

O 53: Focus Session: Electrocatalytic Energy Harvesting and Conversion

Time: Wednesday 10:30–13:15

Location: S052

Topical Talk

O 53.1 Wed 10:30 S052

Insights into Oxygen Evolution Electrocatalysis on Perovskites — •THOMAS J. SCHMIDT — Electrochemistry Laboratory, Paul Scherrer Institute, CH-5232 Villigen PSI, Switzerland — Laboratory of Physical Chemistry, ETH Zürich, CH-8093 Zürich, Switzerland

Oxygen electrodes are playing a key role in electrochemical energy conversion devices such as fuel cells and water electrolyzers. In both acidic and alkaline environment, both the oxygen reduction and oxygen evolution reaction (ORR / OER), respectively, are limiting the overall energy/voltage efficiency due to its sluggish kinetics. [1, 2]

Whereas in acidic environment, mainly precious metals are used to catalyze the OER, the variety of possible catalysts in alkaline electrolyte is significantly increased and also many non-noble metal oxide based systems can be employed. Generally, the oxygen evolution mechanisms are only partly understood independent of the electrolyte environment and material used. In order to help to understand the underlying mechanisms for the reactions and to support the experimental results, very often computational methods are used, mainly using density functional theory (DFT) calculations.

In this talk, some of your recent findings on non-noble metal catalysts, mainly from the perovskite family will be presented employing both electrochemical as well as operando spectroscopic techniques.

[1] A. Rabis, P. Rodriguez, T.J. Schmidt, ACS Catal., 2012, 2 (5), 864-890 [2] E. Fabbri, A. Habereder, K. Waltar, R. Kötz, T.J. Schmidt, Cat. Sci. Tech., 2014, 4, 3800-3821

Topical Talk

O 53.2 Wed 11:00 S052

Using redox agents to enhance the performance of lithium-air batteries and lithium recycling — •NURIA GARCIA-ARAEZ — University of Southampton

Lithium-air batteries can become the next generation of battery technologies, since they can potentially deliver 5 times more energy than current lithium-ion batteries of the same weight, while having a lower cost and being more environmentally friendly. Unfortunately, the performance of the current lithium-air batteries is limited by three fundamental issues: electrode passivation, degradation reactions and poor kinetics of the desired reactions. Luckily, this talk will show that all these issues can be solved by incorporating suitable redox agents, which can act as shuttles and mediators. As the performance of lithium batteries improves, and the global population increases, the demand for lithium can only increase in the future, and therefore lithium recycling and recovery will need to be developed. This talk will also present a new method for lithium recycling that is based on the combination of redox agents and battery materials.

Topical Talk

O 53.3 Wed 11:30 S052

Probing the Femtosecond Dynamics of the Hydrogen Evolution Reaction on Gold — •R. KRAMER CAMPEN, FRANCOIS LAPOINTE, and YUJIN TONG — Fritz Haber Institute of the Max Planck Society, Berlin, Germany

While water electrolysis on gold electrodes was first demonstrated more than 225 years ago, the mechanisms of both the oxygen and hydrogen evolution halves of this process are still controversial. From an experimental point of view part of the challenge has been a lack of methods that allow characterization of transient intermediates. Here we report a novel experimental approach in which we initiate hydrogen evolution at a gold/liquid water interface using an intense, femtosecond, UV pulse to promote an electron from gold's fermi level into water's

conduction band and track the fate of this electron with fs time resolution both optically, using interface specific sum frequency generation spectroscopy, and electrochemically via a double-pump, laser induced perturbation of the open circuit potential. The results of this approach suggest that, at circum-neutral pH, (i) at the gold/water interface the delocalized, conduction band, solvated electron has a lifetime of 150-250 fs depending on surface potential (ii) conduction band electrons relax to form localized solvated electrons the great majority of which have a potential dependent lifetime of 1-18 ps while a small fraction live for much longer, > 40 ps, and drive chemistry. These results furnish a potential-dependent, mechanistic picture of the transfer of electrons from gold into liquid water, the first step in hydrogen evolution.

15 min. break**Topical Talk**

O 53.4 Wed 12:15 S052

The Electrochemical interface - at the atomic scale — •JAN ROSSMEISL — Department of Chemistry, Nano-science center, University of Copenhagen Universitetsparken 5, 2100, København Ø, Denmark

There are presently no atomic scale simulations or analysis that capture all the essential parts of the nature electrochemical interface. Thus the electrochemical solid/liquid interface represents one of the frontiers of atomic scale simulations. The electrolyte is as important for the fundamental properties of the interface as the surface. The challenge is to model the effect of and interplay between potential, pH and ion strength. Thus far these effects have not correctly been accounted for. However, based on a thermochemical analysis it is now possible to account for the effect of pH and ions in the electrolyte on the atomic structure of the interface.

Topical Talk

O 53.5 Wed 12:45 S052

CO₂ Electroreduction over Cu and Au Nanostructured Catalysts: Size, Oxidation State and Interparticle Distance Effects — HEMMA MISTRY^{1,2}, RULLE RESKE³, FARZAD BEHAFARID², ANA SOFIA VARELA³, PETER STRASSER³, and •BEATRIZ ROLDAN CUENYA¹ — ¹Department of Physics, Ruhr-University Bochum, 44708 Bochum, Germany — ²Department of Physics, University of Central Florida, Orlando FL 32816, USA — ³Department of Chemistry, Chemical Engineering Division, Technical University Berlin, 10623 Berlin, Germany

The electrocatalytic reduction of CO₂ to industrial chemicals and fuels is a promising pathway to sustainable electrical energy storage and to an artificial carbon cycle, but is currently hindered by the low energy efficiency and activity displayed by traditional electrode materials. The structure-dependent catalytic activity of Cu and Au nanoparticle (NP) catalysts for the electroreduction of CO₂ is reported here. NPs with well-defined size and interparticle distance were synthesized, and their activity and selectivity measured. A drastic increase in current density was observed with decreasing Au NP size, along with a decrease in selectivity towards CO. Cu NP catalysts also displayed a significant increase in the catalytic activity and selectivity for H₂ and CO with decreasing NP size, while methane and ethylene selectivity was increasingly suppressed. The size dependent trends observed can be rationalized by the increased population of low-coordinated surface sites on smaller NPs. The selectivity of Cu NP catalysts could be tuned by varying the interparticle distance due to mass transport phenomena such as reactant diffusion and readsorption of intermediates.