

**NOMINATION FORM FOR INVENTOR OF THE YEAR — 2012**

**Instructions:** You may nominate as many people as you wish. Please provide one form for each nominee or joint nominee. Please submit two (2) copies of all papers, including this form, that you wish to be considered by the Awards Panel. A nominee: must have one or more issued U.S. patents (the patent(s) preferably should not be the subject of pending litigation); must be favorably disposed to the patent system; and must be respected by his or her professional peers. The Award is made in recognition of an inventor's lifetime contributions to modern society. The nominee should be prepared to attend the NYIPLA Annual Meeting to be held in May 2012, in New York City, where he, she or they will be honored by the NYIPLA.

1. Nominee(s): Dr. Radoslav Adzic (See Bio attached) (1st page)  
Address: Senior Chemist, Chemistry Dept., Brookhaven National Laboratory  
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2. Identify invention(s) forming the basis of the nomination:  
Nanocatalysts with reduced platinum loading  
(See, attached description of the invention at paragraphs 2-5 and 7)

3. List, by number and inventor, the United States Patent(s) with respect to the above invention(s):  
8 U.S. Patents issued, 12 U.S. Patent Applications pending, 2 International  
Applications (PCT) pending (See, paragraph 6 of attached submission)

4. Set forth any known litigation, interference, or other proceeding that involves or has involved the foregoing inventions or patents, and the result:  
None

5. Nominator: Alan M. Sack  
Address: Intellectual Property Attorney, Locke Lord LLP  
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Signature:  Date: December 15, 2011

**Please feel free to provide a summary of the nominee's contributions which form the basis of this nomination, and of any recognition of the nominee's contributions accorded by his or her peers.** Include any additional information you believe the Awards Panel will find helpful. Materials submitted may not be returned. Please forward the nomination materials no later than **Thursday, December 15, 2011** to **Jessica L. Copeland**, Hodgson Russ LLP, The Guaranty Building, 140 Pearl Street, Suite 100, Buffalo, NY 14202, Tel 1.716.848.1461, E-mail [jcopeland@hodgsonruss.com](mailto:jcopeland@hodgsonruss.com) or **Anna Erenburg**, Cadwalader, Wickersham & Taft LLP, One World Financial Center, New York, NY 10281, Tel 1.212.504.6526, E-mail [anna.erenburg@cw.com](mailto:anna.erenburg@cw.com).

## **Radoslav Adzic**

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### **Education:**

University of Belgrade: M.Sci. faculty of Technology 1965  
University of Belgrade: Dr. Sci. Chemistry 1974

### **Professional Employment:**

Institute of Electrochemistry, ICTM, 1965–1992 (Research Director 1978-1983; Director 1983–1992)  
Research Associate, Case Western Reserve University, 1971–1973  
Visiting Faculty, Case Western Reserve University, 6. -9. 1977; 6-9. 1983  
Visiting Professor, Case Western Reserve University, 1988–1990  
Center for Multidisciplinary Studies, U. Belgrade, Professor from, 1990, 1975–1992  
Brookhaven National Laboratory (BNL), Scientist, 1992; Chemist with Tenure, 2001  
BNL, Electrochemistry Group Leader, 2004; Senior Chemist, 2005.  
Stony Brook University, Adjunct Professor, 2006

### **Selected Professional Activities:**

Membership professional organizations: Serbian Chemical Society, The Electrochemical Society, International Society for Electrochemistry (ISE), American Chemical Society  
Organizer 13<sup>th</sup> Yugoslav Symposium on Electrochemistry, Dubrovnik, Yugoslavia, 1983  
Editorial Boards of: *J. Serbian Chem. Soc.*, 1984; *Electrocatalysis*; *J. Transactions SAEST*  
ISE., Co-Chair, Div. Fundamental Interfacial Electrochememistry, 1987–1989  
Co-organizer, Symposium on Oxygen Electrochemistry, Chicago, 1995  
The Electrochemical Society, Executive Committee, Phys. Electrochem. Division, 1995–1999  
Co-organizer, Symposium on Electrocatalysis, Québec City, 2005.  
Member Advisory Board: Energy Materials Center, Cornell U.

### **Honors and Awards:**

Annual Award of the City of Belgrade for Natural Sciences and Mathematics, 1983  
Correspondent Member of the Serbian Academy of Sciences and Arts, 1993  
Honorary Member of the Serbian Chemical Society 1996  
Medal of the Serbian Chemical Society on its 100<sup>th</sup> Anniversary, 1997  
Science and Technology Award, Brookhaven National Laboratory, 2005  
Fellow of The Electrochemical Society, 2005  
Inventor of the Year, Battelle Memorial Institute, 2005  
Energy Technology Award, The Electrochemical Society, 2006  
The SciAm50, 2007  
Department of Energy's Hydrogen Program R&D Award, 2008  
Top Five Discoveries of Brookhaven National Lab. 2010  
Inventor of the Year, Battelle Memorial Institute, 2011

### **Research Interests:**

Surface electrochemistry, electrocatalysis, direct energy conversion, fuel cells

**Publications:** 260 career total, 8 US patents issued

## **NOMINATION FOR INVENTOR OF THE YEAR – 2012**

### **Nominee: Dr. Radoslav Adzic**

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### **1. NOMINATOR**

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### **2. INVENTION(S) FORMING THE BASIS OF THE NOMINATION**

Nanocatalysts with reduced platinum loading

### **3. SUMMARY OF THE POTENTIAL IMPACT OF THE INVENTION(S)**

These newly patented nanocatalysts have the potential to make fuel cell vehicles practical by addressing critical durability and cost barriers. Fuel cells would be a mainstay of a hydrogen economy, and would be used in numerous applications. Fuel cells are already being used to advantage in forklift trucks, where they last longer than batteries. In addition to vehicle applications, they can supply power either connected to the grid or in a grid-independent generator, or they can supply portable power. Other applications include telecommunications and consumer electronics. This increased use of fuel cells would decrease pollution and global warming, as well as decrease U.S. dependence on foreign oil.

