

O 50: Oxide and Insulator Surfaces I

Time: Wednesday 10:30–13:00

Location: WIL A317

O 50.1 Wed 10:30 WIL A317

Elementary steps of water dissociation on α -Al₂O₃(0001) — ●HARALD KIRSCH¹, JONAS WIRTH², YUJIN TONG¹, MARTIN WOLF¹, PETER SAALFRANK², and R. KRAMER CAMPEN¹ — ¹Fritz-Haber-Institut, Abt. Physikalische Chemie, 14195 Berlin, Germany — ²Universitaet Potsdam, Institut fuer Chemie, 14476 Potsdam OT Golm, Germany

Alumina surfaces are ubiquitous in technologically relevant applications and a useful model system for more complicated, environmentally abundant, aluminosilicate phases. Because their properties change dramatically on interaction and reaction with water, water/Alumina chemistry has been studied, both experimentally and theoretically, for decades. In this work, we study the interaction of heavy water (D₂O) with the α -Al₂O₃(0001) surface under ultra high vacuum (UHV) conditions. Hydroxylation of the Al₂O₃(0001) in UHV is performed by dosing D₂O seeded in Helium with a molecular beam source (MBS). For characterization we employ vibrationally resonant sum frequency generation (VSF) spectroscopy to probe the OD stretch response of interfacial species. This technique allows us to distinguish several different OD-species in the OD-stretching region. Comparison of the resulting measured spectra with frequencies and geometries calculated from periodic density functional theory allows us to identify, for the first time, the products of the two theoretically predicted dissociation pathways: we observe the elementary steps of water dissociation on α -Al₂O₃(0001).

O 50.2 Wed 10:45 WIL A317

Optical Characterization of α -Al₂O₃(0001) Surface Structure and Reactivity in Ambient Conditions — ●YUJIN TONG, HARALD KIRSCH, and R. KRAMER CAMPEN — Fritz-Haber-Institut, Abt. Physikalische Chemie, 14195 Berlin, Germany

The surface chemistry of alumina is important in fields such as heterogeneous catalysis, geo- and environmental chemistry. Often these surfaces are not merely passive participants in interfacial chemistry: reaction between species present in adjoining phases at the surface can lead to correlated changes in surface structure and reactivity. While much important chemistry at alumina surfaces occurs in ambient conditions, simultaneously probing surface reconstruction and reactivity in these environments is challenging. In this study, we employ surface specific vibrational sum frequency (VSF) spectroscopy to characterize the reaction of water with the α -Al₂O₃(0001) surface in ambient conditions. Starting with a Al-terminated surface prepared under UHV in the absence of water, we use the evolution of the interfacial OH stretch spectral response to track the presence of dissociatively adsorbed water and that of the surface phonon spectral response to track the accompanying surface reconstruction. All changes in spectral observables are clearly shown to be reversible on heating. We demonstrate that the observed phonon modes are surface specific by their frequencies and symmetry and assign them based on comparison to computation.

O 50.3 Wed 11:00 WIL A317

Water Adsorption at the Tetrahedral Titania Surface Layer of SrTiO₃(110)-(4×1): An STM and Photoemission Study. — ●STEFAN GERHOLD¹, ZHIMING WANG¹, XIANFENG HAO¹, ZBYNEK NOVOTNY¹, CESARE FRANCHINI², EAMON MCDERMOTT³, KARINA SCHULTE⁴, MICHAEL SCHMID¹, and ULRIKE DIEBOLD¹ — ¹Institute of Applied Physics, Vienna University of Technology, Austria — ²Center for Computational Materials Science, University of Vienna, Austria — ³Institute of Materials Chemistry, Vienna University of Technology, Austria — ⁴MAX IV Laboratory, Lund University, Sweden

The interaction of water with oxide surfaces is of great interest for both fundamental sciences and applications. We present a combined theoretical [density functional theory (DFT)] and experimental [Scanning Tunneling Microscopy (STM), photoemission spectroscopy (PES)] study of water interaction with the two-dimensional titania overlayer that terminates the SrTiO₃(110)-(4 × 1) surface and consists of TiO₄ tetrahedra. STM, core-level and valence band PES show that H₂O neither adsorbs nor dissociates on the stoichiometric surface at room temperature, while it dissociates at oxygen vacancies. This is in agreement with DFT calculations, which show that the energy barriers for water dissociation on the stoichiometric and reduced surfaces

are 1.7 and 0.9 eV, respectively. We propose that two-dimensional tetrahedrally coordinated titania overlayers are generally hydrophobic. In addition, enhanced reactivity due to deposited Sr adatoms is discussed. This work was supported by the Austrian Science Fund (FWF, project F45).

