Theory for Surface Processes and Spectroscopies Focus Topic
Room B116 - Session TH2-TuA

Electronic Structure and Reactivity

Moderators: Paul S. Bagus, University of North Texas, **C. Richard Brundle**, CR Brundle and Associates

4:20pm **TH2-TuA-7 Interaction of Hydrogen Species with γ-Al_2O_3 Surfaces***, **Anne Chaka**, K. Khivantsev, T. Ahmed, B. Schmitt, J. Szanyi, L. Kovarik,* Pacific Northwest National Laboratory **INVITED**

The interaction of hydrogen species with active sites in transition aluminas such as γ-Al_2O_3 is responsible for performance of these materials in important applications such as heterogeneous catalysis and hydrogen permeation barriers. Understanding these active sites and their interactions with hydrogen species has been inhibited by a lack of a clear crystal structure, let alone surface terminations, for these aluminas. Theoretical studies have had to make assumptions regarding surface terminations and the structure of active sites, leading to ambiguous spectroscopic interpretation and uncertainty in reaction mechanisms. Recent experimental investigation of hydrothermally synthesized γ-Al_2O_3 rhombus-platelets utilizing state-of-the-art FTIR, high-field solid state ^{27}Al NMR, high resolution TEM, and CO/N_2 activation probes have clarified the nature of the active sites on (100) segments of highly reconstructed (110) faces and irrational surfaces. (Khivantsev *et al., Angew. Chem. Int. Ed*. 2021, 60, 17522–17530.) High resolution FTIR and *ab initio* thermodynamics and molecular dynamics based on density-functional theory are utilized to characterize the structure and reactivity of these sites as well as surface and bulk transport as a function of temperature and partial pressures of H_2, D_2, H_2O, and D_2O.

5:00pm **TH2-TuA-9 Elucidating the Effects of Oxygen Vacancies and Electric Fields on the Adsorption of Species on La-Based Perovskites***, **Ariel Whitten**, J. McEwen,* Washington State University*; E. Nikolla,* University of Michigan, Ann Arbor*; R. Denecke,* University of Leipzig, Germany

Perovskite materials can be used in electrochemical CO_2 reduction processes due to their higher stability than metal catalysts such as Nickel but are limited by their catalytic activity towards CO_2 reduction. For perovskites to be an alternative catalyst for this process, the surface chemistry of perovskites needs to be augmented by the introduction of active sites on the surface such as oxygen vacancies or by applying electric fields. We propose using La-based perovskites ($LaNiO_3$, $LaCoO_3$ and $LaFeO_3$) which are known to be highly active in CO_2 reduction to reduce CO_2 on the surface and we investigate these surfaces using both experimental and theoretical methods. While this proposal specifically focuses on the theoretical nature of the project, we use experimental methods to ground our theoretical calculations. Our first study explored experimental XPS spectra with theoretical calculations that predict the core level binding energy shifts of various adspecies on the surface (H, O, OH, H_2O and CO_2). Adsorption of species on the surface was favorable with considerable charge transfer occurring between the surface and the adspecies. This study is imperative for understanding the surface chemistry of our system before we augment it with oxygen vacancies and electric fields. We found that the higher energy peak for both $LaCoO_3$ and $LaNiO_3$ corresponds to water adsorption while the lower energy peak is due to lattice oxygen. The other species correspond to intermediate satellite peaks. Figure 1 shows the XPS spectra generated for $LaNiO_3$. Literature results and temperature dependent XPS spectra confirmed our results were accurate. We will also investigate the effects of coverage and oxygen vacancies on the XPS spectra for several of our surfaces ($LaNiO_3$ and $LaCoO_3$). Finally, we investigate the effects of oxygen vacancies and electric fields on the surface activity and adspecies adsorption. Our preliminary studies show that oxygen vacancies can increase the adsorption of CO_2 on the surface and electric fields change the plane wave averaged potential of the surface. We expect that the influence of electric fields will strengthen the adsorption of CO_2 due to the increase electrons stabilizing the surface. Further work will be completed to explore the effects of electric fields on adsorption strength of CO_2 as well as the formation of oxygen vacancies.

