

# Platinum Monolayer Electrocatalysts

Project FC141

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Brookhaven National Laboratory

DOE Hydrogen and Fuel Cells Annual Merit Review  
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# Overview

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## Timeline

Start: September 2015

End: October 2019

## Barriers

### A. Catalysts' Durability:

< 40% loss in activity after 30,000 cycles

### B. Catalysts' Performance:

Catalyst activity;  $\geq 0.44$  A/mg<sub>PGM</sub>

### C. Catalysts' Cost:

PGM loading;  $\leq 0.125$  mg PGM /cm<sup>2</sup>

## Budget

Funding received in

FY2018: \$600,000

FY2019: \$500,000

## Collaborators

General Motors

Toyota M. C.

N.E. CHEMCAT Co.

# Relevance

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## Project objective

Developing active, durable core-shell catalysts for the oxygen reduction reaction (ORR) that meet the DOE technical targets (Table 3.4.7)

Activity at 0.9 V  $>0.44$  A/mg<sub>PGM</sub>, loss  $<40\%$  after catalyst and support AST  
 $<30$  mV loss at 0.8 A/cm<sup>2</sup> after catalyst AST (30,000 cycles 0.6-0.95V)  
 $<30$  mV loss at 1.5 A/cm<sup>2</sup> after support AST (5,000 cycles 1-1.5V)

## RDE screening targets

**Activity  $>0.6$  A/mg<sub>PGM</sub> after catalyst AST (this period), including support AST (next goal). ECSA  $>40$  m<sup>2</sup>/g after catalyst AST.**

## Tasks and deliverables

- Innovate and validate new core materials, core-shell structures, and scalable synthesis methods for advancing cathode catalysts/support
- Deliver samples with performance exceeding RDE targets for MEA tests by collaborates

## Status and impact

- Synthesis of active, durable **PtNiN** catalysts is improved based on better understanding of lattice structure and Pt segregation behavior.
- Nitride-stabilized bimetallic catalysts on suitable carbon supports are promising for  $>0.4$  A/g activity after both catalyst and support ASTs.

# Approach

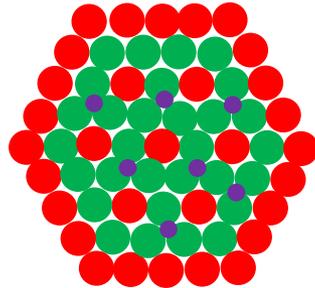
## Two types of catalysts with low and PGM-free cores:



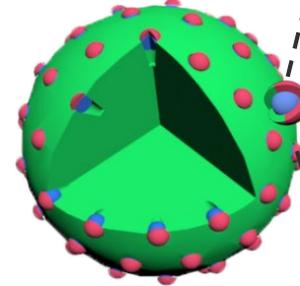
Pt ●

Ni ●

N ●



Pt shells on top of  $\text{NbO}_x$  cores that are partly embedded in carbon



Bright dots for ordered Pt atoms in shell

Gray area for embedded amorphous  $\text{NbO}_x$  core

- Ni is the best activity promoter for ORR, but is prone to dissolution in PEMFC.
- Nitriding stabilizes Ni resulting in high ECSA, activity, and durability.
- Structural advantage of nitride core for stability of monolayer Pt skin catalyst clarified.
- Correlation of performance (ECSA, activity, and durability) with properties (Ni content, lattice phase, and Pt segregation) established.
- Pt binds carbon weakly and catalyzes carbon corrosion, resulting in loss of carbon and ECSA after support AST.
- Embedding  $\text{NbO}_x$  in 4-nm pores on carbon and depositing Pt on top anchors down each of Pt half-shell particles, which minimizes particle agglomeration and carbon corrosion.
  - Small effort in this period
  - Future studies planned for enhancing support durability.

# Tasks and Outline

**Last year status:** The best RDE results exceeded activity and durability targets, but MEA results have not met the two targets concurrently.

	Target	PtNiN			
		MEA			RDE
		GM#1	LANL	GM#2	BNL
MA (A mg <sup>-1</sup> )	> 0.44	0.37		0.15	0.91 / 0.5
MA loss (30K)	< 40%	-19%		-56%	-18%
ECSA (m <sup>2</sup> /g)		27		44	89 / 50
ECSA loss	< 40%	-21%		-50%	-13%
Loss @0.8 Acm <sup>-2</sup>	<30 mV	30	0	75	

Pt-NbO <sub>x</sub> C		
MEA		RDE
UW	GM	BNL
0.12	0.03	0.56
		-4%
	20	66
	+25%	
No loss after support AST		

Before optimizing MEA fabrication for PtNiN, we need to better understand and optimize catalysts.

(1) XRD and TEM characterization for clarifying favorable PtNiN lattice structure and formation of Pt monolayer skin (slides #6-10)

(2) Intermetallic phase for PtNiN on porous Ketjenblack 300J (Slides #11-14)

Summary – RDE screen criteria (slide #15)

Oxidation of NbO<sub>x</sub> at higher temperature may be one of the causes of low MEA activity.

(3) XPS and TEM results confirmed structural model. (Slide #16)

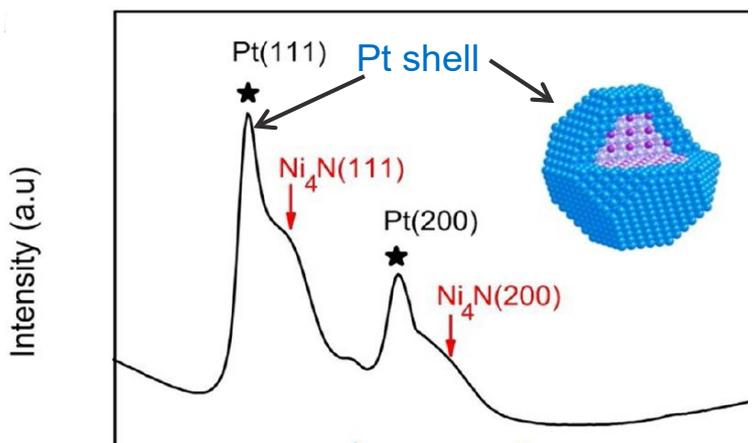
# 1a. Pt distribution: Core-shell or thin skin



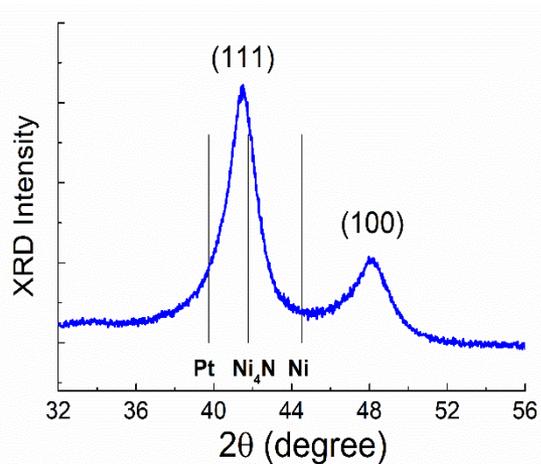
**Core-shell** structure has a **Pt**-only shell and a **Ni(N)**-only core.



