V.A.5 The Science and Engineering of Durable Ultra-Low PGM Catalysts

Fernando H. Garzon (Primary Contact),
Jose-Maria Sansiñena, Mahlon Wilson,
Jerzy Chlistunoff, Ivana Matanovic, Neil Henson,
and Eric L. Brosha
Los Alamos National Laboratory
MPA-11, MS. D429
Los Alamos, NM 87545
Phone: (505) 667-6643
Email: garzon@lanl.gov

DOE Manager
Nancy Garland
Phone: (202) 586-5673
Email: Nancy.Garland@ee.doe.gov

Subcontractors
- Yushan Yan, University of Delaware, Newark, DE
- Abhaya Datye and S. Michael Stewart, University of New Mexico, Albuquerque, NM
- Siyu Ye and David Harvey, Ballard Fuel Cells, Burnaby, BC, Canada

Project Start Date: October, 2009
Project End Date: March, 2014

Overall Objectives

- Development of durable, high mass activity platinum group metal (PGM) cathode catalysts enabling lower cost fuel cells
- Elucidation of the fundamental relationships between PGM catalyst shape, particle size and activity to help design better catalysts
- Optimization of the cathode electrode layer to maximize the performance of PGM catalysts—improving fuel cell performance and lowering cost
- Understanding the performance degradation mechanisms of high mass activity cathode catalysts—provide insights to better catalyst design
- Development and testing of fuel cells using ultra-low loading high activity PGM catalysts—validation of advanced concepts

Fiscal Year (FY) 2014 Objectives

- Optimization of Pt supported on pyrolyzed polypyrrole nanowire catalysts for fuel cell testing
- Quantification of Pt supported on pyrolyzed polypyrrole nanowire cathode fuel cell performance
- Optimization of ceria doping for high performance, low free radical generation cathode catalysts
- Demonstration of lifetime improvement of ceria nanoparticle stabilized fuel cells measured by accelerated stress testing

Technical Barriers

For fuel cells and fuel cell systems to be commercially viable, significant reduction in cost is required. Materials and manufacturing costs for stack components need to be reduced. Low-cost, high-performance catalysts enabling ultra-low precious metal loading, and lower cost, are required to make fuel cell stacks competitive. Polymer electrolyte membrane fuel cells, polybenzimidazole-type fuel cells, and phosphoric acid fuel cells suffer from the necessity of relatively high PGM loading.

- PGM catalysts are difficult to synthesize on high performance alternative corrosion resistant supports
- PGM area specific activity may decrease with decreasing particle size
- Durability may decrease with use of smaller catalyst particles that possess greater PGM surface area to mass ratios

The technical targets for catalyst loading are indicated in Table 1. These targets were formulated with the assumption that fuel cell durability and impurity tolerance would not be impacted by the decreased Pt loadings used in the fuel cells.

TABLE 1. Technical Targets

Characteristic	Units	2011 Status	Targets	
			2017	2020
PGM total content (both electrodes)	g/kW (rated)	0.19	0.125	0.125
PGM total loading	mg PGM/cm^2 electrode area	0.15	0.125	0.125

FY 2014 Accomplishments

- Accomplished large batch synthesis (>2 g) of novel nanowire PGM catalysts
- Completed ceria nanoparticle migration study using advanced photon source synchrotron X-ray microprobe
- Completed oxygen-free radical decomposition catalysis studies for Pr-, Gd- and Zr-doped ceria
- Completed accelerated stress testing of fuel cell membrane electrode assemblies (MEAs) incorporating ceria free-radical scavengers

- Completed characterization of LANL catalyst materials delivered to Ballard Fuel Cells for validation testing
- Performed fuel cell testing using novel nanowire PGM catalysts demonstrating 50-cm^2 single-cell performance with <<0.1 mg Pt/cm^2 that equals or exceeds conventional MEAs with 0.2 mg Pt/cm^2

