Project FC009

Contiguous Platinum Monolayer Oxygen Reduction Electrocatalysts on High-Stability-Low-Cost Supports

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Brookhaven National Laboratory

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BROOKHAVEN NATIONAL LABORATORY

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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

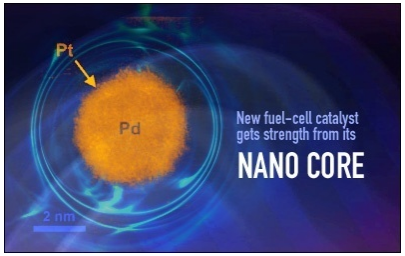
Budget

Funding received in FY14:
$ 650,000
Planned Funding in FY 15:
$ 650,000

Collaborations

Toyota M. C., General Motors, LLC, U. Wisconsin, U. Stony Brook, CFN-BNL, IRD- Fuel Cells, Korean Institute for Energy Research

Relevance



Project objectives:

Synthesizing high performance Pt monolayer (ML) on stable, inexpensive metal or alloy nanostructured electrocatalysts for the oxygen reduction reaction (ORR)

This reporting period:

Increasing activity and stability of Pt monolayer catalysts to meet the DOE technical targets for 2020 by following:

- **Electrodeposition of inexpensive refractory metal alloy nanoparticles on GDLs to fabricate the electrodes of 5, 25, and 50 cm^2 and carrying out MEA tests at BNL and GM.**
- **Further developing the nitriding method to stabilize cores (Pd-Ni) and the stabilization method involving addition of Au to cores.**
- **Demonstrating suitability of Graphene as support for Pt ML catalysts**

Approach

Milestone 1: Verifying new improved synthetic methods

	Completed
❖ Depositing nearly perfect Pt MLs on various cores	100%
❖ Ordering core-monolayer shell interface structure	90%
❖ Nitriding non-noble metal core components for increased stability	80%

Milestone 2: Fabrication of MEAs and tests of selected catalysts

❖ MEA test of Pt/Pd synthesized in ethanol has a PGM activity of 0.4 A/mg; Pt mass activity 0.9 A/mg_{Pt}, at 900mV in O_2.	90%
❖ Pulse – potential deposition of cores on GDL carbon used to obtain 5, 25 and 50 cm^2 electrodes	90%

Milestone 3: The 100% Pt utilization

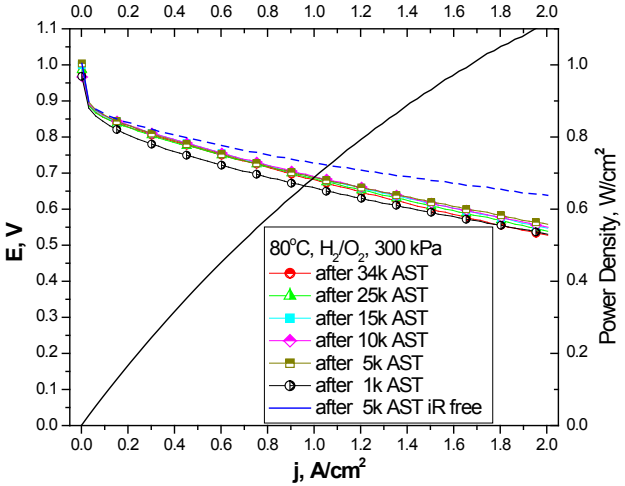
❖ The 100% Pt utilizations has been verified in electrodeposited cores and nanoparticle cores deposited at GDL.	100%

Milestone 4: Graphene as support

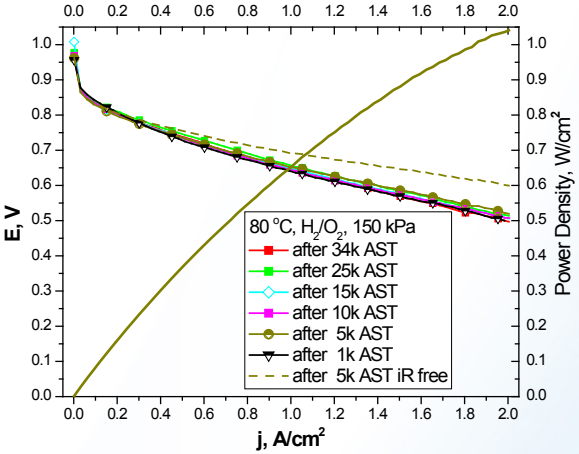
❖ Graphene and reduced Graphene Oxide were successfully used as supports	50%

Accomplishments and Progress: New syntheses of improved catalysts

Co-deposition of W-Ni cores, of the Pt/Pd/WNi catalyst - (Part of Ni displaced by Pd, Pt monolayer placed by UPD Cu displacement)



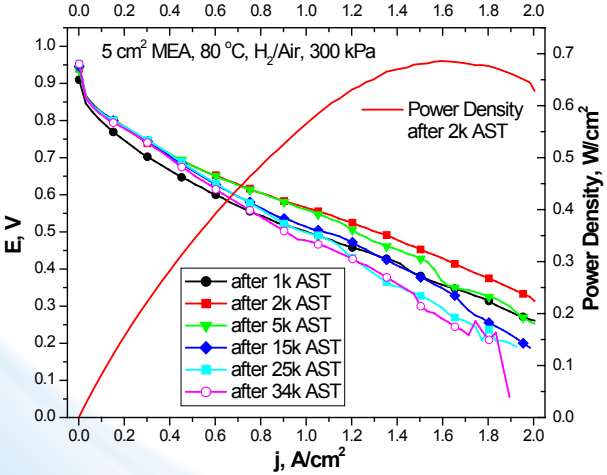
Durability of 5 cm² MEA in H_2/O_2 and H_2/Air

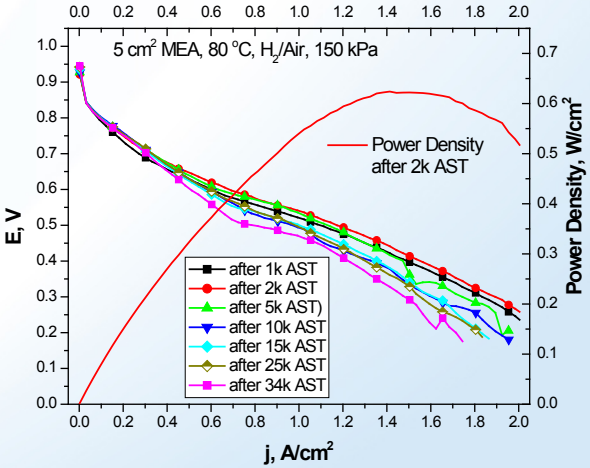


Polarization curves from a 5 cm² MEA with loading of 0.07 mg_{PGM}/cm^2

Pt_{ML}/Pd/WNi/GDL catalyst on the cathode, TKK Pt catalysts (0.05 mg_{Pt}/cm^2) on anode,

Nafion® HP membrane.





- ✓ The mass activity is 0.46 A/mg_{PGM}
- ✓ The loss in the performance at 1.5 A/cm² is only 19 mV after 34000 AST
- ✓ The performance in Air needs to be improved

Accomplishments and Progress: New syntheses of improved catalysts

Durability assessment - summary

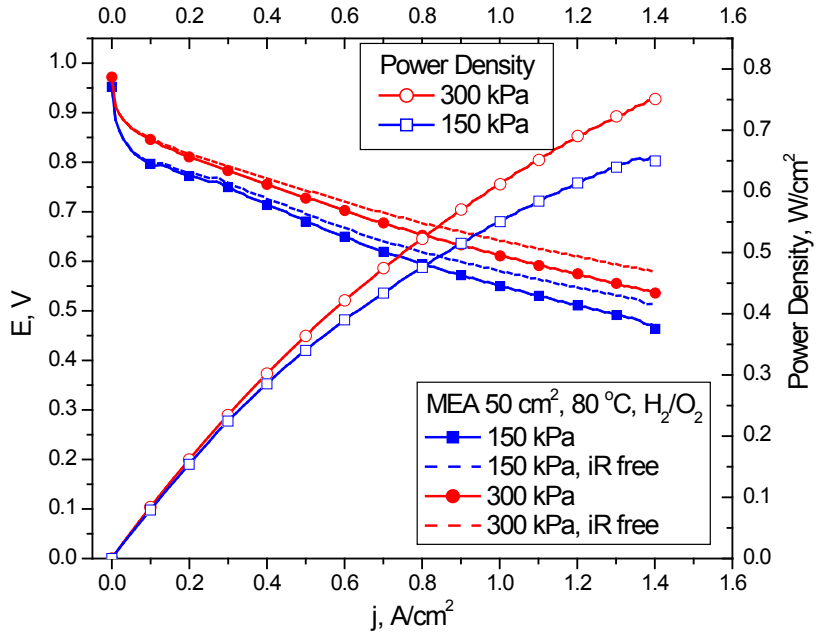
	DOE 2020 targets	Pt_{ML}/Pd/WNi/GDL 80°C, H_2/O_2, 150 kPa	Pt_{ML}/Pd/WNi/GDL 80°C, H_2/O_2, 300 kPa
PGM total loading, mg_{PGM}/cm^2	< 0.125	0.07 mg_{PGM} /cm^2 at the cathode	0.07 mg_{PGM} /cm^2 at the cathode
Loss in performance at 0.8 A/cm^2	< 30 mV	19 mV after 34000 AST	7 mV after 34000 AST
Loss 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

