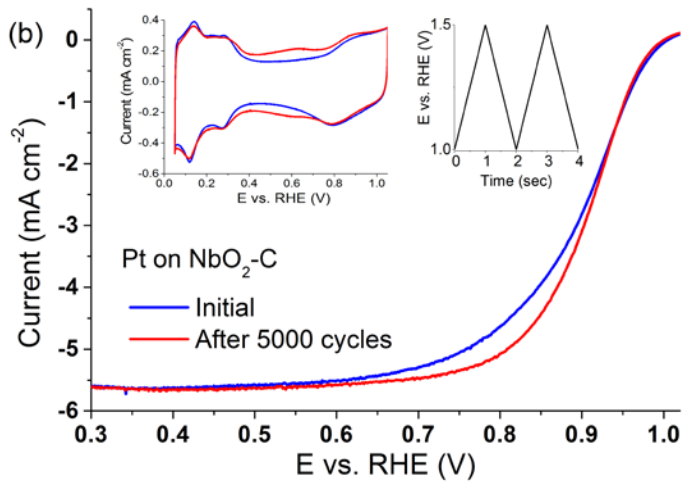
Accomplishments and Progress: ORR activity and durability of Pt on NbO_2-doped carbon

Well-ordered Pt nanoparticles with average diameter about 4 nm were obtained by controlling growth. The catalyst contains **28.9 wt% Pt and ~20 wt% NbO_2** - balance carbon.





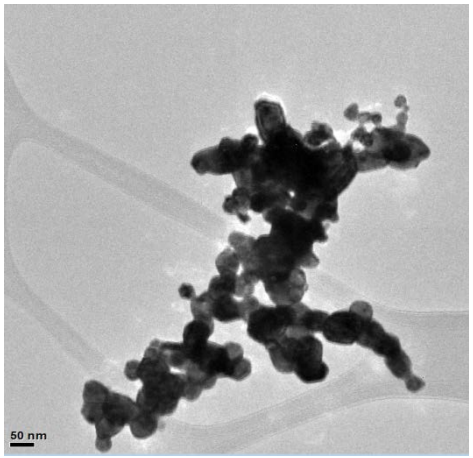
The Pt mass activity at 0.9 V **0.3 to 0.5 A mg^{-1}**



5000 potential cycles from **1 to 1.5V no decay** reflects a very high stability
For Pt/C catalyst
-20 mV shift observed
Pt loading = 26 $\mu g cm^{-2}$

Further activity enhancement is possible with Pt based core-shell catalysts or shaped Pt nanocatalysts.

Accomplishments and Progress: Metallic tungsten nanoparticles as inner cores



Pd6W9/C: 1.04A/mg_{Pt}

0.102A/mg_{PGM}

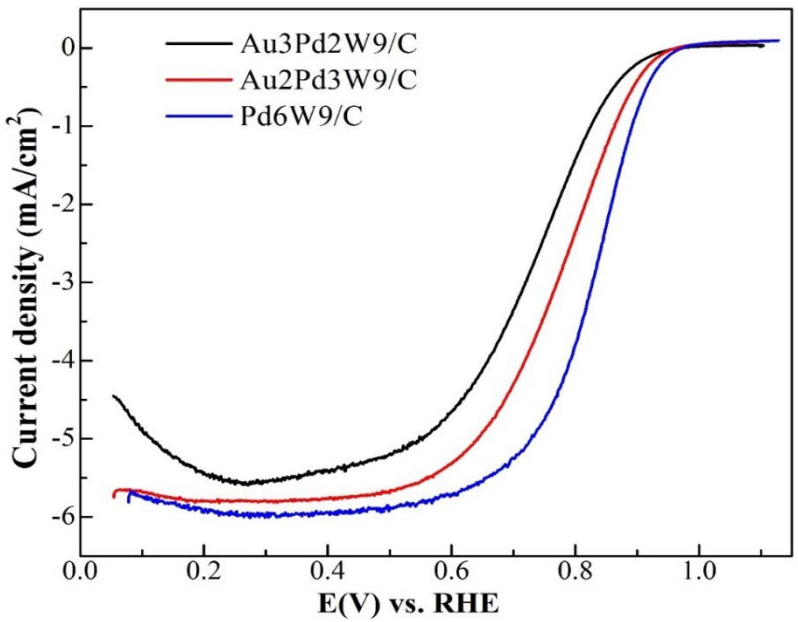
Interlayer of another metal to form a shell is necessary

Propylene carbonate as solvent was used to galvanically displace some W by Pd

Core-shell structure indicated by a lack of W oxidation

Increasing activity as a function of core composition indicate possibility for further improvements

W as a core several obstacles:
1. Synthesis of nanoparticles is complex
2. Half-filled d-band has large electronic effect on adlayers



Pd6W9

Element	Wt %	At %
PdL	28.00	40.19
W L	72.00	59.81

Au3Pd2W

Element	Wt %	At %
PdL	09.11	15.00
W L	66.35	63.19
AuL	24.53	21.81

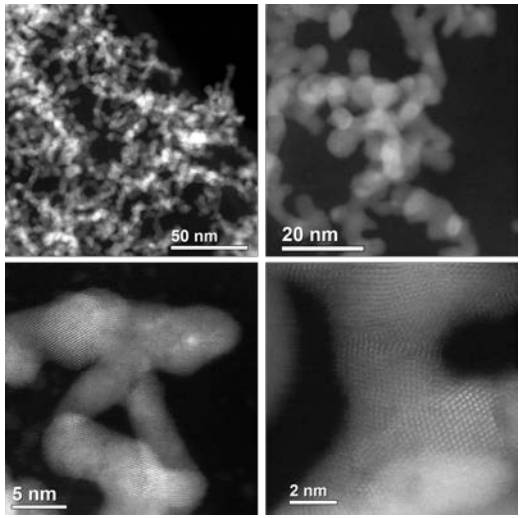
For W NPs preparation: W NPs were prepared via decomposition of fresh prepared tungsten nitrides obtained from WCl_6 in chloroform and NH_3 annealed in NH_3 to 600ºC forms tungsten nitride that decomposes at 800ºC.

