

Surface Science

Room 200 - Session SS1-ThM

Water-Surface Interactions

Moderator: B.D. Kay, Pacific Northwest National Laboratory

8:20am **SS1-ThM1 Metal/Electrolyte Interfaces: In-situ Scanning Tunneling Microscopy Studies**, *K. Wandelt*, University of Bonn, Germany
INVITED

In the years to come more and more processes at solid/liquid interfaces will replace processes which nowadays are carried out by vacuum based methods, like surface modification, thin film growth, nanostructuring, etc.. Among others this is a consequence of the growing number of methods which are capable to provide in-situ information about properties and processes at solid/liquid interfaces with the same precision as we are used to in vacuum. This is particularly true for ElectroChemical Scanning Tunneling Microscopy (ECSTM), which - in combination with in-situ FTIR- and some ex-situ spectroscopies - is used in this work to characterize copper single crystal electrodes interacting with various electrolytes. Firstly, surface structural phase transitions and morphological changes due to the adsorption of simple anions, like Cl, Br, J, S, SO₄²⁻, SCN, etc., will be studied with atomic resolution. Secondly, it will be shown that the halogen and sulphur covered electrode surfaces are interesting primary templates for the formation of thin ordered compound films (e.g. CdCl₂) as well as self-assembled organic nanostructures (e.g. from porphyrins and viologenes). In particular the latter ones are found to form chiral cavitands, which in turn are ideal secondary templates for the design of more complex molecular architectures with nanoscale periodicity and specific functionality.

9:00am **SS1-ThM3 Segregation of Anions at the Alkali Halide Solution/Vapor Interface Investigated by Photoemission Spectroscopy**, *S. Ghosal*, University of California, Irvine; *H. Bluhm*, Lawrence Berkeley National Laboratory; *B.S. Mun*, Lawrence Berkeley National Laboratory, US; *G. Ketteler*, *F.G. Requejo*, *E.L.D. Hebenstreit*, *D.F. Ogletree*, *M. Salmeron*, Lawrence Berkeley National Laboratory; *J.C. Hemminger*, University of California, Irvine

Ion-enhanced interactions with gases at aqueous solution interfaces may play an important role in the chemistry of concentrated inorganic solutions in the atmosphere. Using ambient pressure photoemission spectroscopy (PES) we have measured the concentration of ions at the surface of saturated potassium iodide and potassium bromide solutions. In the case of saturated potassium iodide solutions two iodine 4d peaks that are separated by a binding energy difference of 1.7 eV can be identified in the PES spectrum. Using photon-energy-dependent depth-profiling we have determined that the iodine peak with the higher binding energy is due to an iodine species at the solution interface, while the low binding energy peak is due to iodine from the bulk of the solution. The presence of an anion species at the solution interface is in agreement with our previous ambient pressure PES results that showed an enhancement of the halide anion concentration at the solution interface compared to the literature value for bulk solutions. @footnote 1@ @FootnoteText@ @footnote 1@ S. Ghosal et al., Science 307, 563 (2005).

9:20am **SS1-ThM4 The Growth of Thin Water Films on a Hydrophobic Water Monolayer on Pt(111)**, *G.A. Kimmel*, *N.G. Petrik*, *Z. Dohnalek*, *B.D. Kay*, Pacific Northwest National Laboratory

The growth of amorphous solid water and crystalline ice films on Pt(111) is investigated using rare gas physisorption. For a wide range of growth temperatures (20 - 155 K), the water monolayer wets the Pt(111). However, crystalline ice films grown on the water monolayer do not wet that surface. In contrast, amorphous films grow layer-by-layer for at least the first three layers over a wide range of growth temperatures (20-120 K), probably due to kinetic limitations. Wetting films grown at low temperature that are subsequently annealed to high temperature typically unwet during or after the crystallization of the films. The results are surprising since it is commonly believed that water films wet Pt(111). However, they are consistent with recent theory and experiments suggesting that the molecules in the water monolayer are fully coordinated forming a hydrophobic surface with no dangling OH bonds or lone pair electrons and a low surface energy.

9:40am **SS1-ThM5 The Nature of Water on Oxygen Covered Pt: Low Temperature Activation and Unexpected Structure**, *T. Schiros*, *H. Ogasawara*, Stanford Synchrotron Radiation Laboratory; *L.-Å. Näslund*, *M. Odellius*, *L.G.M. Pettersson*, Stockholm University, Sweden; *A. Nilsson*, Stanford Synchrotron Radiation Laboratory