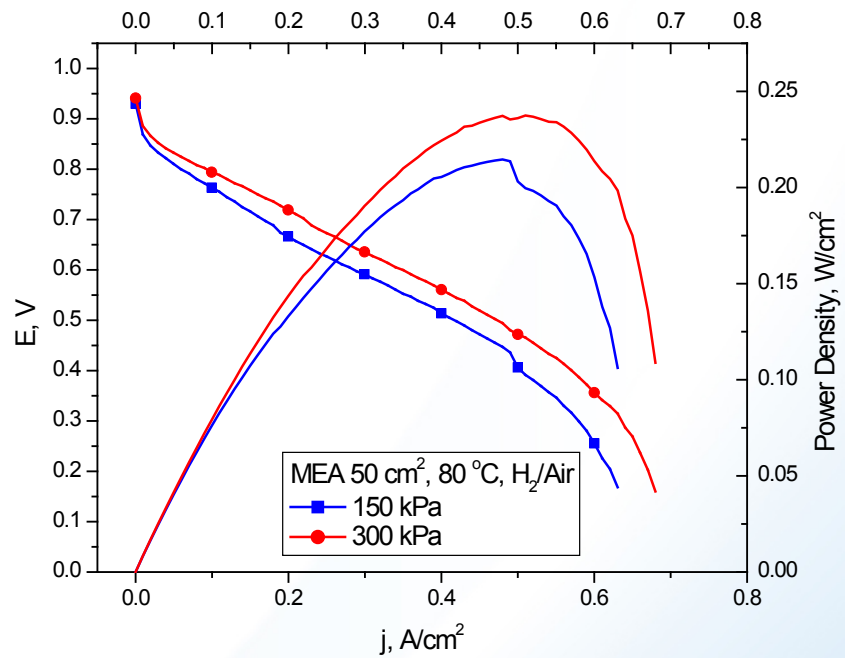
- ✓ Achieved lower PGM loading, and high Pt utilization
- ✓ Surpassed the DOE targets for mass activity, and loss in performance at higher back pressure
- ✓ The performance in Air needs to be further improved

Accomplishments and Progress: New syntheses of improved catalysts

Co-deposition of W-Ni cores, of the Pt/Pd/WNi catalyst

Performance assessment of **50 cm²** MEA





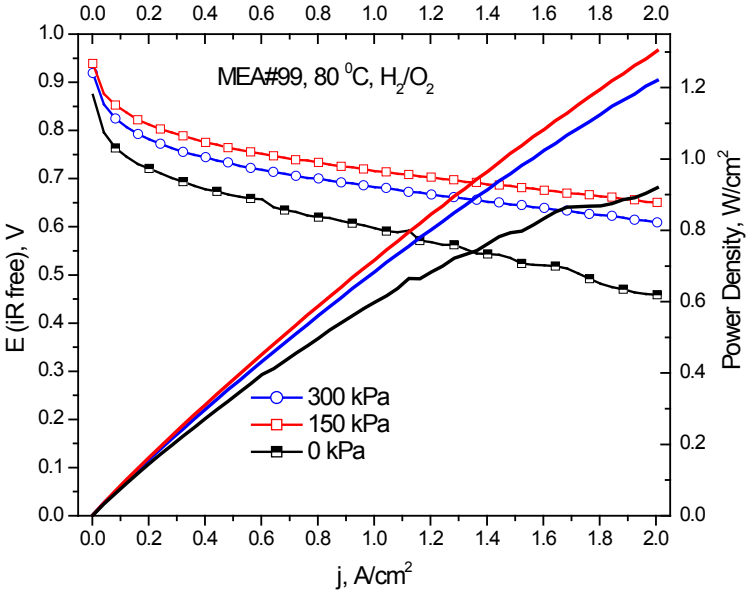
Polarization curves of 50 cm² MEA, assembled with Pt_{ML}/Pd/WNi/GDL cathode, standard Pt/C (TKK 46 %) anode, and Nafion® XL membrane.

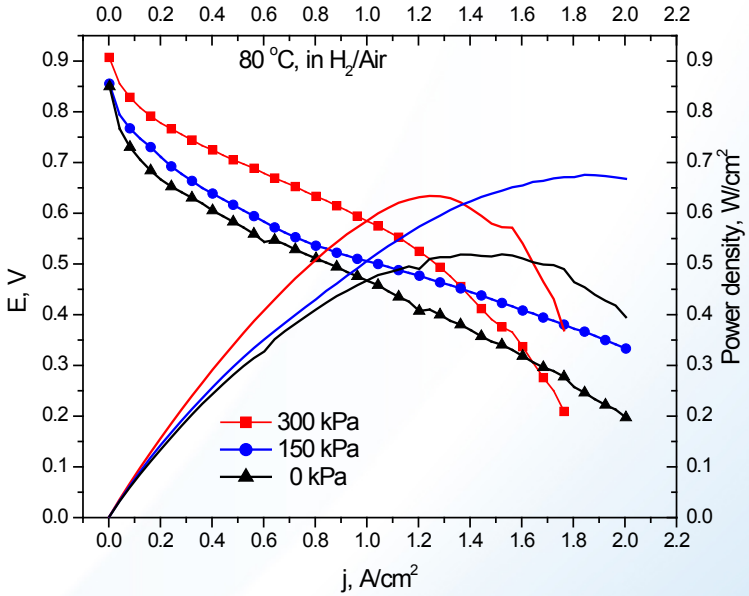
- ✓ Mass activity @ 900mV, iR-free – 0.41 A/mg_{PGM}
- ✓ The performance in Air needs to be improved

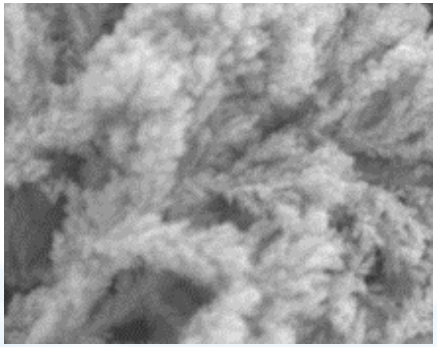
Accomplishments and Progress: New syntheses of improved catalysts

Electrodeposition of **dendritic Pd cores** for zero back pressure of O_2

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







Dendritic Pd deposit , 113 m^2/gr_{Pt}

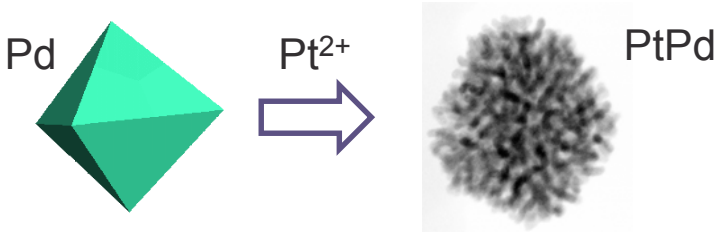
Electrodeposition of dendritic nanostructured cores is a promising strategy for improving the MEAs performance at low or no back pressure, high current density, in H_2/Air feed.

Accomplishments and Progress: New syntheses of improved catalysts

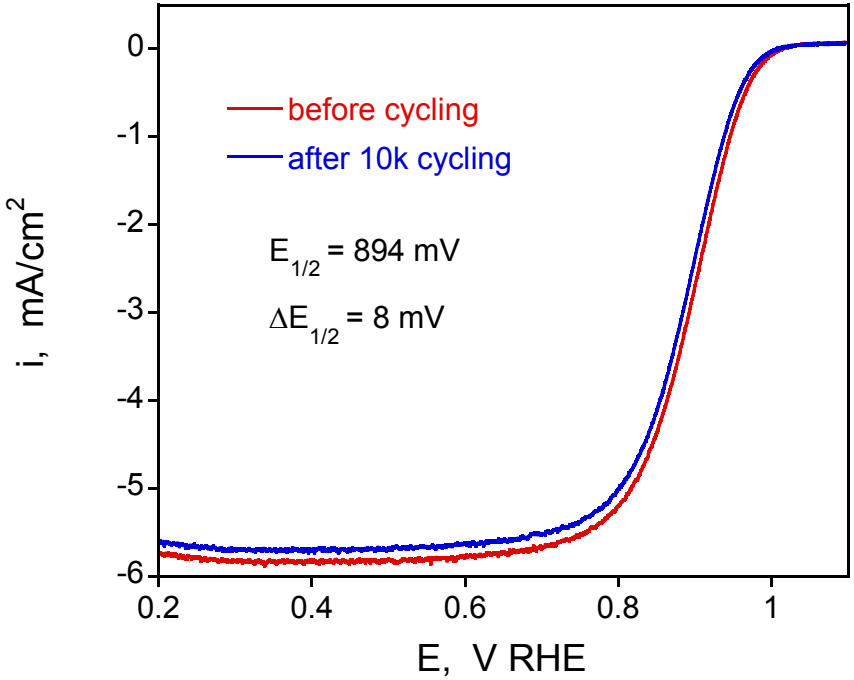
Carbon-supported PtPd dendritic catalysts

- Synthesized by galvanic replacement of Pd on Pd octrahedral template nanoparticles by Pt.

