High-Activity Dealloyed Catalysts

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General Motors Global Product Development
Fuel Cell Activities
Pontiac, MI
May 16, 2013

FC087

Overview

Timeline

- Project start date: 1 Aug 2010
- Project end date: 30 Nov 2013
- Percent complete: 70%

Budget

- Total project funding:$5,952,827
  - DOE share: $4,762,313
  - Contractor share: $1,190,514
- Funding received:
  - FY10&11 $0.68M
  - FY12 $1.76M
- Planned Funding for FY13: $1.13M

Barriers

- Barriers addressed
  - B. Cost
    - Decrease required loading of precious metals including platinum
  - A. Durability
    - Maintain kinetic activity, and later high current density performance, after appropriate accelerated tests
  - C. Performance
    - Achieve and maintain high current densities at acceptably-high voltages

Partners

- Subcontractors:
  - Technical University of Berlin
  - Johnson Matthey Fuel Cells
  - Massachusetts Institute of Technology
  - Northeastern University
  - George Washington University
- Project lead: GM

from 2012 AMR

Relevance

- **Cost**
  - Demonstrate reliable oxygen reduction reaction kinetic mass activities > DOE target 0.44 A/mg_{PGM} in H_2/O_2 fuel cells, using **manufacturable** synthesis and dealloying procedures
  - Achieve high-current-density performance in H_2/air fuel cells adequate to meet DOE heat rejection targets and Pt-loading goals of <0.125 g_{Pt}/kW and <0.125 mg_{Pt}/cm^2_{geo}
- **Durability**
  - Demonstrate durability of the kinetic mass activity against DOE-specified voltage cycling tests in fuel cells
  - Determine where alloying-element atoms should reside with respect to the catalyst-particle surface for durable activity
- **Performance**
  - Demonstrate durability of high-current-density performance
  - Scale up to full-active-area fuel cells, to be made available for DOE testing

Reduce catalyst cost while achieving the required durable performance, allowing fuel cells to become economically competitive with other power sources.

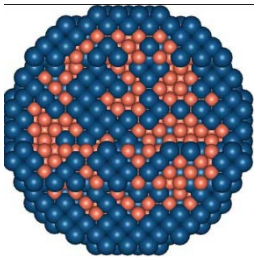
Approach: Basic Concept

M is one or more non-precious metals

precursor **dealloying** catalyst

PtM_3/C ----------> $Pt_{1.5\text{-}5}M/C$

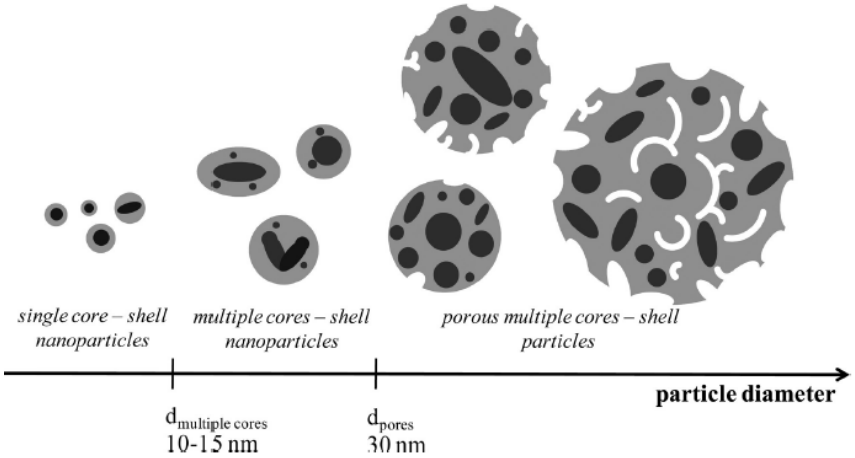
e.g., acid leaching, electrochemically dissol'n



Cross section, Pt in blue

Lattice compression of surface Pt layer

- Erlebacher dealloying of continuous films showed ligament/pore network controlled by relative rates of nonnoble-element dissolution and noble atom *surface* diffusion → tune to improve durability
- Shao-Horn pre-project work suggested high initial non-noble atom concentration generate porous structure
- Strasser pre-project work suggested particle morphology determined by particle size (below)



From M. Oezaslan, M. Heggen and P. Strasser, J. Am. Chem. Soc. 134 (2012) 514 with permission from ACS

Question to be answered

- Activity-morphology relationship
- Desired structure, elements, and composition for durability
- Activity-durability trade-off

Approach: Milestones and Go/No Go

Time	Milestone or Go/No-Go Decision	Status
May-2012	Milestone 1: ORR mass activity >0.44 A/mg_{PGM} reliably achieved with 0.1 mg_{PGM}/cm^2 loading in at least two labs.	Satisfied at two labs with large batches catalysts
Oct-2012	Milestone 2: Durability of kinetic activity. ≥60% of initial mass activity maintained in two labs after 30k cycles 0.6-1.0V RHE in fuel cells	Satisfied at two labs with large batches catalysts
Oct-2012	Go/No-Go: Simultaneously achieve Milestones 1 and 2 with one material	Passed
Dec-2012	Milestone 3: Initial high-current-density performance in H_2/air ≥560 mV at 1.5A/cm^2 with 0.1 mg_{Pt}/cm^2 loading	Satisfied at GM. Still need to achieve in 2nd lab
Nov-2013	Milestone 4: Scale-up and durability of high-current-density performance in short stack in H_2/air under accelerated durability testing and make it available to DOE for independent testing	Optimizations of dealloying process and electrode fabrication method are on-going

Metric	units	2011	2012	2013	2017 DOE target
Mass activity	A/mg_{PGM}@900$mV_{iR\text{-}free}$	0.6 ($PtCu_3$), 0.4 ($PtCo_3$)	0.5 ($PtCo_3$) 0.5 ($PtNi_3$)	0.6-0.75 ($PtCo_3$&$PtNi_3$)	≥0.44
Loss in catalytic activity	% lost after 30k cycles 0.6-1.0V	80% ($PtCu_3$) 40% ($PtCo_3$)	30% ($PtCo_3$) 70% ($PtNi_3$)	0-40% ($PtCo_3$&$PtNi_3$)	≤40%
PGM total content	g_{PGM}/kW_{rated}	0.19 ($PtCu_3$) @1.5Acm^2	0.16 ($PtNi_3$) @1.5Acm^2	0.16 ($PtNi_3$) @ 1.5Acm^2	≤0.125
PGM total loading	mg_{PGM}/cm^2_{geo}	0.15 ($PtCu_3$)	0.15 (*anode still 0.05*)	0.15 (*anode still 0.05*)	≤0.125

Large-batches in blue

Met all DOE 2015 cathode activity target in 100g-batch catalysts !!

Collaborations (subcontractors)

- GM
  - Overall project guidance, testing of catalysts, fabrication and testing of MEAs and fuel cells

- Technical University Berlin (TUB) (university)– Prof. Dr. Peter Strasser
  - née Univ. of Houston (UofH)
  - Selection of new candidate catalyst systems, pre-fuel-cell evaluation, tie-in to theory

- Johnson Matthey Fuel Cells (JMFC) (industry) – Dr. Rachel O'Malley
  - Scale-up of synthesis, improved manufacturability of dealloying, incorporation and MEA testing

- Massachusetts Institute of Technology (MIT) (university) – Prof. Yang Shao-Horn
  - Electron microscopy, dealloying interpretation, alternate preparations of core/shell structures

Northeastern University (NEU) (university) – Prof. Sanjeev Mukerjee
  - X-ray absorption spectroscopy (EXAFS, XANES)

George Washington University (GWU) (university) -- Prof. David Ramaker
  - Theoretical support of x-ray absorption spectroscopy, Δμ XANES

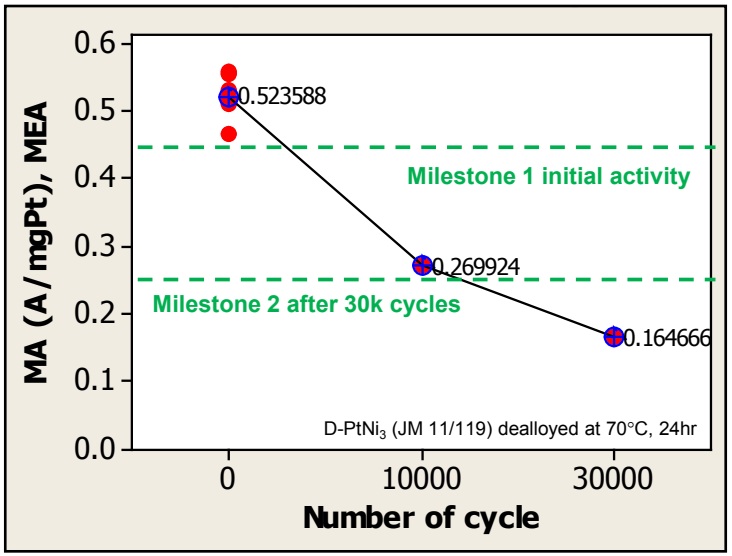
Project is working through iterative cycles of synthesis, scaleup, performance evaluation, and characterization

