FINAL REPORT
Award Number DE-SC0003871
First principles modeling of the metal-electrolyte interface: A novel approach to the study of the electrochemical interface.

1. First Name: Maria

2. Last Name: Fernandez-Serra

3. Email Address: maria.fernandez-serra@stonybrook.edu

4. Number of Postdocs: 0

5. Number of Graduate Students: 1

6. Number of Undergraduate Students: 0

7. Abstract:

The research objective of this proposal is the computational modeling of the metal-electrolyte interface purely from first principles. The accurate calculation of the electrostatic potential at electrically biased metal-electrolyte interfaces is a current challenge for periodic “ab-initio” simulations. It is also an essential requisite for predicting the correspondence between the macroscopic voltage and the microscopic interfacial charge distribution in electrochemical fuel cells. This interfacial charge distribution is the result of the chemical bonding between solute and metal atoms, and therefore cannot be accurately calculated with the use of semi-empirical classical force fields. The project aims to study in detail the structure and dynamics of aqueous electrolytes at metallic interfaces
taking into account the effect of the electrode potential.

Another side of the project is to produce an accurate method to simulate the water/metal interface. While both experimental and theoretical surface scientists have made a lot of progress on the understanding and characterization of both atomistic structures and reactions at the solid/vacuum interface, the theoretical description of electrochemical interfaces is still lacking behind. A reason for this is that a complete and accurate first principles description of both the liquid and the metal interfaces is still computationally too expensive and complex, since their characteristics are governed by the explicit atomic and electronic structure built at the interface as a response to environmental conditions. This project will characterize in detail how different theoretical levels of modeling describer the metal/water interface. In particular the role of van der Waals interactions will be carefully analyzed and prescriptions to perform accurate simulations will be produced.

8. Accomplishments:

A. We have studied the structure and dynamics of liquid water in contact with Pd and Au (111) surfaces using ab initio molecular dynamics simulations with and without van der Waals interactions. Our results show that the structure of water at the interface of these two metals is very different. For Pd, we observe the formation of two different domains of preferred orientations, with opposite net interfacial dipoles. One of these two domains has a large degree of in-plane hexagonal order. For Au, a single domain exists with no in-plane order. For both metals, the structure of liquid water at the interface is strongly dependent on the use of dispersion forces. The origin of the structural domains observed in Pd is associated to the interplay between water/water and water/metal interactions. This effect is strongly dependent on the charge transfer that occurs at the interface and which is not modeled by current state of the art semi-empirical force fields.

B. We have finished the implementation of coupled ab initio molecular dynamics and non equilibrium greens functions calculations, by coupling the SIESTA electronic structure code with the SMEAGOL electronic transport code. Currently it is possible to simulate the electrochemical interface under realistic bias conditions. A manuscript is with the description od the method is currently under review and available at http://arxiv.org/abs/1606.09203#: