

Platinum Monolayer Electrocatalysts

Radoslav Adzic – Original PI, Senior scientist emeritus 2018

Jia Wang – Presenter and Current PI

Miomir Vukmirovic and Kotaro Sasaki – Project Co-PIs

**Co-workers: Zhixiu Liang, Liang Song, Zhong Ma,
and Kurian Kuttiyiel**

**DOE Hydrogen and Fuel Cells Annual Merit Review
June 14, 2018**

Overview

Timeline

Start: September 2015

End: October 2018

Budget

Funding received in

FY2017: \$700,000

FY2018: \$600,000

Barriers

A. Catalysts' Durability:

< 40% loss in activity after 30,000 cycles

B. Catalysts' Performance:

Catalyst activity; ≥ 0.44 A/mg_{PGM}

C. Catalysts' Cost:

PGM loading; ≤ 0.125 mg PGM /cm²

Partners

Los Alamos National Laboratory

Collaborators

General Motors

Toyota M. C.

N.E. CHEMCAT Co.

Korean Institute for Energy Research

University of Virginia

Relevance

Project objective:

Developing active, durable core-shell catalysts for the oxygen reduction reaction (ORR) that meet the DOE technical targets for 2020.

Activities in this period: R&D on 5 electrocatalyst designs

4g-batch synthesis and MEA tests of PtNiN/C catalysts

Four new nanostructured core-shell catalysts

Catalysts' performance targets:

RDE Tests		MYRDD Table 3.4.7 Technical Targets: Electrocatalysts for Transportation Applications			MEA Tests	
↓		Characteristic	Units	2020 Target	↓	
		PGM content at rated power	$g_{\text{PGM}}/kW_{\text{gross}}$ at 150 kPa (abs)	0.125		
		PGM loading	mg_{PGM}/cm^2 total	0.125	●	
3 of 5 ✓		Mass activity	A/mgPGM at 900 mV _{IR-free}	0.44	◆	
5 of 5 ✓		Electrocatalyst stability (0.6 ↔ 0.95 V)	% mass activity loss after 30K cycles	<40	◆	
		Loss at 0.8 A/cm ² (0.6 ↔ 0.95 V)	mV loss after 30K cycles	<30	●	
1 of 1 ✓		Support stability (1.0 ↔ 1.5 V)	% mass activity loss after 5K cycles	<40		
		Loss at 1.5 A/cm ² (1.0 ↔ 1.5 V)	mV after 5K cycles	<30		

One catalyst tested for support stability on RDE

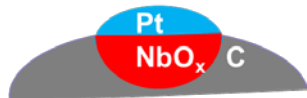
PGM activity & loss after AST measured with H₂/O₂ on MEA ◆

Low-loading, HCD performance vs. Pt/C with H₂/air on MEA ●

Approach

- **Materials:** - Nitriding to stabilize Ni (Topic 1)
 - Stable, PGM-free cores (Topics 2 – 5)Screened many and focused on four most promising ones
- **Advanced core-shell nanostructures:**
 - Pt(ML) on (111) faceted Pd nanosheet (Topics 2 - 3)
 - Pt(111) on Co₂P(001) faceted nanorod (Topic 4)
 - NbO_x core embedded in C, with Pt on top (topic 5)

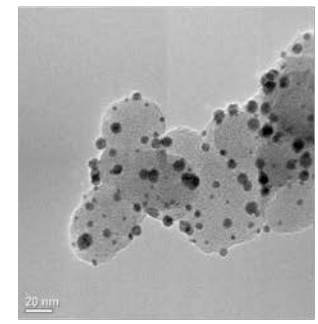
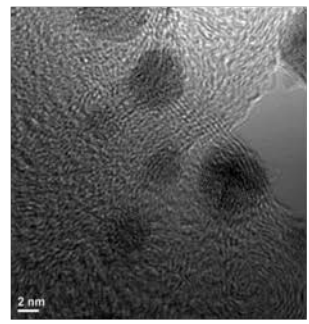
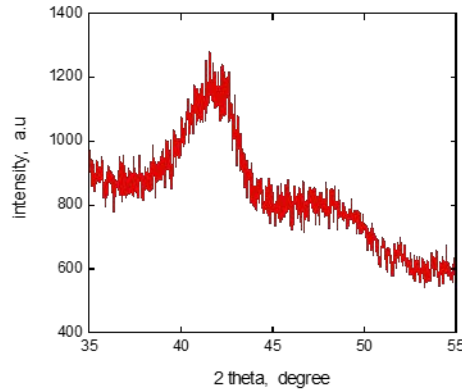
1. PtNiN RDE, gram-batch synthesis, multiple MEA tests
2. Pt_{ML}Pd_{NS}WNI RDE, gram-batch synthesis, MEA test
3. Pt_{ML}Pd_{NS}NbN RDE, gram-batch synthesis, MEA test scheduled
4. Pt₍₁₁₁₎Co₂P_{NR} RDE
5. Pt_{top}-NbO_x-C RDE (plus 5K 1-1.5 V support durability)
MEA tests for use at cathode and anode scheduled



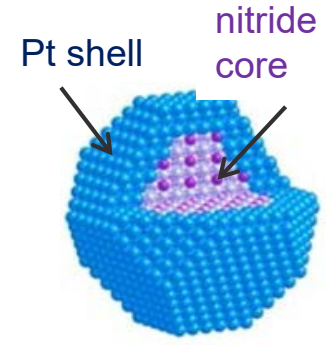
Detailed in the next ten slides of accomplishment and progress

1. PtNiN/C: 3 g/batch synthesis

Pt, Ni precursors and Vulcan XC72 mixed in an organic solution, dried in vacuum at 60 °C, and annealed in NH₃ (510 °C for 2h).

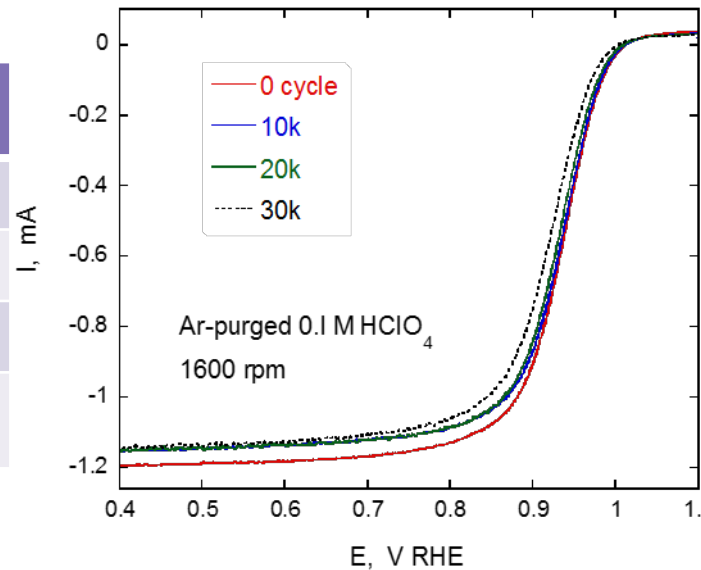


Average size 3.5 nm. Well dispersed on carbon



ORR activity and durability further improved by the new one-step synthesis method

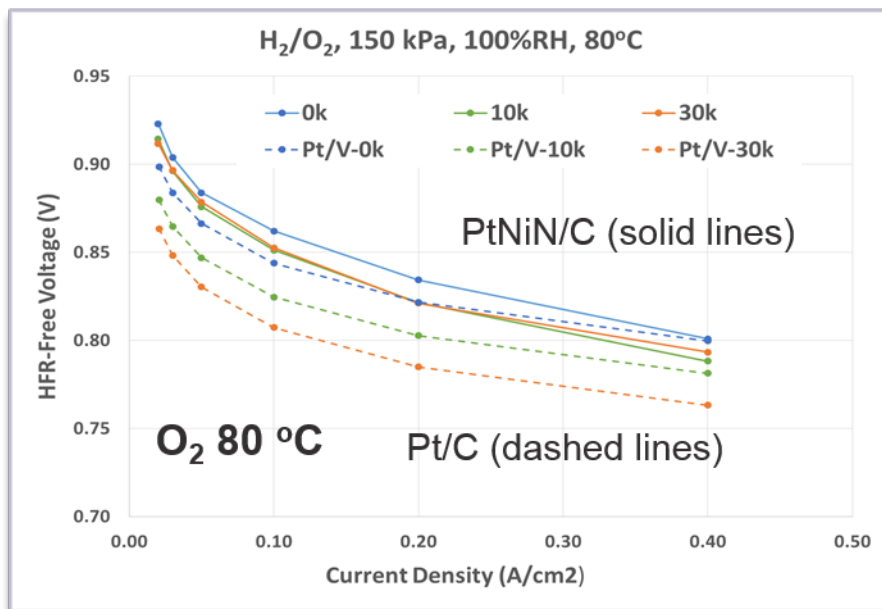
cycle #	MA (A/mg)	E _{1/2} (mV)	ECSA (m ² /g)
0	0.91	932	88.5
10k	0.86	932	83.8
20k	0.78	928	78.9
30k	0.74 -18 %	919 -13 mV	77.2 -13 %



The one-step method yielded higher mass activity (**0.91**) than that (**0.86**) reported previously using the two-step method. **Loss after 30K cycles 18%** also better than the target of <40%.

