

# Monday Morning, November 4, 2002

## Electrochemistry and Fluid-Solid Interfaces

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

## Fuel Cells and Surface Electrochemical Reactions

Moderator: J.G. Chen, University of Delaware

8:20am **EC+SS-MoM1 Imaging of Water Ionization at Platinum Surfaces in High Electric Fields.** C. Rothfuss, V. Medvedev, E.M. Stuve, University of Washington

The high electric field intrinsic to the electrode/electrolyte interface plays an important role in electrochemical surface chemistry. To study these fields, which are of the order of 1 V/Å, we employ a field ionization system in which water and other electrolytic species are adsorbed and ionized on Pt field emitter tips. Ions produced by the applied field are imaged onto microchannel plates and mass resolved with time-of-flight or ExB (Wien filter) mass spectrometers. Water ionization produces hydrated protons with 1-10 water molecules per proton, that are ejected from the tip. Images of ramped field ionization experiments show dramatic differences in ionization of amorphous vs. crystalline water. Below 135 K, where water exists in amorphous form, ionization is random overall, increasing in intensity with increasing field. Above 135 K, where water is crystalline, ionization occurs in long-lived zones that, with increasing field, increase in intensity and number and redistribute themselves about the surface so as to be as far apart as possible. Temperature dependent studies over the range of 80-300 K follow the energetic details of water ionization. Below 170 K the field required for dissociative ionization decreases linearly with increasing temperature. In a ramped field desorption experiment, ionization produces hydrated proton clusters with 2-7 water molecules per cluster. Above 170 K protonated clusters desorb sequentially beginning with the 6-water cluster and followed by progressively smaller clusters as the field increases. The disappearance of an n-water ion cluster results from loss of a water molecule to form cluster n - 1. The respective energies for water removal from clusters of n = 5, 4, and 3 were found to be 0.55, 0.76, and 0.85 eV. These numbers are in excellent agreement with previous measurements of water attachment energies. This work is supported by the Office of Naval Research.

8:40am **EC+SS-MoM2 A Specular He Scattering Study of Water Adsorption, Desorption, and Clustering on Pt(111).** J.L. Daschbach, B.M. Peden, R.S. Smith, B.D. Kay, Pacific Northwest National Laboratory

Specular He atom scattering is used to probe the adsorption, desorption, and clustering kinetics of sub-monolayer H<sub>2</sub>O on Pt(111) over the temperature range 22 K to 185 K. Water deposited on clean Pt at low temperatures is shown to be arranged randomly on the Pt substrate. Over a narrow temperature range, as the clean substrate temperature is raised, the deposited water transforms to a 2-D condensed phase. Rearrangement of randomly adsorbed H<sub>2</sub>O is studied as a function of coverage and temperature. At low initial H<sub>2</sub>O coverage the specular He waveform is dominated by the clustering of the isolated H<sub>2</sub>O molecules. At higher H<sub>2</sub>O coverage and temperature a second feature is manifest, which we interpret as the Oswald ripening of the 2-D islands. Adsorption and desorption kinetics are examined isothermally. Water, when fully clustered in two dimensions, gives rise to a He specular intensity that decreases linearly with coverage. Over essentially the entire sub-monolayer coverage regime the sample coverage changes linearly in time during both adsorption and desorption of H<sub>2</sub>O. This requires that the desorption rate be independent of coverage and thus the desorption kinetics are zero-order. The zero-order kinetics are a consequence of the coexistence of a 2-D H<sub>2</sub>O gas with a 2-D condensed H<sub>2</sub>O phase on the Pt surface. At higher temperatures, depending on flux, non-zero order kinetics are observed which are indicative of a transition to a single H<sub>2</sub>O 2-D phase. Details of the experimental techniques and results will be presented. Pacific Northwest National Laboratory is a multiprogram National Laboratory operated for the Department of Energy by Battelle under Contract DE-AC067-76RLO 1830.