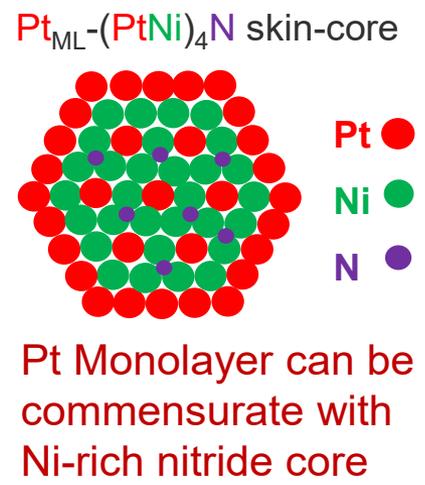
**Pt-skin** structure also has a **Pt**-only shell, but with a **PtNi(N)**-alloy(nitride) core



Shoulder peaks indicate the lattice spacing of  $Ni_4N$  core is smaller than that of the 3-4 ML Pt shell.



A single set of symmetric peaks suggests uniform lattice spacing of alloy or a monolayer Pt skin

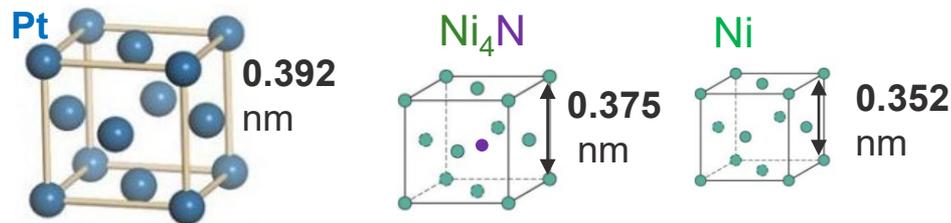
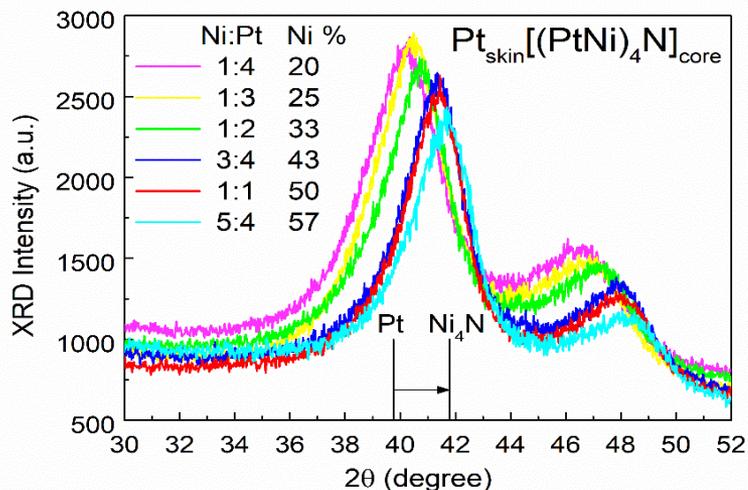


No need to de-alloy Ni in acid for both types of PtNiN catalysts. While similar ECSA can be obtained, a monolayer skin layer is favored for high activity enhancement by subsurface Ni.

How to characterize and optimize thin skin catalysts?

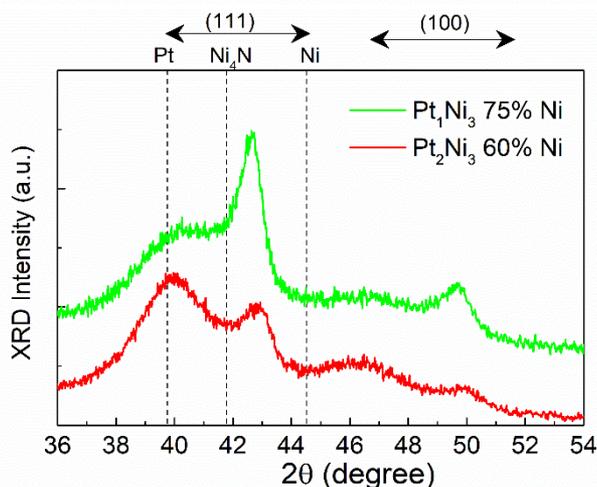
# 1b. Single-phase PtNiN with Ni% up to 57%

Accomplishment

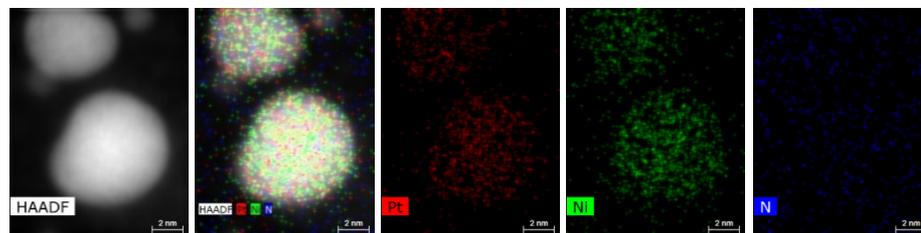


$Ni_4N$  has one N atom at the center of FCC cubic cell, which expands Ni lattice resulting in a reduction of the lattice mismatch with Pt from **-10.2%** to **-4.6%**.

Moderate lattice mismatch between Pt and  $Ni_4N$  facilitates formation of single phase, stable PtNiN particles with high Ni content.



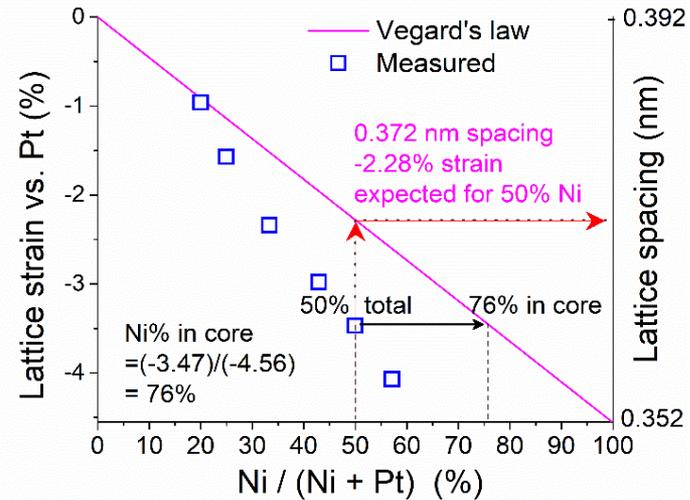
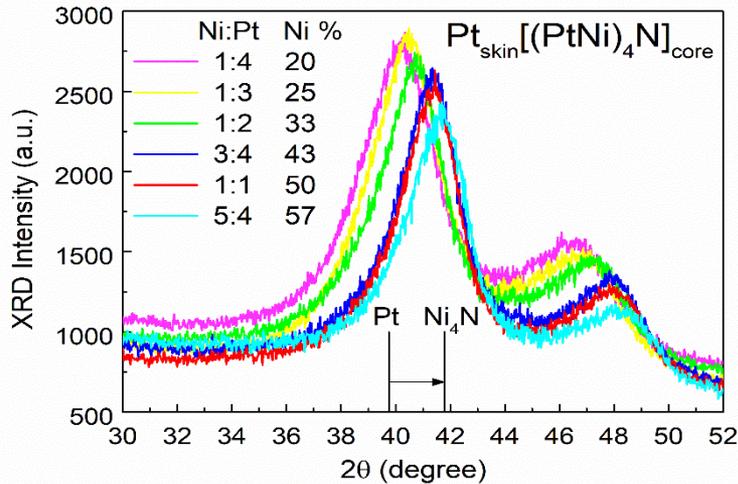
Phase separation occurs with 60% and 75% Ni for PtNiN. Without Pt,  $Ni_3N$  forms.



HAADF and EDS mappings of PtNiN particles (Pt:Ni 4:3) show single phase particles.

