O 18: Focus Session: Frontiers in Reducible Oxide Surface Science II

Time: Monday 15:00–18:15 Location: HE 101

Invited Talk O 18.1 Mon 15:00 HE 101

Surface chemistry of ruthenates — •Ulrike Diebold[1], Daniel Halwidl[1], Wernfried Mayer-Schmözer[1,2], Martin Setvin[1], Florian Mittendorfer[1,2], Josef Redinger[1,2], and Michael Schmid[1] — [1]Institute of Applied Physics, TU Wien, Vienna, Austria — [2]Center for Computational Materials Science, TU Wien, Vienna, Austria

Ternary oxides with a perovskite-type crystal structure are of increasing interest in energy-related applications such as solid oxide fuel/electrolysis cells and (photo-) electrocatalysis. Surface science studies can provide an atomic-scale understanding of relevant fundamental processes, but appropriate model systems with a well-defined surface structure are rare. Here we report our results on the cleaved CaO and SrO-terminated surfaces of the Ruddlesden-Popper materials $Ca_3Ru_2O_7$ and $Sr_3Ru_2O_7$. Surfaces can easily be prepared by exfoliation in UHV, which provides large, defect-free terraces that are ideal for atomic-scale investigations. We used STM and nc-AFM in combination with XPS and DFT to investigate the adsorption of H_2O [1,2] and O_2. We find that results on the related binary oxides give a good first guide for the adsorption behaviour, and that the tilting and rotation of the materials' octahedra strongly influence the ordering of overlayers. [1] D. Halwidl, et al. Nature Mater. 15 (2016) 450. [2] D. Halwidl, et al., Nature Comm. 8 (2017) 23.

Invited Talk O 18.2 Mon 15:30 HE 101

Multiscale modelling of metal oxide interfaces and nanoparticles — •Kersti Hermansson — Department of Chemistry-Ångström Laboratory, Uppsala University, Uppsala (Sweden)

In the scientific literature, a full arsenal of experimental methods are being used to help characterize redox-active metal oxide surfaces and interfaces such interfaces. At the same time, the number of theoretical studies steadily increases, providing mechanistic information at a detail that is hard to beat by experiment. Here the major challenges are (i) how to build a structural model that captures the complexity and imperfections of the real system at hand, and (ii) how to find interaction models that are good enough.

I will discuss some efforts in the development of multiscale modelling approaches for surfaces and interfaces of metal oxides (e.g. CeO2, ZnO, MgO) with and without interacting molecules (e.g. water), including combinations of DFT, tight-binding-DFT, and reactive force-field simulations. Can calculations without explicit electrons really be used instead of quantum-mechanical calculations when the electrons are so closely coupled to the functionality as they are for redox-active metal oxides?

I will also inform about the European Materials Modelling Council (https://emmc.info/), and our efforts to promote the use of materials modelling in industry and the quality of the modelling results; the EMMC is open to everyone interested.

O 18.3 Mon 16:00 HE 101

MnO(001) thin films on Au(111) — •Christoph Möller and Niklas Nilius — Institute of Physics, Carl von Ossietzky University, 26111 Oldenburg, Germany

A variety of oxidation states and a high reactivity make manganese oxide a promising material for applications in heterogeneous catalysis. Using STM and XPS, we have probed the structural and electronic properties of ultrathin MnO films deposited on the Au(111) surface. At low coverage, the oxide crystallizes into regular islands with up to 50 nm diameter. Their surface exposes either a 2x2 reconstruction or various stripe phases, depending on the island height. The MnO band gap was determined to 2.8 eV, while the first field-emission resonance occurs at 3 eV, indicating a drastic decrease of the gold work function upon MnO deposition. With increasing thickness, the oxide grows into a polycrystalline, non-conductive film, whose stoichiometry increasingly deviates from MnO.

O 18.4 Mon 16:15 HE 101

Electrochemical Characterization of Reducible Oxide Surfaces — •Ladislav Kavan — J. Heyrovsky Institute of Physical Chemistry, Dolejskova 3, 182 23 Prague, Czech Republic

The electronic band structure of semiconducting oxides (TiO2 or SnO2) is relevant to photo/electrochemistry and energy applications. The position of conduction band (CB) edge controls reductive photocatalytic reactions (e.g. hydrogen formation from water or CO2-reduction to solar fuels), Li-insertion electrochemistry, recombination blocking in perovskite solar cell and open-circuit potential of dye-sensitized solar cell. Recently, the reduction of CO2 to methane attracted attention for investigation of Mars atmosphere. The ALD-grown TiO2 and SnO2 layers are useful for electron selective contacts in perovskite solar cells. However, there is a considerable controversy about the position of CB in TiO2 (anatase, rutile, including the crystals with distinguished facets). The conflict is rationalized by considering the adsorption of OH- and H+ ions from the electrolyte solution on the electrode surface [5]. The facet specific electrochemistry of water splitting on TiO2 is addressing both the CB position and the electrocatalytic activity of the relevant crystal face. Doping of SnO2 by F- or Sb5+ provides the quasi-metallic (degenerate semiconductor) material, but little is known about similar doping-induced behavior of TiO2. We have recently found purely metal-like electrochemical properties of Ta-doped, optically transparent thin films of TiO2 (anatase) made by pulsed-laser deposition.