### **4. DESCRIPTION OF THE INVENTION(S)**

Dr. Radoslav Adzic and his team at Brookhaven National Laboratory (BNL) have developed nanostructured electrocatalysts that address critical needs of improved durability, lower cost, and higher activity for applications in hydrogen fuel cells. The catalysts are nanometer-scale core-shell particles with monolayers of platinum supported by metal, metal alloy, or nanostructured metal/non-noble metal cores. Proper choice of core material, dopant, and structure result in higher activity and dramatically increased durability of the catalyst compared to traditional platinum electrocatalysts. Because they contain only about one-tenth the platinum of conventional catalysts, these new nanocatalysts are also lower in cost. The advances in these catalysts substantially reduce the technical barriers to durable, economical fuel cells, particularly for

automotive applications that will enable clean hydrogen fuel cell transport alternatives. The BNL team has also developed advanced materials synthesis procedures to enable scale-up production of these well-defined nanostructured catalysts for practical applications in pilot-scale fuel cell testing.

Dr. Adzic and his colleagues designed the first platinum monolayer fuel-cell anode electrocatalyst, which consists of ruthenium nanoparticles with a few platinum islands of monoatomic thickness. (See Figure 1.) This electrocatalyst has long-term stability and the same catalytic activity as a standard, all-platinum electrocatalyst, which contains 10 times more platinum, and is therefore very expensive. This new electrocatalyst has the potential to reduce the cost and increase the efficiency of fuel cells in electric vehicles, among other applications.

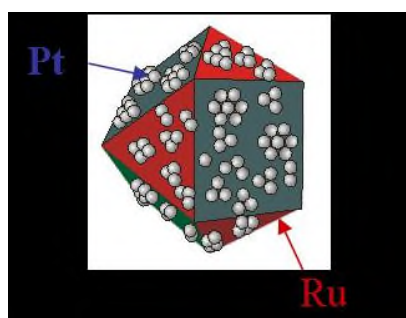


Figure 1: Platinum clusters on a ruthenium nanoparticle.

The initial anode catalyst research demonstrated that the monolayer core-shell design had promise for high activity, low platinum content, and good durability. In a very important second stage of research, Dr. Adzic and his team also developed several types of platinum monolayer cathode electrocatalysts for the difficult oxygen reduction reaction (ORR). The fuel cell cathode has required high platinum loading due to the challenges of ORR kinetics and poor durability of platinum to corrosion. Dr. Adzic and his team have demonstrated that the core-shell catalyst can substantially address these challenges. In basic science research, they demonstrated that high ORR activity could be obtained for platinum monolayers on properly chosen metal substrates, and that the activity could be even higher than that of pure platinum. A very promising example is a platinum monolayer on a palladium substrate. The team then developed synthesis procedures for nanostructured core-shell catalysts based on this concept; see Figures 2 and 3.

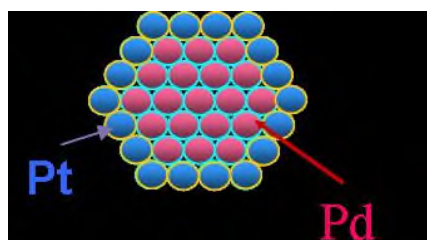


Figure 2: Schematic illustration of a nanoparticle having a platinum monolayer shell on a palladium core ( $Pt_{ML}/Pd$ ).

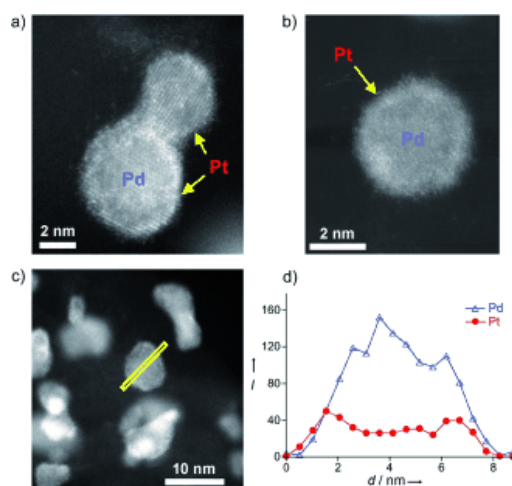


Figure 3: a–c) High-angle annular dark field (HAADF) scanning electron microscope (SEM) images of the  $\text{Pt}_{\text{ML}}/\text{Pd}/\text{C}$  electrocatalyst obtained in a 200mg scaled-up synthesis. d) Distribution of components in a  $\text{Pt}_{\text{ML}}/\text{Pd}/\text{C}$  nanoparticle in (c) obtained by a line-scan analysis using energy dispersive spectroscopy (EDS).

