SIMS Solutions in Materials and Life Sciences
Room Great Lakes C - Session SS-MoA2

Energy Storage II

Moderator: Andrew Giordani, Procter & Gamble Company

2:20pm **SS-MoA2-3 Study of Lithium-Ion Battery Degradation from the Subsurface of Electrodes***, X. Yao,* Advanced Technology Institute, University of Surrey, UK*; **Tomáš Šamořil**, J. Dluhoš,* TESCAN ORSAY HOLDING, Czechia*; J. Watts,* Department of Mechanical Engineering Sciences, University of Surrey, UK*; Z. Du,* Energy and Transportation Science Division, Oak Ridge National Laboratory*; B. Song,* Neutron Scattering Division, Oak Ridge National Laboratory*; R. Silva,* Advanced Technology Institute, University of Surrey, UK*; T. Sui,* Department of Mechanical Engineering Sciences, University of Surrey, UK*; Y. Zhao,* National Physical Laboratory, UK*; D. Miller,* TESCAN USA

In recent years, considerable attention is paid to the improvement of Li-ion batteries (LIBs), currently used as powerful electrical energy storage in a wide spectrum of devices. Their life span related to capacity fade is mainly influenced by the degradation of electrodes associated with the deactivation of active materials and irreversible parasitic reactions. The selection of a suitable analytical technique for LIBs degradation study is very limited by the requirement to provide information about the chemical composition including light elements such as lithium with high surface sensitivity.

Within this contribution, a Scanning Electron Microscope equipped with a Focused Ion Beam (FIB-SEM) uniquely combined with a compact Time-of-Flight Secondary Ion Mass Spectrometer (ToF-SIMS) [1,2] was applied for the high-spatial-resolution study of chemical composition in the cross-sectional interface (see Fig. 1) of pristine and cycled LIB electrodes to identify degradation mechanisms [3]. The ability to correlate SEM observation with ToF-SIMS and other analytical techniques such as Energy Dispersive X-Ray Spectroscopy (EDS) [4] and Raman spectroscopy [5] on the same FIB-SEM system allows extended and correlated analytical capabilities that provide a deeper understanding of degradation processes in LIBs material from the mechanical, chemical, and electrochemical point of view.

[1] J.A. Whitby, et. al., Advances in Mat. Sci. and Eng., (2012), 1-13.

[2] D. Alberts, et. al., Instr. Sci. & Technol. 42, (2014), 432-445.

[3] Yao, et. al., Energy Environ. Mater., (2022), 662-669.

[4] T. Sui, et. al., Nano Energy 17, (2015), 254-260.

[5] D.J. Miller, et. al., Microsc. Microanal. 25, (2019), 862-863.

2:40pm **SS-MoA2-5 Quantification of Transport Function in Solid Ionic Conductors from Concentration Depth Profiles***, **Martin Schäfer**, J. Wiemer, J. Bernzen, V. Gunawan, K. Rein,* Philipps Universität, Germany*; K. Weitzel,* Philipps-Universität Marburg, Germany

One of the powerful applications of SIMS pertains to the quantification of concentration depth profiles as resulting from transport processes. Classical examples can be found in tracer diffusion or ion exchange experiments. A more recent application is the Charge Attachment Induced Transport (CAIT) technique, where a charge carrier beam is directed to a sample surface while the back side of the sample is in contact with a single grounded electrode [1,2]. The charge carriers softly attach to the surface and charge it up to a well-defined electric potential. Attachment of the charge carriers causes gradients of concentration and electric potential which induces the transport of charge carriers in the material. If the ion species attached is chemically different from the native carrier a concentration depth profile arises, where e.g. external K^+ ions may replace native Na^+ ions in a unidirectional transport process [3]. Complementary information can be gained by thermal electropoling experiments, where depletion zones emptied of all alkali ions (and an equal amount of electrons) can be generated [4]. Finally native alkali ions can be replaced by protons over several 100 nm by a modified field assisted ion exchange experiment [5].

All the concentration depth profiles can be quantified by means of time of flight secondary ion mass spectrometry (ToF-SIMS). The analysis of such profiles allows not only to quantify the diffusion coefficients of competing transport channels of solid ionic conductors [6]. It also allows for the first time to gain understanding of the potential energy landscape of ions in such materials [7-9].

[1]M. Schäfer, K.-M. Weitzel, PCCP, 13 20112–20122, (2011).

[2] J. Martin, M. Gräf, T. Kramer, C. Jooss, M.-J. Choe, K. Thornton and K.-M. Weitzel. PCCP.,19, 9762-9769, (2017).

[3] L. Rossrucker, P.V. Menezes, J. Zakel, M. Schäfer, B. Roling and K.-M. Weitzel, ZPC, **226**, 341- 53, (2012).

[4]K. Rein, M. Schäfer, and K.-M. Weitzel, IEEE Transactions on dielectrics and electrical insulation, p. 1422, (2020).

[5] T. Ishiyama, J. Nishii, T. Yamashita, H. Kawazoe, T. Omata, J. Mater. Chem. A, 2, 3940, (2014); and unpublished work from the authors lab.

[6] J. Martin, S. Mehrwald, M. Schäfer, T. Kramer, C. Jooss, K.-M. Weitzel,Electrochimica Acta, 191, 616–623, (2016).

