

Energy Harvesting & Storage

Room Naupaka Salon 5-7 - Session EH-MoM2

Surfaces and Interfaces for Efficient Power Conversion and Batteries

Moderator: David Ginger, University of Washington

10:20am **EH-MoM2-8 Fabrication of Proton-conductive BaCeZrYO_{3-δ} Coatings by Solution Precursor Plasma Spray (SPPS) Method**, *Yen-Yu Chen, W. Zeng, C. Liu, G. Yao*, Chinese Culture University, Taiwan

Perovskite-type proton-conductive ceramic materials have high potentials for the application of sustainable energy fields, such as protonic ceramic fuel cell (PCFC), carbon dioxide conversion, ammonia fuel synthesis, etc. In this study, perovskite-type proton-conductive coatings, BaCeZrYO_{3-δ} (BCZY), were deposited on NiO/BaZrYO_{3-δ} (BZY) substrates by a solution precursor plasma spray (SPPS) method. The precursors were consisted the BCZY species of the nitrate salts and dissolved into de-ionic water. The NiO/BZY substrates were prepared by a die-pressing method. Several properties of the coatings were analyzed, including crystal phases by X-ray diffraction (XRD), microstructures by scanning electron microscope (SEM), electrical properties by electrochemical impedance spectroscopy (EIS), etc. The results of XRD show the coatings after post-coating annealing over 600°C are mainly consisted of perovskite phases. The microstructure analysis of the BCZY coatings characterized by SEM show the coatings are mainly consisted of overlapped splats of BCZY materials and a few of surface pores can be found from the coating layers. The average thickness of the coating layers are about several microns. The formation mechanism of the BCZY coatings can be purposed as the BCZY precursor droplet breakup, liquid-phase evaporation, thermal pyrolysis of precursors, solid particles melting, and then the melting particles splatted and overlapped on the substrate to form the BCZY coatings. The details electrical property analysis of the BCZY coating samples are as mentioned in the following report.

10:40am **EH-MoM2-9 Metal Exsolution and Nanoparticle Self-Assembly Dynamics at Complex Oxide Surfaces**, *Moritz Lukas Weber*, Forschungszentrum Juelich GmbH, Lawrence Berkeley National Laboratory, RWTH Aachen University, Juelich-Aachen Research Alliance; *B. Šmid*, Charles University, Czech Republic; *H. Kersell*, Lawrence Berkeley National Laboratory (LBNL); *U. Breuer*, Forschungszentrum Jülich GmbH, Germany; *M. Rose*, Forschungszentrum Jülich GmbH, RWTH Aachen University, Juelich-Aachen Research Alliance (JARA-FIT, Germany); *N. Menzler*, Forschungszentrum Jülich GmbH, RWTH Aachen University, Germany; *R. Dittmann*, Forschungszentrum Jülich GmbH, Juelich-Aachen Research Alliance (JARA-FIT, Germany); *R. Waser*, Forschungszentrum Jülich GmbH, RWTH Aachen University, Juelich-Aachen Research Alliance (JARA-FIT), Germany; *O. Guillon*, Forschungszentrum Jülich GmbH, RWTH Aachen University, Juelich-Aachen Research Alliance (JARA-Energy), Germany; *C. Lenser*, Forschungszentrum Jülich GmbH, Germany; *S. Nemšák*, Lawrence Berkeley National Laboratory (LBNL); *F. Gunke*, Forschungszentrum Jülich GmbH, Juelich-Aachen Research Alliance (JARA-FIT), Germany

Metal exsolution attracts much attention for the synthesis of nanostructured catalysts. Thermal reduction of doped perovskite parent oxides induces the migration of reducible cations from the oxide bulk to the surface and results in the self-assembly of metallic nanoparticles that serve as catalytic centers. Ideal exsolution-type catalysts therefore dynamically adapt with respect to the oxygen chemical potential. The parameters that influence the kinetics of nanoparticle exsolution, however remain an open question in the scientific community. Furthermore, little is known about the origin of stability limitations of exsolved nanoparticles that are typically anchored at the oxide support.

We employ epitaxial thin films model systems with atomically defined surfaces to investigate the exsolution response of Ni in SrTi_{0.9}Nb_{0.05}Ni_{0.05}O_{3-δ} and SrTi_{0.95}Ni_{0.05}O_{3-δ} of respective *n*-type and *p*-type defect chemistry. Here, we study the mass transfer of dopants towards the surface as well as the morphological evolution of the nanostructured catalysts. Our thin film approach enables to study differences in the exsolution behavior on the basis of well-defined (001) surfaces, eliminating uncertainties regarding the complex microstructure and anisotropy of ceramic oxides and the presence of secondary surface phases.

In order to assess the dynamic changes at the catalyst surface during metal exsolution, we conduct advanced *in-situ* spectroscopy and scattering analyses. In particular, we employ a recently developed technique that allows for the simultaneous analysis of the chemical and structural

evolution of the solid-gas interface based on coupled *in-situ* ambient pressure X-ray photoelectron spectroscopy (AP-XPS) and *in-situ* ambient pressure grazing incidence X-ray scattering (AP-GIXS). Our investigations show that the defect chemistry of the near-surface region determines the dynamics of the exsolution response, where the formation of space charge regions at the perovskite surface plays a major role for the process.