O 50.4 Wed 11:15 WIL A317

Sub-Monolayer Water Adsorption on Alkaline Earth Metal Oxide Surfaces: A First-Principles Study — ●XUNHUA ZHAO, SASWATA BHATTACHARYA, LUCA M. GHIRINGHELLI, SERGEY V. LEVCHENKO, and MATTHIAS SCHEFFLER — Fritz-Haber-Institut der Max-Planck-Gesellschaft

In the present work, we predict atomic structures of adsorbed complexes that should appear on alkaline earth metal oxide (001) terraces in thermodynamic equilibrium with water and oxygen gases. Density-functional theory with the hybrid exchange-correlation functional HSE06 combined with the self-consistent many-body dispersion approach [1] is used to calculate total energies. The choice of this functional is validated by renormalized second-order perturbation theory [2]. An unbiased search for global minima of H_xO_y adsorption is performed using first-principles genetic algorithm for periodic models. x and y as a function of temperature and pressure are determined using *ab initio* atomistic thermodynamics. We find a range of H₂O chemical potentials where one-dimensional adsorbed water structures are thermodynamically stable on CaO(001). On MgO(001) and SrO(001), such structures are not found. The formation of the one-dimensional structures is explained by the balance between water-water and water-surface interactions.—[1] A. Tkatchenko, R. A. DiStasio, Jr., R. Car and M. Scheffler, Phys. Rev. Lett. **108**, 236402 (2012); [2] X. Ren, P. Rinke, G. E. Scuseria, M. Scheffler, Phys. Rev. B **88**, 035120, (2013).

O 50.5 Wed 11:30 WIL A317

A first principles study of halogenated adsorbates on ice — ●MICHEL BOCKSTEDTE and PHILIPP AUBURGER — Lst. Theor. Festkörperphysik, Universität Erlangen-Nürnberg, 91058 Erlangen

Fluid water, water clusters, and water ice possess the fascinating ability to solvate ions and electrons. On ice, the solvated electron facilitates electron-induced reactions of adsorbates via dissociative electron attachment (DEA) that for instance take place in atmospheric chemistry. The simultaneous interaction of the electron with the molecule and the ice surface enhances the cross section as compared with the gas phase. The current understanding of the physical mechanisms at work is rather incomplete, in particular a picture on the molecular scale is missing. Here we investigated the interaction of halogenated hydrocarbons and HCl with prototypical electron traps at the ice surface in the framework of density functional theory (DFT), hybrid DFT, and many body perturbation theory. For the hydrocarbons clear chemical trends across the halogen series, F, Cl, and Br, are found concerning favorable adsorption sites. Depending on the halogen and the electron trap, electron affinity of antibonding adsorbate levels is enhanced. A quenching of electron traps by HCl or Cl⁻, as form during the DEA, is discussed.

O 50.6 Wed 11:45 WIL A317

impact of the vapour pressure of water on the equilibrium shape of zinc oxide nanoparticles: An ab-initio study — ●STEPHANE KENMOE, MIRA TODOROVA, P. ULRICH BIEDERMANN, and JOERG NEUGEBAUER — Max-Planck-Institut für Eisenforschung GmbH, Max-Planck-Straße 1,40237 Düsseldorf ,Germany

ZnO powders and nanoparticles are used as catalysts and have potential applications in gas-sensing and solar energy conversion. A fundamental understanding of the exposed crystal facets, their surface chemistry and stability as function of environmental conditions is essential for rational design and improvement of synthesis and properties. Using density-functional theory calculations we study the adsorption of water on the non-polar low-index (10-10) and (11-20) surfaces of ZnO. Observing both molecular and dissociative H₂O adsorption, we analyse the contributions of water-surface and water-water interactions to the energies of the stable structure. Based on this insight we compute and analyse the impact of water adsorption on surface energies and the equilibrium shape of nanoparticles in a humid environment

O 50.7 Wed 12:00 WIL A317

The role of surfaces and interfaces in the phase separating Li intercalation material $\text{Li}_x\text{FeSiO}_4$ — ●NICOLAS G. HÖRMANN^{1,2} and AXEL GROSS^{1,2} — ¹Helmholtz Institute Ulm (HIU) Electrochemical Energy Storage, Albert-Einstein-Allee 11, 89069 Ulm — ²Universität Ulm, Institut für Theoretische Chemie, Albert-Einstein-Allee 11, 89069 Ulm

Phase separating behavior of electrode materials of secondary Li battery materials is typically assumed to cause low rate capability due to a nucleation and growth process. Nevertheless, cathodes made of LiFePO_4 can show fast charging rates if they consist of nanoscale particles. Several mechanisms have been proposed for this observation, most of which are related to finite size effects such as interfaces or strain [1]. It is, however, still under debate whether e.g. the alignment of phase interfaces is mainly driven by "lattice" or "chemical mismatch" and how the actual interface looks like.

We present ab-initio studies tackling related issues for the promising material $\text{Li}_x\text{FeSiO}_4$ [2] based on density functional theory (DFT). In particular, Li binding energies for different chemical environments - in bulk and near surfaces or interfaces - are determined. Effects of strain are considered by decomposing the interface energy into contributions due to coherency strain and change of the chemical environment. Subtleties such as charge localisation are analysed as well.

