V.P.8 Fundamental Studies of Electrocatalysis for Low Temperature Fuel Cell Catalysts

Nenad M. Markovic (Primary Contact),
V.R. Stamenkovic and H. You

Argonne National Laboratory
9700 S. Cass Ave.
Argonne, IL 60439
Phone: (630) 252-5181; Fax: (630) 252-7777
E-mail: markovic@anl.gov

DOE Program Officer: Richard Kelley

Phone: (301) 903-6051
E-mail: Richard.Kelley@science.doe.gov

Objectives

- Fundamental atomic/molecular level understanding of metal-electrolyte interfaces required for efficient transformation of chemical energy of hydrogen, hydrocarbons and oxygen into electrical energy in fuel cell systems.

- Use and develop state-of-the art ex situ and in situ surface sensitive probes and spectroscopy, in combination with density functional theory calculations to determine the most active and stable sites for adsorption of reactants, reaction intermediates and spectator species.

- From experimental and computational studies on well-characterized single crystals, form the basis for synthesis of nanoscale surfaces to have optimal catalytic properties for the O-O, H-H, O-H, and C-H bond making and bond breaking events in environments of interest for fuel cell technologies.

Technical Barriers

- Fundamental understanding of metal-electrolyte interfaces will transform electrocatalysis from a largely phenomenological subject into a discipline that will be able to address many challenges, opportunities and research needs in the areas of basic science of materials for clean and efficient energy conversion.

- The novel concept of tailored nanoscale oxygen reduction catalysts will significantly reduce noble-metal loading necessary to make the fuel-cell technology economically competitive and sustainable.

- New materials will revolutionize catalyst performance in fuel cell systems, not only for the oxygen reduction reaction, but also for a wide range of reactions that are required for the implementation of a hydrogen-based economy, thereby leading the nation to more secure energy independence and a cleaner environment for future generations.

Abstract

The low rate of the oxygen reduction reaction in low/moderate temperature fuel cell systems is the main limitation for a wide application of this technology. We present here a science-based approach that will allow obtaining predictive understanding of the factors that determine the reactivity and stability of the ORR at electrified metal-solution interfaces at nanoscale dimensions. This approach is based on (i) fine tuning of the electronic properties of metal surface atoms; (ii) systematic alternation of the interfacial properties that constitute the entire electrochemical double layer structure; and (iii) molecular patterning of metal surfaces, aimed at the design of surfaces where the sites of poisonous spectator species are blocked, while providing the sufficient number of free metal sites needed to chemisorb the reactant and reaction intermediates. We demonstrate that depending on the geometric/electronic properties of the catalyst as well as supporting electrolytes (including the nature of anions and cations, temperature and pH) the activities of the ORR and oxidation of small organic molecules can range from 50 fold increase to 50 fold decrease. This behavior is discussed in the light of the role of covalent and non-covalent interactions in controlling spectators' coverage which determine the number of free active sites for high turnover rates of the electrochemical reactions.

Progress Report

(i) Fine tuning of the electronic properties of metal surface atoms; importance of covalent bonds.

(a) Catalytic activity.

Much of the art and science of catalyst development has been based on understanding chemisorption trends of oxygenated species, considering that the kinetics of both the oxygen reduction reaction and of the oxidation of small organic molecules is governed by the nature of *metal-oxygen covalent bonds*. This approach we used in the development of PtNi and PtCo catalysts for the ORR[1,2]. The rate of the ORR, expressed in terms of turn over frequency (TOF, defined as the number of electrons produced per active-site per second), on various of cathode materials (Figure 2) demonstrate that if grown
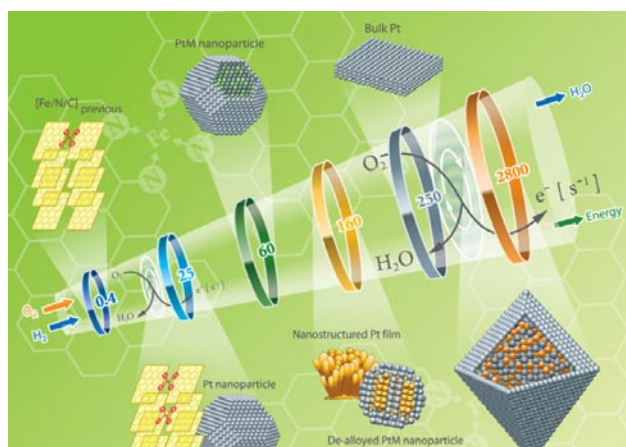
FIGURE 1. The rate of the catalytic electrochemical conversion of the ORR, expressed in terms of turn over frequency (TOF). Science 324 (2009) 47-48[2]