Tech transfer: University ➔ Catalyst manufacturer ➔ Stack integrator

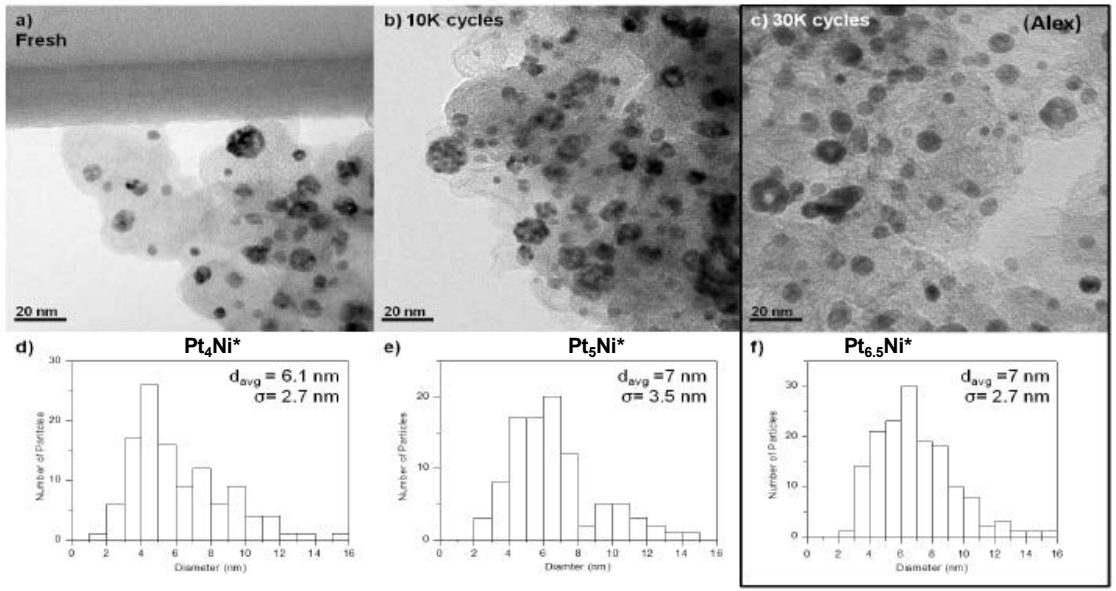
At Last Year's Meeting

- Had worked mostly on large-batch D-$PtCu_3$ and D-$PtNi_3$.
  - ✓ Demonstrated initial ORR activity and H_2/air performance.
  - ✓ Had not met kinetic durability target with JM large-batch materials.
    - TEM revealed unusually broad and non-normal particle-size distribution
      - ➢ JM had focused on single-phase, with and without superlattice – expected to give more uniform dealloying, but have proven difficult to grow.
      - ➢ Porous particles were evident.
- However, met activity & durability with GM *small-batch* D-PtCo and D-$PtCo_3$.

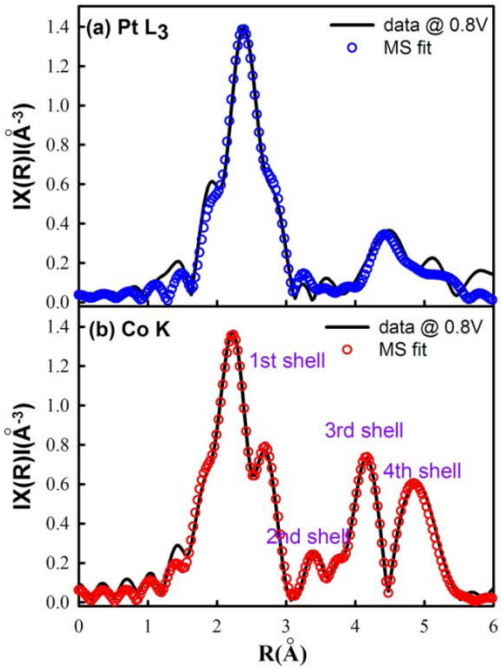
Mass activity during voltage-cycling test (0.6-1.0V)

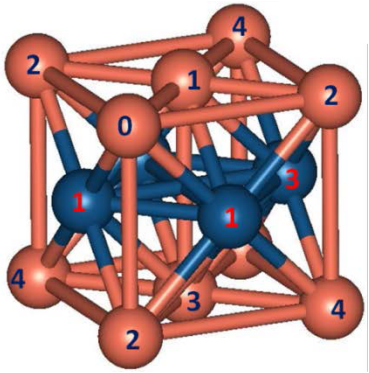


MIT micrographs of 11/176 D-$PtNi_3$ MEAs cycled at GM



in-situ EXAFS: Chemistry/Morphology





Precursor	d (nm)	cycles	R (nm)	Microstructure
GM small-batch PtCo/HSC	4.0?	~100	2.70	Mostly SC-S
GM small-batch $PtCo_3$/HSC	4.0	~100	2.71	50% SC-S, 50% MC-PS
$PtNi_3$/HSC	4.5	~100	2.72	MC-PS w M in PS
$PtNi_3$/HSC	5.5	10k	2.73	MC-PS w < M in PS
$PtNi_3$/HSC	6.5	30k	2.74	MC-PS w << M in PS
Pt/VC	3-5	~100	2.75	Nanoparticle

single core (SC)
shell (S)
multiple-core (MC)
porous shell (PS)

- Coordination number ratios of each element provide the overall particle morphology
- Large-batch D-$PtNi_3$ are mostly multi-core porous-shells agreeing with TEM.
- Cycled catalysts showed little Pt-Ni interactions (most Ni are gone from subsurface), coinciding with increased R_{Pt-Pt} distances (less strain, less activity).

Steps to Improve Durability

- Is $PtCo_3$ intrinsically more corrosion-resistant than $PtNi_3$?
  - Seems unlikely from known corrosion properties and heats of mixing, but JM will make a $PtCo_3$ analog
  - Note: TUB had looked at a wide range of alternate alloying elements in preproject work
- Want more core/shell, less pores, but with high M content in cores
  - Decrease M dissolution rate vs. Pt surface diffusion rate during dealloying
    - Use less aggressive chemical leachant to slow M dissolution and/or higher temperature and/or added complexing ions to increase Pt surface diffusion rate
- Start with more uniform particle sizes
  - JM running 8 different $PtNi_3$ preparation methods
  - TUB low-temperature codeposited $PtNi_3$
- Ternary systems
  - GM has added Au or Ir in bulk, TUB has added Au or Pd on surface
    - To date, not very encouraging results
  - Additional component to increase flux of diffusing Pt adatoms during dealloying
  - JM exploring addition of passivating elements
- Post-dealloying thermal annealing to improve Pt skin

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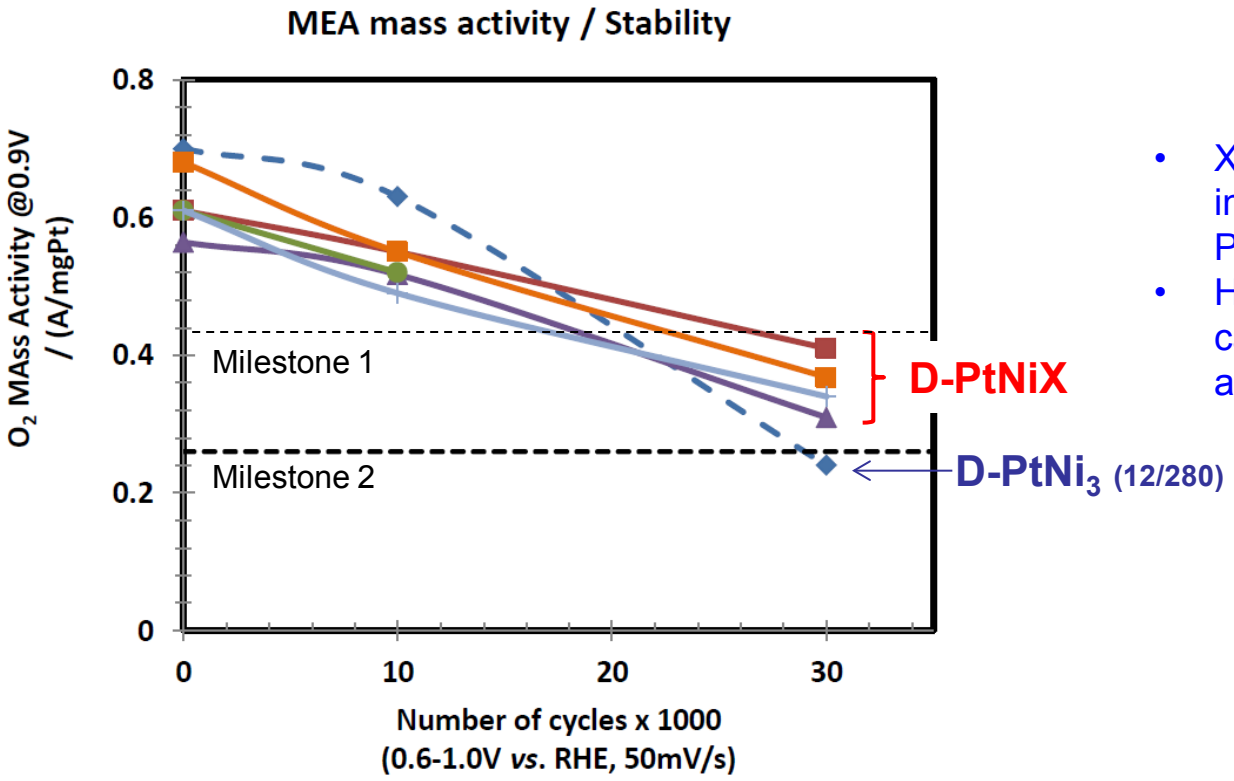
Additional Component to Increase Flux of Diffusing Pt Adatoms During Dealloying



- X is a non-precious metal chosen to increase the flux of surface-diffusing Pt atoms during dealloying.
- However, some X remaining in final catalyst contradicts our original assumption.