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INTRODUCTION

Minimizing the quantity of PGMs used in polymer electrolyte membrane fuel cells is one of the remaining challenges for fuel cell commercialization. Tremendous progress has been achieved over the last two decades in decreasing the Pt loading required for efficient fuel cell performance. Unfortunately, the fluctuations in the price of Pt represent a substantial barrier to the economics of widespread fuel cell use. Durability and impurity tolerance are also challenges that are tightly coupled to fuel cell Pt electrode loading. Polymer electrolyte fuel cell membrane durability is limited by free radical attack generated from oxygen reduction processes. The creation of peroxide via two electron oxygen reduction and subsequent decomposition into hydroxyl and/or hydroperoxyl free radicals may be the major source of nonmetallic fuel cell component chemical degradation. The addition of Ce^{+3} by ion exchange has greatly improved the durability of polymer electrolyte fuel cells. The cerium cations decompose the free radical species at high rates, thus limiting membrane damage and carbon support oxidation. However our recent studies show the Ce ions are very mobile [1]. An alternative approach is the addition of cerium oxide nanoparticles as free radical scavengers. The surfaces of CeO_2 nanoparticles contain appreciable concentrations of Ce^{+3} and Ce^{+4} that may act as catalytic sites for free radical decomposition. However little is known about the effects of particle size and doping on the free radical scavenging rates, and the selectivity towards peroxide decomposition versus secondary free radical generation has not been previously studied. The mobility of cerium generated from the decomposition of the nanoparticles is also unknown. The results of our FY 2014 work are published in greater detail in the references [1-3] listed at the end of this report.

APPROACH

Our approach to new PGM catalyst design is multi-tiered**.** We are designing new low platinum loading catalysts on novel support materials to improve fuel cell performance. Novel shapes; nanoparticles, nanotubes and nanowires are being synthesized in a variety of sizes. We are using contemporary theoretical modeling and advanced computational methods to understand and engineer the new catalysts. We are also modeling and designing appropriate catalyst architectures to maximize the performance of our novel catalysts. Catalyst-support interactions and their effects on durability and mass activity are also investigated. New methods to reduce the free radical attack on fuel cell components, such as catalytic nanoparticle free radical scavengers, are being studied. We also study and test the performance of the catalysts in electrochemical cells, single-cell fuel cells and fuel cell stacks. The new catalysts are be extensively characterized before and after fuel cell operation. The synthesis and characterization of Pt catalysts on carbon nanowires derived from pyrolyzed polypyrrole were reported on last year. In FY 2014 we scaled up the production and delivered catalyst quantities sufficient for Ballard fuel cell testing. The testing results are summarized in our DOE-EERE-FCT FC010 Annual Merit Review presentation. The catalysts showed much superior performance to conventional materials at low loadings, ~0.05 mg Pt/cm^2 and low relative humidity (RH) (30%) conditions.

Ceria and doped ceria nanoparticles were synthesized using acetate solution precursors [2]. Cerium(III)acetate (Strem Chemicals) and Pr or Zr acetates were dissolved in deionized water acidified to obtain a solution of 0.1 M metal ions (Ce + *M*). To the mixture concentrated nitric acid (Fisher) was added until both the cerium and *M* acetates were dissolved. Once both metal acetates were dissolved, a 50 % ammonium hydroxide solution (Alfa Aesar) was added to the solution while it was manually agitated until the solution turned white and opaque. The dried samples were subsequently transferred to a ceramic boat and heated under air at between 200-800°C for 1 hour to achieve a range of particles sizes from 5 to 40 nm. Phase purity, crystal structure, lattice parameters and crystallite size were determined by powder X-ray diffraction measurements. Specific (normalized by Brunauer-Emmett-Teller gas adsorption surface area) hydrogen peroxide decomposition rates were determined by volumetric determination of catalytic oxygen production. To determine the peroxide decomposition to free radical production selectivity, a 6-carboxyfluoroscein dye coupled with ultraviolet visible spectroscopy was used. Fluorine ion emission rates were determined by fluorine ion specific electrode measurements (Orion). Inks were made by mixing a 2% Nafion© solution with a TKK platinum supported on carbon catalyst (47.9 wt% Pt). If pure or doped ceria (2% of the weight of platinum) were also added to the cathode inks, they were incorporated after catalyst mixing. Decals were made by painting catalyst inks onto polymer substrates. The loading of platinum as well as the platinum to cerium ratio was verified using X-ray fluorescence (XRF) spectroscopy; all cathode decal loadings were 0.23 mg Pt/cm^2 and the anode decal loading were 0.18 mg Pt/cm^2.

