

Frontiers of New Light Sources Applied to Materials, Interfaces, and Processing Focus Topic Room A124-125 - Session LS+AS+SS-ThM

Operando Methods for Unraveling Fundamental Mechanisms in Devices Towards Renewable Energies

Moderator: Olivier Renault, CEA-University Grenoble Alps, France

8:00am **LS+AS+SS-ThM-1 X-Ray Insight into Fuel Cell Catalysis: Operando Studies of Model Surfaces and Working Devices**, *Jakub Drnec*, I Martens, European Synchrotron Radiation Facility, France; *T Fuchs*, University of Kiel, Germany; *T Wiegmann*, European Synchrotron Radiation Facility, Germany; *A Vamvakeros*, Finden Ltd., UK; *R Chattot*, European Synchrotron Radiation Facility, France; *O Magnussen*, University of Kiel, Germany

INVITED

Complete physico-chemical operando characterization of electrochemical devices in whole, or its constituent materials separately, is necessary to guide the development and to improve the performance. High brilliance synchrotron X-ray sources play a crucial role in this respect as they act as a probe with relatively high penetration power and low damage potential. In this contribution the new possibilities of using high energy, high intensity X-rays to probe model fuel cell catalysts and energy conversion devices will be presented.

HESXRD (High Energy Surface X-ray Diffraction) [1] and TDS (Transmission Surface Diffraction) [2] provide ideal tools to study structural changes during reaction conditions on single crystal model electrodes. The main advantage of both techniques is the possibility to follow the structural changes precisely with atomic resolution. While HESXRD is ideally used to determine exact atomic position, the TSD is easier to use and allows studies with high spatial resolution. For example, HESXRD can be used to follow the atomic movement of Pt atoms during electrochemical oxidation and dissolution with very high precision, explaining the different catalyst degradation behaviors and suggesting possible routes to improve its durability [3-4]. The TSD is an excellent tool to study advanced 2D catalysts.

To study fuel cells or batteries as a whole, elastic scattering techniques, such as WAXS and SAXS, can be employed as they can provide important complementary information to more standard X-ray imaging and tomography. The advantage is that the chemical contrast and sensitivity at atomic and nm scales is superior. Coupling these technique with the tomographic reconstruction (XRD-CT and SAXS-CT) is much less common as it requires bright synchrotron sources and advanced instrumentation, but allows 3D imaging of operational devices with unprecedented chemical sensitivity. This can be demonstrated on imaging of standard 5 cm² fuel cells during operation. The change in morphology and atomic arrangement of the catalysts, PEM hydration and water distribution can be followed in one experiment as a function of operating conditions. Furthermore, the fundamental processes leading to the catalyst aging can be assessed with high temporal and spatial resolution. These advanced scattering techniques open a door to holistic investigations of operational devices, which are needed to successfully incorporate new materials at the device level.

[1] J. Gustafson et al., *Science* 343, 758 (2014)

[2] F. Reikowski et al., *J. Phys. Chem. Lett.*, 5, 1067-1071 (2017)

[3] J. Drnec et al, *Electrochim. Acta*, 224 (2017),

[4] Chattot et al., *Nature Materials*, 17(2018)

8:40am **LS+AS+SS-ThM-3 Multi-scale Operando X-ray Tomography of Solid-state Li Battery Electrolytes at Elevated Temperatures and Pressures**, *Natalie Seitzman*, Colorado School of Mines; *J Nelson Weker*, SLAC National Accelerator Laboratory; *M Al-Jassim*, National Renewable Energy Laboratory; *S Pylypenko*, Colorado School of Mines

Solid state Li ion conductors are next-generation battery technologies that reap the capacitive benefits of Li metal anodes while mechanically resisting the Li interface evolution and thus prolonging lifetime. Additionally, they are not flammable, offering greater safety than liquid counterparts. However, interface evolution and Li protrusions are observed in solid state batteries despite the mechanical resistance.^{1,2} There is debate as to whether these protrusions nucleate at the Li anode or within the ceramic electrolyte, and there are several factors that affect these protrusions including electrolyte density, pre-existing defects, anode/electrolyte interfacial contact, and imperfect electronic insulation within the electrolyte.³ Understanding the influence of these variables is greatly

enhanced by directly imaging the interior of the ceramic at multiple scales in conjunction with electrochemical experiments.

This talk addresses the contribution of electrolyte density and defects, interfacial contact, and conductivity to structural changes in β -Li₃PS₄ (LPS) ceramic electrolyte in operating cells via 3D X-ray imaging with sub-micron resolution. Cells of Li, LPS, and a blocking contact are constructed and studied *in operando* at 200 psi and 70°C. Because electrolyte density and initial defects depend on the composition and synthesis of the ceramic conductor, two syntheses of LPS with different particle sizes are compared. Also, pressure is a key parameter in the quality and stability of interfacial contact while temperature affects both the ionic and electronic conductivity of the ceramic.