PtNiN/C: MEA tests by GM and LANL

Accomplishment



PtNiN/C

0.105 mg_{Pt} cm⁻²

Pt/C

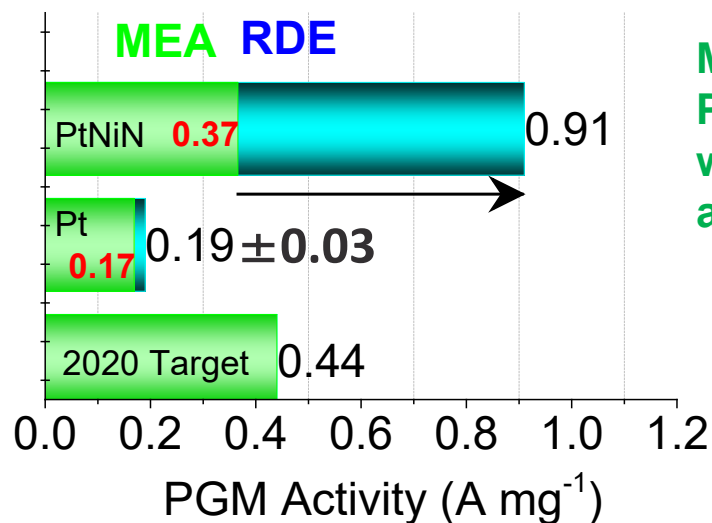
0.120 mg_{Pt} cm⁻²

cycle #	MA (A/mg)	ECSA (m ² /g)	cycle #	MA (A/mg)	ECSA (m ² /g)
0	0.366	26.5	0	0.169	74
10k	0.300	23.2	10k	0.093	27
30k	0.296	18.7	30k	0.058	18
30k/0k	-19 %	-21 %	30k/0k	-66 %	-76 %

cycling: 3s@0.6V, 3s@0.95V

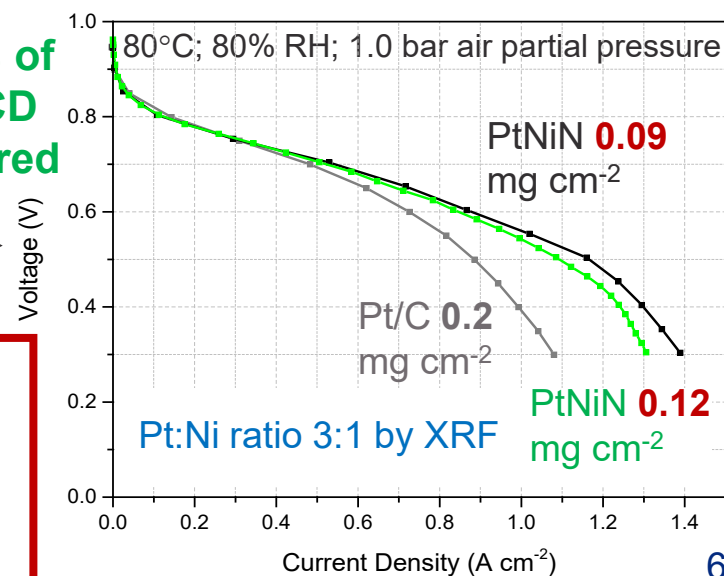
Activity loss (-19%) is 1/3 that of Pt/C, and meets the target of < 40% loss.

>2 times of Pt/C activity at 0.9 V by GM



More than 2 times of Pt/C activity at HCD with H₂/air measured at LANL

Two PtNiN/C samples with half of the Pt/C loading exhibited higher currents.

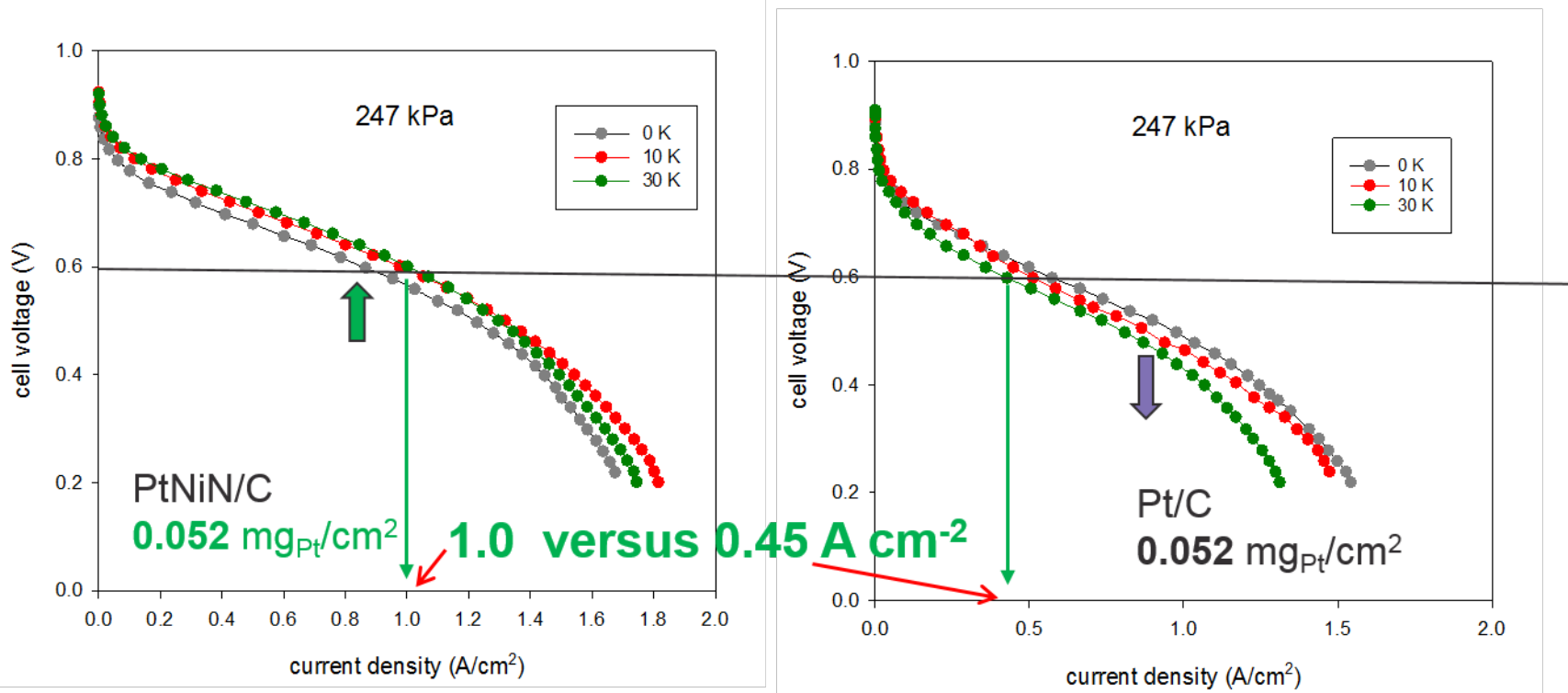


PtNiN/C: Low load, HCD with H₂/air at LANL

Accomplishment

After 30K cycles, **no voltage loss**; Target < 30 mV at 0.8 A cm⁻² met.

Current at 0.6 V with **low loading more than doubled** that of Pt/C



Same low cathode Pt loadings determined by XRF.

Anode catalyst ETEK 20 wt.% Pt/C (0.1 mg_{Pt}/cm²).

Square cycles: 0.6 V (3s) to 0.95 V (3s) at 80 °C, backpressure 105 kPa (abs)

2. Pt_{ML}Pd_{NS}/W_{Ni}/C (4 g synthesis)

Accomplishment

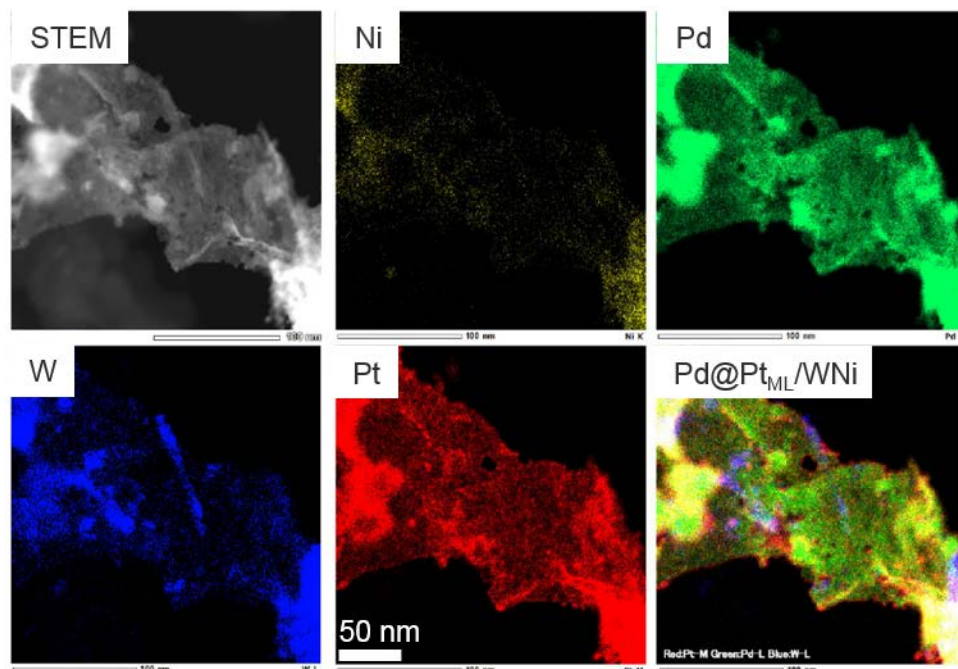
Preparation procedure:

- W & Ni precursors & XC72 mixed in chloroform
- The dried mixture annealed in H₂
- Pd deposited by bubbling CO gas
- Pt deposition via Cu UPD

Scale-up synthesis:

- ❖ 0.8 g per batch of Pd/W_{Ni}/C made at BNL
- ❖ Pt ML deposition 1 batch of 4 g Pd/W_{Ni}/C by NECC

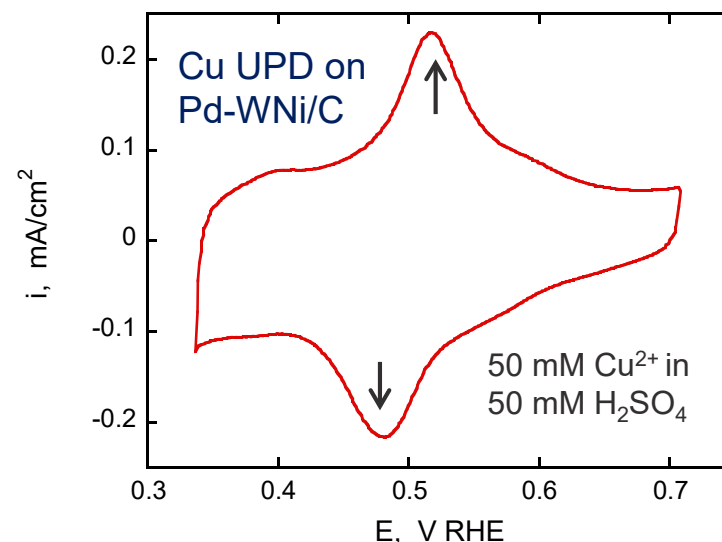
STEM/EDX of 4g/batch Pt_{ML}/Pd_{NS}/W_{Ni}/C



- Broad distribution of **W** and **Ni** on carbon surfaces
- **W****Ni** were well covered by **Pd** nanosheets
- **Pt** goes on top of **Pd**.

Formation of (111) faceted Pd nanosheet (NS) on W_{Ni} by CO gas

Fan et al, *J. Colloid Interface Sci.* 490 (2017) 190



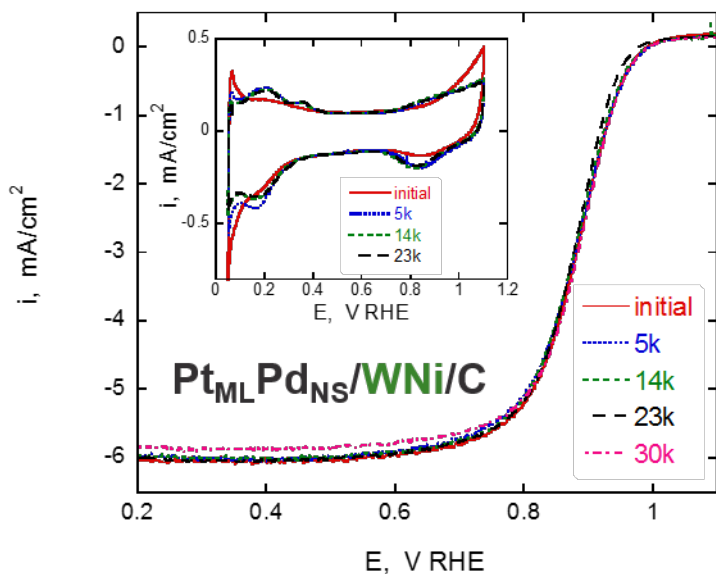
Sharp Cu UPD peaks indicate large Pd(111) facets; good for ORR.

Pd(111) enhances ORR activity of Pt ML:
Pt_{ML}/Pd(111) > Pt_{ML}/Pd(100) & Pt_{ML}/Pd(110)

Gong, et al, *J. Electroanal. Chem.* 2011, 662, 213

Pt_{ML}Pd_{NS}/W_{Ni}/C performance

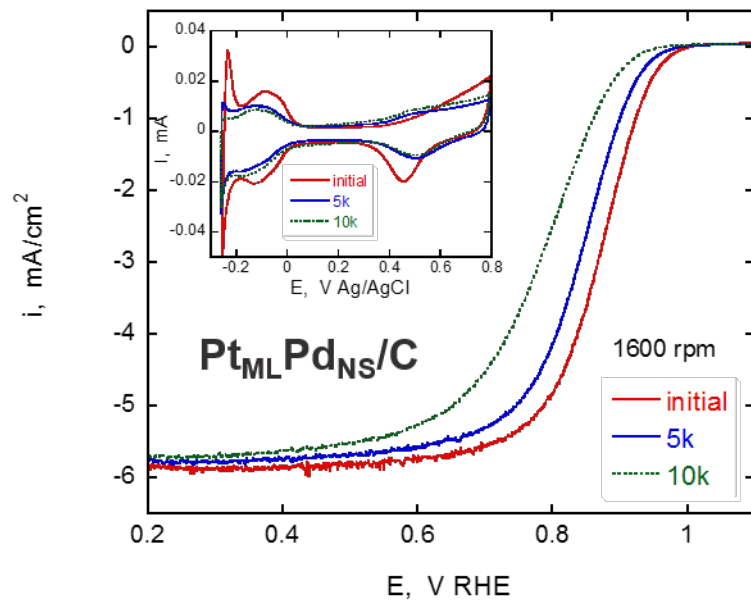
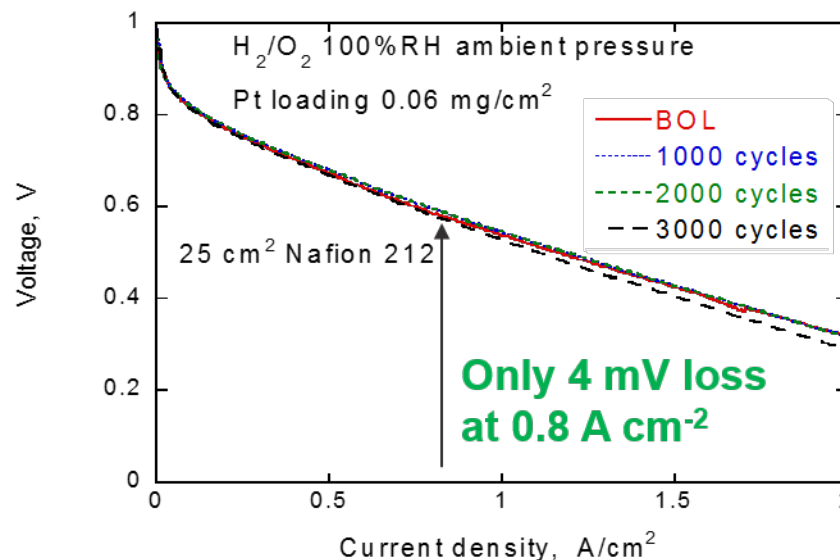
Accomplishment



No discernible loss of ORR activity after 30k cycles for Pt_{ML}/Pd_{NS}/W_{Ni}/C on RDE, while $\Delta E_{1/2} = -86$ mV after 10k cycles for Pt_{ML}/Pd_{NS}/C.

Pt _{ML} /Pd _{NS} /W _{Ni} /C (A/mg)		Pt _{ML} /Pd _{NS} /C
Small batch	4 g batch	Small batch
1.96 Pt	0.68 Pt	2.52 Pt
0.16 PGM	0.22 PGM	0.13 PGM

