# V.A.9 High-Activity Dealloyed Catalysts

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- Yang Shao-Horn, Massachusetts Institute of Technology (MIT), Cambridge, MA
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- Peter Strasser, Technical University Berlin (TUB), Berlin, Germany

Project Start Date: August 1, 2010
Project End Date: September 30, 2014

## 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) 2014 Objectives

- Improve understanding of where alloying-element atoms should reside with respect to the surface of the catalyst particle for simultaneously achieving good activity, durability, and high-current-density performance in air.
- 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 $mg_{PGM}/cm^2$.
- Develop catalyst and optimize electrode to achieve >0.56 V at 1.5 $A/cm^2$ after durability testing.

## 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 2014 Status (50 $cm^2$ at GM) |
|---|---|---|---|
| Mass activity | $A/mg_{PGM}$ @ $900mV_{iR\text{-}free}$ | ≥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 (still 0.05 on anode) |
| 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 2014 Accomplishments

- Developed several large-batch $PtNi_3$ and $PtCo_3$ catalysts 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 lost only 0-40% of its initial activity after 30,000 cycles at 0.6-1.0 V, bettering the target of <40% loss.
- Achieved same $H_2$/air fuel cell performance as 0.4 $mg_{Pt}/cm^2$ electrode with one-fourth the PGM loading with newly developed catalysts. Confirmed improved performance of the newly developed catalyst in a full-active-area automotive stack.

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## INTRODUCTION

The amount of expensive platinum used as the oxygen reduction catalyst in fuel cells must be reduced at least 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 initial 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

During FY 2012 and 2013, we successfully shifted to dealloyed $PtNi_3$ and $PtCo_3$ systems and demonstrated on several large-batch precursors their improved activity and durability in 50-$cm^2$ fuel cells exceeding DOE 2017 targets, and therefore passed the Go/No-Go gate in 2012. During FY 2013 and 2014, we extensively used advanced electron microscopy and synchrotron X-ray techniques in an attempt to correlate atomic-scale structure and composition with catalytic performance in order to improve our understanding in designing a better catalyst. On the other hand, as the loading of Pt in the cathode electrode is reduced, we observed larger voltage loss, especially at high power, than expected. This loss was attributed to low available Pt area for oxygen reduction reaction as Pt loading is reduced. Therefore, we continue to further develop our catalyst to have higher specific Pt area. Meanwhile, iterations of electrode optimization were done and selected catalysts were demonstrated in a full-active-area fuel cell stack.

## RESULTS

We have showed record oxygen reduction reaction (ORR) activities even after accelerated voltage-cycling stability tests. These catalysts were prepared from large batch catalyst precursors from Johnson Matthey and were dealloyed using multiple acid-leaching conditions and post-leaching thermal annealing treatments at GM. A subset of those samples and their respective ORR activity changes with voltage-cycling tests is shown in Figure 1. As reported last year, catalysts made from the old $PtNi_3$ precursor (11/176 type) had poor particle size distribution and showed poor durability. However, catalysts made from the new $PtNi_3$ precursor (12/280 type) had good particle size distribution and showed excellent durability. GM generated MEA samples at different aging stages of these catalysts and sent to the partners for advanced characterization (MIT for transmission electron microscopy [TEM], NEU for extended X-ray absorption fine structure analysis [EXAFS], and GWU for X-ray absorption near-edge spectroscopy [XANES]) in an attempt to deepen our understanding of what is needed to make a high-activity and durable catalyst. Due to limited space, only a few achievements will be highlighted in this report.

The high activity of dealloyed Pt-Ni catalysts can be attributed to the compressive lattice strain of the Pt-shell surface due to the lattice and composition mismatch to the underlayer Ni-rich core. As the Pt shell grows thicker the lattice strain diminishes. On the other hand, certain Pt-shell thickness and quality are necessary to protect the Ni-rich core from degradation in an MEA environment. We have developed methods to evaluate the Pt-shell quality and to correlate micro-composition to the ORR activity.