Images of 2D projection can not tell whether there is a Pt skin layer of 1-2 monolayer thick

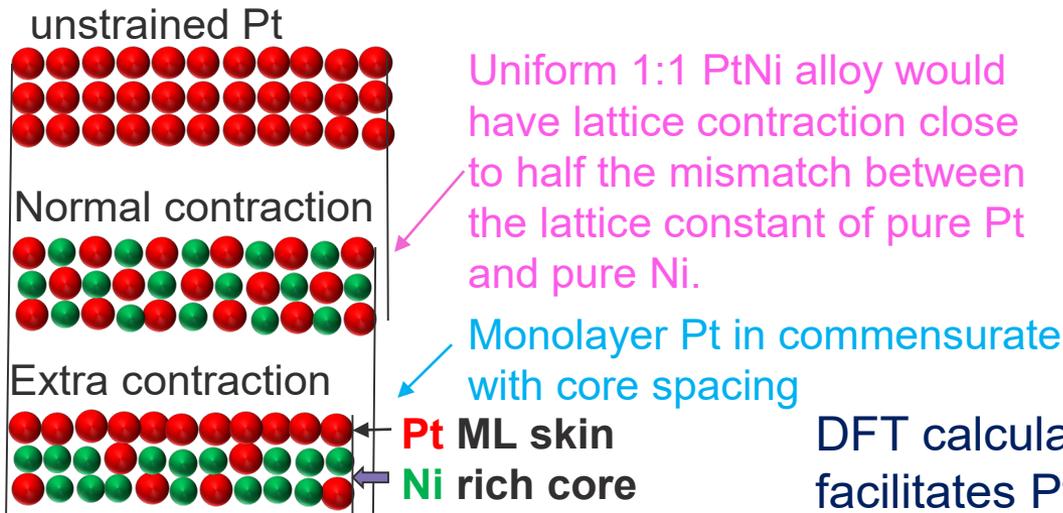
# 1c. Contracted Pt ML skin on PtNiN cores



Middle spacing expected for 50% Ni

XRD peak shifts show lattice contraction increases with increasing Ni atomic %.

Lattice strains (squares) are larger than expected by the linear relationship based on total Ni%.



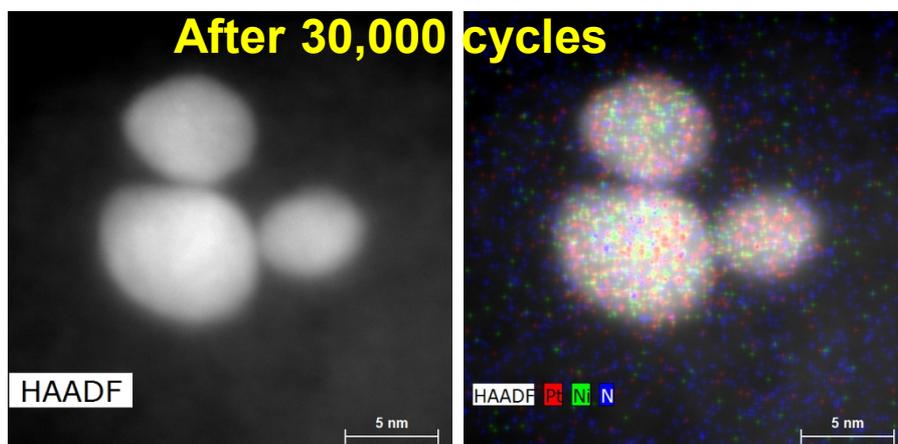
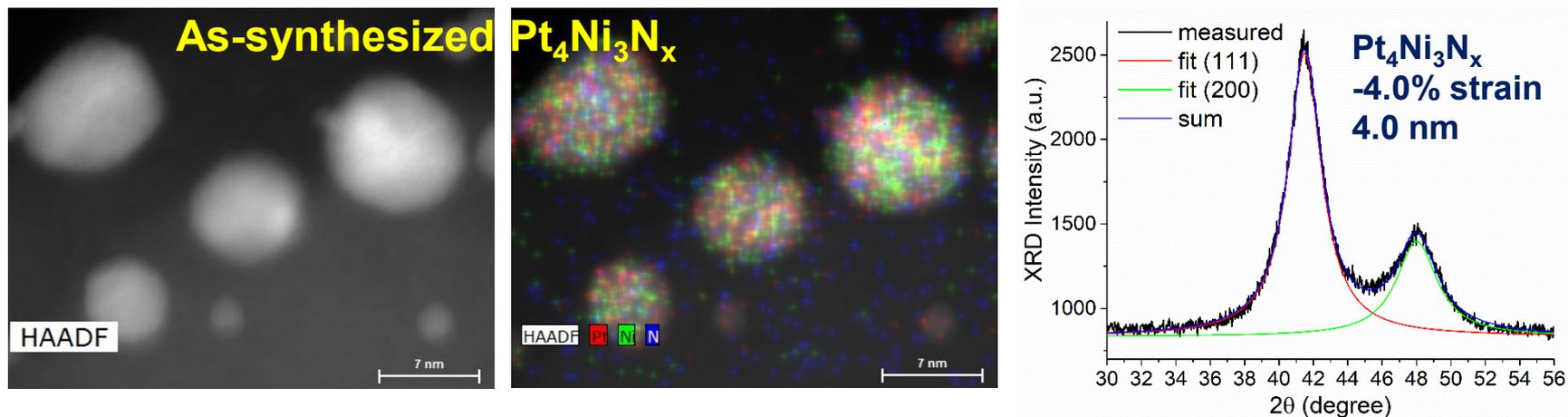
Uniform 1:1 PtNi alloy would have lattice contraction close to half the mismatch between the lattice constant of pure Pt and pure Ni.

Monolayer Pt in commensurate with core spacing

Extra lattice contraction indicates formation of monolayer-like Pt skin layer on Ni-enriched alloy nitride cores.

DFT calculation supports that nitriding facilitates Pt segregation to surface

## 1d. HAADF and EDS of PtNiN on Vulcan



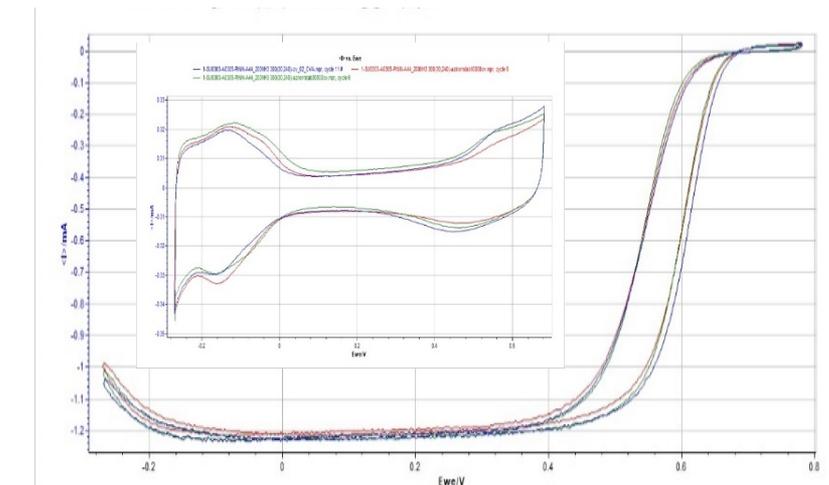
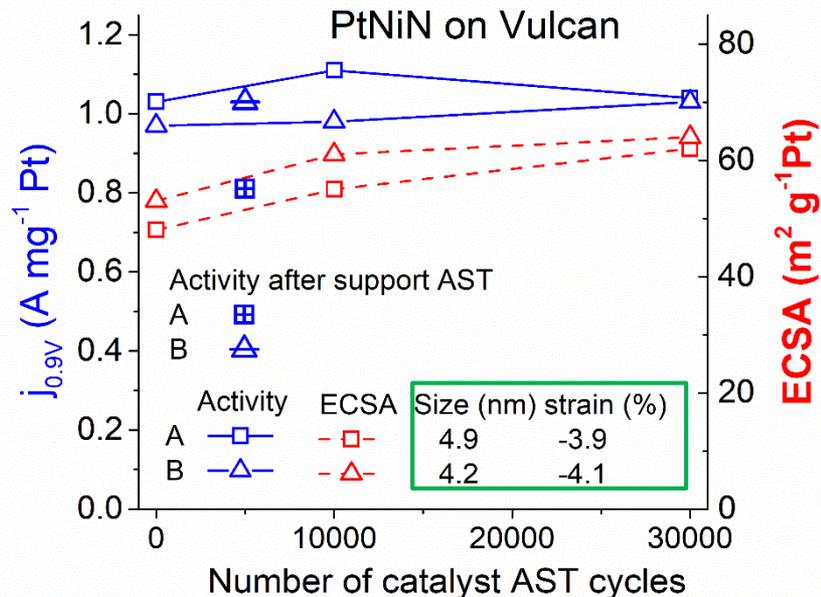
HAADF and EDS mapping confirm even distribution of Pt, Ni, and N and single phase particles.

