

O 30: Surface Chemical Reactions and Heterogeneous Catalysis II

Time: Tuesday 10:30–12:45

Location: PHY C 213

O 30.1 Tue 10:30 PHY C 213

Recent mechanistic insights into the electrochemical CO₂ reduction at platinum electrodes in pyridine containing electrolytes — ●KATRIN R. BICKEL, SIMON FILSER, QI LI, KONRAD SCHÖNLEBER und KATHARINA KRISCHER — Nonequilibrium Chemical Physics, Physics Department, Technical University Munich, Germany

The development of suitable energy storage concepts is essential for the efficient use of renewable energy sources. One promising approach is the electrochemical conversion of CO₂ to liquid or gaseous fuels. However, due to the large activation barrier for the reduction of CO₂, such a process is challenging.

In the 1990s, Bocarsly et al. reported that in the presence of pyridine CO₂ can be electrochemically reduced to methanol on palladium or platinum electrodes at a comparably low overpotential [1]. Despite various electrochemical and theoretical studies, the mechanism of this reduction process is still unclear. In particular, the role of the metal surface and the occurring reaction intermediates are under dispute.

We present recent results of a mechanistic study of the CO₂ reduction in the presence of pyridine, amongst others by rotating disk electrode measurements. We found strong indications for the presence of an adsorbed pyridine species at the metal electrode. Therefore, a particular focus is placed on the nature of this surface species and its role in the reduction process.

[1] G. Seshadri, C. Lin, A. B. Bocarsly; *J. Electroanal. Chem.*, 1994, 372, 145

O 30.2 Tue 10:45 PHY C 213

Anodization of aluminum surfaces — ●FLORIAN BERTRAM¹, JONAS EVERTSSON¹, FAN ZHANG², JINSHAN PAN², FRANCESCO CARLA³, and EDVIN LUNDGREN¹ — ¹Lund University, Division of Synchrotron Radiation Research, Lund, Sweden — ²KTH Royal Institute of Technology, Department of Chemistry, Division of Surface and Corrosion Science, Stockholm, Sweden — ³ESRF, Grenoble, France

Aluminum and Aluminum alloys are used in a broad range of everyday commercial products. For many of these products an efficient corrosion protection is critical. In oxygen or aqueous environment aluminum forms a passivating surface oxide layer with a typical thickness of 2–4.3 nm. This surface oxide already offers some corrosion protection. By increasing the thickness of the surface oxide it is possible to increase the corrosion resistivity. One way to increase the thickness widely used in today's industry is anodization.

Here, we present the results of the anodization of an aluminum single crystal and an aluminum alloy studied by in-situ x-ray reflectivity. The reflectivity studies have been complemented by electrochemical impedance spectroscopy. Both single crystal as well as alloy samples show a linear increase of film thickness with increasing anodization voltage. However, the slope is much higher in the single crystal case.

O 30.3 Tue 11:00 PHY C 213

Improvement of the electrical conductivity of bipolar plates for fuel cells by plasma etching in carbon dioxide environment — ●TATIANA FEDOSENKO, NICOLAS WÖHRL, and VOLKER BUCK — Faculty of Physics, University of Duisburg-Essen, Carl-Benz-Str. 199, 47057 Duisburg, Germany

Bipolar plates for the fuel cells, made of carbon-polymer composites, are one way to distribute the fluid and to conduct the current from the anode of one cell to the cathode of the adjacent cell. However, polypropylene (PP) significantly decreases the contact conductivity between the plates in a stack. It is possible to improve the contact conductivity by etching the PP at the surface in microwave plasma. A microwave plasma source is used in remote mode (CYRANNUS by iplas) that allows plasma treatments up to atmospheric pressure, making the process scalable for industrial applications.

In this study the bipolar plates are etched in carbon dioxide plasma, varying the etching time. SEM and Fourier transform infrared spectroscopy (FTIR) is used to analyze the changes in the surface chemistry. Plasma etching is more advanced than the deposition of the coating of electrocatalytic materials onto the surface of the bipolar plates, since such coating must meet many criteria: a very good adhesion, the coating should not be degraded by high temperatures and water.

Contact resistivity measurements are interpreted with respect to the

etching of the surface and rearrangements of the chemical bonds in the PP due to plasma irradiation of the surface.

