

Monday Afternoon, November 4, 2002

Electrochemistry and Fluid-Solid Interfaces

Room: C-104 - Session EC+SS-MoA

Liquid-Solid Interfaces & Nanoscale Electrochemistry

Moderator: S. Morin, York University

2:00pm **EC+SS-MoA1 Femtosecond Spectroscopy at the Metal/Liquid Interface**, S. Roke, M. Bonn, A.W. Kley, Leiden University, The Netherlands

Vibrational sum frequency generation spectroscopy is an ideal technique to study molecules at surfaces and at buried interfaces with a high degree of molecular specificity. The most powerful feature of this technique is its capability to monitor intramolecular vibrations of the first layer of molecules on the surface: it essentially allows one to look inside the molecules at the interface. The use of femtosecond laser pulses allows one to not only perform frequency domain measurements, but also time domain measurements. We have performed femtosecond time and frequency domain measurements on the acetonitrile/gold interface. Comparison of the time and frequency domain results showed that, although the two approaches are in principle equivalent they are sensitive to different physical aspects of the system. Time domain measurements are more clearly influenced by the inhomogeneity of adsorption sites, whereas frequency domain measurements are more subject to the homogeneous features of the spectral line broadening. To account for this we have extended existing models for calculating SFG spectra and free induction decay measurements. From the combination of the measurements and our model we have obtained information on the orientation and binding of acetonitrile to the gold surface and determined the nature and time scale of the decay of the vibrational polarization of the CH and CN stretch vibrations. The CN oscillators are distributed inhomogeneously across the surface and have a dephasing time of 1.65 ps. The CH stretch vibration however does not feel the inhomogeneity and dephases 2.5 times faster ($T_2 = 610$ fs), because the methyl groups are further away from the interface.

2:20pm **EC+SS-MoA2 Studies of the Interphase Region for Liquid Hexadecane Near a Au Surface**, A.C. Oliver, J.E. Houston, Sandia National Laboratories

In this presentation, we explore the formation and properties of a solid-like "interphase" region near Au surfaces immersed in liquid hexadecane using interfacial force microscopy (IFM). We measure variations of the normal and lateral friction forces, as well as the conductance behavior, as a function of the relative interfacial separation. We show that this interphase layer passivates the normally strong bonding between two Au surfaces even at high applied stresses. In addition, no conduction is seen for this normally insulating layer until appreciable stresses are applied. By placing a voltage between tip and sample, we determine the thickness of the organized film from the behavior of the electrostatic force as a function of relative separation up to film contact. We show that at room temperature the interphase-layer thickness is ~ 7 molecular diameters, which increases with larger bias voltages. In addition, the lateral force shows appreciable friction before film contact for the larger voltages, indicating that the field is causing a local film organization. Data taken as a function of temperature indicates a decrease in the film organization. We discuss the implication of these results in the general context of the interaction of surface in liquid environments. Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin company, for the DOE under Contract DE-AC04-94AL85000.

2:40pm **EC+SS-MoA3 Surface Forces at Electrified Interfaces**, J. Frechette, T.K. Vanderlick, Princeton University

Electrodes specifically designed for the surface forces apparatus were developed to study adhesion between mica and polycrystalline gold at different applied potentials. Pull-off forces were a strong function of applied potential and dominated by electrostatic interactions. Adhesion measurements increased six-fold in a 150 mV window around the potential of zero charge. We compared these measurements using DLVO and JKR (Johnson-Kendall-Roberts) theory in the case of dissimilarly charged surfaces. We also investigated the effect of potential dependent adsorption, such as pyridine on gold, on electrostatic forces and adhesion. We observed a stronger influence of the adsorbate on adhesion measurements than on surface forces.