15 min. break

O 18.5 Mon 16:45 HE 101

Mixed nano-oxides: microscopic mechanisms behind their structural and electronic characteristics — •Claudine Noguera, Jacek Goniakowski, and Ha-Linh T. Le — Institut des Nanosciences de Paris CNRS and Université Pierre et Marie Curie, Paris, France

Doped and especially mixed (ternary) oxides represent promising materials with many potential applications in spintronics, materials for energy and environment, etc. Indeed, combining two cations of different size and/or electronegativity is expected to allow modulating the structural and electronic properties of the resulting alloy. However, there are presently large gaps in our understanding of the formation and properties of such mixed-oxides, especially at the nanoscale.

In this context, considering the technological importance of titanium and other transition metal oxides, we have focused on mixed transition metal oxides of XYO3 stoichiometry, within two architectures displaying low dimensional effects. Relying on first principles simulations, we analyze and compare the electronic properties of Ti2O3/X2O3 heterostructures and TiXO3 honeycomb monolayers deposited on an Au(111) substrate (X=V, Cr, Fe) and we highlight the driving forces toward mixing.

O 18.6 Mon 17:00 HE 101

Improving Adhesion at weakly-interacting metal/oxide interfaces — Ha-Linh T. Le[1], •Jacek Goniakowski[1], Claudine Noguera[1], Alexey Koltsov[2], and Jean-Michel Mataigne[2] — [1]Institut des Nanosciences de Paris, CNRS, 75005 Paris — [2]ArcelorMittal Maizières Research, 57280, Maizières lès Metz

The control of adhesion at metal/oxide interfaces is of a key importance for a large variety of applications, involving either 2D or 3D metal deposits on oxide substrates. More recently it has also been addressed in the context of anti-corrosive zinc coating of advanced high strength steels. Indeed, selective oxidation and surface segregation of strengthening elements, such as Al, may lead to a formation of an oxide film on the steel surface which dramatically reduces zinc adhesion.

In this context, we report a thorough ab initio and Monte Carlo study of adhesion at a zinc/alpha-alumina(0001) interface. We find that the interaction of zinc with bare non-polar terminations of alumina is indeed weak but that it can be improved by either surface pre-hydroxylation or by metallic buffers. While the performance of single-component buffers may degrade upon oxidation, that of realistic multi-component ones (e.g. stainless steel) remain satisfactory under a large span of oxidizing conditions due to the separation of metal and oxide components in the buffer and the suppression of the weak oxide/zinc and moderately strong alumina/metal interfaces. More generally, thanks to the possibility of selective oxidation and component segregation, multi-component buffers appear as promising solutions for improving adhesion at weakly interacting metal/oxide interfaces.

O 18.7 Mon 17:15 HE 101

A DFT study of the (011) and (110) surfaces of rutile VO_2 — •Florian Mittendorfer[1,2], Jakub Planer[1,2], Wernfried Mayr-Schmölzer[1,2], and Josef Redinger[1,2] — [1]Center for Computational Materials Science, TU Wien, Vienna, Austria — [2]Institute of Applied Physics, TU Wien, Vienna, Austria

Vanadium dioxide is a promising material with potential applications for fast electronic or optical switching. These applications are related to a structural and electronic transition from monoclinic to a rutile phase at 340K. Our results show that standard DFT (PBE) approaches give a reasonable description of the metallic rutile phase, while more advanced approaches, such as meta-GGA+U (SCAN) or hybrid functionals are needed to obtain the correct band gap of ∼0.7 eV for the monoclinic phase. In addition, I will discuss the stability of various terminations for the rutile VO_2(011) and (110) surface and compare them to recent experimental STM data.