[7] M. Schäfer, K.-M. Weitzel, Materials Today Physics, 5, 12–19, (2018).

[8] M. Schäfer, D. Budina, K.-M. Weitzel, PCCP., 21, 26251, (2019).

[9] J. L. Wiemer, M. Schäfer, K.-M. Weitzel, J. Phys. Chem. C, 125, 4977-4985, (2021).

3:00pm **SS-MoA2-7 High Five: UHV SIMS with Plasma Primary & Simultaneous Positive and Negative Secondary Ion Detection***, S. Fearn,* Imperial College London, UK*; R. Chater,* Imperial College of Science, Technology and Medicine, UK*; **Graham Cooke**,* Hiden Analytical Ltd., UK*; N. Smith,* Oregon Physics

High Five is a recently completed SIMS instrument at Imperial College London that provides dynamic secondary ion mass spectrometry (SIMS) measurements at multi-scale lengths from nm's to several 100microns using a novel gas plasma focused ion-beam source and column from Oregon-Physics.The SIMS detector configuration is unique as both positive and negative SIMS compositional information is recorded by two synchronised quadrupole mass (QMS) filter detectors.

The performance of the primary ion source on target is reported for both mass and neutral filtered oxygen and xenon ion beams at energies from 2keV to 30keV.These beams have been used for both SIMS measurements, i.e. both mass spectra and SIMS imaging for depth profiling.SIMS results in High-Five are obtained from either surfaces that are 'as-prepared' or by sputter-polishing processes 'in-situ' using high-current well focused ion-beams from the plasma source.

Performance results for simultaneous positive and negative secondary ion detection from High-Five are illustrated using air-sensitive solid-state lithium electrode and electrolyte material from an active research program in the Materials Department, Imperial College London.

In High-Five, the primary ion source can be configured to produce an electron beam for both non-destructive feature selection and surface processing.The performance of the primary source for this mode is reported and illustrated with imaging of complex oxides used in fuel cell electrode and electrolysers.These materials are readily amorphized & reduced with ion beam bombardment.Suitable site locations for SIMS are found using imaging for lattice orientation contrast prior to SIMS analysis.

3:20pm **SS-MoA2-9 Indigenous Organic Molecular Biosignatures are Detectable via ToF-SIMS of a Kerogen-rich Jurassic Clay***, M. Pasterski,* University of Illinois Chicago*; M. Lorenz, A. Ievlev,* Oak Ridge National Laboratory*; R. Wickramasinghe, **Luke Hanley**, F. Kenig,* University of Illinois Chicago

Organic molecular biosignatures (OMBs) detected within Mars Sample Return (MSR) samples could provide strong evidence for the existence of extraterrestrial life[1]. The utility of any OMB depends on its character, which can be: indigenous or syngenetic; non-indigenous or incorporated during sub-surface fluid migration; or contaminant. OMB character can be determined via its spatial distribution within a host rock [2, 3], but gas chromatography - mass spectrometry (GC-MS) does not readily preserve spatial information. ToF-SIMS imaging is effective at determining the spatial distribution of OMBs in various sediments [4, 5]. Ancient indigenous sterane molecular ions and fragments ions of isorenieratene derivatives (all suspected OMBs) are detected using ToF-SIMS within a kerogen-rich sample, the 164 million-year-old Oxford clay. Previous work compared ToF-SIMS of the Oxford Clay with results from laser ablation photoionization mass spectrometry imaging [6]. Data from GC-MS, ToF- SIMS, energy dispersive X-ray spectroscopy (EDS), and traditional micrographic imaging were compared using statistical packages within the data analysis platforms R and Python.

Steranes are detectable in ToF-SIMS spectra via their molecular ions and reflect a subset of the complex sterane mixture that dominates the saturated/unsaturated hydrocarbons of the extractable fraction observed via GC-MS. ToF-SIMS spectra and MS images indicate that steranes are heterogeneously distributed on the micron scale. Additionally, typical fragment ions of isorenieratene derivatives appear within ToF-SIMS spectra from regions with observable sterane ions. These isorenieratenes are the dominant constituents of the extracted aromatic fraction. EDS analysis indicates that the regions containing OMBs are high in organic carbon, likely reflecting the previously observed sulfur-rich kerogen [7]. The restricted spatial distribution of the OMBs to regions containing kerogen indicates that they are indigenous to the sample.

Indigenous OMBs are detectable via ToF-SIMS in ancient, kerogen-rich samples. The presence of an OMB molecular ion strengthens the interpretation of ToF-SIMS data of complex natural material as does the spatial coincidence of kerogen and potential indigenous OMBs in ancient sediments.

1) Neveu, *et al.* (2018) *Astrobiology, 18,* 1375.

2) Brocks (2011) *Geochim. Cosmochim. Acta,* 75, 3196.

3) Medina Ferrer (2018) *Org. Geochem., 124,* 112.

4) Thiel and Sjovall (2011) *Planetary Sci., 39,* 125.

5) Siljeström, *et al.* (2017) *Org. Geochem., 109,* 14.

6) Wickramasinghe, *et al.* (2021) *Anal. Chem., 93,* 15949.

7) Kenig, *et al.* (1994) *J. Geo. Soc. Lon., 151,* 139.

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