In related work, Dr. Adzic and his team demonstrated that platinum catalyst durability could be dramatically improved by doping with gold. This doping, which was done in a manner that formed small gold clusters on the platinum, improved the resistance to oxidative corrosion during voltage cycling, which is a challenge in automotive fuel cell applications due to stop-and-go driving cycles. (Zhang, *Science* 2007; U.S. Patent No. 7,704,919)

The innovations in platinum monolayer catalysts and the gold doping were recently combined to demonstrate both high activity with low platinum content and high durability. Platinum monolayer catalysts were formed on gold-doped palladium cores. These electrocatalysts have high activity and extremely low platinum content. (See Sasaki, *Angew. Chem. Int. Ed.* 2010.) This work is a practical demonstration that gold doping the palladium core accomplishes the same dramatic increase in durability for a core-shell catalyst as seen in the original case of gold clusters on solid platinum catalysts.

The team has incorporated the  $\text{Pt}/\text{Pd}/\text{C}$  electrocatalysts into a membrane electrode assembly (MEA) for use in a fuel cell to test the activity and durability of the electrocatalysts under operating conditions. Figure 4 shows the distribution of platinum and palladium in an MEA as fabricated (a) and after 100,000 potential cycles (b, c, d). The core-shell catalysts retain their structure during the test (c, d), while they move somewhat within the MEA (b).

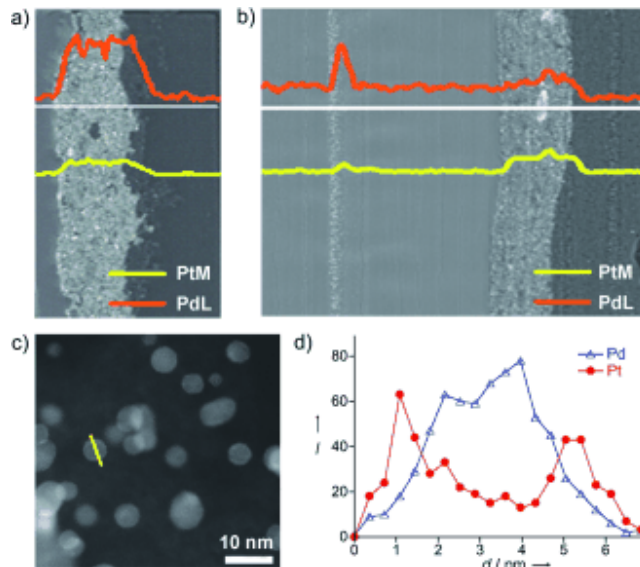


Figure 4: Cross-section of a membrane electrode assembly (MEA) incorporating the Pt<sub>ML</sub>/Pd/C electrocatalysts showing the concentration profiles for Pd and Pt before (a) and after 100 K potential cycles (b). c) HAADF image of Pt<sub>ML</sub>/Pd/C particles and d) the distribution of a Pt monolayer on a Pd core/shell nanoparticle, obtained by line analysis of EDS after the test.

The U.S. Department of Energy (DOE) target for platinum mass catalytic activity for the oxygen reduction reaction is 0.44 A/mg at 0.9 V. Figure 5 shows activity (a) and electrochemical surface area (b) measurements for the Pt/Pd/C catalysts incorporated into the MEA. Initial platinum mass activity is two to three times higher for the Pt/Pd/C compositions than for Pt/Ketjen or Pt/C catalysts. The loss in mass catalytic activity during cycling can be explained by a reduction in electrochemical surface area (SA) for all three types of catalyst.

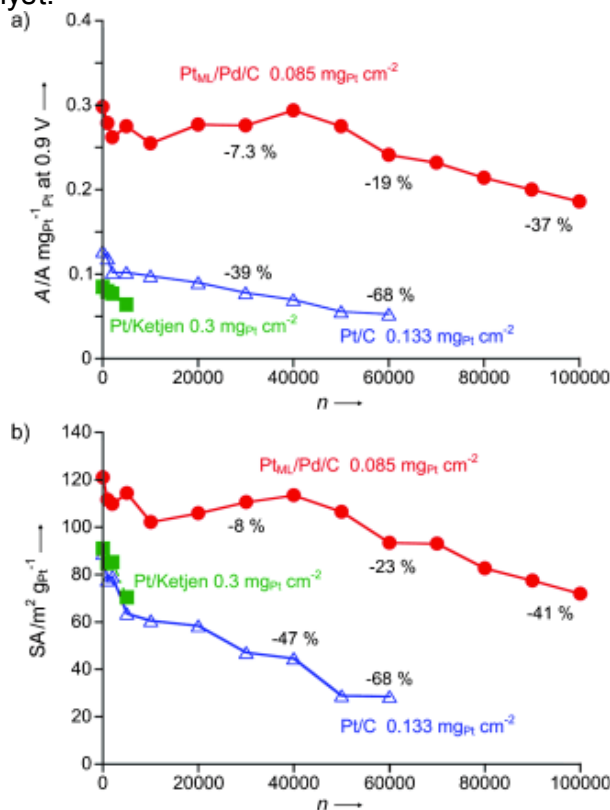


Figure 5: The Pt mass activity  $A$  for the oxygen-reduction reaction (ORR) as a function of the number of potential cycles  $n$  during fuel cell testing of the Pt<sub>ML</sub>/Pd/C electrocatalyst. The limits of the potential cycle were 0.7 and 0.9 V (RHE), with a 30-s dwell time at 80 °C. The results with Pt/C and Pt/Ketjen carbon

catalysts are shown for comparison. b) The electrochemical surface area (SA) of the three catalysts as a function of number of potential cycles.

