

## O 25: Poster: Metal Substrates

Time: Monday 18:00–20:00

Location: P2/EG

O 25.1 Mon 18:00 P2/EG

**Ab initio design of Pt-Ir based novel bifunctional electrocatalysts for fuel cell applications** — ●HALIL IBRAHIM SÖZEN<sup>1</sup>, MEHTAP OEZASLAN<sup>2</sup>, and THORSTEN KLÜNER<sup>1</sup> — <sup>1</sup>Institute of Chemistry, Carl-von-Ossietzky University of Oldenburg, D-26129 Oldenburg, Germany — <sup>2</sup>Technische Universität Braunschweig, Braunschweig 38106, Germany

Electric vehicles powered by polymer electrolyte membrane fuel cells (PEMFC) have a great potential to reduce a large portion of CO<sub>2</sub> emissions from the transportation sector and facilitate the advent of the hydrogen economy worldwide. However, highly dynamic conditions during the operation of PEMFC in the heavy-duty sector cause hydrogen starvation at the anode electrode, resulting in cell reversal events (< -1.5 V) and therefore carbon oxidation reaction (COR). In this work, we aimed to develop novel bifunctional electrocatalysts for the anode electrode based on Pt-Ir alloys. Our innovative approach involves unifying two functionalities, the hydrogen oxidation reaction (HOR) and oxygen evolution reaction (OER), as an alternative reaction for proton and electron formation to the COR in only one nanoparticle on the same support material. Density functional theory (DFT) based chemisorption energies of H\*, O\*, OH\*, H<sub>2</sub>O\* and OOH\* are reported with the effect of hydroxyl species presence and the effect of pH. Calculated chemisorption energies are implemented to model HOR and OER and plot Gibbs free energy diagrams. Various surfaces such as Pt(111), Pt<sub>3</sub>Ir(111), PtIr(111) and Ir(111) have been considered for electrocatalytic reactions and their relative performance is compared.

O 25.2 Mon 18:00 P2/EG

**2D Lattice Gas Order-Disorder Transition Observed by LEED and Vibrational Sum Frequency Generation Spectroscopy** — ●ZHIPENG HUANG, TOBIAS ROOS, YUJIN TONG, and R. KRAMER CAMPEN — Faculty of Physics, University of Duisburg-Essen

Order-disorder phase transition of monoatomic superstructures on single crystal surfaces is commonly described by Ising or lattice-gas model. The molecular orientation needs to be considered for modeling the order-disorder transition of diatomic superstructures on single crystal surfaces, but it is challenge to be accessed by experiments.

Here we present our studies on CO ordered overlayers on Pt(111) surface by the surface sensitive thermal desorption spectroscopy (TDS), low-energy electron diffraction (LEED) and polarization dependent sum-frequency generation spectroscopy (SFG). An order-disorder phase transition of CO overlayer is observed by LEED under in-situ heating. The CO stretch vibrational frequency shifts suddenly when the transition happens. Combining LEED superstructure patterns and polarization dependent sum-frequency generation spectroscopy results, we reveal the changes of CO molecular orientation on Pt(111) surface during the order-disorder phase transition. We model the sudden CO stretch frequency shift caused by phase transition and the systematic shift as a function of coverage. These results demonstrate how the CO intermolecular interactions influence the molecular orientation and the stretch vibrational frequency. They provide insights on the change of microscopic potential energy level during the order-disorder phase transition.

