PHYSICAL CHEMISTRY 2012

11th International Conference
on Fundamental and Applied Aspects of
Physical Chemistry

Under the auspices of the
University of Belgrade

Proceedings

The Conference is dedicated to
Professor Ivan Draganić

September 24-28, 2012
Belgrade, Serbia

CONTENTS

COMPUTATIONAL CHEMISTRY APPLIED TO PROBLEMS IN ELECTROCHEMISTRY – SELECTED EXAMPLES AND PERSPECTIVES

I. A. Pašti[a]*, D. D. Vasić[b], N. M. Gavrilov[a], S. V. Mentus[a,c]

[a] *University of Belgrade, Faculty of Physical Chemistry, Studentski trg 12-16, 11158 Belgrade, Serbia*
[b] *University of Belgrade, Vinča Institute of Nuclear Sciences, Laboratory for Physical Chemistry, Mike Petrovića Alasa 12, 11000 Vinča, Serbia*
[c] *Serbian Academy of Science and Arts, Knez Mihajlova 35, 11000 Belgrade, Serbia*
* e-mail: igor@ffh.bg.ac.rs

Abstract

Computational approach in electrochemistry, being complementary to the experimental one, provides important information regarding the electrode processes on atomic level. In this contribution, applicability of computational approach to the problems related to electrocatalysis at different levels of complexity is demonstrated Starting with simple problem of modification of Pd(111) surface with other metal atoms, the data regarding electronic structure and periodic trends upon surface functionalization with p-elements have been offered. Next, Cl adsorption on Pd_3M alloys (M = Fe, Co, Ni, Pd, Rh) and Pd monolayers over (111) surfaces of coinage metals has been analyzed. Besides strong correlation of adsorptive properties and electronic structure, structural changes invoked by Cl adsorption are predicted. Brief overview of mechanistic analysis of ORR on Pt(hkl) surfaces is provided, allowing identification of rate determining steps on different surfaces and reaction paths, finally resulting in simulation of stationary ORR currents. Possibilities and strategies of computational approach in rational design of new electrocatalytic materials are discussed.

Introduction

With the increasing demand for energy on a global level, electrochemistry is expected to play one of the crucial roles in following years. With special interest in energy conversion, research is directed towards i) accumulation of fundamental knowledge and ii) application of this knowledge for development of new highly efficient power sources. Development of new experimental techniques and instrumentations has been followed by significant advance of theoretical methods and computer power. This resulted in application of theoretical methods in surface science and electrochemical studies providing data on atomic level, being complementary to experimental results. Although computational approach is still limited to relatively simple systems and invokes certain degree of approximation, rather important data can be obtained quickly and easily with significant advantage over the experiment: system composition can be controlled to perfection. In

addition, time necessary for *in silico* experiment is usually much shorter compared to conventional experiment.

In this contribution we offer new results obtained using computational approach regarding different problems in electrocatalysis. These problems are listed with regard to their complexity. Starting with relatively simple problem of investigation of electronic structure modification upon functionalization of Pd(111) surface with selected p-elements, we proceed to the investigation of adsorption of Cl on Pd_3M alloys (M = Fe, Co, Ni, Pd, Rh) and Pd monolayers over (111) surfaces of coinage metals and subsequent processes. Then follows a mechanistic analysis of oxygen reduction reaction (ORR) on selected Pt(hkl) surfaces and full simulation of stationary ORR curves. Finally, we discuss the computational approach in rational design of new materials for electrocatalysis.

Methods

Presented results have been obtained using pwscf code of QUANTUM Espresso distribution [1]. Surfaces were modeled in semi-infinite manner using periodic boundary conditions in combination with plane wave basis sets. Convergence was achieved by adjusting kinetic energy and charge density cut-off values. First 2D Brillouin zone has been sampled by appropriate set of k points generated through the general Monckhorst-Pack scheme [2].

Results and Discussion

a) Surface functionalization and periodic trends

Surface functionalization presents an important concept in electrochemistry and electrocatalytic studies. Number of studies has been offered so far demonstrating the effects of surface modification with foreign atoms and molecules on electrocatalytic performance [3]. The most interesting cases here are underpotential deposition (UPD) of metals and formation of surface alloys on single crystal surfaces [4]. This offers the possibilities of investigation of electrocatalytic processes on the level of model systems. UPD of p-metals has been investigated for long time for the case of oxidation of lower alcohols and CO oxidation. Nevertheless, the understanding of all effects is not fully completed. This is due to an altered energetics of adsorption of reactive species and intermediates on modified surfaces invoked by alteration of electronic structure of the surface, changes in adsorbate-adsorbate interactions, changes of work function and so on. Computational approach can provide deep insight into all these quantities, providing data complementary to the ones obtained by electrochemical measurements. In addition, it enables investigation of vast number of systems, some of them being only hypothetical, which allows separation of important factors that govern electrocatalytic activity.