Accomplishments and Progress: Pt Monolayer on /PdNi Aerogel

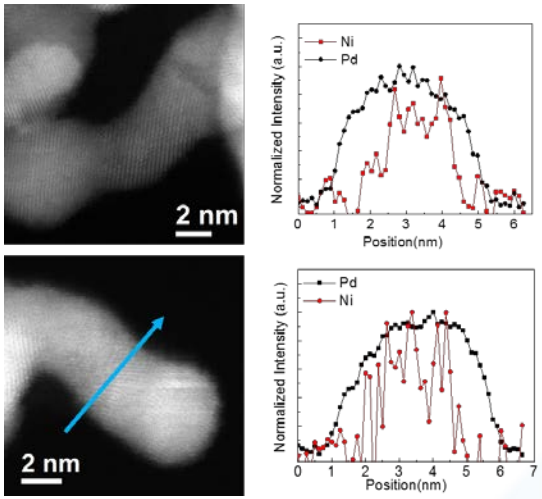
Aerogel synthesis in collaboration with Bin Cai and Alexander Eychmüller, TU Dresden

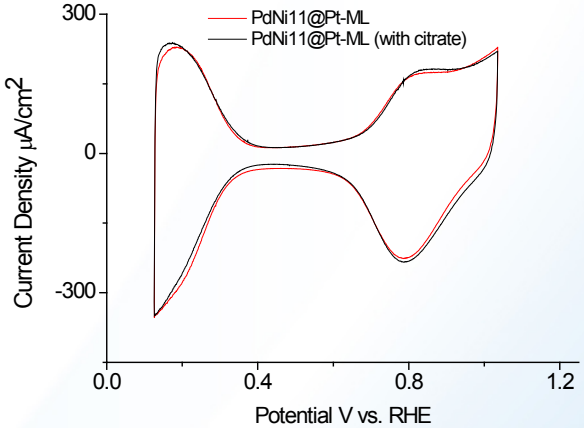
Metallic aerogels advantages: i) rapid electron transfer, ii) large surface area, high porosity (accelerate mass transfer), iii) no support corrosion.

