V.A.10 High-Activity Dealloyed Catalysts

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Project Start Date: August 1, 2010
Project End Date: November 30, 2013

Overall Objectives

- Demonstrate, in 50-cm^2 membrane electrode assemblies (MEAs) in fuel cells using catalyst precursors prepared in large batch size, a dealloyed catalyst that satisfies DOE 2017 catalyst goals.

- Determine, at the atomic scale, where alloying-element atoms should reside with respect to the surface of the catalyst particle for simultaneously good activity, durability, and high-current density performance in air.

- Develop and demonstrate electrodes giving high current density performance in air adequate to meet the DOE platinum group metal (PGM) loading targets of <0.125 g$_{PGM}$/kW$_{rated}$ and <0.125 mg$_{Pt}$/cm$^2_{geo}$.

- Scale up of synthesis and dealloying. Test durability of activity and power density in full-active-area cells.

Fiscal Year (FY) 2013 Objectives

- Optimize manufacturable procedures for precursor synthesis and dealloying of the catalyst powders.

- Demonstrate electrodes made from dealloyed catalysts that give good high current density performance using air as the oxidant: >0.56 V at 1.5 A/cm^2 when tested with the DOE-targeted cathode loadings ≤0.1 mg$_{PGM}$/cm^2.

- Improve understanding of where alloying-element atoms should reside with respect to the surface of the catalyst particle for simultaneously good activity, durability, and high-current-density performance in air.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

(B) Cost

(A) Durability

(C) Performance

Technical Targets

TABLE 1. Progress towards Meeting Technical Targets for Electrocatalysts for Transportation Applications

Characteristic	Units	2017 DOE Stack Targets	Project 2013 Status (50 cm^2 at GM)
Mass activity	A/mg$_{PGM}$ @ 900 mV$_{iR-free}$	≥0.44	0.6-0.75 (PtNi&PtCo)
Loss in catalytic (mass) activity	% lost after 30k cycles 0.6-1.0 V	≤40%	0-40% (PtNi&PtCo)
PGM Total Content	g$_{PGM}$/kW$_{rated}$	≤0.125	0.16 @1.5 A/cm^2 in H$_2$/air
PGM Total Loading	mg$_{PGM}$/cm$^2_{geo}$	≤0.125	0.15 (still 0.05 on anode)
Performance @ rated power	mW/cm^2	1,000	945
Performance @ 0.8 V	mA/cm^2	300	240

FY 2013 Accomplishments

- Developed several catalysts derived from large-batch PtNi$_3$ and PtCo$_3$ achieving initial mass activities of 0.60-0.75 A/mg$_{PGM}$, substantially exceeding the target of 0.44 A/mg$_{PGM}$.

- The above catalysts, demonstrated in two labs, lost only 0-40% of its initial activity after 30,000 cycles (0.6-1.0 V), bettering the target of <40% loss.

- MEAs made with large-batch catalysts at 0.1 mg_{PGM}/cm^2 gave 0.58 V at 1.5 A/cm^2. Although higher than the project milestone of 0.56 V, there is still some room for improvement. Voltage after 30,000 cycles (0.6-1.0 V) was still lower than the target of 0.56 V.

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INTRODUCTION

The amount of expensive platinum used as the oxygen reduction catalyst in fuel cells must be reduced about 4-fold to make proton exchange membrane fuel cells cost-competitive with other power sources. Pt-alloy catalysts, typically prepared with a composition of Pt_3M (M being a non-precious metal) have historically provided about half of the necessary activity gain vs. state-of-the-art pure-Pt/carbon catalysts. Prior to this project, team member Peter Strasser's group had shown, in small-scale laboratory experiments, that additional activity gains could be obtained by first synthesizing alloys with excess M and then removing most of the M by an electrochemical treatment [1]. They hypothesized that this treatment leaves the surface Pt atoms closer to one another than they are in pure Pt, causing electronic structure changes that accelerate the reduction of oxygen [2]. This project has developed manufacturable means of scaling up these dealloyed catalysts, confirming that most of the activity gains seen in ex situ laboratory experiments can also be achieved in practical fuel cells at GM, which satisfy the DOE catalyst activity target. However, we identified severe problems: (1) lack of durability and (2) poor performance in hydrogen/air fuel cells at high current density, associated with the use of the alloying element, copper, which had seemed most attractive in ex situ experiments. In FY 2012 we successfully shifted to other alloying elements, cobalt and nickel, which avoid one of the mechanisms whereby copper caused problems. We continue to pursue ideas to solve the durability shortfall that we have seen to date for the large-scale dealloyed $PtNi_3$ and $PtCo_3$ materials.