We conclude that the mass transfer during metal exsolution and therefore the nanoparticle self-assembly at the perovskite surface is surface-controlled by interaction with the energy landscape of the complex oxide surface. Derived from our investigations, we propose a mechanistic model that describes how metal exsolution is mediated by the surface defect chemistry and we demonstrate surface engineering of the topmost atomic layers can be utilized as a novel strategy for the active control of the exsolution behavior. Moreover, our observations indicate that the different nature of the surface potential may influence the stability of exsolved nanoparticles.

11:00am **EH-MoM2-10 Characterization of Surfaces and Interfaces in Polymer Electrolyte Membrane Electrolyzers**, *Svitlana Pylypenko*, Colorado School of Mines

Polymer electrolyte membrane water electrolyzers (PEMWEs) are of significant importance towards enabling the large-scale utilization of renewable hydrogen. Fabrication and integration of components, advancement of scalable manufacturing techniques, elucidation of degradation mechanisms, and development of degradation mitigation strategies all require extensive characterization of materials, components, and devices. The complexity of the systems and problems combined with the multitude of relevant scales require multi-technique characterization and motivate further developments of characterization methods and novel approaches. This talk will discuss some of our recent studies on both catalyst layers (CLs) and porous transport layers (PTLs) for application in PEMWEs. Specifically, this presentation will highlight the complementary nature of electron and X-ray microscopy and spectroscopy methods for the investigation of surfaces, interfaces, and interactions within the CLs comparing results for Ir and IrO₂-based CLs, and fresh and aged or tested CLs. Similarly, the characterization of PTLs requires advanced characterization to properly assess the elemental distribution and chemical speciation of PTLs and protective coatings.

11:20am **EH-MoM2-11 Design and Manufacture of Air-Silicon Batteries and the Impact of Plasma-Processed Silicon on the Efficiency of These Batteries**, *Marziyeh Gholami*, Shahid Beheshti University, Iran (Islamic Republic of)

Silicon, as the second most abundant material on earth, is a significant option as an anode material in air metal batteries, so the theoretical energy density is very high at about 8470 Wh kg⁻¹. The discharge products of this battery are non-toxic and environmentally friendly. The final battery is light in weight and will be used in wet or very dry areas. Also, due to the lack of cathode in these batteries, less space will be occupied and the weight of the battery will be light. These advantages, along with the low cost, have made this battery one of the brightest prospects in the field of energy storage devices. In this primary battery, porous carbon, a catalyst, and a polymer as a cathode play an important role in the structure of the battery. An alkaline solution is used as the electrolyte. If plasma-untreated silicon is used in this battery, it has a lower OCV and a short discharge cycle. So, the research carried out in this project was the processing of silicon surface with plasma in order to increase the effective cross-section of silicon in contact with the electrolyte and increase the open-circuit voltage of the battery due to the increase in voltage that we will have at the sharp points. Surface roughness is also guaranteed by plasma etching.

11:40am **EH-MoM2-12 Insights into the Interfacial Reactions of High Voltage MgV₂O₄ Cathodes for Rechargeable Magnesium Batteries**, *D. Nguyen, V. Prabhakaran*, Pacific Northwest National Laboratory, Joint Center for Energy Storage Research (JCESR); *V. Shutthanandan*, Pacific Northwest National Laboratory; *J. Hu*, Pacific Northwest National Laboratory, Joint Center for Energy Storage Research; *G. Alexander, J. Cabana-Jimenez*, University of Illinois at Chicago, Joint Center for Energy Storage Research; *K. Mueller*, Pacific Northwest National Laboratory, Joint Center for Energy Storage Research; *Vijayakumar Murugesan*, Pacific Northwest National Laboratory, Joint Center for Energy Storage Research
Interfacial reactions driven by charge transfer occurring at the electrode – electrolyte interface contribute to the formation of complex interphasic layers that govern the performance of energy storage devices. These interfacial reactions are influenced by various factors such as surface chemistry of electrode, electrochemical properties of the electrolyte

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solution, and the working potential of the device. Precise capturing of critical interfacial reactions and subsequent evolution of solid-electrolyte interphase components is extremely challenging due to the complexity and heterogeneity of the interphasial reactive components, the reaction dynamics under variable potentials, and the smaller dimensions of interphase region. Probing complex interfacial processes requires the integration of advanced spectroscopies within an electrochemical device to monitor interfacial reactions and structural changes during operation. In this study, we investigated the interphasial evolution of MgV_2O_4 cathodes for rechargeable magnesium batteries using both *in situ* and *ex situ* X-ray photoelectron spectroscopy while also probing structural transformation of interphasial chemical species using *operando* Raman spectroscopy. Our study revealed that the solid electrolyte interphase layer on MgV_2O_4 was formed mainly by the decomposition of electrolyte anions that occurred at a very early stage of the initial charging process. The interphase layer also thickened with increased cell potential as well as repeated cycling. Post surface analysis of the MgV_2O_4 cathode after 20 cycles also confirmed surface conditioning processes that is well supported by its electrochemical performance in early cycles. Our study revealed insights into the surface evolution of MgV_2O_4 , which provides crucial information for development of an oxide cathode for rechargeable magnesium batteries as well as other battery chemistries that involve sodium and lithium ions.

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