into "gigantic" 30 nm octahedra our Pt_3Ni nanoparticles with TOF≈2800 s^{-1} would be expected to yield 10-fold higher Pt mass activities than current Pt/C. The mechanism of improvement/deactivation occurs through the change of electronic properties (*d*-band center and work function) of the nanosegregated Pt-Ni surface alloys. By studying the ORR on $Pt_3Ni(1099)=20(111)$ x(100) and $Pt_3Ni(1077)=8(111)$x(100) stepped surfaces (Figure 2) we find that to preserve the TOF of $Pt_3Ni(111)$ minimum width of (111) facets should be 20 Pt atoms.

(b) Stability.

The design of cathode catalysts must be guided by two equally important fundamental principles: optimization of their catalytic properties as well as the ability of their surfaces to preserve nobility in hostile electrochemical environments. In our experiments,
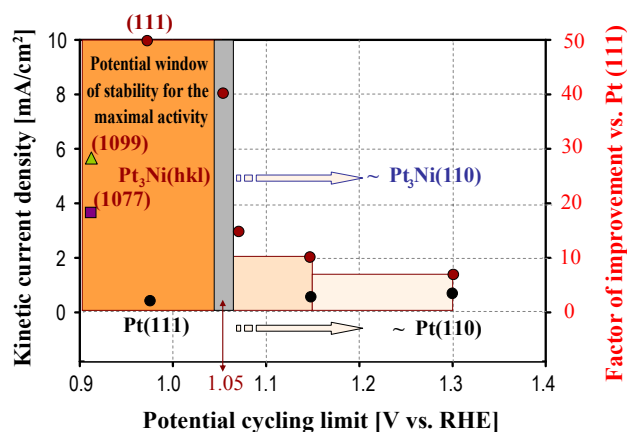
stability of bimetallic surfaces is monitored as the potential-induced relaxation and disordering of the surface structure, which is examined by utilizing a combination of surface x-ray scattering, scanning tunneling microscopy and electrochemical methods. Figure 2 summarizes electrochemical measurements, which show that $Pt_3Ni(111)$ and stepped surfaces are stable up to 1.05 V.

(ii) Fine tuning of the electrochemical double layer structure: importance of non-covalent bonds.

Classical models of metal electrode-electrolyte interfaces have generally focused on covalent interactions between adsorbates and the corresponding solid surfaces (see previous section). Recently, we have demonstrated that these traditional models for describing the catalytic activity of the electrochemical interfaces is not sufficient[3], and to understand electrocatalytic trends in the oxygen reduction reaction (ORR), the hydrogen oxidation reaction (HOR), and the oxidation of methanol on Pt surfaces in alkaline electrolytes, *noncovalent interactions*, such as hydrogen bonding, cation-water, and cation-OH_{ads} bonding, must also be taken into consideration. All these systems are generally applicable in alkaline fuel cells.

We used a combination of experimental and theoretical techniques to find that cation-specific noncovalent interactions between hydrated alkali-metal cations $M^+(H_2O)_x$ and adsorbed OH species increase in the same order as the hydration energies of the corresponding cations and likely result in an increase in the concentration of OH_{ad}-$M^+(H_2O)_x$ or $(H_2O)_{x-1}M^+ \cdots H_2O \cdots OH_{ad}$ clusters relative to the bulk (Figure 2). These trends are inversely proportional to the activities of the ORR, the HOR and the oxidation of methanol on Pt: $Cs^+ > K^+ > Na^+ \gg Li^+$.

(iii) Molecular patterning of metal surfaces.