- Passed both Milestone 1 (initial ≥0.44 A/mg$_{PGM}$) and Milestone 2 (post-30k cycle ≥0.26 A/mg$_{PGM}$), as well as DOE goal for loss of ≤40% of initial activity.
- GM confirmed ORR durability in MEAs → *first catalyst to satisfy gate criteria*

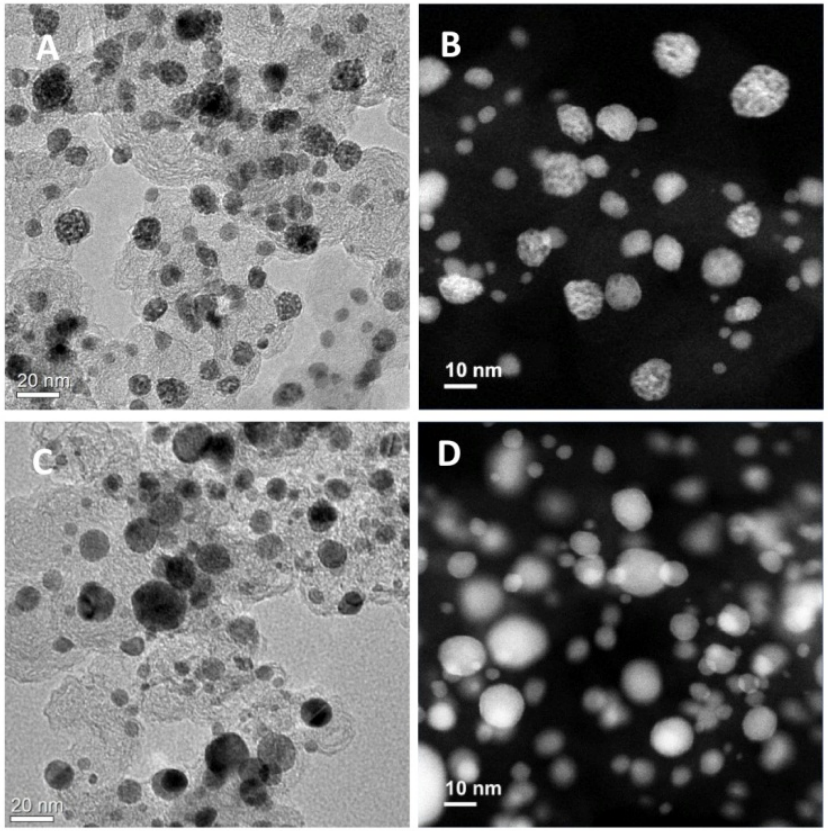
Provisional Patent filed

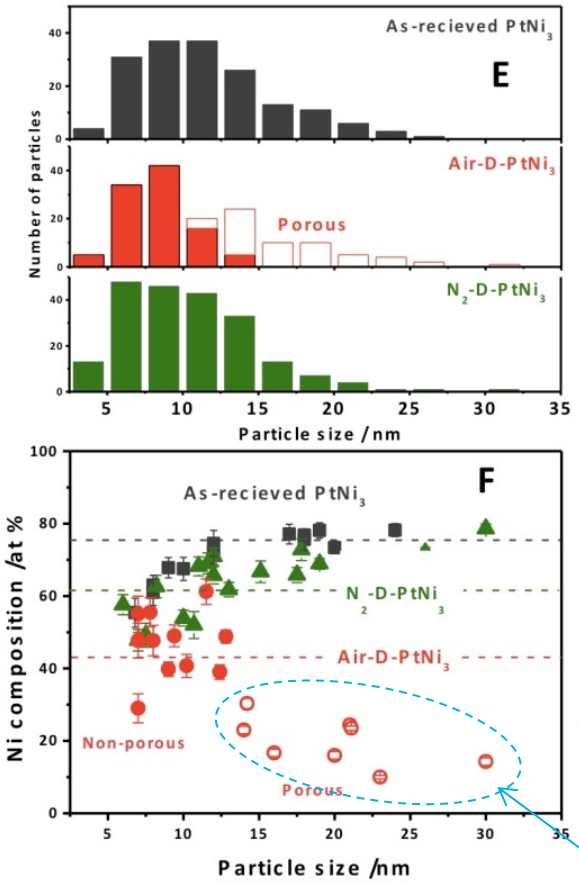
Technical Accomplishment:

Leaching under less-oxidizing condition: TUB showed that etching in 25°C H_2SO_4 under air gave porous particles, but under N_2 gave nonporous

Air-dealloyed

N_2-dealloyed





$PtNi_3$ 11/176

precursor

N_2-dealloyed

Air-dealloyed

Porous and low-Ni content

- Air-dealloyed: porous large particles and solid small particles.
- N_2-dealloyed: all solid particles → succeeded in decreasing Ni dissolution rate!?
- N_2-dealloyed gave slightly better V-cycling stability in RDE.
- GM's MEA tests showed small improvement but insufficient to reach durability target.

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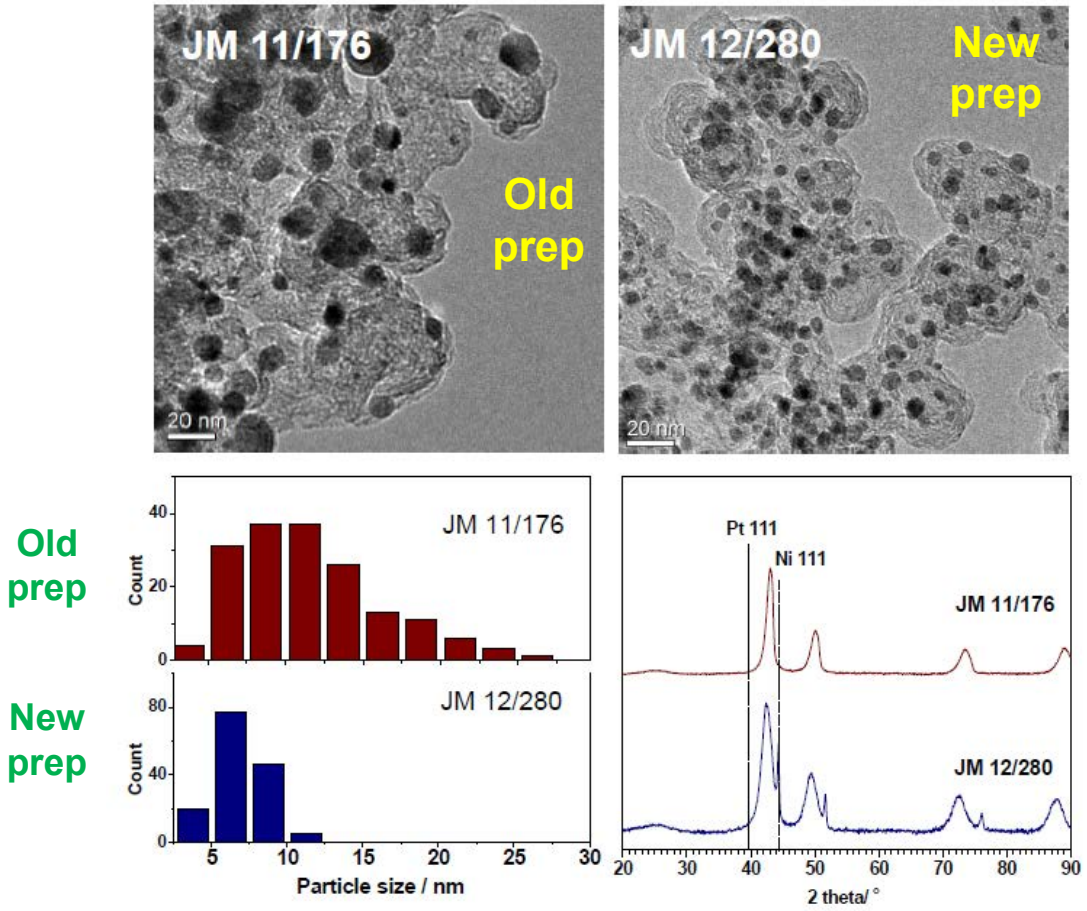
JM Improved Particle-Size Distribution of Large-batch $PtNi_3$