3:00pm **EC+SS-MoA4 A New View of Ion Adsorption at Mineral-Fluid Interfaces with Synchrotron X-Ray Scattering**, P. Fenter, Argonne National Laboratory, Z. Zhang, Northwestern University, M.L. Schlegel, Commissariat à l'Energie Atomique, France, C.Y. Park, L. Cheng, Argonne National Laboratory, K.L. Nagy, University of Colorado at Boulder, D.J. Wesolowski, Oak Ridge National Laboratory, M. Machesky, Illinois State Water Survey, M.J. Bedzyk, Northwestern University, N.C. Sturchio, University of Illinois at Chicago **INVITED**

Ion adsorption at mineral-water interfaces is a key component of the electrical double-layer, a classic problem in surface science, and is fundamental for understanding the mobility of elements in the environment. We describe direct in-situ measurements of the systematic trends in ion adsorption near rutile- and muscovite-water interfaces using synchrotron X-ray scattering techniques (X-ray standing waves and X-ray reflectivity). These minerals represent two extremes in terms of location and origin of surface charge. The surface charge on rutile, an oxide, is determined by surface protonation reactions and is located above the mineral surface. In contrast, the surface charge of muscovite, a phyllosilicate, is determined by the permanent negative charge due to isomorphous lattice substitution below the mineral surface. The location of Zn^{2+} , Sr^{2+} and Y^{3+} ions were fully triangulated at the rutile(110)-water interface revealing unexpected differences in their adsorption geometries. Separate measurements were made of K, Cs^+ , Ca^{2+} , Ba^{2+} and Zn^{2+} ion heights with respect to the muscovite(001)-water interface. Systematic trends in adsorption behavior will be discussed in the context of classical pictures of ion-mineral interactions (e.g., inner sphere vs. outer-sphere complexes) and by contrasting the different ion adsorption behavior at the rutile and muscovite surfaces. Research sponsored by the U.S. Department of Energy, Office of Basic Energy Science: Division of Chemical Sciences, Geosciences and Biosciences.

3:40pm **EC+SS-MoA6 Solution Composition Effects on Calcite Dissolution and Growth Processes**, A.S. Lea, J.E. Amonette, D.R. Baer, N.G. Colton, Pacific Northwest National Laboratory

We have examined the influence of a number of solution impurities on step motion and shape of pits during dissolution and growth on the cleavage surface of calcite. Mg^{2+} , in contrast to the other impurities (Ca^{2+} , Mn^{2+} , Sr^{2+} , Co^{2+} , Mg^{2+} , and CO_3^{2-}) we have studied, exhibits unique behavior by uniformly enhancing dissolution rather than retarding dissolution. Of the impurities that retard dissolution, Sr^{2+} and CO_3^{2-} demonstrate selective sorption to the most sterically accessible step site resulting in a substantial slowing of dissolution of this type of step. Mn^{2+} and Co^{2+} , however, retard dissolution uniformly due to non-selective step sorption. For Mn^{2+} , Sr^{2+} , Co^{2+} , and Ca^{2+} , little impact on dissolution rate is seen until a threshold concentration is reached, whereupon near complete frustration of dissolution occurs upon further increase in impurity concentration. These results can be explained using a simple terrace-ledge-kink model that incorporates site-blocking and works equally well with metal ion or carbonate ion pair concentrations. This site-blocking model cannot explain the enhanced dissolution behavior of calcite in the presence of Mg^{2+} . In calcite growth processes, Ca^{2+} ions demonstrate preferred kink sorption sites, manifested by the unique pit shape observed during pit fill-in.

This work was supported by the Office of Basic Energy Science, Geosciences Research Program, U.S. Department of Energy. The work was conducted in the Environmental Molecular Sciences Laboratory, a U.S. Department of Energy user facility located at Pacific Northwest National Laboratory.