9:00am **EC+SS-MoM3 Surface Chemistry of Solid Oxide Fuel Cells.** R.J. Gorte, University of Pennsylvania **INVITED**

Fuel cells are an attractive method for electrical power generation because they offer the possibility of very high efficiencies compared to normal heat engines. One of the major hurdles preventing their implementation for a wide variety of applications is the fact that, until recently, only H<sub>2</sub> could be used as the fuel. We have recently demonstrated that stable power generation, without either internal or external reforming, can be achieved through the direct oxidation of hydrocarbons, including liquids, using a solid-oxide fuel cell (SOFC).<sup>1</sup> The anodes in these direct-oxidation SOFC

were composites made of Cu, ceria, and yttria-stabilized zirconia (YSZ). In this talk, the methods for preparing these anodes will be described. It will be demonstrated that surface chemistry and structure are crucial for improved performance of these fuel cells. Attempts to control the surface chemistry and structure will then be discussed.

<sup>1</sup> S. Park, J. M. Vohs, and R. J. Gorte, *Nature*, 404 (2000) 265.

9:40am **EC+SS-MoM5 Strategies for the Study of Methanol and CO Electrocatalysis on Solid Electrodes and Nanometer-Scale Supported Catalysts.** C. Korzeniewski, G. Vijayaraghavan, L. Gao, Texas Tech University **INVITED**

The electrochemical oxidation of methanol and related small molecules has been of special interest in relation to fuel cell research. The development of fuel cells that operate below 100 °C on methanol, or H<sub>2</sub> has stimulated interest in the reaction steps involved in methanol and carbon monoxide oxidation at metal electrodes. In addition to being a by-product of methanol oxidation, carbon monoxide can also be present as an impurity in H<sub>2</sub>. Adsorption of carbon monoxide on the anode catalyst generally degrades its performance. We have approached the study of methanol and carbon monoxide oxidation with the use of electrochemical techniques in combination with in situ infrared spectroscopy, atomic force microscopy (AFM) and wet-analytical methods. This presentation will focus on the surface electrochemistry of methanol and carbon monoxide at supported Pt and Pt-Ru catalysts. In situ infrared measurements are being performed with Vulcan carbon supported fuel cell catalysts. The carbon supported materials are adsorbed onto a smooth gold electrode to enable infrared sampling in a standard reflectance geometry. A thermostated cell allows in situ infrared measurements between ambient and 80 °C. Similar to the bulk metals, thermal effects on methanol oxidation at nanometer-scale catalysts are stronger for Pt-Ru (atomic percent Ru = 50%) than Pt. The influence that metal particle size distribution and spatial arrangement on carbon supports has on methanol oxidation pathways is being investigated by depositing metal particles on highly ordered pyrolytic graphite. The surface electrocatalytic properties of the supported particles are investigated with cyclic voltammetry. AFM is used to determine the catalyst size distribution and spatial arrangement at different stages of preparation and electrochemical characterization. Properties of nanometer-scale metal particles in relation to methanol oxidation pathways will be discussed.

10:20am **EC+SS-MoM7 Potential Application of Tungsten Carbides as Direct Methanol Fuel Cell (DMFC) Electrocatalysts.** H.H. Hwu, J.G. Chen, University of Delaware

The Pt/Ru anode in direct methanol fuel cells (DMFC), though effective, is disadvantageous in terms of its prohibitively high costs and limited supplies. In this work, we are evaluating the effectiveness of tungsten and molybdenum carbides as alternatives to Pt/Ru electrocatalysts by studying their reactivities towards methanol, water, and carbon monoxide. Using Temperature Programmed Desorption (TPD) and High-Resolution Electron Energy Loss Spectroscopy (HREELS) the reaction pathways of these DMFC molecules on carbide-modified Mo(110), W(110), and W(111) can be understood. On both W(110) and W(111) carbide surfaces, methanol readily decomposes into gas-phase CO, methane, hydrogen, and surface carbon and oxygen. In addition, both tungsten carbide surfaces are active toward the dissociation of CO and water. Preliminary studies on the Mo(110) carbide surface also show strong decomposition activity toward methanol, but through a different pathway than either the W(110) or W(111) carbide surfaces. Results from parallel studies of DMFC molecules on thin film tungsten carbides will also be presented.

10:40am **EC+SS-MoM8 Ru Nanoparticles Prepared by Decomposition of Ru<sub>3</sub>(CO)<sub>12</sub> on Au (111): Structural Characterization and Chemical Properties.** T. Cai, Z. Song, Z. Chang, G. Liu, J.A. Rodriguez, J. Hrbek, Brookhaven National Laboratory

Supported ruthenium metal particles prepared from ruthenium carbonyl have been shown as a most active catalyst for ammonia synthesis. In the emerging field of nanoscience, a goal is to make nanostructures with interesting functional properties. We have started a research program using metal carbonyls as precursors in the synthesis of nanoparticles on well-defined templates. In this study, we prepared and characterized a Au-supported Ru model catalyst under UHV by depositing metallic Ru on a Au (111) surface using triruthenium dodecacarbonyl, Ru<sub>3</sub>(CO)<sub>12</sub>, as a molecular precursor. We used the reconstructed Au (111) surface as an inert template for metallic cluster growth. Carbonyl adsorbs molecularly on the surface at 90 K and starts to dissociate at 280 K by CO elimination, as shown in TPD studies. The complete decomposition of the carbonyl occurs above 500 K, leaving metallic Ru on the surface with no significant C or O as detected by

XPS. Such an atomically clean Ru deposit is also obtained on Au (111) by MOCVD of  $\text{Ru}_3(\text{CO})_{12}$  at an elevated substrate temperature of 550 K. The morphology of the Ru nanoparticles investigated by STM and their chemical reactivity toward simple molecules ( $\text{CO}$ ,  $\text{N}_2$ ,  $\text{NH}_3$ ,  $\text{O}_2$ ,  $\text{NO}_2$ ) studied by XPS and TPD will be discussed. The research was carried out at BNL under Contract No. DE-AC02-98CH10086 with the U.S. DOE (Division of Chemical Sciences).

**11:00am EC+SS-MoM9 Development of a Microreactor System for Electrocatalytic Studies of Methanol Oxidation, N. Arvindan, E.M. Stuve, University of Washington**

We report on the development of a microreactor for studies of methanol electro-oxidation on platinum catalysts. One of the primary benefits of the microreactor is the ease of temperature control and low consumption of reactants. Temperature can be adjusted and controlled nearly instantaneously over the range of 20 to 100 C. Higher temperatures are possible depending on the pressure limitations of the fluidic connections to the microreactor. The microreactor enables studies of methanol electro-oxidation at high temperatures to achieve accelerated kinetics and freedom from CO poisoning. Methanol oxidation is measured at constant potential following a step from a non-reacting potential. Accumulation of surface species like CO is subsequently measured by linear sweep voltammetry. These two measurements enable the overall oxidation rate of methanol to be compared with the CO oxidation rate. Initial results demonstrate clean voltammetry of polycrystalline platinum electrodes for all temperatures. Reaction studies over the range of 80 to 100 C show that methanol oxidation occurs at the same rate as CO oxidation, consistent with the series reaction path (methanol to CO to carbon dioxide) being the dominant mechanism. The results conclusively show that thermal desorption of CO is insignificant, even at temperatures as high as 95 C. At 95 C turnover rates vary from 0.1 to 1 per second for the respective potential range of 400 to 600 mV vs. RHE. These results show that unmodified polycrystalline platinum is an effective catalyst for methanol oxidation at 95 C and support the feasibility of high temperature direct methanol fuel cells. This work is supported by the National Science Foundation and the UW Center for Nanotechnology.

**11:20am EC+SS-MoM10 Combined Atomic Force Microscope and Acoustic Wave Devices: Application to Electrodeposition, J.-M. Friedt, L. Francis, K.-H. Choi, A. Campitelli, IMEC, Belgium**

We here present the development of an instrument based on a new combination of techniques including scanning probe microscopy (atomic force microscopy, AFM, in our case) and acoustic wave devices (quartz crystal microbalance - QCM - and acoustic wave resonators). We display the ways these two measurement techniques interact and show that their performances are not degraded through interaction. Using finite element analysis, we explain observations compatible with the generation of longitudinal acoustic waves in the liquid, creating standing wave patterns between the QCM sensing electrode and the AFM cantilever holder leading to resonance frequency instabilities of the QCM. QCM electrode vibration in liquid is also shown not to degrade AFM lateral resolution. We then show measurement results from electrodeposition of copper and silver on gold electrode obtained using this instrument, and demonstrate how the data from both techniques (QCM-D and AFM) are complementary. Since QCM-D allows simultaneous measurement of the resonance frequency at several overtones of the quartz crystal resonator as well as the dissipation (quality factor) of each of these overtones, we show how the relative frequency shifts of the overtones informs on the kind of interactions between the oscillating acoustic wave device and the surrounding media (electrodeposited layer and solution used for electrochemistry). This combined measurement was performed on AT-cut quartz resonators (QCM), SH-SAW lithium tantalate and quartz acoustic wave devices and Love mode quartz acoustic wave devices. Finally, we show that after identifying the types of interactions we can efficiently use electrodeposition as a mean of calibrating the sensitivity of acoustic wave devices. Sensitivities close to the theoretical values and compatible with previous values given in the literature are presented.

