

Fundamental Aspects of Material Degradation Focus Topic Room A212 - Session DM+BI+SS-ThM

Material Stabilities and Technology for Degradation Protection

Moderators: Markus Valtiner, Vienna University of Technology, Austria, Gareth S. Parkinson, TU Wien, Austria

8:00am **DM+BI+SS-ThM-1 Extremely Thin Protective Oxide Layer for Reflective Silver Thin Films**, *Midori Kawamura, E Kudo, Y Sasaki, T Kiba, Y Abe, K Kim*, Kitami Institute of Technology, Japan; *H Murotani*, Tokai University, Japan

Silver (Ag) thin films possess high electrical and optical properties, but their low stability should be resolved. We have developed a highly stable Ag thin film where thermal agglomeration can be suppressed, by utilizing nanometer thick surface Al layers. Then we have confirmed that Al surface nanolayer deposited Ag films show a high optical reflectance as well as Ag single film. Here, the Al nanolayer was oxidized to be Al oxide nanolayer, being transparent in visible region, by natural oxidation in air. In the present study, we investigate durability of the Ag films with surface nanolayers under high humidity condition.

We prepared Ag single layer (150 nm), Ti (1, 3 -nm) / Ag films and Al (1, 3 -nm) / Ag films on glass substrate by rf magnetron sputtering in Ar discharge. In addition, vacuum evaporation method was also used for the preparation of Al (1, 3 -nm) / Ag films. A difference on degradation of the films by different fabrication methods was investigated. The samples were kept for 16 hrs in a chamber where temperature and humidity was set to 55°C and 90%RH, respectively.

After the test, agglomeration occurred in Ag single layer and optical reflectance was decreased. On the other hand, Ti or Al nanolayer covered Ag films kept smooth surface even after the test. The surface roughness observed using AFM was as small as 1.0 nm. As a result, we have found that both Al and Ti surface nanolayers can play significant role as protective layer under high humidity condition. However, Ti / Ag films showed a lower reflectance due to light absorption by TiO₂ layer formed on the surface, and the samples with Al surface nanolayer showed a higher optical reflectance.

By XPS analysis, very thin Ag sulfide formation was observed in Ag single film after the humidity test, but not in Ti or Al covered Ag films. This suggests very thin Al oxide or Ti oxide nanolayer prevented contact of Ag atoms and SO₂ gas in air. However, Ag signal was detected in the surface oxide layers, which indicates onset of outward diffusion of Ag atoms.

8:20am **DM+BI+SS-ThM-2 Influence of the Electric Double Layer on Degradation of Materials**, *Dominik Dworschak, M Valtiner*, Vienna University of Technology, Austria

Corrosion and adhesion science usually focuses on the solid side of a liquid/solid or solid/adhesive interface. However, the only some nanometer thick interface itself is the complex transition region which drives many important processes in corrosion and delamination. The electric double layer (EDL) is a key part of the interfacial region but remains mostly neglected as a potential key player in degradation processes. Here, we will demonstrate that the EDL has an important influence on the corrosion mechanism of passivating materials in the transpassive region (material dissolution at potentials where the passive film breaks down).

We utilize an electrochemical flow cell combined with an inductively coupled mass spectrometer (ICP-MS) to enable the in-situ study of the time-resolved release of elements into solution. This provides detailed insights into the nature of the passive and transpassive condition. As model systems, we use nickel based alloys. These are essential to modern industry and uniquely tailored for a wide range of applications, which rely on high corrosion and heat resistance. In particular, we polarized a series of Ni₇₅Cr₁₆Fe₉, Ni₈₆Cr₅Fe₉ as well as Ni₇₄Cr₁₆Fe₉Mo₁ model alloys in order to understand the effect of chromium concentration and molybdenum on transpassive dissolution

In the transpassive regime we can detect the presence of protective species of chromium and molybdenum on the surface. Unexpectedly, we can demonstrate significant corrosion resistance above a critical potential where the passive film breaks down. This is traditionally known as trans passive region with bulk dissolution of metal alloys. However, we find that the EDL forms a transient passivating solution side protective layer in the transpassive region – i.e. we characterize an electric double layer induced corrosion resistance, which solely – and surprisingly – lies in the structure of

the solution side. This finding has general important implications for designing degradation resistance in highly corrosive environments.