The nature of the adsorbed water layer on surfaces has been a topic of interest due to its relevance for many practical fields, including corrosion, electrochemistry, environmental science and heterogeneous catalysis. Recently the behavior of adsorbed water under the presence of oxygen has garnered increasing interest in connection to the triple phase boundaries problem in fuel cell catalysis. Here, we studied the co-adsorption of water and oxygen on Pt(111) with X-ray photoemission and X-ray absorption spectroscopy in an ultra high vacuum environment combined with electronic structure calculations in the frame work of density functional theory. While water absorbs intact on clean metal surfaces at low temperature, @footnote 1-3@ an oxidized Pt surface activates and splits adsorbed water even at low temperature. We propose a new structure model for the activated water on Pt(111). We find that the activated water aligns the molecular axis perpendicular to the surface and is hydrated in the equatorial plane. @FootnoteText@ @footnote 1@ H. Ogasawara et al, Phys. Rev. Lett. 89 (2002) 276102. @footnote 2@ K. Andersson et al, Phys. Rev. Lett. 93 (2004) 196101. @footnote 3@ K. Andersson et al, Surf. Sci. Lett. In press (2005).

10:00am **SS1-ThM6 DFT Calculations of Interaction of Water Molecules with Pt(111) Surface**, *L. Árnadóttir*, University of Washington; *H. Jónsson*, University of Iceland; *E.M. Stuve*, University of Washington

The interaction of water molecules with the Pt(111) surface has been studied using DFT and the PW91 functional. Early stages of ice crystal nucleation and the possibility of dissociation on flat terrace, kink and steps have in particular been addressed. In the lowest energy configuration, a water molecule sits on top of a Pt atom and donates an electron pair into an empty d-orbital on the Pt. The binding energy is found to be 0.30 eV. Small water clusters of two and three water molecules also have lowest energy configuration on top of a Pt atom. In those small clusters one water molecule is centered on the top of a Pt surface atom and is tilted with the hydrogen atoms pointing about 16° away from the surface plane and the other water molecules about 0.5 Å further away from the surface. While the dissociation of water molecules is uphill by 0.72 eV on the flat terrace, it is almost neutral energetically at the step but has an activation energy of 0.91 eV. The dissociation will, however, not occur thermally because desorption will occur more readily. As the temperature is raised, the diffusion of single water molecule is predicted to become active on the time scale of seconds at a temperature of 43 K which is in good agreement with recent experimental results of Kay and coworkers. @footnote 1@. The binding at steps and kinks on the Pt(111) surface is substantially stronger than at the flat terrace, by 0.16 eV and 0.25 eV, respectively, and the lowest energy configuration has the water molecule sitting on top of edge or kink atoms. At low coverage, clusters of water molecules would, therefore, be expected to line the upper side of step edges. This is consistent with experimental STM images taken by Morgenstern et al. @footnote 2@ @FootnoteText@ @footnote 1@ Daschbach, J. L., Peden, B. M., Smith, R. S., Kay, B. D., J. Chem. Phys., 2004. 120(3): p. 1516-1523 @footnote 2@ Morgenstern, M., Michely, T., Comsa, G., Phys. Rev. Lett., 1996. 77(4): p. 703-706

10:20am **SS1-ThM7 The Effect of Incident Collision Energy on the Phase, Crystallization Kinetics, and Porosity of Vapor Deposited Amorphous Solid Water Films**, *T. Zubkov*, *R.S. Smith*, *Z. Dohnalek*, *B.D. Kay*, Pacific Northwest National Laboratory

Molecular beam techniques that allow for the precise control of the impingement flux, deposition angle, and incident collision energy are used to grow nanoscale films of amorphous solid water (ASW). The phase (amorphous or crystalline), porosity, and subsequent crystallization kinetics of the ASW films are probed using temperature programmed desorption, inert gas physisorption, and infrared spectroscopy. We find that for films grown at 20 K and normal incidence, the incident collision energy (up to 2 eV) has no effect on the phase of the deposited film or the subsequent crystallization kinetics. On the other hand, the incident beam energy does affect the porosity of the deposited films. At low beam energy (0.05 eV), the porosity of the vapor deposited film depends strongly on the incident growth angle. Films with structures from non-porous to highly porous can be grown by increasing the angle of incidence of the impinging molecules. The porosity of the ASW films decrease with increasing beam energy. The results of these experiments and their implications for the physical

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properties of ASW are presented and discussed. Pacific Northwest National Laboratory is operated by Battelle for the U.S. Department of Energy.

10:40am **SS1-ThM8 Ionization of Water-Ice Layers on Platinum: Effect of Carbon Monoxide**, *R.A. Manghani, V.K. Medvedev, E.M. Stuve*, University of Washington

Field ionization of water on a platinum field emission tip was studied in the presence of carbon monoxide (CO) as co-adsorbate. Water adlayers 5 - 400 Å thick were grown under field-free conditions at 108 K by exposure of cryogenically cooled emitter tip to water vapor in ultrahigh vacuum. Onset of field ionization of water layers was probed by ramped field desorption (RFD) on platinum and CO saturated platinum emission tip. Onset field for water ionization on CO saturated platinum was found to be lower than that for water adsorbed on bare platinum. Facilitation of ionization by saturated CO on platinum was attributed to enhancement in the local field. The effect decreased with increasing water thickness, but existed for thick water layers. Effect of CO on water ionization is discussed and a model is presented.