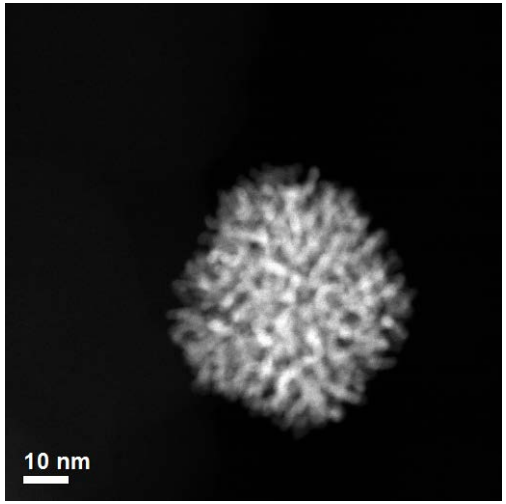
Surfactant:
CTAC (cetyltrimethylammonium chloride)
Reductant: ascorbic acid

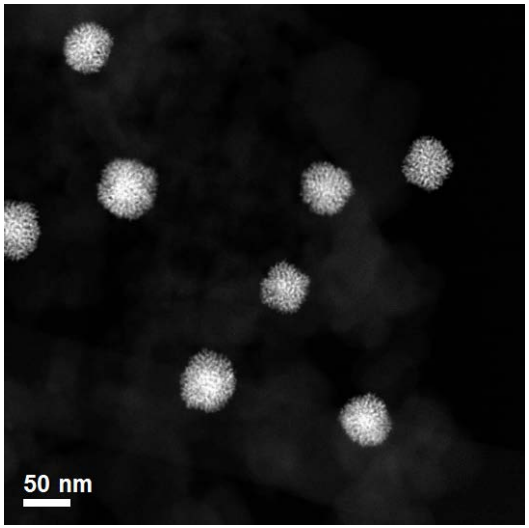


Hong et al., 6(3) ACS Nano, 2410



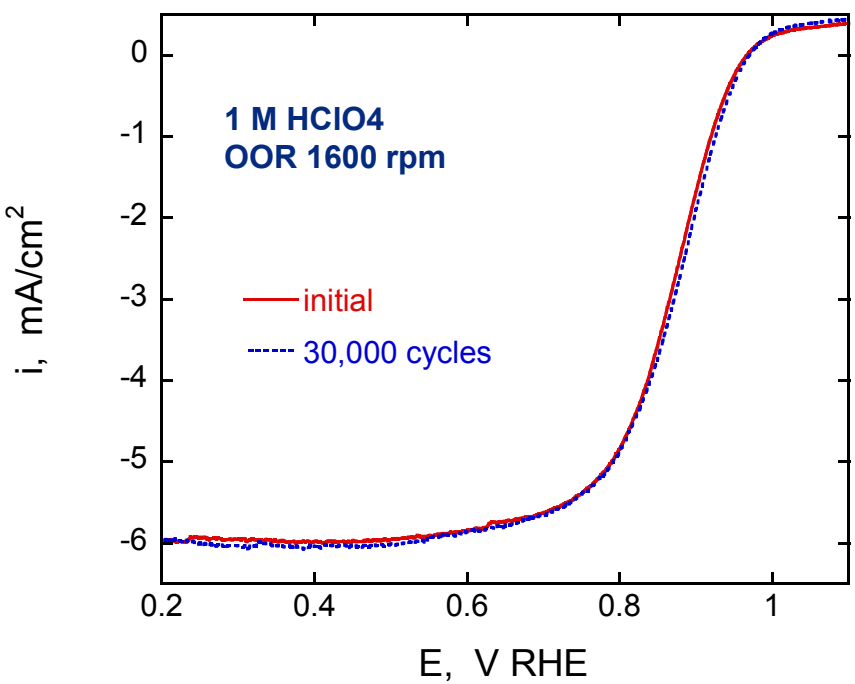
MA: 0.57 A/mg$_{Pt}$
0.39 A/mg$_{PGM}$
SA: 7.9 A/m^2





Using Au to stabilize various cores

Pt_{ML} on Au-modified W compounds



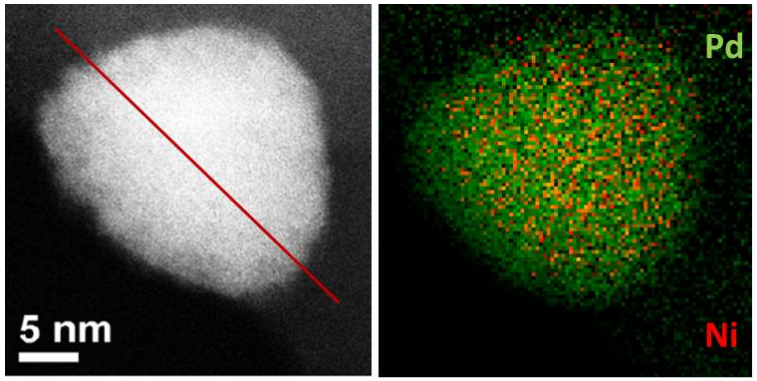
Thermal procedure to modify cores

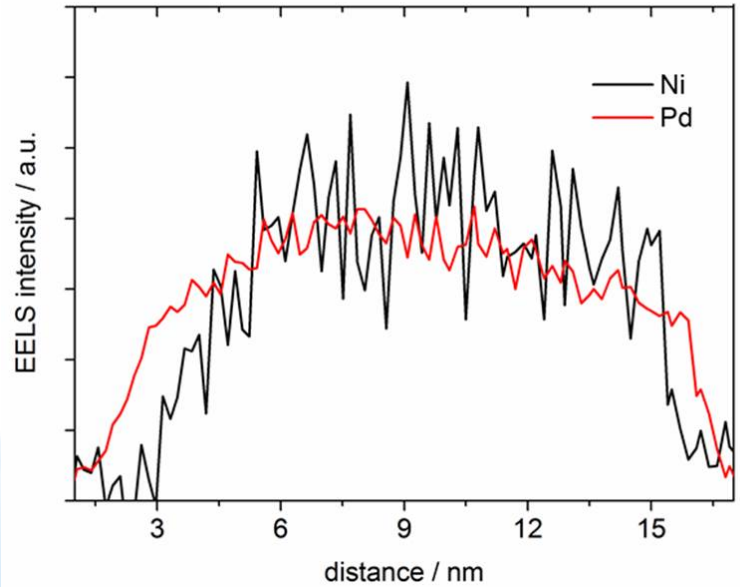
- **Pt ML on Au-W compounds** shows enhanced ORR performance
- No degradation in 30,000 cycles - high stability - **selected for further tests**

Pt Mass Activity: 0.72 A/mg_{Pt}
(Pt + Au) Mass Activity : 0.33 A/mg

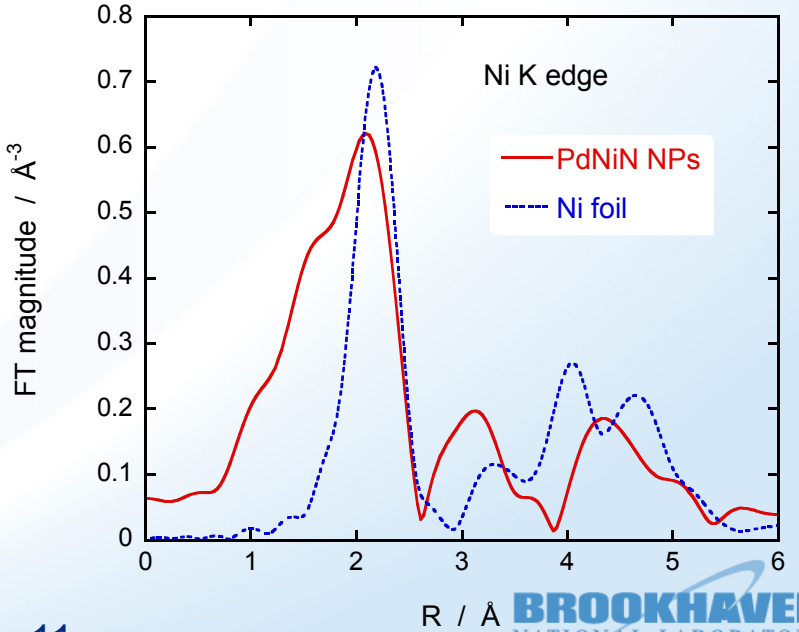
Accomplishments and Progress: **Nitride-stabilized non-noble** core components

Pt_{ML} on nitride-stabilized PdNi core catalysts





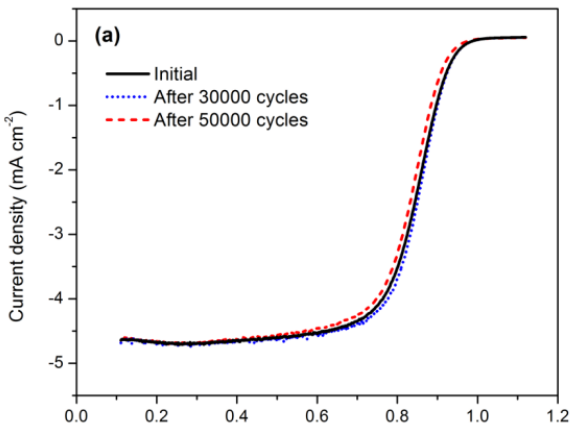
- **$Pd_{50}Ni_{50}/C$** calcinated in N_2 at 250° C for 1 hr and in NH_3 at 510° C for 2 hrs
- STEM/EELS show that Pd atoms segregate on the surfaces
- XAS shows a decrease in Ni bonding due to the formation of Ni nitride