Pd-Ni11%
HAADF-STEM imaging

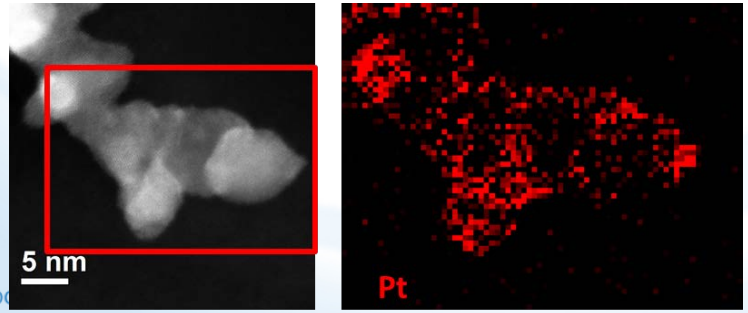


STEM-EELS line scan show a Pd shell and Pd/Ni core

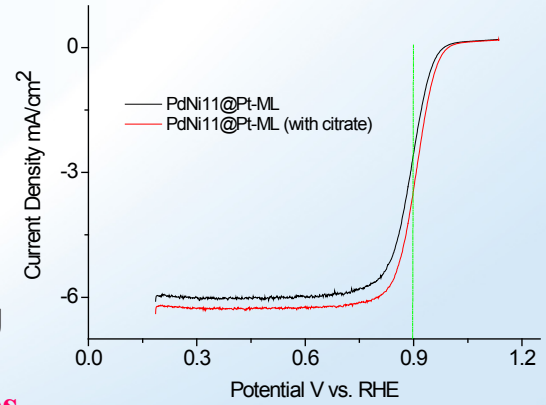




Pt Monolayer on Pd-Ni11%



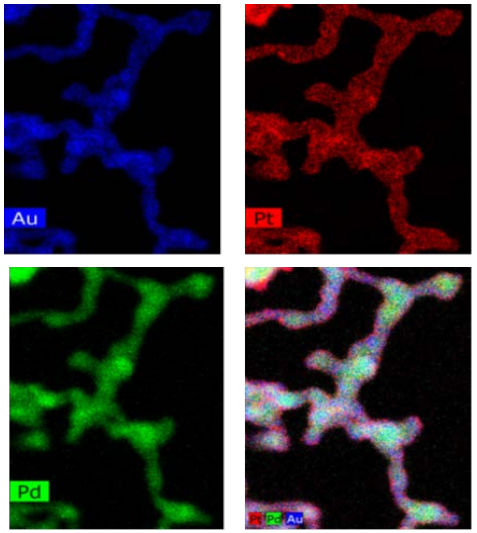
STEM-EELS mapping



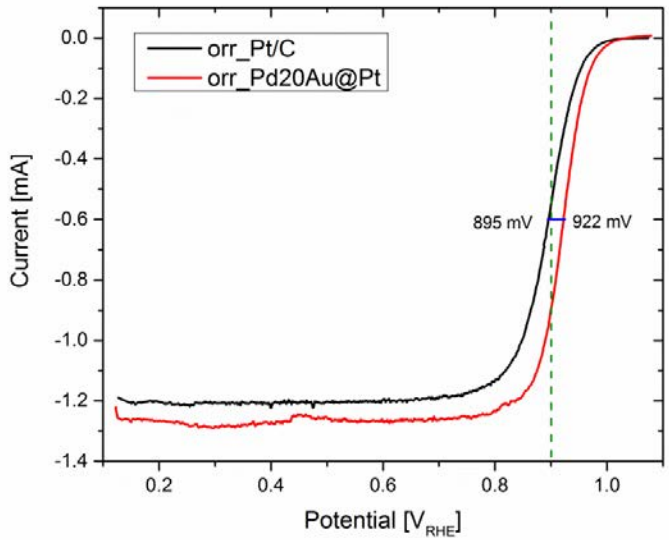
Twinning boundaries beneficial for the ORR

Accomplishments and Progress: Pt Monolayer on $Pd_{20}Ni$ Aerogel

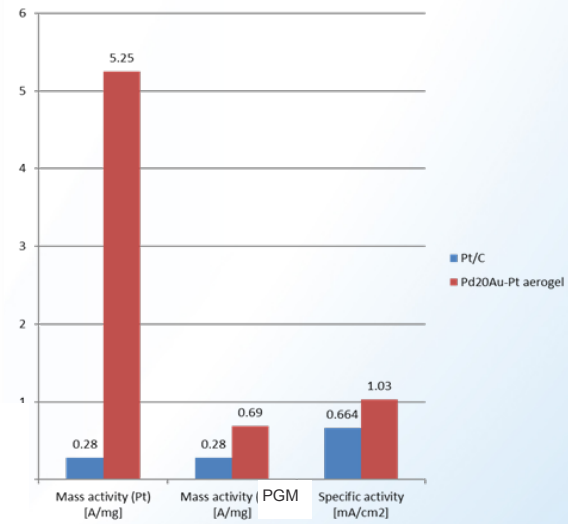
TEM ; EDX Mapping $Pd_{20}AuPt$



RDE test of $Pt/P_{d20}Au$ catalyst



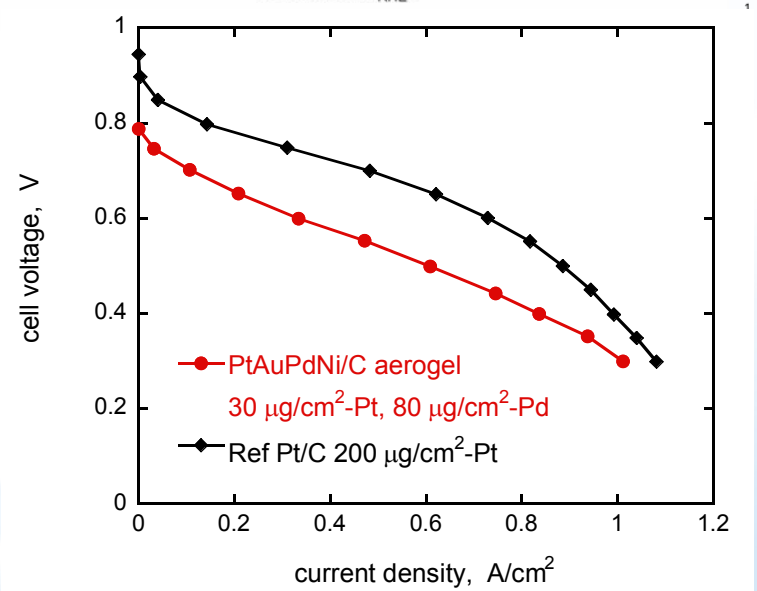
Mass activity
5 A/mg_{Pt}
0.75A/mg_{PGM}



MEA test

Low activity is apparently caused by damage of aerogel structure in making MEA and low Pt content 30 $\mu g/cm^2$-Pt

Cathode: BNL Pt_{ML}/AuPdNi/C, **30 $\mu g/cm^2$-Pt**, 80 $\mu g/cm^2$-Pd, air 200 sccm, 1.0 bar partial pressure, ionomer/carbon (I/C) = 0.4



Core-shell aerogels amplify the enhancement factors of core-shell and aerogel structures

Responses to the Previous Year's Reviewers' Comments

Q1 The project should reduce reliance on RDE testing which does not always predict behavior in MEAs

Q2 BNL needs to move faster toward durability experiments

A1,2 We completely understand these comments and a considerable effort was spent on MEA and durability testing.

Q3 The project would benefit from more formal collaboration with catalysts manufacturers and fuel cells developers for scale up synthesis and MEA testing. The project should interact with the Fuel Cell Consortium for Performance and Durability.

A3 We agree with this comment and actually we are acting along these directions. Separate industrially-funded CRADA efforts are in place with GM and Toyota.

Q4 The project should seek to minimize Au and Pd as much as possible.

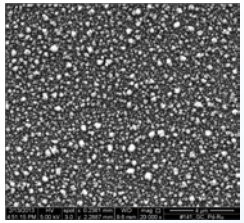
A4 Much of our recent studies have been focused exactly on that point. With some systems a 50% decrease of Pd content has been achieved. Durability tests will follow.

Collaborations

Partners

Los Alamos National Laboratory, Piotr Zelenay PI, Ulises Martinez, co-worker; Catalysts characterization, MEA tests, results discussion and future work.