11:00am **SS1-ThM9 Electron-Stimulated Production of Molecular Oxygen in Thin Films of Amorphous Solid Water on Pt(111)**, *N.G. Petrik*, Pacific Northwest National Laboratory; *A.G. Kavetsky*, Khlopin Radium Institute, Russia; *G.A. Kimmel*, Pacific Northwest National Laboratory

The electron-stimulated reactions in amorphous solid water (ASW) films leading to the production of molecular oxygen were investigated. Thin (0-400 ML) amorphous films of H@sub 2@@super 16@O, H@sub 2@@super 18@O, and D@sub 2@O deposited on Pt(111) were irradiated with 87 eV electrons, and the electron-stimulated desorption (ESD) of O@sub 2@ was measured versus film thickness and isotopic composition. The O@sub 2@ ESD yield is low for small coverages, has a maximum at ~20 ML, and decreases to a coverage independent level for coverages greater than ~50 ML. The O@sub 2@ and H@sub 2@ ESD yields versus ASW coverage are similar, indicating that both originate from mobile electronic excitations produced in the bulk of the ASW film that subsequently diffuse to the ASW/Pt and ASW/vacuum interfaces where they induce reactions. However in contrast to H@sub 2@, experiments with layered films of H@sub 2@@super 16@O and H@sub 2@@super 18@O show that O@sub 2@ is produced only near the ASW/vacuum interface. The O@sub 2@ molecule is produced via a relatively fast radiation-induced process from a stable precursor, perhaps HO@sub 2@ or H@sub 2@O@sub 2@, which accumulates at the ASW/vacuum interface. The results suggest that mobile electronic excitations produce a reactive species at the ASW/Pt interface, such as OH, which subsequently diffuses through the film to the ASW/vacuum interface where further reactions produce the stable precursors for the O@sub 2@ molecules.

11:20am **SS1-ThM10 A Comparison of H@sub 2@O and D@sub 2@O Adsorption on MgO(100) Under Ambient Conditions**, *M.C. Foster, N.J. Ward, D. Passno*, University of Massachusetts - Boston

Transmission Fourier transform infrared spectroscopy is used to investigate both H@sub 2@O and D@sub 2@O adsorbed on the (100) face of MgO under ambient conditions. A sample cell has been constructed such that many of these infrared transparent surfaces are investigated while the volume of gas phase molecules probed is minimized. A number of crystals, obtained by cleaving with a hammer and chisel a larger single crystal boule under a nitrogen purge, are placed in this cell, which is essentially a hollow stainless steel tube with IR windows on either side. Water is introduced at the desired pressure and allowed to establish a dynamic equilibrium with the MgO(100). The adlayer formed on the crystal faces is observed by transmission Fourier transform infrared (FTIR) spectroscopy. Any IR absorption stemming from molecules in the gas phase in the resulting spectrum is easily subtracted out. From these measurements, we find that water reversibly adsorbs to MgO(100) creating liquid-like layers at room temperature with slight hysteresis seen during a complete adsorption / desorption cycle. The adsorption isotherm of water on MgO(100) resembles a typical BET plot, which coupled with by the fact that IR absorption due to either the OH or OD stretch of the adsorbed water does not change as a function of coverage, suggests that the layer grows in via three-dimensional island formation. Special attention has been paid to the issue of dissociative adsorption of water on the surface, either reversible or permanent with no evidence seen under these experimental conditions.

11:40am **SS1-ThM11 Water Adsorption on a Polymer Surface**, *L.G. Rosa¹*, University of Nebraska-Lincoln; *Ya.B. Losovyj*, Louisiana State University; *I.N. Yakovkin*, Institute of Physics of National Academy of Sciences of Ukraine; *P.A. Dowben*, University of Nebraska-Lincoln, US

Water absorption and adsorption on the thin films of the ferroelectric copolymer polyvinylidene fluoride with 30% trifluoroethylene, P(VDF-TrFE,70:30) has been explored by angle resolved thermal desorption, angle resolved photoemission spectroscopy, high resolution photoemission spectroscopy and x-ray diffraction. We observe that water is absorbed into the polymer bulk. When the near surface region is saturated, an ice layer at the surface of the polymer can be formed. Strong dipole - dipole interactions between the dipole of water and the dipole of the ferroelectric polymer play an important role in absorption and desorption, including but not limited to, isotopic exchange and dielectric properties. Adsorbed water seems to be a spectator to the many phase transition of the ferroelectric polymer particularly the ones at the surface and bulk.

¹ Morton S. Traum Award Finalist

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