After catalyst AST, little change in particle size and element distribution.

Formation of Pt monolayer skin layer on Ni-enriched nitride core leads to large lattice contraction (XRD) and high structural stability (TEM-EDS), which enhance activity and durability of PtNiN catalysts.

# 1e. Performance of PtNiN on VC

A typical set of ORR and CV curves on RDE

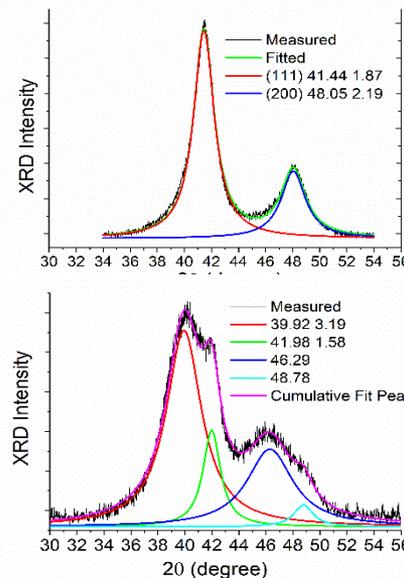


# of cycles: 0 (blue), 10k (red), 30k (green)

Sample A has higher Pt wt% than B.  
Both have Ni/(Ni+Pt) atomic% ~44%.

**No loss of activity and durability after catalyst and support ASTs**  
**Activity >0.8 A/mg, ECSA >50 m²/g**

Structure-performance correlation clarified but remains complicated and will be further tuned.

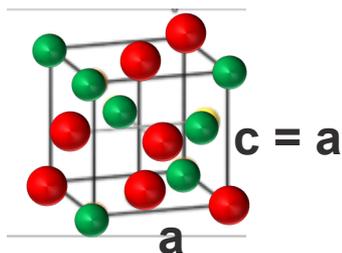


Samples having a single set of symmetric XRD peaks are far more active and durable than those having two sets of peaks because a thick Pt shell with little lattice contraction is less active and lattice mismatch at core-shell interface reduces structural stability.

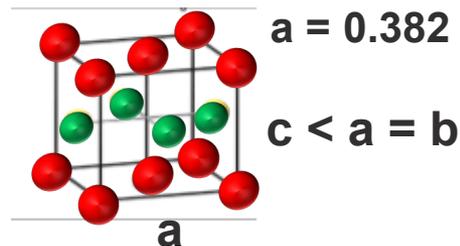
## 2a. PtNiN intermetallic on Ketjenblack 300J

Significantly improved activity and durability have been shown by long-range chemical ordered intermetallic, e.g.,  $L_{1_2}$ -Pt<sub>3</sub>Co,  **$L_{1_0}$ -Pt<sub>1</sub>Co<sub>1</sub>**,  $L_{1_0}$ -Pt<sub>1</sub>Ni<sub>1</sub>

Regular alloy  
 $c/a = 1.0$

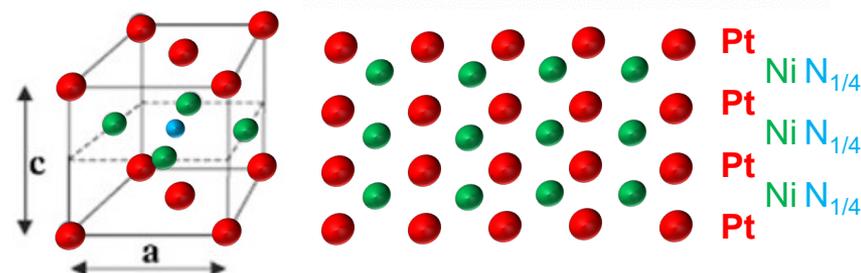
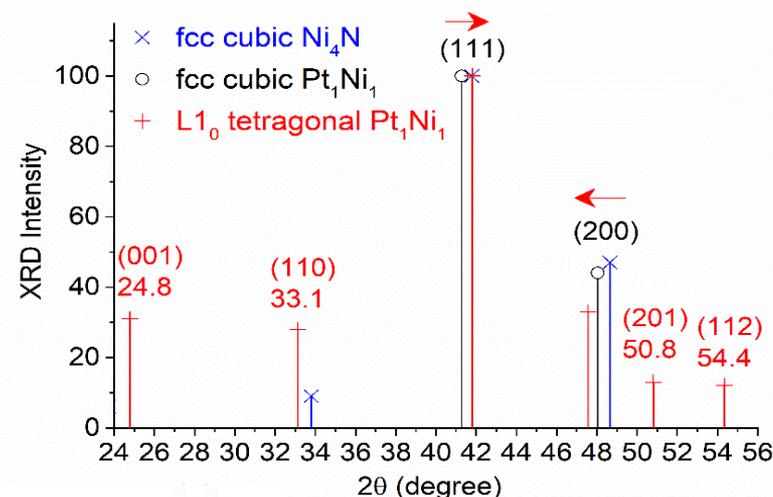


$L_{1_0}$  Intermetallic  
 $c/a = 0.94$   
 $c = 0.359$  nm  
 $a = 0.382$  nm



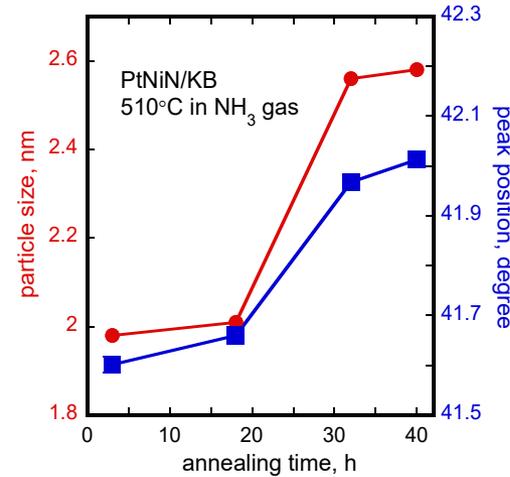
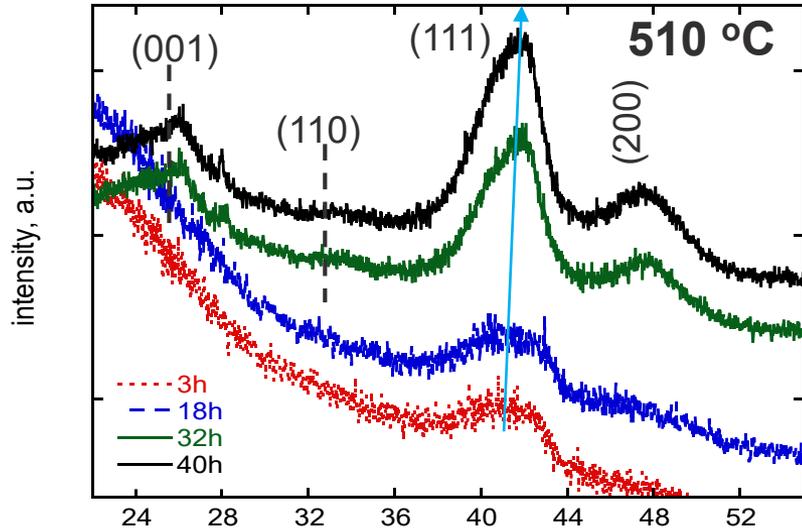
Higher temperature and longer anneal time often cause too large particle size.