8:40am **DM+BI+SS-ThM-3 Key Issues for the Stability of Protective Surface Oxides**, *Philippe Marcus*, CNRS - Chimie ParisTech, France **INVITED**

This lecture will focus on a surface science approach of corrosion and protection of metals and alloys, with emphasis on the structure and growth of surface oxide layers, a central theme in corrosion science.

Understanding early stage oxidation of metal surfaces at atomic or nanometric scale is a key to a better design and an improved control of engineering metals.

The following topics will be addressed:

- Nanostructure of ultra-thin oxide layers (passive films) on metals,
- Early stage oxidation of stainless steels,
- Local electronic properties of passive films,
- Mechanisms of initiation of localized corrosion, with emphasis on the role of surface defects in localized attack leading to corrosion,

The data that will be presented are obtained by using *in situ* Scanning Tunneling Microscopy (STM), Scanning Tunneling Spectroscopy (STS), X-Ray Photoelectron Spectroscopy (XPS), Time-of-Flight Secondary Ions Mass Spectrometry (ToF-SIMS) combined with electrochemical techniques and DFT calculations.

9:20am **DM+BI+SS-ThM-5 Controlling and Observing Localized Dealloying Corrosion and Dissolution via Lateral Modification of Surfactant Inhibitor Layers**, *S Neupane*, Hasselt University, Belgium; *Frank Uwe Renner*, IMEC vzw. Division IMOME, Belgium

Corrosion processes on metals and alloys may result in substantial degradation and loss of functionality. Mitigation strategies include alloy design, to allow for passivation, or the application of inhibitors to protect materials but they are often causing irreversible damage and potential catastrophic failure at more severe corrosion conditions. The ultimate understanding of the involved fundamental processes including the initial stages of corrosion attacks is still lacking, in particular on the important atomic and molecular scale. Surfactant inhibitors protect surfaces from corrosion by forming molecular layers or so-called self-assembled monolayers separating the material from the corrosive environment. Yet, with inhibitors *localized dealloying* takes place at higher electrochemical potentials [1]. To address the fundamental nature of the site of initiation of dealloying corrosion we have recently introduced different strategies for novel surface-science approaches [2]. On the one hand the inhibitor layer can be laterally modified by using a sequential application combining different steps of micro-contact printing and solution backfilling [3]. In consequence an array of artificial defects such as patch boundaries or displacements by overprinting using foreign impurity molecules can be obtained in a well-controlled way. On the other hand the molecular stability may be locally probed by molecular-scale force measurements employing AFM techniques. In the retract force curve molecular fishing events are eventually visible which can be correlated to the inhibition efficiency. We here exemplify both aspects on noble metal model systems such as Cu-Au and more reactive surfaces including Cu-Zn and pure Cu. On Cu-Au surfaces initial dealloying pits are occurring along patch boundaries formed by sequential application of thiol inhibitors [4]. On Cu surfaces we applied different mercapto-benzimidazoles and could indeed link the observed layer stability with the actual corrosion behavior.

[1] A. Pareek et al., J. Am. Chem. Soc.133 (2011) 18264–18271. [2] B. Shresta et al., Faraday Discuss. 180 (2015), 191. [3] S. Neupane et al., Langmuir. 34 (2018) 66–72. [4] S. Neupane et al., submitted.

9:40am **DM+BI+SS-ThM-6 In Situ Characterization of Interactions at Polymer/Metal Oxide Interfaces Under Aqueous Conditions by a Spectro-electrochemical Approach**, *Sven Pletincx*, Vrije Universiteit Brussel, Belgium; *L Fockaert, A Mol*, Delft University of Technology, Netherlands; *H Terryn, T Hauffman*, Vrije Universiteit Brussel, Belgium

The mechanisms governing coating/metal oxide delamination are not yet fully understood, although strong and durable adhesive interactions at the interface are considered to be an important prerequisite for good coating durability. Achieving adequate adhesion strengths between an organic and inorganic system in various operating conditions is one of the complex challenges of interface engineering. However, obtaining local chemical information at this solid/solid interface is challenging, since common surface sensitive analysis techniques only operate under vacuum conditions, making it impossible to probe environmental effects *in situ*.¹

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The analysis of this so-called buried interfaces is achieved by characterizing ultrathin polymer films onto a metal oxide substrate by ambient-pressure photoelectron spectroscopy (APXPS).² Here, we show that APXPS with a conventional X-ray source can be used to study the effects of water exposure on the interaction of acrylic coatings with aluminum oxide. This is done by making the polymer layer sufficiently thin to probe the interface non-destructively.

