O 35: Poster Session III: Surface dynamics I: Phase transitions and elementary processes

Time: Tuesday 10:30–12:30 Location: P

O 35.1 Tue 10:30 P

Interphase Formation in Solid Oxide Electrolysis Cells - A Close-up on the YSZ/LSM Grain Boundary — •Hanna Tuerk, Karsten Reuter, and Christoph Scheurer — Fritz-Haber-Institute of the Max-Planck-Society

Solid oxide electrolysis cells (SOECs) are among the most efficient technologies for water splitting from fluctuating renewable electricity sources. While SOECs are in principle well adapted to intermittent operation, cell performance and lifetime is severely limited by degradation of the anode. This degradation goes hand in hand with the oxygen evolution reaction 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.

Here, we take a first step to elucidate the TPB structure by performing molecular simulations of the underlying interface between the oxygen-ion conducting electrolyte yttria-stabilized zirconia (YSZ) and the typical electrode material strontium-doped lanthanum manganite (LSM). Parallel-tempering Monte Carlo with a cumulatively growing swapping region centered at the interface yields an efficient simulation approach capable of addressing the structural complexity of this grain boundary region. Our experimentally validated results clearly evidence the formation of an extended interphase region with partial loss of crystalline order and distinct segregation profiles.

O 35.2 Tue 10:30 P

Time-Resolved 2D IR Pump-Probe Spectroscopy — Michael Lackner, •Marvin Hille, Tim Lämmerzahl, Nelli Kremer, and Eckart Hasselbrink — University of Duisburg-Essen, Essen, Germany

Internal vibrational energy distribution (IVR) in molecules is fundamental for understanding their chemical reactivity and research in this field has gained a lot of popularity in the past. It is, however, still fair to say that predictive power over the energy flow in vibrationally excited molecules has yet to be obtained. We will present newest findings regarding the energy flow dynamic of a fatty acid Langmuir-Blodgett film on a picosecond scale. Vibrational sum frequency generation (vSFG) spectroscopy allows precise monitoring of resonant vibrations of an adsorbate monolayer. In our setup we use a resonant ps narrowband IR laser pulse for pumping and a fs broadband IR-visible pulse pair for vSFG probing of the monolayer. Using this pump-probe setup we observed a very fast (< 2ps) energy transfer to the other modes when pumping the anti-symmetric methyl or methylene stretch, followed by a longer decay (~85 ps) into presumably bending and internal rotational modes.

O 35.3 Tue 10:30 P

Atomic Diffusion in O(2x2) on Ru(0001) - Spiral High Speed STM — •Leonard Gura[1], Joachim Paier[2], Zechao Yang[1], Florian Kalass[1], Matthias Brinker[1], Heinz Junkes[1], Markus Heyde[1], and Hans-Joachim Freund[1] — [1]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany — [2]Humboldt Universität zu Berlin, Berlin, Germany

The diffusion of atomic oxygen on Ru(0001) has been studied over the last decades. Conventional Scanning Tunneling Microscopy (STM) gave hopping rates for oxygen vacancies in an O(2x2) adlayer in the order of 1/100 s [1].

Here we present new results on the dynamics in the O(2x2) layer on Ru(0001) at room temperature. We used a novel STM spiral scan pattern to avoid internal resonance frequencies of the microscope body. With this approach we increased the frame rate to 40 Hz.

Thanks to the high frame rate we were able to observe frequent jumps in the O(2x2) adlayer with hopping rates in the order of 1/1 s. In addition, we resolved intermediate states during single jump events. Based on Density Functional Theory (DFT) calculations, we provide a plausible O migration pathway.

Ideas for future studies include oxygen coverage and temperature dependent measurements. With refined spiral geometries and tip velocities we hope to further increase the scan speed to then monitor more dynamic processes at the atomic scale.

[1] Wintterlin, J. et al. (1997). Surface science, 394(1-3), 159-169 and references therein.

O 35.4 Tue 10:30 P

Free energy QM/MM simulations of on-surface reaction pathways — •Aurelio Gallardo[1,2], Jesus Mendieta[1], and Pavel Jelínek[1,2] — [1]FZU of the CAS, Prague, Czech Republic — [2]RCPTM, Palacký University, Olomouc, Czech Republic

On-surface chemistry represents a fast-growing field allowing to synthetize molecular structures not available by traditional wet chemistry. In combination with high-resolution scanning probe technique providing the unprecedented spatial resolution, individual products of reactions can be precisely identified. Nevertheless, a deep understanding of the reaction mechanism under the conditions imposed by the substrate remains unknown. Widely adopted energy reaction path techniques will only describe the potential energy landscape at zero Kelvin, while the free energy landscape at given temperature enables a more appropriate description of the reaction. Such simulations including temperature effect include the effect of entropy, vibrations modes, concerted motion, etc. Consequently, such simulations avoid local minima and allows to explore different states, revealing lower energy pathways. We will present QM/MM simulations of strain-induced isomerization in one-dimensional metal-organic chains on Cu(111) surface [1]. The simulation demonstrates the importance of the temperature effect on proper description of the reaction mechanism.

[1] M. Telychko, J. Su, A. Gallardo, Y. Gu, J. I. Mendieta-Moreno, D. Qi, A. Tadich, S. Song, P. Lyu, Z. Qiu, H. Fang, M. Joo Koh, J. Wu, P. Jelínek J. Lu, Strain-Induced Isomerization in One-Dimensional Metal-Organic Chains, Angew. Chem 58, 8591-18597 (2019).

O 35.5 Tue 10:30 P

Nonadiabatic quantum dynamics of diffusion and scattering at metal surfaces — •James J Gardner, Svenja M Janke, and Reinhard J Maurer — University of Warwick, Coventry, United Kingdom

Dynamics at molecule-metal interfaces involve a close coupling between the electronic and nuclear degrees of freedom, violating the Born-Oppenheimer approximation. The Anderson-Holstein Hamiltonian provides a standard model for describing the nonadiabatic dynamics encountered at the metal surface. We present two forms of this Hamiltonian that encompass surface diffusion and scattering, both having an explicit structure for the electronic bath depending on only two parameters. With these models, we identify and analyse different parameter regimes in which quantum tunnelling and nonadiabatic effects are important. We further calculate quantum rates and scattering probabilities at different levels of theory. Our results provide a benchmark for the performance of existing and future simulation methods to describe accurate quantum reaction rates at metal surfaces.