Pt/Pd/Ru/C by RSD



Collaborators

U. Wisconsin (University) **Manos Mavrikakis,** DFT studies

U. Connecticut, Radenka Maric, reactive spray catalysts deposition (RSD); Finishing equipment construction to avoid any oxidation of refractory metal cores

BNL, Dong Su, Lijun Wu and Yimei Zhu, SOTA characterization of nanoparticles using TEM, STEM,

Ping Liu, DFT calculations

GM (Industry): **Anu Kongkanand, Yun Cai,** MEA tests

Korean Institute for Energy Research, Gu-Gon Park, Catalysts syntheses, nitriding at high preasure.

Technology Transfer

N.E. Chemcat Co. (Industry) **Catalysts synthesis. Licensing agreement for four patents.**

Proposed Future Work

FY 17 and beyond

1. **Optimization of verified synthesis, scale up, and MEA stability tests of Pt ML catalysts having following cores:**
   - NbN-based non-noble metal cores
   - Stabilization of cores by NbO_2 doping carbon.
   - W, WN inner cores covered by tailored outer core for ultimately low cost, high activity and
   - stability ORR catalyst. Optimization helped by DFT calculations

2. Doping Pt ML shell, doping core constituents

- Doping Pt ML catalysts by Au 2D clusters
- Ir doping of Pd or Pd alloy cores, based on its stabilization effects in other reactions. .

Milestone 1 Pt ML catalysts on non-noble metal core to meet the 2020 targets *Completed 20%*

3. Novel strategies to synthesize high performance, Pt monolayer electrocatalysts

- Electrodeposition of refractory metal alloys and earth metals using aqueous, ionic liquids
- and/or non-aqueous solvents.
- Nitriding will be used at ambient and high pressure to stabilize non-noble metal cores.
- Reactive spray deposition of non-noble metal alloys without oxidation of components.
- Improving catalysts response at high CD using Aerogel, functionalized CNTs and designing
- a 3D catalyst layers.

Milestone 2 Improve catalysts response at high CD regions by 80%, from 1.1 to 2 A/cm^2 *Completed 10%*

Summary

MEA tests were carried out with promising Pt ML catalysts including Pt/Pd/C, Au-doped Pt/Pd/C, Aerogel Pt/PdAu and nitride-stabilized Pt/PdNiN/C.

Pt/PdNiN/C similar performance as the control catalyst with higher Pt loading, but below expectation based on the RDE data. Decreased humidification improved its activity to better than that of the control. Improved catalysts are under investigation.

Au-doped Pt ML catalyst showed outstanding activity, with considerably better response in the high current density region (40%) than control.

Aerogel Pt/PdAu poorly performed in MEA possibly because a low Pt content 30 $\mu g/cm^2$, or damaged structure in making MEA. The aerogel supports offer very promising possibilities for future studies.

Two Nb-based cores: NbN is stable core that can support a high activity Pt ML. NbO_2-doped carbon black prevents carbon corrosion up to 1.5 V, while retaining the good catalyst activity.

W as inner core can be modified by outer cores (a thin layer of Pd, or PdAu) is a good possibility to obtain active, stabile catalyst with ultimately low noble metal content.

Publications

Journals:

1. K. A Kuttiyiel, YM. Choi, K. Sasaki, D. Su, SM. Hwang, SD. Yim, T.H. Yang, G.G. Park, R. R Adzic, "Tuning electrocatalytic activity of Pt monolayer shell by bimetallic Ir-M (M=Fe, Co, Ni or Cu) cores for the oxygen reduction reaction", *Nano Energy*, **29** (2016) 261-267.
2. GY. Chen, K. A. Kuttiyiel, D. Su, M. Li, CH. Wang, D. Buceta, CY. Du, YZ. Gao, GP. Yin, K. Sasaki, M. B. Vukmirovic, R. R. Adzic, "Oxygen Reduction Kinetics on Pt Monolayer Shell Highly Affected by the Structure of Bimetallic AuNi Cores", *Chemistry of Materials*, **28** (2016) 5274-5281.
3. M. B. Vukmirovic, K. A. Kuttiyiel, H. Meng, R. R. Adzic, "Controllable Deposition of Platinum Layers on Oxide Surfaces for the Synthesis of Fuel Cell Catalysts", *ChemElectroChem*, **3** (2016) 1635 - 1640.
4. X. L. Tian, J. M. Luo, H. X. Nan, H. B. Zou, R. Chen, T. Shu, X. H. Li, Y. W. Li, H. Y. Song, S. J. Liao, R. R. Adzic, "Transition Metal Nitride Coated with Atomic Layers of Pt as a Low-Cost, Highly Stable Electrocatalyst for the Oxygen Reduction Reaction", *Journal of the American Chemical Society*, **138** (2016) 1575-1583.
5. Y. Li, K. A. Kuttiyiel, L. Wu, YM. Zhu, E. Fujita, R. R. Adzic, K. Sasaki, "Enhancing Electrocatalytic Performance of Bifunctional Cobalt-Manganese-Oxynitride Nanocatalysts on Graphen", *ChemSusChem*, **10** (2017) 68-73.
6. K. E. Ayers, J. N. Renner, N. Danilovic, J. X. Wang, Y. Zhang, R. Maric, H. Yu, "Pathways to Ultra-Low Platinum Group Metal Catalyst Loading in Proton Exchange Membrane Electrolyzers", *Catalysis Today*, **262** (2016) 121-132.
7. M. E. Scofield, YC. Zhou, SY. Yue, L. Wang, D. Su, X. Tong, M. B. Vukmirovic, R. R. Adzic, S. S. Wong, "Role of Chemical Composition in the Enhanced Catalytic Activity of Pt-Based Alloyed Ultrathin Nanowires for the Hydrogen Oxidation Reaction under Alkaline Conditions", *ACS Catalysis*, **6** (2016) 3895-3908.
8. M. E. Scofield, C. Koenigsmann, D. Bobb-Semple, J. Tao, X. Tong, L. Wang, C. S. Lewis, M. B. Vukmirovic, YM. Zhu, R. R. Adzic, S. S. Wong, "Correlating the Chemical Composition and Size of Various Metal Oxide Substrates with the Catalytic Activity and Stability of As-Deposited Pt Nanoparticles for the Methanol Oxidation Reaction", *Catalysis Science & Technology*, **6** (2016) 2435-2450.

