

## O 94: Poster Session VII: Poster to Mini-Symposium: Electrified solid-liquid interfaces II

Time: Thursday 10:30–12:30

Location: P

O 94.1 Thu 10:30 P

**Peeling graphite layer by layer to study the charge exchange dynamics of ions inside a solid on the fs time scale** — ●ANNA NIGGAS<sup>1</sup>, SASCHA CREUTZBURG<sup>2</sup>, JANINE SCHWESTKA<sup>1</sup>, BENJAMIN WÖCKINGER<sup>1</sup>, PEDRO L GRANDE<sup>3</sup>, BERNHARD C BAYER<sup>4,5</sup>, JOSÉ P MARQUES<sup>6</sup>, FRIEDRICH AUMAYR<sup>1</sup>, ROBERT BENNETT<sup>7</sup>, and RICHARD A WILHELM<sup>1</sup> — <sup>1</sup>Institute of Applied Physics, TU Wien, Vienna, Austria — <sup>2</sup>Institute of Ion Beams and Materials Research, HZDR, Dresden, Germany — <sup>3</sup>Instituto de Física, Universidade Federal do Rio Grande do Sul, Porto Alegre, Brazil — <sup>4</sup>Institute of Materials Chemistry, TU Wien, Vienna, Austria — <sup>5</sup>Faculty of Physics, University of Vienna, Vienna, Austria — <sup>6</sup>BioISI - Biosystems & Integrative Sciences Institute, Faculdade de Ciências da Universidade de Lisboa, Lisbon, Portugal — <sup>7</sup>Department of Physics and Astronomy, University of Glasgow, Glasgow, UK

Charge exchange is one of the many effects taking place when particles penetrate through matter. For a long time experiments were limited to studying secondary particles because observation of the ion inside a solid is not possible. We perform highly charged ion transmission through single-, bi- and trilayer graphene to study the ions' exit charge state after intaction. Thereby we address the charge state changes in graphite with monolayer precision. Following our results of two independent approaches, accompanied by a first-principles model on interparticle de-excitation, we find that the ultra-fast neutralisation dynamics depend only on the time the ion interacts with material layers and neutralisation happens primarily in the topmost surface layers.

O 94.2 Thu 10:30 P

**Electrooxidation of Isopropanol on Pt and Ru Single Crystals: an *In situ* X-Ray Diffraction Study** — ●XIN DENG<sup>1,2</sup>, RALF SCHUSTER<sup>1</sup>, LEON JACOBSE<sup>2</sup>, VEDRAN VONK<sup>2</sup>, YAROSLAVA LYKHACH<sup>1</sup>, OLAF BRUMMEL<sup>1</sup>, ANDREAS STIERLE<sup>2</sup>, and JÖRG LIBUDA<sup>1</sup> — <sup>1</sup>Interface Research and Catalysis, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstr. 3, D-91058 Erlangen — <sup>2</sup>Deutsches Elektronen-Synchrotron DESY, Notkestr. 85, D-22607 Hamburg

By combining isopropanol fuel cells with liquid organic hydrogen carriers, it is possible to convert chemically bound hydrogen into electricity without generation of gaseous gas. Platinum is the best catalyst for alcohol oxidation, however, partial poisoning by the product acetone impacts the activity. The addition of ruthenium increases the reaction rates, however, the origin of the beneficial effect is not clear so far. In this work, we investigated the electrochemical oxidation of isopropanol on Pt(111) and Ru(0001) single crystals by employing high-energy grazing incidence X-ray diffraction. The existence of isopropanol does not influence the oxidation of Pt(111) as the crystal truncation rods (CTRs) show similar shapes in the electrolyte with and without isopropanol. Platinum is severely roughened by potential cycling with an upper potential limit higher than 1.35 V, while Ruthenium is much stable. Further analysing the XRD data of Ru(0001) by fitting the CTRs will help us understand its behavior.

O 94.3 Thu 10:30 P

**Resolving the structure of oxidized Cu surfaces with machine-learned Gaussian Approximation Potentials** — ●NICOLAS BERGMANN<sup>1</sup>, NICOLAS G. HÖRMANN<sup>1,2</sup>, and KARSTEN REUTER<sup>2</sup> — <sup>1</sup>Technische Universität München, Garching, Germany — <sup>2</sup>Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

Copper was recently shown to exhibit promising capabilities toward electrochemical CO oxidation [1], yet only after undergoing activating surface morphological changes. The detailed structure and composition of the formed surface oxidic layer is hitherto unknown, preventing further mechanistic analyses. Here we use the high computational efficiency of machine-learned Gaussian Approximation Potentials (GAPs [2]) to systematically investigate the Cu(111) surface structure with varying concentrations of adsorbed oxygen. The potentials are trained with density-functional theory data of bulk CuO<sub>x</sub> and molecular dynamics generated slab structures.

While low oxygen coverages do not alter the Cu substrate significantly, we find dramatic morphological changes above a critical coverage of ~ 25% monolayer: Surface copper atoms are extruded from the top layer, forming CuO<sub>x</sub> islands, while at the same time the amount

of subsurface oxygen increases. A detailed analysis of local atomic environments reveals predominant local structural motives resembling those in well known bulk copper oxides.

[1] A. Auer *et al.*, Nature Catal. **3**, 10, (2020). [2] A.P. Bartok and G. Csanyi, Int. J. of Quantum Chem. **115**, 16 (2015).

O 94.4 Thu 10:30 P

**Under potential deposited Hydrogen on Pt(111) is both terminal and bridge-bonded** — GREGOR ZWASCHKA<sup>1,2</sup>, YUJIN TONG<sup>1,2</sup>, and ●R. KRAMER CAMPEN<sup>1,2</sup> — <sup>1</sup>Fritz Haber Institute of the Max Planck Society, Berlin, Germany — <sup>2</sup>University of Duisburg-Essen, Duisburg, Germany

Despite decades of effort, finding catalysts for either half reaction of electrolytic water splitting that are reactive, stable and inexpensive has proven remarkably challenging. For the hydrogen evolution half reaction (HER) in acidic solution platinum meets the first and second of these goals remarkably well but understating why it does so, *i.e.* understanding the mechanism of the HER on Pt, has proven challenging.

H adsorbs on Pt at potentials positive of those at which H<sub>2</sub> appears. Understanding the potential-dependent structure of this underpotential-deposited (UPD) H, how it differs from H adsorbed on Pt in UHV, and its relationship to H<sub>2</sub> generation is a necessary step in understanding the HER mechanism. Here we perform vibrational sum frequency spectroelectrochemistry to collect the potential dependent Pt-H spectral response on single crystal Pt(111) electrodes in acidic solution. In contrast to suggestions from UHV and previous infrared spectroelectrochemical studies, we find that both terminal and bridge-bonded H appear throughout the UPD region and that, depending on the defect density, distinct types of terminal-bonded hydrogen can be observed. Intriguingly, for pristine Pt(111) surfaces we also observe an interfacial hydronium species heretofore only predicted in calculation.

O 94.5 Thu 10:30 P

**Characterization of excitonic behaviour of MoS<sub>2</sub> on gold electrode by final state resonant sum frequency spectroscopy** — ●TAO YANG, ERIK POLLMANN, MARIKA SCHLEBERGER, YUJIN TONG, and RICHARD KRAMER CAMPEN — University of Duisburg-Essen, Faculty of Physics, 47057 Duisburg, Germany

Two dimensional (2D) materials are promising candidate electrocatalysts for the hydrogen evolution reaction (HER) because of their large surface area and tunable electronic properties. Particularly MoS<sub>2</sub>, a transition metal dichalcogenide, has been intensively studied in this context showing comparable efficiency for the HER as Pt. While continuous breakthroughs in HER activity of MoS<sub>2</sub> have been achieved, less attention has been devoted to the mechanistic investigation, *e.g.*, charge transfer between a metal electrode and the MoS<sub>2</sub>. Here we use final state resonant sum frequency spectroscopy to study the optical response of MoS<sub>2</sub> exfoliated on a gold electrode in aqueous solution as a function of applied bias. The results show the evolution of the A and B excitons with electron doping. Together with Raman and electrochemical characterization, the current study provides important insights into understanding the relationship between electronic structure, atomic configuration and electron transfer at metal/MoS<sub>2</sub>/aqueous electrolyte interface.