APPROACH

Because of the poor durability of $D-PtCu_3$ and anode poisoning due to dissolved Cu crossing over and plating, last year we shifted our efforts to other alloying elements, cobalt and nickel. Small-batch GM-made $D-PtCo_3$ and D-PtCo catalysts met, in 50-cm^2 fuel cells at GM, both the initial activity and the durability DOE 2017 targets, however, large-batch JMFC-made $D-PtNi_3$ catalysts met only the initial activity target. To understand this discrepancy, this year, advanced electron microscopy and synchrotron X-ray techniques were applied to tested and aged electrodes to correlate atomic-scale structure and composition with differences in activity and durability between individual catalysts, thereby guiding further catalyst development. Extensive work was done modifying catalyst precursor synthesis and dealloying procedure to generate durably active dealloyed catalysts. Demonstrated at two labs, several catalysts made from at least two large-batches of $PtNi_3$ and $PtCo_3$ precursors simultaneously satisfied both DOE 2017 initial activity and durability targets, and therefore we passed the Go/No-Go gate in October 2012.

RESULTS

To resolve the discrepancy in the durability observed between GM-made small-batch $D-PtCo_3$ and JMFC-made large-batch $D-PtNi_3$, in situ extended X-ray absorption fine structure was employed by NEU and GWU. The findings are summarized in Table 2. It was found that while GM $D-PtCo_3$ and D-PtCo show a large fraction of single-core with a shell structure, the JMFC $D-PtNi_3$ show mostly multi-core with porous-shell structure. With voltage cycling, Pt-Ni interaction decreases indicating loss of Ni from the shell. Pt-Pt distance was also seen to increase approaching that of pure Pt. Losses of Ni and Pt strain explain the loss of oxygen reduction reaction (ORR) activity after voltage cycling for JM $D-PtNi_3$. Transmission electron microscopy (TEM) analyses by MIT on these catalysts confirmed these findings.

TABLE 2. Structure and Composition Determined by Extended X-Ray Absorption Fine Structure Measurement of Different Catalysts at Different Number of Cycles

Precursor	d (nm)	Cycles	R_{Pt-Pt} (Å)	Microstructure
GM small-batch D-PtCo/HSC	4.0	~100	2.70	Mostly SC-S
GM small-batch D-PtCo$_3$/HSC	4.0	~100	2.71	50% SC-S, 50% MC-PS
D-PtNi$_3$/HSC	4.5	~100	2.72	MC-PS w M in PS
D-PtNi$_3$/HSC	5.5	10k	2.73	MC-PS w < M in PS
D-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)