Book chapters:

9. K. Sasaki, K. A. Kuttiyiel, J. X. Wang, M. B. Vukmirovic, R. R. Adzic, "Recent Advances of Platinum Monolayer Electrocatalysts for the Oxygen Reduction Reaction" in Electrocatalysts for Low Temperature Fuel Cells: Fundamentals and Recent Advancements, T. Maiyalagan, S. S. Viswanathan (eds) Wiley-VCH Verlag Gmbh & Co. KGaA, Germany, in print.
10. K. Sasaki, "Electrochemical cells for in situ XAS studies" in International Tables for Crystallography: Volume I, X-ray Absorption Spectroscopy and Related Techniques, C. T. Chantler, B. Bunker, F. Boscherini (eds), the International Union of Crystallography (Chester, UK), in print.

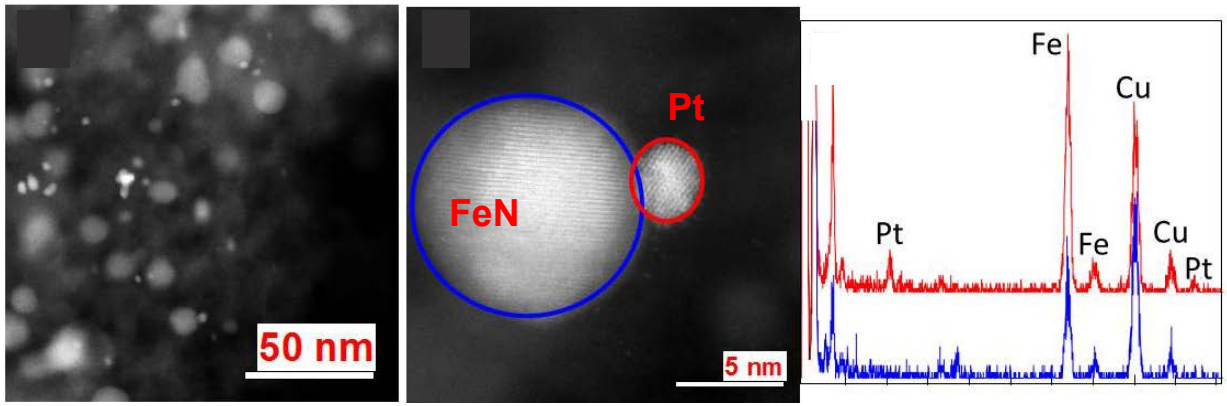
Back up slides

Electrodeposited Janus Nanoparticles for the ORR

Graphene is an interesting support. Pyrolyzed Fe-porphyrin on graphene to compare with carbon.

Potential pulse deposition of Pt on 5% Fe-Porphyrin pyrolyzed at 700ºC in NH_3 on graphene giving FeNC nanoparticles

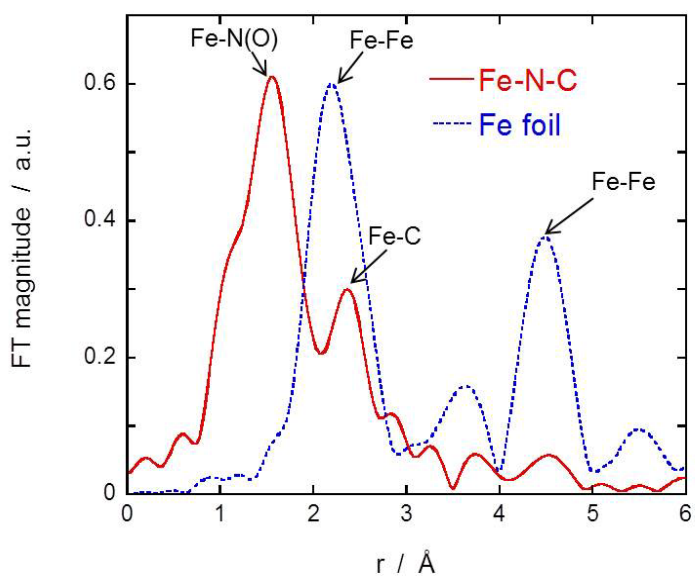
Nucleation of Pt occurs preferentially on Fe.



STEM-HAADF image and EDS of particles after 25000 cycles show large Fe and small Pt particles.

Janus structures - two materials bonded into a single particle.

Synergistic effect increases the durability of the catalyst.



Pt deposition 5 pulses of 1 sec from 0.4-0.9V (RHE), then OCP for 30sec.