MEA test by NECC: No loss of MA at 0.9 V

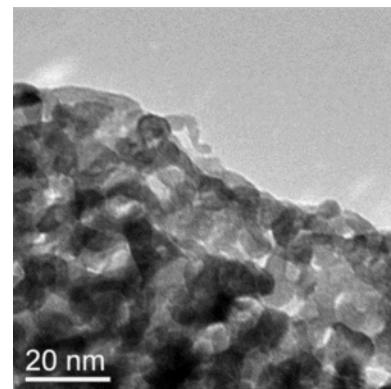


cycles	Pt (A/mg)	PGM (A/mg)	ECSA (m ² /g)
0	0.208	0.067	79
3000	0.215	0.069	60

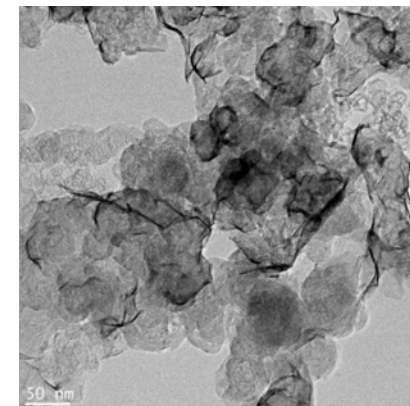
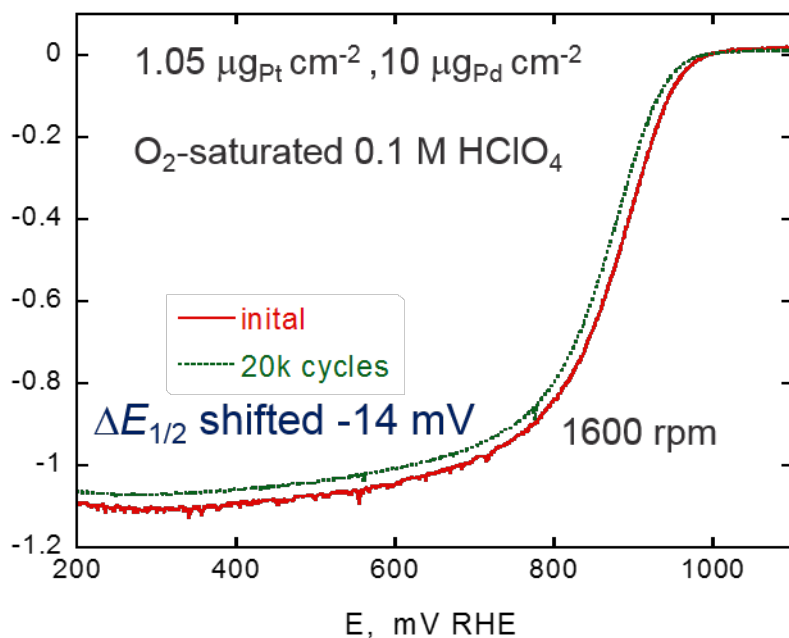
3. Pt_{ML}Pd_{NS}/NbN/C (4 g synthesis)

- ✓ Synthesized by ammonolysis of NbCl₅ and nitridation in NH₃ at 600°C ~ 800°C
- ✓ The conductivity NbN NPs is ~20 S/cm, as high as carbon support
- ✓ NbN nanoparticles are interconnected into aerogel-like nano-frames with 5 – 15 nm pores & high surface area (63.5 m²/g)

NbN nano-frames



20-60 nm Pd nanosheets

Pt_{ML}Pd_{NS}/NbN/C (small batch)

Pd nanosheet deposited on NbN by CO at BNL.
 Pt ML deposition of 4g sample made by NECC.

Small batch	4g batch
2.58 Pt	1.17 Pt
0.25 PGM	0.36 PGM

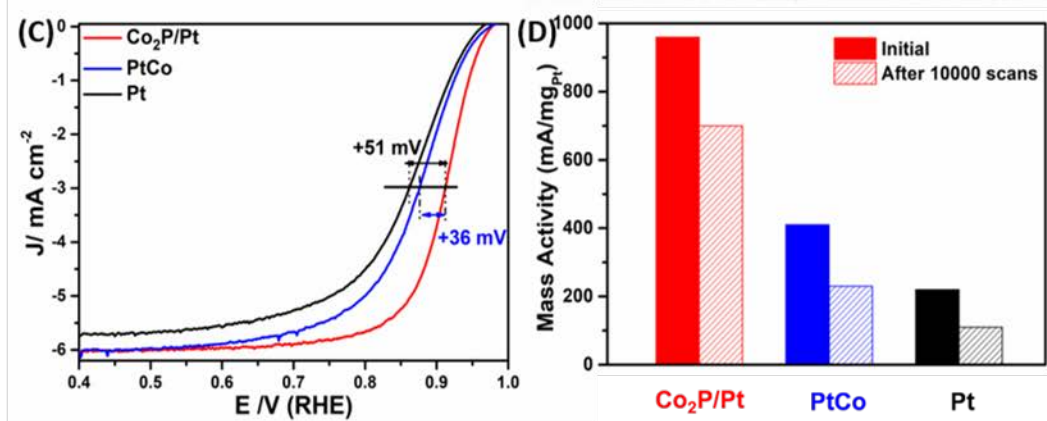
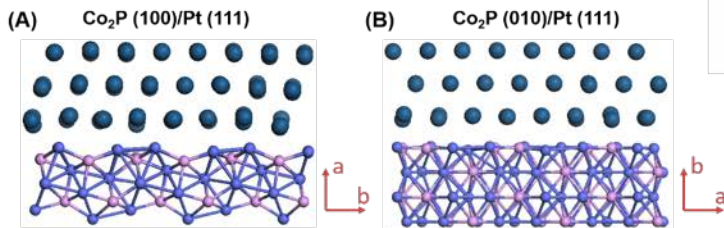
NbN, similar to WNi, enhances durability.
 $\Delta E_{1/2}$ shifted -14 mV after 20 K cycles.

Scale up synthesis of Pt_{ML}/Pd_{NS} with WNi or NbN is feasible, but PGM activity needs improvement.

4. Pt₍₁₁₁₎Co₂P nanorods

Pt mass activity of 0.96 A mg⁻¹ more than double that of PtCo.

After 10K 0.6 – 1V cycles, 0.70 A mg⁻¹ > 0.44 target



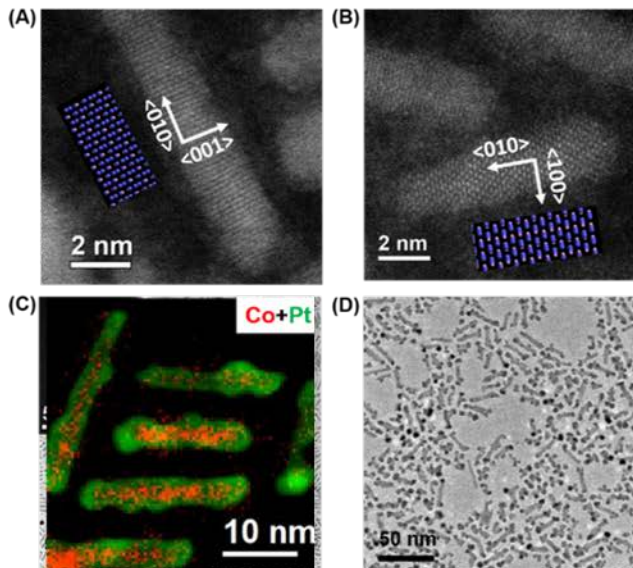
Using shape control to maximize favorable core-shell interface

Pt(111)/Co₂P(001) interface has the most favorable O-binding energy for ORR, while Co₂P(010) facet deactivates Pt for ORR.

Co₂P Nanorods have (001) plane at the sides and (010) at the ends.

The high (001):(010) area ratio of Co₂P nanorods enhances the ORR activity.

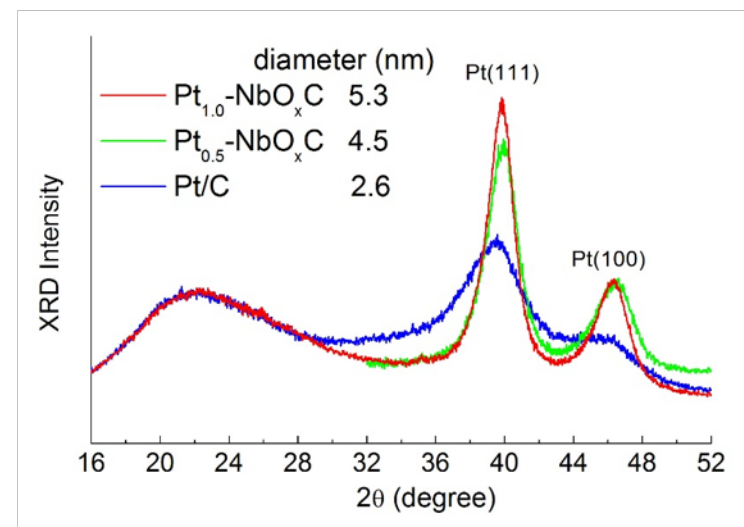
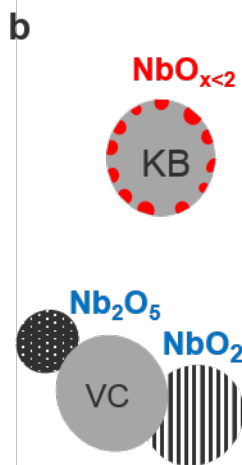
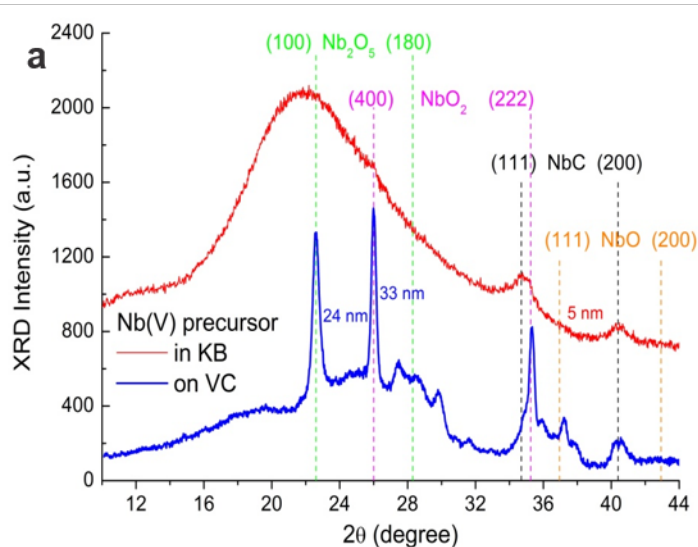
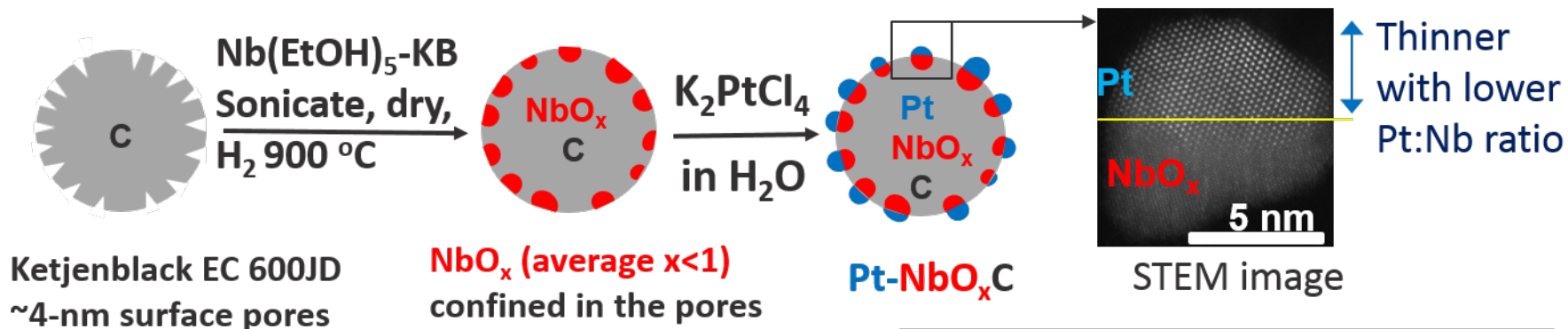
Pt(111) formation promoted by Fe(CO)₅.