All MEAs were assembled using 50-cm^2 Dupont™ XL proton exchange membranes. To create un-stabilized MEAs,

the XL membranes were first boiled in NaOH. The washed membranes were partially dried at 80°C for 10 minutes, then hot pressed between the decals at 120 psi/cm^2 at 212°C for 5 minutes, then allowed to cool to room temperature in air. The pressed MEAs were then boiled in 1 M sulfuric acid to remove the cerium cations. The removal of the silica and cerium ions was confirmed by XRF and energy dispersive spectrometer measurements. Fuel cells were assembled using a SGL 25BC gas diffusion layer (SGL Group) with graphite current collectors.

Open circuit voltage testing at low RH is well known to accelerate membrane degradation. Cells were conditioned by running at 80°C and 100 % RH overnight. Beginning of life testing was carried out after conditioning at both 30°C and 100% RH, and 80°C and 30% RH. For beginning-of-life testing, the high frequency resistance, limiting current, power-density, and impedance spectroscopy were performed with hydrogen. The cells were allowed to operate under open circuit at 80°C, 30% RH, except when tested every 24 to 72 hours to assess cell degradation. A jacketed condenser was used to remove water vapor from the exhaust gases so that the fluorine emission rate of both the anode and cathode could be measured. The accelerated stress test was stopped when open circuit potential dropped beneath 0.7 V, at which point impedance spectroscopy and limiting current measurements were impossible, or the crossover current appeared ohmic, which was indicative of a gas crossover leak in the cell.

Unmodified Dupont™ XL membranes were used as received, containing both cerium cations and silica fibers, and were also subjected to stress testing to determine baseline behavior. Unlike the unstabilized membranes, the control XL membranes were not pretreated by boiling in sodium hydroxide or sulfuric acid; the as-received membranes were used to fabricate MEAs using ink decal transfer, and then conditioned and tested the in the same manner as the other cells. An FEI Quanta 400F scanning electron microscope (SEM) equipped with an energy dispersive spectrometer was used to acquire scanning electron microscope images of membranes after conditioning and stress testing. 5 KeV electrons were used, and both backscattered and secondary electrons images were recorded.

RESULTS

Figures 1 and 2 show the inverse selectivity versus reactivity for praseodymium, zirconium, and doped cerium oxide, respectively. On each plot, the performance of cerium oxide is plotted in red for comparison. An ideal catalyst would be one that maximizes reactivity while minimizing inverse selectivity; the particle size that gives the fastest peroxide decomposition rate while producing the least free radicals.

Un-doped cerium oxide exhibits interesting trends in specific activity and inverse selectivity. The red markers representing the pure ceria samples, clearly show a trend of

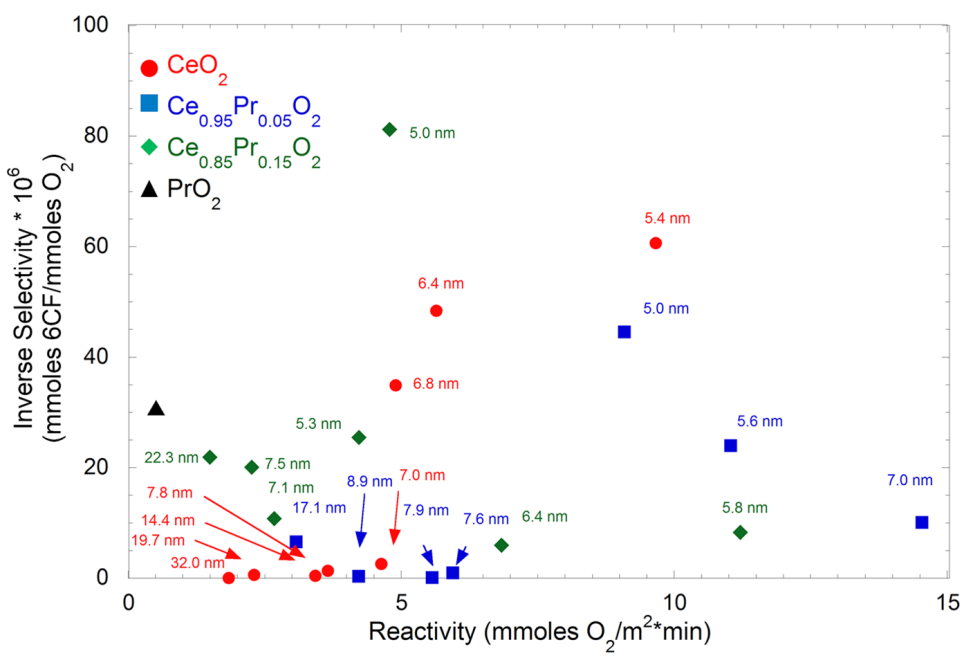

FIGURE 1. Inverse selectivity versus activity for peroxide decomposition by different particle sizes of cerium oxide (circle), $Ce_{0.95}Pr_{0.05}O_2$ (square), $Ce_{0.85}Pr_{0.15}O_2$ (diamond), and bulk PrO_2 (triangle). Particle sizes for the different doped and undoped cerium oxides are listed beside the data points [2].

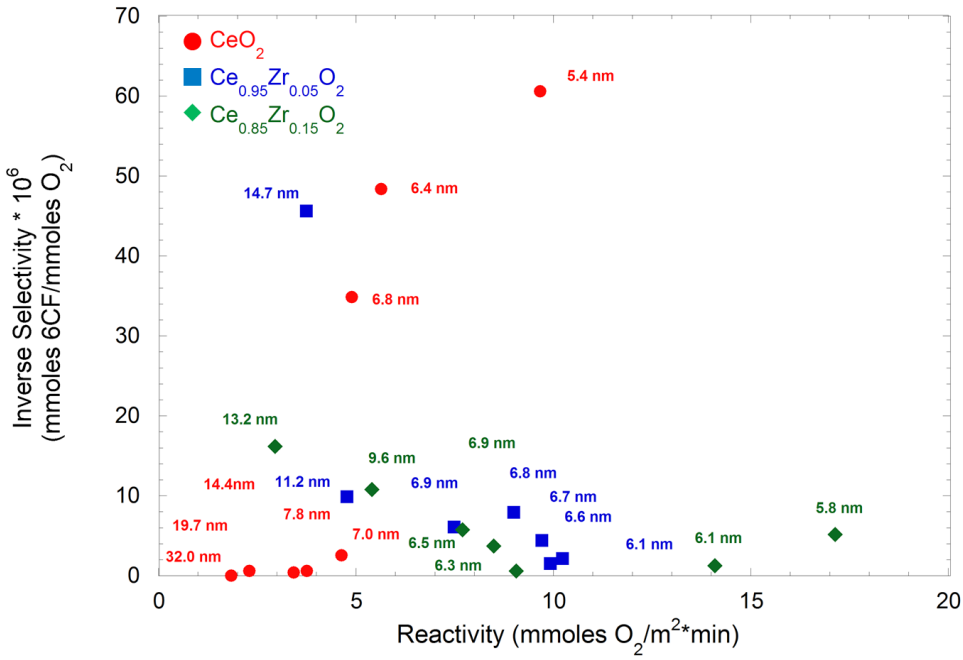

FIGURE 2. Inverse selectivity versus activity for peroxide decomposition by different particle sizes of cerium oxide (circle), $Ce_{0.95}Zr_{0.05}O_2$ (square), and $Ce_{0.85}Zr_{0.15}O_2$ (diamond). Particle sizes for the different doped and undoped cerium oxides are listed beside the data points [2].

increasing area specific activity with decreasing particle size, however the free radical production rate increases for the smaller ~8 to 5 nm particle size range. The largest particle sizes produce no measurable free radicals, however it is desirable for fuel cell performance to minimize the volume of MEA components that do not contribute to multiphase transport.

As compared to pure cerium oxide, when praseodymium is incorporated into the nanoparticle at 5 at%, the optimal reactivity is seen for circa 7 nm without any loss in selectivity, with smaller and larger crystallite sizes giving worse activity. Similarly for 15 at% Pr incorporation, the optimal crystallite size is closer to 6 nm with a loss of activity and selectivity seen above and below this crystallite size. For the 15 at% Pr particles, the activity and selectivity of the particles approaches that of pure praseodymium for the 22.3 nm particles, whereas the 5 at% Pr particles, while beginning to become less selective and active for larger crystallite sizes, do not reproduce the behavior of pure praseodymium at 17.1 nm. However, the 5 at% particles gave better performance over pure cerium oxide and 15 at% nanoparticles. For zirconium doping, unlike praseodymium, there is no loss in activity and selectivity with decreasing crystallite size as seen in Figure 2. In fact, decreasing particle size and increasing zirconia content improve both activity and selectivity in these nanoparticles, and suggests that any cerium-zirconium nanoparticles beneath 7 nm would be useful for selectively decomposing hydrogen peroxide.