Using the microscopic results from TEM at MIT and GM, the elemental measurement results from GM, and micro-composition analysis from EXAFS at NEU, GWU developed XANES delta mu technique to evaluate the quality of the Pt shell. They identified a specific feature in the XANES spectra that belongs to direct and indirect Ni-O bonds. Measuring this feature at different electrochemical potentials on the different catalysts after different aging stages, GWU found that it was easier for oxygen to penetrate through the Pt-shell on the catalyst made from the old

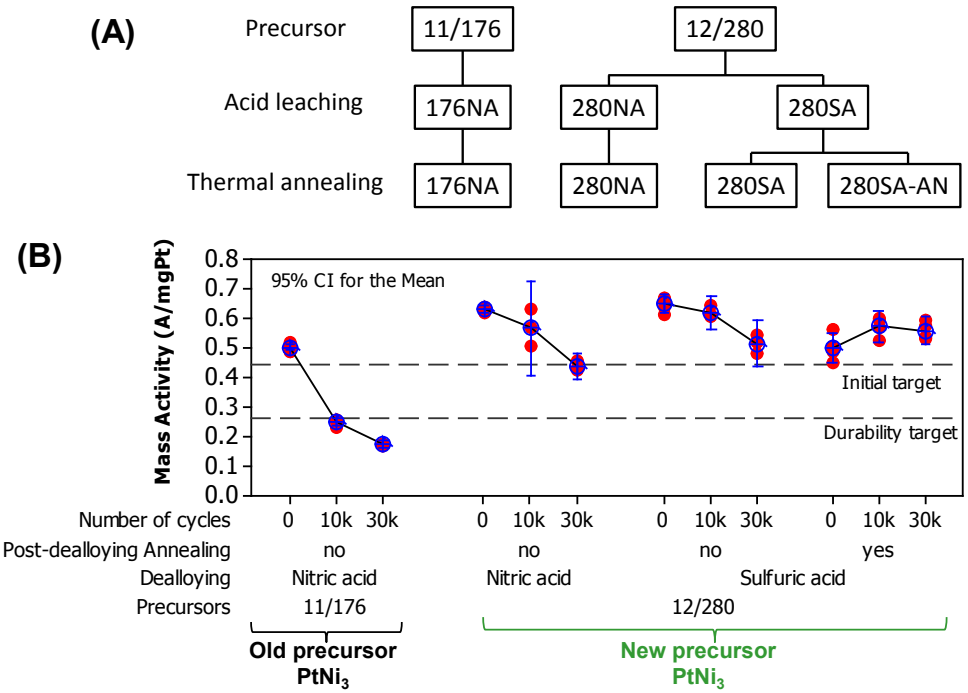



**FIGURE 1.** (A) Schematic showing selected catalysts. The precursors were either treated in: (1) 1 M nitric acid at 70°C for 24 h in air (176NA and 280NA) or, (2) 0.5 M sulfuric acid at 80°C for 24 h in nitrogen (280SA). After the dealloying, some 280SA catalysts were thermally annealed at 400°C for 4 h in 5% $H_2$ and 95% $N_2$, marked as 280SA-AN. (B) GM 50-$cm^2$ MEA mass-activity data for the different catalysts as a function of voltage cycles. Error bars represent 95% confidence intervals for the means.

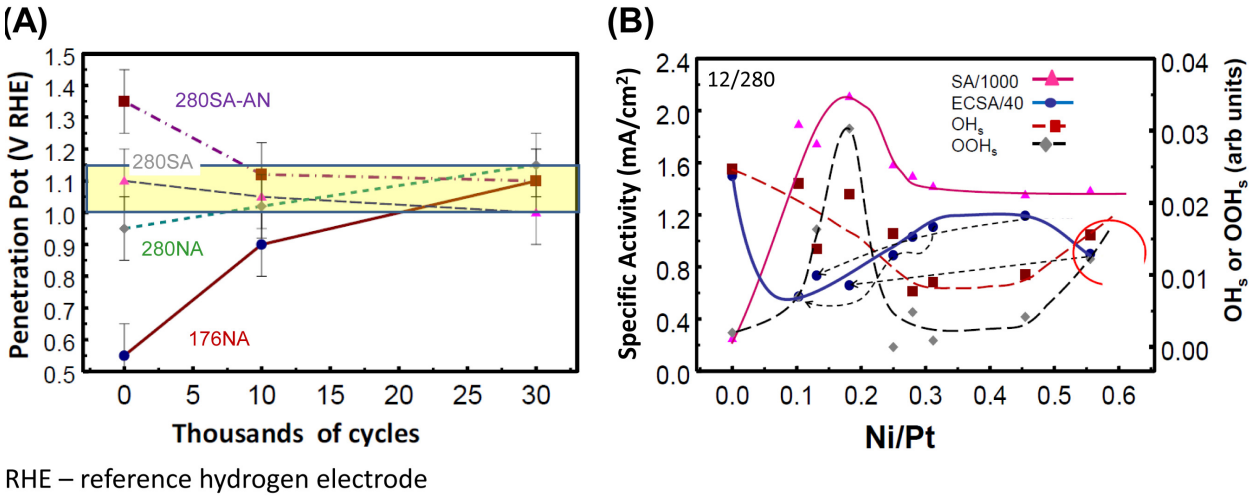
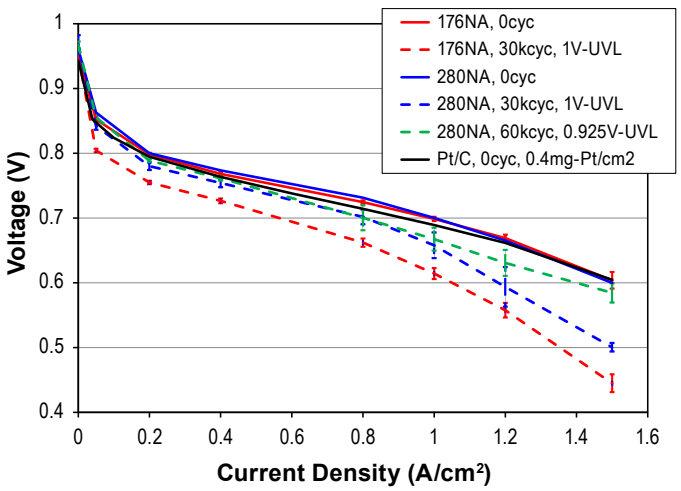