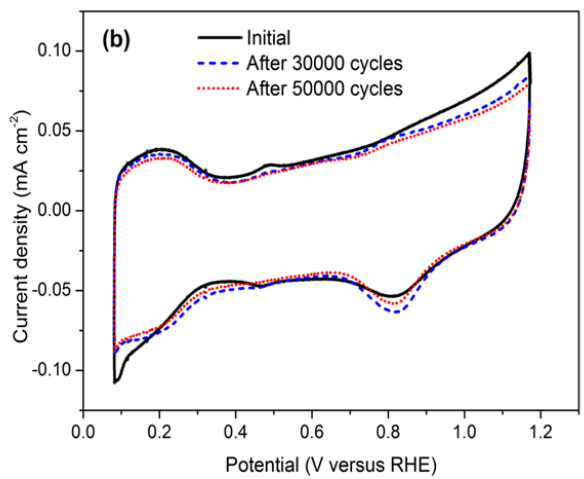


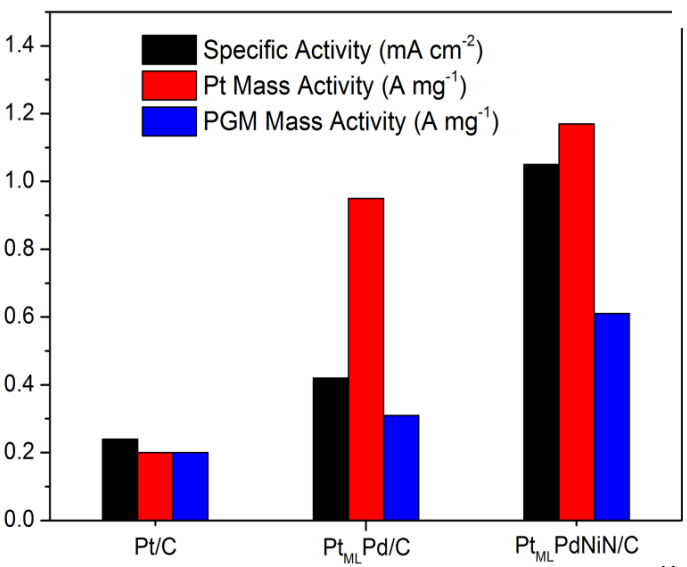
Accomplishments and Progress: **Nitride-stabilized** non-noble core components

Pt_{ML} on nitride-stabilized PdNi core catalysts

Stability : Ni nitride formation stabilizes Ni







Pd content is reduced by 50% in comparison with Pt/Pd/C catalyst, while stability and activity are enhanced

Catalyst	Pt_{ML} $Pd_{50}Ni_{50}$
Pt mass activity j_k/ A mg^{-1}	**1.05**
PGM mass activity j_k/ A mg^{-1}	**0.61**
Specific activity mA/cm^2	**1.17**
ECSA m^2/g $_{Pt}$	**90**
Particle size XRD (nm)	**13**
$E_{1/2}$ / (mV) Initial/ After 50,000 cycles	**850 / 840**

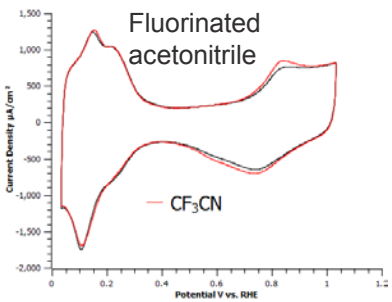
K. A. Kuttiyiel, K. Sasaki, Y. Choi, D. Su, P. Liu, R. R. Adzic, *Nano Letters* 12 (2012) 6266-6271.

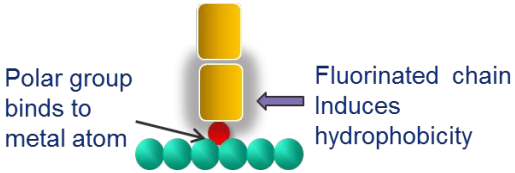
Accomplishments and Progress: Adsorption of fluorinated molecules at Pt and ORR

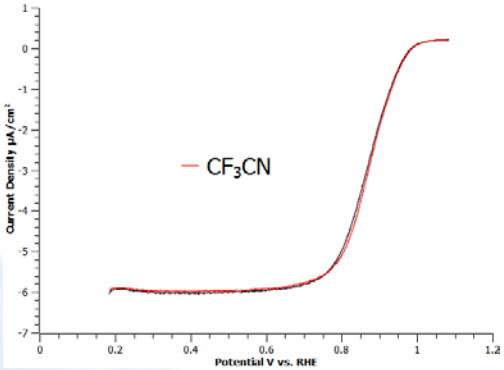
$CF_3(CF_2)_7CH_2CH_2SH$
$CF_3(CF_2)_3CH_2CH_2SH$
CF_3CH_2SH
$(CF_3)_2CHOH$
$(CF_3)_2CO$

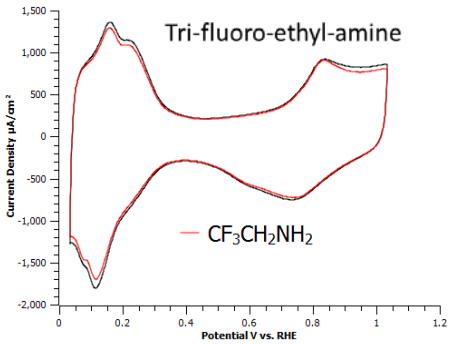
Expected decrease of H_2O activity on Pt similarly as in Yeager's "dry cave" proposition

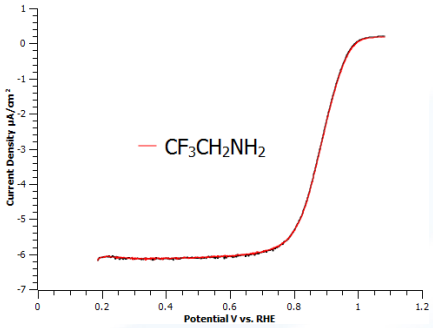
At small coverage of CF_3, a negligible enhancement is observed; inhibition at larger Approach deserves a short additional attention

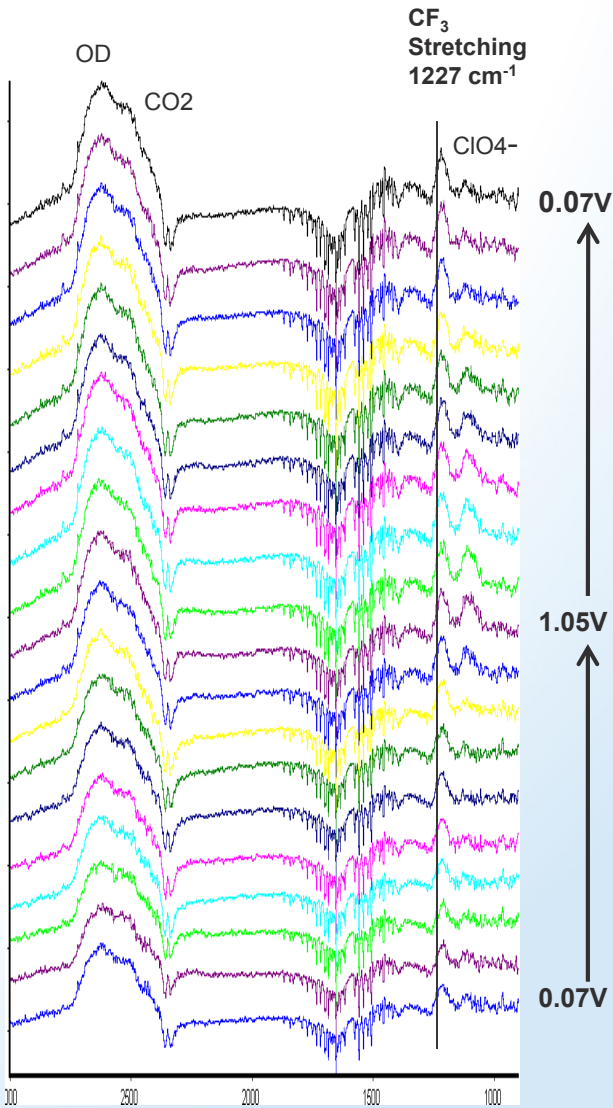












Kanamura, Tanaka, Gervasio, Kennedy, Adzic, Yeager, Burton, Gunerante, Perfluoro – ethylene -1,2-bis-phosphonic acid fuel cell electrolyte. J.Electrochem. Soc. 143, 2765- 2770 (1996).

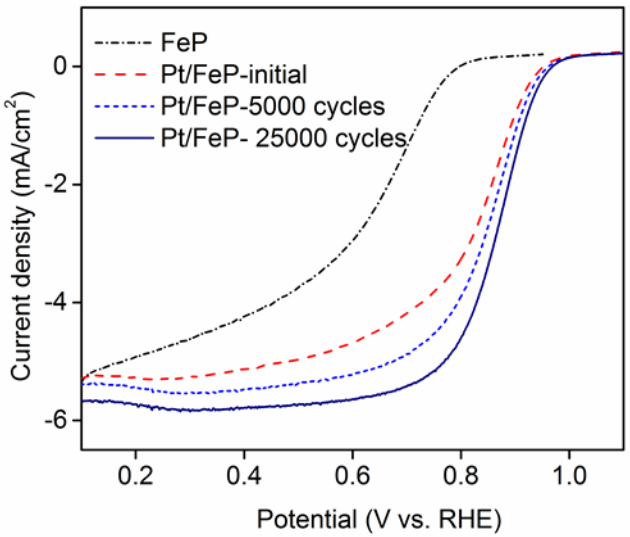
Reductive adsorption of CH_3CN on Pt Morin, Weaver, Conway, J. E.A.C., 421, (1997) 213-220.

