

Announcing the Final Examination of Nagendra Dhakal for the Degree of Doctor of Philosophy in Physics

Date: Friday, April 7, 2017

Time: 01:00 – 3:00 P.M.

Room: PSB 146

Dissertation title: Computational Approach to Electrocatalysis

ABSTRACT

The main objective of this work is to understand the basis of the rational design of the electrocatalyst used in fuel cells for the conversion of chemical energy stored in hydrogen molecules into the electrical energy. It needs the understanding of the relationship among the compositions of the materials under consideration, their electronic structure and catalytic activities. The first principle computational approach is implemented to achieve the goal.

Our work is focused first on the issues in hydrogen oxidation reaction taking place in anode compartment of the cell. Next comes up with the issues with Oxygen Reduction Reaction taking place in cathode compartment. Finally, we focus on mechanisms underlying binding of small molecules on substrates.

Platinum perfectly catalyzes hydrogen oxidation reaction on the hydrogen fuel cell anodes. However, it has at least two drawbacks: a) it is too expensive; b) it has a low tolerance to CO poisoning. Pt-Ru bi-functional catalysts are more tolerant to CO, but they are still very expensive. In this work, we performed first-principle studies of stability reactivity of M/W (110) structures, where M = Pd, Ru, Au monolayers. All three systems are found to be stable: formation energy of MLs is significantly higher than cohesive energy of the M-elements. The calculated binding energies of H, H₂, OH, CO, and H₂O were used to obtain the reaction free energies. Analysis of the free energies suggests that Au-W bonding does not activate sufficiently Au monolayer, whereas Ru/W(110) is still too reactive for the CO removal. Meanwhile, Pd/W (110) is found to catalyze hydrogen oxidation and at the same time to be highly tolerant to the CO poisoning. The latter finding is explained by the fact that CO binds much weaker to Pd on W (110) than to Pt, while the OH binding energy is strong enough to ensure CO oxidation. The obtained results are traced to the electronic structure of the systems.

Oxygen Reduction Reaction (ORR) is the heart core reaction in fuel cells, Proton Exchange Membrane Fuel cell and DEMFC. However, the reaction is not so obvious and need suitable electrocatalyst. Pt or Pt-based catalysts are found to be the best catalyst so far. But, its cost and shortage make it not feasible economically. Moreover, lower onset potential (maximal electrode potential at which the reaction can proceed) of such catalysts is offering another limitation to fuel cell performance. Research has been conducted in many directions for lowering the cost by replacing the Pt with some other elements of lower cost or reducing the Pt-content in the material; and even more finding the material performing better than Pt. In this paper, we've tried to understand the ORR mechanism and look for the material that could be potential option to Pt. Our calculations suggest that for monolayer of Pd on Nb or Mo the onset potential is

the same as for Pt, while cost of these systems are much lower than that of Pt. Presence of water changes the reaction rate very minimum. Rational design method facilitates the research of selecting the appropriate catalyst and saves time and effort significantly. The result shows that the d-band center model is not accurate to describe the reactivity of the catalyst.

For decades, adsorbates' binding energy (E_B) has been used as an indicator of the adsorbate–substrate bond strength (E_{BF}). Thus – although one can compute accurately any E_B – models to gauge bond-strength are developed and applied to rationalize and anticipate E_B 's because that is a key aspect in the rational search for efficient catalysts. Yet bond-strength alone fails to predict E_B trends. Therefore, quantifying and understanding the difference between E_B and E_{BF} is essential to catalysts design. Indeed, the adsorbate-substrate bond formation perturbs the substrate's electronic charge density, which reduces E_B by the energy attached to such perturbation: E_{pert} . Here, with the example of carbon monoxide adsorption on metal-doped graphene, we show that E_{pert} may exceed 1 eV and render an unusual situation: although the E_B of CO to the Au-doped graphene indicates that binding does not happen, we find evidence of a strong bond between CO and the substrate. Thus, in this case, the large E_{pert} totally *disrupt the equivalency between E_{BF} and E_B* we also propose a method to compute E_{pert} that bypasses dealing with an excited electronic state of the system.

Outline of Studies:

Major: Physics

Educational Career:

M. S. University of Southern Mississippi, USA, 2009

B. S. Tribhuvan University, Nepal, 2003

Committee in Charge:

Dr. Sergey Stolbov (Chair)

Dr. Talat S. Rahman

Dr. Masahiro Ishigami,

Dr. Artem Masunov (External Committee Member)

Approved for distribution by Dr. Sergey Stolbov, Committee Chair, in March 31, 2017.