4:00pm **EC+SS-MoA7 Investigation of Binary Oxide (V_2O_5) Thin Films as Electrodes for Rechargeable Micro Batteries using Li**, A. Talledo, H. Valdivia, Universidad Nacional de Ingeniería, Peru, C. Benndorf, University of Hamburg, Germany

We report on the preparation of V_2O_5 thin films, their characterization and their application as electrodes in rechargeable micro batteries using lithium as counter electrode. The V_2O_5 thin films were deposited onto SnO coated glass by reactive rf sputtering of a V cathode using an Ar + O_2 atmosphere. The electrodes were characterized by their electrochemical behavior (IV-curves during charging and recharging using LiClO_4 + PC as electrolyte), X-ray diffraction (XRD), X-ray and UV induced photoelectron spectroscopy (XPS and UPS) and infrared (IR) measurements. XRD measurements demonstrated that unannealed V_2O_5 films were amorphous with no sharp reflexes. Annealing to 350°C was sufficient to produce crystalline β - V_2O_5 . XPS spectra revealed the expected V/O ratio and the correct line positions. However, the O 1s peak was splitted into two components, one from the V_2O_5 component (530.8 eV). The other at 533.1 eV is attributed to the uptake of water from the atmosphere. The large uptake of water is consistent with a porous structure of the V_2O_5 thin film. The charged micro

battery resulted in a maximum voltage of 3.4 V for the currentless circuit and a capacity of 34.5 mC/cm². With XPS we could demonstrate the migration of Sn into the V₂O₅ layer for the electrodes charged with Li. Further, UPS spectra from uncharged and charged V₂O₅ indicate a band gap narrowing due to the Li uptake, which is consistent with optical measurements. Our investigation contributes to the understanding and application of vanadium oxide thin films as cathodes for micro batteries.

4:20pm **EC+SS-MoA8 Creating Beakers without Walls: Formation of Deeply-Supercooled Binary Liquid Solutions from Nanoscale Amorphous Solid Films**, *P. Ayotte, R.S. Smith, G. Teeter, Z. Dohnálek, G.A. Kimmel, B.D. Kay*, Pacific Northwest National Laboratory

Supercooled liquids are metastable and their lifetimes are dictated by the kinetics for crystallization. Traditional experimental studies have used a variety of methods to suppress crystallization while cooling from the liquid phase. An alternate approach is to heat an amorphous solid above its glass transition temperature, T_g , whereupon it transforms into a deeply-supercooled liquid prior to crystallization. We employ molecular beams, programmed desorption (both TPD and isothermal) and FTIR vibrational spectroscopy to synthesize and characterize compositionally tailored nanoscale films of glassy methanol and ethanol. We demonstrate that these films exhibit complete diffusive intermixing and suppressed crystallization when heated above T_g . Furthermore, the resulting container-less liquids evaporate as continuously mixed ideal binary solutions while retaining their solid-like macroscopic shapes. This approach provides a new method for preparing deeply-supercooled liquid solutions in metastable regions of their phase diagram and for studying the kinetics of their phase separation and crystallization as they approach thermodynamic equilibrium. The applicability of this technique for studying aqueous liquid solutions will also be presented and discussed. P. A. is an NSERC Postdoctoral Fellow. Pacific Northwest National Laboratory is a multiprogram National Laboratory operated for the U. S. Department of Energy by Battelle Memorial Institute under contract DE-AC06-76RLO 1830.

4:40pm **EC+SS-MoA9 Using Nanomechanical Responses in Individual Systems from a Single C-C Bond to Single Cell**, *J. Gimzewski*, University of California, Los Angeles **INVITED**

: The capability of the atomic force microscope has recently been extended as powerful tool to not only image molecules in real space in but also to explore the mechanical properties of single molecules in a wide range of environments ranging from ultra high vacuum to in vivo. In this talk I will present a series of experiments that span from individual cells in growth media to the forced rotation of a single carbon-carbon bond in a organic molecule, using AFM based techniques such as non-contact dynamic AFM. I will show that the ability to measure small forces and amplitudes in a range of environments enables unique insights into nanomechanical process such as the determination of the zepto Joule forces for molecular switches and the ability to monitor cell function. Additionally, I will also span these two extremes using liquid based nanomechanical probes of proteomic and genetic recognition processes.

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