5. Pt-NbO_x-C half-embedded core-shell

Accomplishment

Motivation: Prevent carbon corrosion and particle agglomeration during fuel cell's start-ups and shut downs (up to 1.5 V) by using embedded NbO_x to minimize Pt-carbon contact and to prevent Pt particle agglomeration.

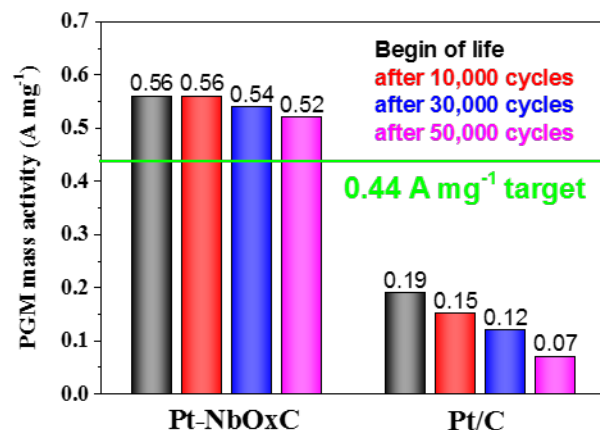
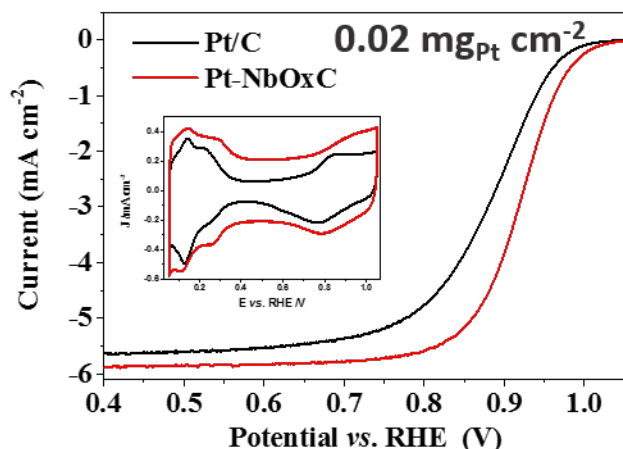


With Nb(5+) precursor confined in nm-sized pores, highly dispersed NbC or NbO particles were obtained.

NbC/NbO acted as the reducing agent for Pt selective deposition on ~5 nm NbO_x embedded particles.

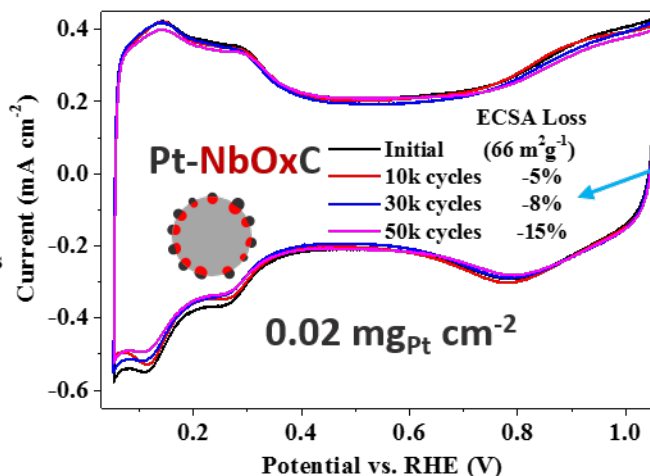
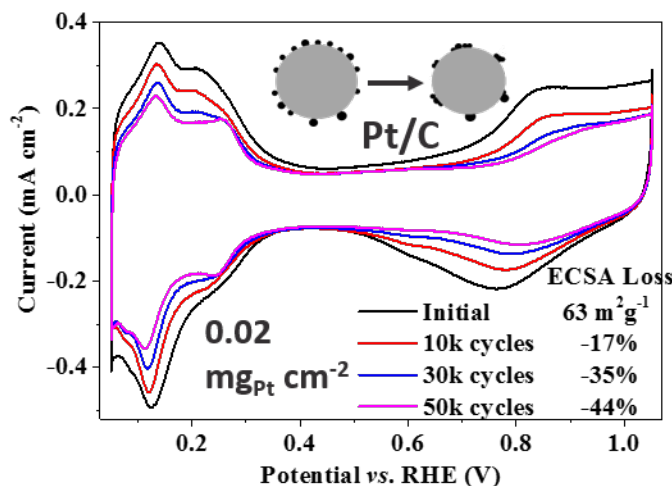
ORR Activity and Durability of Pt-NbO_x-C

Accomplishment



Highly sustainable activity: after 50 K cycles, 0.52 A mg⁻¹ above the 0.44 A mg⁻¹ target.

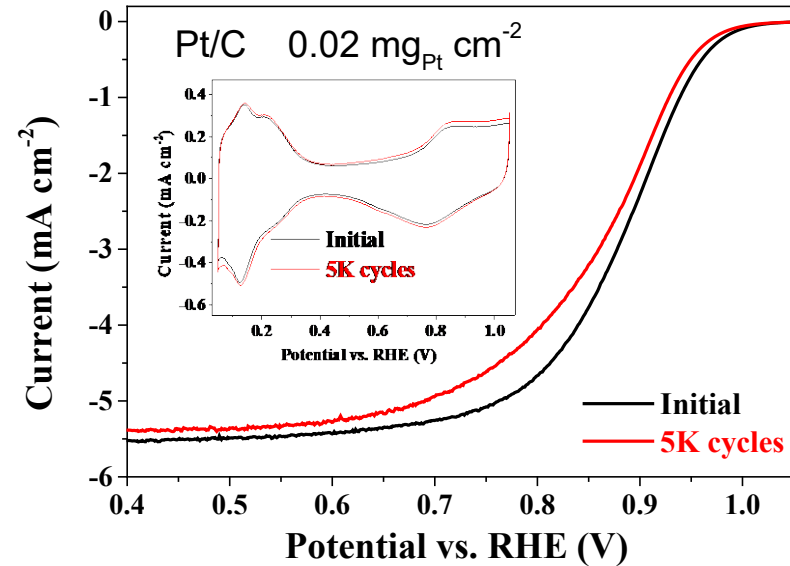
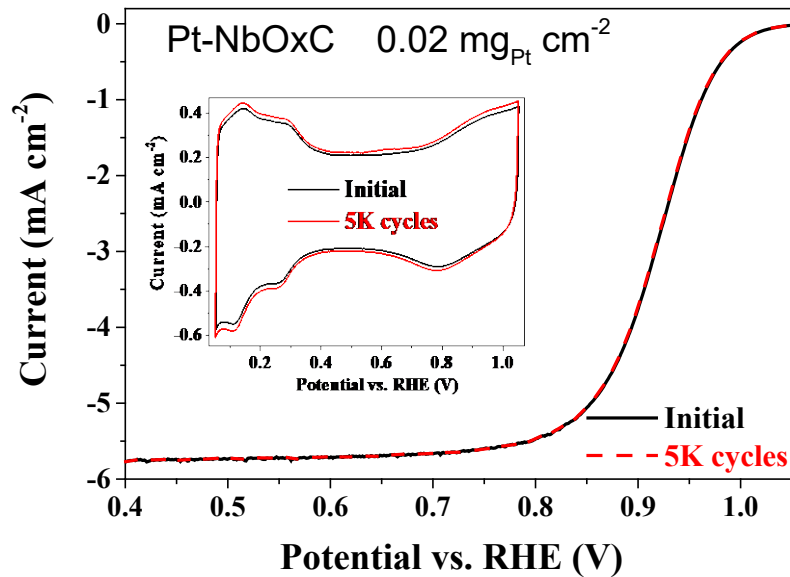
Pt 14.1 wt% determined by ICP, Nb ~18 wt%. AST: 0.6 -1 V, 50 mV s⁻¹



Very low losses of activity (-4%) and ECSA (-8%) after 30K cycles, much better than the up to -40% targets and that of Pt/C.