**FIGURE 2.** (A) Potentials where indirect Ni-O interaction become dominant (penetration potentials) determined by Ni K edge XANES for the different catalysts. (B) Plot of δ|Δμ| for $OOH_n$* at 0.7 V in $O_2$ and |Δμ| for OH* at 0.9 V in $N_2$, along with the specific activity ($mA/cm_{Pt}$) at 0.9 V, as a function of Ni/Pt content.

precursor (176NA) than on those made from the new precursor (Figure 2A). Post-dealloying thermal annealing (280SA-AN) was also found to enhance Pt-shell quality. Interestingly, after extensive voltage cycling, all catalysts showed a similar characteristic shell quality. This may indicate the minimum Pt shell thickness needed for any catalyst to be sufficiently stable in a fuel cell environment.

Furthermore, XANES analysis on the Pt $L_3$ edge allows quantification of adsorbed species on the Pt surface. Of particular interest, adsorbed OH, OOH, and HOOH

are believed to strongly correlate with ORR activity. A comprehensive picture appeared when measurements on the different catalysts at different aging stages were done (Figure 2B). The specific activity measured in MEAs (pink solid line) correlates with OOH surface species in lieu of OH dominating. This points to a relatively lower Pt-O bond strength on the dealloyed catalysts. More importantly, it explains how the activity of the 12/280-type catalyst increases before it decreases as the Ni content decreases but the activity of the 11/176-type catalyst monotonically decreases. This suggests that the catalyst should start at a slightly high Ni content to maintain high activity for an extended period of time.




UVL – upper voltage limit

**FIGURE 3.** GM 50-cm$^2$ MEA polarization curves of D-PtNi$_3$ (color lines) and Pt/C (black line) catalysts, before (solid lines) and after (dashed lines) voltage-cycling tests as indicated in the legend. Operating conditions were $H_2$/air, 80°C, 100/100% relative humidity$_{in}$, stoichiometry 1.5/2, 170/170 kPa$_{abs}$.

In the previous year, we reported encouraging $H_2$/air fuel cell performance but noted that the high-power performance was still lower than what one would expect from such highly active catalysts. Since then, GM conducted multiple iterations of electrode optimization. Figure 3 shows comparative polarization curves of the different catalysts after optimization. Dealloyed catalysts 176NA (red solid line) and 280NA (blue solid line) at 0.1 mg$_{PGM}$/cm$^2$ cathode loading gave comparable performance as a Pt/C catalyst (black solid line) at four times the loading. This demonstrates good utilization of the new catalysts.

After 30,000 voltage cycles, 176NA lost more activity than 280NA (also showed in Figure 1, first and second triads) and hence larger voltage (red vs. blue dashed lines). Interestingly, we found that one could mitigate the performance loss by constraining the upper voltage limit during the voltage cycling from 1 V to 0.925 V. Doing so, we were able to mitigate the performance loss at 1.5 A/cm$^2$ to only 20 mV after 60,000 cycles. This highlights the highly intimate interaction between materials and system and the necessity of optimizing one in correlation with the other.