We developed a new approach that can be used for the rational design of cathode catalysts for phosphoric
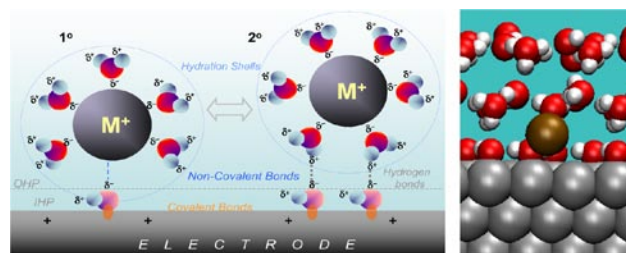

FIGURE 2. The rate of the ORR on $Pt_3Ni(111)$, $Pt_3Ni(1099)$ and $Pt_3Ni(1077)$ and factor of improvement vs. Pt(111). Potential window of stability is around 1.05 V, exemplified as the "grey zone.

FIGURE 3. Left: Models for noncovalent interactions between hydrated alkali-metal cations and adsorbed OH and the formation of OH_{ad}-$M^+(H_2O)_x$ or $(H_2O)_{x-1}M^+ \cdots H_2O \cdots OH_{ad}$ clusters. Right: DFT activity mapping. Nature Chemistry 1 (2009) 466-472[3]
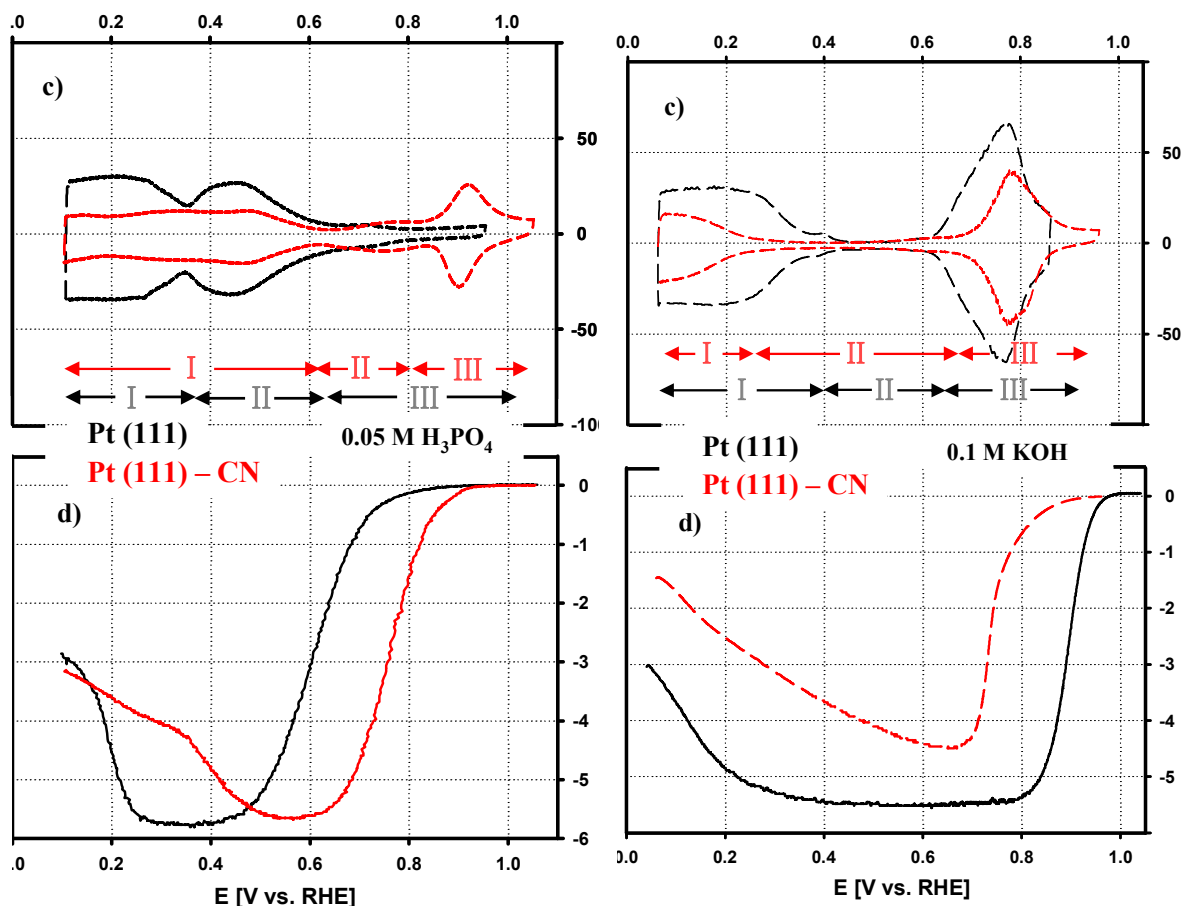
FIGURE 4. Cyclic voltammograms and polarization curves for the ORR on Pt(111) and Pt(111)CN$_{ad}$[4].

