

O 49: Oxide Surfaces 1

Time: Wednesday 15:00–17:30

Location: S053

O 49.1 Wed 15:00 S053

Revised Chen's derivative rule for efficient simulations of scanning tunneling microscopy: New results on surface oxides — ●KRISZTIÁN PALOTÁS¹, YUNJAE LEE², TAEHUN LEE², and ALOYSIUS SOON² — ¹Wigner Research Center for Physics, Budapest, Hungary — ²Yonsei University, Seoul, Republic of Korea

Advanced simulation tools of scanning tunneling microscopy (STM) are vital for the proper understanding of various physical and chemical processes at material surfaces. For this reason Chen's derivative rule for electron tunneling has been revised [1] to build a computationally efficient STM simulation tool, based on ab initio electronic structure. This STM simulation method enables (i) the weighting of tunneling matrix elements of arbitrary tip-orbital composition, (ii) arbitrary tip geometrical orientations to mimic asymmetric tip-sample relations, and (iii) the possibility of quantitative analysis of tip-orbital interference contributions to the tunneling current. Recently, this method has been applied to diverse complex surface oxides [2,3,4], where a better agreement with STM experiments has been achieved than obtained with the Tersoff-Hamann (spherical tip orbital) model.

[1] G. Mándi and K. Palotás, *Phys. Rev. B* 91, 165406 (2015). [2] T. Lee et al., *Nanoscale* 11, 6023 (2019). [3] T. T. Ly et al., *J. Phys. Chem. C* 123, 12716 (2019). [4] Y.-J. Lee et al., *Appl. Surf. Sci.* 562, 150148 (2021).

O 49.2 Wed 15:15 S053

Hydrogen Atom Scattering at Aluminium Oxide — ●MARTIN LIEBETRAU and JÖRG BEHLER — Universität Göttingen, Institut für Physikalische Chemie, Theoretische Chemie, Tammannstraße 6, 37077 Göttingen, Germany

The adsorption of atomic hydrogen is important in many fields, from heterogeneous catalysis via hydrogen storage to nuclear fusion. Here, we report molecular dynamics simulations of high-energy hydrogen atom scattering at the α -Al₂O₃(0001) surface. Employing a high-dimensional neural network potential, which allows us to include the full-dimensional thermal motion of the surface atoms, we are able to calculate a large number of trajectories with the accuracy of density-functional theory at a small fraction of the computational costs. Investigating different kinetic energies, surface temperatures and incident angles, we are able to characterize the scattering process in detail.

O 49.3 Wed 15:30 S053

Adsorption of Gases on β -Ga₂O₃ Surfaces — ●JONATHAN K. HOFMANN^{1,2}, CELINA S. SCHULZE¹, MARTIN FRANZ¹, NIPIN KOHLI¹, DOROTHEE ROSENZWEIG¹, ZBIGNEW GALAZKA³, and HOLGER EISELE¹ — ¹Technische Universität Berlin, Institut für Festkörperphysik, Germany — ²Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, Germany — ³Institut für Kristallzüchtung, Germany

β -Ga₂O₃ is a wide band gap material, which is promising for high power and UV (opto-)electronics. The typical *n*-type doping is controllable via the growth parameters, intentional doping, or post-growth heat treatment. In this contribution, we address the question of its surface properties under typical ambient conditions, i. e., under H₂O and O exposure. The β -Ga₂O₃ single crystals were grown with the Czochralski method [1]. Using Auger electron spectroscopy (AES), and scanning tunnelling microscopy/spectroscopy (STM/STS), we show how the different adsorbed atoms/molecules change the structure and electronic properties of β -Ga₂O₃ (100) and (001) surfaces under UHV-conditions. On the (100) surface, large clusters of H₂O with an undisturbed surface in between were observed. However, STS showed no change in the electronic states. On the (001) surface, oxygen covered almost the complete surface. STS showed that O lifts the band bending inherent in clean β -Ga₂O₃ surfaces.

The project was supported by the Leibnitz Association, Leibnitz Science Campus GraFOX, project C2-3.

[1] Z. Galazka *et al.* *ECS J. Solid State Sci. Technol.* 6 (2017) Q3007

O 49.4 Wed 15:45 S053

Atomic scale studies of chromium species on Fe₃O₄(001) — ●MORITZ EDER¹, PANUKORN SOMBUT¹, CHUNLEI WANG¹, MATTHIAS MEIER², JIRI PAVELEC¹, CESARE FRANCHINI^{2,3}, MICHAEL SCHMID¹, ULRIKE DIEBOLD¹, and GARETH PARKINSON¹ — ¹Institute of Ap-

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Chromium (Cr) ferrite catalysts are industrially employed for the water gas shift reaction in order to provide large amounts of molecular hydrogen.[1] However, the European REACH legislation requires the removal of hexavalent Cr from all catalysts used in industrial processes due to its toxicity. Consequently, alternative metals are sought to fulfill the role of Cr species in the corresponding compounds.[2] To this end, one needs a fundamental understanding of Cr on iron oxides. We present the investigation of Cr species on Fe₃O₄(001) by means of STM and XPS at room temperature. We show the behavior during exposure to water gas shift reactants and upon high-temperature treatment. The results are compared to the behavior of other transition metals[3] and discussed with respect to implications for applied catalysis.

[1] Häussinger, Lohmüller, Watson, *Hydrogen*, 2. Production. In: Ullmann's Encyclopedia of Industrial Chemistry, 2011

[2] Glassner, *Int. Surf. Technol.* 14, p. 36, (2021)

[3] Bliem et al., *Phys. Rev. B* 92, p. 075440 (2015)

O 49.5 Wed 16:00 S053

Adsorption and structural behaviour of thymine on Ce₂O₃ and Ce₆WO₁₂ — ●SASCHA MEHL — Elettra Sincrotrone, Trieste, Italy

Reducible oxides are of particular interest in the field of biological systems and nanotechnology application for instance in biosensors, bio medicine and catalysis. The aim is to design novel nano-size structured thin cerium oxide films that possess bio recognition and bio catalytic properties to detect macro molecules e.g. nucleic acids. Model studies of simplified systems such as nucleobases on well-defined oxide surfaces play a major role for understanding and development of these highly promising bio analytical devices. We utilized synchrotron radiation photo electron spectroscopy (SRPES), resonant photo electron spectroscopy (RPES) and X-ray absorption spectroscopy (XAS) which provide ideal conditions to obtain oxidation states, structural and geometrical information on thin organic ad layers. Furthermore, the focus was on the adsorption behavior, electronic structure and thermal stability in the temperature range of 25 * 250 °C of thymine on reduced cerium oxide model systems: thymine/Ce₂O₃(111)/Cu(111) and thymine/Ce₆WO₁₂(100)/W(110). We distinguished two different adsorbed species of thymine on cerium oxide: one strongly bound chemisorbed type and a second weakly bound physisorbed species in the multi layer regime which desorbs at 75 °C. Further investigations have shown that chemisorbed thymine binds to the surface via N-atoms independent of elementary composition and stoichiometry of the substrate.

O 49.6 Wed 16:15 S053

Interaction of organic acids with magnetite surfaces - the DFT perspective — KAI SELLSCHOPP¹, WERNFRIED MAYR-SCHMÖLZER¹, SOMAK BANERJEE¹, JOHANN FLEISCHHAKER¹, ROBERT MEISSNER², and ●GREGOR VONBUN-FELDBAUER¹ — ¹Institute of Advanced Ceramics, TU Hamburg, Germany — ²Institute of Polymers and Composites, TU Hamburg, Germany

Magnetite nanoparticles have a high potential for diverse applications like waste-water treatment, catalysis, and hybrid materials. Formic acid and phosphoric acid can be viewed as the smallest representatives of the acids, which are used to functionalize magnetite nanoparticles. Here, we present results from density functional theory (DFT) calculations on the adsorption of such acids on magnetite low index surfaces. For modelling the adsorption, the configuration space is a challenge and here an approach is presented which allows to sample the adsorption configuration space and to select configurations as input for DFT calculations using unsupervised machine learning approaches. The resulting structures allow for in-depth analyses of the systems including structural and electronic effects.

O 49.7 Wed 16:30 S053

Role of surface termination and orientation on the activity of CoFe₂O₄(001) and (100) surfaces for water oxidation —

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CoFe₂O₄ plays an important role as an anode material for electrochemical water splitting, necessitating detailed understanding of the mechanism of oxygen evolution reaction (OER). This inverse spinel contains alternating layers of octahedral Co and Fe in the (001) direction and mixed Co and Fe layers along the (100) orientation. Here, we employ density functional theory calculations with an onsite Hubbard *U* term (DFT+*U*) to investigate the OER performance of CoFe₂O₄(100) and iron-rich (001) surfaces and compare to the cobalt-rich (001) surface [1]. While the overpotentials of Fe reaction sites are above 0.44 V, octahedral Co shows the lowest overpotential: 0.38 V at the Co-rich (001) surface and even 0.20 V at the mixed Co-Fe (100) surface when terminated with an additional tetrahedral Fe-layer. This reduction of overpotential correlates with a Co²⁺ oxidation state at the surface and a stabilization of the *OOH intermediate due to hydrogen bonding to neighboring sites. Support by the German Science Foundation (DFG), CRC/TRR 247, project B04 and a computational grant at MagnitUDE are gratefully acknowledged.