[1] Malik, R et al., *J. Electrochem. Soc.*, **160**, 5, A3179-A3197, **2013**

[2] Hörmann, N.G. and Groß, A., *J. Solid State Electrochem.*, accept.

O 50.8 Wed 12:15 WIL A317

In-situ x-ray investigation of solid oxide fuel cell model electrodes — ●SERGEY VOLKOV^{1,2}, MARKUS KUBICEK³, VEDRAN VONK¹, DIRK FRANZ^{1,2}, JÜRGEN FLEIG³, and ANDREAS STIERLE^{1,2} — ¹Deutsches Elektronen-Synchrotron DESY, 22603 Hamburg, Germany — ²Fachbereich Physik, Universität Hamburg, 20355 Hamburg, Germany — ³Institut für Chemische Technologien und Analytik, Technische Universität Wien, 1060 Vienna, Austria

The performance of high temperature solid oxide fuel cell (SOFC) electrodes depends strongly on the structure and composition of yttria stabilized zirconia (YSZ) surfaces. In addition, on the fuel cell cathode side the interface between the perovskite electrode and the YSZ electrolyte plays an important role during the oxygen incorporation process. Our studies focus on the cathode side of SOFCs, which is mimicked by the YSZ (100) surface, as electrolyte, and pulsed laser deposition grown $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$, as electrode, were studied. In order to track structural changes in-situ surface x-ray diffraction experiments were performed at the ESRF, beamline ID03. A special x-ray diffraction chamber was developed, which allows contacting the electrode and applying a controlled voltage across the electrolyte. Anomalous scattering at the Y and Zr K-edges was used to enhance the scattering contrast. The analysis of the crystal truncation rod data has revealed a noticeable change in intensity depending on different oxygen pressure, temperature and voltage conditions. These intensity changes mostly refer to the changes in the composition and vacancy concentration below the electrode, what will be presented in detail.

O 50.9 Wed 12:30 WIL A317

Structural, electronic and thermodynamic properties of $\text{YBaCo}_4\text{O}_{7+\delta}$ from DFT+U calculations — ●JAKUB GOCLON and BERND MEYER — Interdisciplinary Center for Molecular Materials and Computer-Chemistry-Center, FAU Erlangen-Nürnberg

In the past decade, one of the main goals in solid oxide fuel cell (SOFC) research was to develop intermediate-temperature SOFCs (IT-SOFCs) operating at 600–800 °C. Recently, a new family of layered cobalt oxide compounds based on the YBaCo_4O_7 structure has been proposed for application as cathode material in IT-SOFCs. The compounds are able to adsorb in a reversible way up to $\delta=1.5$ oxygen atoms per unit formula, both at low and high temperatures.

We performed DFT+U calculations for different YBaCo_4O_7 bulk structures based on structural models proposed in the literature. We then focused on the bulk properties of the oxygen-rich phases after oxygen incorporation, searching for the most favorable positions of the additional oxygen atoms. In the second part of this work we determined the most stable termination (structure, chemical composition) of the $\text{YBaCo}_4\text{O}_7(001)$ surface based on thermodynamic analysis. Analogical calculations were performed for oxygen adsorption on $\text{YBaCo}_4\text{O}_8(001)$. The local electronic structure and the local distribution of the cobalt cations in close vicinity of the additional oxygen atoms has been carefully analyzed and will be discussed. In addition, results from corresponding calculations for the bulk and low-index surfaces of Co_3O_4 will be shown as reference.

O 50.10 Wed 12:45 WIL A317

Ab-initio study of the wurtzite terminated rocksalt $\text{CoO}(111)$ polar surface: Facing a DFT bulk dilemma — FLORIAN MITTENDORFER and ●JOSEF REDINGER — Inst. f. Applied Physics, Vienna University of Technology, Vienna, Austria

Evidenced by LEED, the polar (111) surface of CoO is terminated by a wurtzite like top Co-O bilayer, which from experimental and theoretical evidence is believed to become metallic to compensate polarity [1]. An ab-initio DFT investigation of such a mechanism is not only complicated by the polarity of the surface, but also by the correlated nature of the Co 3d electrons, which have to be treated by PBE+U type approaches or by employing hybrid functionals like HSE06. Using the VASP code slabs of various thickness have been treated and the preference for a wurtzite like termination could be established. However, this outcome should be taken with caution, since already for the CoO bulk system PBE+U and HSE06 find a preference for the wurtzite (or zincblende) structure over the experimental slightly distorted rocksalt structure, similar to the case of MnO [2]. We present an analysis of our HSE06 and PBE+U results also for different double counting corrections and conclude that only for unreasonably high values of U the correct bulk phase order can be established.

[1] K Heinz and L Hammer, *J. Phys.: Condens. Matter* **25**, 173001 (2013 Review)

[2] A. Schrön, C. Rödl, and F. Bechstedt, *Phys. Rev. B* **82**, 165109 (2010)