A *spectroelectrochemical* setup of *in situ* ATR-FTIR Kretschmann and Odd Random Phase Electrochemical Impedance Spectroscopy (ORP-EIS) on a complementary model system is used to characterize and monitor the formed bonds at the metal oxide/polymer interface.³ A nanometer thin aluminum layer is sputtered on an IR transparent crystal, such that the IR signal reaches the oxide/polymer interface, obtaining a near-interface spectrum. This way, we have direct access to the interface, and the influence of an above-the-polymer electrolyte (i.e. H₂O) is probed. Simultaneously the protective properties and corrosion processes of the overall hybrid system are monitored by ORP-EIS.

This work shows that by using ultrathin films in combination with a set of recently developed techniques, it is possible to non-destructively and *in situ* probe interfacial changes in hybrid systems.

1. Watts, J. F. The Interfacial Chemistry of Adhesion: Novel Routes to the Holy Grail? *Adhes. Curr. Res. Appl.* 1–16 (2006). doi:10.1002/3527607307.ch1

2. Pletincx, S. *et al.* In Situ Characterization of the Initial Effect of Water on Molecular Interactions at the Interface of Organic/Inorganic Hybrid Systems. *Sci. Rep.* **7**, 45123 (2017).

3. Pletincx, S. *et al.* In Situ Methanol Adsorption on Aluminum Oxide Monitored by a Combined ORP-EIS and ATR-FTIR Kretschmann Setup. *J. Phys. Chem. C* **122**, 21963–21973 (2018).

11:00am **DM+BI+SS-ThM-10 Design of Corrosion Resistant High Entropy Alloys**, *Gerald Frankel*, *C Taylor*, *W Windl*, The Ohio State University; *J Scully*, University of Virginia; *J Locke*, The Ohio State University; *P Lu*, Questek Innovations

INVITED

The corrosion resistance of a metal alloy is dictated by the exposure environment as well as the alloy structure, composition, and details of the surface condition such as the presence of a passive film. The design of new alloys with improved corrosion resistance must take all of these factors into account. As a result, the degrees of freedom in alloy design are so numerous that the standard process of trial and error is extremely lengthy, even using high throughput methods. This is particularly true for emerging materials such as high entropy alloys (HEAs) and bulk metallic glasses. The complexity of the corrosion process makes integrated computational materials engineering (ICME) for corrosion resistance very challenging. In this work we describe an approach for design of corrosion resistant alloys (CRAs) using ICME. The work has focused on HEAs because of the vast, multidimensional compositional and processing space associated with HEAs. The ultimate goal of CRA design is a combination of multiscale, multiphysics models that accurately describe the details of each of the controlling mechanisms and chemical/physical interactions in the degradation process. However, progress can be made using computational approaches coupled with empiricism. Calculation of Phase Diagrams (CalPhaD) methods are extremely useful in this regard. Furthermore, a number of relevant calculable parameters, such as metal-metal and metal-oxygen bond strength or chloride ion adsorption energies, can be used to create correlations with corrosion metrics that enable prediction of corrosion properties of alloys in previously unexplored compositional space. We will present the methodology used for the design of an extremely corrosion resistant HEA as well as a series of HEAs that are less resistant, but allow for the assessment of critical parameters controlling corrosion resistance in HEAs.

11:40am **DM+BI+SS-ThM-12 Determination of Hydrogen in High Strength Steels using Scanning Kelvin Probe Force Microscopy**, *Ines Traxler*, *G Schimo-Aichhorn*, CEST Competence Centre for Electrochemical Surface Technology, Austria; *A Muhr*, *G Luckeneder*, *H Duchaczek*, *K Stellnberger*, voestalpine Stahl GmbH, Austria; *D Rudomilova*, *T Prosek*, University of Chemistry and Technology Prague, Czech Republic; *B Lutzer*, CEST Competence Centre for Electrochemical Surface Technology, Austria; *D Stifter*, *S Hild*, Johannes Kepler University Linz, Austria

High-strength steels are important materials for the automotive industry. Due to their good formability and high strength they are used for the manufacture of light weight and fuel-efficient automotive parts. A disadvantage of high strength steels is their proneness to hydrogen

embrittlement. Even small amounts of hydrogen can cause a deterioration of mechanical properties. Therefore, the effect of hydrogen on the steel microstructure is of great interest and it is important to study and visualize the effects and mechanisms of hydrogen in steels. For this purpose, Scanning Kelvin Probe Force Microscopy (SKPFM) is a promising technique for the investigation of hydrogen in the steel microstructure with a very good spatial resolution.