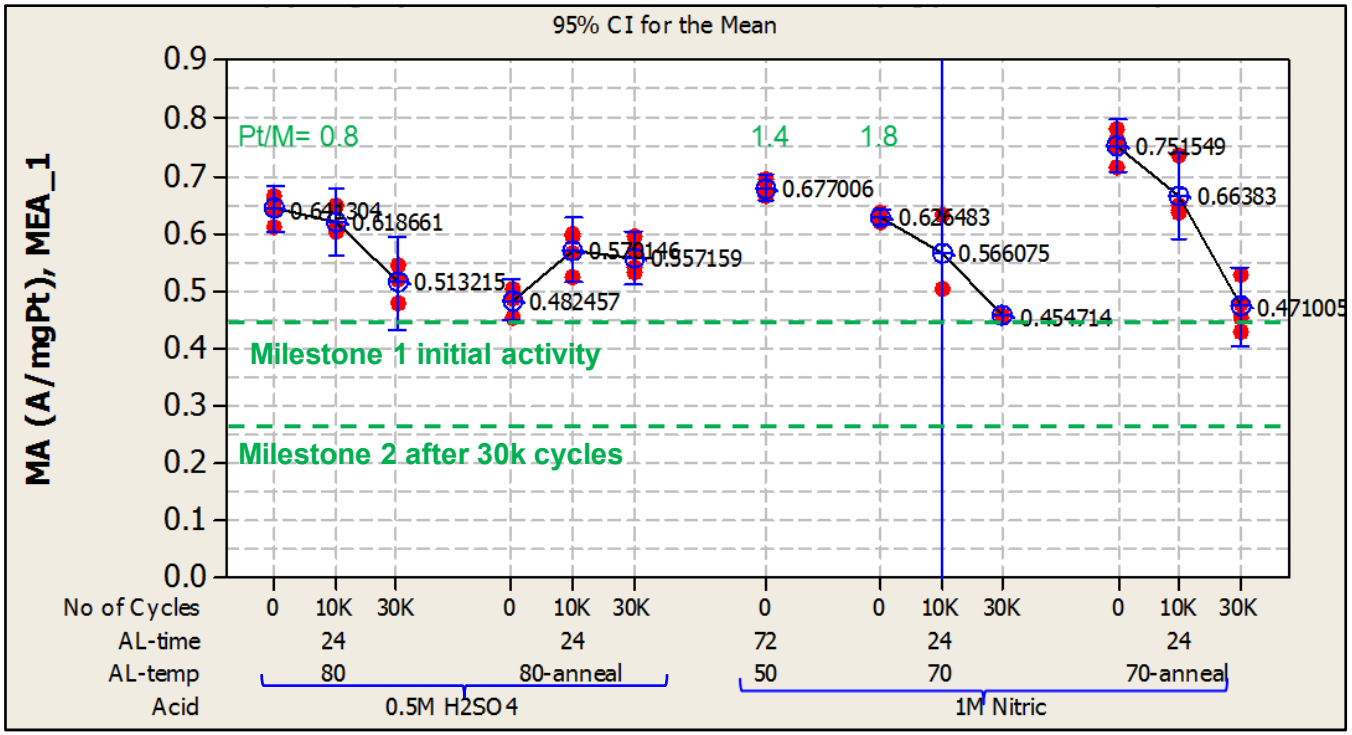


- One of 8 new preparation paths that JM has tried.
- Improved PSD and smaller mean particle size.
- Not a single Pt_xNi phase. Pure Ni phase is present.
- This and one other scalable approach are being carried forward. Currently at 100g batch.

Technical Accomplishment:

Passed Milestone 2 with Several Treatments of JM New $PtNi_3$ Precursor in MEAs

Mass activities as a function of voltage cycles



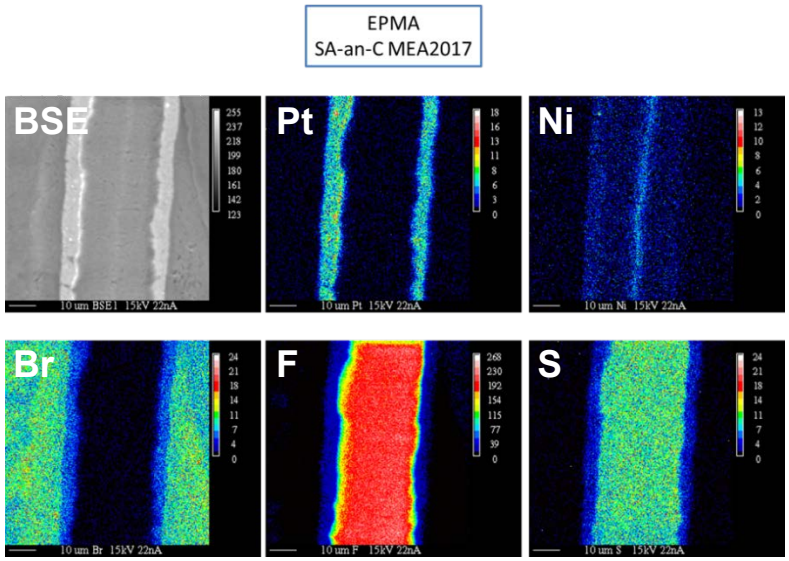
Cathode loadings:
0.082-0.100 mg_{Pt}/cm^2

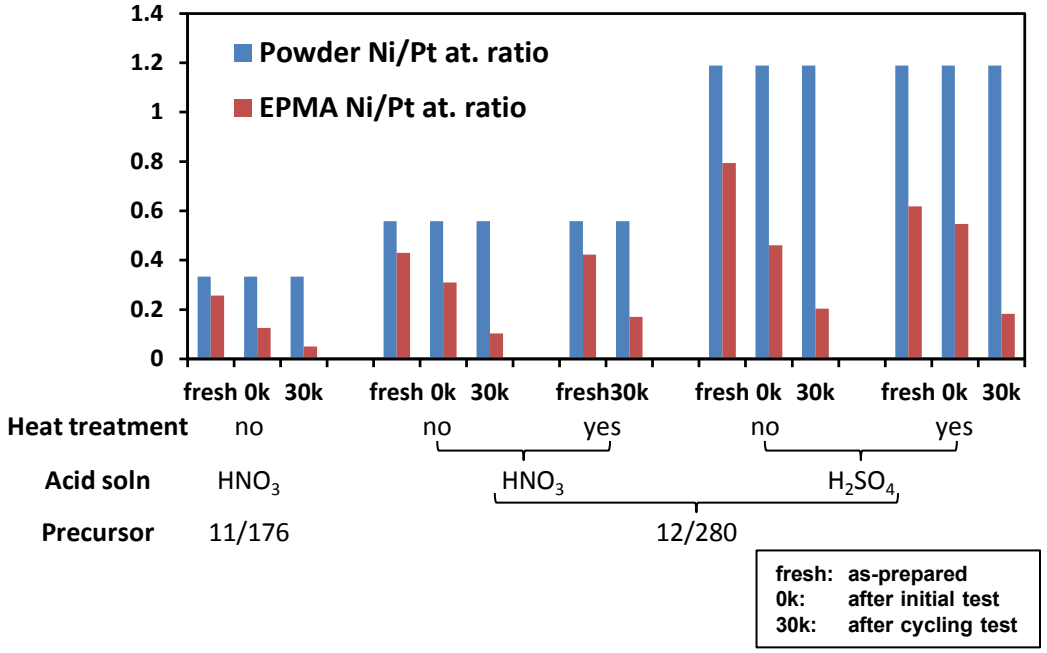
Thermal annealing:
5% H_2/N_2 at 400 C for 4hrs

- All MEAs satisfied Milestones 1 and 2 as well as DOE goal of ≤40% loss of initial activity.
- *Passed* Go/No-go gate Nov 2012.