Further improvement of this catalyst involved using a PdAu alloy as a core that increased catalyst stability. A uniform alloy causes a positive shift in the Pd oxidation, in accord with its stabilization potential, and reduced PdOH formation. This effect is evidenced from voltammetry and *in situ* extended X-ray absorption fine structure (EXAFS) studies, in particular confirming the changes in coordination number of Pd-O. Potential cycling did not entail any decrease in Pd, Pt, or Au content. The Pt mass activity of the Pt/Pd<sub>9</sub>Au<sub>1</sub>/C electrocatalyst in a test involving 200,000 potential cycles decreased about 30%. The DOE's target for 30,000 potential cycles under the same protocol is a loss of 40%. For comparison, the mass activity of a commercial Pt/C catalyst shows a terminal loss below 50,000 cycles.

The group has invented three different types of electrochemical cells for manufacturing the monolayer-coated nanoparticle catalysts. They have also scaled up production of the electrocatalysts to pre-commercial levels. Batches of tens of grams can be reliably produced with uniform properties, including catalytic activity and durability. (Sasaki, *Electrochim. Acta* 2010) This scale-up activity has proven that these materials will work well, not only in the laboratory, but also in the field.

Recently Dr. Adzic and his team have been studying the effects of lattice strain, surface coordination, and shape on the activity and durability of nanocatalysts. Engineering nanocatalyst structures to take advantage of these effects promises to yield further improvements in fuel cell catalysts for both oxygen reduction and fuel oxidation. For instance, after setting the stage with the initial design, the team under Dr. Adzic's direction has continued to develop the technology over the last three years. They have fabricated the monolayers on substrates of several materials and shapes, including high surface area carbon, transition metal oxides, nanorods, nanowires, and palladium tetrahedra, to name a few. (Xing 2010; Gong 2010)

To conclude, the new concepts have now been tested in fuel cells to demonstrate dramatic durability improvement, lowered platinum loading, and higher activity. (See Figure 6.) These results are regarded as very promising by the original equipment manufacturer (OEM) partners, and are subject to licensing discussions for automotive applications as the OEMs plan for introduction of fuel cell vehicles in limited production quantities in 2015.

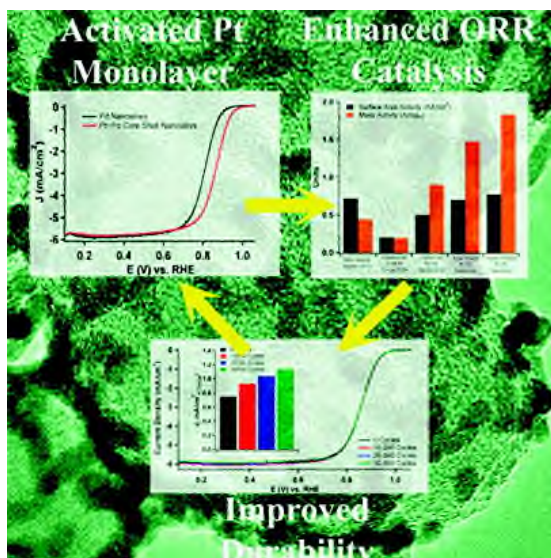


Figure 6: Pt<sub>ML</sub>/Pd catalysts offer improved activity and durability over pure Pt nanowires.

## **5. POTENTIAL FOR SOCIETAL AND/OR ECONOMIC BENEFIT**

The newly patented nanocatalysts will likely greatly increase the durability and reduce the cost, as well as potentially increase the efficiency of fuel cells in electric vehicles, as well as in stationary power applications. Fuel cells are expected to become a major source of clean energy. As a number of major automobile OEMs prepare to introduce fuel cell vehicles in limited quantities starting in 2015, Brookhaven Science Associates, LLC is currently in licensing discussions with catalyst producers who hope to supply automotive fuel cell needs and regard the BNL innovations as valuable elements for successful fuel cell catalyst design. Broadly, concerns about climate change and the need for renewable energy have made this research particularly relevant today.

The techniques used in these nanocatalysts for reducing platinum content can be applied in other areas of platinum-based catalysis. The catalysts are currently being tested in electrolyzers for the production of hydrogen. BNL envisions potential applications in other heterogeneous catalytic reactions as well.