When compared to an un-stabilized membrane cell, large cerium oxide nanoparticles have stabilizing effects, which results in a lower loss in performance over time. Both medium and small cerium oxide nanoparticles also show some initial stabilization. However, ultimately they have detrimental effect on the lifetime of the fuel cells during accelerated stress testing, causing an increase in hydrogen cross over, fluorine emission, and exponential loss in open circuit voltage. As predicted from selectivity and activity performance, ~7.0 nm pure cerium oxide nanoparticles incorporated in the cathode catalyst layer impart the same stabilization for fuel cells as cerium cations dispersed in the membrane; Figures 3 and 4 illustrate this effect. However, this improvement is short lived. The loss in performance in attributed to the loss of cerium oxide due to dissolution, which increases for decreasing particle size [3]. After 350 hrs the cerium oxide particle sizes become smaller, perhaps changing the energetics of the cerium oxide oxidation states, so that the selectivity of the cerium oxide for free radical decomposition becomes too low and the peroxide decomposition on cerium oxide, generates an increasing amount of free radicals. A parallel study by the authors using spatially resolved XRF observed cerium migration in both membrane ion-exchanged and ceria nanoparticle stabilized fuel cells after accelerated stress testing in very short time periods [1]. While future work remains on the stabilization effects of zirconium doped cerium oxide nanoparticles in fuel cells, research focusing on the changes in selectivity and activity of doped nanoparticles for hydrogen peroxide

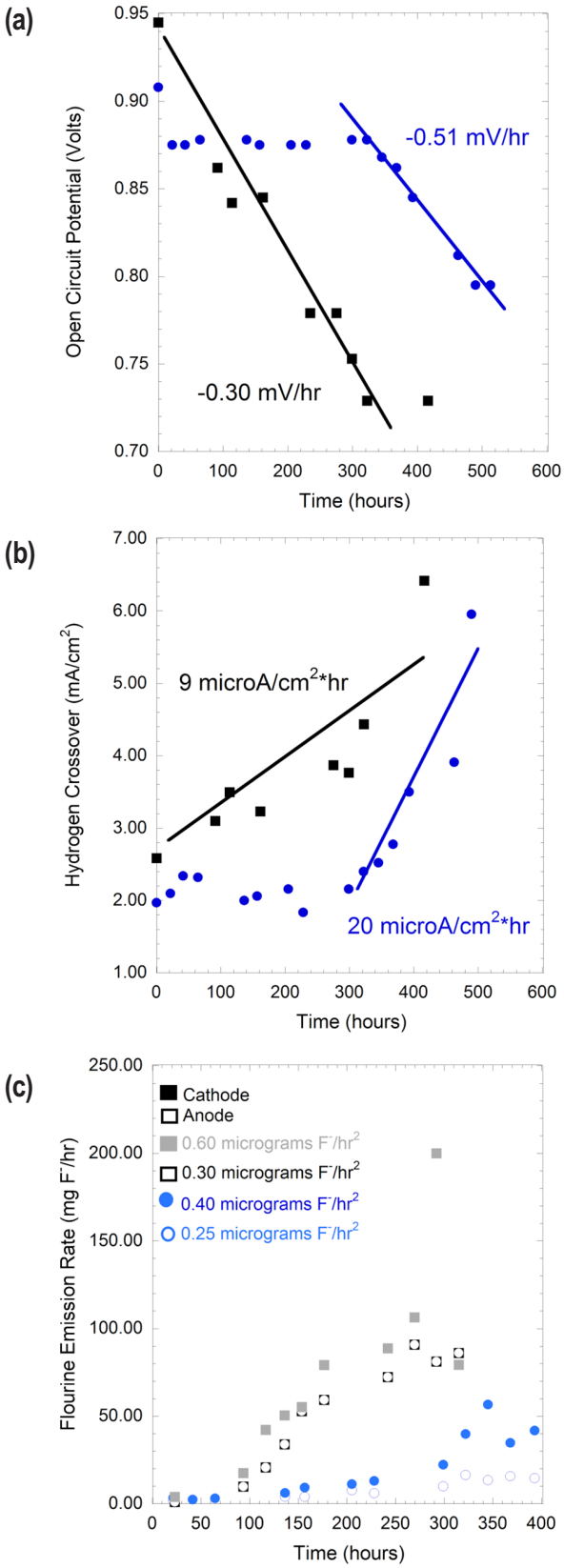

FIGURE 3. Un-stabilized membrane fuel cell open circuit voltage accelerated stress test with 7 nm ceria particles (circles) addition to cathode versus XL un-stabilized membrane fuel cell (squares) a) open circuit voltage, b) hydrogen crossover, c) fluorine ion emission [3].