Technical Accomplishment:

Post-testing ICP and EPMA

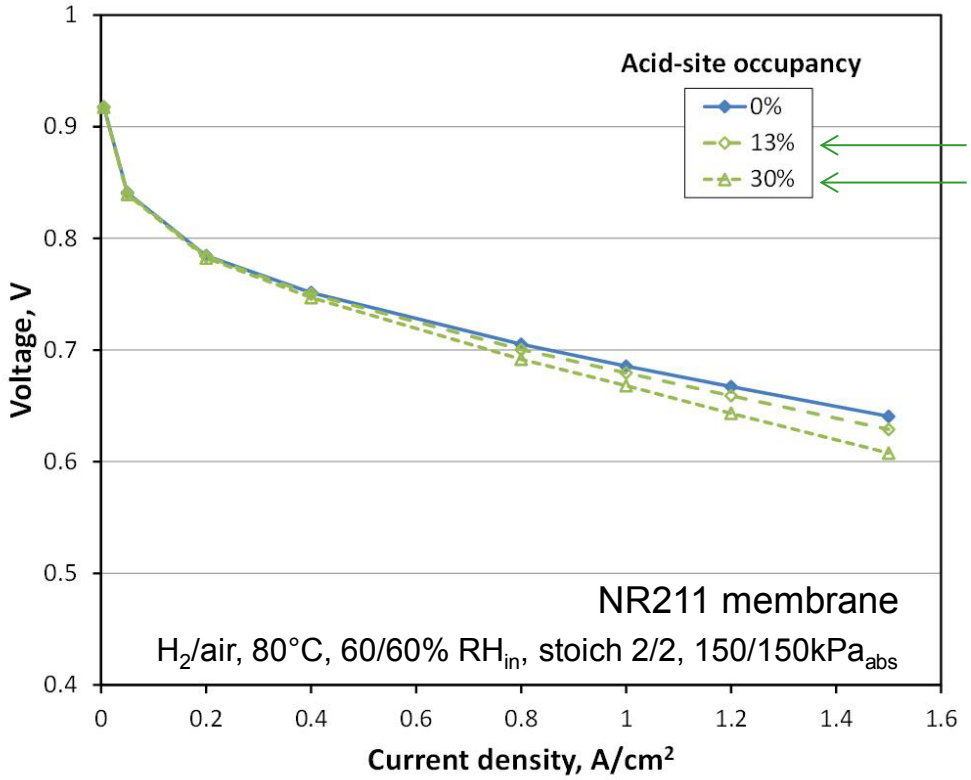




- ICP and EPMA were used to determine Pt and Ni contents in the electrodes and membranes.
- Noticeable amount of Ni leached out from the cathode into the membrane after MEA lamination.
- Larger amount of Ni left the cathode into the membrane during operation. 11/176 catalyst lost more Ni into the membrane. MIT confirmed using TEM/EDS.
- Despite the Ni losses, ORR activities were still very high for 12/280 derivatives. → robust

Kukreja data

Simulated Impact of Dissolved Ni on Air Performance

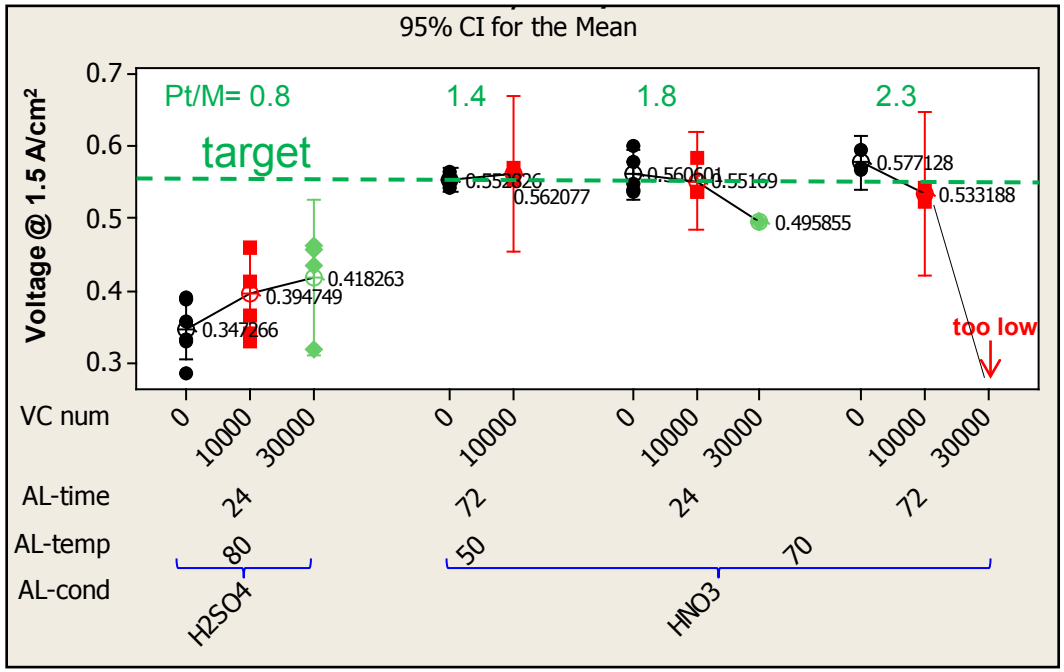


* Greszler, Moylan, Gasteiger. Handbook of Fuel Cells, Wiley, 2009, vol. 6, p. 728

- Used model* validated on high-Pt-loaded electrode with pre-incorporated cation-containing membranes. The model is based on cations electromigrate to cathode, displacing proton and slowing ORR.
- Model predicts voltage losses ~40 mV for reasonably large amounts of dissolved Ni^{2+}.

Air Performance on New-Precursor-derived Catalysts

Voltage at 1.5A/cm² under H_2/air as a function of voltage cycles

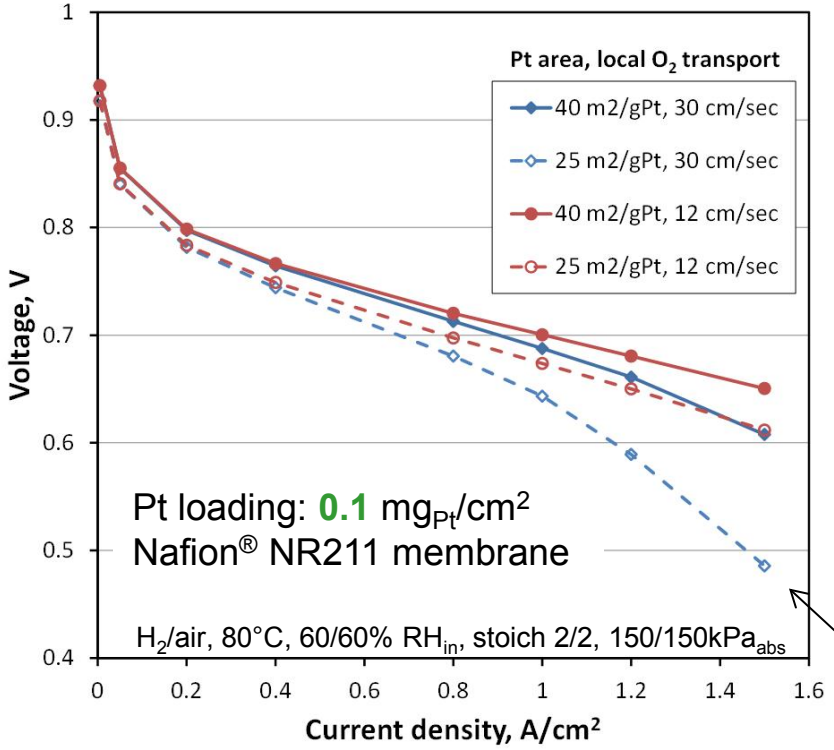


Measurement:
H_2/air, 80°C, 100/100% RH_{in}, stoich 2/2, 170/170kPa$_{abs}$
Cycling:
0.6-1.0V, 50mV/s, H_2/N_2, 80°C, 100% RH
Cathode loadings:
0.082-0.100 mg$_{Pt}$/cm²

- Initial air performance of new precursor (12/280) has not yet matched the older precursors.
- Extended acid leaching up to 72hrs at 70°C gave slightly higher initial air performance but durability appeared worse.
- All catalysts showed good ORR retention (>0.38A/mg after cycled) with Pt area decreasing from 45 to 25 m²/g. → Cation-model prediction and this result suggest that the observed large voltage loss is likely driven by other complications, e.g., **unoptimized electrode** induced by Ni^{2+}.
- 0.6-1.0V cycling is *too aggressive* for vehicle operation. Could induce carbon corrosion.

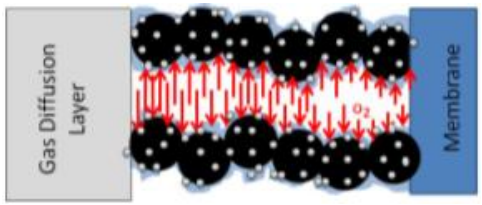
Technical Accomplishment:

Local O_2 Transport Resistance and Pt Surface Area

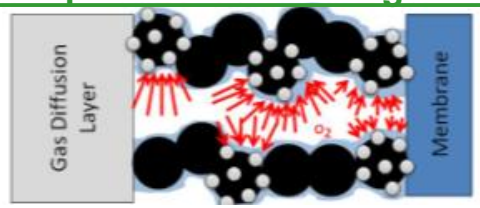


Modeled by Greszler, *et al.*, *J. Electrochem. Soc.*, F831 (2012)

Well-dispersed & High roughness factor



Poorly-dispersed & Low roughness factor



Cartoon from DOE transport proj, Wenbin Gu

- In fact, because the electrodes we've developed have low Pt roughness factor (Pt loading × Pt-specific surface area) the 'local O_2 transport resistance' described by other groups begins to become relevant.
- The source of this resistance is unclear but is often attributed to O_2 transport at air/ionomer or ionomer/Pt interfaces.
- Fortunately this type of voltage loss can be mitigated by increasing Pt surface area and/or improved electrode fabrication. → suggest targeting Pt area of >50m^2/g_{Pt} at end-of-life for a robust system.