Pt loading: 2.1 μg/cm^2

Pt clusters on Fe-N-C nanoparticles encapsulated in graphene layers make stable catalyst for the ORR. **First example in electrocatalysis.**

XAS indicates formation of FeNC

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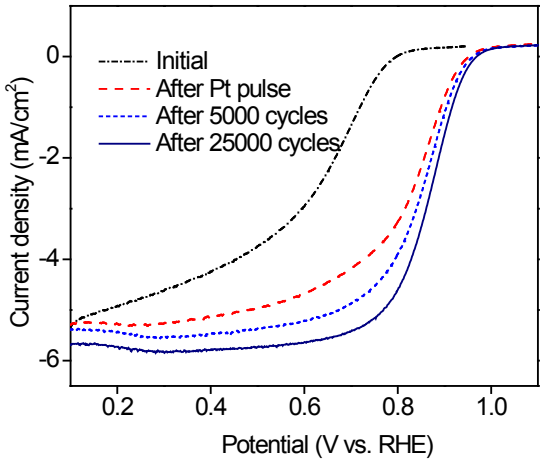
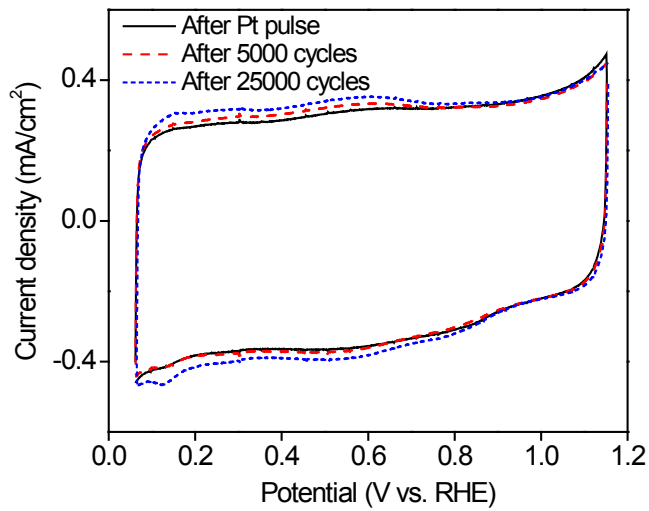
Electrodeposited Janus Nanoparticles for the ORR (cont'd)

New approach to designing of efficient, stable, low-cost electrocatalysts





RDE loading 0.2mg/cm^2
Cycling at 50mV/s from 0.6-1.0 V in air

MA=0.69 - 0.85 A/mg$_{Pt}$

Half wave potentials (mV)		A/mg$_{Pt}$
Initial	633	
After Pt pulse	838	0.69
After 5000 cycles	853	0.73
After 25000 cycles	869	0.85

Increase in synergy between Pt and FeNC changes the electronic structure of Pt and thus increases the ORR activity.

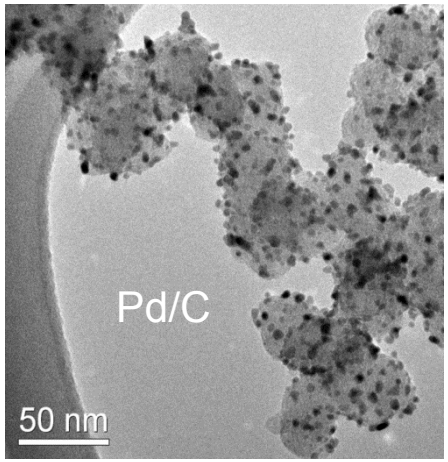
Janus structures play a bifunctional role of tuning Pt and increasing the durability by bonding at the Pt-FeNC interface.

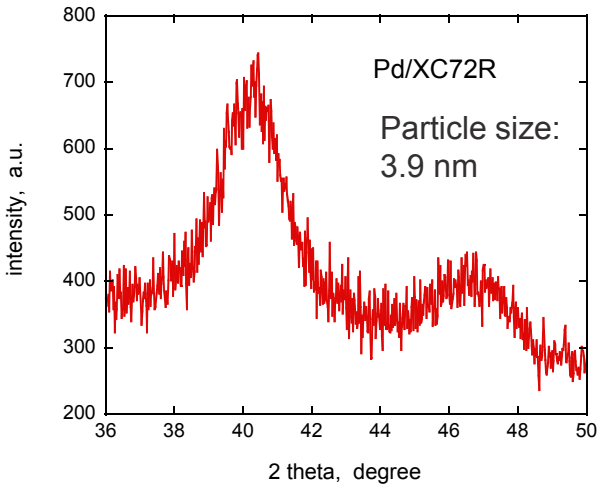
Kuttiyiel, et al., Chem. Comm., 2017,53, 1660

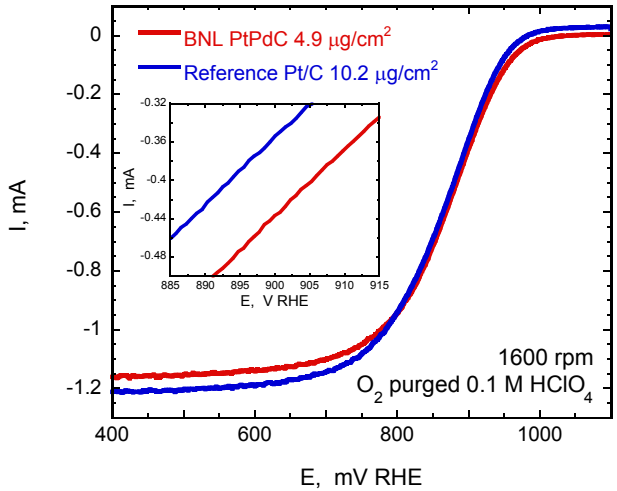
RDE performance of scaled-up BNL Pt_{ML}/Pd/C

