

## Surface Science Division

### Room D136 - Session SS1+HC-MoM

#### Electrochemistry

Moderators: Jan Balajka, TU Wien, Sefik Suzer, Bilkent University, Turkey

8:20am **SS1+HC-MoM-1 Surface Inhomogeneities and Ordering Phenomena of (Pr,Ba)CoO<sub>3-δ</sub> Thin Film Electrocatalysts Induced by High Temperatures and Oxygen Partial Pressures**, David Mueller, M. Giesen, T. Duchon, C. Schneider, Forschungszentrum Jülich GmbH, Germany  
Complex transition metal oxides are used ubiquitously in (electro-)catalysis, ternary and quaternary compounds of the perovskite structure showing especial promise for increasing the efficacy of a plethora of redox reactions. The perovskite structure ABO<sub>3</sub> being able to accommodate a huge range of elements on both A- and B-site allows to tune the electronic and physicochemical properties and tailor those towards a certain catalytic application by careful design of the chemistry. This rational design paradigm has led to the identification of simple descriptors that offer structure-property-activity predictions. These descriptors, mostly derived from the electronic states near the Fermi level, can, for example, be elucidated through X-Ray absorption (XAS) or photoemission spectroscopy.<sup>1</sup>

The catalyst surfaces, however, are dynamic in technologically relevant conditions. Design rules thus have to consider structural, chemical and electronic rearrangements at the surface during catalysis or catalyst processing. Adding to this complexity, spatial inhomogeneities may arise from decomposition pathways that are not found in the bulk, and occur on length scales that can not be resolved by standard electrochemical or spectroscopic techniques.

Here, we investigate (Pr,Ba)CoO<sub>3-δ</sub> (PBCO) as a prototypical example material that exhibits both promising catalytic properties towards the oxygen evolution reaction in solid electrochemical cells<sup>2</sup> as well as a rich structural and chemical complexity depending on oxygen content.<sup>3</sup> Exposing epitaxial thin films grown by pulsed laser deposition to elevated temperatures and oxygen partial pressures typically present in operation, we could identify severe chemical rearrangements at the nanoscale using X-Ray absorption photoelectron microscopy (X-PEEM). We employ principal component analysis on the spatially resolved XAS spectra of all constituents to unambiguously identify correlations of chemical and electronic inhomogeneities.<sup>4,5</sup> Even though PBCO has been found to be thermodynamically stable in the cubic phase over a wide range temperature and oxygen partial pressures in the bulk, our data suggests a Cahn Hillard type decomposition process confined to the surface after mere hours of exposure. The decomposition products show a considerable lateral inhomogeneity of both A-site chemistry and the electronic structure at the surface, emphasizing that activity descriptors derived from this through spatially averaging techniques have to be heavily scrutinized.

<sup>1</sup>J. Suntivich *et al.*, *Science* **334**, 1383–1385 (2011); <sup>2</sup>A.Grimaud *et al.*, *Nat. Commun.* **4**, 2439 (2013); <sup>3</sup>C. Frontera, *Chem. Mater.*, **17**, 5439-5445 (2005); <sup>4</sup>M. Giesen *et al.*, *Thin Solid Films* **665**, 75-84(2018). <sup>5</sup>D. N. Mueller *et al.*, *J. Phys. Chem. C* **125**, 2021, 10043-10050

8:40am **SS1+HC-MoM-2 Understanding the Influence of Electrolyte and the Buried Interface on the Stability of Hybrid Systems: A Spectro-Electrochemical Approach**, Tom Hauffman, N. Madelat, B. Wouters, A. Hubin, H. Terry, Vrije Universiteit Brussel, dept. Materials and Chemistry, Belgium

The stability of the interface between (organic) coatings and metal (oxides) is of crucial importance for the durability and efficiency of hybrid structures in numerous applications, e.g. in food packaging, automotive, ... This interface is a challenging zone to analyze: from both sides covered with micro- to millimeter thick layers, surface sensitive spectroscopic techniques cannot unravel its characteristics in a non-destructive way. Moreover, the change of this interface due to environmental influences remains challenging to reveal.

In this work, we propose the use of a combined electrochemical and spectroscopic method: Odd Random Phase Multisine Electrochemical Impedance Spectroscopy in combination with Infrared Spectroscopy in a Kretschmann geometry. This fusion allows to correlate the global electrochemical characteristics of the system – such as water uptake and ion diffusion – with enhanced interfacial information.

The concept of this approach is proven on ultrathin PAA and PMMA layers on aluminium oxide<sup>1</sup>, clearly elucidating the surface sensitivity of the

Kretschmann geometry and unravelling the enhanced adhesion effect of water on short time scales.

The combined characterization tool has been employed on “industrial -like” organic coatings on model engineering metals. Here, the influence of water uptake, the possibility to make a distinction between water ingress and water diffusion, the influence of both species on delamination and corrosion and the influence of the tuned buried interface will be presented<sup>2,3,4</sup>.

1. Pletincx S. et al., An in situ spectro-electrochemical monitoring of aqueous effects on polymer/metal oxide interfaces, *Journal of Electroanalytical Chemistry* **848** (2019).
2. Wouters B. et al., Monitoring initial contact of UV-cured organic coatings with aqueous solutions using odd random phase multisine electrochemical impedance spectroscopy, *Corrosion Science* **190** (2021).
3. Madelat N. et al., Differentiating between the diffusion of water and ions from aqueous electrolytes in organic coatings using an integrated spectro-electrochemical approach, *Corrosion Science* **212** (2022).
4. Madelat N. et al., An ORP-EIS approach to distinguish the contribution of the buried interface to the electrochemical behaviour of coated aluminium, *Electrochimica Acta* **455** (2023).