It is reported by several groups that the morphology of a catalyst can be affected by many factors such as precursor composition, size, and dealloying condition [3-5]. On a flat system, Erlebacher showed that morphology can be governed by the relative rate of nonnoble-element dissolution and noble atom surface diffusion [5]. TUB attempted to tune this rate by conducting acid treatment in sulfuric acid in presence of air or nitrogen gas (Figure 1). In air, O_2 creates a corrosion potential of ~1 V (higher than ~0.6 V in the N_2 case) and enhances Ni dissolution, and therefore removes more Ni. Large numbers of porous particles were observed
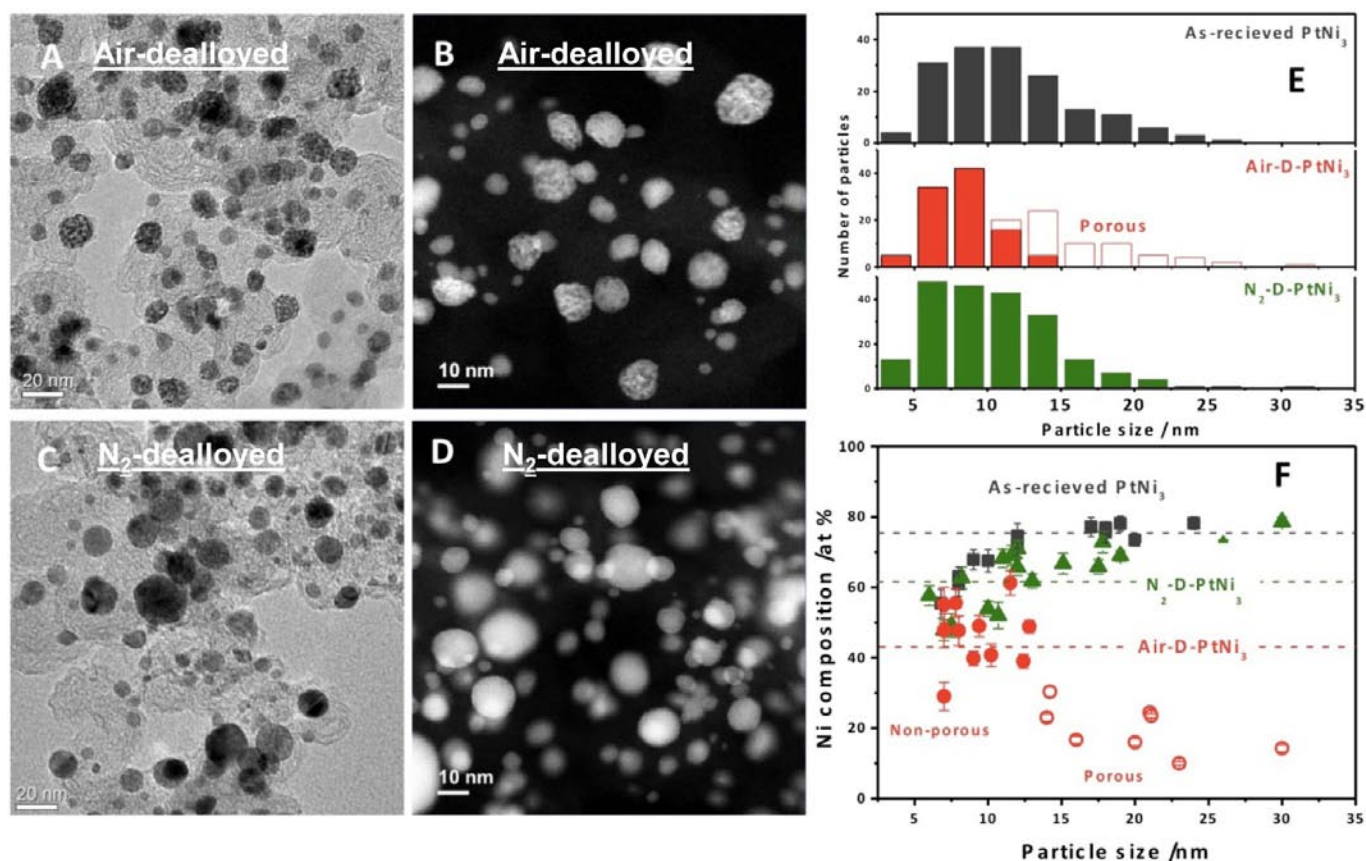
FIGURE 1. (A) TEM image and (B) High-angle annular dark-field (HAADF)-Scanning TEM (STEM) image of air-dealloyed-PtNi$_3$ 11/176 catalyst. (C) TEM image and (D) HAADF-STEM image of N$_2$-dealloyed-PtNi$_3$ catalyst. (E) Particle size distributions. (F) Size-composition-porosity relationships, where the horizontal dash lines represent the average compositions. It is shown that porous particles begins to form at particle larger than 13 nm and shows less residual Ni in air-dealloyed-PtNi$_3$ catalyst.

when dealloyed in air. Interestingly, only particles with its size larger than about 13 nm were seen to be porous. Smaller particles were solid and retained more Ni. These results indicate that particle size plays a significant role in determining the particle morphology and perhaps smaller particles are more stable than larger ones.

JMFC studied more than eight different preparation paths in order to improve the particle size distribution of its precursors. Figure 2 compares TEM images of JMFC old and new precursors. The particle size distribution is clearly improved in the new precursor. However, the new precursor is no longer single phase, showing some amount of pure Ni phase. Although our original approach was to make a single-phase alloy which was thought to give a more uniform dealloying process, it was very challenging to achieve acceptable particle size distribution with a single phase. JMFC now also made progress in eliminating the pure Ni phase which may induce complication during MEA fabrication.

