

## Fundamental Aspects of Material Degradation Focus Topic Room A212 - Session DM2+BI+SS-ThA

### Fundamentals of Catalyst Degradation: Dissolution, Oxidation and Sintering

**Moderator:** Gareth S. Parkinson, TU Wien, Austria

4:00pm **DM2+BI+SS-ThA6 Stability Challenges in Electrocatalysis, Serhiy Cherevko**, Forschungszentrum Jülich GmbH, Germany **INVITED**

Many industrially important electrochemical energy conversion technologies, such as electrolysis and fuel cells, rely on expensive noble metal electrocatalysts to accelerate reactions, and thus, improve energy conversion efficiency. Despite their relatively high stability, even noble metals are not completely immune. Indeed, the latter fact represents a considerable challenge in the wide-spread commercialization of electrolyzers and fuel cells. Electrocatalyst or support corrosion, particle agglomeration and detachment, Ostwald ripening, structural and morphological changes are just a few examples of possible degradation processes.<sup>1</sup> These processes clearly illustrate the level of complexity one has to deal with in order to understand and circumvent degradation in real devices. Thus, it is difficult to imagine modern electrocatalysis research without advanced analytical tools. In this talk I will demonstrate that the application of on-line inductively coupled plasma mass spectrometry, on-line electrochemical mass spectrometry, and identical location transmission electron microscopy in electrocatalysis research can assist in clarifying the mechanisms leading to degradation. As some representative examples I will show degradation of the state-of-the-art and advanced platinum based catalysts in fuel cells and iridium based catalyst in water electrolysis.<sup>2-4</sup> Time will also be devoted to discussing application of alternative non-noble metal catalysts in the energy conversion technologies and their stability. Finally, stability in other electrocatalytic systems, e.g. photo-electrochemical water splitting or carbon dioxide reduction will be touched.

Literature:

- 1 Cherevko, S. *Current Opinion in Electrochemistry***8**, 118-125 (2018).
- 2 Cherevko, S. *et al. Nano Energy***29**, 275-298, (2016).
- 3 Kasian, O. *et al. Angewandte Chemie***57**, 2488-2491 (2018).
- 4 Geiger, S. *et al. Nature Catalysis***1**, 508-515 (2018).

4:40pm **DM2+BI+SS-ThA8 Self-limited Growth of an Oxyhydroxide Phase at the Fe<sub>3</sub>O<sub>4</sub>(001) Surface in Liquid and Ambient Pressure Water, Florian Kraushofer**, TU Wien, Austria; *F. Mirabella*, TU Wien, Austria, Germany; *J. Xu, J. Pavelec, J. Balajka, M. Müllner, N. Resch, Z. Jakub, J. Hulva, M. Meier, M. Schmid, U. Diebold, G.S. Parkinson*, TU Wien, Austria

Atomic-scale investigations of metal oxide surfaces exposed to aqueous environments are vital to understand degradation phenomena (e.g. dissolution and corrosion) as well as the performance of these materials in applications. Here, we utilize a new experimental setup for the UHV-compatible dosing of liquids to explore the stability of the Fe<sub>3</sub>O<sub>4</sub>(001)-(√2 × √2)R45° surface following exposure to liquid and ambient pressure water, using low energy electron diffraction (LEED), x-ray photoemission spectroscopy (XPS) and scanning tunnelling microscopy (STM).

Short-time exposure of the surface to clean H<sub>2</sub>O results in hydroxylation of the surface, which is not observed in UHV. After longer exposure times, we observe lifting of the (√2 × √2)R45° reconstruction with LEED and stronger hydroxylation of the surface with XPS, in agreement with previous reports. However, scanning tunnelling microscopy (STM) images reveal a more complex situation than simply reverting to a bulk-truncation, with the slow growth of an oxyhydroxide phase, which ultimately saturates at approximately 40% coverage. We conclude that the new material contains OH groups from dissociated water coordinated to Fe cations extracted from subsurface layers, and that the surface passivates once the surface oxygen lattice is saturated with H because no further dissociation can take place.

5:00pm **DM2+BI+SS-ThA9 The Impact of W on the Early Stages of Oxide Evolution for Ni-Cr Alloys, C. Volders, V.A. Avincola**, University of Virginia; *I. Waluyo*, Brookhaven National Laboratory; *J. Perepezko*, University of Wisconsin - Madison; *Petra Reinke*, University of Virginia

Ni-Cr alloys are highly coveted as they exhibit superior corrosion resistance due to the formation of a passive chromia film which helps protect the underlying alloy from degradation. The properties of this system are

further enhanced through the addition of minor alloying elements such as Mo or W. For example, Mo is known to reduce catastrophic events such as pitting and crevice corrosion, thereby enhancing overall corrosion resistance. The ideal composition for technical Ni-Cr alloys has been optimized over many decades, however, the mechanistic understanding for the role of alloying elements such as Mo and W has not been fully developed. The primary objective of this work is to formulate a better mechanistic understanding of how the addition of W impacts the early stages of oxidation for this system and eventually use this information for further improvement of Ni-Cr alloys.

