

O 24: Focus Session: Structure and Chemistry of Metal-Oxide Surfaces I

Time: Tuesday 10:30–13:15

Location: MA 005

Invited Talk

O 24.1 Tue 10:30 MA 005

Modelling Photo-electrochemistry on Oxide Surfaces — ●HARALD OBERHOFER — Technical University Munich, Garching, Germany

The role computer modelling plays today in understanding and optimising catalysts for photo-electrochemical reactions is undisputed. Yet, state of the art simulation approaches tend to rely on a number of assumptions and simplifications which—especially on oxide surfaces—may not be fully justified. For example, simulation of the all-important water oxidation reaction is mainly based on idealised surfaces and the computational hydrogen electrode (CHE) approach, which evaluates the thermodynamic feasibility of a catalyst looking at pathways where each hydrogen abstraction is coupled to the removal of one electron (PCET). The precise reactive site of the catalyst is thereby viewed as irrelevant, based on the premise of idealised surfaces. Yet, specifically on semi-conducting oxides both the assumption of PCET and of pristine, defect-free surfaces are not necessarily fulfilled.

In my presentation I will outline some of the steps necessary to augment theoretical approaches that so far have been geared towards the simulation of metal surfaces under ideal conditions to oxides under realistic conditions. There, the focus will lie on the nature of the reactive site—considering e.g. defects able to attract reaction-driving localised charge carriers—and the appearance of free energy barriers and their influence on reaction kinetics. Finally, for a realistic model of photo-electrochemical reactions occurring on the solid-liquid interface I will examine the role the solvent itself.

O 24.2 Tue 11:00 MA 005

Vanadium dioxide as high work function electrode — ●RONGBIN WANG^{1,2}, KEKE FU¹, TAKAYOSHI KATASE^{3,4}, HIROMICHI OHTA³, STEFFEN DUHM¹, and NORBERT KOCH^{1,2} — ¹Institute of Functional Nano & Soft Materials (FUNSOM), Soochow University, China — ²Institut für Physik, Humboldt-Universität zu Berlin, Germany — ³Research Institute for Electronic Science, Hokkaido University, Japan — ⁴Laboratory for Materials and Structures, Tokyo Institute of Technology, Japan

VO₂ is a rather unique metal oxide as it exhibits a first-order metal-insulator (MI) transition from an insulating phase with monoclinic structure to a metallic phase with tetragonal rutile structure near 340K. The evolution of valence bands and core levels of VO₂ thin films upon sputtering and annealing with or without residual O₂ atmosphere was monitored by ultraviolet and X-ray photoemission spectroscopy. Sputtering and subsequent annealing in vacuum introduced lower oxidation state V species, leading to an increased density of V 3d derived bands close to the Fermi level. However, annealing under O₂ results in stoichiometric VO₂ with a high work function of up to 6.7 eV. In addition, the temperature dependent photoemission results illustrate the electronic structure evolution of VO₂ during the metal-insulator transition.

O 24.3 Tue 11:15 MA 005

Atomic-scale structure of the Hematite α -Fe₂O₃(1-102) surface — ●FLORIAN KRAUSHOFER, ZDENEK JAKUB, MAGDALENA BICHLER, JAN HULVA, MARTIN SETVIN, MICHAEL SCHMID, ULRIKE DIEBOLD, PETER BLAHA, and GARETH S. PARKINSON — Vienna University of Technology, Vienna, Austria

Hematite (α -Fe₂O₃) is a promising material for technological applications due to its abundance, low cost and chemical stability. Its 2.2 eV bandgap makes it potentially ideal as a photoanode for photoelectrochemical water splitting, but performance is hampered by slow reaction kinetics and the need for a significant overpotential.

To date, most surface science studies of α -Fe₂O₃ have focused on the (0001) facet, but preparing a stoichiometric surface under UHV conditions has proven problematic. Some authors have investigated the equally relevant (1-102) surface, and reported that a (1x1) and a reduced (2x1) termination can be reversibly prepared. Several models have been proposed for the (2x1) reconstruction, but as of now no scanning probe data exists to support or refute them.