Accomplishments and Progress : Graphene as catalysts support

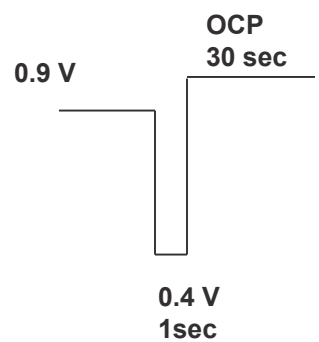
ORR on Pt on annealed Fe Porphyrine (FeP) on Graphene (Gr)

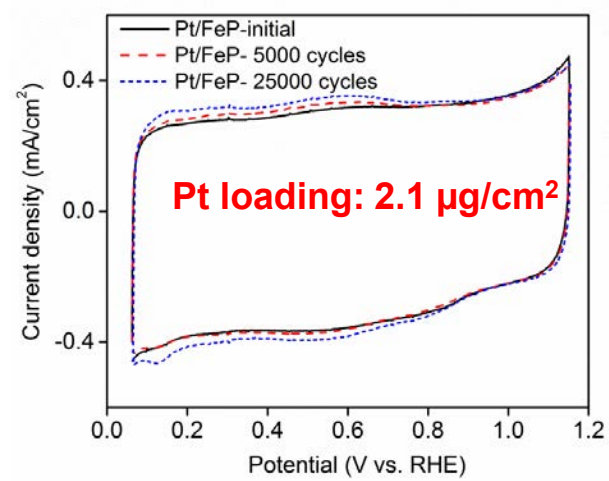
Motivation: Electronic properties of graphene are easily modified by dopants and affect Pt monolayer

Annealing of 5% of FeP on Gr at 700° C in NH_3



Potential pulse deposition of Pt





$E_{1/2}$(mV)		A/mg_{Pt}
FeP	633	
Pt/FeP	838	0.69
Pt/FeP 5000 cycles	853	0.73
Pt/FeP 25000 cycles	869	0.85

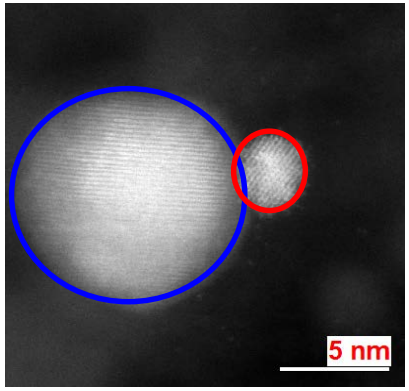
RDE loading 0.2 mg/cm^2
Potential cycling at 50 mV/s from 0.6-1.0 V in air

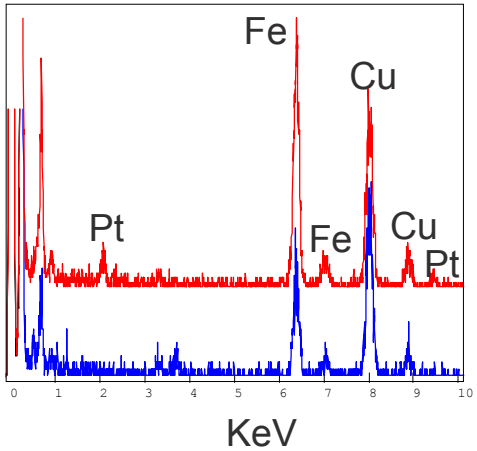
FeP on Gr shows an excellent performance in alkaline solutions

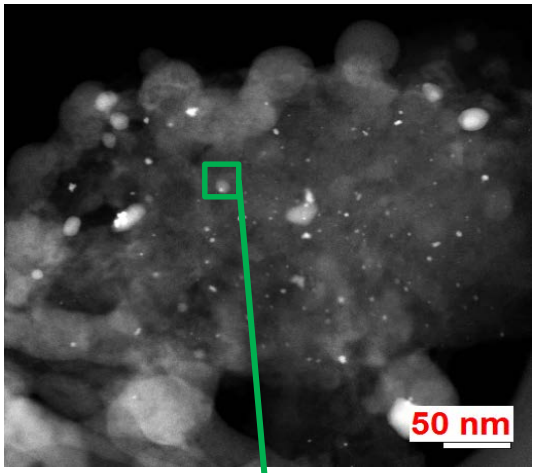
Accomplishments and Progress: Graphene as catalysts support

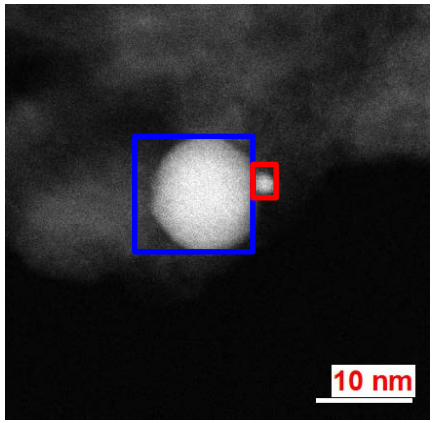
Potential pulse Pt deposition on 5% FeP on Graphene

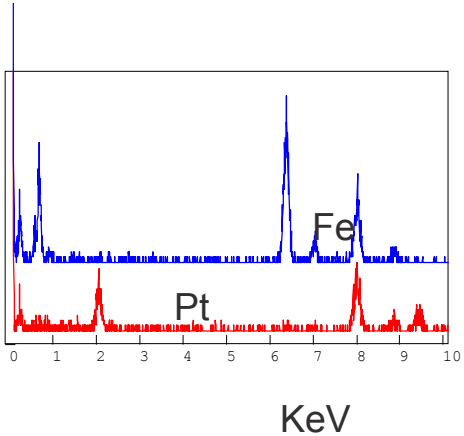
Nucleation of Pt occurs preferentially on Fe;

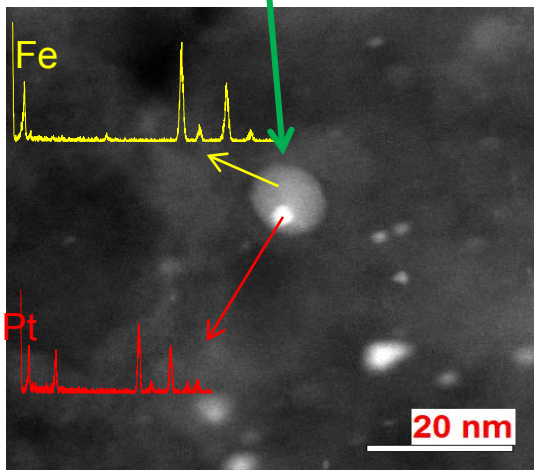












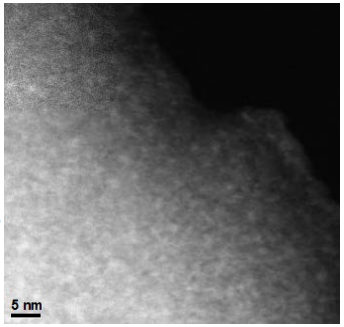
STEM-HAADF image and EDS of particles after 25,000 cycles show large Fe and small Pt particles.

Accomplishments and Progress: Graphene as catalysts support

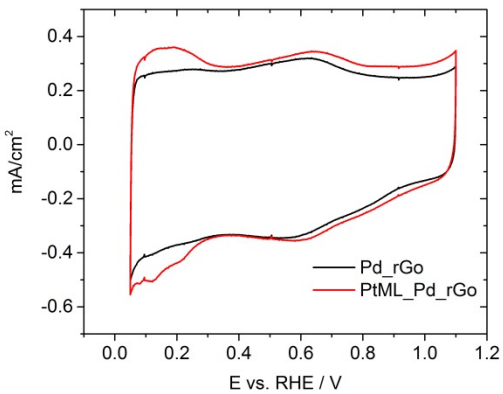
Pt ML on Pd core on reduced Graphene oxide (rGO)

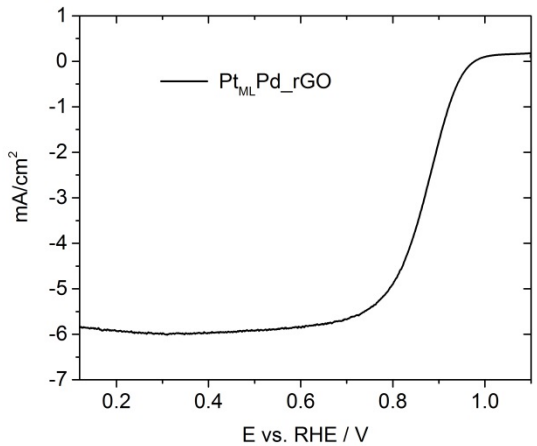
Pd deposited on Reduced Graphene oxide using *Cation, Pb^{2+}, adsorption, Pb^0 displacement* method .

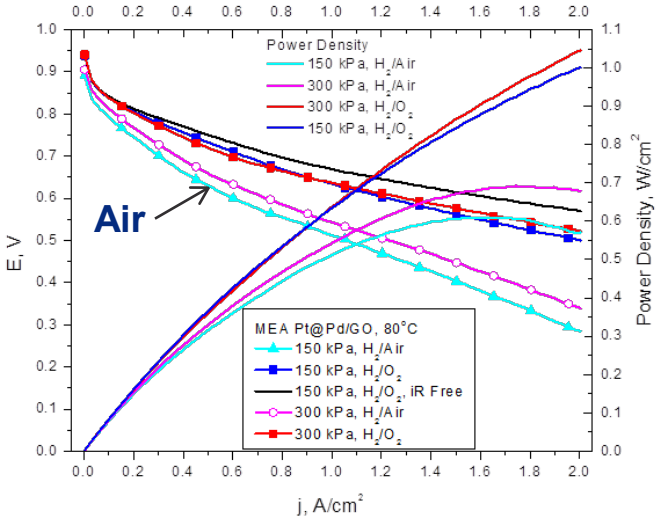
Clusters of Pb deposited on rGO are smaller than 1 nm.