Ketjenblack EC-300J was used as support partly for keeping particles small during long nitriding time.  
Two sets of samples made: 510 °C for **2–40** h and 560 °C for **2–18** h.

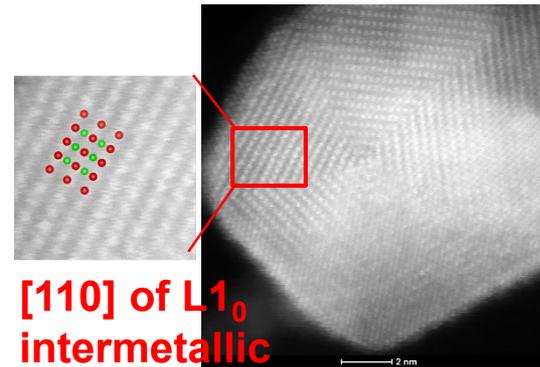
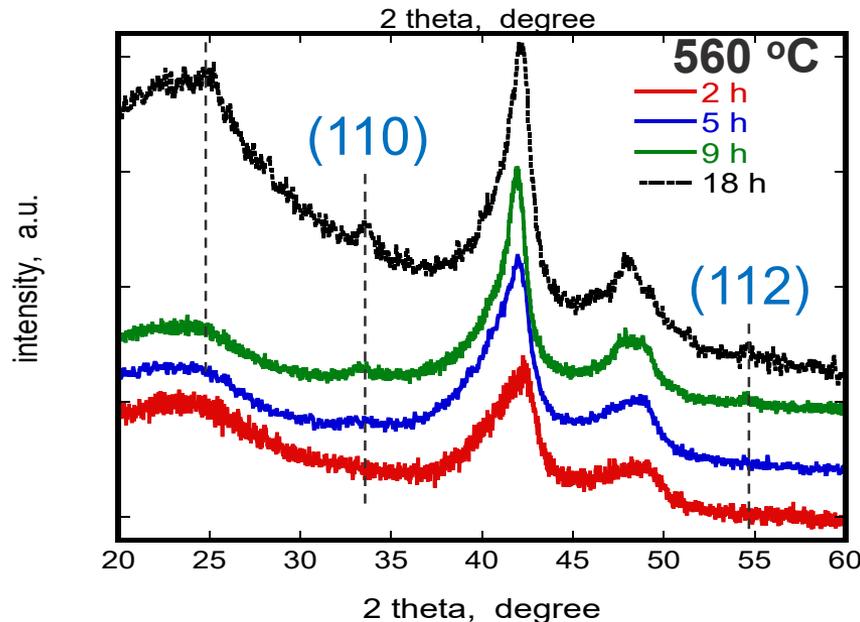


Similar XRD pattern expected for  $L_{1_0}$  Pt<sub>1</sub>Ni<sub>1</sub>N intermetallic; N at the center further stabilizes ordered structure. The x-y planes are alternately occupied by Pt and Ni atoms, causing  $a=b > c$  and thus (111) and (200) shift in opposite directions

## 2b. XRD of intermetallic PtNiN on KB



The (111) peak shifting to larger angle with increase of annealing time.



A high resolution image shows the [110] of L<sub>10</sub> lattice spacing.

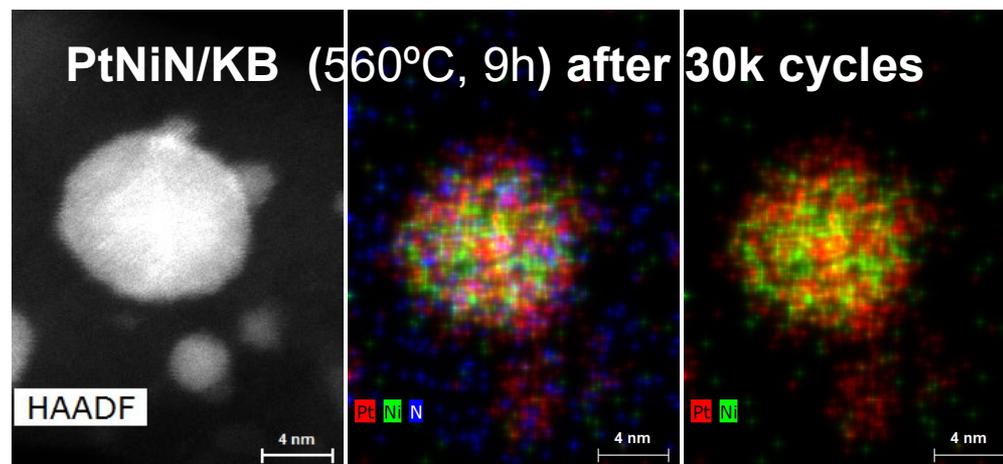
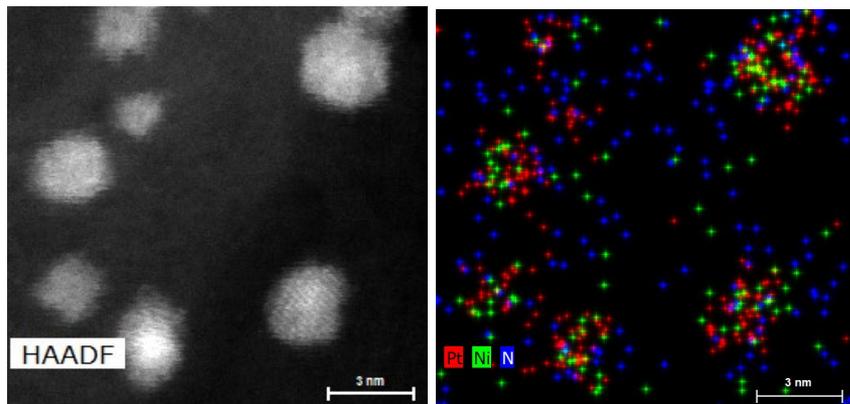
(110) and (112) peaks emerged  
(200) peak shifts to smaller angle

With total Pt:Ni 4:3, some particles form **L<sub>10</sub> Pt<sub>2</sub>Ni<sub>2</sub>N** cores.