O 94.6 Thu 10:30 P

**Effect of water co-adsorption on the electrochemical stability of H-covered Pt(111)-water interfaces** — ●SUDARSAN SURENDRALAL, MIRA TODOROVA, and JÖRG NEUGEBAUER — Max-Planck-Institut für Eisenforschung, Max-Planck-Str. 1, 40237 Düsseldorf, Germany

Using density functional theory based molecular dynamics simulations we study the relation between H-coverage and electrode potential at the Pt(111)/water interfaces. We find that chemisorbed water molecules strongly interact with the H-adatoms and strongly impact the electrode potential. Above a critical H adsorbate coverage, chemisorbed water becomes unstable at these interfaces. The loss of co-adsorbed water molecules results in a steep increase in the electrode potential, making the interface thermodynamically unstable. The presence of a critical upper H concentration well below 1 ML has been observed experimentally but is absent in surface science modeling. This

allows for the first time to understand the mechanisms that limit H adsorption on these surfaces and that lead to the onset of the hydrogen evolution reaction (HER).

S.Surendralal, M. Todorova, and J. Neugebauer, (under review).

O 94.7 Thu 10:30 P

**Implicit solvation limitations and beyond for potential-dependent electrochemical interfaces modelling** — •ARTHUR HAGOPIAN<sup>1,2</sup> and JEAN-SÉBASTIEN FILHOL<sup>1,2</sup> — <sup>1</sup>ICGM, University of Montpellier, CNRS, ENSCM, Montpellier, France — <sup>2</sup>RS2E French network on Electrochemical Energy Storage, FR5439, Amiens, France

In recent years, processes at solid/liquid interfaces have attracted considerable attention due to their major role in scientific and engineering applications. In the battery domain, solid/liquid interfaces are critical for the development of high energy density batteries such as lithium-metal batteries (LMB), which are the current missing key to a large-scale vehicle electrification and renewable energy generation. In LMB, the interface of interest corresponds to the interface between a lithium metal anode and an organic electrolyte, where in this particular case, the solid electrolyte interphase (SEI) layer is formed between the solid and liquid phases. Despite decades of research, our knowledge on the atomistic structure and chemical evolution of the SEI is still rather limited. In this work, we investigate the particular case of LiF, one of the most commonly found SEI phases in lithium-based batteries. A polarizable continuum model (PCM) is used to describe the solvent dielectric response and a grand canonical DFT approach is used to simulate potential variation. We show that in the case of LiF, which is a highly polar surface, PCM suffers limitations due to its inability to simulate chemical reactivity. We highlight that these limitations are

also found while investigating charged interfaces. We finally propose a hybrid implicit/explicit model to overcome PCM limitations.

O 94.8 Thu 10:30 P

**Doping of Free-standing Graphene Measured with Kelvin Probe Force Microscopy under Electrochemical Reaction Conditions** — •SALMA KHATUN, SIDNEY COHEN, IRIT GOLDIAN, and BARAN EREN — Weizmann Institute of Science, Rehovot, Israel

Solid-liquid interfaces play a central role in electrochemistry, electrolysis, and catalysis. The electrical double layer (EDL) which forms at the solid-electrolyte interface, plays a key role in moderating these processes. Due to the difficulty in probing this thin layer, very few experimental mechanistic studies under realistic reaction conditions have been reported. We know, free-standing single layer graphene (SLG) is transparent to both electrons and photons. When used as the solid interface in an electrochemical environment, a variety of microscopic and surface-sensitive spectroscopic techniques can be used to probe that interface from the upper side. Our study examines some of the fundamental issues in such a set-up. We have built an electrochemical micro-reactor cell enclosed by a SLG membrane. The double layer thickness is varied controllably by changing the pH of the aqueous NaOH solution. Since our SLG is not doped via any support or contaminants, the changes occur only due to doping from applied electric field. KPFM measurements are used to monitor the shift of Fermi-energy. Due to cleanliness of our technique, the result can be described fairly well by a model considering the applied electrochemical potential, modified by the capacitive drop in the EDL. Differences between experimental values and those predicted by the model can be explained by electrochemical doping during the evolution of O<sub>2</sub> and H<sub>2</sub>.