The improved JMFC precursor was then dealloyed and treated under a series of conditions at GM. The PtNi$_3$ precursor was either leached in 1M nitric acid under air or 0.5M sulfuric acid under nitrogen. The acid-leaching temperature and time were also changed to obtain the Pt/Ni atomic ratio in the range suitable for fuel cell testing (Pt/Ni ~0.8-3). Post-dealloying thermal annealing was shown in rotating-disk experiment that could improve activity and stability [6]. A similar procedure was also applied to the catalysts in this study. Figure 3 shows the mass activities of the resultant catalysts as a function of voltage cycle. Nitric-acid/air 70°C, 24 hours (second triad from the right) was the same dealloying condition that was applied to the old precursors (11/176) last year that showed mass activity of 0.17 A/mg$_{PGM}$ after 30,000 cycles. The catalyst prepared from the new precursor showed excellent activity and durability, fulfilling Milestone 1 (initial activity ≥0.44 A/mg$_{PGM}$), Milestone 2 (activity after 30k cycles ≥0.26 A/mg$_{PGM}$), and the DOE target of ≤40% loss of initial activity after 30k cycles. In fact, all of the catalysts in Figure 3 (save the one leached at 50°C) fulfilled the same. Sulfuric-acid/N$_2$ dealloying is a less oxidative condition than nitric-acid/air and therefore requires higher acid-leaching temperature to remove sufficient Ni. However, still higher Ni was retained in the particles. High resolution-TEM analyses by MIT on these particles showed a formation of Pt shell that might stabilize
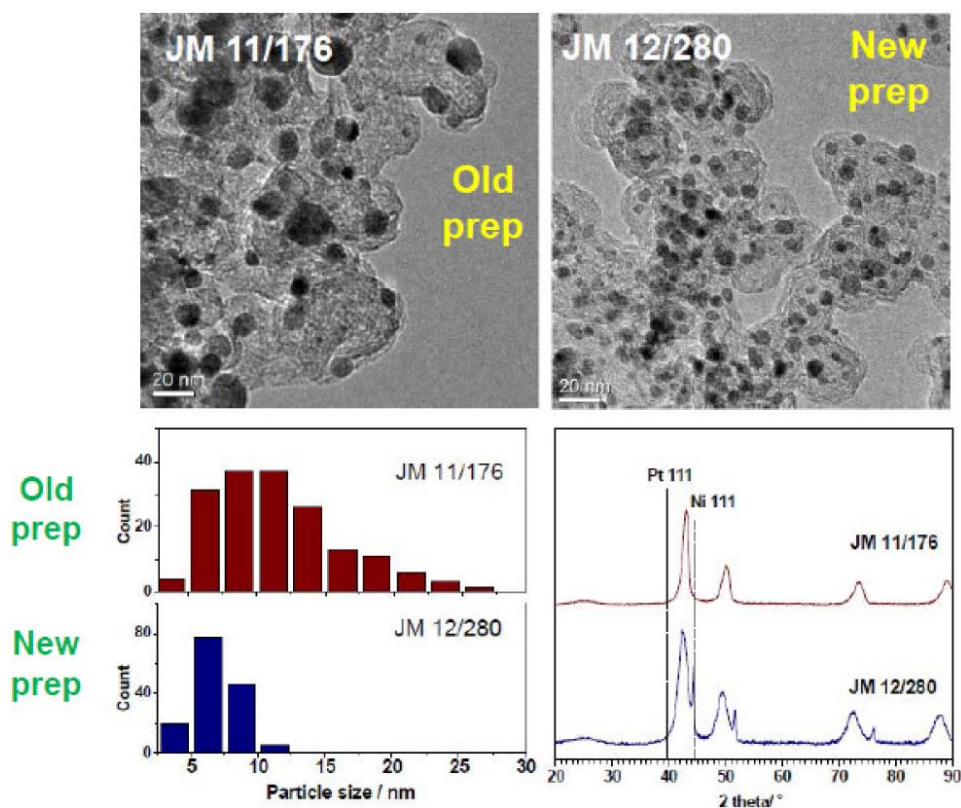
FIGURE 2. TEM images, particle-size histograms, and powder X-ray diffractogram of JMFC's old and new PtNi$_3$ precursors. The vertical lines in the diffractogram show the diffractions of Pt and Ni phases.
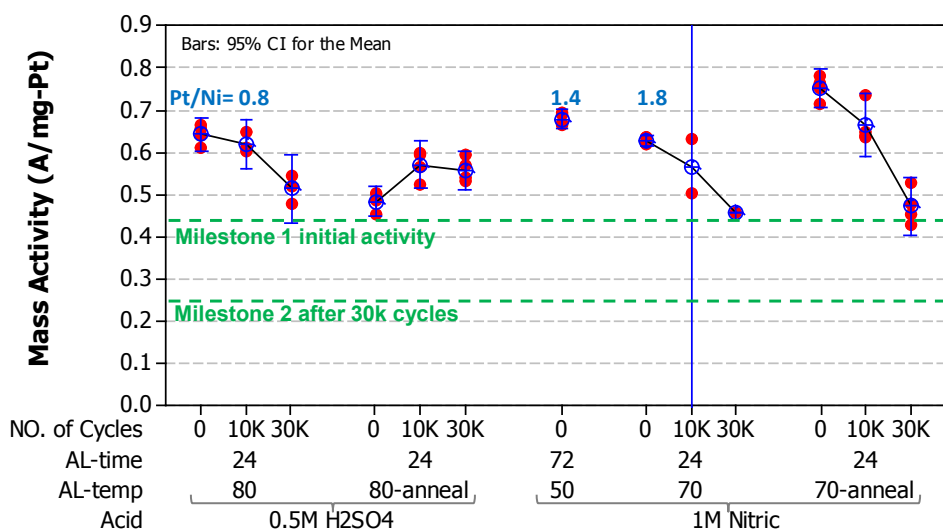