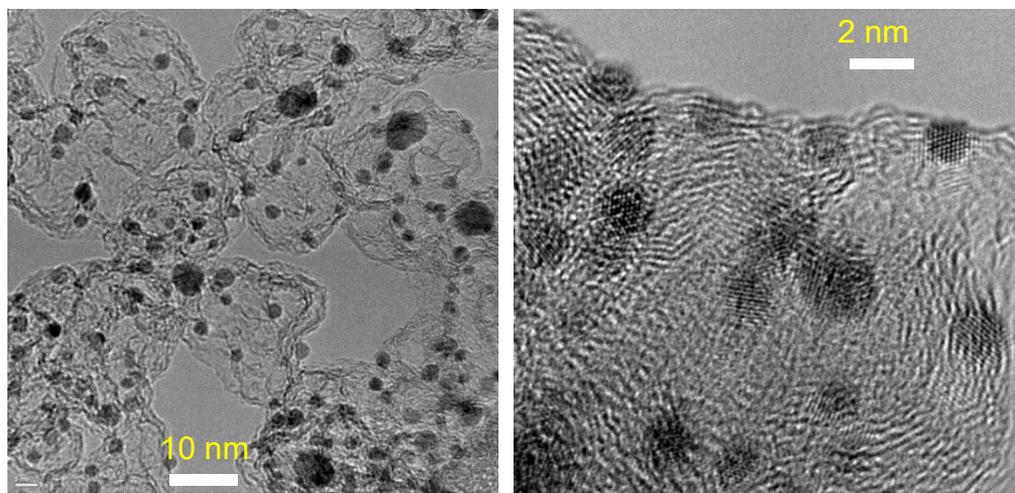
## 2c. EDS and TEM of PtNiN on KB (vs on VC)

Accomplishment

PtNiN / KB 560°C 9h

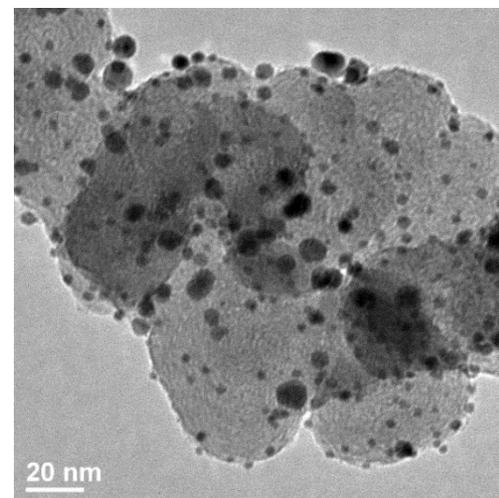


PtNiN on KB300 560 °C 9h



Many but not all embedded in graphitized carbon

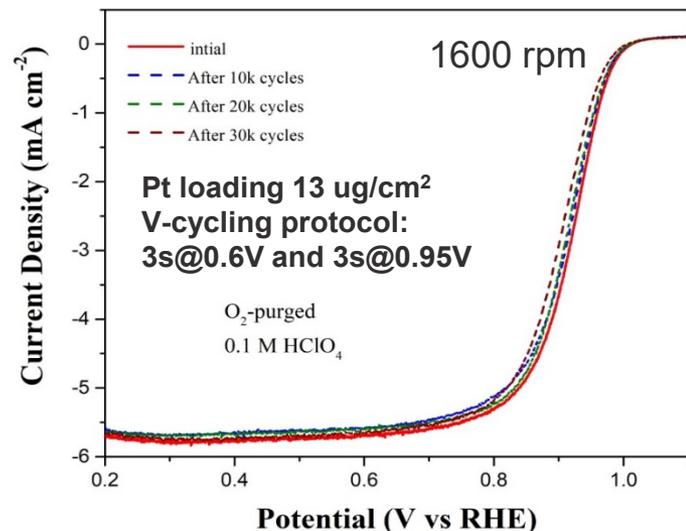
PtNiN on VC 510 °C 2h



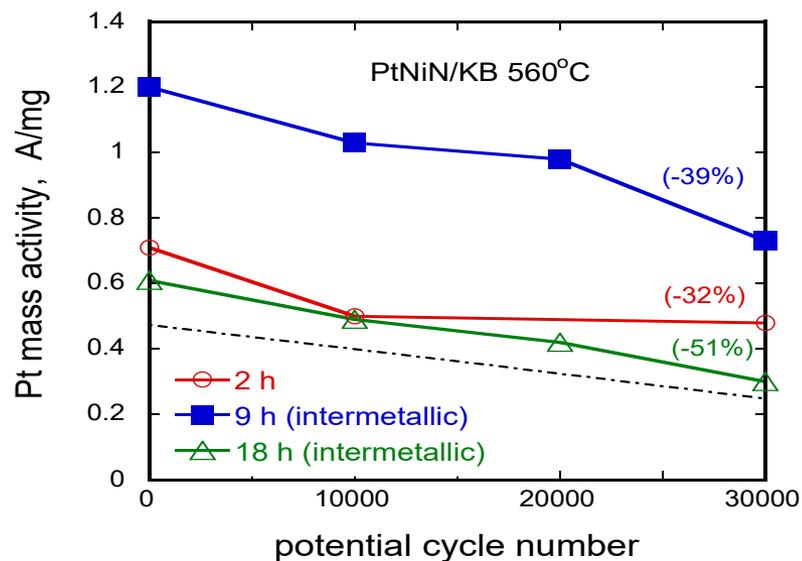
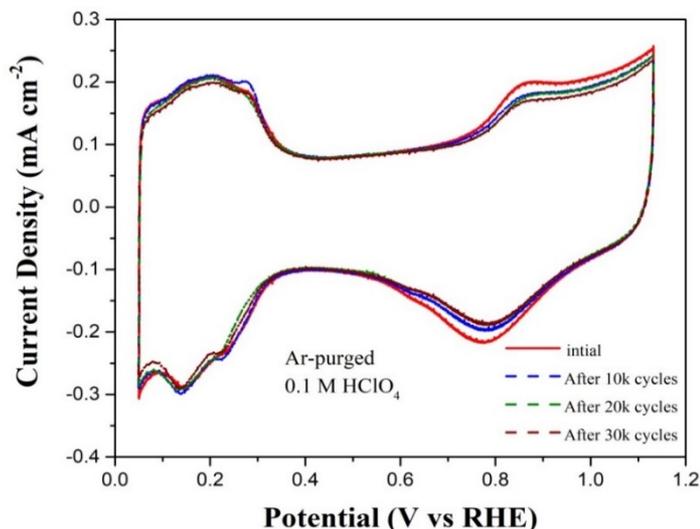
Most attached on surface

# 2d. ORR on RDE for intermetallic PtNiN on KB

Accomplishment



	560°C 9h		510°C 32h	
V-cycle	MA (A/mg)	ECSA (m <sup>2</sup> /g)	MA (A/mg)	ECSA (m <sup>2</sup> /g)
0	1.20	61	0.59	58
10k	1.03	63	0.87	61
20k	0.98	60	0.56	61
30k	0.73 (-39%)	59 (-3%)	0.54 (-8%)	54 (-8%)

