

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 H₂O 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 H₂O is studied as a function of coverage and temperature. At low initial H₂O coverage the specular He waveform is dominated by the clustering of the isolated H₂O molecules. At higher H₂O 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 H₂O. 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 H₂O gas with a 2-D condensed H₂O 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 H₂O 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 H₂ 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).¹ 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.

¹ 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 H₂ 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 H₂. 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 Ru₃(CO)₁₂ 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, Ru₃(CO)₁₂, 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 (CO , N_2 , NH_3 , O_2 , 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_{SCE} . Scans taken during the overpotential deposition process at potentials negative of -0.070 V_{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.

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