acid fuel cells. This approach is based on molecular patterning of metal surfaces with inert CN adsorbates[4]. We find that on Pt(111) modified by irreversibly adsorbed CN activities of the ORR can go from *25-fold increase* in the presence of sulfuric acid anions and *10-fold increase* in the presence of phosphoric acid anions (Figure 4 left), to *no effect* in the presence of weakly adsorbing perchloric acid anions. Interestingly *50-fold decrease* is observed in alkaline solutions (Figure 4 right). This enormous increase in activity suggests that the CN$_{ad}$ molecules can block the sites for adsorption of spectator phosphoric acid anions but still provide sufficient number of free Pt sites needed first to chemisorb the O$_2$ molecule and then to break the O-O bond (Figure 5b). Equally dramatic deactivation in alkaline solution is rationalized based on anticipated blocking effect of CN$_{ad}$-M$^+$(H$_2$O)$_x$ clusters for adsorption of O$_2$ molecule and reaction intermediates[4] (Figure 5c).

Future Directions

We will continue to *(i) create* novel states of catalytic materials by manipulating both covalent and non-covalent interactions at electrochemical interfaces;
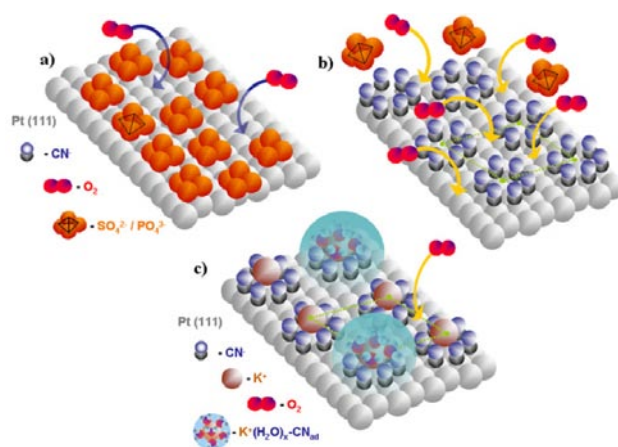

FIGURE 5. Schematic presentation of the availability of Pt surface atoms for adsorption of O$_2$ molecules on CN-free and CN-covered Pt(111)[4].

(ii) characterize, electronic properties of nanostructured interfaces by developing and using ex-situ and in-situ surface characterization techniques and theoretical

methods; *(iii) understand* fundamental principles that govern efficient bond making and bond breaking events at electrochemical interfaces; and *(iv) optimize* the active sites by an iterative process, guided by the fundamental understanding of electrochemical interfaces.

References

1. V. Stamenkovic, B. Fowler, B.S. Mun, G. Wang, P.N. Ross, C. Lucas, and N.M. Markovic, *Science.*, **315** (2007) 493-497.

2. H. Gasteiger and N.M.markovic, *Science,* **324** (2009) 48-49.

3. D. Strmcnik, K. Kodama, D. van der Vliet, J. Greeley, V. Stamenkovic and N.M. Markovic, *Nature Chemistry* **1** (2009) 466-472.

4. D. Strmcnik, M. Escudero, K. Kodama, V. Stamenkovic, A. Cuesta, and N.M. Markovic, *Nature Chemistry*, to be published (2010).

Publications (including patents) acknowledging the grant or contract

Referred Journals-since 2007

V. Stamenkovic, B. Fowler, B.S. Mun, G. Wang, P.N. Ross, C. Lucas, and N.M. Markovic, *Science.*, **315** (2007) 493-497.

1. V. Stamenkovic, B.S. Mun, M. Arenz, K.J.J.Mayrhofer, C. Lucas, G. Wang, P.N. Ross, and N.M. Markovic, *Nature Materials.*, **6** (2007) 241-247.