## **6. US PATENTS, PATENT APPLICATIONS/STATUS and SIGNIFICANT PUBLISHED PAPERS AND ARTICLES**

*8 Issued U.S. Patents (6 since 2009):*

U.S. Patent No. 6,183,894 issued 2/6/2001

Inventor(s): Radoslav R. Adzic and Nebojsa S. Marinkovic

U.S. Patent No. 6,670,301 issued 12/30/2003

Inventor(s): Radoslav Adzic, Stanko Brankovic and Jia Wang

U.S. Patent No. 7,507,495 issued 3/24/2009 (foreign counterparts granted and pending)

Inventor(s): Jia X. Wang and Radoslav R. Adzic

U.S. Patent No. 7,632,601 issued 12/15/2009 (foreign counterparts pending)

Inventor(s): Radoslav Adzic and Tao Huang

U.S. Patent No. 7,691,780 issued 4/6/2010

Inventor(s): Radoslav Adzic, Junliang Zhang, Yibo Mo and Miomir Branko Vukmirovic

U.S. Patent No. 7,704,918 issued 4/27/10

Inventor(s): Radoslav Adzic, Miomir Vukmirovic and Kotaro Sasaki

U.S. Patent No. 7,704,919 issued 4/27/10 (foreign counterparts pending)

Inventor(s): Radoslav Adzic and Junliang Zhang

U.S. Patent No. 7,855,021 issued 12/21/2010

Inventor(s): Radoslav Adzic, Yibo Mo, Miomir Vukmirovic and Junliang Zhang

*12 U.S. Patent Applications pending, some with foreign counterparts (10 since 2009)*

U.S. Patent Application Serial No. 11/132,378 filed 5/19/2005 and published as U.S.

Patent Application Publication No. US 2006/0263675 on 11/18/2006

U.S. Patent Application Serial No. 11/853,368 filed 9/11/2007 and published as U.S.

Patent Application Publication No. US 2009/0068505 on 3/12/2009

U.S. Patent Application Serial No. 12/603,216 filed 10/21/2009 and published as U.S.

Patent Application Publication No. US 2010/0097742 on 4/22/2011

U.S. Patent Application Serial No. 12/581,430 filed 10/20/2009 and published as U.S.

Patent Application Publication No. US 2010/0099012 on 4/21/2011

U.S. Patent Application Serial No. 12/709,836 filed 2/22/2010 and published as U.S.

Patent Application Publication No. US 2010/0177462 on 7/15/2010

U.S. Patent Application Serial No. 12/708,226 filed 2/18/2010 and published as U.S.

Patent Application Publication No. US 2010/0197490 on 8/5/2010



U.S. Patent Application Serial No. 12/709,910 filed 2/22/2010 and published as U.S. Patent Application Publication No. US 2010/0216632 on 8/26/2010  
U.S. Patent Application Serial No. 13/033,764 filed 2/24/2011 and published as U.S. Patent Application Publication No. US 2011/0151356 on 6/23/2011  
U.S. Patent Application Serial No. 13/000,800 filed 12/22/2010  
U.S. Provisional Patent Application Serial No. 61/466,842 filed 3/23/2011  
U.S. Provisional Patent Application Serial No. 61/466,853 filed 3/23/2011  
U.S. Provisional Patent Application Serial No. 61/537,814 filed 9/22/2011

*2 PCT Patent Applications in the International Stage*

PCT/US2011/29773 filed 3/24/2011

PCT/US2011/43901 filed 7/13/2011

*Book Chapter:*

Kotaro Sasaki, Minhua Shao, and Radoslav Adzic, "Dissolution and Stabilization of Platinum in Oxygen Cathodes," in *Polymer Electrolyte Fuel Cell Durability*, Springer New York (2009)

*Major Journal Articles—Foundations:*

- S. R. Brankovic, J. X. Wang, and R. R. Adžić, "Metal monolayer deposition by replacement of metal adlayers on electrode surfaces," *Surf. Sci.*, **474**(1-3), pp. L173-L179 (2001)
- S. R. Brankovic, J. X. Wang, and R. R. Adžić, "Pt Submonolayers on Ru Nanoparticles: A Novel Low Pt Loading, High CO Tolerance Fuel Cell Electrocatalyst," *Electrochem. Solid-State Lett.*, **4**(12), pp. A217-A220 (2001)
- Brankovic, S. R., J. McBreen, and R. R. Adžić, "Spontaneous deposition of Pt on the Ru(0001) surface," *J. Electroanalytical Chemistry*, **503**(1-2), pp. 99-104 (2001)
- K. Sasaki, Y. Mo, J.X. Wang, M. Balasubramanian, F. Uribe, J. McBreen, R.R. Adzic, "Pt submonolayers on metal nanoparticles—novel electrocatalysts for H<sub>2</sub> oxidation and O<sub>2</sub> reduction," *Electrochimica Acta*, **48**(25-26), pp. 3841-3849 (2003)
- Wang, J. X., Brankovic, S.R., Zhu, Y., J.C. Hanson, and Adžić, R.R., "Kinetic Characterization of PtRu Fuel Cell Anode Catalysts Made by Spontaneous Pt Deposition on Ru Nanoparticles," *J. Electrochemical Society*, **150**(8), pp. A1108-A1117 (2003)
- K. Sasaki, J.X. Wang, M. Balasubramanian, J. McBreen, F. Uribe, R.R. Adzic, "Ultra-low platinum content fuel cell anode electrocatalyst with a long-term performance stability," *Electrochimica Acta*, **49**(22-23), pp. 3873-3877 (2004)
- J. Zhang, Y. Mo, M. B. Vukmirovic, R. Klie, K. Sasaki, and R. R. Adzic, "Platinum Monolayer Electrocatalysts for O<sub>2</sub> Reduction: Pt Monolayer on Pd (111) and on Carbon-supported Pd Nanoparticles," *J. Phys. Chem. B.*, **108**(30), pp. 10955-10964 (2004)
- Junliang Zhang, Miomir B. Vukmirovic, Kotaro Sasaki, Anand Udaykumar Nilekar, Manos Mavrikakis, and Radoslav R. Adzic, "Mixed-Metal Pt Monolayer Electrocatalysts for Enhanced Oxygen Reduction Kinetics," *J. Am. Chem. Soc.*, **127**(36), pp. 12480-12481 (2005)
- J. Zhang, F. H. B. Lima, M. H. Shao, K. Sasaki, J. X. Wang, J. Hanson, and R. R. Adzic, "Platinum Monolayer on Nonnoble Metal-Noble Metal Core-Shell Nanoparticle Electrocatalysts for O<sub>2</sub> Reduction," *J. Phys. Chem. B.*, **109**(48), pp. 22701-22704 (2005)