0.1 M $HClO_4$
$E_{1/2}$ = 0.870V







Half Wave potential: 870 mV
Pt Mass Activity: 0.8 A/mg

Cathode- Pt/Pd/GO with PGM loading of 0.114 mg/cm²;
MA_{pgm} = 0.3 A/mg - activation was not sufficient

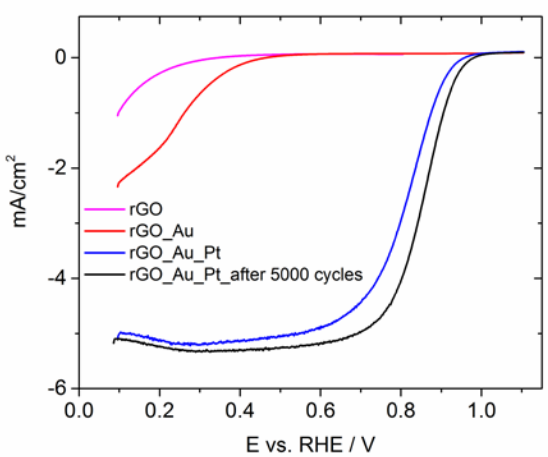
Atomic level control of metal deposition using *Cation adsorption/reduction, atom displacement* is possible with rGO; MEA with rGO has promising properties

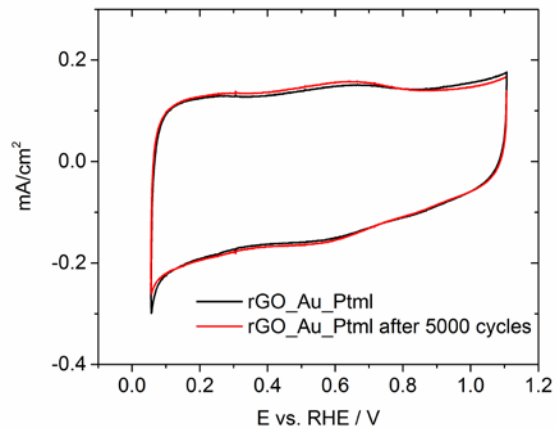
Accomplishments and Progress: Graphene as catalysts support

Pt ML on Au core on reduced Graphene oxide (rGO)

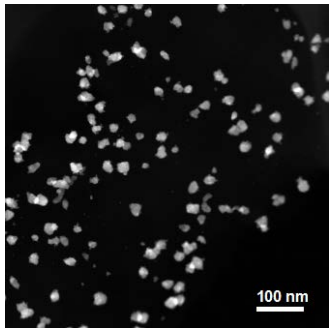
Au deposited on Reduced Graphene oxide using
Cation, Pb^{2+}, adsorption, Pb0 displacement method.

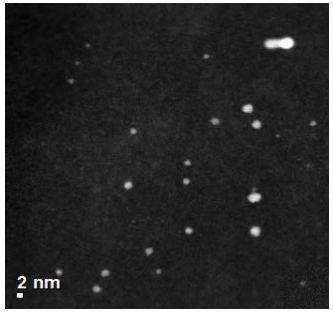
Activity increases, no change in surface area

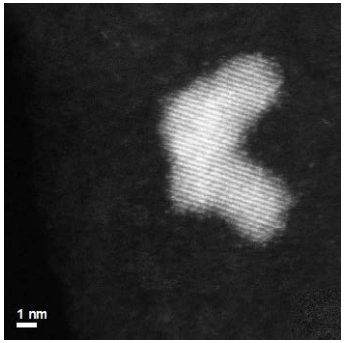




Pt deposited on Au using Cu upd technique
Pt: 2.1 μg/cm²
Pt mass activity after 5000 cycles: 0.6 A/mg



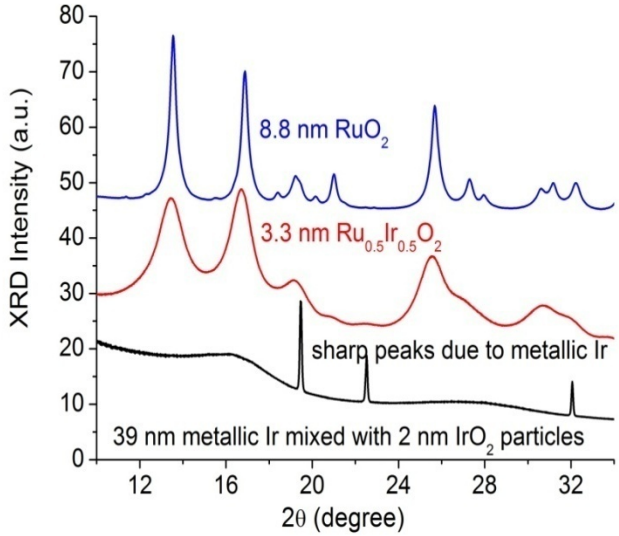


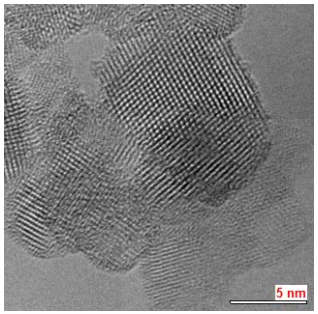


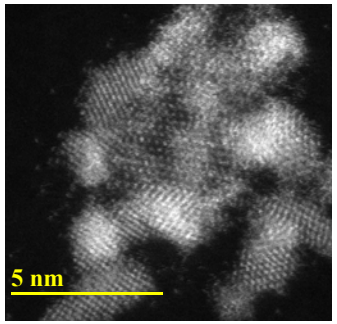
PtML on Au deposited on rGO (after 5000 potential cycles)

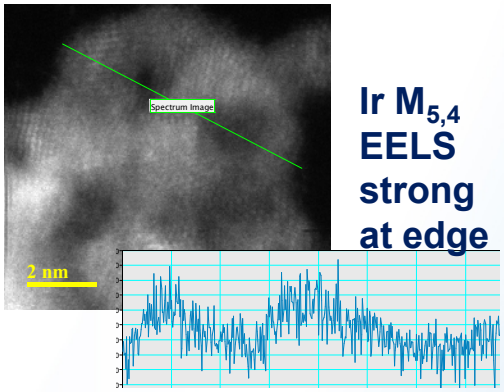
Technical Accomplishments and Progress

Facile synthesis of unsupported RuO_2 and $Ru_{0.5}Ir_{0.5}O_2$ for oxygen evolution





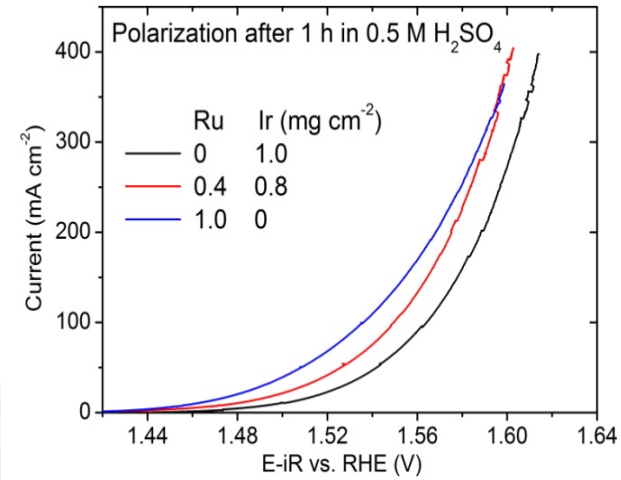




Ir $M_{5,4}$ EELS strong at edge

Clean, ordered, uniform RuO_2

$Ru_{0.5}Ir_{0.5}O_2$
Some core-shell, some mixed



Ru/C → (400 °C, in air, 1 h) → **RuO_2**

Ru/C + H_2IrCl_6 → (400 °C, in air, 1 h) → **Ru@IrO_2**

Formed with a spike of high temperature while carbon is burned out within 10 min, the metal oxide particles are **small in size** and **highly ordered** compared to other thermal synthesis methods, which are important for obtaining a **high surface area, durable** oxide nanocatalysts.

$Ru_{0.5}Ir_{0.5}O_2$ is more active than IrO_2 over large potential region.

Summary

Improvements of Pt ML catalysts, increased understanding of MEAs fabrication, developing new cores and stabilization methods, and using Graphene as support have been accomplished.

Pulse – potential deposition of cores on GDL carbon used to obtain 5, 25 and 50 cm^2 electrodes; the procedure has been further improved.

The MEA mass activity and durability of some catalysts exceed the DOE 2020 targets. Air performance needs improvement.

Stabilization of cores based on nitriding method and Au addition has been improved.

Dendritic deposits cores provide enhanced mass transport conditions for air and improve performance at high current densities.

At small coverage, short chain fluorinated molecules cause a negligible enhancement of the ORR; inhibition is observed at larger ones.

Graphene and reduced Graphene Oxide can be useful supports. Atomic level control of metal deposition using *Cation adsorption/reduction, atom displacement* is possible.

High activity $Ru_{0.5}$-$Ir_{0.5}O_2$ catalyst for the OER has been developed.