Hydrogen diffusion in different high-strength steels was investigated using SKPFM. Hydrogen entry at cut edges and coating defects was studied as well as the influence in the individual steel grains. The measurements were carried out with different salt solutions on the backside of CP1000 (complex phase), DP1000 (dual phase) and zinc coated DP1000 steels to induce corrosion and promote hydrogen entry into the steel. The permeating hydrogen was measured on the upper side of the sample by repeated surface scans and the effect on the contact potential difference (CPD) was studied. Furthermore, SKPFM measurements with different relative humidity were carried out, monitoring the effects of corrosion. Additionally, Scanning Kelvin Probe (SKP) measurements were done for comparison.

With SKPFM, the preferred diffusion pathways of hydrogen through the steel microstructure could be visualized as well as the effect of zinc coatings on hydrogen permeation.

12:00pm **DM+BI+SS-ThM-13 Reflection Mode Interferometry for studying interfacial processes**, *Kai Schwenzfeier*, *P Bilotto*, *M Lengauer*, *C Merola*, *H Cheng*, *M Valtiner*, TU Wien, Austria

Molecular level processes at electrified solid|liquid interfaces play a critical role in corrosion and degradation processes. These include adsorption of ions, evolution of electrochemical double layers, oxidation/dissolution of metals, screening effects as well as liquid properties at an interface. However those processes/effects are notoriously hard to measure due to long integration times or too small probe with many available analysis techniques.

We refined Multiple Beam Interferometry (MBI) to enable time resolved *in situ* and *operando* measurement of processes at solid|liquid interfaces in both transmission and reflection geometry. In this presentation dynamic interfacial processes such as changes of refractive indices in small (nanometer sized gaps), a micro-to-angstrom scale view into corrosion processes and surface oxidation, as well as specific and non-specific potential driven ion adsorption in aqueous solutions will be discussed in detail. We will relate these measurements to molecular resolution AFM imaging and force spectroscopy at solid|liquid interfaces.

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Low Fouling Interfaces and Environmental Degradation

Moderator: Axel Rosenhahn, Ruhr-University Bochum

2:20pm DM1+BI+SS-ThA-1 Utilizing Experimental and MD Simulation Approaches in the Understanding and Design of Low Fouling Interfaces, *Paul Molino*, University of Wollongong, Australia **INVITED**

Biofouling is a ubiquitous problem for a diverse suite of industries, impacting the functionality of materials and devices. Diverse approaches taken in the design of materials and interfaces to prevent microbial fouling often rely on atomic and molecular scale processes, however the fundamental mechanism/s underlying these processes, and their mode of action, in many cases continue to elude researchers. Highly hydrophilic chemistries such as polyethylene glycol and zwitterion-based chemistries, have long been used to generate interfaces that prevent biological interactions at surfaces. Such surface chemistries have been proposed to function through a combination of molecular water organisation and steric repulsion at the interface. Experimental approaches have confirmed the presence of hydration layers associated with hydrophilic polymer-based surfaces, yet the fundamental mechanisms underlying their capacity to inhibit surface fouling, and how such hydration layers differ from equally hydrophilic interfaces that do not prevent surface fouling is still unclear. Molecular dynamic (MD) simulations have gone some way to provide critical insights into their respective mechanism/s of action, however experimental approaches capable of adequately resolving features at a suitable spatial resolution to corroborate and build on these models have been lacking. Herein I will present a highly biofouling resistant coating composed of silica nanoparticles functionalised with a short chain hydrophilic silane. To understand the interfacial environment at the hydrated nanoparticle surface, frequency modulation – atomic force microscopy was used to provide sub-atomic resolution of the water structuring about the nanoparticle interface, which we validate using all-atom molecular dynamic simulations that strikingly predict similar structures of water layers on the original and ultralow fouling surfaces. The convergence of experimental and modelling data reveals that suitably spaced, flexible chains with hydrophilic groups interact with water molecules to produce a connective, *quasi-stable* layer, consisting of dynamic interfacial water, that provides a basis for antifouling performance of ultrathin, hydrophilic surface chemistries. This approach provides a road map for the future development and optimisation of interfacial chemistries and materials designed to combat biofouling and biodegradation.