**11:40am EC+SS-MoM11 Study of Bismuth Thin Film Electrodeposition and Oxide Formation on Au(111), C.A. Jeffrey, D.A. Harrington, University of Victoria, Canada, S. Morin, York University, Canada**

Bismuth and bismuth oxide films have been well studied due to their magnetoresistive and semiconducting properties. In this work, the formation of electrodeposited bismuth thin films is studied using in-situ scanning tunneling microscopy (STM). Their growth mode and morphology provide useful information for the production of well-defined bismuth thin films. Electrodeposition of bismuth is performed on Au(111) in acidic solution and the bismuth film transformation to bismuth oxide in alkaline solution is

studied using in-situ atomic force microscopy (AFM). Our study of the underpotential deposition process indicate that the reconstruction of Au(111) is lifted by the adsorbed bismuth, resulting in the formation of gold islands at potentials negative of 0.170  $V_{\text{SCE}}$ . Scans taken during the overpotential deposition process at potentials negative of -0.070  $V_{\text{SCE}}$  reveal 'needle' growth starting at step edges. These needles propagate over the surface and eventually form relatively uniform films. Atomic resolution images of the needle structures show the nearly rectangular unit cell 3.9 Å x 4.3 Å that contains one bismuth atom. The shorter side of the unit cell lies in the direction of the growth axis of the needle. This reduced spacing results in preferential incorporation of surface diffusing atoms at the needle tip, as opposed to along the edge, and accounts for the anisotropic growth. Bismuth oxide was formed by first forming the bismuth layer in acidic solution followed by a gradual shifting of the solution pH to a value of 10. Under these conditions, the transformation to the oxide film is monitored as the potential is made more positive. Close to the potential where the formation of bismuth oxide is expected, the morphology changes abruptly; small isolated protrusions form on the needle structures and cover the entire surface. The surface oxide formed can be reduced back to bismuth and this results in a disordered Bi film.

# 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  $\sim 7$  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  $\text{Zn}^{2+}$ ,  $\text{Sr}^{2+}$  and  $\text{Y}^{3+}$  ions were fully triangulated at the rutile(110)-water interface revealing unexpected differences in their adsorption geometries. Separate measurements were made of K,  $\text{Cs}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$  and  $\text{Zn}^{2+}$  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.  $\text{Mg}^{2+}$ , in contrast to the other impurities ( $\text{Ca}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{CO}_3^{2-}$ ) we have studied, exhibits unique behavior by uniformly enhancing dissolution rather than retarding dissolution. Of the impurities that retard dissolution,  $\text{Sr}^{2+}$  and  $\text{CO}_3^{2-}$  demonstrate selective sorption to the most sterically accessible step site resulting in a substantial slowing of dissolution of this type of step.  $\text{Mn}^{2+}$  and  $\text{Co}^{2+}$ , however, retard dissolution uniformly due to non-selective step sorption. For  $\text{Mn}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Ca}^{2+}$ , 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  $\text{Mg}^{2+}$ . In calcite growth processes,  $\text{Ca}^{2+}$  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 ( $\text{V}_2\text{O}_5$ ) 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  $\text{V}_2\text{O}_5$  thin films, their characterization and their application as electrodes in rechargeable micro batteries using lithium as counter electrode. The  $\text{V}_2\text{O}_5$  thin films were deposited onto SnO coated glass by reactive rf sputtering of a V cathode using an Ar +  $\text{O}_2$  atmosphere. The electrodes were characterized by their electrochemical behavior (IV-curves during charging and recharging using  $\text{LiClO}_4$  + 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  $\text{V}_2\text{O}_5$  films were amorphous with no sharp reflexes. Annealing to 350°C was sufficient to produce crystalline  $\beta$ - $\text{V}_2\text{O}_5$ . XPS spectra revealed the expected V/O ratio and the correct line positions. However, the O 1s peak was split into two components, one from the  $\text{V}_2\text{O}_5$  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  $\text{V}_2\text{O}_5$  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/cm<sup>2</sup>. With XPS we could demonstrate the migration of Sn into the V<sub>2</sub>O<sub>5</sub> layer for the electrodes charged with Li. Further, UPS spectra from uncharged and charged V<sub>2</sub>O<sub>5</sub> 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.