Here we present an atomic-scale scanning tunnelling microscopy (STM) study of the (1x1) and (2x1) surfaces of α -Fe₂O₃ (1-102). The data acquired for the (1x1) termination support a bulk termination model, as predicted by previous publications, but STM and nc-AFM

images of the (2x1) reconstruction are inconsistent with previously proposed models. We propose a new model based on ordered oxygen vacancies, the plausibility of which is confirmed by density functional theory (DFT) results.

O 24.4 Tue 11:30 MA 005

The (O12) surfaces of hematite and their interactions with water - a DFT study — ●MAGDALENA BICHLER¹, FLORIAN KRAUSHOFER², ZDENEK JAKUB², GARETH PARKINSON², and PETER BLAHA¹ — ¹Institute of Materials Chemistry, TU Wien — ²Institute of Applied Physics, TU Wien

Hematite (α -Fe₂O₃) is abundant all over the world and might be used for several applications, including photo electrochemical water splitting.

We focus our study on the (1-102) surface of hematite (R-cut). For this surface two different terminations exist. On the one hand, there is a (1x1) bulk terminated stoichiometric surface, but at low O₂ pressure, a (2x1) reconstruction with missing oxygen atoms is formed.^{1,2}

We carried out ab initio calculations by using the WIEN2k code³. Based on our DFT calculations, we present a new model of the (2x1) reconstruction, which is energetically more stable than the one that has been proposed so far⁴ and agrees well with experiment (including STM simulations).

We also present our results of water adsorption on both surface terminations, including a (1x3) superstructure for water on the bulk terminated surface and discuss these data together with experimental findings.

¹ M. A. Henderson et al., Surf. Sci. 1998, 417, 66-81

² F. Kraushofer et al., JPCC, 2017, accepted

³ <http://www.wien2k.at>

⁴ M. A. Henderson, Surf. Sci. 2010, 604 1197-1201

Invited Talk

O 24.5 Tue 11:45 MA 005

Potential-Specific Structure at the Hematite-Electrolyte Interface — MARTIN E. MCBRIARTY¹, JOANNE E. STUBBS², PETER J. ENG², GUIDO VON RUDORFF³, JOCHEM BLUMBERGER³, and ●KEVIN M. ROSSO¹ — ¹Pacific Northwest National Laboratory, Richland, WA, USA — ²Argonne National Laboratory, Lemont, IL, USA — ³University College London, Bloomsbury, London, England, UK

The structure of transition metal oxide interfaces with aqueous electrolyte regulates the reactions fundamental to (photo)electrochemical energy conversion and electrode degradation. Measurements that provide atomically precise structural models of ion and solvent arrangements are essential, but most rely on static conditions not operating conditions far from equilibrium. Using a novel cell, the structure of the hematite (α -Fe₂O₃) (1-102)-electrolyte interface was measured under controlled electrochemical bias using synchrotron crystal truncation rod X-ray scattering. At increasingly cathodic potentials, charge-compensating protonation of surface oxygen groups increases the coverage of bound water while adjacent water layers displace outwardly and became disordered. Returning to open circuit potential leaves the surface in a persistent metastable state. Thus, the flux of current and ions across the interface is regulated by multiple electrolyte layers whose structure changes in the applied potential. The study reveals the complex environment underlying the simplified electrical double layer models used to interpret electrochemical measurements and emphasizes the importance of condition specific structural characterization for properly understanding catalytic processes at these interfaces.

Invited Talk

O 24.6 Tue 12:15 MA 005

Photoelectrochemistry on hematite: a first-principles view — ●ANDERS HELLMAN — Department of Physics and the Competence Centre for Catalysis, Chalmers University of Technology, Sweden

Fe₂O₃ is an abundant n-type semiconductor that has excellent stability in neutral and alkaline electrolytes, but so far the reported solar-to-hydrogen conversion efficiency is far from the theoretical limit [1]. Major factors hampering the performance of Fe₂O₃ are high recombination rate and poor oxygen evolution kinetics.