Proposed Future Work

FY 15 and beyond

1. **Synthesis and MEA tests**

   Selected Pt ML on nitride, or Au stabilized cores of non-noble and refractory metal alloy, and Graphene-supported cores in 50 cm^2 electrodes. Tests are at BNL and GM.

Milestone one ----------Completed 30%

2. **Stack tests at GM**

Pt_{ML}/Pd/WNi and the catalysts selected from the above MEA tests.

Milestone two ----------Completed 20%

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

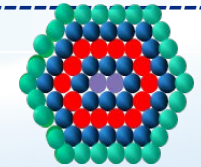
Electrodeposition of refractory metal alloys using aqueous and/or **non-aqueous solvents**.
Nitriding to stabilize non-noble metal cores. Nitriding at **high pressure**.
Graphine as tunable nanoparticle support.
Reactive spray deposition of non-noble metal alloys **without oxidation of components.**

Milestone three ----------Completed 30%

4. **Approaching 1.23V**

   Onion-structured nanoparticles with new cores of multiple metal layers to tune Pt monolayer properties and shift E° closer to 1.23 V. Supporting DFT calculations have been completed.

Milestone four ----------Completed 20%



Collaborations

Toyota Motor Company (Industry) **Makoto Adachi, Toshihiko Yoshida** MEA tests.

U. Wisconsin (University) **Manos Mavrikakis,** collaboration on theoretical calculations

U. Connecticut, Radenka Maric, reactive spray catalysts deposition

Center for Functional Nanomaterials, BNL Ping Liu, DFT calculations;
Eli Sutter, Dong Su and Yimei Zhu, TEM, STEM

GM (Industry) **Anu Kongkanand, Yun Cai**

IRD Fuel Cells, (Industry) **Madeleine Odgaard**

Korean Institute for Energy Research, Gu-Gon Park

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

Publications

1. Flame-Based Synthesis of Core-Shell Structures Using Pd-Ru and Pd Cores, J. Roller, H. Yu, M.B. Vukmirovic, S. Bliznakov, P.G. Kotula, C.B. Carter, R.R. Adzic, R. Maric, Electrochim. Acta, 138 (2014) 341–352.
2. Electrocatalysts for the Oxygen Reaction, Core-Shell Electrocatalysts, Miomir B. Vukmirovic, Encyclopedia of Applied Electrochemistry, Gerhard Kreysa, Ken-ichiro Ota, and Robert F. Savinell (Eds.), Springer, New York (2014), pp. 437-443.
3. Electrochemical Atomic-Level Controlled Syntheses of Electrocatalysts for the Oxygen Reduction Reaction, Stoyan Bliznakov, Miomir Vukmirovic, Radoslav Adzic, Atomically-Precise Methods for Synthesis of Solid Catalysts, Sophie Hermans and Thierry Visart de Bocarme (Eds.), RSC Catalysis Series No. 22, The Royal Society of Chemistry, 2015, 144-166.
4. High Performance Pt Monolayer Catalysts Produced via Core-Catalyzed Coating in Ethanol, Yu Zhang, Yu-Chi Hsieh, Vyacheslav Volkov, Dong Su, Wei An, Rui Si,Yimei Zhu, Ping Liu, Jia X. Wang, and Radoslav R. Adzic, ACS Catal. 2014, 4, 738−742.
5. Gold Nanocrystal Surfaces Reveal Anomalous Four-electron Oxygen Reduction in Alkaline Solution, Fang Lu, Yu Zhang, Deyu Lu, Dong Su, Mingzhao Liu, Yugang Zhang, Jia X. Wang, Radoslav R. Adzic, and Oleg Gang submitted to Nature Chemistry.
6. Enhancement of the oxygen reduction on nitride stabilized Pt-M (M=Fe, Co, and Ni) core–shell nanoparticle electrocatalysts, K.A. Kuttiyiel, Y.M. Choi, S.-M. Hwang, G.-G. Park, T.-H. Yang, D. Su, K. Sasaki, P. Liu, R.R. Adzic, Nano Energy(2015) 13, 442–449.
7. Au–Promoted Structurally Ordered Intermetallic PdCo Nanoparticles for the Oxygen Reduction Reaction, K. A. Kuttiyiel, K. Sasaki, D. Su, L. Wu, Y. Zhu, R.R. Adzic, Nature Communications, 5 (2014) 5185, DOI: 10.1038/ncomms6185.

Patents

1. K. Sasaki, W.-F. Chen, J.T. Muckerman, R.R. Adzic, “Molybdenum and Tungsten Nanostruc-tures and Methods for Making and Using Same”, Patent # 8,927,453, issued on 1/6/2015.
2. K. A. Kuttiyiel, K. Sasaki, R.R. Adzic, “Synthesis of Au-induced Structurally Ordered AuPdCo Intermetallic Core-Shell Nanoparticles and their use as Oxygen Reduction Catalysts”, BSA14-24, ROI

Responses to the Previous Year's Reviewers' Comments

Q1 Pure transition metal cores should be excluded from the scope; it has been shown multiple times that they dissolve..

A1 We agree with the view on dissolution of non-noble metal cores. For that reason we are developing ordered intermetallic compounds, gold alloys and nitride-stabilized core constituents. Stability of these species is being determined in current MEA tests.

Q2 It would be nice to see the high stability of the nitride-stabilized Pt-M core-shell catalyst in MEA. A benchmark against commercial Pt/C and PtCo/C with similar Pt loading is missing.

A2 These experiments are being conducted. The delay was caused by relocation of the laboratory.

Q3 Improvement in air performance would be good.

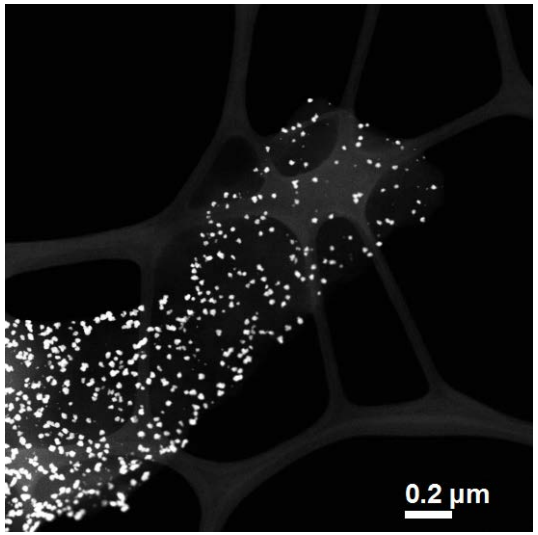
A3 Yes, we are redesigning the electrode structure to improve it. Guidelines provided by dendritic porous deposits. It works with air without back-pressure.

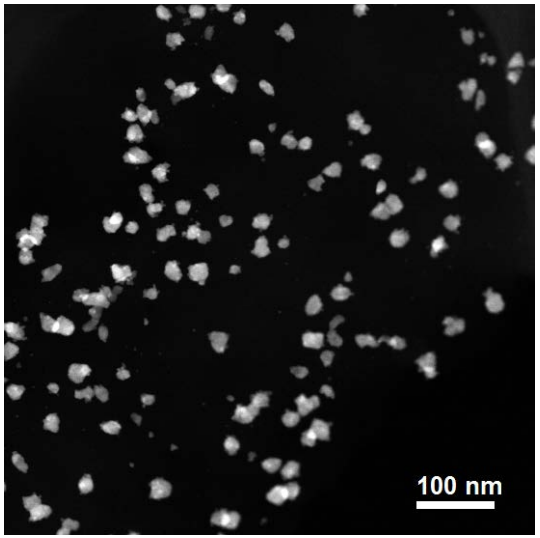
Q4 The hollow core-shell concept was expected to see progress.

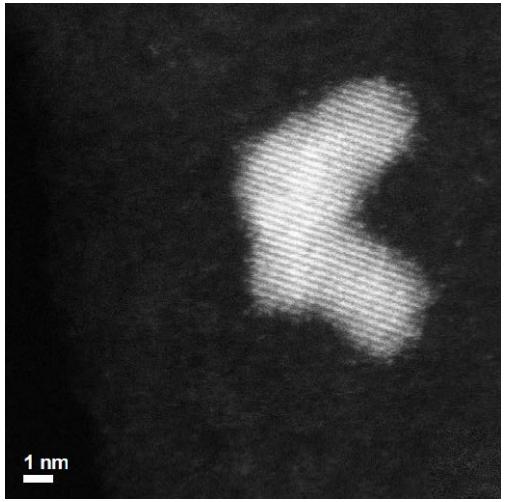
A4 This topic won BNL's technology maturation project and is being researched intensively. We will mention it in the presentation.