Here we present the results regarding functionalization of Pd(111) surface with selected p-elements. Results obtained indicate there is significant periodicity in these cases. Namely, Ga and In tend to segregate to bulk, while Ge, Sn, Pb, As,

Sb and Te tend to form surface alloys. Remaining atoms, S and Se, favor adsorption on Pd(111). Electronic structure of modified surfaces, described through the position of d-band center and band width, differs greatly (Fig. 1).
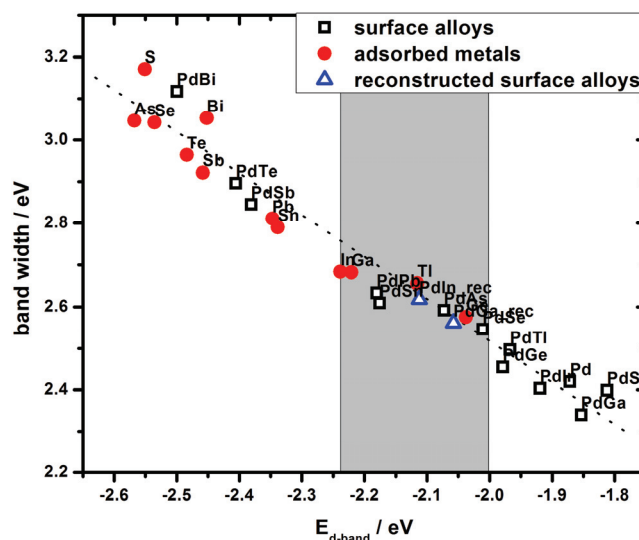

Figure 1. Position of d-band center ($E_{d\text{-band}}$) and band width of Pd(111) modified in different manners with p-elements. Shaded region indicates electronic structure desirable for efficient oxygen reduction.

Besides the data necessary for the understanding of electrocatalytic reactions on selected surfaces, the data regarding surface stability and electronic structure could be used for rational design of new electrocatalysts (see section d).

b) Adsorption of spectator species and stability of alloy surfaces

It has been widely accepted thus far that the adsorption of spectator species on electrocatalyst surfaces affects electrocatalytic activity either through the decrease of the number of available active sites or by invoking electronic effect. The well known example is OH specie in the case of oxygen reduction reaction (ORR). Nevertheless, other species can also affect electrocatalytic performance of given surface, such as chloride ion in the case of ORR investigated in $HClO_4$ solution [5]. Platinum and palladium alloys have been investigated for ORR performance as due to altered electronic structure with respect to clean host metals which hinders adsorption of OH and enhances ORR performance. However, important question arises regarding other spectator species and whether their presence can induce structural changes in surface layers. We investigated adsorption of Cl on Pd_3M alloys (M = Fe, Co, Ni, Pd, Rh) and Pd monolayers over (111) surfaces of coinage metals [6,7]. Obtained results display both altered electronic structure and adsorption properties, which are mutually dependent (Fig. 2).
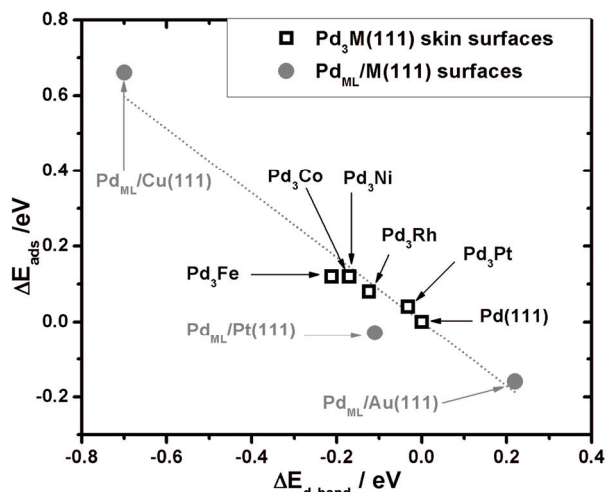
Figure 2. Correlation of Cl adsorption energies, ΔE_{ads}, to the surface electronic structure parameters, $\Delta E_{d\text{-}band}$ of Pd_3M alloys (M = Fe, Co, Ni, Pd, Rh) and Pd monolayers over (111) surfaces of coinage metals .