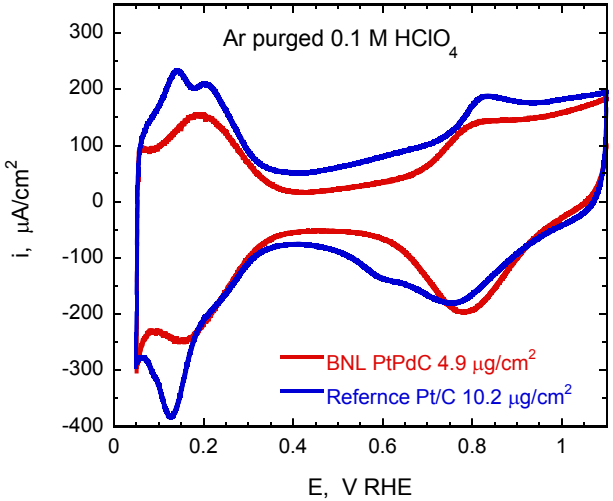
13.8 wt-% Pt, 24.1 wt-% Pd, bal C

- Pd deposited on XC72R by formic acid at room temperature
- Pt monolayers deposited by galvanic replacement of UPD Cu









	MA (A/mg_{Pt})	SA (mA/cm^2)	ECSA (m^2/g)
BNL Pt/Pd/C	0.60	0.45	132
Reference Pt/C	0.24	0.34	72

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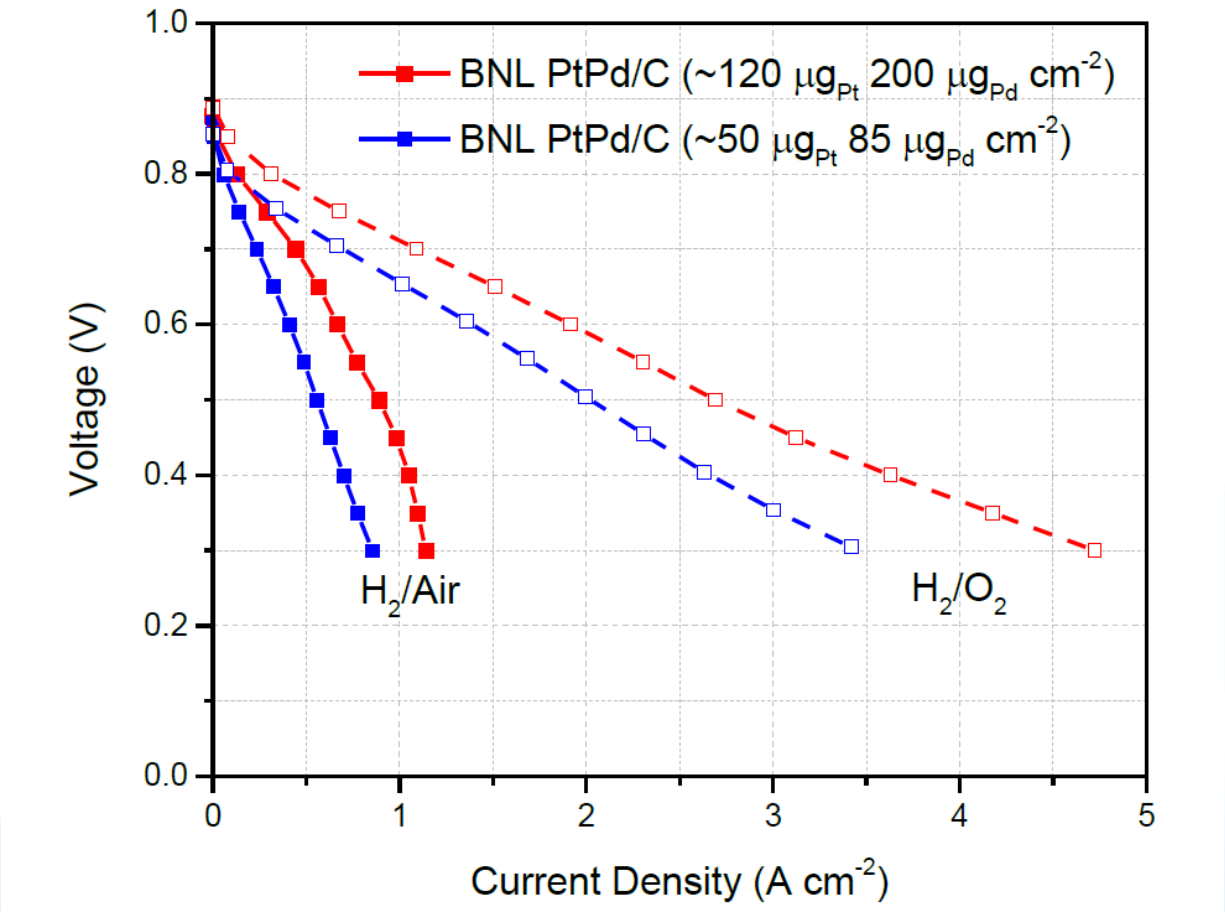
Pt_{ML}/Pd/C recent MEA study

Cathode: BNL Pt_{ML}Pd/C ca. 50-120 $ug_{Pt}cm^{-2}$, 85-200 $ug_{Pd}cm^{-2}$, air or O_2, 200 sccm, 1.0 bar air or O_2 partial pressure; **Anode**: Commercial GDE ca. 0.3 $mg_{Pt}cm^{-2}$, H_2, 200 sccm; 1.0 bar H_2 partial pressure; **Membrane**: Nafion®211; Cell: 80°C; **Reference Fuel Cell**: 0.1 mg cm^{-2} anode; 0.2 mg cm^{-2} cathode; 47 wt.% Pt/C (TKK).