## Tuesday Afternoon Poster Sessions

### Electrochemistry and Fluid-Solid Interfaces Room: Exhibit Hall B2 - Session EC-TuP

#### Poster Session

**EC-TuP1 A Potentiodynamic Study of the Influence of Chloride and Chromate on Passive Films on Copper.** *M.A. Hossain, M.Y.A. Mollah, Lamar University, D.E. Mencer, Wilkes University, R. Schennach, Technical University of Graz, Austria, H. McWhinney, Prairie View A&M University, D.L. Cocke, Lamar University*

Copper is being increasingly studied today because of its use for electronic interconnects, its resistance to corrosion and its structural and alloying properties even though it undergoes pitting corrosion in the presence of aggressive ions including chloride and bromide. In a research program to delineate the physical and chemical processes that control metal and alloy oxidation, we have found it necessary to explore in detail the oxidation of copper. Although the electrochemical oxidation of copper has been much studied, there is a need to examine the nature of the oxidation product films developed in the process in light of recent discoveries of the importance of the intermediate oxide,  $\text{Cu}_3\text{O}_2$ . In this study, the electrochemical oxidation of copper is examined in neutral solution by cyclic voltammetry and linear sweep voltammetry. The influences of chloride and chromate ions have been investigated. Chloride has been found to strongly influence the passive film and to produce additional chemical species in the product films. Chromate influences the electrochemical properties of the passive films by increasing resistance to corrosion and increasing resistance to electrochemical reduction during linear sweep voltammetry. The structural and chemical influences have been examined by SEM and XPS. The chemical and structural changes in the product films will be discussed in terms of the increasing body of information being determined on the nature of oxidation produced films on copper by thermal, electrochemical and plasma means.

**EC-TuP2 Electrochemical Characterization and Preparation of Nanoporous Model Catalysts Produced from the Alloy  $\text{Cu}_{77}\text{Zn}_{12}\text{Mn}_7\text{Ni}_4$ .** *M. Kesmez, M.A. Hossain, Lamar University, D.E. Mencer, Wilkes University, H. McWhinney, Prairie View A&M University, D.L. Cocke, Lamar University*

In a research program to explore the preparation of model catalysts by the electrochemical oxidation of alloys, we have examined the oxidation of the  $\text{Cu}_{77}\text{Zn}_{12}\text{Mn}_7\text{Ni}_4$  alloy to produce a nanoporous copper manganese oxide catalyst with supported nickel. This has been accomplished by the selective dezinification of the alloy under oxidative potential control. The electrochemical properties of the alloy have been examined by cyclic voltammetry and linear sweep voltammetry to establish the mechanisms of corrosion and the characteristics of the oxidized films. The electrochemical characteristics needed for catalyst design will be delineated. The structural and chemical properties of the product films have been examined by SEM and XPS before and after thermal treatments to produce the active catalysts. The electrochemical preparation of the model hopcalite catalyst will be discussed in terms of the previous preparation of the catalyst by thermal and plasma chemical means. The potential of electrochemically controlled dezinification of this type alloy will be discussed for the production of new nanoporous model catalysts.

**EC-TuP3 The Electrode Processes of Iron at Potentials Beyond the Stability Limits of Water.** *S.R. Pathak, Lamar University, J.R. Parga, Instituto Tecnológico de Saltillo, Mexico, D.E. Mencer, Wilkes University, G. Irwin, D.L. Cocke, Lamar University*

The increasing use of iron electrodes in electrochemical processes that operate beyond the stability limit of water has created a critical need for the delineation of the irreversible interfacial processes affecting performance. These include the production of a range of aqueous iron species, a number of oxyhydroxides and several oxides that are released to the aqueous phase or remain attached to the electrode surfaces. We have examined the performance of iron electrodes in a five electrode arrangement with three bipolar and two monopolar electrode systems. The electrochemical reactor has been examined by the Cell Design 2000 software by LChem® to produce potential distribution and current distributions. The local electrochemicals are compared to the model calculations. The electrode surfaces residues have been examined by linear sweep voltammetry. The solids have been characterized by SEM, XRD, FTIR and Mossbauer Spectroscopy. The iron oxide and oxyhydroxide phases produced display strong dependence on pH. The results will be discussed in the context of the prevalent chemical and physical mechanisms and the influence on the performance of systems

such as electrocoagulation, electrodecantation and electroflotation will be delineated.