To achieve our goal, a series of oxidation experiments with the direct comparison between Ni-15Cr and Ni-15Cr-6W (weight percent) samples were performed and analyzed with the use of X-ray photoelectron spectroscopy (XPS). The first set of experiments employed an *in-operando* XPS approach where the modulation of alloy and oxide composition and bonding was observed over an extended period of time delivering a detailed view of the reaction pathways. The key results from this work include the observation of Cr surface segregation in the alloys prior to oxidation, which contributes to a rapid nucleation of Cr oxide species in the first reaction steps. The more intriguing result was the addition of W to the alloy resulted in a near complete suppression in the formation of Ni oxide, while further enhancing the formation of a pure chromia phase, which has been attributed to the addition of W increasing the supply of Cr to the surface and will be discussed.

A second series of XPS experiments focus on oxidation as function of crystallographic orientation of individual, large grains for Ni-15Cr and Ni-15Cr-6W. The differences in atom density and surface energies as a function of orientation lead us to expect significant differences in reactivity which will impact passivation and oxide performance. This has been demonstrated for aqueous corrosion of NiCr and NiCrMo alloys by Scully *et al. J. Phys. Chem. C*, **2018**, 122 (34), 19499-19513, and our work is complementary for thermal oxidation studies. In this work, Ni-15Cr and Ni-15Cr-6W samples were thermally oxidized and we will present and discuss the difference in oxidation products for various grain orientations for both samples.

5:20pm **DM2+BI+SS-ThA10 The Stability of Platinum in Non-aqueous Media, J. Ranninger, S. Wachs, J. Möller, K. Mayrhofer, Balázs Berkes**, Forschungszentrum Jülich GmbH, Germany

Many basic reactions in electrochemistry, like the hydrogen oxidation reaction, oxygen reduction reaction, water oxidation or CO<sub>2</sub> reduction reaction has been thoroughly studied in aqueous electrolytes. To these fundamental studies well defined experimental conditions have been chosen: smooth or single crystal electrodes with known surface structures, ultrapure electrolytes and very clean experimental apparatus. In many respects electrocatalysis in organic solvents is much less advanced than its understanding in aqueous systems.

The example of LIBs shows us, however, clearly how much potential of non-aqueous electrochemistry holds, in this particular example for the development of energy storage devices. Other important and possible technical applications are new type of batteries, electro-organic synthesis including electrochemical reduction of CO<sub>2</sub>, electrodeposition, supercapacitors or electrochemiluminescence.

Stability of electrochemical systems is a particularly important question in electrocatalysis. No matter if it is a fuel cell, a battery, a supercapacitor, a construction subject to corrosion or an electrode used for synthesis, economic considerations require a certain lifetime of these systems. Therefore, it is also important to understand electrocatalysis especially the aspect of stability in non-aqueous electrolytes. To this end very sophisticated, often in situ and real-time analysis methods are required. In this work we show a powerful approach to study dissolution phenomena in non-aqueous electrochemical systems on the example of platinum.

Platinum is often considered to be a model electrode and catalyst material. This metal is probably the most thoroughly studied one in electrochemistry, however, it still shows many interesting yet not well understood features. This is also true for the stability of the metal during potential cycling. The electrochemical stability window of organic electrolytes is usually much higher than that of water enabling the simultaneous cycling and downstream analysis of dissolution in a higher potential range. As a result, even the electrochemistry of platinum shows hitherto unveiled phenomena regarding its dissolution mechanism especially when using electrolytes with ultra-low (1 ppm) water content. In this work, we focus on the effect of water, anions, cations and organic solvent molecules on the anodic and cathodic dissolution behavior of

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platinum. To demonstrate the benefits of this novel method on the field of non-aqueous electrochemistry the stability of other non-aqueous systems will be discussed shortly, too.

5:40pm **DM2+BI+SS-ThA11 Stabilizing Transparent Conductive Oxides as a Route to Long-Lived Thin Film Photovoltaics: A Case Study in CIGS**, *N.C. Kovach*, Colorado School of Mines; *R. Matthews*, *E.B. Pentzer*, Case Western Reserve University; *L. Mansfield*, National Renewable Energy Laboratory; *T.J. Peshek*, NASA Glenn Research Center; *Ina Martin*, Case Western Reserve University

Degradation of the aluminum-doped zinc oxide (AZO) top contact is a known failure mode in Cu(In,Ga)Se<sub>2</sub> (CIGS) solar cells. The degradation of the AZO can be observed in device and module current-voltage characteristics as an increase in series resistance and decrease in fill factor. Due to its low cost and earth abundance, AZO is a good choice for the TCO in thin-film solar cells. However, it has one of the higher degradation rates of TCOs under damp heat stress. 3-aminopropyltriethoxysilane (APTES) was used to modify the AZO top contacts in CIGS solar cells. Results demonstrate that the application of the nm-scale modifier mitigates AZO degradation in damp-heat exposure, and further, arrests the degradation of the full CIGS device.

APTES modification of thick (~0.8 μm) AZO films significantly impedes the electrical degradation of the material caused by DH exposure, without significantly affecting the initial optical, electrical, or structural properties of the AZO films. Upon 1000 h of DH exposure, resistivity of both systems increased and can be attributed only to decreased mobility, as carrier concentration was consistent. APTES modification slowed the increase in AZO resistivity over 1000 h of DH exposure; however, the protective nature of APTES modification became critical after 1500 h. At this extended exposure time, macroscopic degradation was observed only for bare AZO including pitting and delamination and was accompanied by an increase in resistivity and decrease in carrier concentration. X-ray photoelectron spectroscopy (XPS) data show that the APTES layer stabilizes the oxygen binding environment of the AZO surface, suggesting that covalent passivation of AZO surface sites by silanization essentially “caps” reactive moieties, thereby improving the stability of the material.

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