- M. H. Shao, T. Huang, P. Liu, J. Zhang, K. Sasaki, M. B. Vukmirovic, and R. R. Adzic, "Palladium Monolayer and Palladium Alloy Electrocatalysts for Oxygen Reduction," *Langmuir*, **22**(5), pp. 10409-10415 (2006)
- Min-Hua Shao, Kotaro Sasaki, and Radoslav R. Adzic, "Pd-Fe Nanoparticles as Electrocatalysts for Oxygen Reduction," *J. Am. Chem. Soc.*, **128**(11), pp. 3526-3527 (2006)
- J. Zhang, K. Sasaki, E. Sutter, R. R. Adzic, "Stabilization of Platinum Oxygen-Reduction Electrocatalysts Using Gold Clusters," *Science*, **315**(5809), pp. 220-222 (2007)
- B. Vukmirovic J. Zhang, K. Sasaki, F. Uribe, M. Mavrikakis, R. R. Adzic, "Platinum Monolayer Electrocatalysts for Oxygen Reduction," *Electrochim. Acta*, **52**, 2257 (2007)
- J. Zhang, K. Sasaki, E. Sutter, R. R. Adzic, "Stabilization of Platinum Oxygen Reduction Electrocatalysts Using Gold Clusters," *Science*, **315**, 220 (2007).
- R. R. Adzic, J. Zhang, K. Sasaki, M. B. Vukmirovic, M. Shao, J.X. Wang, A.U. Nilekar, Mavrikakis, J. A. Valerio, F. Uribe, "Platinum Monolayer Fuel Cell Electrocatalysts," *Topics in Catalysis*, **46**, 249-262 (2007).
- M. Shao, K. Sasaki, N. S. Marinkovic, L. Zhang, R. R. Adzic, "Synthesis and Characterization of Platinum Monolayer Oxygen-Reduction Electrocatalysts with Co-Pd Core-Shell Nanoparticle Supports," *Electrochem. Comm.*, **9**, 2848-2853 (2007)
- J. X. Wang, J. Zhang, R. R. Adzic, "Dual-Trap Kinetic Equation for the Oxygen Reduction Oxidation Reaction on Pt (111) in Acidic Media," *J. Phys. Chem. A*, **111**, 12702-12710 (2007)
- R. R. Adzic, J. Zhang, K. Sasaki, M. B. Vukmirovic, M. Shao, J. X. Wang, A. U. Nilekar, M. Mavrikakis, J. A. Valerio, F. Uribe, "Platinum Monolayer Fuel Cell Electrocatalysts," *Topics in Catalysis*, **46** (3-4), pp. 249-262 (2007)

*Major Journal Articles—Recent Work:*

- K. Sasaki, L. Zhang and R. R. Adzic, "Niobium oxide-supported platinum ultra-low amount electrocatalysts for oxygen reduction," *Phys. Chem. Chem. Phys.*, **10**, pp. 159-167 (2008)
- A. Kowal, M. Li, M. Shao, K. Sasaki, M.B. Vukmirovic, J. Zhang, N. S. Marinkovic, P. Liu, A.I. Frenkel, R. R. Adzic, "Ternary Pt/Rh/SnO<sub>2</sub> Electrocatalysts for Oxidizing Ethanol to CO<sub>2</sub>," *Nature Materials*, **8**, 325 (2009)
- J. X. Wang, H. Inada, L. Wu, Y. Zhu, Y. Choi, P. Liu, W-P. Zhou, and R. R. Adzic, "Oxygen reduction on well-defined core-shell nanoparticles: Size, facet, and Pt shell thickness effects," *J. Am. Chem. Soc.*, **131**, 17298 (2009)
- Sasaki, K., Naohara, H., Cai, Y., Choi, Y. M., Liu, P., Vukmirovic, M. B., Wang, J. X. and Adzic, R. R., "Core-Protected Platinum Monolayer Shell High-Stability Electrocatalysts for Fuel-Cell Cathodes," *Angewandte Chemie International Edition*, **49**, 8602–8607 (2010)
- Tanushree Ghosh, Miomir B. Vukmirovic, Francis J. DiSalvo, Radoslav R. Adzic, "Intermetallics as Support for Pt Monolayer O<sub>2</sub> Reduction Electrocatalysts: Potential for Significantly Improving Properties," *J. Am. Chem. Soc.*, **132**, 906 (2010)
- Kuanping Gong, Wei-Fu Chen, Kotaro Sasaki, Dong Su, Miomir B. Vukmirovic, Weiping Zhou, Elise L. Izzo, Carmen Perez-Acosta, Pussana Hirunsit, Perla B. Balbuena, Radoslav R. Adzic, "Platinum-monolayer electrocatalysts: Palladium interlayer on IrCo alloy core improves activity in oxygen-reduction reaction," *J. Electroanal. Chem.*, **649**, 232 (2010)
- M. Li, A. Kowal, K. Sasaki, N. Marinkovic, D. Su, E. Korach, P. Liu, R. R. Adzic, "Ethanol oxidation on the ternary Pt-Rh-SnO<sub>2</sub>/C electrocatalysts with varied Pt:Rh:Sn ratios," *Electrochimica Acta*, **55**, 4331 (2010)