**EC-TuP4 Microstructure in Selective Electrodeposition of Copper on Indium-Tin-Oxide Film.** *S. Asakura, M. Hirota, A. Fuwa, Waseda University, Japan*

This paper describes the use of electrodeposition process to fabricate copper micropatterns on indium tin oxide (ITO) surface using patterned self-assembled monolayers (SAMs) as templates. Thin film ITO has good conductivity and excellent transparency in the visible region, but very few attempts have been made on fabrication of SAMs and electrodeposition of copper on ITO substrates. Micropatterned copper, which has been widely used because of its high electrical conductivity and low cost, is a key requirement since copper provides us with the electronic circuit wires which send signals to the functional molecules on them, electrochromic materials like a part of display, and biosensor. In our study, the organosilane SAMs have been prepared from octadecyltrimethoxysilane (ODS) by chemical vapour deposition (CVD) and irradiated through a TEM grid as a photomask by vacuum ultraviolet (VUV, 172 nm) light for removal of selected SAMs region and creation of electrode region for copper deposition. Lateral force microscopy (LFM) has been used to evaluate the friction differences between photoirradiated and unirradiated areas. SAMs and ITO regions have been also characterized by cyclic voltammetry (CV), from which we could decide selectively electrodeposition condition. It has been found possible to have micropatterned copper utilizing SAMs blocking effect in preventing electron transfer from species in solution through electrodeposition.

**EC-TuP5 Characteristics of the Polymer formed on via Sidewall during RIE Process and its Removal.** *J. Song, J. Kim, Samsung Electronics Co., Ltd., Korea, H. Seo, Y. Kim, H. Jeon, Hanyang University, Korea*

Via contact holes, act as electrical connection between the upper and lower metal layers through inter-metal dielectric, are generally patterned by photo lithography and reactive ion etching (RIE) processes, and the patterned photoresist after the formation of via holes is conventionally removed by the combination of remote plasma ashing and wet organic stripping. It is very critical to remove completely polymer formed on via sidewall and bottom during RIE process to have reliable metal filling and good contact resistance. Via holes were formed by using RIE process with  $\text{CHF}_3/\text{CF}_4$  gas under the same processing conditions for the state-of-the art DRAM process. The surface morphology of polymer before and after cleaning process was observed by using in-line scanning electron microscopy (SEM), vertical SEM and transmission electron microscopy (TEM). The chemical compositions and structures of polymer were analyzed by using energy dispersive spectroscopy (EDS) and Auger electron spectroscopy (AES). TEM and EDS study revealed that the side wall polymer were grown from the cap TiN layer on Al and showed the truncated cone shape with the thickness in the range of 200–400 Å. This indicates that via polymer layer becomes a very critical issue when the etch stop layer is TiN. Bottom polymer layer showed double layer structure with two distinct chemical compositions. The lower layer with the thickness of about 50 Å showed a similar chemical characteristic to the side wall polymer while the upper polymer layer with the thickness of about 200 Å showed no fluorine content. In this study, we will investigate the removal characteristics of polymer during RIE process at various ashing and stripping conditions. Preliminary results indicated that the low temperature remote oxygen plasma ashing and hydroxylammoniumsulfate based wet stripping were very effective to remove polymer formed on the side and bottom of via holes during RIE process.

# Authors Index

**Bold page numbers indicate the presenter**

## — A —

Amonette, J.E.: EC+SS-MoA6, **3**  
Arvindan, N.: EC+SS-MoM9, **2**  
Asakura, S.: EC-TuP4, **5**  
Ayotte, P.: EC+SS-MoA8, **4**

## — B —

Baer, D.R.: EC+SS-MoA6, **3**  
Bedzyk, M.J.: EC+SS-MoA4, **3**  
Benndorf, C.: EC+SS-MoA7, **3**  
Bonn, M.: EC+SS-MoA1, **3**