4.5-nm-diameter disks are better than 2.6-nm particles for ORR because flat surface is more active and stable than low-coordinated sites at edge.

Pt-NbO_x-C Durable with 1-1.5 V cycles



Capacitance currents in CV increased slightly for both samples, which is related to carbon corrosion at potential higher than 1 V.

No loss of ORR activity for Pt-NbO_x-C after 5000 cycles 1-1.5V, 0.5 V s⁻¹ because Pt particles were anchored by embedded NbO_x, preventing agglomeration of Pt particles. Loss of activity occurred for the Pt/C where Pt particles were weakly attached on carbon.

MEA tests scheduled for Pt-NbO_x-C as durable anode and cathode catalysts

Summary

	Target	PtNiN	Pt _{ML} Pd _{NS} WNi	Pt _{ML} Pd _{NS} NbN	PtCo ₂ P nanorod	Pt-NbO _x -C
Mass Activity (A mg ⁻¹ PGM)	> 0.44	0.91 RDE 0.37 MEA	0.22 RDE 0.07 MEA	0.36 RDE	0.96 RDE	0.56 RDE
MA loss (30K 0.6-0.95 V)	< 40%	-18% RDE -19% MEA	0% RDE 0% MEA	-20% RDE	-30% RDE	-4% RDE
MA loss (1-1.5V)	< 40%					0% RDE
Loss @0.8 Acm ⁻²	<30 mV	0 mV	4 mV			
Activity rank		excellent	need to improve		excellent	good
Durability rank		excellent	excellent	good	fair	excellent

- Ni₄N and Co₂P (3d M compounds) are stable, activity-enhancing cores.
- Favorable facets and core-shell interface boost performance.
- Embedding cores into carbon surface prevent particle agglomeration.
- ✓ RDE tests found promising materials and nanostructures.
- ✓ Significant progress made in scaling up and MEA test/optimization.

Responses to Previous Year Reviewers' Comments

- C1 Risk of running too many directions, short of a ranking to indicate the most promising direction to achieve goals.
- R1 We did quick screening, focused on fewer catalysts, and provided a comparison table in summary.
- C2 Need to work more on cores with substantially reduced PGM or PGM-free cores.
- R2 We worked on using PGM-free cores and Pd interlayer.
- C3 Need to scale up catalyst synthesis and do more MEA-level tests and physical characterization.
- R3 We increased efforts in scaling up catalyst synthesis and had more MEA tests. These are time consuming.
Collaboration with NECC and GM helped.

Collaboration and Technology Transfer

Partners within Hydrogen and Fuel Cell Program

Los Alamos National Laboratory, Piotr Zelenay (PI), Ulises Martinez, and Yu Seung Kim (L'Innovator), MEA tests, composition by XRF

Collaborators (Universities and institutions)

BNL: Dong Su, Lijun Wu and Yimei Zhu, TEM, STEM

University of Virginia: Sen Zhang, Synthesis of Pt-Co₂P nanorods

Korean Institute for Energy Research: Gu-Gon Park

Collaborators (Industry)

General Motor: Anu Kongkanand and Yun Cai, MEA tests, EPMA

Toyota Motor: Hisao Kato

N.E. Chemcat: Hiroshi Igarashi and Kiyotaka Nagamori,
Synthesis, RDE test, and characterization (SEM/EDX)

Technology Transfer (Four BNL Pt(ML) patents licensed)

N.E. Chemcat Co. (2012) Recent RDE of 10kg/batch Pt_{ML}Pd/C

Pt MA A/mg	PGM A/mg	SA mA/cm ²	ECSA m ² /g _{Pt}
2.40	1.0	1.53	157

Remaining Challenges and Barriers

Challenges remain for low-PGM catalysts

Pt_{ML}Pd: High PGM activity and durability concurrently

Facet optimization: Difficult to scale up shape-controlled synthesis

PtNiN/C and Pt-NbO_x-C:

Scale up synthesis with high uniformity and reproducibility

MEA fabrication optimization

Confirming durability with post-test analysis of MEA

Further activity and durability enhancement

Challenges for PGM-free catalysts

Low volume activity

H₂O₂ formation

Low durability

Proposed Future Work

PtNiN/C

- Octahedral PtNiN to further enhance the activity
- High pressure nitriding to further improve the stability
- Technology transfer to catalyst producers
- MEA optimization and post-test analysis of MEA

Pt-NbO_x-C

- MEA tests and optimization, scale up synthesis
- Including Ni or Co in NbO_x core to enhance activity

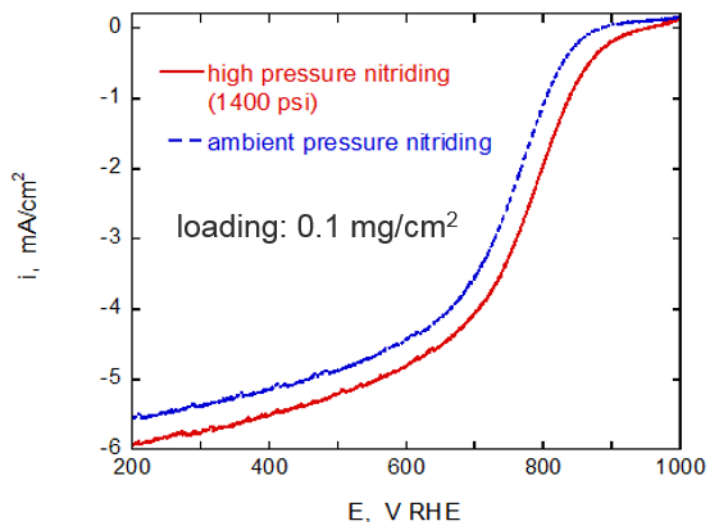
Pt-NiN-C

- Replacing NbO_x with activity-enhancing PGM-free cores

Any proposed future work is subject to change based on funding levels

Proposed Studies of PGM-free Catalysts

PGM-free ORR catalysts via high pressure nitriding

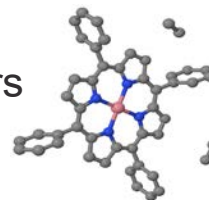


ORR activity of Fe-N-C synthesized in NH₃ at 900°C at 1400 psi (red curve) is higher than that synthesized in NH₃ at ambient pressure (blue curve)

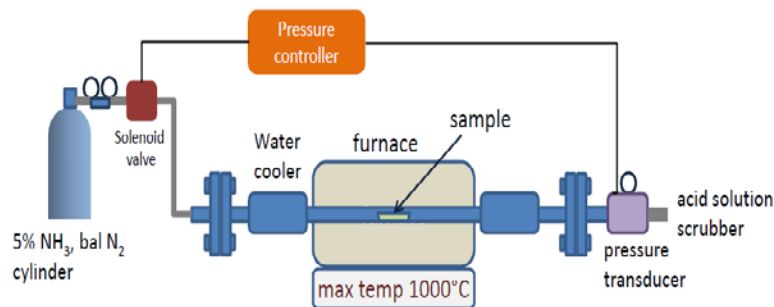
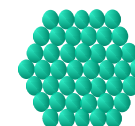
$E_{1/2}$ increased by 761-730 = 31 mV

EXAFS indicates that Fe-N-C comprises Fe-N₄ centers and Fe nanoparticles – a similar structure reported in Mukerjee *et al.*, *JACS* 135 (2013) 15443.

Fe-N₄
centers



Fe NPs



Identify critical factors of the activity enhancement by comparing the atomic structures of high & ambient pressure-nitrided Fe-N-C catalysts:

Density of Fe-N₄ moieties and/or role of Fe NPs?

