

Electrochemistry and Fluid Solid Interfaces

Room 326 - Session EC+SS-TuM

Water at Interfaces I: Structure and Electrochemistry

Moderator: E.M. Stuve, University of Washington

8:20am EC+SS-TuM1 A Microreactor System for Electrocatalytic Kinetics: Methanol Oxidation on Platinum Electrodes at Elevated Temperature, N. Arvindan, L. Arnadottir, E.M. Stuve, University of Washington

We describe a silicon-based microreactor for measurement of electrocatalytic rate constants for methanol oxidation on platinum and modified platinum electrodes. The device consists of silicon and pyrex wafers bonded together by a Teflon treatment to create an enclosed flow channel 0.25 mm deep, 1.5 mm wide, and 25 mm long. The flow channel includes deposited platinum lines for fluid heating, temperature measurement, and a counter electrode. A separate palladium line serves as a reference electrode. The working electrode is inserted into an opening in the flow channel. The working electrode can be a single crystal, polycrystalline sample, or actual supported catalyst. The microreactor can accommodate mixed metallic catalysts such as PtRu. 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. 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 effect catalyst for methanol oxidation at 95 °C and support the feasibility of high temperature direct methanol fuel cells.

8:40am EC+SS-TuM2 In Situ Characterization of Nucleation and Growth During Electrochemical Deposition of Copper, A. Radisic, Johns Hopkins University; M.J. Williamson, University of Virginia, Charlottesville, current address Lawrence Berkeley National Laboratory; M.C. Reuter, S.J. Chey, R.M. Tromp, F.M. Ross, IBM T.J. Watson Research Center; P.C. Searson, Johns Hopkins University

In current copper metallization technology, copper is electrodeposited onto a barrier layer pre-covered by a thin copper seed layer. As the feature sizes of the trenches and vias continue to shrink, strategies for direct deposition of copper onto the barrier layer need to be explored. Copper electrodeposition on diffusion barrier layers occurs through 3D island growth, and hence nucleation and growth play an important role in determining the properties of metallization. We have studied nucleation and growth processes during electrochemical deposition of copper using the in situ transmission electron microscopy. This is a real time, high resolution imaging technique that allows us to study the evolution of island density with time, as well as the spatial and temporal correlations between islands. In this study we report on the nucleation and growth parameters for copper electrodeposition, obtained using both ex situ and in situ experimental techniques. We examine the relationship between potential, solution chemistry, and island density. Furthermore, we show that under appropriate experimental conditions, a high density of copper islands and a continuous thin copper film can be obtained at the surface. F. M. Ross, Growth processes and phase transformations studied by in situ transmission electron microscopy. IBM Journal of Research, 44, 489-501, 2000

9:00am EC+SS-TuM3 Electrochemical Synthesis of Multifunctional Building Blocks for Nanosystems, P.C. Searson, Johns Hopkins University

INVITED

Electrochemical synthesis is an important tool in the fabrication of multicomponent or layered structures with high aspect ratio. Nanometer size particles, such as nanorods or nanowires exhibit many unique properties associated with their inherent shape anisotropy. For example, ferromagnetic (FM) nanowires exhibit unique and tunable magnetic properties due to the shape anisotropy and the small wire dimensions. The introduction of multiple segments along the length of a nanowire can lead to further degrees of freedom associated with the shape of each segment and the coupling between the layers. For example, modifying the diameter,

composition, and layer thicknesses in multilayer FM/NM (NM = nonmagnetic material) nanowires it is possible to tailor the orientation of the magnetic easy axis and properties such as the Curie temperature, coercivity, saturation field, saturation magnetization, and the remanent magnetization. The unique properties of multisegment nanowires can also be exploited in suspensions where the manipulation and assembly of nanometer scale particles has become an important tool in nanotechnology. The ability to bind molecules with different functionalities to different components in multisegment nanowires introduces an additional degree of freedom that is potentially important in enhancing surface reactions, immobilizing molecules, and assembling scaffolds for tissue engineering.

9:40am EC+SS-TuM5 Photoexcited Electrodeposition of Cu Structures on p-Si(001), C. Scheck, Y.-K. Liu, P. Evans, The University of Alabama; G. Zangari, University of Virginia; R. Schad, The University of Alabama

Selective growth of metals on semiconductors has recently raised considerable interests, due to its possible application in the direct formation of interconnects on Si. We produced small structures by photoexcited electroless plating of Cu on p-type Si(001). The p-type substrate forms a Schottky barrier with the solution which inhibits the plating process. Local illumination creates minority carriers which become available to discharge metal ions. The illumination was done by converging a 1-5 mW laser beam to a 1-2mm focus diameter on the substrate in the plating solution using an optical microscope. We analyzed the diameter of the growing dots as a function of laser light wavelength and intensity, illumination duration, composition of the solution and charge carrier lifetime in the substrate. The dimensions of the dots are determined by the diffusion length of the excited minority carriers. The lateral dimensions of the produced structures are found to decrease with reduced laser wavelength or intensity but is independent of the duration of the illumination. Shorter minority carrier lifetimes in the semiconductor substrate lead to a further reduction of structure dimensions. The effect of spontaneous background precipitation on the Si surface is studied as a function of solution composition. The optical reflectivity can be related to the fractal surface roughness.