## — C —

Cai, T.: EC+SS-MoM8, **1**  
Campitelli, A.: EC+SS-MoM10, **2**  
Chang, Z.: EC+SS-MoM8, **1**  
Chen, J.G.: EC+SS-MoM7, **1**  
Cheng, L.: EC+SS-MoA4, **3**  
Choi, K.-H.: EC+SS-MoM10, **2**  
Cocke, D.L.: EC-TuP1, **5**; EC-TuP2, **5**; EC-TuP3, **5**  
Colton, N.G.: EC+SS-MoA6, **3**

## — D —

Daschbach, J.L.: EC+SS-MoM2, **1**  
Dohnálek, Z.: EC+SS-MoA8, **4**

## — F —

Fenter, P.: EC+SS-MoA4, **3**  
Francis, L.: EC+SS-MoM10, **2**  
Frechette, J.: EC+SS-MoA3, **3**  
Friedt, J.-M.: EC+SS-MoM10, **2**  
Fuwa, A.: EC-TuP4, **5**

## — G —

Gao, L.: EC+SS-MoM5, **1**  
Gimzewski, J.: EC+SS-MoA9, **4**  
Gorte, R.J.: EC+SS-MoM3, **1**

## — H —

Harrington, D.A.: EC+SS-MoM11, **2**  
Hirota, M.: EC-TuP4, **5**  
Hossain, M.A.: EC-TuP1, **5**; EC-TuP2, **5**  
Houston, J.E.: EC+SS-MoA2, **3**  
Hrbek, J.: EC+SS-MoM8, **1**  
Hwu, H.H.: EC+SS-MoM7, **1**

## — I —

Irwin, G.: EC-TuP3, **5**

## — J —

Jeffrey, C.A.: EC+SS-MoM11, **2**  
Jeon, H.: EC-TuP5, **5**

## — K —

Kay, B.D.: EC+SS-MoA8, **4**; EC+SS-MoM2, **1**  
Kesmez, M.: EC-TuP2, **5**  
Kim, J.: EC-TuP5, **5**  
Kim, Y.: EC-TuP5, **5**  
Kimmel, G.A.: EC+SS-MoA8, **4**  
Kleyn, A.W.: EC+SS-MoA1, **3**  
Korzeniewski, C.: EC+SS-MoM5, **1**

## — L —

Lea, A.S.: EC+SS-MoA6, **3**  
Liu, G.: EC+SS-MoM8, **1**

## — M —

Machesky, M.: EC+SS-MoA4, **3**  
McWhinney, H.: EC-TuP1, **5**; EC-TuP2, **5**  
Medvedev, V.: EC+SS-MoM1, **1**  
Mencer, D.E.: EC-TuP1, **5**; EC-TuP2, **5**; EC-TuP3, **5**  
Mollah, M.Y.A.: EC-TuP1, **5**  
Morin, S.: EC+SS-MoM11, **2**

## — N —

Nagy, K.L.: EC+SS-MoA4, **3**

## — O —

Oliver, A.C.: EC+SS-MoA2, **3**

## — P —

Parga, J.R.: EC-TuP3, **5**  
Park, C.Y.: EC+SS-MoA4, **3**  
Pathak, S.R.: EC-TuP3, **5**  
Peden, B.M.: EC+SS-MoM2, **1**

## — R —

Rodriguez, J.A.: EC+SS-MoM8, **1**  
Roke, S.: EC+SS-MoA1, **3**  
Rothfuss, C.: EC+SS-MoM1, **1**

## — S —

Schennach, R.: EC-TuP1, **5**  
Schlegel, M.L.: EC+SS-MoA4, **3**  
Seo, H.: EC-TuP5, **5**  
Smith, R.S.: EC+SS-MoA8, **4**; EC+SS-MoM2, **1**  
Song, J.: EC-TuP5, **5**  
Song, Z.: EC+SS-MoM8, **1**  
Sturchio, N.C.: EC+SS-MoA4, **3**  
Stuve, E.M.: EC+SS-MoM1, **1**; EC+SS-MoM9, **2**

## — T —

Talledo, A.: EC+SS-MoA7, **3**  
Teeter, G.: EC+SS-MoA8, **4**

## — V —

Valdivis, H.: EC+SS-MoA7, **3**  
Vanderlick, T.K.: EC+SS-MoA3, **3**  
Vijayaraghavan, G.: EC+SS-MoM5, **1**

## — W —

Wesolowski, D.J.: EC+SS-MoA4, **3**

## — Z —

Zhang, Z.: EC+SS-MoA4, **3**