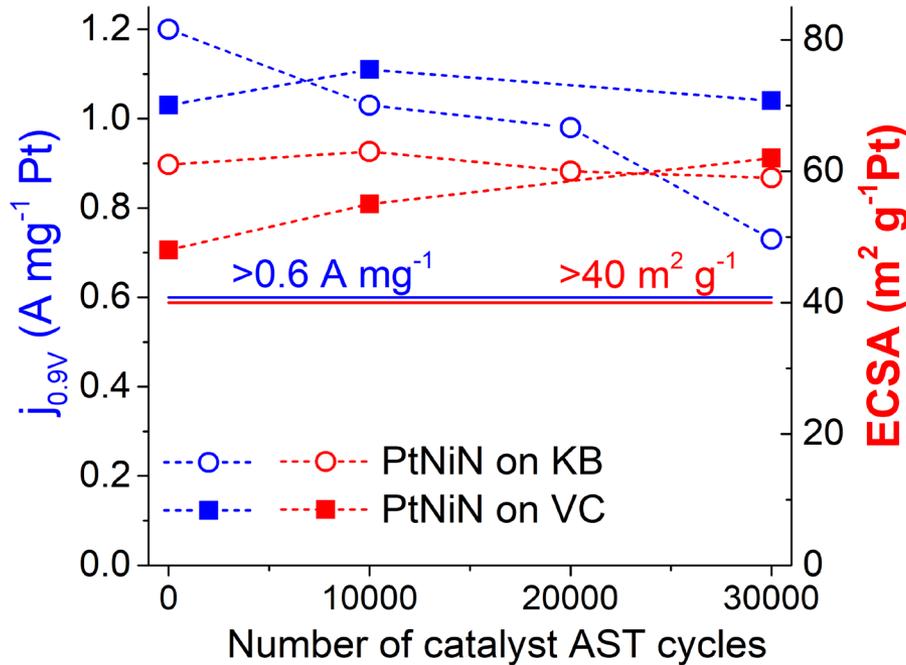


Pt mass activity  $\geq 0.7$  A/mg and ECDSA  $> 50$  m<sup>2</sup>/g after 30,000 cycles

Range of synthesis parameters narrowed down.

# RDE screening PtNiN samples for MEA tests

Accomplishment



RDE screening criteria for PtNiN on VC and KB: **Activity >0.6 A/mg** and **ECDSA > 40 m<sup>2</sup>/g** after catalyst AST on RDE.

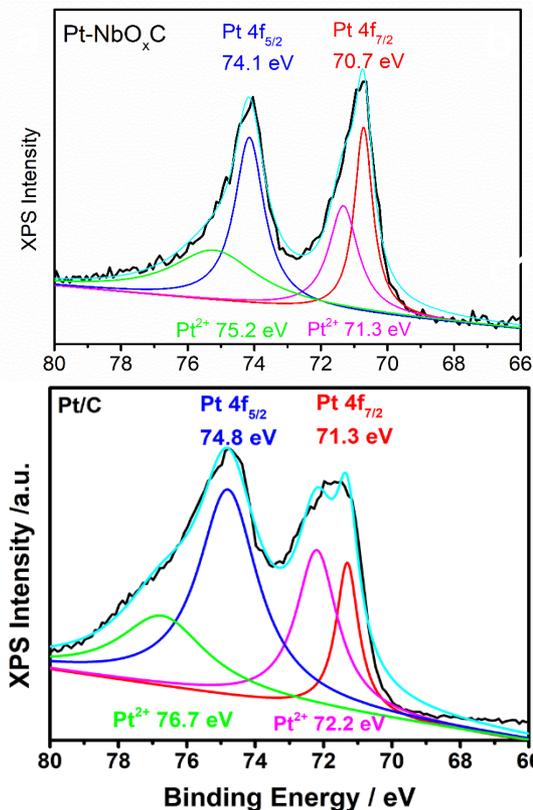
DOE target after catalyst AST: Activity >0.27 A/mg and ECDSA loss <40%

Carbon effect found by MEA tests will guide future study for durability including support AST.

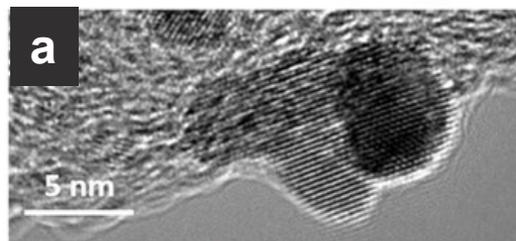
No loss of activity and ECDSA for PtNiN on VC after catalyst and support ASTs on RDE at ambient temperature show promise to include support AST in MEA tests.

If the superior durability is confirmed in MEA tests, PtNiN will offer an opportunity for active bimetallic catalysts passing both catalyst and support ASTs.

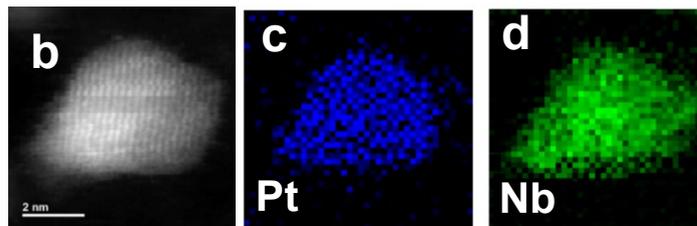
### 3. Characterization of Pt-NbO<sub>x</sub>C (KB600)



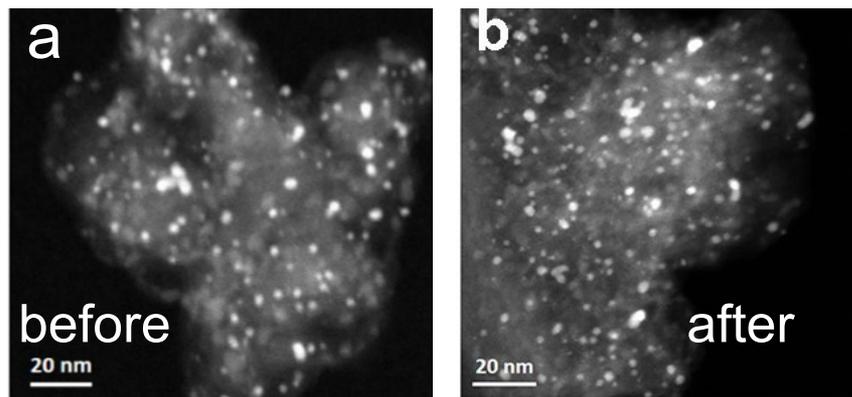
The 0.6 eV shift of XPS peak suggest partial charge transfer for NbO<sub>x</sub> to Pt, supporting that Pt is in contact with NbO<sub>x</sub>.



Pt shells (ordered) on top of NbO<sub>x</sub> (amorphous) cores that are partly embedded in carbon



EELS mapping of Pt and Nb elements of a single particle



No significant change in particle size and density after durability tests.

KB600 can eliminate particles larger than 5 nm, but disappointing MEA results suggested that NbO<sub>x</sub> oxidation under fuel cell operating conditions were not fully prevented.

No go with NbO<sub>x</sub>. Nb nitrides and porous carbon will be used in future research.

# Proposed Future Work

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## Remaining challenges:

MEA validation and optimization need to be completed

Synthesis of PtNiN on corrosion-resistant supports

## Future work

- Further optimization based on feedback of MEA tests and explore more favorable structure and synthesis methods
- Explore approaches for making highly active nitride catalysts on corrosion-resistant support to meet durability requirement for catalyst and support AST concurrently.

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

# Responses to Previous Year Reviewers' Comments

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## Comments:

Demonstrated improved durability and PGM activity with stable metal nitride, phosphide, and oxide cores on RDE results, but have not fully validated in MEA.

Need more structural characterization and fundamental understanding

Validating the performance of PtNiN in MEA should be a top priority.

## Response:

RDE served as fast screening method for exploring new materials/structures. Out of five types of catalysts, PtNiN was selected for further development and validation in MEA.

Structural analysis clarified the benefits of nitriding and guided synthesis studies for further improving PtNiN catalysts.

Major effort and progress were made in establishing correlation between key structural parameters and catalytic performance, which ensured high quality of samples for MEA tests.

Samples were delivered to GM. MEA tests will be conducted in May and optimization will follow.