FIGURE 3. GM 50-cm^2 MEA mass-activity data for JMFC PtNi$_3$ new precursor (12/280) dealloyed under different times/temperatures/acid-types, with and without a post-dealloying anneal of the powder (4 h 400°C in 5% H$_2$/N$_2$). Blue error bars showing 95% confidence interval for the mean are large when only two samples have been completed due to large multiplier of standard deviation for only two samples.
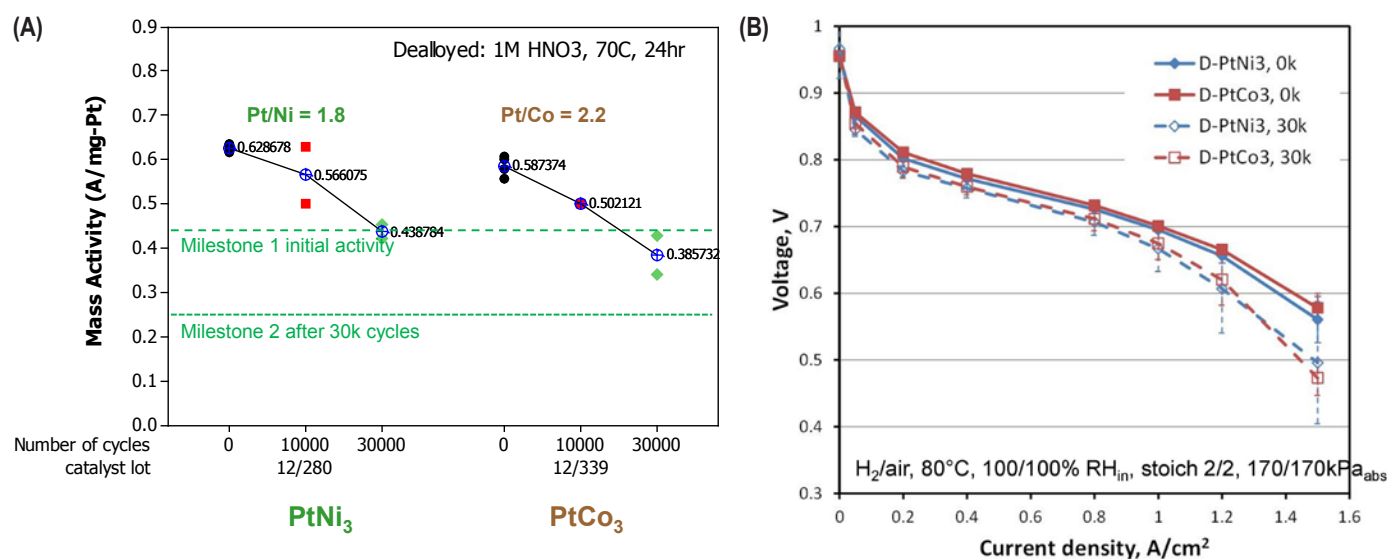
FIGURE 4. GM 50-cm^2 MEA (A) mass-activities and (B) H$_2$/air polarization curves of D-PtNi$_3$ and D-PtCo$_3$ catalysts as a function of voltage cycles. Both were dealloyed using the same condition (1M HNO$_3$, air, 70°C, 24 h).