9:00am **SS1+HC-MoM-3 Controlling CO<sub>2</sub> Reduction and Electrocatalysis Reactivity Using Alloy and Polymer-modified Electrodes**, Andrew Gewirth, University of Illinois at Urbana Champaign

INVITED

This talk addresses the reactivity associated with CO<sub>2</sub> and nitrate electroreduction. Electrodeposition of metals from plating baths containing 3,5-diamino-1,2,4-triazole (DAT) as an inhibitor yields highly porous materials exhibiting enhanced activity for electrochemical reactions. Electrodeposition of Cu or CuAg and CuSn, alloy films from such plating baths yields high surface area catalysts for the active and selective electroreduction of CO<sub>2</sub> to multi-carbon hydrocarbons and oxygenates. Alloy films containing Sn exhibit the best CO<sub>2</sub> electroreduction performance, with the Faradaic efficiency for C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>5</sub>OH production reaching nearly 60 and 25%, respectively, at a cathode potential of just -0.7 V vs. RHE and a total current density of ~-300 mA/cm<sup>2</sup>. *In-situ* Raman and electroanalysis studies suggest the origin of the high selectivity towards C<sub>2</sub> products to be a combined effect of the enhanced destabilization of the Cu<sub>2</sub>O overlayer and the optimal availability of the CO intermediate due to the Ag or Sn incorporated in the alloy. Sn-containing films exhibit less Cu<sub>2</sub>O relative to either the Ag-containing or neat Cu films, likely due to the increased oxophilicity of the admixed Sn. A related effect is found for nitrate reduction on alloy-modified Cu electrodes. Modification of the Cu electrode with certain polymers yields substantially enhanced CO<sub>2</sub> reduction reactivity, due in part to control of the Cu<sub>2</sub>O layer and elevated surface pH. Polymer-composite electrodes exhibit enhanced reactivity over a wide range of proton-involved electrochemical reactions. As an example, methanol oxidation reactivity is substantially enhanced with polymer-modified Pt electrodes.

9:40am **SS1+HC-MoM-5 Enhancement of CO<sub>2</sub> Reduction Reaction Activity and Selectivity of Sub-2 nm Ag Electrocatalysts by Electronic Metal-Carbon Interactions**, Xingyi Deng, D. Alfonso, T. Nguyen-Phan, D. Kauffman, National Energy Technology Laboratory

We show that the activity and selectivity of sub-2 nm Ag electrocatalysts for electrochemical CO<sub>2</sub> to CO conversion is drastically improved by electronic metal-support interactions (EMSI). The EMSIs between Ag and carbon support, created by deposition of Ag onto heavily sputtered, highly oriented pyrolytic graphite (HOPG), were revealed by X-ray photoelectron spectroscopy (XPS), and supported by computational modeling based on density functional theory (DFT). While sub-2 nm Ag electrocatalysts lack of EMSIs showed selectivity (CO Faradaic efficiency FE<sub>CO</sub> < 2%) toward the electrochemical CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR), similar sized Ag electrocatalysts with EMSIs demonstrated ~100% FE<sub>CO</sub> and more than 15-fold increase of CO turnover frequency (TOF<sub>CO</sub>). Our calculations elucidated that the electronic Ag-C interactions led to a significant charge transfer (1.02 e) from Ag to carbon support and subsequently lowered the potential-limiting step in CO<sub>2</sub>RR by 0.41 eV. Our results provide the direct evidence of improving CO<sub>2</sub>RR performances of electrocatalysts through EMSIs, particularly between metal and carbon. The EMSIs help break the limit of size-dependent CO<sub>2</sub>RR activity in Ag nanoparticles, hinting at a new approach for creating active and selective electrocatalysts.

# Monday Morning, November 6, 2023

10:00am **SS1+HC-MoM-6 Super Structure and Surface Reconstructions with High-Energy Surface X-Ray Diffraction**, *Gary Harlow*, University of Oregon; *D. Gajdek*, University of Malmo, Sweden; *G. Abbondanza*, *A. Grespi*, Lund University, Sweden; *H. Wallander*, University of Malmo, Sweden; *A. Larsson*, University of Lund, Sweden; *L. Merte*, University of Malmo, Sweden; *E. Lundgren*, Lund University, Sweden

The performance of an electrocatalyst (its activity, selectivity, and stability) is strongly dependent on the electrode structure and composition, particularly in the near surface region. A successful approach in trying to understand the impact of structure is the use of well-defined model electrodes such as single crystals, to isolate how various changes in structure and composition impact upon the catalyst behavior. Surface x-ray diffraction gives the average surface structure of an isolated facet, whereas real catalysts often contain multiple facets and edge sites. This contribution will discuss the application of high energy surface x-ray scattering to quickly map out large volumes of 3D reciprocal space and then extract crystal truncation rods. These truncation rods can then be used to determine atomic coordinates of surface atoms, in operando.

Examples during methanol oxidation on both Pt(111) and Au(111) surfaces will be presented. As well as measurements on the the stability of ultra-thin Fe oxide layers on Pt(111) after transfer from vacuum to our in situ electrochemical cell.

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