10:00am EC+SS-TuM6 Ultrahigh Vacuum Studies of Static and Dynamic Solid Oxide Electrocatalysts by Field Ionization and Spectroscopic Techniques, R.A. Manghani, V.K. Medvedev, E.M. Stuve, University of Washington

Understanding solid oxide fuel cell reactions and electrochemical promotion of catalysts requires a complete description of the three-phase boundary (catalyst/electrolyte/fluid) under both static and dynamic (that is, reacting) conditions. We have undertaken two approaches to examine solid oxide electrocatalytic surfaces under well-defined, ultrahigh vacuum (UHV) conditions. The first method uses field ionization and field emission methods to probe the static properties of the three-phase boundary. A platinum field emitter tip of radius 35 nm was studied in a highly oxidized state and in the form of a Pt/ceria supported catalyst. Subsurface oxygen, which has been implicated in the NEMCA effect, was prepared on the platinum tip by oxygen ion sputtering at high temperature. Local work function measurements were performed by field emission microscopy to examine the oxide surface with and without chemisorbed oxygen. Pt/ceria surfaces were prepared by coating the Pt tip with a ceria adlayer and then evaporating platinum onto the ceria coating. The reactions of hydrocarbons (methane and butane) and water were examined on the Pt/ceria substrates by field ionization microscopy and mass spectrometry (time-of-flight and Wien filter modes). The second method uses a full solid oxide fuel cell (SOFC) operating in an ultrahigh vacuum system. The UHV-SOFC permits study of solid oxide anodes for direct oxidation of hydrocarbons such as methane and butane. The anode consists of a ceria coated YSZ pellet (5 mm diameter), which has a sealed tube on the cathode side to deliver oxygen at approximately 1 mbar. The anode side was studied by x-ray photoelectron spectroscopy, Auger electron spectroscopy, and quadrupole mass spectrometry while being exposed to the hydrocarbon reactant. The UHV-SOFC thus allows surface analysis of a dynamic electrocatalyst surface. This work is supported by the Office of Naval Research.

10:20am EC+SS-TuM7 Molecular Ordering at Liquid-Liquid Interfaces, M.L. Schlossman, University of Illinois

INVITED

Our view of molecular ordering in Langmuir monolayers at the water-vapor interface influences our understanding of molecular ordering at other interfaces, including liquid-liquid interfaces for which structural information is scarce. We present a comparative study of monolayers of long-chain alkanols at the water-vapor and water-hexane interfaces using

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x-ray reflectivity to highlight significant differences between these two interfaces. The molecules in the Langmuir monolayer form an ordered phase of nearly rigid rods. In contrast, at the water-hexane interface the alkanol molecules form a condensed phase with progressive disordering of the chain from the hydroxy to the methyl group. Surprisingly, at the water-hexane interface the density in the head group region is 10 to 15% greater than either bulk water or the ordered head group region found at the water-vapor interface. It is conjectured that this higher density is a result of water penetration into the head group region of the disordered monolayer. The alkanol monolayers at the water-hexane interface also undergo a solid to gas phase transition as a function of temperature. X-ray off-specular diffuse scattering is used to directly probe the statistical distribution of domains in monolayers of a fluorinated alkanol near the transition temperature. Evidence that the domains are of equilibrium size suggests that the domain line tension can be determined from these measurements.

11:20am **EC+SS-TuM10 Water-Graphite Interaction and the Behavior of Water near Graphite Surface**, *M. Grunze, A.J. Pertsin*, Universität Heidelberg, Germany

A new, orientation-dependent water-graphite potential, which reproduces MP2-level quantum chemistry calculation results for the water-graphite complex, is suggested. The potential is used in grand canonical Monte Carlo simulations of the behavior of water confined between graphite surfaces. Comparative simulations using an isotropic potential are made to see the manifestations of the orienting effect of the water-graphite interaction in the structural and thermodynamic properties of the interfacial region. The shear behavior of water confined between the graphite surfaces is also explored to gain a better understanding of the effect of water on the friction and wear of graphitic carbons.

11:40am **EC+SS-TuM11 Molecular Structure at Interfaces between Water and Metal, Metal Oxide, or Polymer Studied by Sum Frequency Generation Spectroscopy**, *K. Uosaki, R. Yamamoto, S. Nihonyanagi*, Hokkaido University, Japan

Sum frequency generation (SFG) measurement was carried out to investigate the molecular structure at the interfaces between aqueous solution and metal, metal oxide, or polymer. Potential dependent water structure at metal electrode, photo-induced hydrophilicity at titanium dioxide and the conformation of molecular chain of polyelectrolyte brush under various environment were studied.

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