Alternative Metal Oxide Supports for Cathode Catalyst Powder in Automotive PEMFCs

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ORR Catalysts: Activity and Durability

- Cost and durability: primary vehicle-related barriers to fuel cell vehicle commercialization
  - State-of-the-art fuel cell MEAs use higher loading than the published 2020 DOE target of 0.125 mg_{Pt}/cm^2
  - Life-limiting failure modes are commonly associated with the cathode catalyst layer: Pt or Pt alloy dissolution / agglomeration, support corrosion

- How can the specific activity (uA/cm^2_{Pt}) of Pt for ORR be increased?
  – Alloy that compresses Pt-Pt distance (ensemble effect)
  – Alloy/other species that donates e^- to the Pt site (ligand effect)
  – Added species that helps with O adsorption
  – Better coordination of Pt (<u>extensive surface</u>, alternative particle shape, larger particle)
  – Optimized crystallite surface
  – Removal of poisons (e.g. sulfate or sulfonate anions)
  – Improved proton transport from ionomer/water to Pt surface

- Besides specific activity increases, how can the mass activity (A/g_{Pt}) of Pt for ORR be increased?
  – Minimize atomic layers (conformal coating, core-shell)
  – High surface area support

Concepts for extensive Pt surfaces on stable substrates…

FLAT SAMPLES

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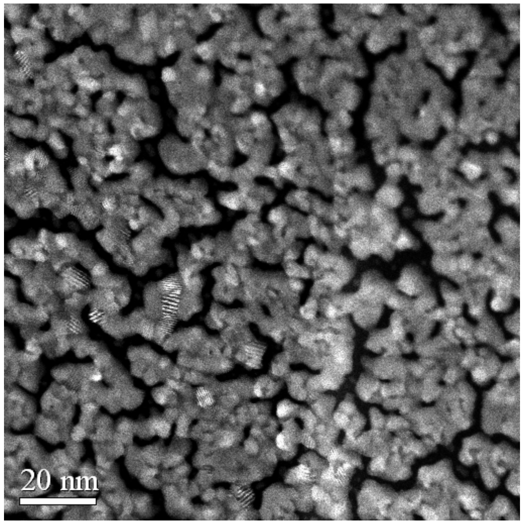
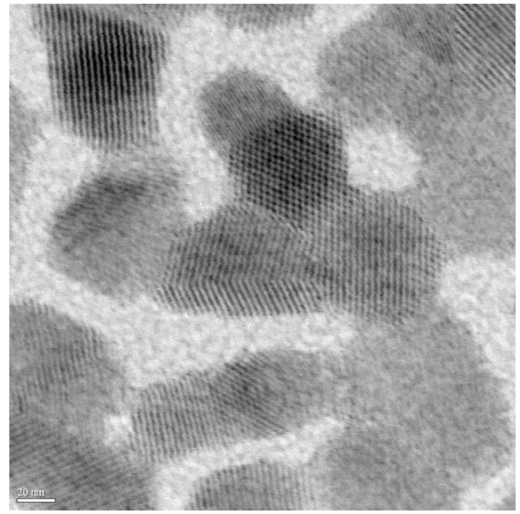
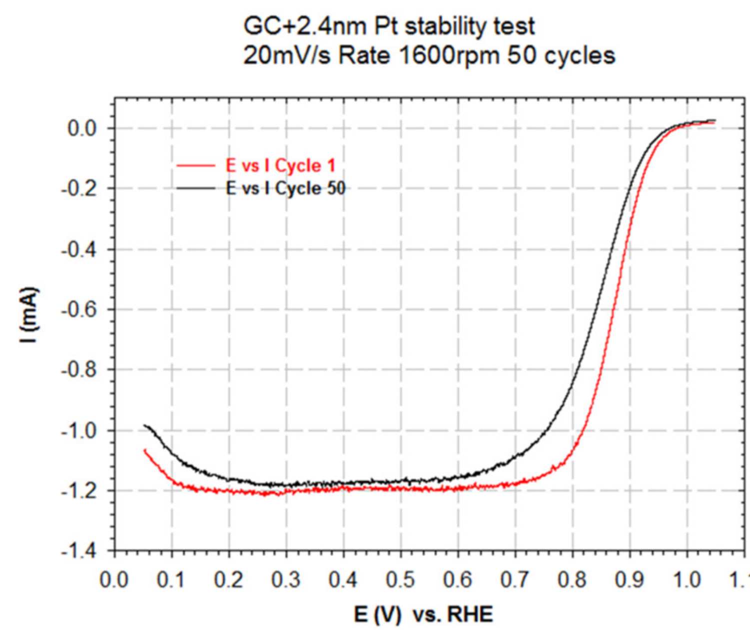
Is It Possible to Generate 2-D Connected Pt Network at Low Pt Loading?





Magnetron sputtering of 24 Å Pt (nominal) on graphene can yield a 2-D connected Pt network…

…But it is not durable. After 50 RDE cycles (0.1-1.05 V), activity deteriorates.



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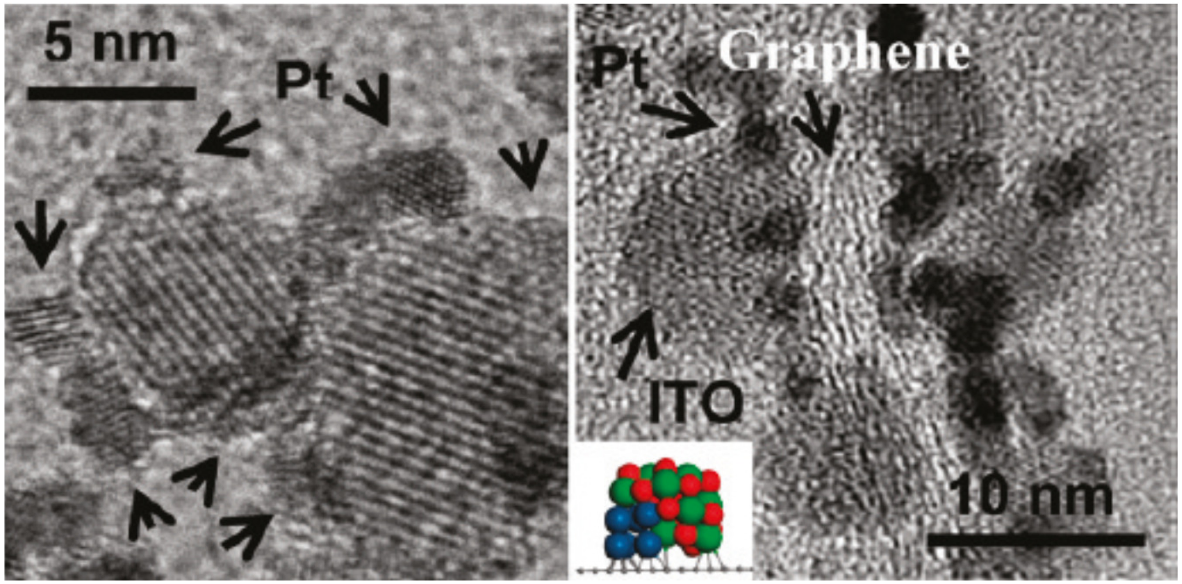
Stabilizing Pt on Graphene



In-Sn-O is a conductive metal oxide, which has been used successfully in stabilizing Pt nanoparticles (6 atom clusters) on graphene as ORR catalyst, with enhanced activities.

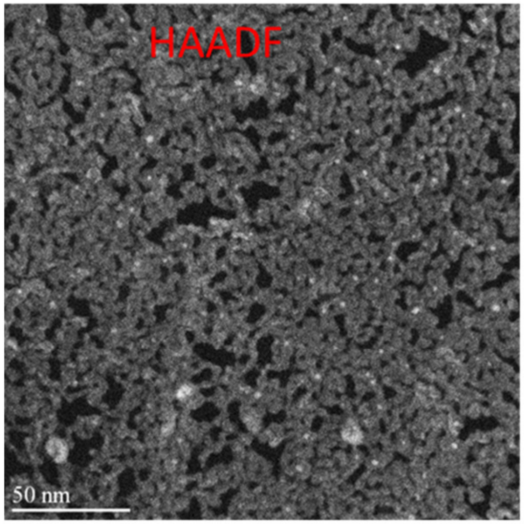
Kou *et al.*, *J. Am. Chem. Soc.* **133** (2011) 2541-2547

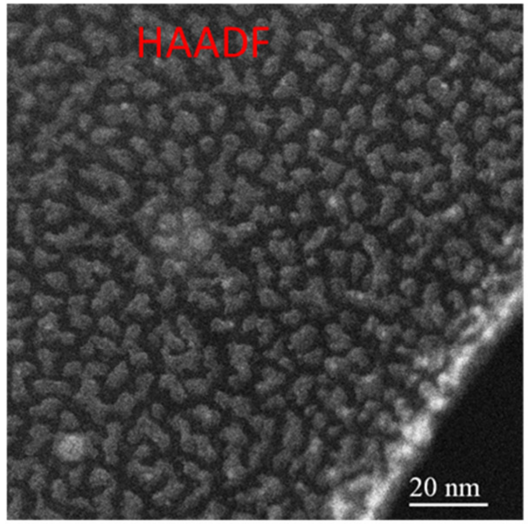
Two issues:

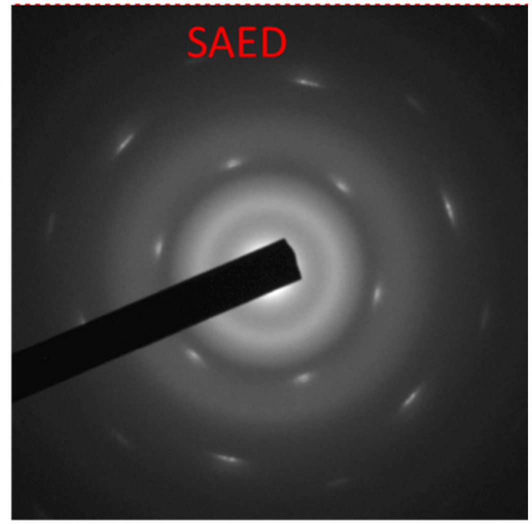
- ITO is not durable in PEMFC working conditions
- Wet chemical method used to produce stabilized Pt nanoparticles

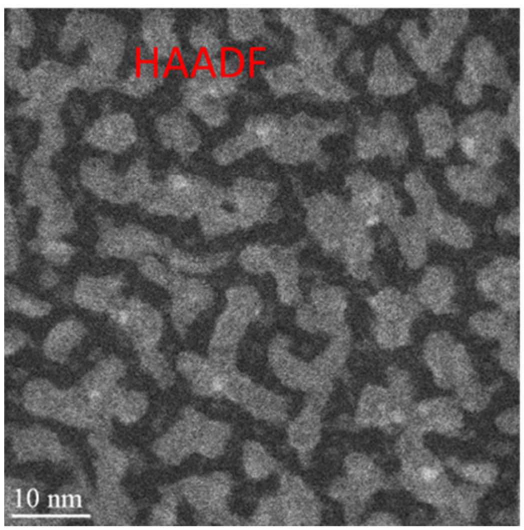
Can we find other *conductive stable oxides* (in fuel cell) that increase activity and facilitate the durability of the ORR catalysts?