Oxynitride catalysts for ORR in alkaline media

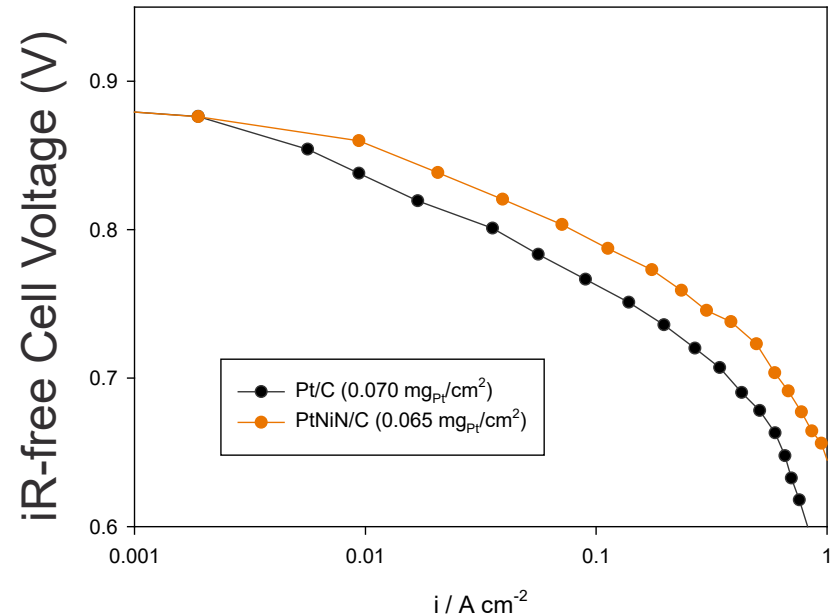
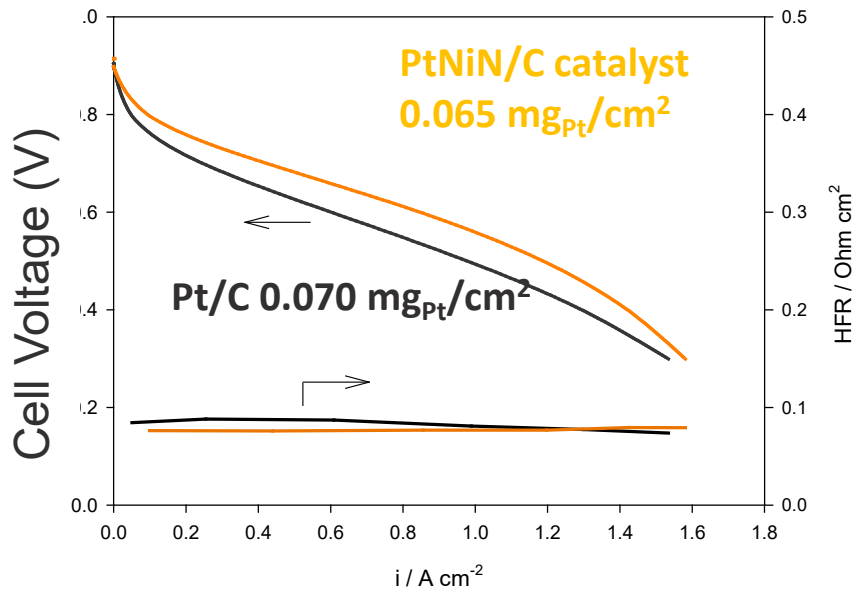
Li, Kuttilyiel, Fujita, Adzic, Sasaki *et al.*, *ChemSusChem* 2017, 10, 68

Any proposed future work is subject to change based on funding levels

Technical Back-Up Slides

PtNiN/C – Another MEA test (H₂/air) at LANL

Higher activity than Pt/C at all currents and with air

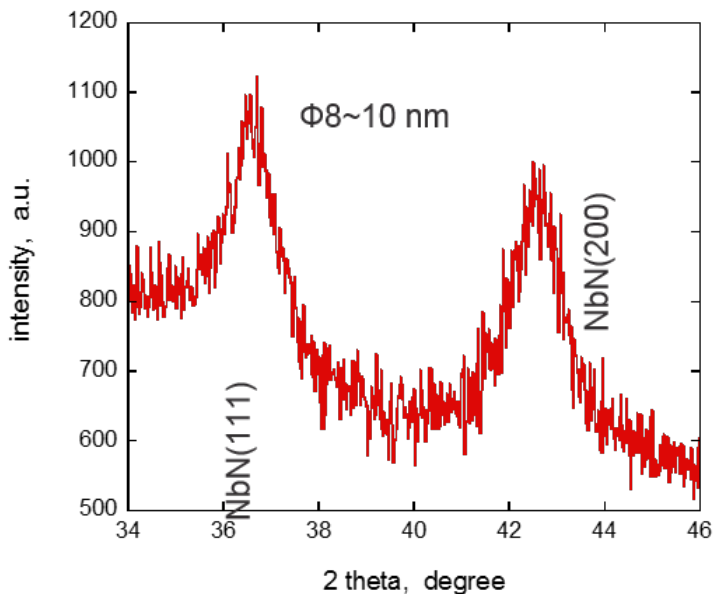


Catalyst: BNL PtNiN/C catalyst or commercial ETEK 20wt.% Pt/C
Pt loading determined by XRF, close to half of 0.125 mg/cm^2

Test condition: 80 °C, backpressure 142 kPa

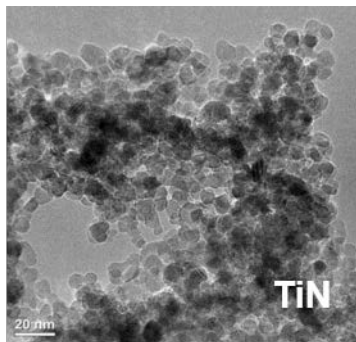
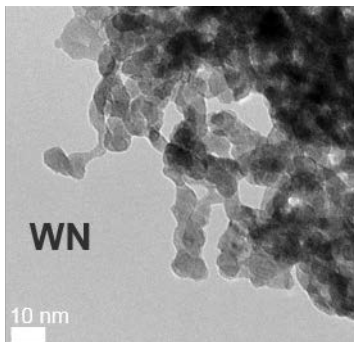
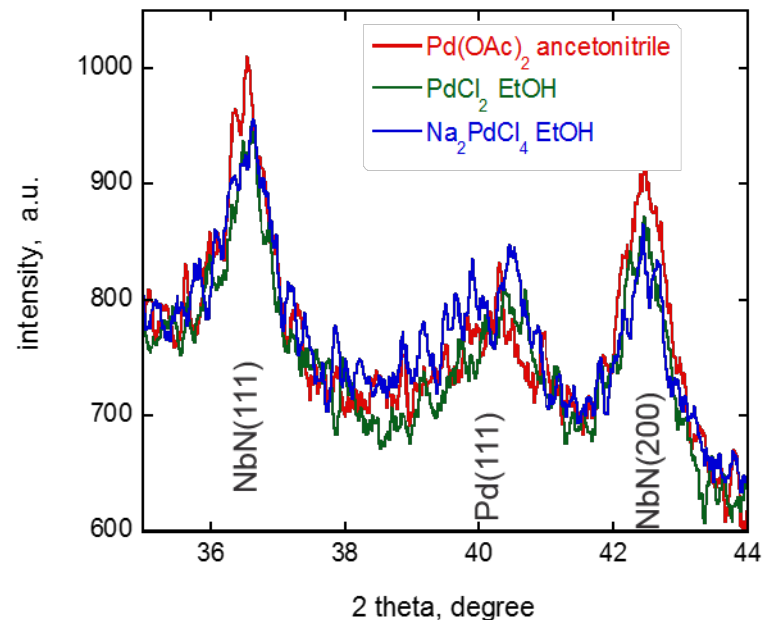
Anode catalyst ETEK 20 wt.% Pt/C (0.1 $\text{mg}_{\text{Pt}}/\text{cm}^2$)

Metal nitride nanoframes



NbN XRD peaks observed

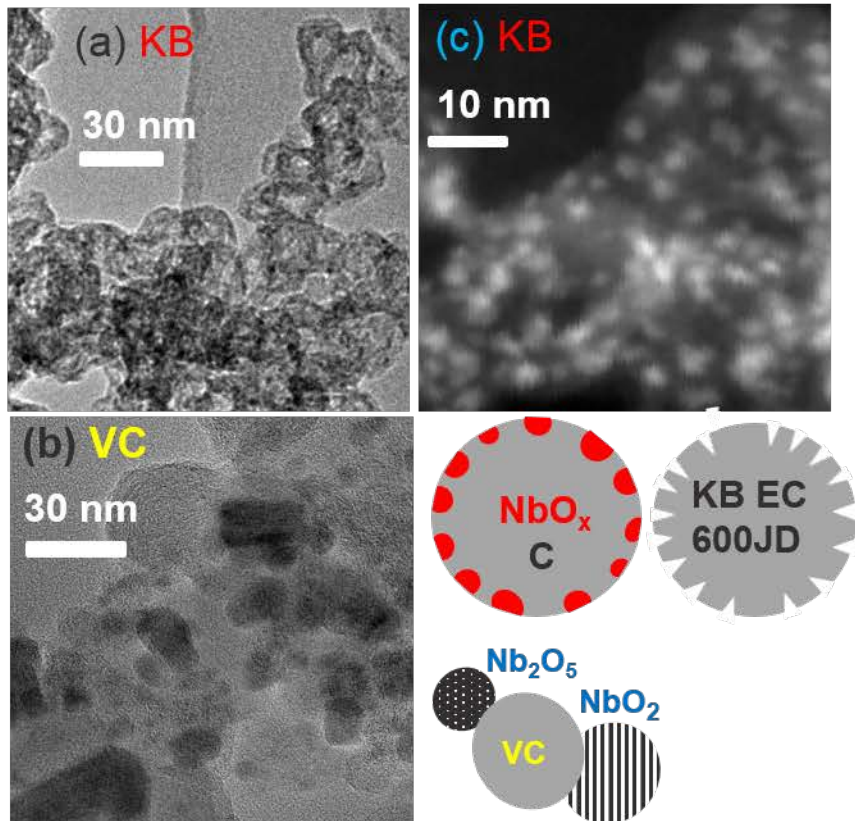
Pd(111) nanosheets



NbN synthesis method was used to produce WN, TiN, CrN, VN, and TaN.