O 30.4 Tue 11:15 PHY C 213

Photo-catalytic water splitting with co-catalysts: beyond proton-coupled electron transfer — ●HARALD OBERHOFER, MARKUS SINSTEIN, RAN JIA, and KARSTEN REUTER — Technische Universität München, Germany

Efficient, sustainable production of molecular hydrogen—a promising alternative to batteries in terms of energy storage—is still an unsolved problem. Recently, we presented [1] a novel screening method for viable combinations of photocatalysts and metal co-catalysts based on the computational hydrogen electrode approach pioneered by Nørskov and Rossmeisl.[2] In this thermodynamic approach charge-neutral proton-coupled electron transfer (PCET) pathways are generally assumed. Any screening approach resting on this assumption may therefore falsely rule out viable catalysts following other, uncoupled pathways.

Using an implicit solvent model we recently implemented into the FHI-aims DFT package,[3] we extend our screening scheme to uncoupled reaction paths, where due to the occurrence of charged intermediates solvent screening effects can no longer be neglected. We present first results of our screening efforts and show that even for charge-neutral PCET pathways solvent effects can not be neglected.

[1] H. Oberhofer, K. Reuter, *J. Chem. Phys.* **139**, 44710 (2013).

[2] A. Valdes *et al.*, *J. Phys. Chem. C* **112**, 9872 (2008).

[3] V. Blum *et al.*, *Comp. Phys. Commun.* **180**, 2175 (2009).

O 30.5 Tue 11:30 PHY C 213

Towards Heterogeneous Catalysis Beyond the Born-Oppenheimer Approximation: LDFA and beyond — ●SIMON P. RITTMAYER¹, J. IÑAKI JUARISTI², KARSTEN REUTER¹, and JÖRG MEYER¹ — ¹TU München, Germany — ²Deppto. & Centro de Física de Materiales (CSIC-UPV/EHU), San Sebastián, Spain

Inspired by the need of a more efficient and thus responsible use of energy, an age of light-enhanced heterogeneous catalysis is dawning. Even photons from sunlight can be used to accelerate surface reactions, if their energy is selectively and efficiently transferred into distinct nuclear degrees of freedom [1]. However, on metal catalysts resulting athermal mode populations are generally challenged by rapid energy dissipation in particular into the continuum of easily accessible electron-hole pair excitations. *Ab initio* molecular dynamics simulations beyond the Born-Oppenheimer approximation can assess corresponding lifetimes and therewith answer important questions as to the feasibility and efficiency of such light enhancement of catalytic reaction steps. On the way to establishing a numerically tractable approach even for complex surface processes we pursue the local density friction approach (LDFA) [2] and extend it beyond the hitherto inherent independent-atom and frozen-surface approximation. We apply this new scheme to the non-adiabatic damping of adsorbate vibrations on transition metal surfaces and critically discuss it by comparing the results to other theoretical approaches as well as experimental data.

[1] S. Linic *et al.*, *Acc. Chem. Res.* **46**, 1890 (2013).

[2] J. I. Juaristi *et al.*, *Phys. Rev. Lett.* **100**, 116102 (2008).

O 30.6 Tue 11:45 PHY C 213

Ligand-controlled electrocatalytic response in the oxygen reduction reaction in iron-based 2D metal-organic structures — DORIS GRUMELLI¹, ●BENJAMIN WURSTER¹, SEBASTIAN STEPANOW¹, RICO GUTZLER¹, and KLAUS KERN^{1,2} — ¹Max Planck Institute for Solid State Research, D-70569 Stuttgart, Germany — ²Institut de Physique de la Matière Condensée, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland

In this work we present the electrochemical characterization of single iron atoms coordinated by either tetracyanoquinodimethane (TCNQ), bis-pyridyl-bipyrimidine (PBP) or phthalocyanine (Pc) on Au(111).

The samples were prepared under ultra-high vacuum (UHV) conditions by evaporating either FePc or the organic ligands together with iron, which subsequently self-assemble and form two-dimensional metal-organic coordination networks. By scanning tunneling microscopy in UHV the composition and structure of the networks and FePc layer were controlled and characterized. The sample is brought from UHV to the electrochemical cell through a transfer chamber in

a controlled environment, in which the catalytic activity towards the oxygen reduction reaction in alkaline media is studied. Linear voltammetry experiments show that depending on the coordination environment of Fe the mechanism of the reduction of O_2 is changed. TCNQ-Fe catalyzes the reduction towards H_2O_2 on a $2e^-$ pathway. For PBP-Fe and FePc the complete reduction to H_2O is observed. PBP-Fe catalyzes on a $(2+2)e^-$ pathway, while FePc on a direct $4e^-$ pathway.