Ni. The post-dealloying thermal annealing appeared to improve the stability when the precursors were sulfuric-acid/ N$_2$-dealloyed, although it is unclear whether it offered any advantage when the precursors were nitric-acid/air-dealloyed.

To compare the activity and durability of PtNi and PtCo catalysts, JMFC prepared PtCo$_3$ precursor using the same synthetic path as the PtNi$_3$ new precursor (12/280) and then GM applied the same dealloying treatment to both precursors and evaluated them in 50-cm^2 MEAs. Figure 4 compares the durability of the ORR activity and H$_2$/air performance of these two catalysts. It is obvious that both catalysts perform very similarly over the course of testing. This is consistent with our original expectations based on the similarities of their known corrosion properties and heats of mixing between the two systems.

Two trips to the synchrotron beamlines (eight days at the National Synchrotron Light Source at Brookhaven National Laboratory, four days at the APS) were made in April this year to conduct X-ray absorption measurements by GWU and NEU on the above-tested and aged D-PtNi$_3$ catalysts, to correlate atomic-scale structure and composition with differences in activity and durability, to guide the further catalyst development. The analyses are underway.

CONCLUSIONS AND FUTURE DIRECTIONS

- The initial activity and durability criteria were met with multiple, large-batch, dealloyed catalysts thereby passing the gate decision.

- The particle size of the precursors was the dominant factor influencing durability. Catalysts prepared from smaller particle-size precursors resulted in Pt-shell over alloy-core morphology which appeared to have greater durability over the porous analogues.

- Both D-PtNi$_3$ and D-PtCo$_3$ showed very similar initial activity and retention of activity.

- In FY 2014, we will focus our effort to
  - Optimize manufacturable syntheses/treatments for uniform particle size and high surface area to maximize H$_2$/air fuel cell performance with low-Pt-loaded electrodes.
  - Perform durability testing on full-active-area cells and deliver to DOE for validation.
  - Perform advanced characterization to correlate atomic-scale structure and composition with activity and durability.

PATENTS ISSUED

1. U.S. Provisional Application No. 61/823,032, "Ternary dealloyed catalyst" Joint patent JMFC-GM.

FY 2013 PUBLICATIONS/PRESENTATIONS

Presentations and Published Abstracts

1. Strasser, P., "Materials for Fuel Cell Catalysts", American Chemical Society, San Diego, CA, March 26, 2012.

2. Strasser, P., "Core-Shell Nanoparticle Catalyst Concepts for High Performance Polymer Electrolyte Membrane Fuel Cells", keynote presentation at the Grove Fuel Cells 2012 Science & Technology Conference, Berlin, Germany, April 11, 2012.

3. Gan, L.; Heggen, M.; Rudi, S.; and Strasser, P., "Core-Shell Compositional Fine Structures of Dealloyed $Pt_{1-x}Ni_x$ Nanoparticles and their Impact on Oxygen Reduction Catalysis",Goettingen ETEM Workshop on Heterogeneous Catalysis, Surface Science and Energy Research, July 9–11, 2012, Goettingen, Germany.

4. Strasser, P., "Oxygen Electrocatalysis on Nanostructured Metal and Oxide Nanoparticles", Summer School on Electrocatalysis on Nanoparticles, August 5–9, 2012, Copenhagen, Denmark.

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1. H.L. Xin, J.A. Mundy, Z. Liu, R. Cabezas, R. Hovden, L.F. Kourkoutis, J. Zhang, N.P. Subramanian, R. Makharia, F.T. Wagner, D.A. Muller, Atomic-resolution spectroscopic imaging of ensembles of nanocatalyst particles across the life of a fuel cell, Nano Letters, 12 (2012) 490-497.

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15. Gan L; Cui CH; Rudi S; Strasser P (2013) Core-shell and nanoporous particle architectures and their effect on the activity and stability of Pt ORR electrocatalysts. Top Catal (Submitted)

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