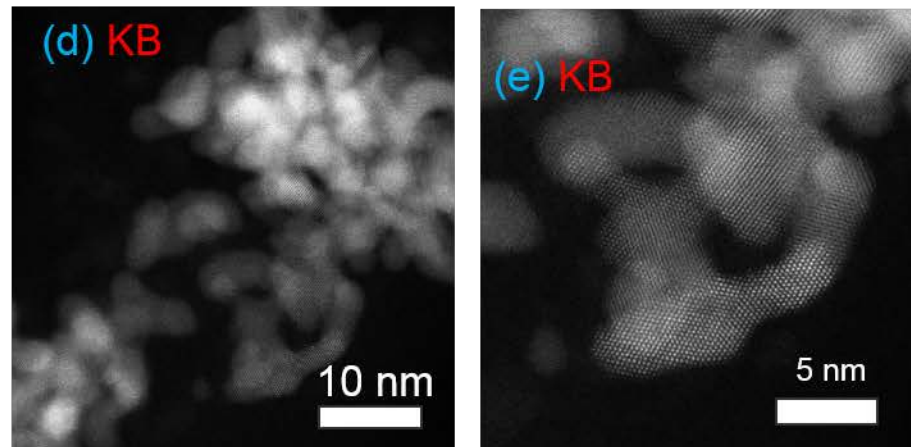
XRD profiles for Pd_{NS}NbN/C samples made using different Pd precursors and solvents.

TEM and STEM of NbO_x-C



(a, b) TEM images for samples made with Ketjenblack and Vulcan differ distinctly: Dark edge of ~30 nm carbon particles due to heavier Nb embedded in the nanopores on carbon surface (a) versus many irregular >10 nm particles (b).

STEM of Pt-NbO_x-C

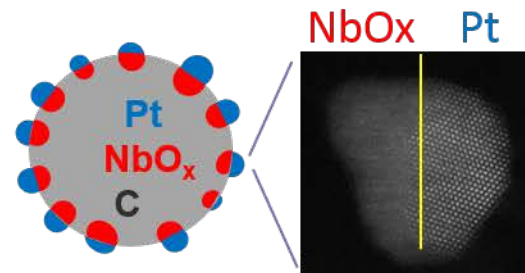


(c-e) STEM images made carbon invisible.

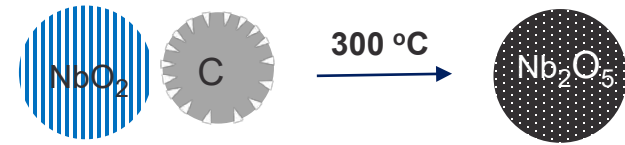
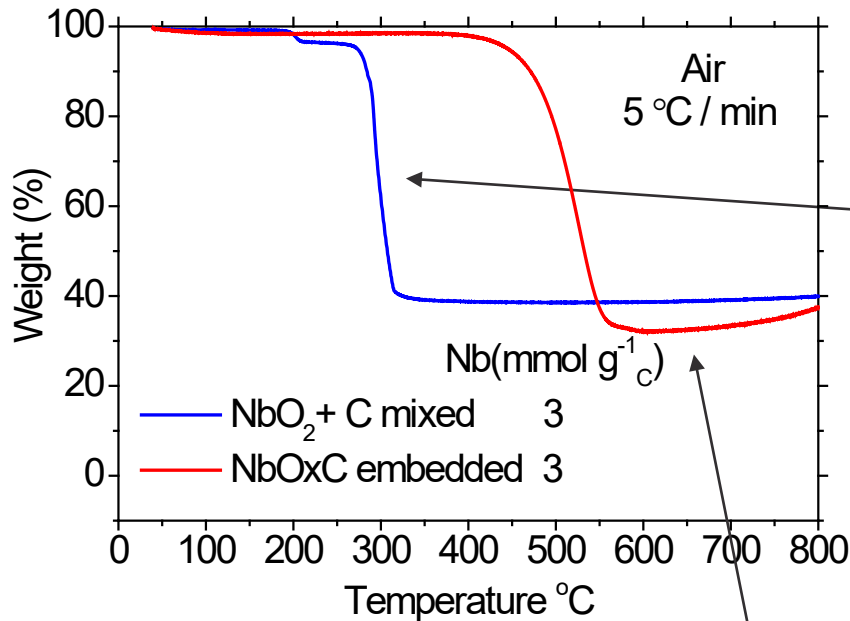
(c) <5 nm amorphous NbO_x

(d) Similar size and distribution for Pt-NbO_x-C

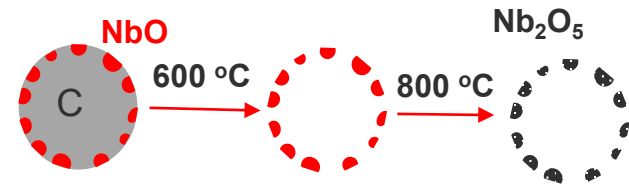
(e) Pt lattice are visible on most particles for the samples after Pt deposition



NbO_x embedded in carbon as evidenced by thermogravimetric analysis (TGA)



Exposed NbO₂ oxidizes at low temperature, triggering carbon burning off below 350 °C.



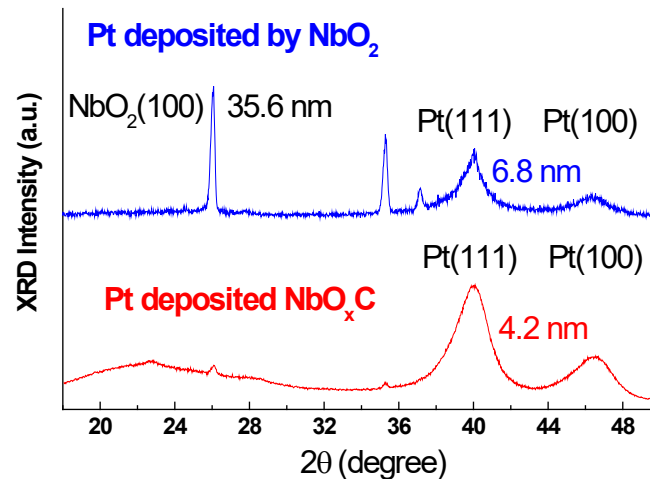
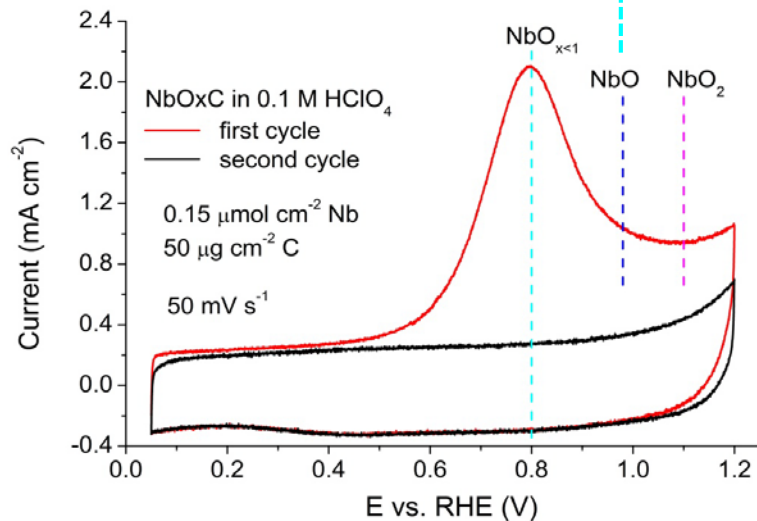
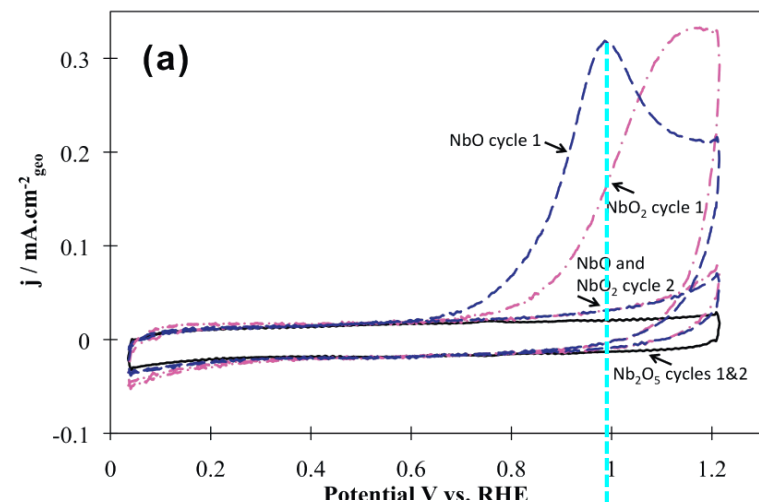
The weight loss due to carbon oxidation to gaseous CO₂ occurs at higher temperature for the sample with embedded NbO_x than that by physically mixed NbO₂ and C because embedded NbO_x are less exposed and thus less active in initiating oxidation at low temperatures.

Small weight gain above 600 °C for the sample with embedded, low-oxidation-state NbO_x is due to oxidation of NbO_x to Nb₂O₅.

Low Nb oxidation state and spontaneous Pt deposition

Surface oxidation of NbO occurs at lower potential (peak at 0.98 V) than that of NbO₂ (close to 1.1 V).

L. Zhang, et al. *J. Phys. Chem. C*, Vol. 114, No. 39, 2010



Samples made by stirring **NbO₂ particles** (blue curve) and **NbO_xC** (red curve) in K₂PtCl₄ aqueous solution overnight exhibited Pt XRD peaks, confirming Pt deposition by not-fully-oxidized Nb.

Our measurements found peak potential at 0.8 V, lower than that for NbO suggesting amorphous NbO_x contains NbC and NbO with **average number of O, x < 1**.