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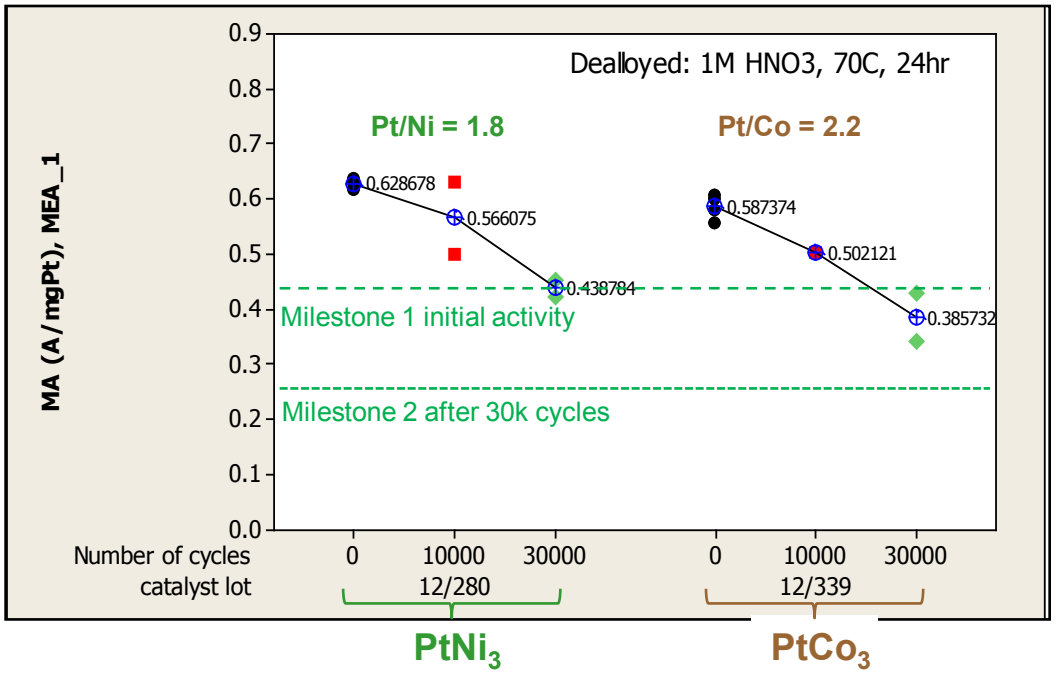
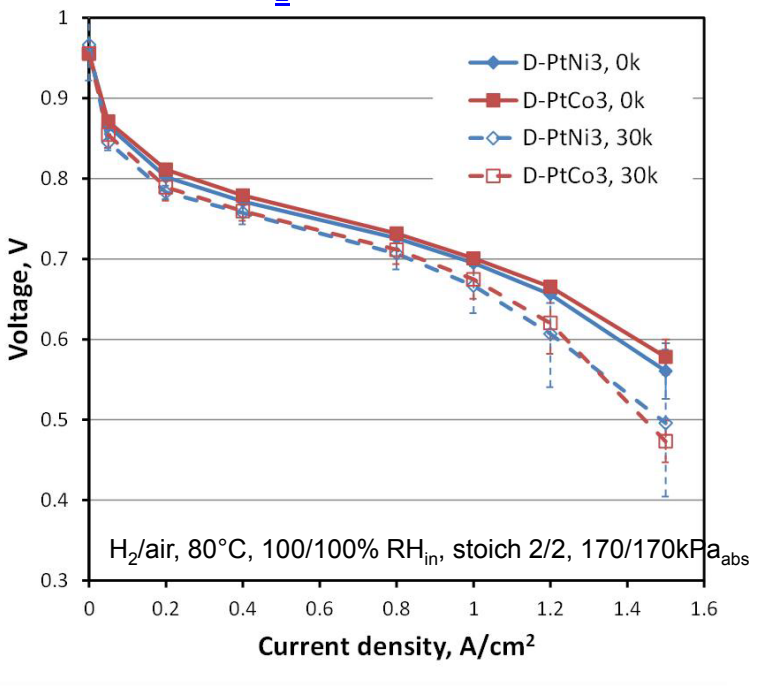
D-$PtNi_3$ vs D-$PtCo_3$ from New JM Large-Batch Precursors

Mass activities



H_2/air performance



- Used same dealloying condition (air, 1M HNO_3, 70°C, 24hr) for both precursors resulted in similar Pt/M ratios (1.8 and 2.2 for Pt/Ni and Pt/Co).
- Both catalysts gave similar ORR activities and air performance which is consistent with our expectations based on similarities of their known corrosion properties and heats of mixing.

Summary

- The initial activity and durability criteria were met with multiple, large-batch, dealloyed catalysts thereby passing the gate decision.
- The particle sizes of the precursors appear to be a dominant factor influencing durability; the initial and aged activities were similar.
- Although these catalysts maintain their high activities, large amounts of Ni are leached into the membrane.
- The Pt-shell over alloy-core morphology appears to have greater durability over the porous analogues.
- Although still insufficient, reducing the rate of non-noble metal dissolution vs. Pt surface diffusion could help to drive the catalyst structure.
- Both D-$PtNi_3$ and D-$PtCo_3$ showed very similar initial activity and retention of activity. We'll continue to investigate both catalysts.
- Modeling has suggested that dissolved base metal(s) from the catalyst(s) alone are not responsible for the observed voltage losses under H_2/air. More electrode optimization is needed.

Future work:

Initial air performance (Milestone 3: >560 mV@1.5A/cm^2 at 0.1 mg$_{PGM}$/cm^2 in >49 cm^2 cell)

- Alternate $PtNi_3$ syntheses/treatments for improved PSD and high surface area. (JM/TUB)
  - Reduce alloying temperature of the precursor
  - Decrease precursor metal content
- Fine-tune dealloying and electrode fabrication for improved high-current-density air performance of Milestone-2-compliant catalysts (GM)
- Adopt a thinner membrane to allay concerns from reviewers (GM/JM)
- Collaborate with DOE transport team. Fabrication and theory on low-Pt-loaded electrode (GM)

Durability of air performance (Milestone 4: >560 mV@1.5A/cm^2 at 0.1 mg$_{PGM}$/cm^2 in short stack)

- Continue development of binary and ternary dealloyed systems (TUB/JM)
- More relevant tests than 30k cycles at 0.6-1.0 V are probably required (GM)
  - Draw on GM and FCTT experience for vehicle-relevant protocol
- Final deliverable: durability testing on full-active-area short stack (JM/GM)
  - Project scheduled to end Nov 2013, expect delays in short-stack testing capability due to move of GM Fuel Cells from NY to MI.