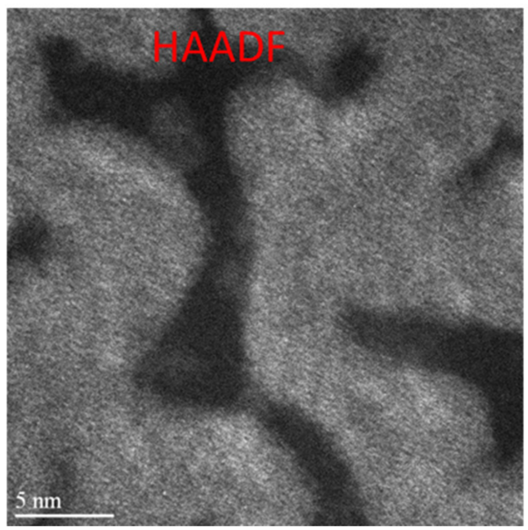
Amorphous Conductive NbO_x Deposited onto Graphene











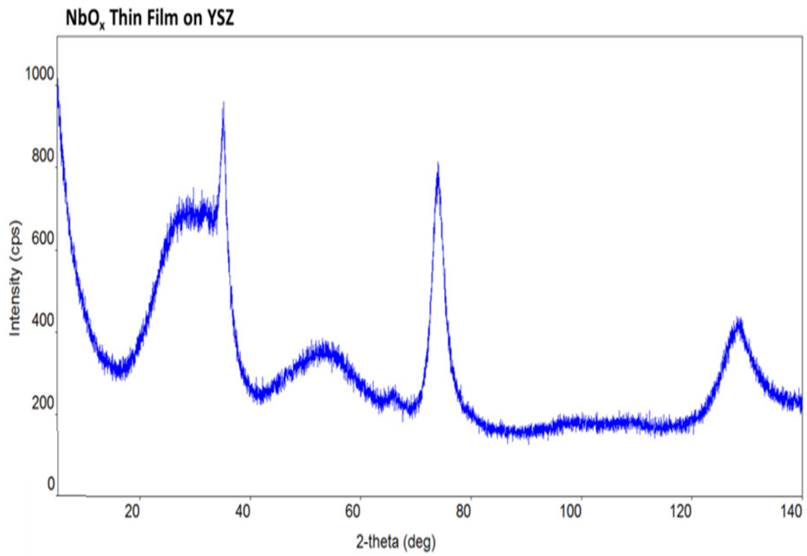
30 Å NbO_x grows into amorphous, isolated, worm-shaped islands on graphene

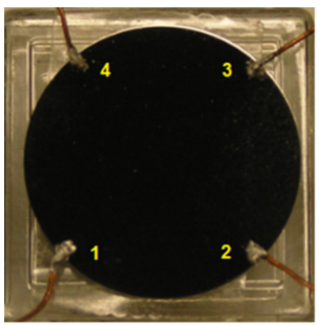
HAADF = high-angle annular dark field TEM
SAED = selected area electron diffraction

NbO_x Films: Amorphous and Conductive

NbO_x deposited in same manner on single crystal YSZ

XRD showed that the deposited film of NbO_x on single crystal YSZ is amorphous.





Van der Pauw Equation and Technique

$$exp\left(-\frac{\pi \cdot R_a}{R_S}\right)+exp\left(-\frac{\pi \cdot R_b}{R_S}\right) = 1$$

The sheet resistance *Rs* can be obtained from the two measured characteristic resistance R_a and Rb

$$R_a = \frac{V_{14}}{I_{23}} \qquad R_b = \frac{V_{34}}{I_{12}}$$

Conductivity $\sigma = \frac{1}{\rho} = \frac{1}{R_s t}$

NbOx (x=2.0 ~2.5)

At RT (22°C), $\boldsymbol{\sigma = 0.089\ S/m}$

At 80°C, $\boldsymbol{\sigma = 0.22\ S/m}$

Graphite

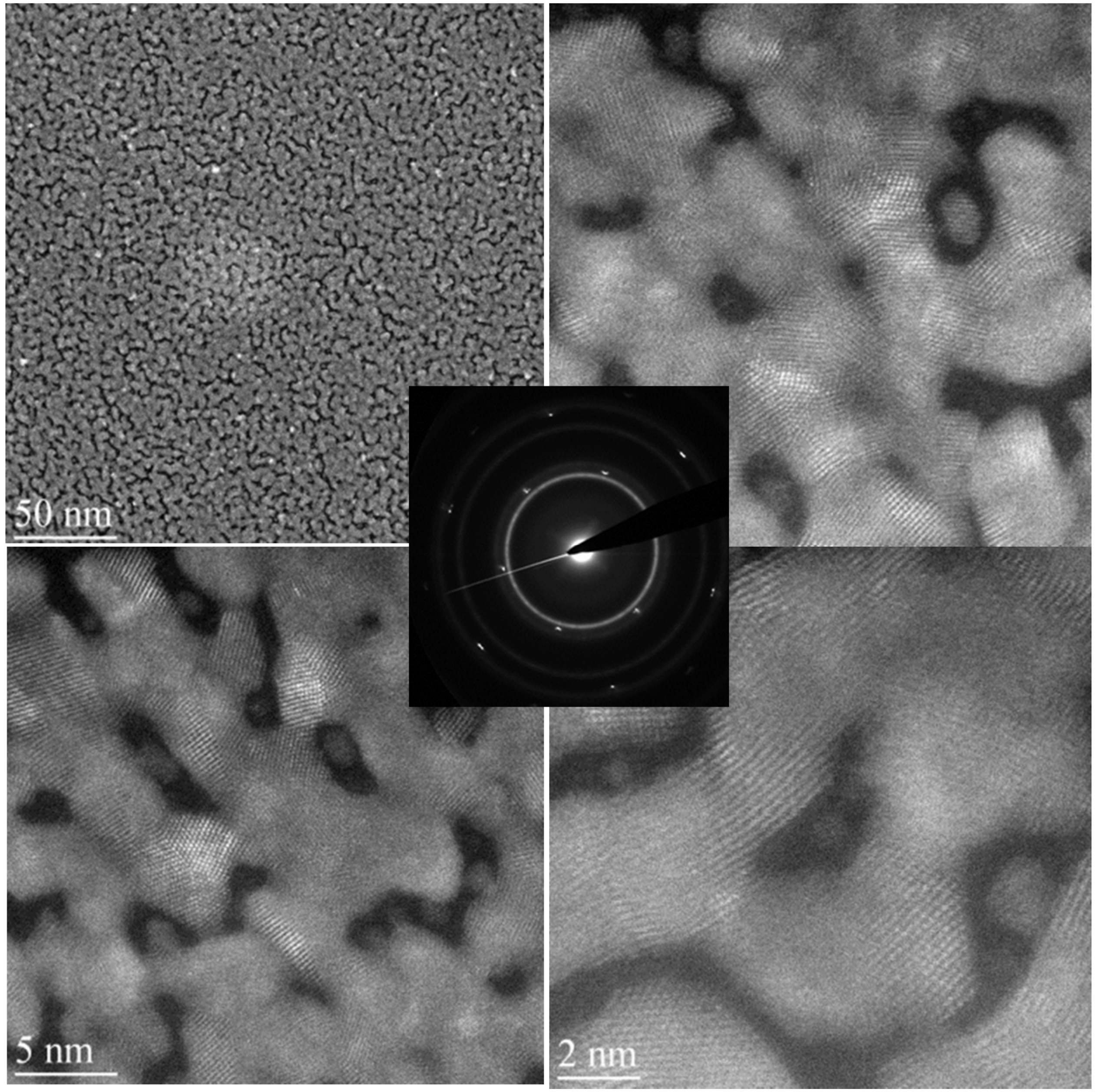
$\sigma_{//} = 2.0{\sim}3.0 \times 10^5\ S/m$

$\sigma \perp = 3.3 \times 10^2\ S/m$ ⊥ basal plane

Amorphous NbO_x is electronically conductive, but has 3 orders of magnitude less conductivity than graphite perpendicular to the plane.

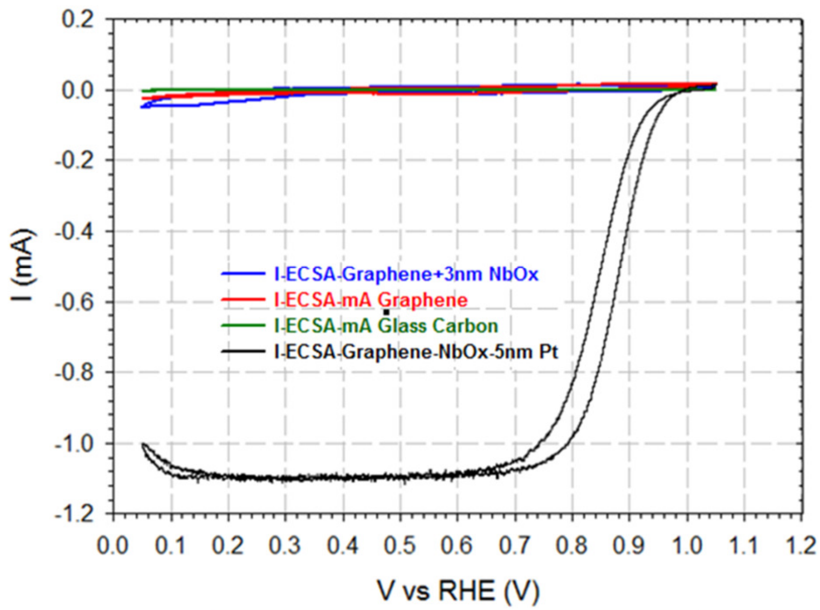
30 Å NbOx Templates 24 Å 2-D Connected Pt Network

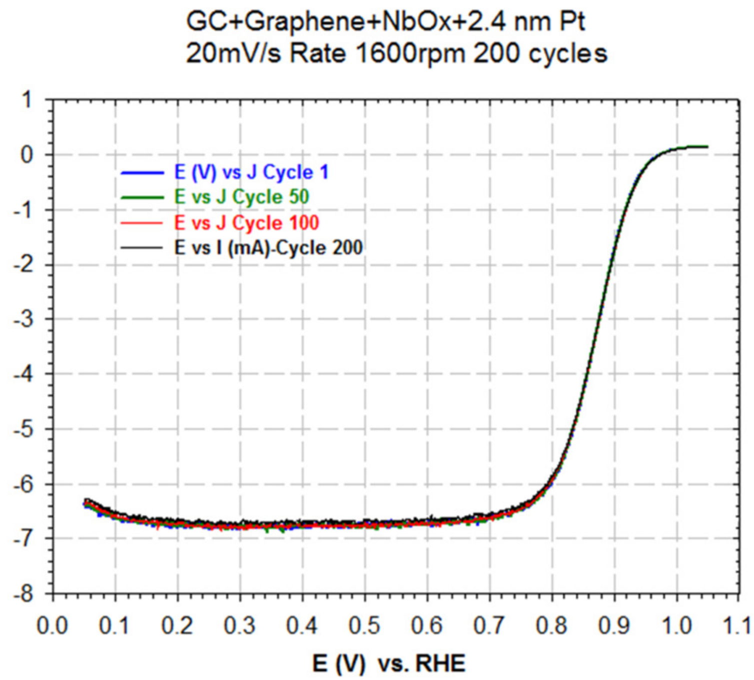
Further coating of 24 Å Pt onto the 30 Å a-NbO_x / graphene forms a 2-D connected Pt network