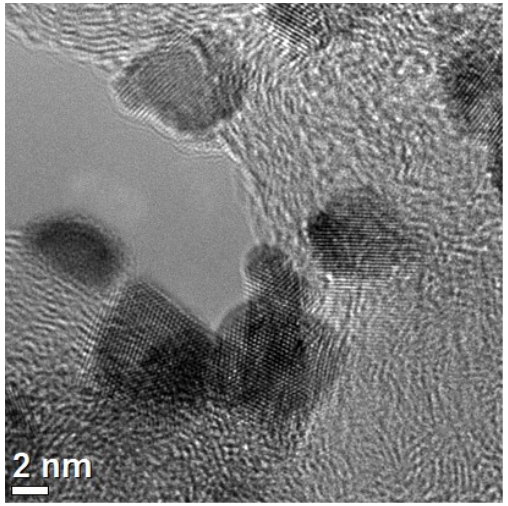


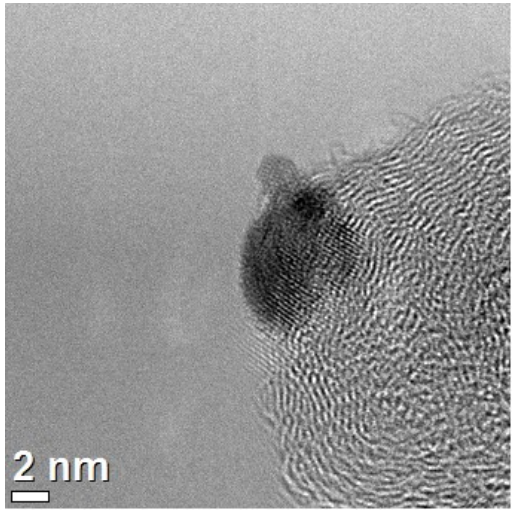
Improving mass transport is necessary with this catalyst in this MEA

Great potential of this catalyst is indicated by 5A/cm2 current density observed with H2/O2 feed

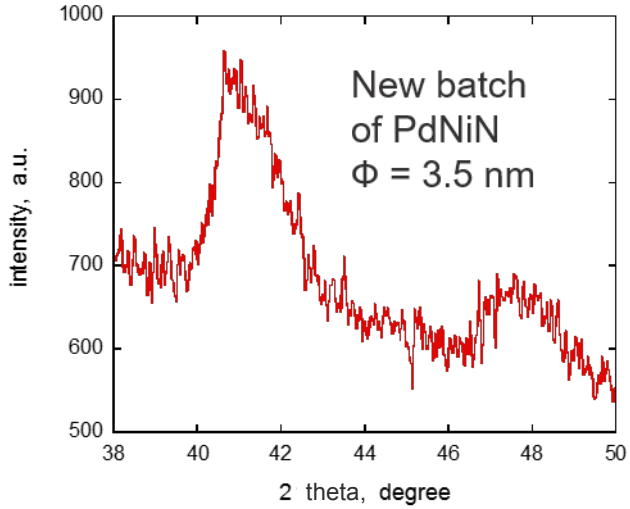
Fuel cell performance for 50 and 120 $\mu g_{Pt}/cm^2$ loadings under oxygen and air

Improvements of Pt_{ML}/PdNiN/C

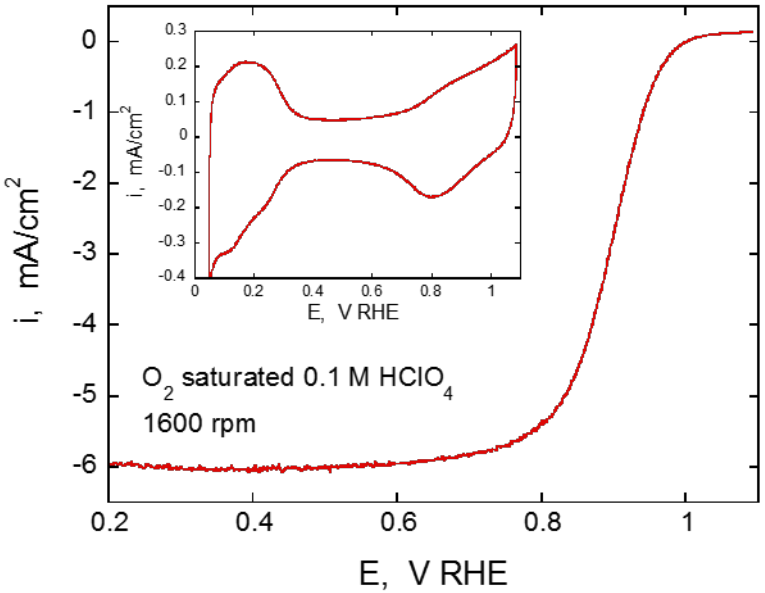




- Improved PdNi synthesis by chemical reduction
  - Use a larger quantity of surfactant (sodium citrate)
  - Slow injection of $NaBH_4$
    - ✓ Smaller particle & narrower distribution



MA (A/mg)	0.55
SA (mA/cm^2)	0.43
ECSA (m^2/g)	129



The sample of this latest batch will be tested in MEAs

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