More important results arise from the analysis of stability of Pd_3M surfaces with adsorbed Cl. Namely, at elevated temperatures, these surface tend to form Pd skin in the first layer due to thermodynamic tendency of M to segregate to bulk. This provides thermodynamic stability of the surface in ORR media and high electrocatalytic activity. Investigation indicates that the presence of adsorbed Cl can induces structural changes of first two layers, lifting aforementioned reconstruction. This process is to be followed by M dissolution from the first layer, resulting in the loss of activity for ORR. This prediction is yet to be confirmed experimentally.

c) Mechanistic analysis of selected electrocatalytic reactions
Computational studies allow investigation of individual steps of complex electrode reactions. This provides a chance to analyze different mechanisms proposed for the same reaction, analyze single reaction on different metallic surfaces, or to investigate structural sensitivity on the surfaces of the same metal but with different crystallographic orientations. Here we analyzed ORR on low-index Pt surfaces. With complete free energy diagrams (an example is given in Fig. 3) constructed for different mechanisms and different surfaces it was possible to determine preferred reactions paths which differ mutually for the investigated surfaces and to indentify rate determining steps for ORR on different Pt surfaces.
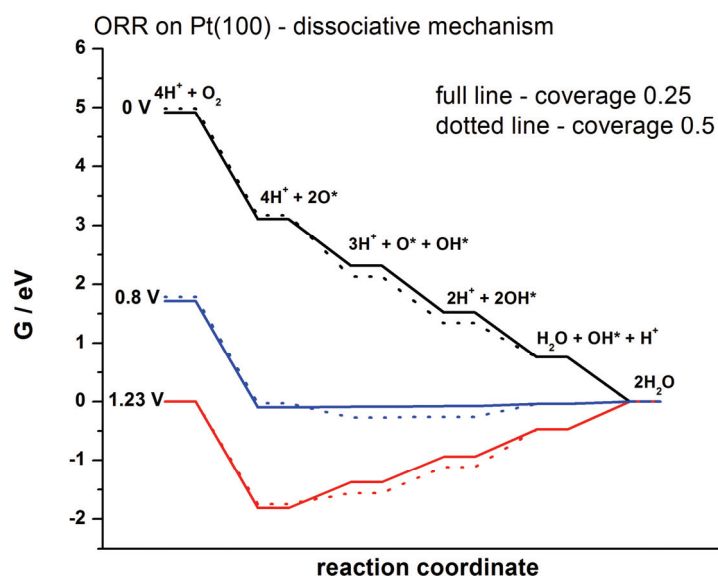
Figure 3. Free energy profiles for ORR on Pt(100) surface under the assumption of dissociative mechanism at three different electrode potentials. Counter electrode is reversible hydrogen electrode in equilibrium, pH = 0.
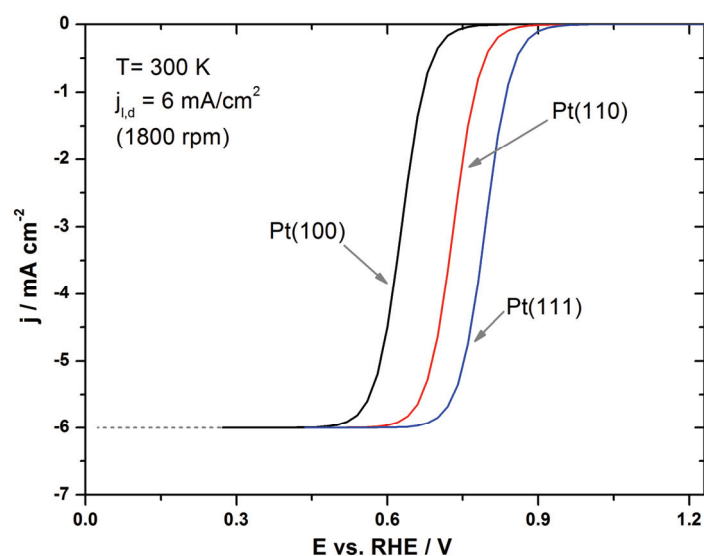

Figure 4. Simulated stationary I-E curves for ORR on rotating single crystal Pt disks with different crystallographic orientation in acidic solution (pH = 0) with the assumption that imposed diffusion limitation correspond to disk rotation rate of 1800 rpm, with electrolyte viscosity, O_2 diffusion coefficient and solubility of 0.1 M $HClO_4$ solution.