High Activity and Durability of 24 Å Pt on 30 Å NbOx on Graphene

- Exhibiting Pt bulk activity and high mass activity with improved durability





Specific Pt transfered charge	210	μC/cm²	Stability checked in 200 cycles with 20mV/s scan rate		
ECSA scan rate	200	mV/s	Measurement using 0.1 M $HClO_4$		
Temperature	30	°C	Pt Loading	2.0 μg/cm²	for 1nm thickness
ORR scan rate	20	mV/s	Scan range	0.05 V to 1.05 V	
Geom. planar area of tip	0.196	cm²	Rotation	1600 rpm	

Sample	Roughness	J (μA/cm²)	J_k (μA/cm²)	Mass Activity (A/g-$_{Pt}$)
24 Å Pt on 30 Å NbO_x on graphene on glassy carbon	0.9	1765	2377	495
24 Å Pt on graphene on glassy carbon	1.2	1562	2192	456
24 Å Pt on glassy carbon	1.3	1058	1345	280

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Converting flat sample activity and stability into practice…

POWDER SAMPLES

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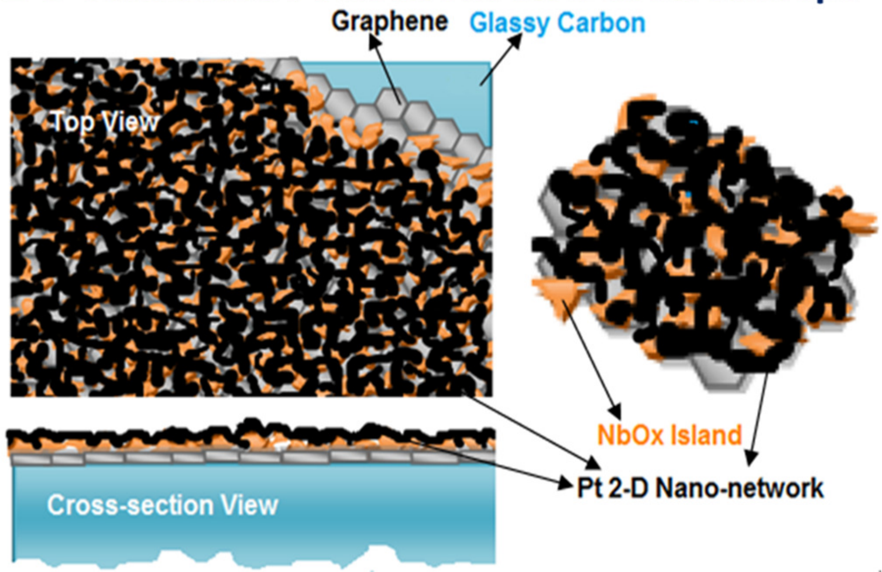
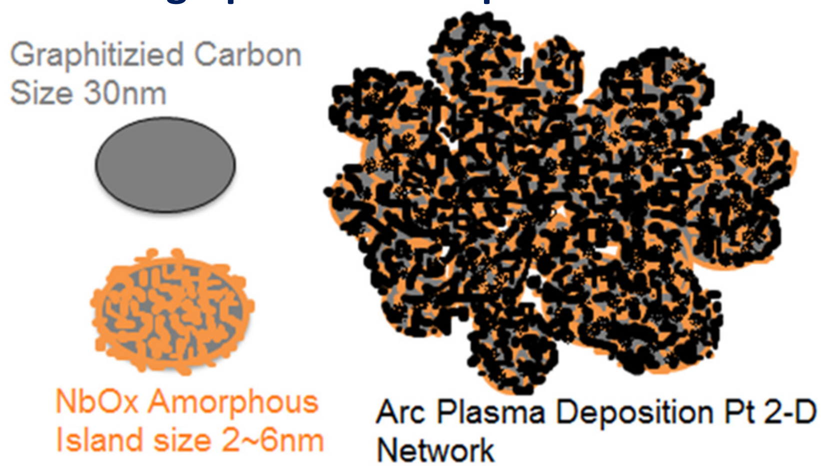
Implementing Concept ORR Catalysts onto Graphitic Carbon Powders

2-D connected Pt-network on a-MOx concept



The industry convention is to incorporate ORR catalyst powders into ink , so powders are preferred

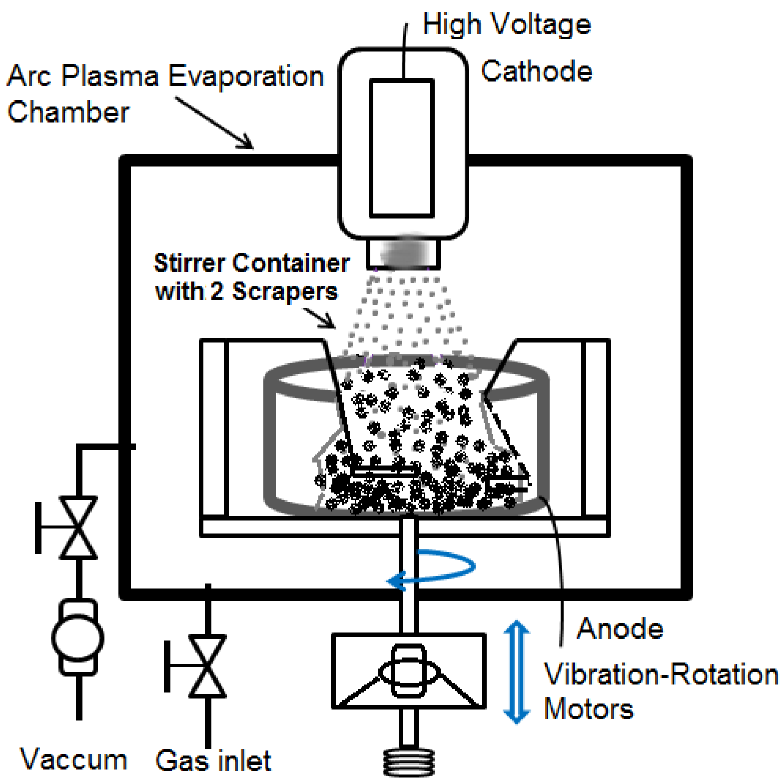
2-D connected Pt-network templated by a-MOx on graphitic carbon powders

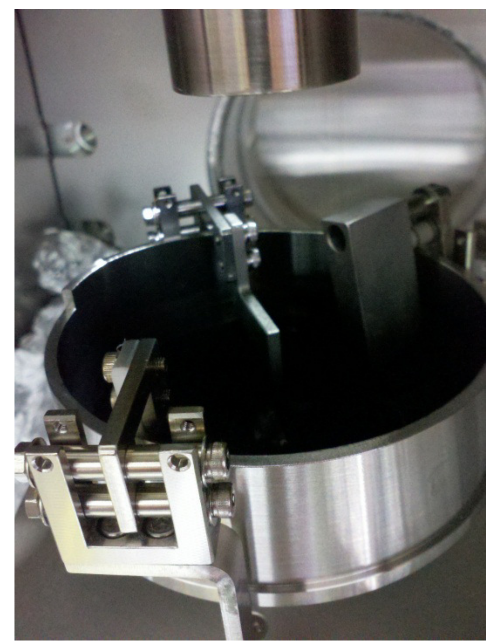


The challenge is implementing the desired amorphous NbO_x templated Pt 2-D connected network onto individual graphitic carbon nano-powders

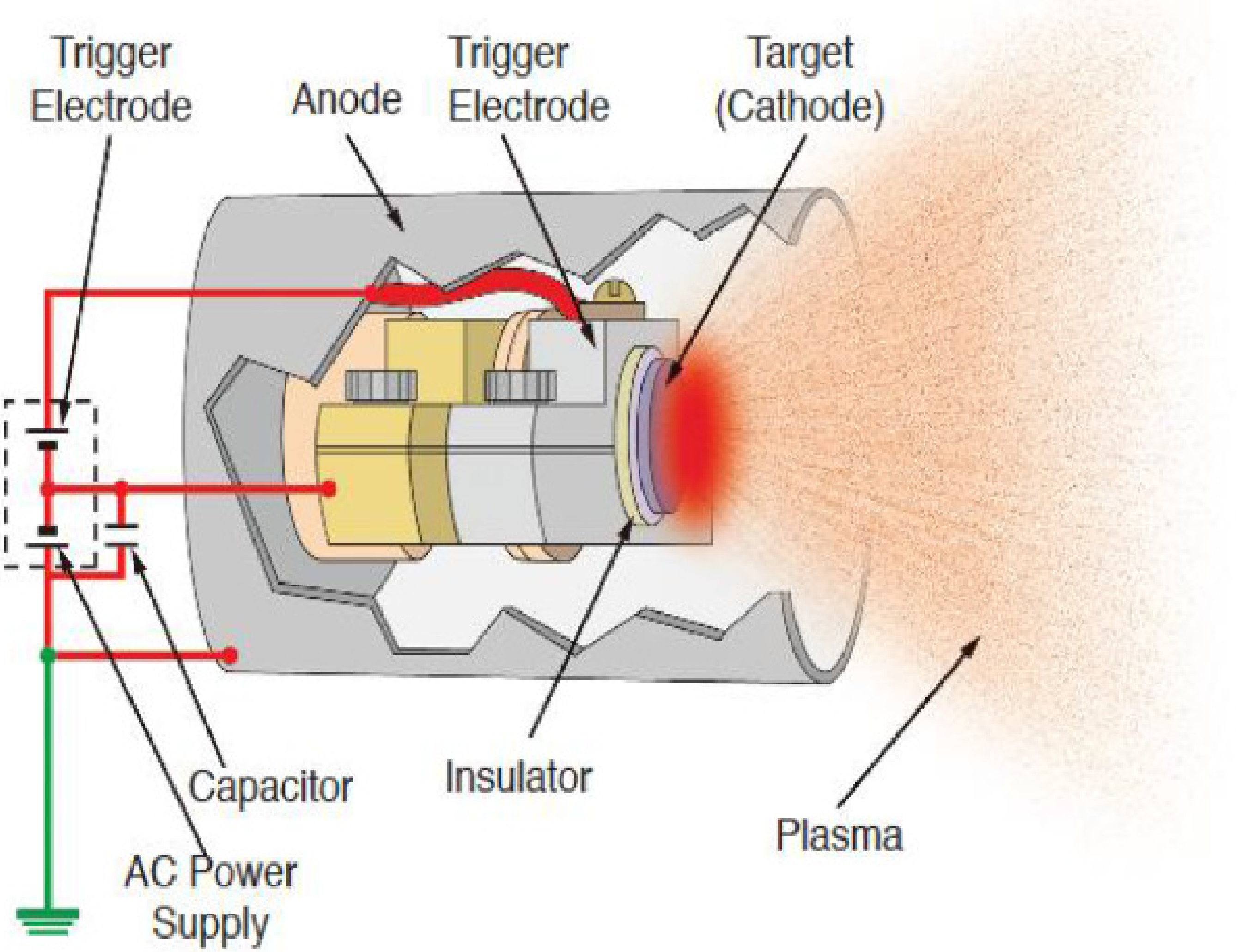
Challenges in Coating Carbon Nano-powders

- It is challenging to flow the graphitic carbon nano-powders using ultrasonic vibration, so a mechanical way has to be adopted to agitate the powders for sputtering. The deposition of NbOx onto carbon powders tends to agglomerate the nano-powders, so an effective powder breakup system has to be in place.
- ULVAC has an APD sputtering system, that can heat up the powder to 350 ^{0}C, flowing the powders, and breaking up the agglomerated powders, with 3 sputtering guns under a vacuum of 10^{-6} Torr.