Synchrotron micro-tomography is combined with synchrotron transmission x-ray microscopy to study the cells with spatial resolution in the hundreds of nanometers and tens of nanometers. Image analysis of these data has identified sites of Li microstructure growth⁴ and now isolates variable-dependent trends such as pressure-dependent void formation in the Li anode. Linking structural changes observed *in operando* to these factors that contribute to Li evolution will guide the design of robust ceramic electrolytes with improved performance and safety.

1. L. Porz, T. Swamy, B. W. Sheldon, D. Rettenwander, T. Frömling, H. L. Thaman, S. Berendts, R. Uecker, W. C. Carter, and Y.-M. Chiang, *Adv. Energy Mater.*, 7, 1701003 (2017).

2. E. J. Cheng, A. Sharafi, and J. Sakamoto, *Electrochim. Acta*, 223, 85–91 (2017).

3. F. Han, A. S. Westover, J. Yue, X. Fan, F. Wang, M. Chi, D. N. Leonard, N. J. Dudney, H. Wang, and C. Wang, *Nat. Energy* (2019).

4. N. Seitzman, H. Guthrey, D. B. Sulas, H. A. S. Platt, M. Al-Jassim, and S. Pylypenko, *J. Electrochem. Soc.*, 165, 3732–3737 (2018).

9:00am **LS+AS+SS-ThM-4 Correlating the Atomic and Electronic Structure in the Formation 2DEGs in Complex Oxides**, *Jessica McChesney*, *X Yan*, *F Wrobel*, *H Hong*, *D Fong*, Argonne National Laboratory

Using a multimodal approach, we investigate the interplay of the atomic and electronic structure of the formation of 2-D electron gas (2DEG) in complex oxide systems. Using hybrid molecular beam epitaxy for synthesis and in-situ synchrotron x-ray scattering atomic precision of the growth is obtained. The electronic structure then characterized via a combination of resonant soft x-ray angle-resolved photoemission and core level spectroscopy and compared with transport measurements.

9:20am **LS+AS+SS-ThM-5 Uncover the Mystery of Oxygen Chemistry in Batteries through High-Efficiency mRIXS and Theory**, *Wanli Yang*, Lawrence Berkeley National Laboratory

INVITED

Energy storage through electrochemical devices (batteries) is under pressure to be greatly improved for today's sustainable energy applications, especially the electric vehicles and power grid using renewable energy sources. A battery utilizes transition-metal (TM) oxides as one of the critical electrodes, the positive electrode, which is often the bottleneck of the energy density. In general, the operation of battery cycling is based on reduction and oxidation (Redox) reactions of TMs and a recently proposed oxygen, which involve the changes on the electron occupation numbers in TM-3d and O-2p states, as well as the evolution of the electronic configuration. However, technical challenges are formidable on probing these states directly, especially for the unconventional oxygen redox states.

This presentation will start with a brief introduction of several needs and grand challenges of battery devices related with oxygen states, which is followed by soft X-ray spectroscopic experiments for providing relevant information. The focus of this presentation is on an active debate of the oxygen states in charged electrodes. We will explain the limitations on conventional soft X-ray absorption spectroscopy (sXAS) for characterizing the important oxygen states, then showcases the power of full energy-range mapping of resonant inelastic X-ray scattering (mRIXS) for clarifying the oxygen redox behaviors in batteries.

We show that mRIXS provides the ultimate probe of the intrinsic oxygen redox reactions in the lattice of battery electrodes [1], which is associated with transition-metal configurations [2]. These spectroscopic results could be quantified to decipher the electrochemical capacity [3], providing both the rationality of the device performance and evidences for understanding the fundamental mechanism of electrochemical materials for energy applications. Furthermore, the mRIXS results indicate a universal driving force of the oxygen redox reactions [4], which could be tackled through

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combined studies of mRIXS and theoretical calculations [5]. We show that such a spectroscopic and theoretical collaboration could deliver unprecedented information for both fundamental understanding and practical optimization on grand challenges in developing high-performance battery devices.

[1] Gent et al., *Nat Comm* 8, 2091 (2017)

[2] Xu et al., *Nat Comm* 9, 947 (2018)

[3] Dai et al., *Joule* 3, 518 (2019)

[4] Yang & Devereaux, *J. Power Sources* 389, 188 (2018)

[5] Zhuo et al., *JPLCL* 9, 6378 (2018)

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