- Zhou, W.-P.; Sasaki, K.; Su, D.; Zhu, Y.; Wang, J. X.; Adzic, R. R., "Gram-Scale-Synthesized Pd<sub>2</sub>Co-Supported Pt Monolayer Electrocatalysts for Oxygen Reduction Reaction," *J. Phys. Chem. C*, **114**, 8950 (2010)
- K. Sasaki, J.X. Wang, H. Naohara, N. Marinkovic, K. More, H. Inada, R.R. Adzic, "Recent advances in platinum monolayer electrocatalysts for oxygen reduction reaction: Scale-up synthesis, structure and activity of Pt shells on Pd cores," *Electrochimica Acta*, **55**, 2645 (2010)
- Koenigsmann, C.; Zhou, W.-P.; R. R. Adzic; Sutter, E.; Wong, S. S., "Size-dependent enhancement of electrocatalytic performance in relatively defect-free, processed ultrathin platinum nanowires," *Nano. Lett.*, **10**, 2806 (2010)
- Seth L. Knupp, Miomir B. Vukmirovic, Pradeep Haldar, Jeffrey A. Herron, Manos Mavrikakis, and Radoslav R. Adzic, "Platinum Monolayer Electrocatalysts for O<sub>2</sub> Reduction: Pt Monolayer on Carbon-Supported PdIr Nanoparticles," *Electrocatal.*, **1**, 213 (2010)
- Kotaro Sasaki, Hideo Naohara, Yun Cai, Yong Man Choi, Ping Liu, Miomir B. Vukmirovic, Jia X. Wang and Radoslav R. Adzic, "Core-Protected Platinum Monolayer Shell High-Stability Electrocatalysts for Fuel-Cell Cathodes," *Angew. Chem. Int. Ed.*, **49**, 8602 (2010)
- Yangchuan Xing, Yun Cai, Miomir Vukmirovic, Wei-Ping Zhou, Jia Wang, Radoslav Adzic, Hiroko Karan, "Enhancing Oxygen Reduction Reaction Activity via Pd-Au Alloy Sublayer Mediation of Pt Monolayer Electrocatalysts," *J. Phys. Chem. Lett.*, **1**, 3238 (2010)
- Kuanping Gong, Dong Su, and Radoslav R. Adzic, "Platinum-Monolayer Shell on AuNi<sub>0.5</sub>Fe Nanoparticle Core Electrocatalyst with High Activity and Stability for the Oxygen Reduction Reaction," *J. Am. Chem. Soc.*, **132**, 14364 (2010)
- Seung Woo Lee, Shuo Chen, Jin Suntivich, Kotaro Sasaki, Radoslav R. Adzic and Yang Shao-Horn, "Role of Surface Steps of Pt Nanoparticles on the Electrochemical Activity for Oxygen Reduction," *J. Phys. Chem. Lett.*, **1**, 1316 (2010)
- Kuanping Gong, Miomir B. Vukmirovic, Chao Ma, Yimei Zhu, Radoslav R. Adzic, "Synthesis and catalytic activity of Pt monolayer on Pd tetrahedral nanocrystals with CO-adsorption-induced removal of surfactants," *J. Electroanal. Chem.* (2011)
- Stoyan Bliznakov, Miomir Vukmirovic, Lijun Yang, Eli Sutter, and Radoslav R. Adzic, "Pt Monolayer on Electrodeposited Pd Nanostructures-Advanced Cathode Catalysts for PEM Fuel Cells," *ECS Trans.*, **41** (1), pp. 1055-1066 (2011)
- Christopher Koenigsmann, Alexander C. Santulli, Kuanping Gong, Miomir B. Vukmirovic, Wei-ping Zhou, Eli Sutter, Stanislaus S. Wong, and Radoslav R. Adzic, "Enhanced Electrocatalytic Performance of Processed, Ultrathin, Supported Pd-Pt Core-Shell Nanowire Catalysts for the Oxygen Reduction Reaction," *J. Am. Chem. Soc.*, **133** (25), pp. 9783-9795 (2011)
- Wei-Ping Zhou, Meng Li, Christopher Koenigsmann, Chao Ma, Stanislaus S. Wong, Radoslav R. Adzic, "Morphology-dependent activity of Pt nanocatalysts for ethanol oxidation in acidic media: Nanowires versus nanoparticles," *Electrochim. Acta*, (2011)
- Yun Cai, Chao Ma, Yimei Zhu, Jia X. Wang, and Radoslav R. Adzic, "Low-Coordination Sites in Oxygen-Reduction Electrocatalysis: Their Roles and Methods for Removal," *Langmuir*, **27** (13), 8540-8547 (2011)
- Jia X. Wang, Chao Ma, YongMan Choi, Dong Su, Yimei Zhu, Ping Liu, Rui Si, Miomir B. Vukmirovic, Yu Zhang, and Radoslav R. Adzic, "Kirkendall Effect and Lattice Contraction in Nanocatalysts: A New Strategy to Enhance Sustainable Activity," *J. Am. Chem. Soc.*, **133** (34), 13551-13557 (2011)