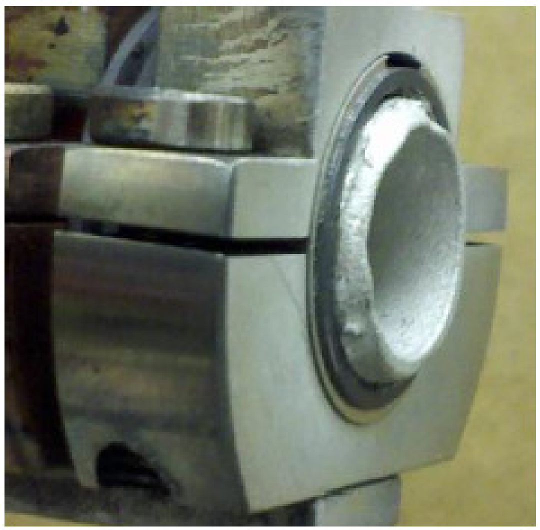
Arc Plasma Deposition (APD) Source

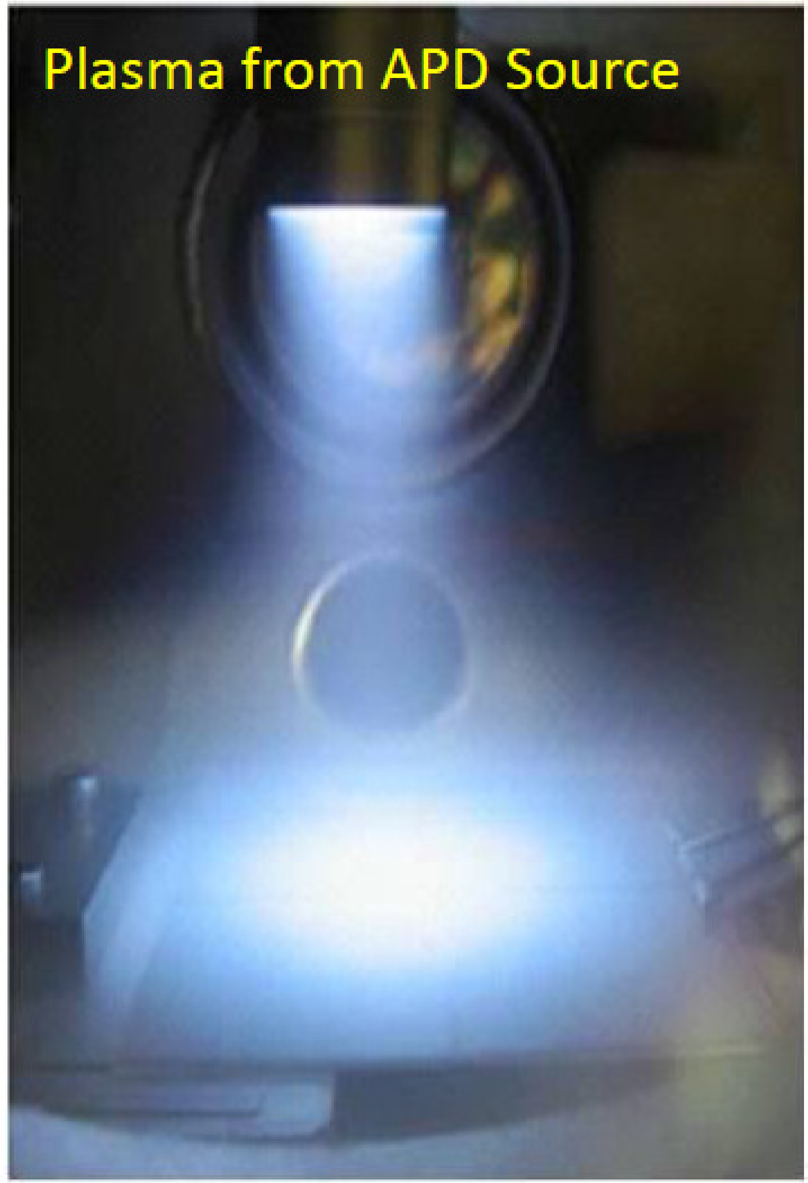


Arc Plasma Deposition (APD) Source

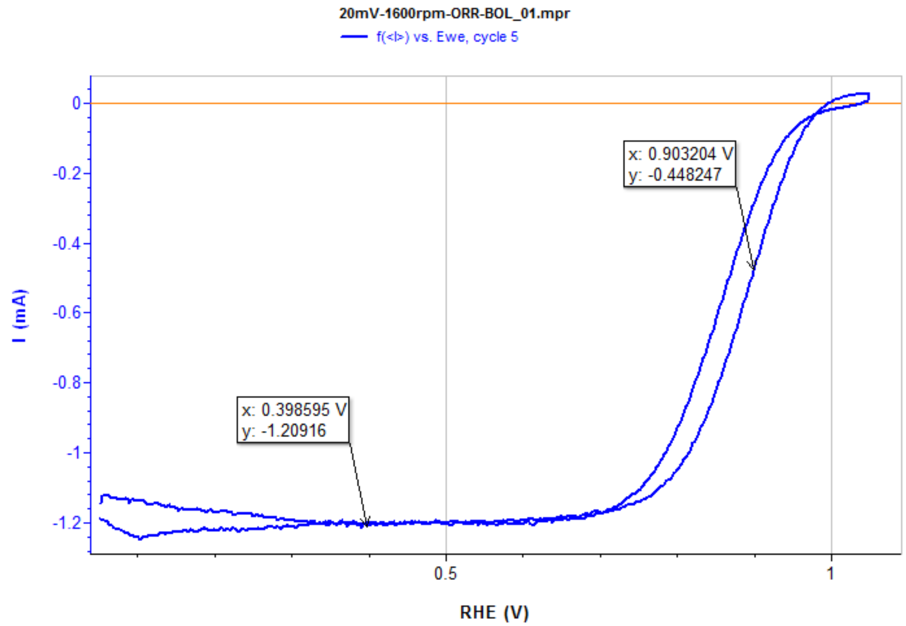
New Tube Target

Used Tube Target





Baseline: TKK EA50 Catalysts



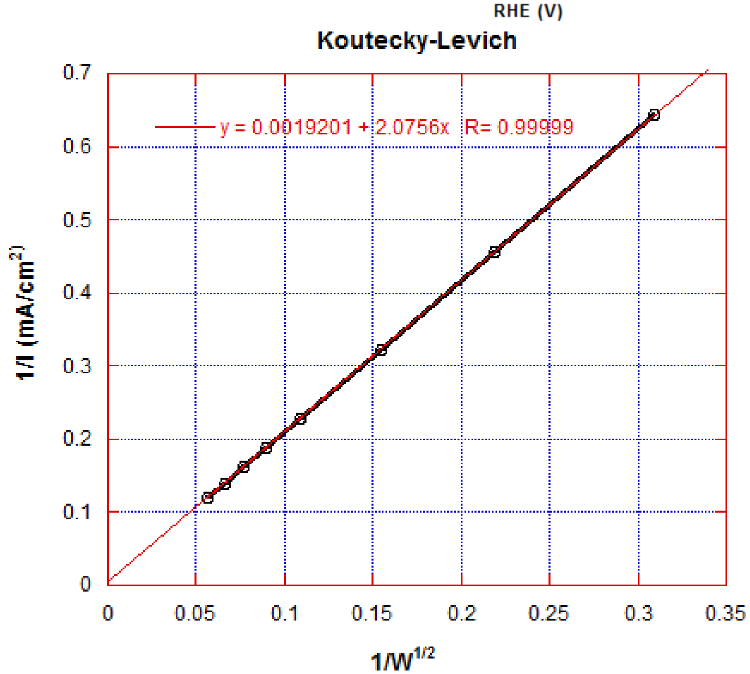
TKK Catalyst 46.8% (C/Pt) Loading about 16.0 ug/cm^2