# Collaboration

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## University and institution collaborators

BNL: Dong Su, Lijun Wu and Yimei Zhu, Xueru Zhao

High resolution TEM images and element mapping

University of Waterloo: Zhongwei Chen and Zhong Ma

Pt-NbO<sub>x</sub>C synthesis and characterization

Korean Institute for Energy Research: Gu-Gon Park

## Facilities at BNL

Center for Functional Nanomaterials

National Synchrotron Light Source (II)

## Industrial collaborators

**General Motor:** Anu Kongkanand and Yun Cai MEA tests

Toyota Motor: Hisao Kato

N.E. Chemcat: Hiroshi Igarashi and Kiyotaka Nagamori

# Summary

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## Relevance

Aiming at concurrently meeting activity targets at 0.9 V and at high current densities and durability targets after catalyst and support ASTs

## Approach

Exploring low-PGM or PGM-free core materials and novel core-shell structures using economically viable synthesis methods

## Accomplishments

- Clarified beneficial effect of nitriding for PtNi bimetallic nanocatalysts
- Illustrated the advantages of Pt skin catalyst with bimetallic nitride core,  $\text{Pt}_{\text{ML}}\text{-}[(\text{PtNi})_4\text{N}]_{\text{core}}$ .
- Several grams of PtNiN samples made with VC and KB as supports delivered for MEA tests.
- RDE tests showed that PtNiN likely to be more stable than PtNi and more active than PtCo.

## Proposed future research

- Optimize PtNiN based on feedback of MEA tests by GM
- Synthesize active PtNiN with corrosion-resistant supports to achieve durability targets against ASTs for catalyst and support

# Technical Back-Up Slides

## RDE Testing Protocols (0.1 M HClO<sub>4</sub> solutions)

**ECSA** measured by average of H adsorption and desorption charges  $(Q_- + Q_+)/2/0.21$ , where  $Q_-$  and  $Q_+$  are integration of negative and positive currents after subtracting double layer currents.

**ORR polarization** taken in positive sweep at 10 mV s<sup>-1</sup>, 1600 rpm, iR-corrected using HFR near 0.4 V.

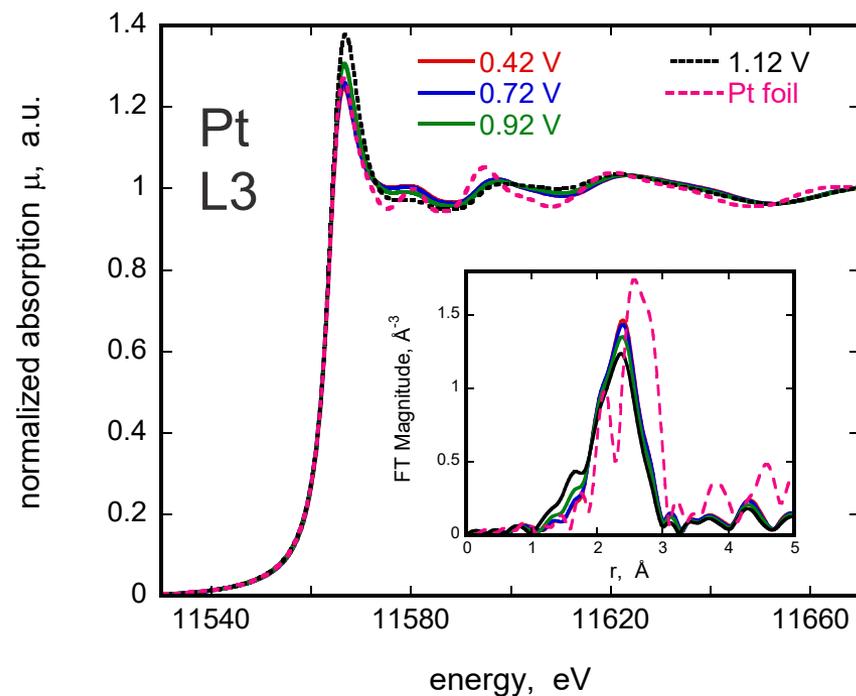
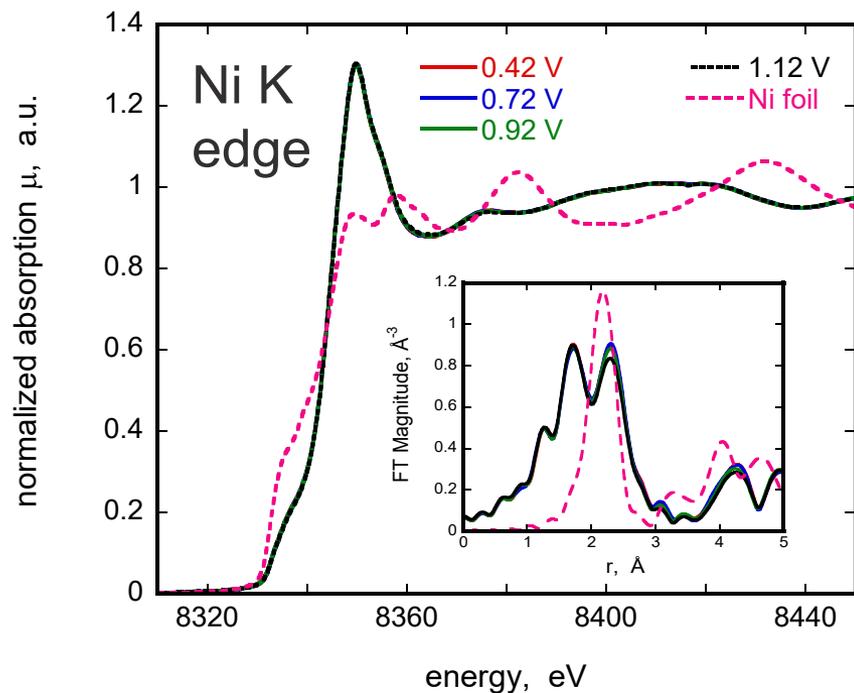
**AST for Catalyst:** 0.6 V (3s) – 0.95 V (3s) with 700 mV/s sweep rate between 0.6 and 0.95

**AST for support:** 1.0 - 1.5 V at 500 mV/S

MYRDD Table 3.4.7 Technical Targets: Electrocatalysts for Transportation Applications		
Characteristic	Units	2020 Target
PGM content at rated power	$g_{\text{PGM}}/\text{kW}_{\text{gross}}$ at 150 kPa (abs)	0.125
PGM loading	$\text{mg}_{\text{PGM}}/\text{cm}^2$ total	0.125
Mass activity	A/mgPGM at 900 mV <sub>iR-free</sub>	0.44
Electrocatalyst stability (0.6 ↔ 0.95 V)	% mass activity loss after 30K cycles	<40
Loss at 0.8 A/cm <sup>2</sup> (0.6 ↔ 0.95 V)	mV loss after 30K cycles	<30
Support stability (1.0 ↔ 1.5 V)	% mass activity loss after 5K cycles	<40
Loss at 1.5 A/cm <sup>2</sup> (1.0 ↔ 1.5 V)	mV after 5K cycles	<30

# *In situ* XAS of intermetallic PtNiN/KB at 560°C in NH<sub>3</sub>

Using our electrochemical cell with 1 M HClO<sub>4</sub> at QAS beamline of NSLS-II



- ❑ No changes in Ni K edge spectra with increasing potentials from 0.42 V to 1.12 V, indicating that Ni is not oxidized due to protection of thin Pt shells, which is oxidized with increasing potentials as the white line intensity of Pt L3 spectra increases
- ❑ FT EXAFS of Ni K edge and Pt L3 from intermetallic PtNiN/KB catalysts show significant differences from their bulk structures. Detailed structural analysis is being made.