2. B. Blizanac, V. Stamenkovic, and N.M. Markovic, *Z.Phys.Chem.* . **221**(2007) 1379-1391.

3. D. Strmcnik, P. Rebec, M. Gaberscek, D. Tripkovic, V. Stamenkovic, C. Lucas. and N.M.Markovic, *J. Phys. Chem. C*, **111**(2007) 18672-18678.

4. K.J.J.Mayrhofer, D. Strmcnik, B.B. Blizanac, V. Stamenkovic, M. Arenz, and N.M. Markovic, *Electrochi. Acta* . **53**(2008) 3181-3188.

5. D. Tripkovic, D. Strmcnik, D. van der Vliet, V. Stamenkovic and N.M. Markovic, *Faraday Discuss*., **140** (2008) 25-40.

6. C. Lucas, M. Cormack, M. Gallagher, A. Brownrigg, P. Thompson, B. Fuler, Y. Grundet, J. Roy, V. Stamenkovic and N.M. Markovic, *Faraday Discuss*., **140** (2008) 41-58.

7. B. Fowler, C. Lucas, A. Omer, G. Wang, V. Stamenkovic and N.M. Markovic, *Electrochim.. Acta* . **53**(2008) 6076-6080.

8. D. Strmcnik, D. Tripkovic, D. van der Vliet, V. Stamenkovic and N.M. Markovic, *"Electrochemistry Comm..* **19** (2008) 1602-1605.

9. D. Strmcnik, D. Tripkovic, D. van der Vliet, K_C Chang, V. Komanecky, H. You, G. Karapetrov, J. Greeley, V. Stamenkovic and N.M. Markovic, *J. Am. Chem. Soc.*, **130** (2008) 15332-15339.

10. H. Gasteiger and N.M. Markovic, *Science,* **324** (2009) 48-49.

11. C. Lucas, P. Thomson , M. Cormack, A. Brownrigg, B. Fowler, D. Strmcnik, V. Stamenkovic, J. Greeley, A. Menzel, H. You, and N.M. Markovic, *J. Am. Chem. Soc.*, **131** (2009) 7654-7661.

12. D. Strmcnik, K. Kodama, D. van der Vliet, J. Greeley, V. Stamenkovic and N.M. Markovic, *Nature Chemistry* **1** (2009) 466-472.

13. V. Komanicky, H. Iddir, K.-C. Chang, A. Menzel, G. Karapetrov, D. Hennessy, P. Zapol, H. You, *J. Am. Chem. Soc.*, 131 (2009) 5732.

14. D. Strmcnik, N. Hodnik, S. B. Hocevar, D. van der Vliet, M. Zorko, V.R. Stamenkovic, B. Pihlar and N.M. Markovic,, *J. Phys. Chem. C*, **114**(2009) 2640-2644.

15. H. Iddir, V. Komanicky, P. Zapol and H. You, *Electrochimca Acta* (in press).

16. D. Strmcnik, M. Escudero, K. Kodama, V. Stamenkovic, A. Cuesta, and N.M. Markovic, *Nature Chemistry*, to be published (2010).

Book Chapters and Proceedings

1. V. Stamenkovic and N.M. Markovic, in Fuel Cell Catalysis: a Surface Science Approach; Editor: Marc T.M. Koper, Leiden University, The Netherlands,; Publisher: John Wiley and Sons, Inc., New Jersey, USA, *2009*.

2. V. Stamenkovic and N.M. Markovic, Model Systems in Catalysis: From Single Crystals and Size Selected Clusters, Editor: Robert M. Rioux, Harvard University, USA,; Publisher: Elsevier Science, Amsterdam, The Netherlands, *2009*.

3. V. Stamenkovic and N.M. Markovic, Handbook of Fuel Cell Volume 5,; Editor: W. Vielstich, H.A. Gasteiger, H. Yokokawa, Publisher: John Wiley and Sons Lim., Chichester, United Kingdom, *2009*.

4. D.Strmcnik, D.vanderVliet, C.Lucas, G.Karapetrov, N.M.Markovic and V.Stamenkovic,*"Fine Tuning of Activity for Nanoscale Catalysts"*Proceedings of the 9th International Symposium on Electrode Processes, Editor: P.Strasser, October 2008, 214th ECS Meeting Honolulu, Hawaii.