[1] H. Hajiyani, R. Pentcheva, ACS Catalysis, 8, 11773-11782 (2018).

O 49.8 Wed 16:45 S053

Complexion Induced Active Phase Evolution in High-Temperature Solid Oxide Cells — ●HANNA TÜRK, FRANZ-PHILIPP SCHMIDT, THOMAS GÖTSCH, ROBERT SCHLÖGL, AXEL KNOP-GERICKE, THOMAS LUNKENBEIN, CHRISTOPH SCHEURER, and KARSTEN REUTER — Fritz-Haber-Institut der MPG, Berlin, Germany
Solid oxide cells (SOCs) are among the most efficient technologies for energy-to-hydrogen conversion from fluctuating renewable electricity sources. While SOC are in principle well adapted to intermittent operation, cell performance and lifetime in electrolysis mode is severely limited by degradation of the anode. This degradation goes hand in hand with the oxygen evolution reaction (OER) taking place at the triple-phase boundary (TPB) between the anode, the solid electrolyte and the gas phase. Up to now, the atomistic structure of this active catalyst region is essentially unknown though, which prevents a detailed analysis of the actual degradation mechanisms.

Recently, we took the first step in elucidating the TPB structure by revealing a complexion at the underlying solid|solid interface of the sintered anode[1], featuring partial amorphization and varying elemental distributions deviating from the confining bulk phases. Based on this finding, we now expand our force field based Monte-Carlo simulations to the OER active site. Our experimentally validated results show unexpected compositional changes with respect to the thermodynamic equilibrium, that combined with a spatially resolved diffusion study indicate a hitherto unknown deactivation mechanism of the anode.

[1] H. Türk et al., Adv. Mater. Interfaces 8, 2100967 (2021).

O 49.9 Wed 17:00 S053

Synergistic Effects of Co and Fe on the Oxygen Evolution Reaction Activity of LaCo_xFe_{1-x}O₃ — ●ACHIM FÜNGERLINGS and ROSSITZA PENTCHEVA — Universität Duisburg-Essen, Fakultät für Physik, Lotharstr. 1, 47057 Duisburg

The efficiency of the perovskite LaCo_xFe_{1-x}O₃ as a catalyst for the oxygen evolution reaction was investigated by DFT+*U* calculations. The overpotential required to drive the reaction is significantly reduced upon Co incorporation, with a subsequent nonmonotonic behaviour for larger amounts of Co. This is supported by electrocatalytic measurements of phase-pure LaCo_xFe_{1-x}O₃ samples [1]. With the deprotonation of adsorbed *OH being the potential determining step in all cases, the reason for the observed trend is twofold: Co turns out to be a more favorable reaction site than Fe, whereas the overpotential of the latter is decreased upon Co substitution. Variations of the magnetic moments of the Co and Fe cations during OER reveal the participation of several, particularly Co, cations up to several layers below the surface. This extends the concept of the active site.

[1] A. Füngelings, A. Koul, M. Dreyer, A. Rabe, D. M. Morales, W. Schuhmann, M. Behrens, R. Pentcheva, Chem. Eur. J. 27, 17145-17158 (2021)

O 49.10 Wed 17:15 S053

Hydrophobic pockets on an oxide surface: In₂O₃(111) — HAO CHEN^{1,2}, MATTHIAS BLATNIK^{1,3}, MICHAEL SCHMID¹, BERND MEYER⁴, ULRIKE DIEBOLD¹, and ●MARGARETA WAGNER^{1,3} — ¹TU Wien, Vienna, Austria — ²University of the Chinese Academy of Sciences, Beijing, China — ³CEITEC BUT, Brno, Czechia — ⁴FAU Erlangen-Nürnberg, Erlangen, Germany

Indium oxide, a transparent conductive oxide (TCO), is widely used in semiconductor industry but it also displays promising performance in electro- and photocatalytic reactions. In all applications, surrounding water molecules may influence chemical processes at the atomic scale, and understanding the interaction of water with In₂O₃ is important.

We focus on In₂O₃(111), which has an intrinsically large unit cell composed of a hydrophilic and a hydrophobic area. We test the reactivity of these areas by unraveling the interfacial water structures for the whole range of water coverages in UHV, from single dissociated molecules to multilayers, employing TPD, XPS, STM and AFM. Even at high coverages we clearly see hydrophilicity and hydrophobicity within the unit cell, both in experiments and calculations. Local accumulation and depletion of water is confirmed by DFT calculations and ab initio molecular dynamics (MD) simulations for ordered structures consisting of up to 18 water molecules per unit cell. This first water layer shows ordering into nanoscopic 3D water clusters separated by hydrophobic pockets. Going beyond UHV conditions, our MD simulations of a liquid layer show the robustness of the strongly hydrophobic area in the unit cell.