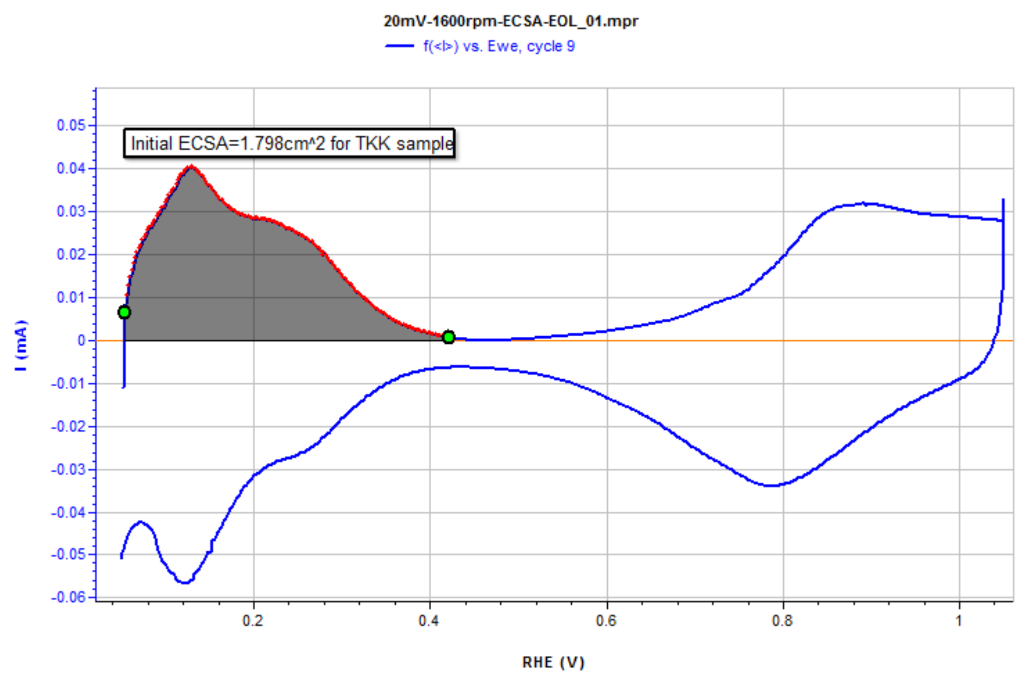
Initial

ECSA ~ 58.10 m^2/g

Mass activity ~ 200 A/g$_{pt}$

Specific activity ~300 uA/cm^2





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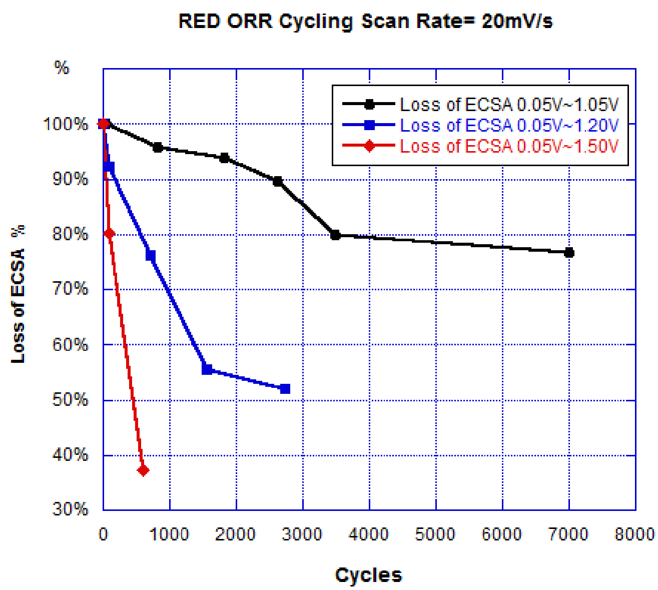
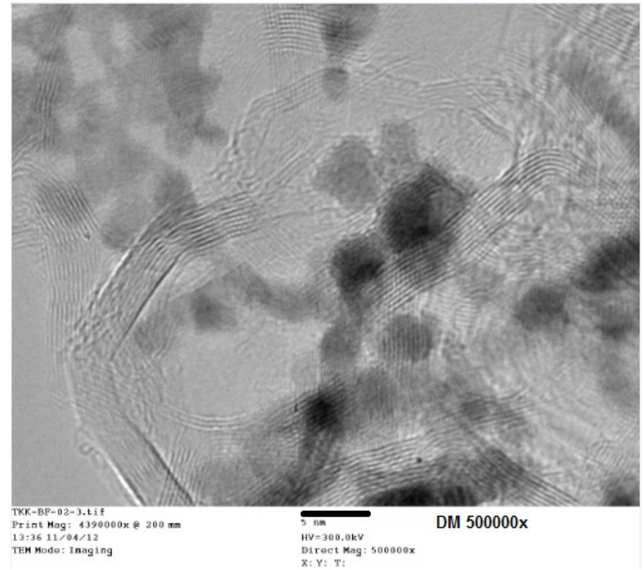
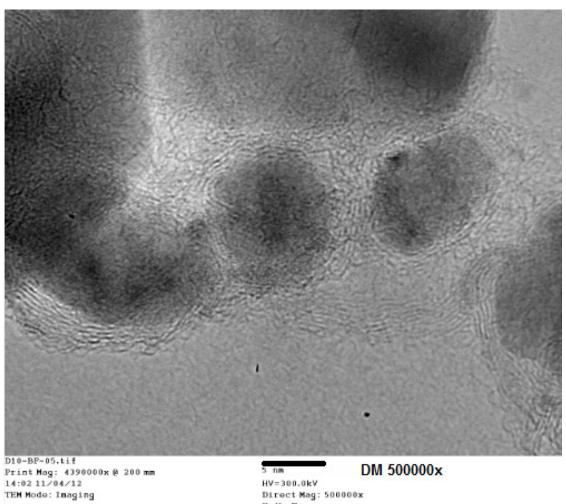
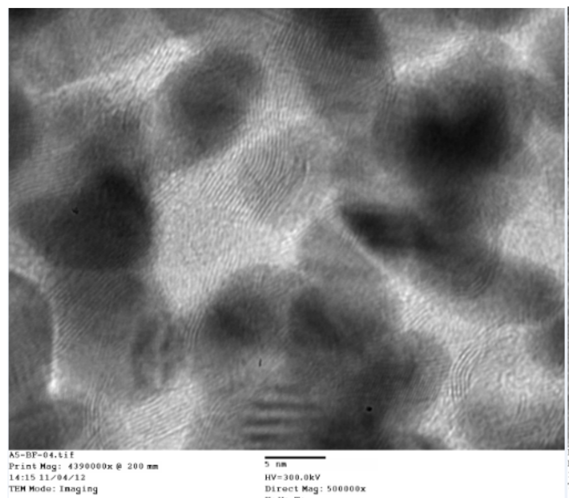


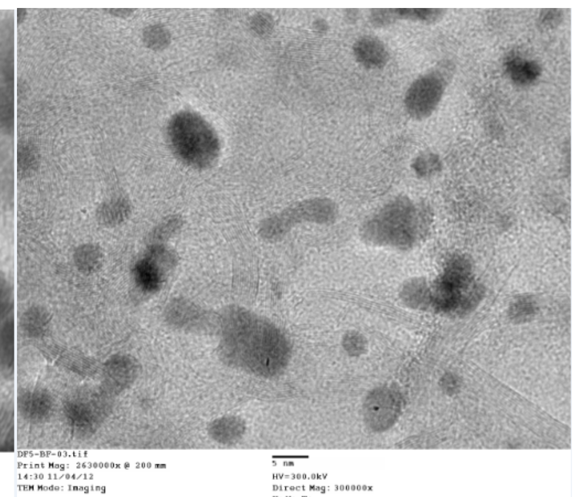




7000 Cycles in O2 0.05 to 1.05V, Pt increases 3 to 5 times



2700 Cycles in O2 0.05 to 1.2V, Pt increases 3 to 5 times



620 Cycles in O2 0.05 to 1.5V, Pt increases 2 to 3 times

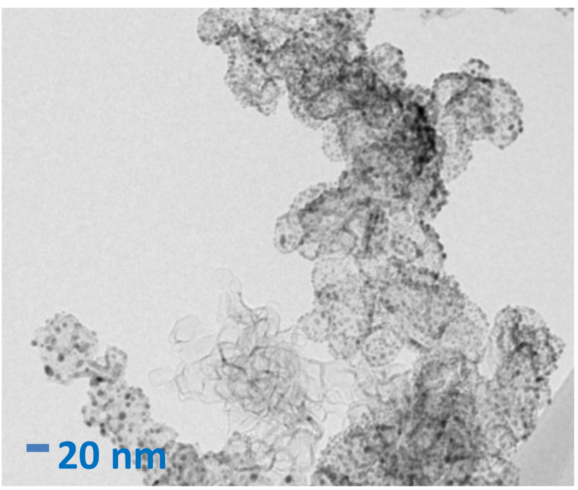
APD Deposition of Pt on Graphitic Carbon

20K pulse Pt/C: 20% ECSA loss after 4000 0.05-1.05 V cycles

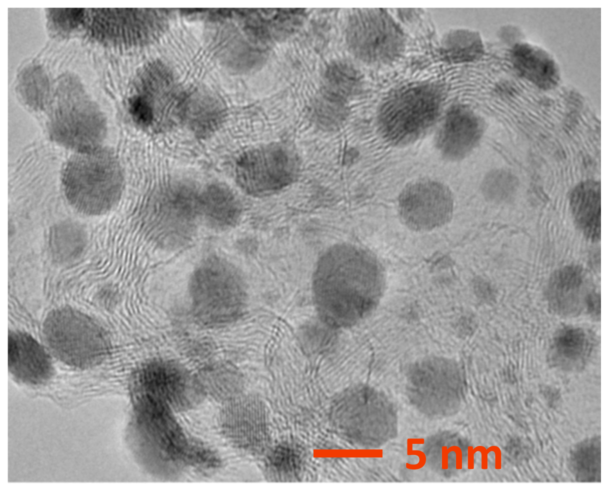
	EOL	4000 cycles
Total Pt Loading (ug/cm^2)	9.48	9.48
ECSA (m^2/g)	82.76	66.27
ORR I@ 0.4V (mA)	1.138	1.138
ORR I@ 0.9V(mA)	0.424	0.395
Roughness	7.8	6.3
Specific Activity (mA/cm^2)	0.442	0.493
Mass Activity (A/gPt)	366	327

40K pulse Pt/C: 17% ECSA loss after 2500 0.05-1.05 V cycles

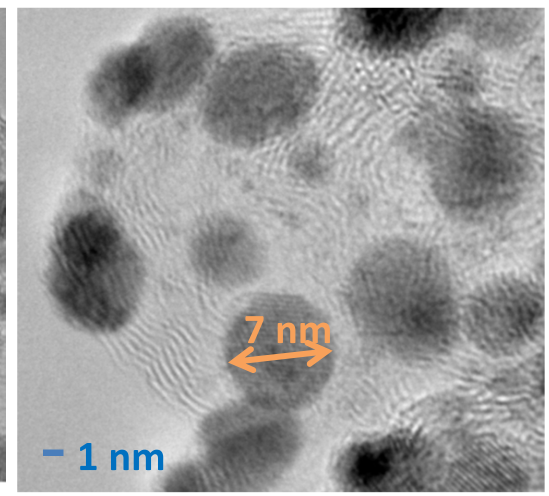
	BOL	2500 cycles
Total Pt Loading (ug/cm^2)	23.36	23.36
ECSA (m^2/g)	46.51	38.65
ORR I@ 0.4V (mA)	1.171	1.176
ORR I@ 0.9V(mA)	0.553	0.505
Roughness	10.9	9.0
Specific Activity (mA/cm^2)	0.492	0.500
Mass Activity (A/gPt)	229	193



40K pulse sample as-made



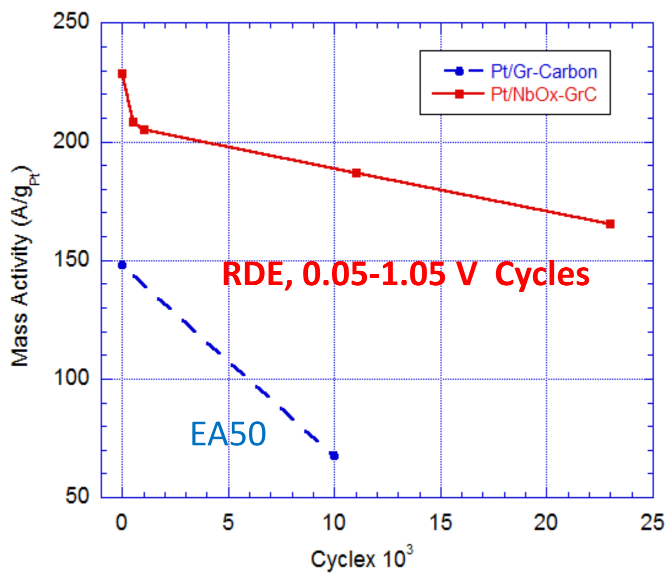
40K pulse sample as-made

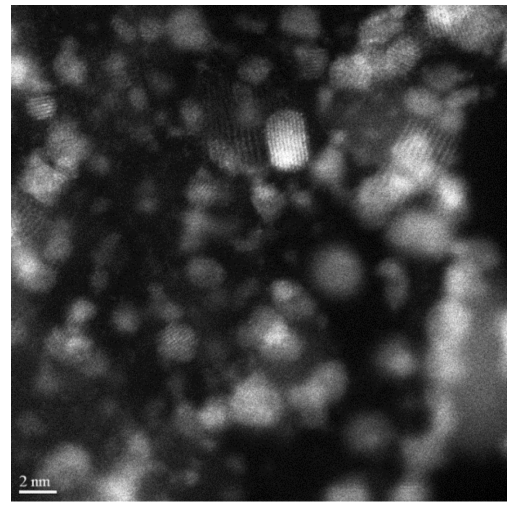


3200 cycles

As with TKK EA50, the APD Pt on graphitic carbon is not stable

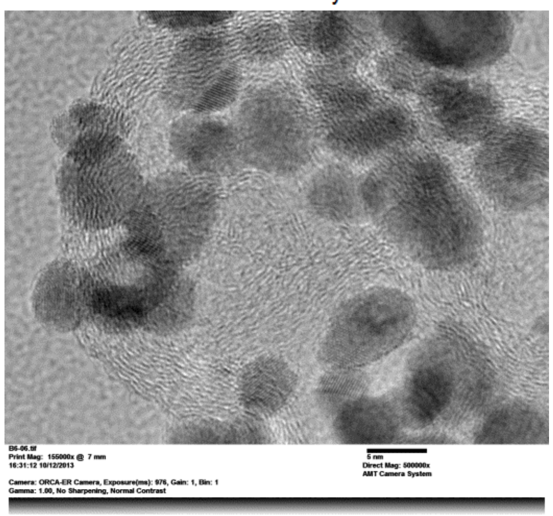
Sequential Deposition of 20K NbO_x and 20K Pt



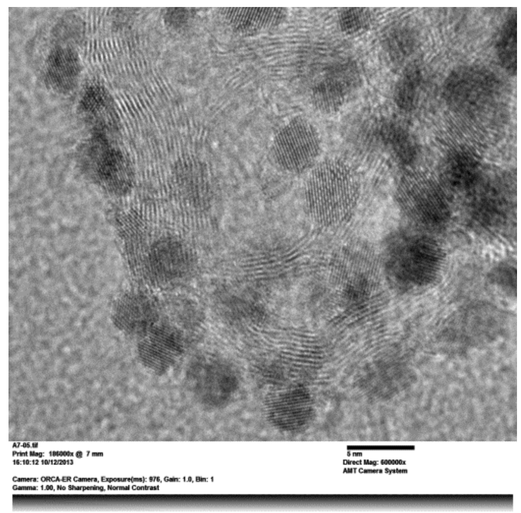


As made 20K NbO_x, 20K Pt powders

Pt pinned by amorphous NbO_x as deposited, partially formed 2-D connected network.