Once the reaction paths have been indentified on different single crystal surfaces it was possible to simulate ORR currents on these surfaces (Fig. 4) using the approach described by Nørskov et al. [8], achieving excellent agreement with experiments [9]. Obtained results provide an insight in structural sensitivity of selected surfaces for ORR and shed the light on its origins, but also provide important information when concerned with rational design of new electrocatalysts.

d) Rational design of new materials

Rational design of new catalysts and electrocatalysts present an ultimate goal for computational studies in electrochemistry. Once the set of candidates for new electrocatalysts is defined, two possible directions may follow. The first one is presented in section c. Interactions of all reactive intermediates with selected surfaces is investigated and the most active candidates are further considered. This is often time-consuming and impractical due to high dimensionality of the problem. The second possible direction is to identify electrocatalytic descriptor(s) and investigate limited number of parameters on large number of systems. As an example, hydrogen adsorption energy can be mentioned as a catalytic descriptor for hydrogen evolution reaction. The application of catalytic descriptor significantly reduces dimensionality of the problem and enables true power of computational approach to be realized. The problem can possible be even more simplified if adsorptive properties of studied surfaces are connected with the electronic structure (Fig. 2). In this way the problem of search for new electrocatalytic materials simplifies to a problem of the search of new materials with predefined electronic structure. Of course, when second approach is applied, strong interdependence between theory and experiment must exist, and these two have to be integrated in a functional entity providing each other mutual feed-back.

Conclusions

In this contribution we have demonstrated applicability of computational approach in problems related to electrocatalysis at different levels of complexity. Starting with simple problem of modification of Pd(111) surface we have provided the data on modification of electronic structure and periodic trends regarding surface functionalization. Then we analyzed Cl adsorption on Pd_3M alloys (M = Fe, Co, Ni, Pd, Rh) and Pd monolayers over (111) surfaces of coinage metals. Besides strong correlation of adsorptive properties and electronic structure we were able to predict structural changes invoked by Cl adsorption. We also provided brief overview of mechanistic analysis of ORR on Pt(hkl) surfaces which allows identification of rate determining steps on different surfaces and reaction paths, finally resulting in simulation of stationary ORR currents. We discussed possibilities and strategies of computational approach in rational design of new electrocatalytic materials, an ultimate goal of computational material science.

One may expect that following years will bring exponential development of computational methods in material science and electrochemistry, resulting in applicability of these methods in progressively more complicated systems.

Nevertheless, this progress must be followed by equivalent evolution of experimental techniques in order to provide mutual feed-back.

References

[1] P. Giannozzi, S. Baroni, N. Bonini et al., J. Phys. Condensed Matter, 2009, 21, 395502.
[2] H. J. Monkhorst, J. D. Pack, Phys. Rev. B, 1976, 13, 5188–5192.
[3] V. Climent, N. García-Aráez, J.M. Feliu, Clues for the Molecular-Level Understanding of Electrocatalysis on Single-Crystal Platinum Surfaces Modified by p-Block Adatoms in Fuel Cell Catalysis: A Surface Science Approach (Ed. M. T. M. Koper), John Wiley & Sons, 2009.
[4] I. Pašti, S. Mentus, Mater. Chem. Phys., 2009, 116, 94-101.
[5] M. Arenz, V. Stamenkovic, T. J. Schmidt, K. Wandelt, P. N. Ross, N. M. Markovic, Surf. Sci. 2003, 523, 199-209
[6] I. A. Pašti, S. V. Mentus, Electrochim. Acta, 2010, 55, 1995–2003.
[7] I. Pašti, N. Gavrilov, S. Mentus, Adv. Phys. Chem., 2011, ID 305634, 8 pp.
[8] J. K. Nørskov, J. Rossmeisl, A. Logadottir, L. Lindqvist, J. R. Kitchin, T. Bligaard, H. Jónsson, J. Phys. Chem. B, 2004, 108, 17886–17892
[9] N.M. Marković, P.N. Ross Jr., Surf. Sci. Rep. 2002, 45, 117-229.