Videos or published descriptions of the invention(s)

<http://www.bnl.gov/bnlweb/pubaf/bulletin/2011/bb011411.pdf> (pp. 1-2)

<http://www.nsls.bnl.gov/newsroom/science/2009/02-387.htm>

[http://www.bnl.gov/bnlweb/pubaf/pr/PR\\_display.asp?prID=1134](http://www.bnl.gov/bnlweb/pubaf/pr/PR_display.asp?prID=1134)

[http://www.bnl.gov/bnlweb/pubaf/pr/PR\\_display.asp?prID=808](http://www.bnl.gov/bnlweb/pubaf/pr/PR_display.asp?prID=808)

[http://www.bnl.gov/bnlweb/pubaf/pr/PR\\_display.asp?prID=07-52](http://www.bnl.gov/bnlweb/pubaf/pr/PR_display.asp?prID=07-52)

## 7. BACKGROUND ON STATE OF THE ART IN THIS FIELD

Dr. Adzic's work has been pioneering and is widely cited. (See Figure 7.) He also collaborates broadly. In a very real sense, this work represents the state of the art in the field of electrocatalysts for fuel cell applications.

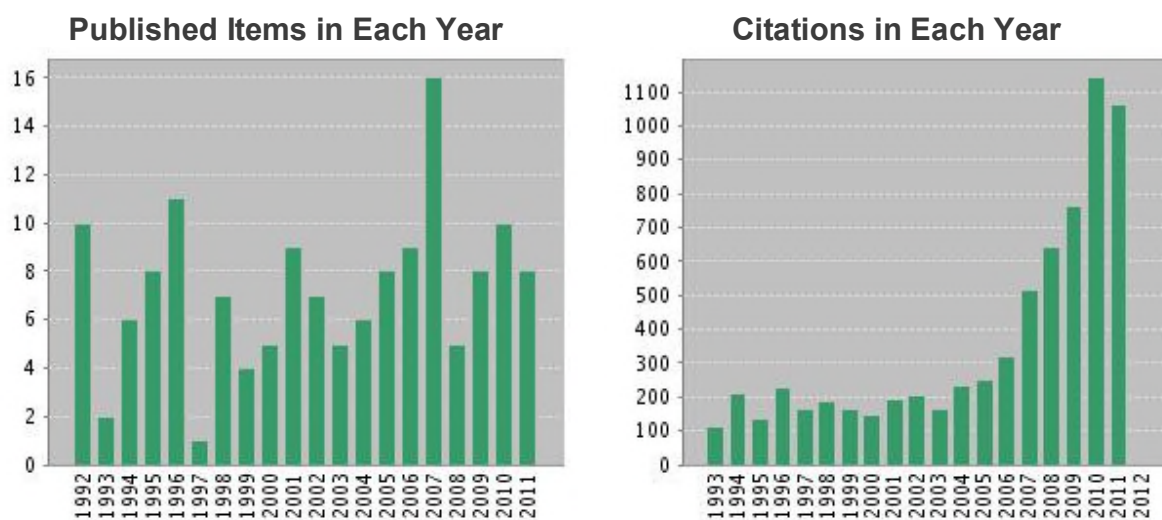


Figure 7: The two charts show Dr. Adzic's publishing history over the past twenty years, and his citation history over the same period. Dr. Adzic has over 260 publications, including over 20 pending applications and issued patents. According to the Web of Science<sup>SM</sup>, his work has been cited 7,613 times excluding citations by his own group.

Conventional Pt/C electrocatalysts require a loading of 0.133 mg of Pt per square centimeter. Commercial catalysts, Pt/Ketjen, have a loading of 0.3 mg<sub>Pt</sub>/cm<sup>2</sup>. Dr. Adzic's catalysts have a loading of 0.085 mg<sub>Pt</sub>/cm<sup>2</sup>. (See Figure 5.) At these loading levels, the initial mass catalytic activity of Pt/Ketjen catalysts is just under 0.1 A/mg<sub>Pt</sub> at 0.9 V, that of Pt/C is about 0.12 A/mg<sub>Pt</sub>, and that of the Pt<sub>ML</sub>/Pd/C catalysts is 0.3 A/mg<sub>Pt</sub>.

Pt/Ketjen experiences failure after only a few thousand cycles. Pt/C activity falls by 68% over 60,000 cycles. The Pt<sub>ML</sub>/Pd/C catalysts retain 59% of the initial activity for at least 100,000 cycles. DOE has established goals for activity and durability of fuel cell catalysts. The DOE's target for 30,000 potential cycles under a test protocol is a loss of 40%. As mentioned previously, the new catalysts developed by Dr. Adzic's group meet or exceed this target.

## 8. FUNDING

The basic science underlying the innovation was done at BNL under U.S. Department of Energy (DOE) Office of Science Basic Energy Sciences (BES) funding. The applied research that leveraged the science to create improved catalysts was also carried out by BNL researchers, under DOE Office of Energy Efficiency and Renewable Energy

(EERE) funding. The fuel cell testing and post-test characterization were carried out in collaboration with other national laboratories (LANL) and industry.