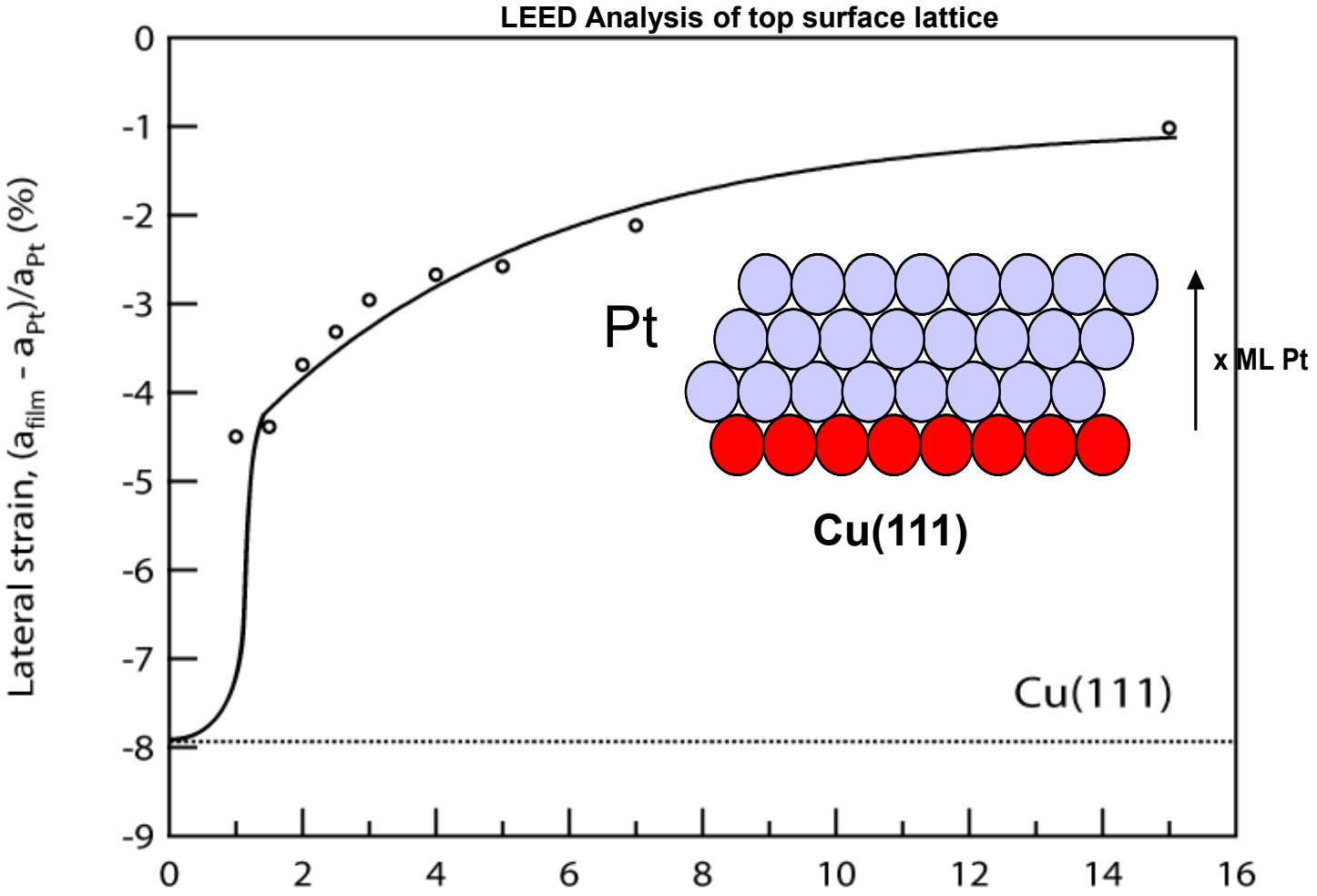
Advanced characterization

- Performance/structure correlations from good/bad pairs of durability-tested MEAs (NEU/GWU/MIT)
  - Rush of fascinating used-MEA samples will make up for recent drought of materials for characterization
  - Pt shell thicknesses and lattice compressions, core alloying-element concentrations, subsurface layer alloying atom concentrations and movement, changes in oxygen adsorbates

Technical Back-Up Slides

Background information: Compressive strain in (111) model 'Cu core – Pt shell' structures

- LEED study shows that *lattice strain is longer range than ligand effects*, > 10 layers
- **surface compression can be thermodynamically stable**



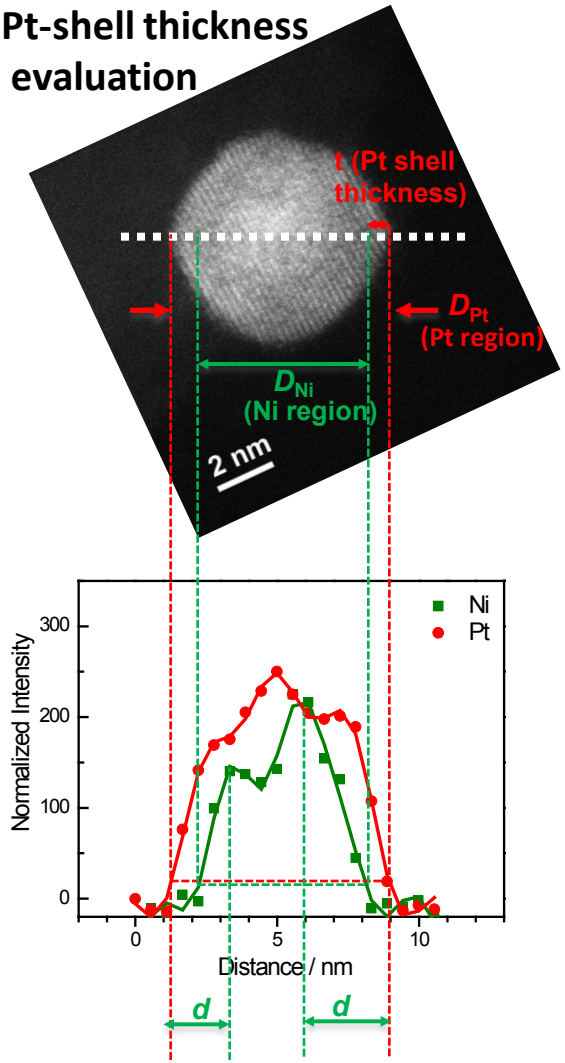
Also used as a backup slide for last year's AMR presentation

Adapted by first author from Strasser …Nillson, Nature Chemistry 2 (2010) 454 (supplemental material)

Technical Accomplishment:

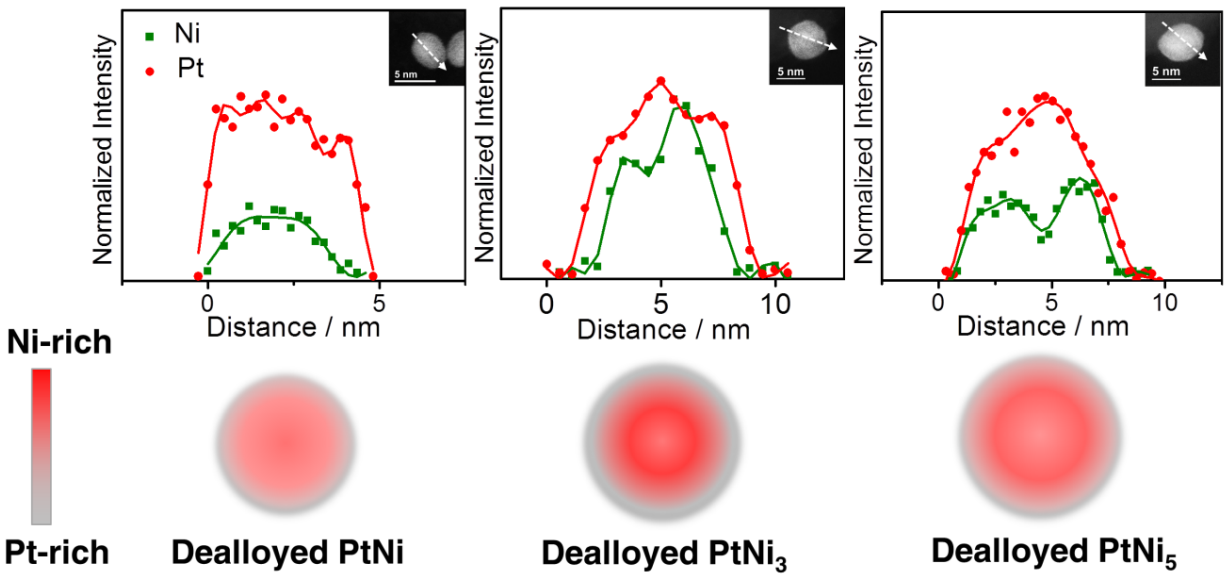
Ni-enriched Inner Shell Formed During Dealloying on RDE

Pt-shell thickness evaluation



d: Depth of Ni-Composition Maxima

Ni-enriched inner shells identified by aberration-corrected STEM/EELS



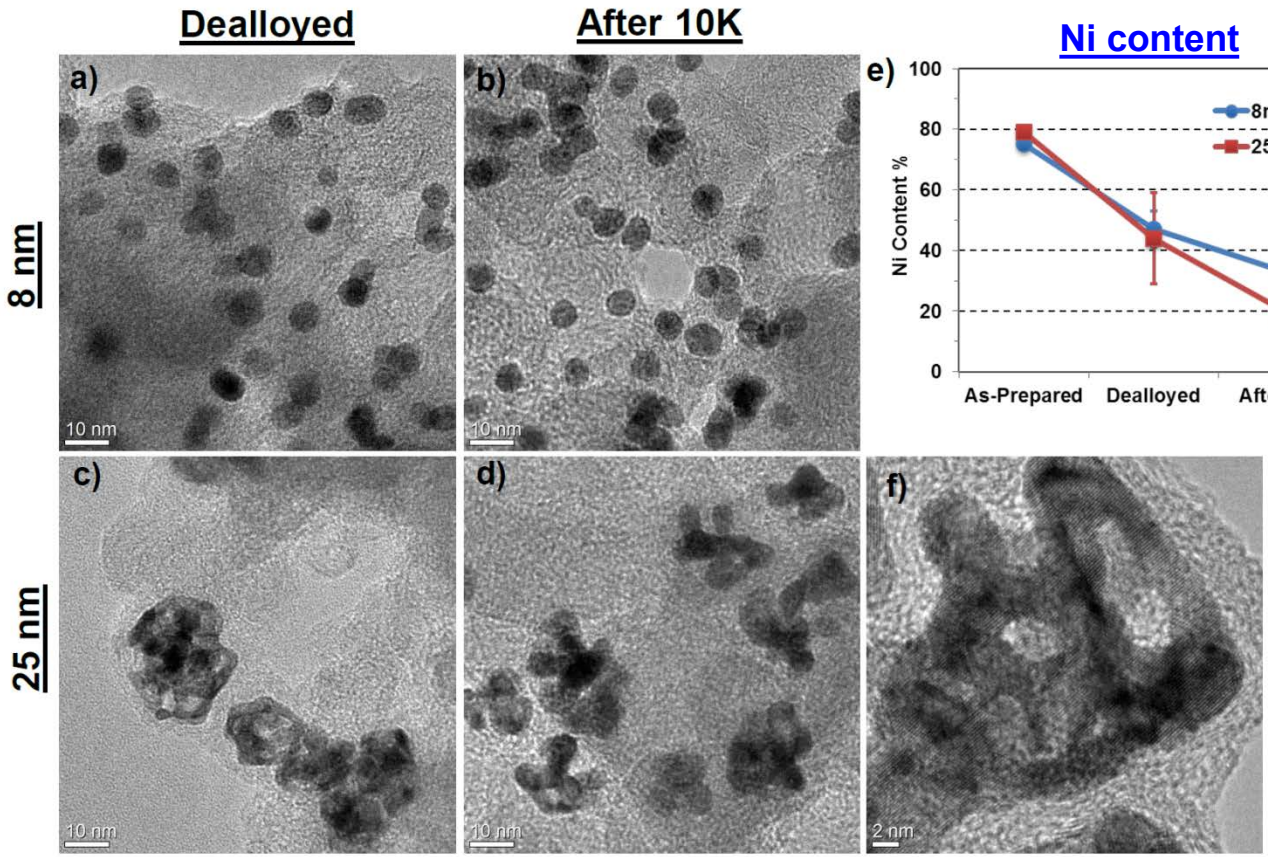
Catalyst	Pt shell thickness (nm)	Maximum Ni composition at the subsurface	Depth of the Ni-composition maxima (nm)	Specific activity (mA/cm^2 Pt)
D-PtNi	0.5 ± 0.2	34 ± 7 %	2.5 ± 0.4	1.90 ± 0.10
D-$PtNi_3$	0.8 ± 0.2	47 ± 11 %	2.6 ± 0.4	2.27 ± 0.13
D-$PtNi_5$	0.4 ± 0.2	40 ± 11%	2.0 ± 0.3	1.81 ± 0.10