3:00pm DM1+BI+SS-ThA-3 Study of Environmental Exposure Effects on Pristine and DC Magnetron Sputtering Metallic Coated 3D Printed Polymers, *D Mihut, Arash Afshar, P Chen*, Mercer University

Three dimensional printing is a promising technique for producing complex geometries and high precision structures from different types of materials. The technique is particularly attractive for polymeric materials due to the cost effectiveness; however when compared to other manufacturing techniques the resulting structures have low mechanical properties and low performance as exposed to harsh environmental conditions. ABS (acrylonitrile butadiene styrene) and PLA (polylactic acid) are common thermoplastic polymers used for many applications (e.g. electrical and electronic assemblies, medical devices, implants, toys). For this research, the ABS and PLA specimens for tensile and flexural testing were 3D manufactured according to standards and their mechanical properties were tested using hardness tester, and Mark-10 tensile testing equipment. In order to simulate outdoor environmental conditions while avoiding the uncertainties associated with it, specimens were exposed to controlled environmental chamber. Accelerated exposure was performed using a UV radiation/condensation (Q-Lab QUV/basic) accelerated weathering tester. ABS and PLA samples were exposed to UV radiation, high temperature and moisture cycles for different time intervals. Some ABS samples were coated with optically thick metallic materials (silver and copper) using high vacuum DC magnetron sputtering deposition system and were later exposed to UV radiation, high temperature and moisture cycles using same conditions as for un-coated samples. The surface and cross section morphology of samples and the adhesion of metallic layers to the polymer substrates were examined using scanning electron microscopy and laser scanning microscopy. The crystalline structure of the metallic coatings was analyzed using X-ray Diffraction technique. The mechanical properties were characterized using flexural and hardness tests over the exposure time. The

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metallic thin films improved the surface resistance of the substrate materials and enhanced the mechanical behavior of samples exposed to harsh environmental conditions.

3:20pm DM1+BI+SS-ThA-4 Reaction Mechanism of Chloride-induced Depassivation of Oxide Films: a Density Functional Theory Study, *Q Pang, H DorMohammadi, K Oware Sarfo, P Murkute, Y Zhang, O Isgor, J Tucker, Linye Árnadóttir*, Oregon State University

A protective iron oxide film (passive film) forms on the surface of iron in alkaline environment, such as in reinforced concrete. Chloride and other aggressive ions can cause the breakdown of the passive film (depassivation) in the same environment, leading to active corrosion. The mechanism of the Cl-induced depassivation is studied on flat and stepped $\alpha\text{-Fe}_2\text{O}_3$ (0001) surfaces because $\alpha\text{-Fe}_2\text{O}_3$ has been suggested to be one of the dominant oxides in the outer layer of the passive film.

The oxidation state of the surface metal atoms plays an important role in Cl-surface interactions and depassivation. Cl binds more strongly to metal atoms at lower oxidation state and these adsorption sites can facilitate higher local coverage. Defect sites, such as on a step edge or next to a O vacancy have lower oxidation states, suggesting an important role of defects in the depassivation process. Two main mechanisms of depassivation have been proposed in the literature, the point defect model that proposes a depassivation through Cl enhanced Fe vacancy formation on the surface and void formation at the metal oxide/metal interface, and the ion exchange model, which proposes a depassivation mechanism through subsurface Cl. Our studies of the thermodynamics of Cl ingress into the passive film, Fe vacancy formation, and bulk vacancy stability all support the point defect model for iron oxide. The initial stages of Cl-induced depassivation are proposed through a combination of reactive force field molecular dynamics simulations and DFT calculations.

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-ThA-6 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.¹ 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.²⁻⁴ 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).

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4:40pm **DM2+BI+SS-ThA-8 Self-limited Growth of an Oxyhydroxide Phase at the Fe₃O₄(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 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 Fe₃O₄(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 H₂O 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-ThA-9 The Impact of W on the Early Stages of Oxide Evolution for Ni-Cr Alloys**, *Cameron Volders*, *V Avincola*, University of Virginia; *I Waluyo*, Brookhaven National Laboratory; *J Perepezko*, University of Wisconsin - Madison; *P 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-ThA-10 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 CO₂ 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 CO₂, 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 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-ThA-11 Stabilizing Transparent Conductive Oxides as a Route to Long-Lived Thin Film Photovoltaics: A Case Study in CIGS**, *N Kovach*, Colorado School of Mines; *R Matthews*, *E Pentzer*, Case Western Reserve University; *L Mansfield*, National Renewable Energy Laboratory; *T 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)Se₂ (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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— H —