O 18.8 Mon 17:30 HE 101

identification of active sites for water oxidation with extremely low overpotential on multicomponent spinel $\mathrm{Co_xNi_{1-x}Fe_2O_4}$(001) surfaces — •hamidreza hajiyani and rossitza pentcheva — Department of Physics and Center for Nanointegration (CENIDE), University of Duisburg-Essen

Using density functional theory calculations with an on-site Hubbard term (DFT+U) we explore the effect of cation substitution and surface termination on the performance of $\mathrm{Co}_x\mathrm{Ni}_{1-x}\mathrm{Fe_2O_4}$(001) as an anode material in the oxygen evolution reaction (OER). To identify the active sites, we investigated the performance of different reaction sites (Fe, Co, Ni and O) at the B-layer with 5-fold coordinated Co/Ni and with an additional 0.5 ML Fe at the (001) spinel surface. Our results indicate that mixing of Co and Ni in equal concentrations (x=0.5) lowers the overpotential over the end members for the majority of reaction sites. Comparison of the overpotentials indicates that surface Co cations on the 0.5 ML Fe termination are the most active sites with the lowest theoretically reported overpotential of 0.30 V. We have shown that this beneficial performance correlates with the modification of the binding energies of intermediate species to the surface. Analysis of the electronic properties and spin densities indicate that the oxidation state of Fe changes from +3 in the bulk to +2 on the 0.5 ML Fe surface, while Co and Ni cations at this termination preserve the bulk oxidation states of +2. Funding by the DFG within SPP1613 is gratefully acknowledged.

O 18.9 Mon 17:45 HE 101

Activation of O_2 adsorbed on $\mathrm{(Ca,Sr)_3Ru_2O_7}$ surfaces: a DFT study — •Wernfried Mayr-Schmölzer[1,2], Daniel Halwidl[2], Florian Mittendorfer[1,2], Ulrike Diebold[2], Josef Redinger[1,2], and Michael Schmid[2] — [1]Center for Computational Materials Science, TU Wien, Vienna, Austria — [2]Institute of Applied Physics, TU Wien, Vienna, Austria

Transition metal perovskite oxides are promising materials for a wide range of applications as diverse as fuel cells and catalysts. Surprisingly not much work has been done on their surface properties regarding oxygen transport and redox properties. Recently the adsorption of O_2 as a charged molecule has been predicted by DFT on defective $SrTiO_3$[1], and La_2NiO_4[2] surfaces. Here, we present a theoretical analysis including many-electron methods of O_2 adsorption on defect-free rocksalt-like SrO and CaO surfaces of Ruddelsden-Popper type $Sr_3Ru_2O_7$(001) and $Ca_3Ru_2O_7$(001). We observe the adsorption of molecular O_2 as a charged superoxo species on both defect-free materials. The DFT adsorption energies are high, up to 1.4 eV on both oxides, which we attribute to the overestimation of the electron affinity of O_2 by standard semi-local functionals, making the charging of the O_2 adsorbate too easy. Using beyond-DFT methods such as hybrid (HSE) functionals and advanced many-electron methods (RPA, G_0W_0) to properly describe the adsorption properties, we calculate an RPA adsorption energy of 0.72 eV in very good agreement with experimental values.

[1] Staykov, A., Chemistry of Materials, 27(24), 8273-8281.

[2] Akbay, T., J. Mater. Chem. A, 4(34), 13113-13124.

O 18.10 Mon 18:00 HE 101

In-situ studies of the reduction of ultrathin $BaTiO_3$ on Pt(111) — •Jonas Pantzer[1], Stefan Förster[1], Jan Ingo Flege[2], Jens Falta[2], and Wolf Widdra[1,3] — [1]Martin-Luther-Universität Halle-Wittenberg, 06120 Halle, Germany — [2]Universität Bremen, 28359 Bremen, Germany — [3]Max-Planck-Institute for Microstructure Physics, 06120 Halle, Germany

Reduced ultrathin films derived from the prototypical perovskite oxides $BaTiO_3$ and $SrTiO_3$ have recently attracted attention due to the their transformation into two-dimensional oxide quasicrystals (OQCs) on a hexagonal metal support [1]. For $BaTiO_x$ on Pt(111), the OQC formation proceeds in two steps via an amorphous two-dimensional wetting layer[2].

Here we report on in-situ low energy electron microscopy (LEEM) studies of morphological changes starting from stoichiometric $BaTiO_3$(111) islands on Pt(111). At 1350 K the genesis and movement of a diffusion front of an amorphous two-dimensional wetting layer on the bare platinum is observed, which starts at the $BaTiO_3$(111)-islands. Subsequently, a second, much slower, diffusion front is observed at the edges of the $BaTiO_3$(111)-islands, indicating a crystallisation of the wetting layer into differently oriented $BaTiO_3$(111).

[1] Förster et al., Nature 502, 215 (2013)

[2] Förster et al. Ann. Phys. 529, 1600250 (2017)