10K 0.05-1.05 V Cycles



10K Cycle 1.0-1.5 V SW Cycles

10K 0.05-1.05 V cycles: Pt particle size increase, but mostly still pinned by NbO_x

10K 1.0-1.5 V cycles: stable

Further Improving the Activity

Sample	Pt loading Wt. %	Roughness (cm^2/cm^2)	ECSA(m^2/g)	**SA ($\mu A/cm^2$)**	**MA(A/g_{pt})**
Baseline Pt/GC	47.00%	9.37	49.4	311	153
2.4APt/NbOx/GR/GLC (flat)	2.4 nm*	1.10	22.9	2377	495
2.4APt/NbTiOx/GR/GLC (flat)	2.4 nm	1.29	25.1	**2416**	**606**
APD Pt/GC	8.99%	1.19	28.4	749	213
APD Pt/GR	10.50%	1.65	27.1	871	235
APD Pt/NbO_x/GC	19.70%	4.58	37.1	**790**	**293**
APD Pt/NbOx/GC	7.54%	2.26	34.0	604	296
APD Pt/NbO_x/GR	10.50%	2.10	34.3	1003	345
APD Pt/NbO_x/GR-L	3.93%	1.01	33.6	**1178**	**391**

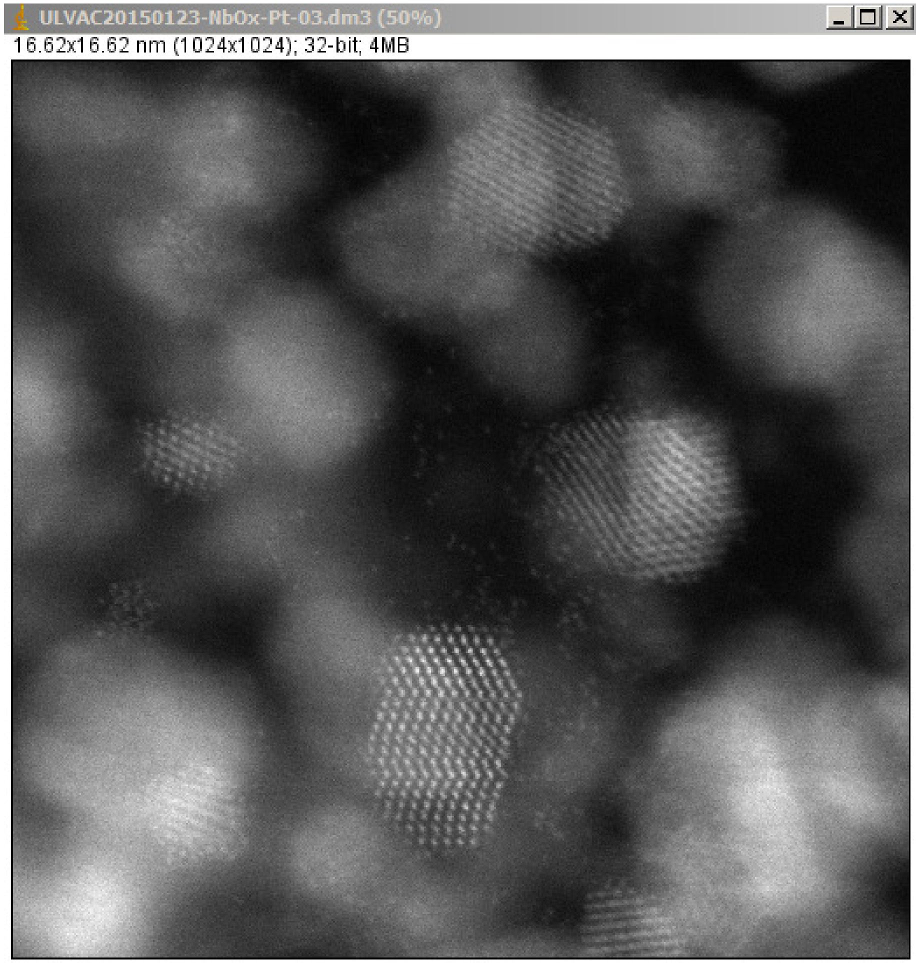
Specific activity of Pt/NbO_x/C ORR catalyst on **graphitic carbon (GC)** is about **800**, on **graphene (GR)** about **1200** $\mu A/cm^2$. Their respective mass activities are about **300** and **400** A/g_{Pt} .

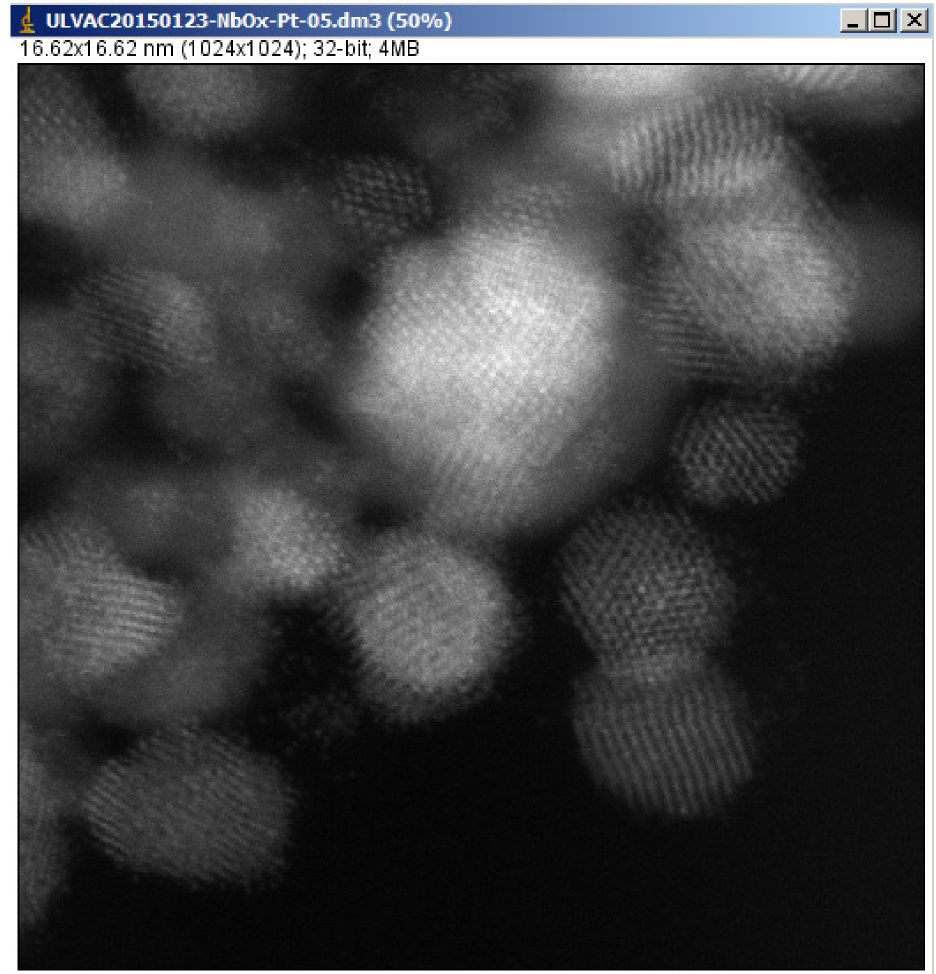
Specific activity on flat sample was **2400** $\mu A/cm^2$ and mass activity was **600** A/g_{Pt}.

The achieved specific activity indicates that the 2-D Pt network is not fully formed yet

Further Increasing The Specific Activity and Durability

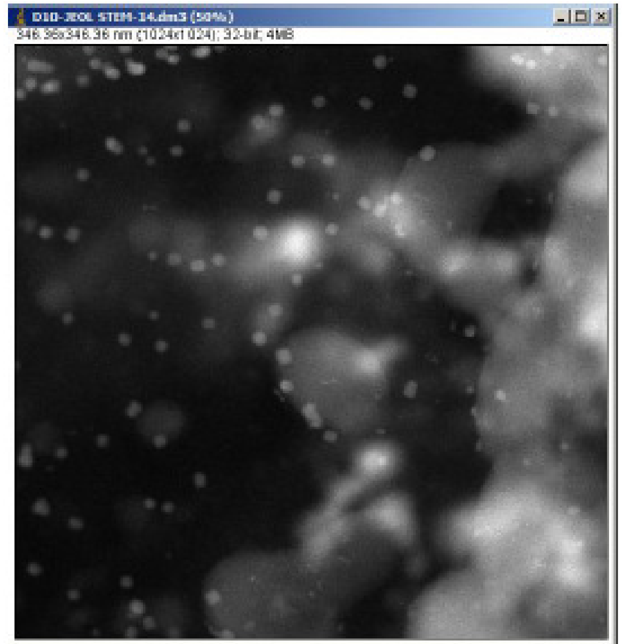
- Using graphene powders and increasing the NbO_x concentration