Hauffman, T: DM+BI+SS-ThM-6, 1
Hild, S: DM+BI+SS-ThM-12, 2
Hulva, J: DM2+BI+SS-ThA-8, 4

— I —

Isgor, O: DM1+BI+SS-ThA-4, 3

— J —

Jakub, Z: DM2+BI+SS-ThA-8, 4

— K —

Kawamura, M: DM+BI+SS-ThM-1, **1**
Kiba, T: DM+BI+SS-ThM-1, 1
Kim, K: DM+BI+SS-ThM-1, 1
Kovach, N: DM2+BI+SS-ThA-11, 4
Kraushofer, F: DM2+BI+SS-ThA-8, **4**

Kudo, E: DM+BI+SS-ThM-1, 1

— L —

Lengauer, M: DM+BI+SS-ThM-13, 2
Locke, J: DM+BI+SS-ThM-10, 2
Lu, P: DM+BI+SS-ThM-10, 2
Luckeneder, G: DM+BI+SS-ThM-12, 2
Lutzer, B: DM+BI+SS-ThM-12, 2

— M —

Mansfield, L: DM2+BI+SS-ThA-11, 4
Marcus, P: DM+BI+SS-ThM-3, **1**
Martin, I: DM2+BI+SS-ThA-11, **4**
Matthews, R: DM2+BI+SS-ThA-11, 4
Mayrhofer, K: DM2+BI+SS-ThA-10, 4
Meier, M: DM2+BI+SS-ThA-8, 4
Merola, C: DM+BI+SS-ThM-13, 2
Mihut, D: DM1+BI+SS-ThA-3, 3
Mirabella, F: DM2+BI+SS-ThA-8, 4
Mol, A: DM+BI+SS-ThM-6, 1

Molino, P: DM1+BI+SS-ThA-1, **3**

Möller, J: DM2+BI+SS-ThA-10, 4

Muhr, A: DM+BI+SS-ThM-12, 2

Müllner, M: DM2+BI+SS-ThA-8, 4

Murkute, P: DM1+BI+SS-ThA-4, 3

Murotani, H: DM+BI+SS-ThM-1, 1

— N —

Neupane, S: DM+BI+SS-ThM-5, 1

— O —

Oware Sarfo, K: DM1+BI+SS-ThA-4, 3

— P —

Pang, Q: DM1+BI+SS-ThA-4, 3
Parkinson, G: DM2+BI+SS-ThA-8, 4
Pavelec, J: DM2+BI+SS-ThA-8, 4
Pentzer, E: DM2+BI+SS-ThA-11, 4
Perepezko, J: DM2+BI+SS-ThA-9, 4
Peshek, T: DM2+BI+SS-ThA-11, 4

Pletincx, S: DM+BI+SS-ThM-6, **1**

Prosek, T: DM+BI+SS-ThM-12, 2

— R —

Ranninger, J: DM2+BI+SS-ThA-10, 4

Reinke, P: DM2+BI+SS-ThA-9, 4

Renner, F: DM+BI+SS-ThM-5, **1**

Resch, N: DM2+BI+SS-ThA-8, 4

Rudomilova, D: DM+BI+SS-ThM-12, 2

— S —

Sasaki, Y: DM+BI+SS-ThM-1, 1

Schimo-Aichhorn, G: DM+BI+SS-ThM-12, 2

Schmid, M: DM2+BI+SS-ThA-8, 4

Schwenzfeier, K: DM+BI+SS-ThM-13, **2**

Scully, J: DM+BI+SS-ThM-10, 2

Stellnberger, K: DM+BI+SS-ThM-12, 2

Stifter, D: DM+BI+SS-ThM-12, 2

— T —

Taylor, C: DM+BI+SS-ThM-10, 2

Terry, H: DM+BI+SS-ThM-6, 1

Traxler, I: DM+BI+SS-ThM-12, **2**

Tucker, J: DM1+BI+SS-ThA-4, 3

— V —

Valtiner, M: DM+BI+SS-ThM-13, 2;

DM+BI+SS-ThM-2, 1

Volders, C: DM2+BI+SS-ThA-9, **4**

— W —

Wachs, S: DM2+BI+SS-ThA-10, 4

Waluyo, I: DM2+BI+SS-ThA-9, 4

Windl, W: DM+BI+SS-ThM-10, 2

— X —

Xu, J: DM2+BI+SS-ThA-8, 4

— Z —

Zhang, Y: DM1+BI+SS-ThA-4, 3