In an attempt to demonstrate the newly developed catalyst in a real fuel cell system, selected catalysts were integrated with other state-of-the-art components and were fabricated into a full-active-area stack. Figure 4 shows the power density for the dealloyed PtNi$_3$ and PtCo$_3$ catalysts tested under Fuel Cell Tech Team recommended conditions. Noticeable voltage loss at dry condition indicates needs for more electrode optimization. Note that one can easily boost the voltage by testing at higher pressure which was recently advised by DOE funded system modeling. We intend to test

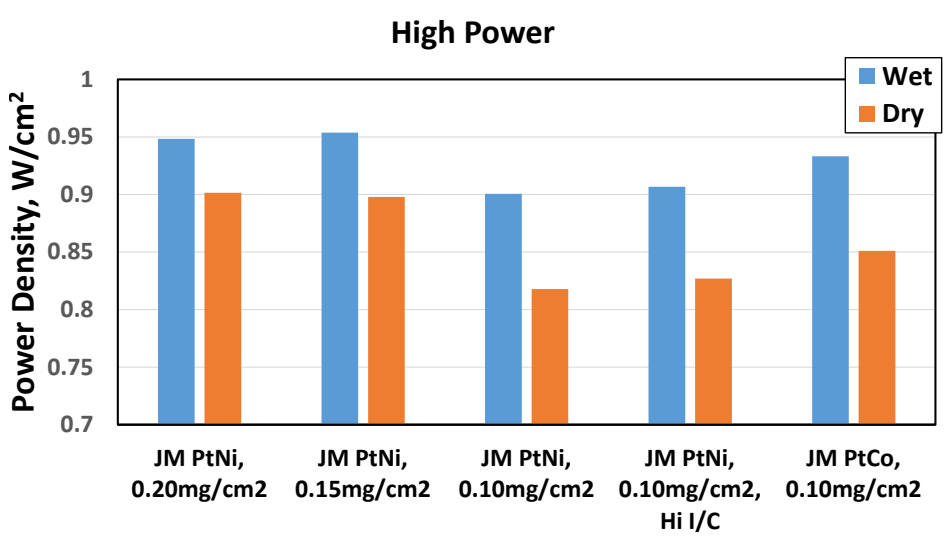



**FIGURE 4.** Full-active-area stack high-power performance of the dealloyed PtNi$_3$ and PtCo$_3$ catalysts under Fuel Cell Tech Team recommended conditions.

at this higher pressure in the near future. In addition, using a relatively high anode loading (0.05 $mg_{Pt}/cm^2$), we currently achieved a PGM total content of 0.16 $g_{PGM}/kW$ (Table 1). If we reduced the anode loading to 0.025 $mg_{Pt}/cm^2$, we would approach the DOE target of 0.125 $g_{PGM}/kW_{rated}$.

## CONCLUSIONS AND FUTURE DIRECTIONS

- Developed and used XAFS techniques to characterize Pt shell and subsurface metals in a fuel cell-relevant environment. Identified factors important in designing a durable highly-active catalyst.
- Demonstrated that dealloyed catalysts developed under this project might be sufficiently durable if we suppressed the upper-limit voltage.
- Successfully transferred and further developed catalyst technology from academia, to catalyst supplier, and to stack integrator in ~3 years. Confirmed improved performance of the newly developed catalyst in a full-active-area automotive stack.
- This project is ending in September FY 2014. However, some future activities will be focused on:
  - Perform durability testing on full-active-area stack.
  - Develop catalyst with higher surface area.
  - Consult with Argonne National Laboratory-led DOE project ("Rationally Designed Catalyst Layers for PEMFC Performance Optimization") to improve the understanding on the effect of leached Ni on fuel cell performance.

## FY 2014 PUBLICATIONS/PRESENTATIONS

### Presentations and Published Abstracts

**1.** D.E. Ramaker, X-ray Absorption Spectroscopy, an in operando probe of reactions in fuel cells and batteries, 245th ACS meeting, April 7–11, 2013, New Orleans, LA.

**2.** Invited talk: "X-ray absorption spectroscopy: An in operando probe of electrode reactions in fuel cells and batteries" D.E. Ramaker 245th National Meeting and Exposition of the American Chemical Society, April 7–11, 2013, New Orleans, LA

**3.** "Preparation of Dealloyed Catalysts with Durably High Oxygen Reduction Activity", J.E. Owejan, E.L. Thompson, A. Kongkanand, Z. Lui, J. Ziegelbauer, F.T. Wagner, A. Martinez, S. Thorpe, W. Turner, R. O'Malley, L. Gan, S. Rudi, C. Cui, P. Strasser, C. Carlton, A. Han, Y. Shao-Horn, Q. Jia, S. Mukerjee, K. Caldwell, and D.E. Ramaker, National Electrochemical Society Meeting, May 12–16, 2013 Toronto, CN.