O 25.3 Mon 18:00 P2/EG

**Formation of solid electrolyte interface from polycaprolactone** — ●KAZEM ZHOUR<sup>1</sup>, ANDREAS HEUER<sup>1</sup>, and DIDDO DIDDENS<sup>2</sup> — <sup>1</sup>WWU Münster, Münster, Germany — <sup>2</sup>Institute Münster (IEK-12) Forschungszentrum Jülich GmbH, Münster, Germany

As for liquid electrolytes, studying the formation of the solid-electrolyte interface and its implications is one of the most important topics in solid-state batteries. In this study, DFT and AIMD calculations were performed to study the decompositions of polycaprolactone, one main constituent of the electrolytes, and its ending groups at the

interface. Additionally, the computational lithium electrode method was applied to study the formation of the SEI under external voltage. The AIMD results suggest that the fragments are highly reactive on the Lithium slab where the fragmentation can be observed in less than 1 ps. The decomposition was triggered by the electrons transferred from the slab to the fragments. The electrochemical mechanism shows only slightly weaker energetics with respect to the non-electrochemical one, showing that Li anode readily reacts with the polymer. After the formation of passivation layers (Li<sub>2</sub>O, LiF or Li<sub>2</sub>CO<sub>3</sub>) on top of the anode, the calculations show that only one monolayer protects the molecules from being decomposed at the interface at short interval of time, where the LiF layer seems to have the most robust protection as compared to the other layers. The electrochemical window and the decomposition of the polymer fragments in the presence of a Li cation, TFSI anion, or LiTFSI ion pair without explicit interface have also been investigated.

O 25.4 Mon 18:00 P2/EG

**Single-molecule study of Heck coupling on a Cu(111) surface** — ●DONATO CIVITA<sup>1</sup>, FRIEDRICH ESCH<sup>2</sup>, and LEONHARD GRILL<sup>1</sup> — <sup>1</sup>Department of Physical Chemistry, University of Graz, Austria — <sup>2</sup>Faculty of Chemistry, TU München, Germany

The interaction of organic molecules with metallic structures is particularly important in heterogeneous catalysis where metallic particles or surfaces help to overcome energy barriers of chemical reactions. This concept is specifically important for Heck cross-coupling, which relies on a palladium catalyst to form a carbon-carbon bond between two different reagents. Model heterogeneous catalysis reactions can be investigated by scanning tunneling microscopy (STM) on metal single crystals. The role of active sites could be determined [1,2], and Heck coupling could be induced thermally [3].

We studied the cross coupling between vinyl-naphthalene (VN) and different halogenated molecules on a Cu(111) surface by STM at low temperatures (7 K). We investigated the bond of the de-halogenated molecules to different atomic structures of the copper surface as well as the thermally induced cross coupling reaction. By the statistical analysis of the products, and STM manipulation of a single metal-organic intermediate we obtain insight into the catalytic activity of the copper surface, and the dependence on the surface morphology.

[1] Hla, S.-W., et al., Phys. Rev. Lett., 85(13) (2000)

[2] Zambelli, T., et al., Science, 273 (1996)

[3] Shi, K.-J., et al., Organic Letters, 19(11) (2017)

O 25.5 Mon 18:00 P2/EG

**Cobalt Island Growth on Metallic Surfaces** — ●BENSU GÜNAY, CHRISTOPHE NACCI, and LEONHARD GRILL — University of Graz, Graz, Austria

Molecular-beam epitaxy is an important technique for the fabrication of epitaxial films with reduced dimensionality in the low coverage regime under ultra-high vacuum conditions [1]. Various parameters are important for the morphology of the nanostructures: the flux of the incident atoms, the surface temperature, the source/substrate geometry, and diffusion of the atoms on the surface [2]. In this study, we investigated the growth of cobalt islands on Cu(111) and Au(111) surfaces using different (K-cell and e-beam evaporator) evaporators. The resulting surfaces were then studied by complementary methods: x-ray photoemission spectroscopy (XPS) to analyze the chemical composition of the surface and scanning tunneling microscopy (STM) to investigate the morphology of the islands. The results show how different deposition conditions change the Co growth on the surface.

[1] Prieto, J. E., de La Figuera, J., & Miranda, R. (2000). Surface energetics in a heteroepitaxial model system: Co/Cu (111). Physical Review B, 62(3), 2126. [2] Negulyaev, N. N., Stepanyuk, V. S., Bruno, P., Diekhöner, L., Wahl, P., & Kern, K. (2008). Bilayer growth of nanoscale Co islands on Cu (111). Physical Review B, 77(12), 125437.