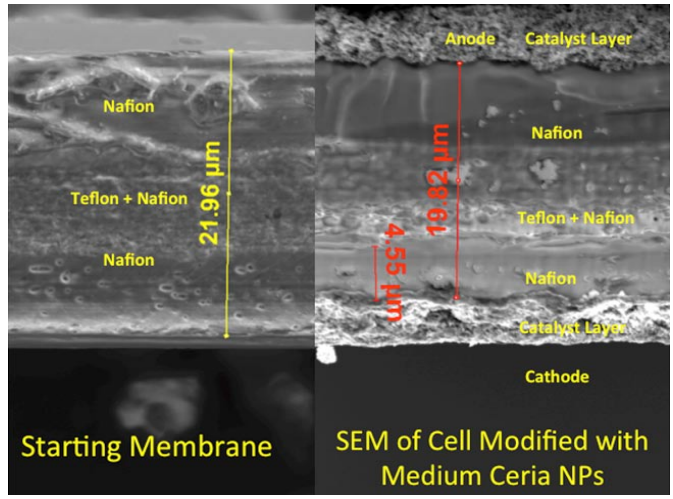

FIGURE 4. SEM images of fuel cell membrane electrode assembly before and after 500 hrs testing [4].

decomposition provides insight into their predicted behavior. Of the two dopants, zirconium cations are the only dopants that demonstrate ideal behavior for fuel cell dopants; increasing selectivity and activity with decreasing particles size, with no lower limit on particle size. In summary, the nanoparticle additives were shown to decompose peroxide and in some cases, improve ionomer durability. The catalytic activity and reaction pathway of cerium oxide towards hydrogen peroxide decomposition was strongly influenced by the crystallite size and the doping of cerium oxide nanoparticles. For both cerium oxide and doped cerium oxide, the size and doping of ceria nanoparticles is also shown to play an important role on their ability to improve membrane durability.

CONCLUSIONS AND FUTURE DIRECTIONS

- Carbon nanowires derived from the pyrolysis of polypyrrole exhibited excellent properties for Pt fuel cell cathode performance optimization
- MEAs incorporating carbon nanowires will benefit from further optimization strategies
- The doping of ceria nanoparticles improves the stability and selectivity of the free radical scavenging catalyst
- The optimal concentration of doped ceria nanoparticles for fuel cell lifetime improvements needs to be determined

FY 2014 PUBLICATIONS/PRESENTATIONS

Publications

1. Stewart, S.M.; Spernjak, D.; Borup, R.; Datye, A.; Garzon, F., Cerium Migration through Hydrogen Fuel Cells during Accelerated Stress Testing. *ECS Electrochemistry Letters* **2014,** *3* (4), F19-F22.

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3. Banham, D.; Ye, S.; Cheng, T.; Knights, S.; Stewart, S.M.; Wilson, M.; Garzon, F., Effect of CeOx Crystallite Size on the Chemical Stability of CeOx Nanoparticles. *Journal of The Electrochemical Society* **2014,** *161* (10), F1075-F1080.

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5. Matanovic, I.; Kent, P.R.C.; Garzon, F.H.; Henson, N.J., Theoretical Study of the Structure, Stability and Oxygen Reduction Activity of Ultrathin Platinum Nanowires. *ECS Transactions* **2013,** *50* (2), 1385-1395.

6. Matanovic, I.; Kent, P.R.C.; Garzon, F.H.; Henson, N.J., Density Functional Study of the Structure, Stability and Oxygen Reduction Activity of Ultrathin Platinum Nanowires. *Journal of the Electrochemical Society* **2013,** *160* (6), F548-F553.

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8. Ogumi, Z.; Matsuoka, H.; Garzon, F.; Kim, H.; Wan, L.-J.; Tamao, K.; Nakamura, M., Electrochemistry 80th Anniversary Special Issue. *Electrochemistry* **2013,** *81* (3), 140-197.

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