O 30.7 Tue 12:00 PHY C 213

Non-adiabatic effects in the oxidation of ultrathin crystalline Mg films: quantum size effects and hot charge carrier distribution — ●ULRICH HAGEMANN and HERMANN NIENHAUS — Faculty of Physics and Center for Nanointegration (CeNIDE), University of Duisburg-Essen, D-47048 Duisburg, Germany

The low-temperature oxidation of ultrathin Mg films in the thickness range between 5 and 30 monolayers (ML) epitaxially grown on Si(111)- 7×7 substrates is studied applying the chemi-current method. The well-ordered films are characterized by electron diffraction and quantum well photoelectron spectroscopy. The exothermic reaction of O_2 molecules with Mg surfaces creates electron-hole pairs which are detected in the Mg:*p*-Si Schottky diodes as a chemi-current. For metal layer thicknesses of approximately 8 and 12 ML the chemically induced current is significantly enhanced by a factor of up to three. We show that this result can be explained by an increased initial reactivity due to the normal confinement of the electrons. The resulting quantum well states lead to larger electron densities of states at the Fermi level for 8 and 12 ML. By fabricating different Mg/Si Schottky diodes with varying barrier heights the energy distribution of the excited hot charge carriers for the Mg oxidation is probed. The distribution exhibits an exponential behaviour which may be described by a Boltzmann-type function with an effective temperature of approximately 1600K.

O 30.8 Tue 12:15 PHY C 213

Kinematic effects in the non-adiabatic energy dissipation during oxidation of Al surfaces — ●ACHIM GERSTENBERG, ULRICH HAGEMANN, and HERMANN NIENHAUS — University of Duisburg-Essen and Center for Nanointegration (CENIDE), Duisburg, Germany

There is a long-standing controversial debate on the nature of the low

initial sticking of oxygen molecules on Al(111) surfaces [1]. In the present study, the reaction is investigated for low substrate temperatures with respect to the kinetic energies of the impinging oxygen molecules using the chemi-current method. The released reaction energy is partly dissipated non-adiabatically by generation of electron-hole pairs in the metal surface. The created hot charge carriers are detected as a chemi-current in large-area Al/*p*-Si (111) Schottky diodes with Al films of 4 to 20 nm thickness. The homogeneous Schottky barrier height is determined to be 0.45 eV. Upon exposure to a hyperthermal molecular beam of oxygen molecules seeded in He gas the temporal evolution of the chemi-current exhibits a maximum in agreement with the low initial reaction probability and in accordance to a nucleation and growth kinetics. When the kinetic energy of the molecules is raised from 50 to 250 meV the respective chemi-current increases strongly. This kinematic current enhancement is still observed after longer exposures for the partially oxidized Al(111) surface.

[1] M.Kurahashi and Y.Yamauchi, PRL 110 (2013) 246102 and ref. therein.

O 30.9 Tue 12:30 PHY C 213

Temperature programmed desorption from chemoelectronic nanodiodes — ●JAN PHILIPP MEYBURG, IEVGEN NEDRYGAILOV, ECKART HASSELBRINK, and DETLEF DIESING — Fakultät für Chemie, Universität Duisburg-Essen, Essen, Germany

Chemoelectronic nanodiodes based on metal-oxide-semiconductor thin film structures allow the in-situ detection of energy release on the top metal electrode of the devices when a surface reaction takes place. This energy can be transported through the nanodiode by hot charge carriers that lead to a detectable current. While the contribution of hot carriers during oxidation and adsorption processes is already reported, the involvement of hot carriers during desorption processes is still to be observed. In this context, temperature programmed desorption from the surface of Pt-SiO₂-*n*-Si chemoelectronic nanodiodes is demonstrated using a heating method that allows for desorbing locally from the Pt top electrode. For this purpose, the 5 nm Pt top electrode is directly heated from 80 to 300 K by a current flow. Simultaneously the temperature is monitored by measuring the Pt film resistance. Reproducible results for water desorption are obtained using this method.