In a recent publication, we showed that joining different oxides provide the possibility of control the recombination rate [2]. The mechanism relies on the formation of dipole-like electric fields at the interface which, depending on the field direction, attract or repel minority car-

riers from the interface. Here we investigate the built-in electric field generated at the interfaces of using first-principles methods. The results show how electronic band alignment and defects doping at the interface determine the direction and strength of the built-in field. We also comment how these can affect the oxygen evolution kinetics via the overpotential. Our understanding of the oxide nanostructures can be employed for designing and improving the performance of water-splitting photoelectrodes.

[1]: D. K. Bora, A. Braun, E. C. Constable, *Energy Environ. Sci.*, 2013, 6, 407. [2]: B. Iandolo, B. Wickman, E. Svensson, D. Paulsson, and A. Hellman, *Nano Lett.*, 2016, 16, 2381.

O 24.7 Tue 12:45 MA 005

Coverage-dependent Water Agglomerates on $\text{Fe}_3\text{O}_4(001)$: Insights from Experiments — •ZDENEK JAKUB¹, MATTHIAS MEIER^{1,2}, JAN HULVA¹, JIRI PAVELEC¹, MARTIN SETVIN¹, MICHAEL SCHMID¹, ULRIKE DIEBOLD¹, CESARE FRANCHINI², and GARETH S. PARKINSON¹ — ¹Institute of Applied Physics, TU Vienna, Austria — ²Faculty of Physics and Center for Computational Materials Science, University of Vienna, Austria

The interaction between iron oxides and water plays a key role in many natural and technological processes. Recent water adsorption studies have found significant complexity on metal oxides, with reports of mixed-mode adsorption and hydrogen bonding. Here we present a multi-technique study of water adsorption on $\text{Fe}_3\text{O}_4(001)$ surface. Quantitative temperature programmed desorption (TPD) and X-ray Photoelectron Spectroscopy (XPS) experiments reveal four partially dissociated phases in the submonolayer regime, corresponding to coverages of 9, 8, 6 and 3 molecules per surface unit cell. These are investigated by non-contact atomic force microscopy (nc-AFM) with tip functionalized by CO molecule. This approach is highly convenient to study water agglomerates on metal oxide surfaces, and we

can clearly demonstrate the existence of dimers and trimers, and a complex hydrogen-bonded network at lower coverage. These images can be further interpreted by DFT-based calculations, which will be presented in a separate talk.

O 24.8 Tue 13:00 MA 005

Transition metal clusters on tetragonal and monoclinic zirconia (ZrO_2) surfaces — •ZHIYU ZOU, PETER LACKNER, SABRINA MAYR, ULRIKE DIEBOLD, and MICHAEL SCHMID — Institute of Applied Physics, TU Wien, 1040, Vienna, Austria

Zirconia (ZrO_2) is widely used in heterogeneous catalysis, gas sensors and solid oxide fuel cells, where it is interfaced to transition metals. However, most investigations of ZrO_2 /metal systems focus on powder samples, where surface-science techniques of high spatial (e.g. STM) or energetic (e.g. XPS) resolution are limited by the morphology and insulating nature of the samples.

We have developed a method to prepare clean, atomically flat ZrO_2 films (5-6 trilayers) with a precise control of phases (tetragonal or monoclinic) on Rh(111). The films are thin enough for STM and XPS measurements, yet show bulk-like crystallography. Transition metal (Rh, Fe, Au, Ag) clusters were deposited on both phases of ZrO_2 . STM and XPS indicate Ag has the weakest interaction with the substrates, and Fe the strongest. In comparison with ultrathin (single-trilayer) ZrO_2 films on Pt_3Zr and $\text{Pd}_3\text{Zr}[1]$, here Fe and Au are less affected by the underlying metallic substrate, resulting in higher density of Fe clusters and 3D cluster growth of Au. On tetragonal films, XPS shows small shifts of Zr3d and O1s core-level peaks; they shift much more on monoclinic films. Our work indicates the possibility of tailoring the electronic properties of transition metals by manipulating oxide support thickness and phases.

[1] J. J. Choi, et al. *J. Phys. Chem. C* 2016, 120, 9920