A higher Ni-composition in the subsurface layers resulted in higher activity

Nano Letters 2012,12 (10): 5423-5430

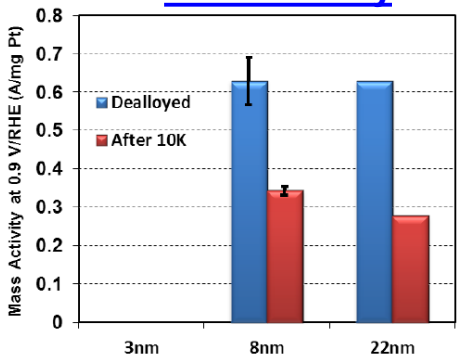
Technical Accomplishment:

EC-dealloying in RDE Yields Solid Small and Percolated Large Particles



Ni content

Mass activity



- The 25nm-NPs shows a similar activity as the 8nm-NPs after dealloying, but lower stability after 10 K.

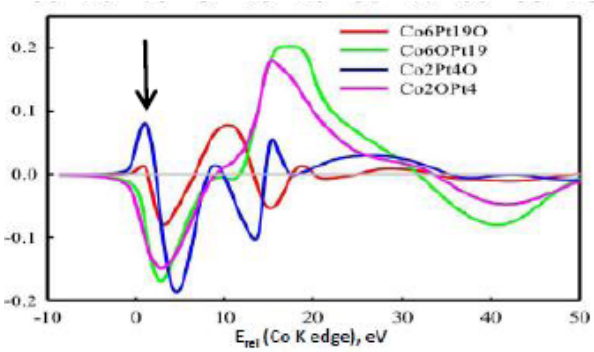
- The 8nm-NPs retains the solid structures and a higher Ni content after 10K cycles, which is consistent with its higher stability
- The pore structure in the 25nm-NPs changed significantly after 10K cycles, demonstrating a structural instability, which is accompanied with the compositional instability (larger extent of Ni loss)

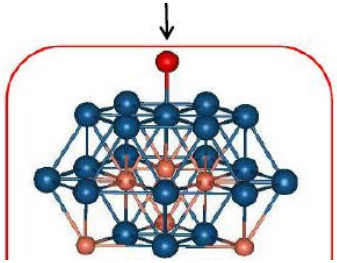
Technical Accomplishment: **from 2012 AMR**

X-ray Absorption Spectroscopy Refined as Tool for Characterizing Atomic-Scale Structure and Composition of Catalysts Used in MEAs

- Developed methodology for electrochemical XAS of used cathode electrodes from MEAs
  - − ions dissolved into the membrane had confounded analysis
  - − run durability of catalyst coated diffusion media (CCDM), separate CCDM from membrane, build CCDM into $HClO_4$ electrochemical cell

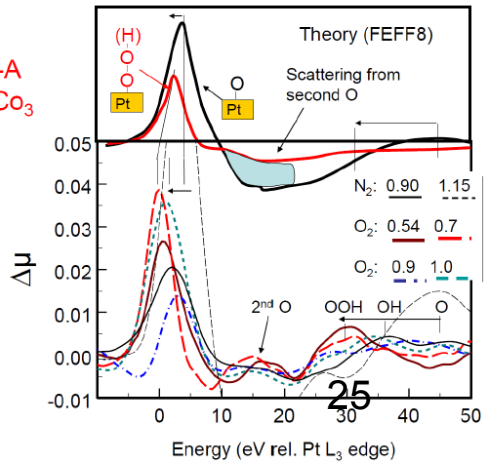
- Δμ XANES signature identified for oxygen bound to Pt atom above alloying elements in second layer
  - − chance to quantify, in practical nanoparticles, alloying-element atoms in positions with strongest effects on activity
  - − chance to quantify near-surface motion of alloying-element atoms



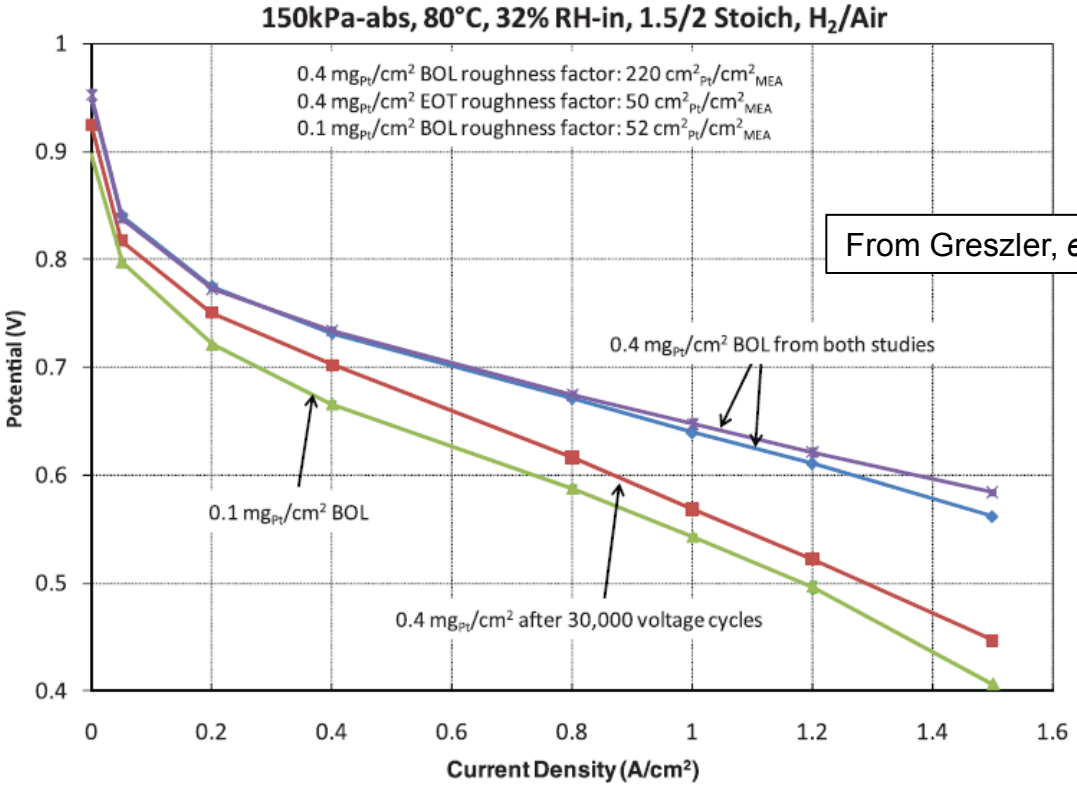


- Δμ XANES signature identified for adsorbed dioxygen species
  - − correlate activity with surface concentration of a possible intermediate

de-A $PtCo_3$



Impact of Pt Roughness Factor on Air Performance



From Greszler, *et al.*, *J. Electrochem. Soc.*, F831 (2012)

- 'Local O_2 transport resistance' can create a significant performance loss in cathode with low Pt roughness factor (Pt loading x Pt-specific surface area).
- For the system we work with, free-cation-related voltage losses are smaller than that expected from local O_2 transport resistance.
- The source of this resistance is unclear but often is attributed to O_2 transport at air/ionomer or ionomer/Pt interface.