**4.** "Understanding the Durability and ORR Reactivity of Four Different De-alloyed PtNi Cathodic Catalysts" David E. Ramaker, Keegan Caldwell, Qingying Jia, Sanjeev Mukerjee, and Joseph M. Ziegelbauer, Presentation at 224th ECS meeting, San Francisco, CA, Oct. 27 – Nov. 1, 2013.

**5.** "What we learned and paths forward on dealloyed catalysts" Anusorn Kongkanand, Presentation to Deborah Myers team at Argonne National Lab, Oct. 16, 2013.

**6.** "Advanced Fuel Cell Catalyst Development for Automotive Application" Anusorn Kongkanand, at University of Akron, Jan. 23, 2014 (small section on dealloyed catalysts).

**7.** "Characterization of Dealloyed Catalysts in PEMFC" A. Kongkanand, R. Kukreja, T.E. Moylan, J. Ziegelbauer, A. Martinez, S. Thorpe, W. Turner, R. O'Malley, L. Gan, S. Rudi, C. Cui, P. Strasser, C. Carlton, A. Han, Y. Shao-Horn, Q. Jia, S. Mukerjee, K. Caldwell, and D.E. Ramaker, National Electrochemical Society Meeting, May 11–16, 2014 Orlando, FL.

**8.** "Are we there yet? Pt-alloy catalysts" A. Kongkanand, S. Kumaraguru, at the DOE Catalyst and Durability Working Groups, Washington, DC, Jun. 16, 2014 (small section on dealloyed catalysts).

### Publications

**1.** Q. Jia, D.E. Ramaker, J.M. Ziegelbauer, N. Ramaswamy, A. Halder, S. Mukerjee, Fundamental Aspects of ad-Metal Dissolution and Contamination in Low and Medium Temperature Fuel Cell Electrocatalysis: A Cu Based Case Study Using In Situ Electrochemical X-ray Absorption Spectroscopy, The Journal of Physical Chemistry C, 117 (2013) 4585-4596

**2.** Cui, C.; Ahmadi, M.; Behafarid, F.; Gan, L.; Neumann, M.; Heggen, M.; Cuenya, B. R.; Strasser, P.: Shape-selected bimetallic nanoparticle electrocatalysts: evolution of their atomic scale structure, chemical composition, and electrochemical reactivity under various chemical environments. Faraday Discuss. 2013, 162, 91-112.

**3.** L. Gan, S. Rudi, C. Cui, P. Strasser, Ni-Catalyzed Growth of Graphene Layers during Thermal Annealing: Implications for the Synthesis of Carbon-Supported Pt-Ni Fuel-Cell Catalysts. ChemCatChem, 2013, 5, 2691-2694.

**4.** D. Ramaker, K. Caldwell, Q. Jia, J. Ziegelbauer, S. Mukerjee, "Observed molecular adsorbates on Pt-bimetallic surfaces during electrocatalysis" Angew. Chem Int Ed.

**5.** Cui, C.; Gan, L.; Heggen, M.; Rudi, S.; Strasser, P.: Compositional segregation in shaped Pt alloy nanoparticles and their structural behaviour during electrocatalysis. Nat Mater 2013, 12, 765-771.

**6.** Lin Gan, Marc Heggen and Peter Strasser. Subsurface Enrichment of Highly Active Dealloyed Pt-Ni Catalyst Nanoparticles for Oxygen Reduction Reaction. ECS Trans. 2013 volume 50, issue 2, 1627-1631.

**7.** C. Cui, L. Gan, M., Neumann, M. Heggen, B. R. Cuenya, P. Strasser, J. Am. Chem. Soc. 2014, 136, 4813–4816.

**8.** A. Kongkanand, W. Gu, F.T. Wagner, Electrocatalyst Design in Proton Exchange Membrane Fuel Cells for Automotive Application, in: F. Tao, W. Schneider, P. Kamat (Eds.) Heterogeneous Catalysis at the Nanoscale for Energy Applications, Wiley-VCH, 2014. (one section on dealloyed catalyst)

**9.** Lin Gan, Chunhua Cui, Stefan Rudi, and Peter Strasser. Core-shell and nanoporous particle architectures and their effect on the

activity and stability of Pt ORR electrocatalysts. Topics in Catalysis 2014, 57, 236-244.

## REFERENCES

**1.** Koh, S. and P. Strasser, *Electrocatalysis on bimetallic surfaces: Modifying catalytic reactivity for oxygen reduction by voltammetric surface dealloying.* Journal of the American Chemical Society, 2007. **129**(42): p. 12624-12625.

**2.** Strasser, P., et al., *Lattice-strain control of the activity in dealloyed core-shell fuel cell catalysts.* Nature Chemistry, 2010. **2**(6): p. 454-460.