5:20pm **TH2-TuA-10 Theory of Magnetic Impurities in Oxides. Complex Problem, Pragmatic Solutions***, **Gianfranco Pacchioni**,* Università di Milano-Bicocca, Italy

Dopants in insulating and semiconducting oxides are of fundamental importance for the design of new materials and often lead to the presence of holes or trapped electrons in particular sites. The correct identification of these paramagnetic centers is crucial for understanding the optical, magnetic, photocatalytic and transport properties of oxides. The nature of magnetic impurities can be investigated by comparing DFT calculations using hybrid functionals with electron paramagnetic resonance, EPR, measurements. We will provide a historical perspective on the description of holes in the O 2p valence band of SiO_2 as a paradigmatic example of interaction between theory and experiment. Then we will discuss N-dopants in TiO_2, ZnO, SnO_2, ZrO_2 and MgO. A comparison with the EPR data allows one to evaluate the accuracy of the DFT calculations. At high N-dopant concentrations the presence of magnetic ordering in some of these materials has been suggested, implying the existence of magnetic interactions between the isolated defects. The use of hybrid functionals allows to adequately describe the nature of the isolated magnetic defects in the oxides, and shows that no magnetic ordering is expected for the dopant concentrations used in the experiments. Problems related to the theoretical treatment in DFT of magnetic impurities in insulating and semiconductor oxides are discussed.

5:40pm **TH2-TuA-11 Dynamics of Electrical Potential Distribution in Ionic Liquid Based Electrochemical Systems at Extended Time and Length Scales, Observed by Myriad of Experimental Techniques Awaits for Theoretical Attention***, **Pinar Aydogan Gokturk**,* Koc University, Turkey*; S. Suzer,* Bilkent University, Turkey

Ionic liquid systems exhibit rich dynamic responses on electrified surfaces. A long-standing question is why these materials display widely different time constants, ranging from nanoseconds to several hours, which can be attributed to the complex interplay of chemical and physical factors, including steric and molecular interactions. Recent theoretical approaches have concentrated in the faster temporal- and shorter lateral-variations. Although a collection of experimental evidences have been reported the presence of longer length and time-dependent processes, understanding of the molecular nature of them is still elusive. Our group use X-ray photoelectron spectroscopy to directly probe the local electrical potential variations, extracted from the binding energy shifts of the corresponding core levels, for obtaining lateral- and temporal-responses on electrified cells in non-invasive and chemically-resolved fashion[1]. Others have used electrochemical, microscopic, terahertz imaging, X-ray and Neutron scattering techniques. Use of electrochemical force microscopy have given new input into the dynamics of charge screening at the solid-aqueous interfaces by identifying multiple time constants and relatively larger length scales of up to 10 microns[2]. But again, such distances are still small to represent real-life electrochemical devices. Moreover, information not only at the interfaces but in the bulk electrolyte covering the entire electrochemical cell is needed. Recent theoretical progress has shed new light on the time dependency, particularly nonlinear response of thin double layer in a parallel plate configuration, where Bazant et al., using a modified version of the Poisson−Nernst−Planck (PNP) equation, had identified different time scales controlled by geometric and ionic diffusion properties of the chemical moieties within such devices[3]. Most of these approaches have been developed and tested for small electrical potentials and relatively dilute aqueous solutions, while extension to higher voltages and highly concentrated electrolytes, as in the case of ionic liquids, still remains a challenging task due to the high interaction energy and long-range Coulombic forces. We will review some of the recent experimental findings, including those from our own work, and the theoretical work mentioned above and highlight some of issues waiting for attention.

1.Aydogan Gokturk, P.; Suzer, S., J. Phys. Chem. C 2021, 125, 17, 9453–9460.

2.Collins, L.; Kilpatrick, J. I.; Kalinin, S. V.; Rodriguez, B. J., Rep. Prog. Phys. 2018, 81 (8), 086101.

3.Bazant, M. Z.; Thornton, K.; Ajdari, A., Phys. Rev. E 2004, 70 (2), 021506

6:00pm **TH2-TuA-12 Sub-eV Electron Inelastic Mean Free Path: A Second Inverted Trend ?***, **Hagai Cohen**,* The Weizmann Institute, Israel

The dependence on kinetic energy of the electron inelastic mean free path (IMFP) parameter has already been studied extensively, showing a drastic qualitative difference between the high-energy regime (above e.g. 100 eV) and the low-energy regime (below e.g. 40 eV). In fact, definitely opposite energy dependencies are exhibited by the two ‘arms’ of the corresponding λ(Ek) universal curve. Extension of these studies to very low energies, below e.g. 5 eV, is by far more challenging experimentally. Hence, only few works have addressed this challenge so far.

Here, a new technique is applied, resulting in an interesting observation. XPS-based experiments with nanometrically thin self-assembled monolayers (SAMs) systematically indicate on a second *inversion* in the derivative of energy dependence, appearing as a common general feature of the sub-eV regime. Using a simple theoretical model, these results are explained and further propose interesting applications for future studies of hot-electron interactions with dielectric layers.

Author Index

Bold page numbers indicate presenter