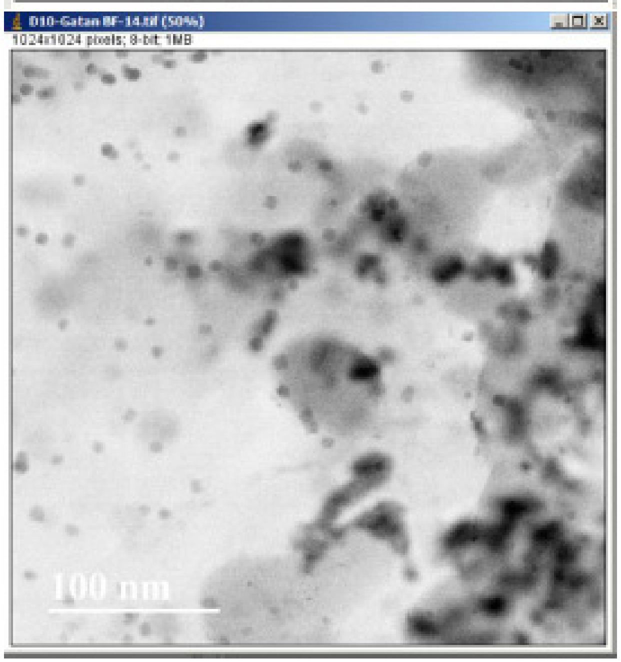


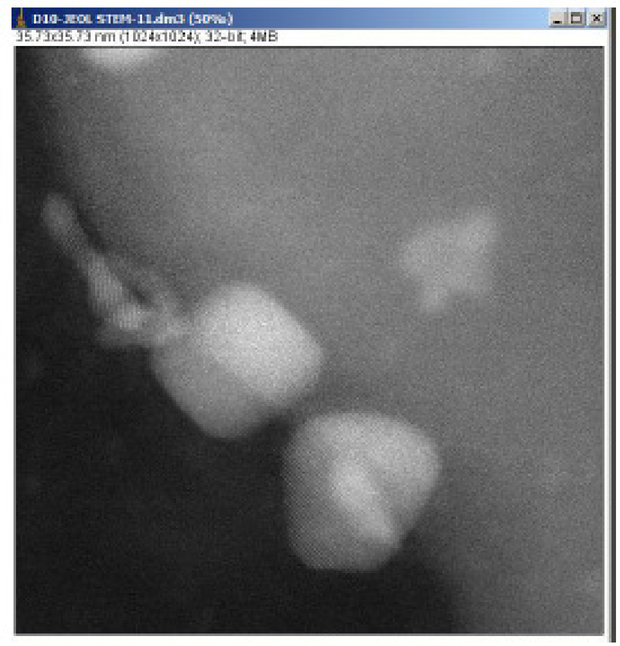
With higher loading of NbO_x (12 wt.%), and with NbO_x forming 2-D connected network, about 5 wt.% of Pt is needed to start forming 2-D connected network with improved specific activity and mass activity

How a-NbOx Enhances Durability

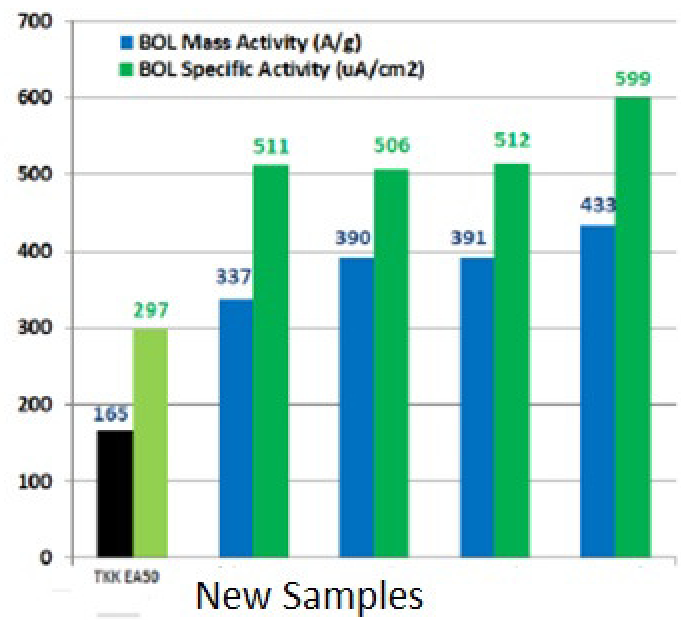


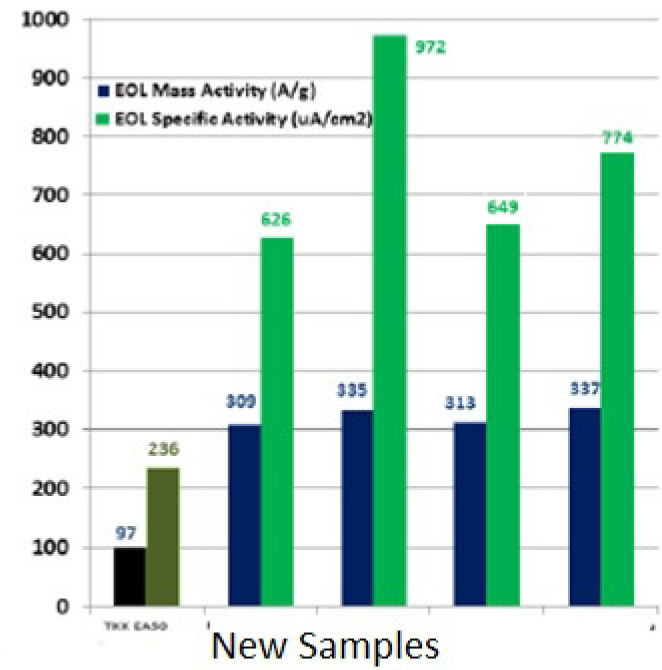
a-NbOx pinned down Pt, preventing excessive agglomeration, probably due to its intermediate surface energy in between those of Pt and Carbon

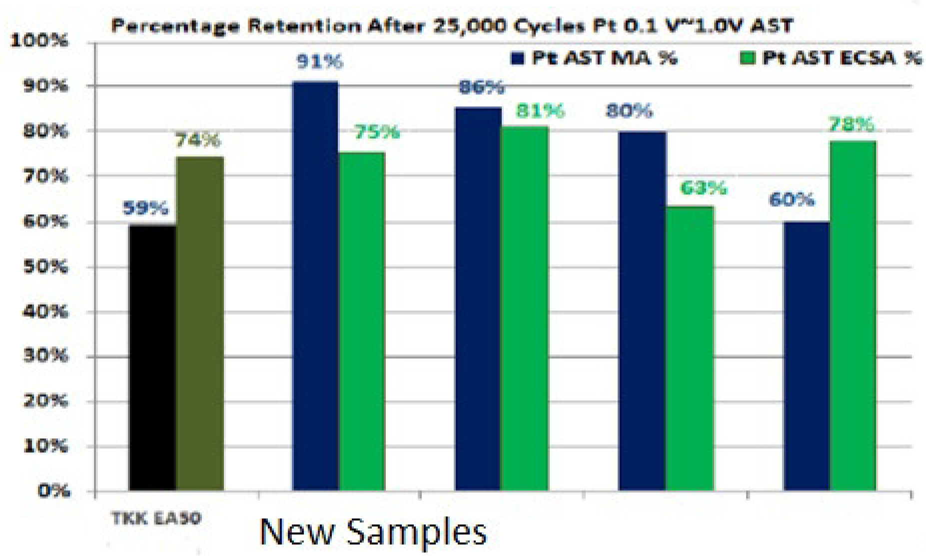




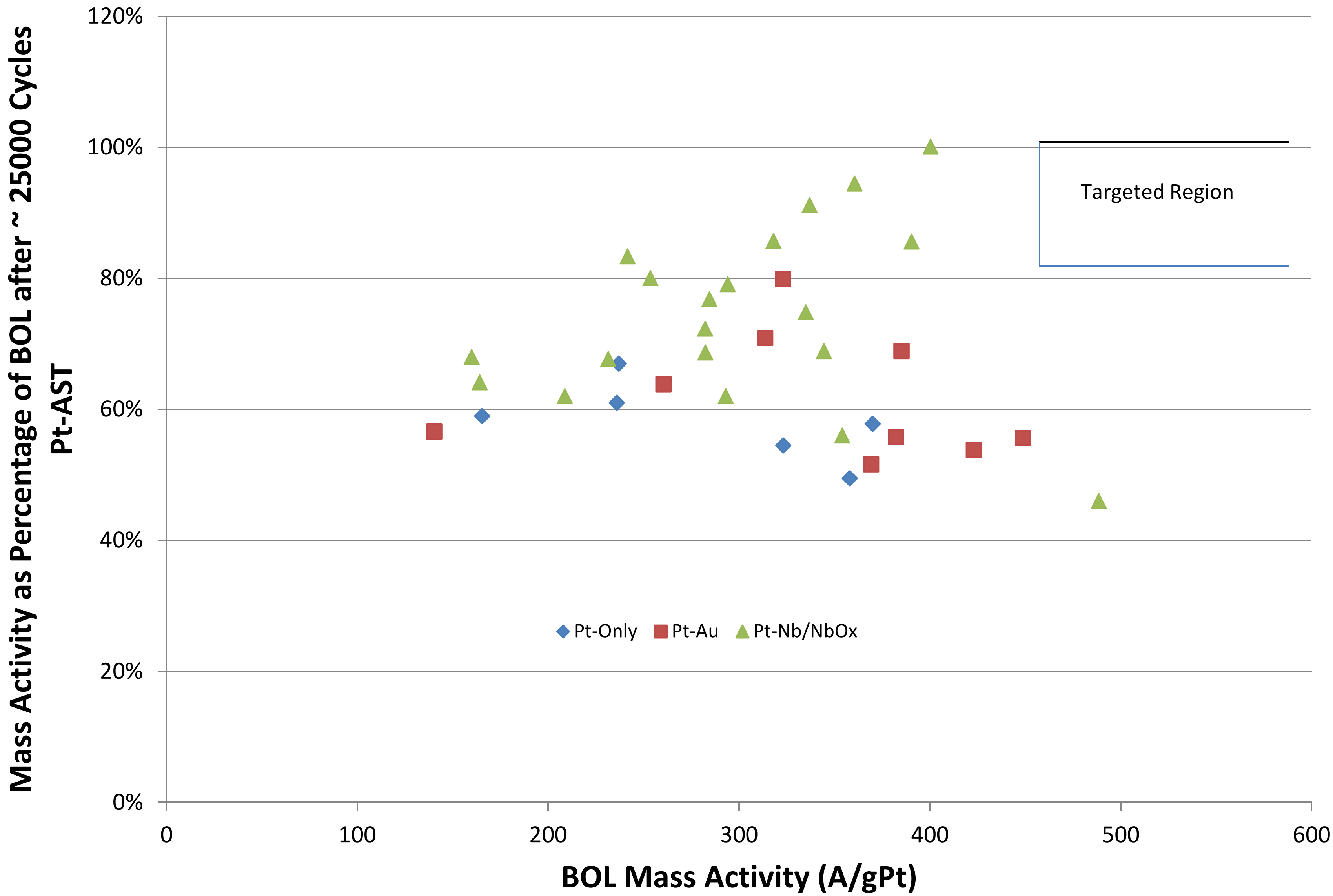
Further Improvements on Activity & Durability







Further Increasing The Specific Activity and Durability
- Using graphene powders and increasing the NbO_x concentration



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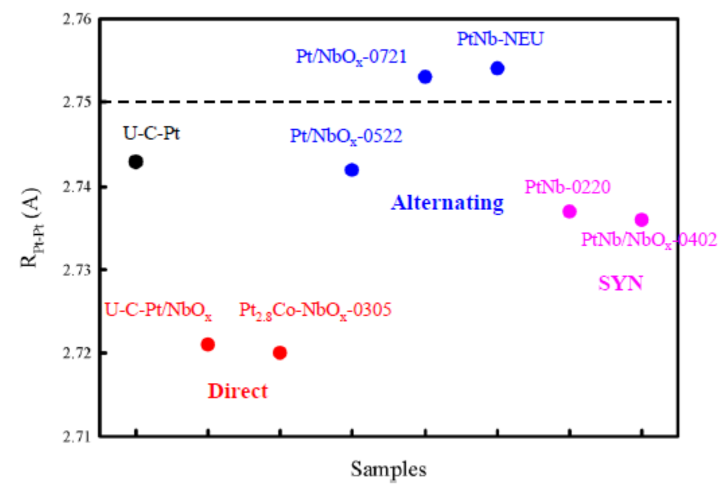
But why would the activity increase?

XAS AND DFT STUDIES

What Contributes to the Improved Activity and Durability

	Pt/NbOx/GC	Pt/GC
R Pt-Pt (Å)	**2.721**	2.740
R Pt-Nb (Å)	**2.737**	
N Pt-Pt	**6.5**	8.3
N Pt-Nb	**0.5**	

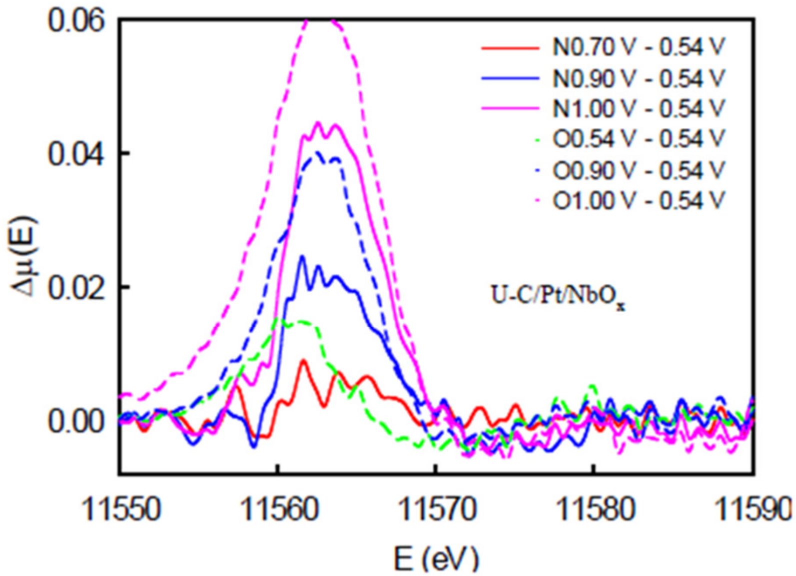
Pt-Pt bond distance

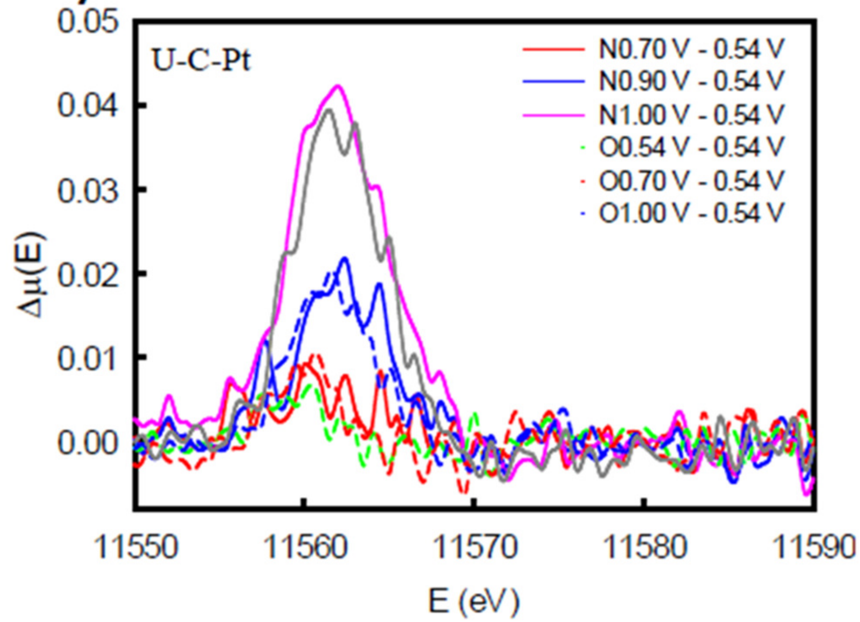


Amorphous NbO_x intrinsically changed the atomic environment of Pt in the ORR catalyst, reducing the Pt-Pt distance (**favorable for activity**) but also lowered the nearest neighbor of Pt. This phenomena is consistent for graphitic carbon or graphene.

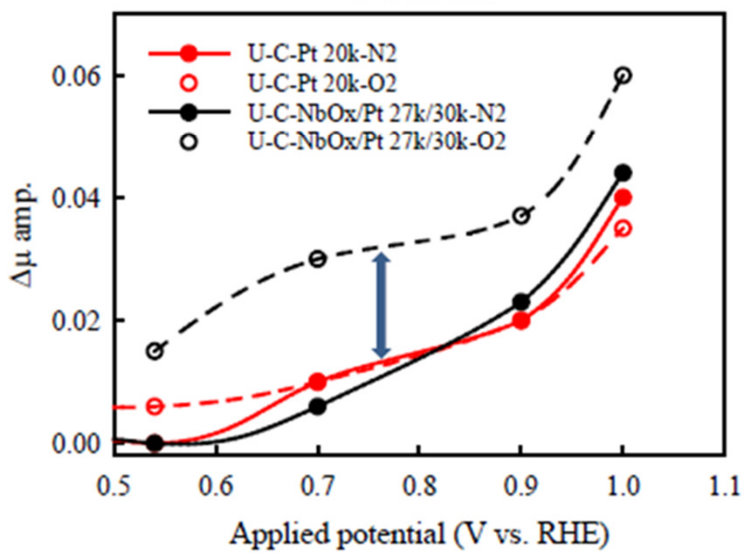
Δμ Analysis at NEU

Δμ analysis





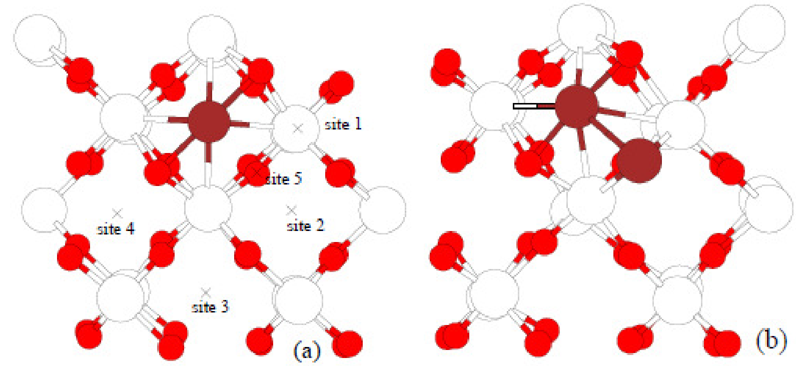
U-C-Pt-20k



1. Reduced OH coverage on Pt-NbO_x compared to Pt was not observed, in line with previous Pt-NbO_x samples.
2. OH coverage on Pt in N_2 and O_2 are about the same.
3. OH coverage on Pt-NbO_x in O_2 is higher than that in N_2.

OH coverage on Pt-NbOx in O_2 is higher that that in N_2, indicating better activity with amorphous NbOx

DFT Modeling at NWU



DFT modeling indicates Pt prefers to sit on top of O sites in amorphous MOx (b) than in crystalline (a) of the same composition

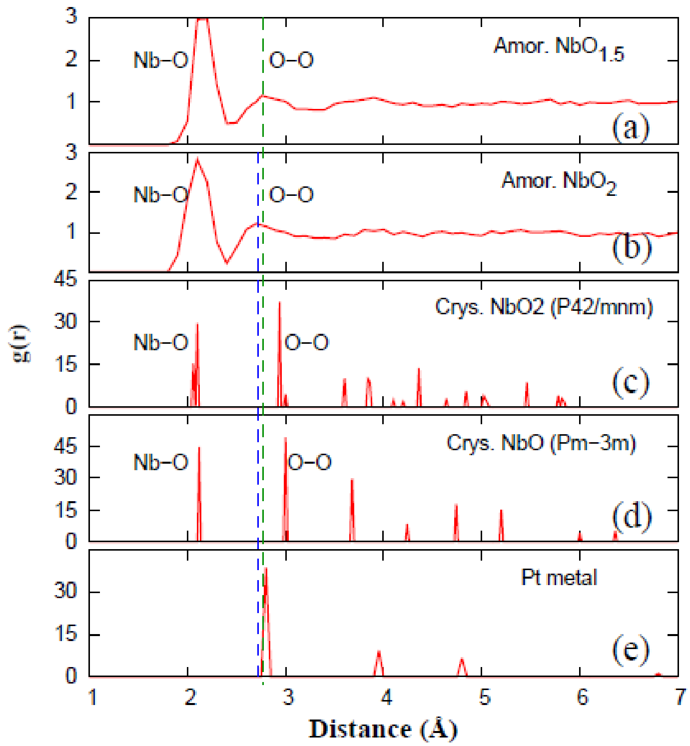


Figure 4: Comparison of radial distribution function of amorphous $NbO_{1.5}$, amorphous NbO_2, crystal NbO, crystal NbO_2, and Pt metal.

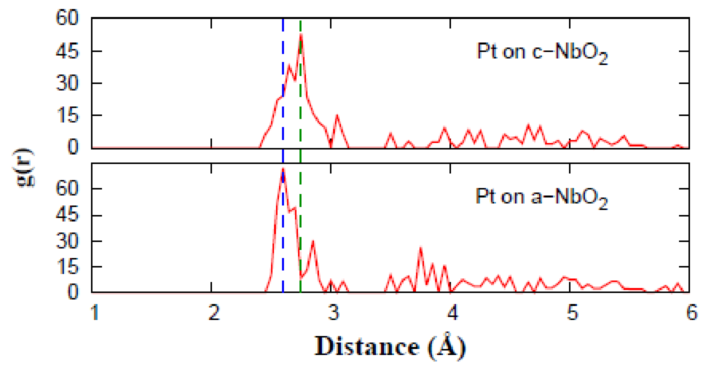


Figure 3: Comparison of radial distribution function of Pt metal on amorphous NbO_2 and crystalline NbO_2.

Amorphous NbO_x leads to shorter O-O distances than in crystalline NbO_x → Amorphous NbO_2 should lead to shorter Pt-Pt distances versus crystalline NbO_2

Summary

- A novel ORR Catalyst for PEMFC has been developed using amorphous stable NbOx worm-shaped islands to template a thin layer of Pt, forming 2D connected Pt network. This microstructurally engineered ORR catalysts posses high specific and mass activity and much improved durability.

- ULVAC APD sputtering with stirring and powder breakage mechanism has been used in replicating this ORR concept onto graphitic carbon and graphene powders of 30 to 50 nanometers, achieving a mass activity of about 400 A/g-Pt and a mass activity retention of more than 90% after 25000 Pt-stress cycles at 0.1-1.0 V V Pt-stress tests in 0.1M HClO4 acid. However, the specific activity is not up to those achievable for Pt 2D connected network. Room still exists for further improvements .

- The improved durability of the novel ORR catalysts comes from the pinning effects of a-NbOx on Pt due to its surface energy in between those of Pt and graphitic carbon.

- The amorphous NbOx has shorter O-O distance compared to its crystalline counterpart, which in turn dictates the Pt-Pt distance shorter , enhancing the ORR activity.