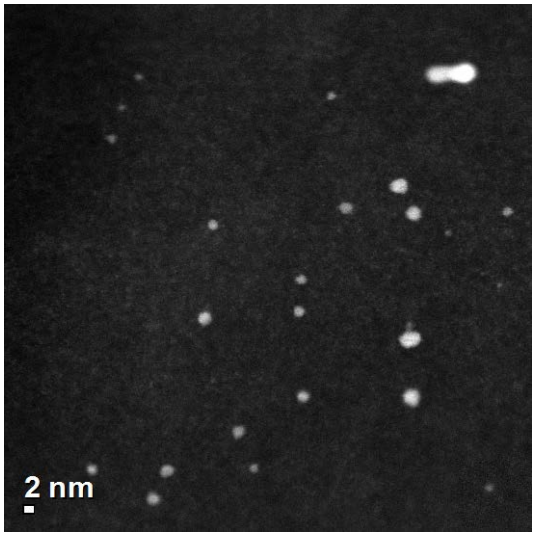
Technical back-up slides

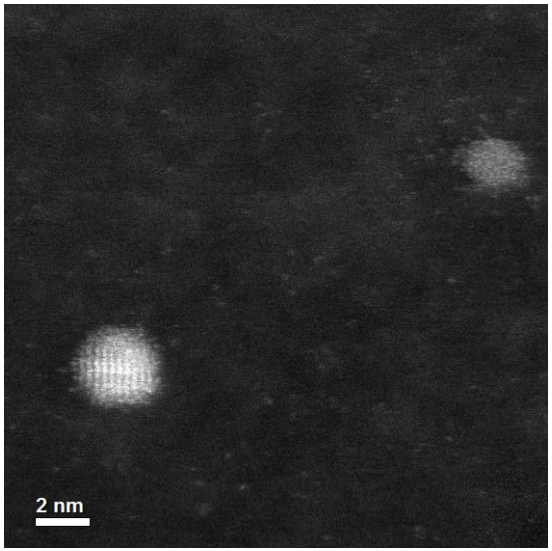
PtML on Au deposited on rGO (after 20,000 potential cycles)

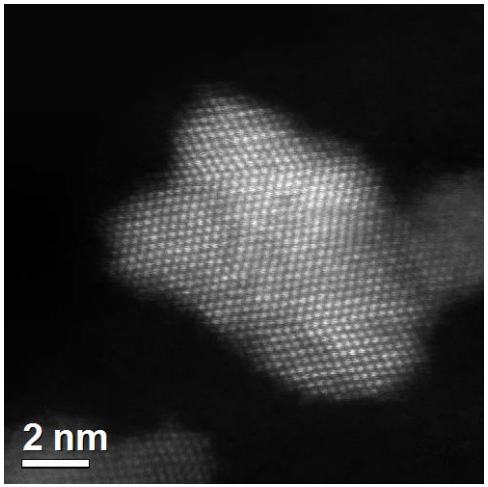




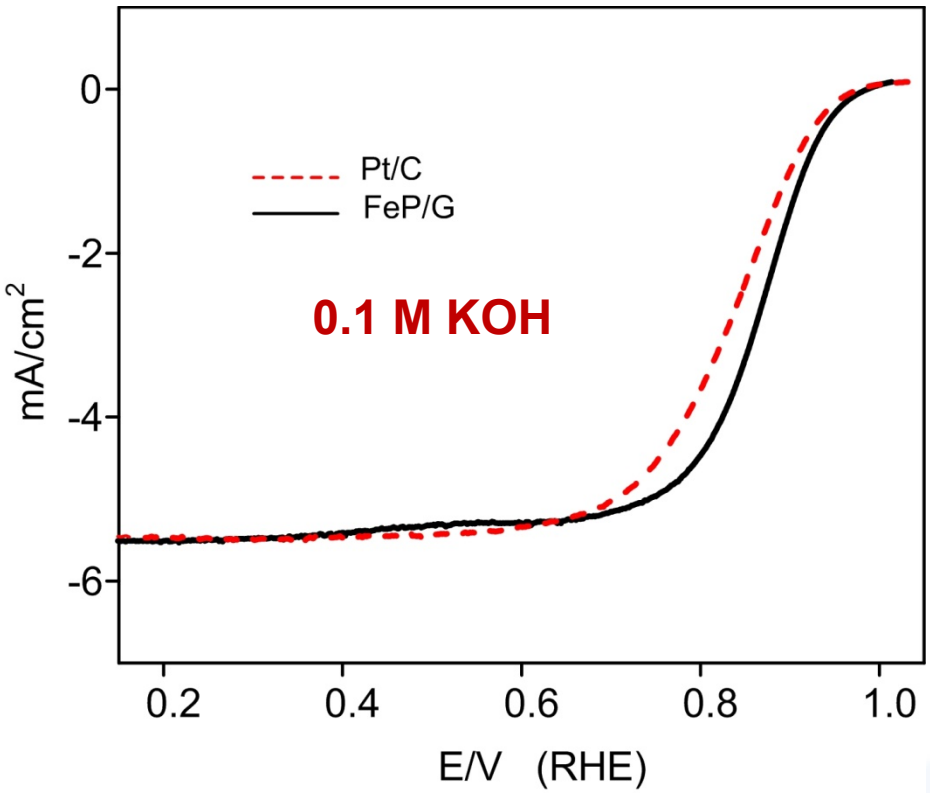


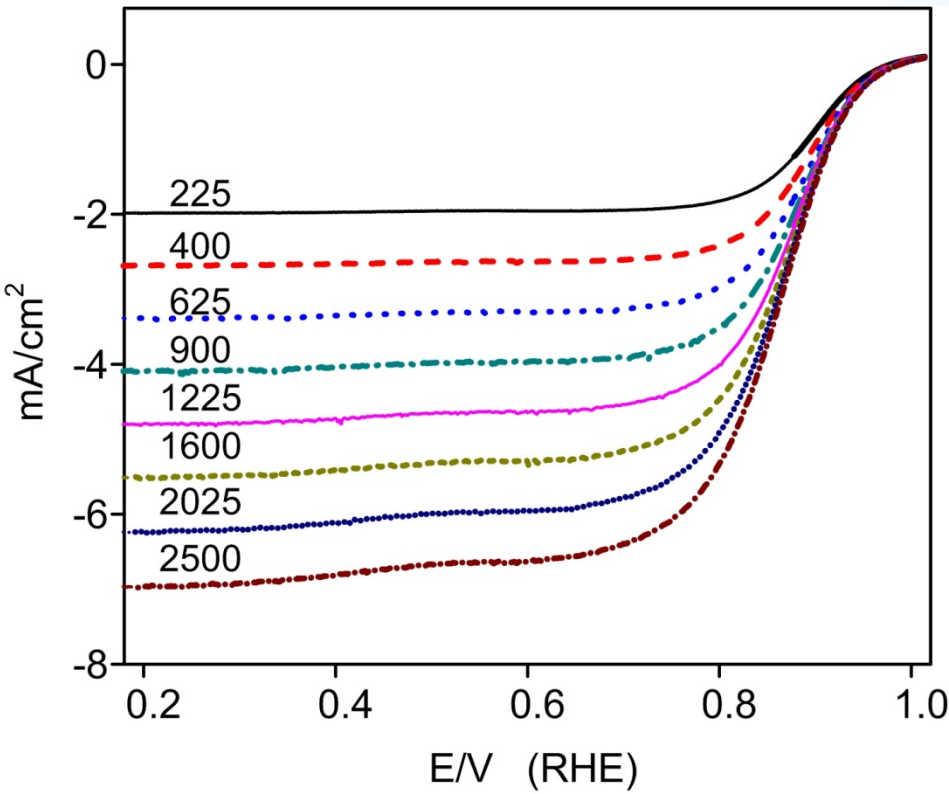






ORR on Fe Porphyrin on Graphene treated in Ammonia at 900ºC





Pt loading: 6.0 ug/cm²
FeP + graphene loading: 0.4 mg/cm²

Half-wave potentials @1600 rpm
ETEK Pt/C : 840mV
Fe P/G : 868 mV

ORR on Metal Porphyrins on Graphene in 0.1 M KOH

Catalyst / (loading)	Onset Potential (V)	Half Wave Potential (mV)	Half Wave Potential after **5000 cycles** (mV)
CoFeP/G (0.4 mg/cm^2)	0.97	880	867
CoP/G (0.4 mg/cm^2)	0.92	845	840
FeP/G (0.4 mg/cm^2)	0.99	870	860
Pt/C (0.1 mg/cm^2) Pt: 10.2 ug/cm^2	0.97	868	838

Electrolyte: 0.1 M KOH; Scan rate: 10mV/s ; Cycling: 0.65 – 1.0 V in air

Technical backup

Facile synthesis of unsupported RuO_2 and $Ru_{0.5}Ir_{0.5}O_2$

The Adams fusion method produces stable IrO_2 nanoparticles with high surface area, but often contains some Ir metal particles due to inhomogeneity in the mixture of H_2IrCl_6 (metal precursor) and $NaNO_3$ (oxidant).

We used carbon powder as the template to make completely oxidized Ru and $Ru_{0.5}Ir_{0.5}O_2$ nanocatalysts. Carbon was completely eliminated from Ru/C after Ru oxidization in air at 350-450ºC as the weight changes were consistent with the value calculated using the mass for two oxygen per Ru minus the weight of carbon when we used Ru/C with Ru weight percent between 20-40%.

The $Ru_{0.5}Ir_{0.5}O_2$ catalyst was made by mixing Ru/C with H_2IrCl_6 in ethanol solution and dried at 80ºC before calcinated at 400ºC for 1h. The weight of obtained catalyst was also consistent with that for RuO_2 and IrO_2 without carbon.

Ru/C	Ru	Ru	RuO2	Ir	IrO2	sum	weight	**deviation**	Temp	time
mg	wt%	mmol	mg	mmol	mg	mg	mg	**%**	℃	min
70.9	40	281	37.3	0	0	37.3	36.9	**-1.2**	400	10
79	40	313	41.6	0	0	41.6	43	**3.3**	350	30
175	40	693	92.2	0	0	92.2	95	**3.1**	400	60
86	40	341	45.3	0	0	45.3	43	**-5.1**	450	60
145	20	287	38.2	0	0	38.2	39	**2.1**	450	60
502	10	497	66.1	0	0	66.1	70.5	**6.6**	350	30
63	20	125	16.6	146	32.7	49.3	47	**-4.7**	350	30