

## SIMS Solutions in Materials and Life Sciences

### Room Great Lakes C - Session SS-MoM3

#### Energy Storage I

Moderator: Andrew Giordani, Procter & Gamble Company

10:00am **SS-MoM3-1 SIMS Study of Interfacial Degradation in Lithium Thiophosphate-Based Composite Cathodes for All-Solid-State Lithium-ion Batteries**, Felix Walther, J. Sann, J. Janek, M. Rohnke, Institute of Physical Chemistry, Justus Liebig University Giessen, Germany

All-solid-state lithium-ion batteries (ASSBs) have gained strong attention in recent years, as they are considered one of the most promising candidates for future energy storage devices. By replacing the liquid electrolyte in conventional lithium-ion batteries (LIBs) with a solid, lithium metal could be enabled as anode material, which in turn could lead to higher energy densities compared to conventional LIBs. At the same time, safety aspects could be improved, since flammable organic electrolytes are avoided, making ASSBs highly attractive for the mobility sector. Particularly lithium thiophosphate-based solid electrolytes are considered promising, as such materials typically exhibit a high ionic partial conductivity and advantageous mechanical properties (i.e., malleability) for large-scale industrial processing. However, several problems remain to be solved before this technology can be transferred to practical application. On the positive electrode side, interfacial reactions of the cathode active material with the thiophosphate solid electrolyte are one of the main reasons for strong capacity loss and poor long-term stability. Although it is known that coatings on the cathode active material have a positive effect on such interfacial reactions, the underlying mechanisms (with and without coating) are still largely unknown.

In this work, we show that the combination of the complementary methods ToF-SIMS and XPS is very powerful to study degradation phenomena in  $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ - and lithium thiophosphate-based composite cathodes [1-3]. ToF-SIMS in particular plays a key role in this context, as it can provide detailed insights beyond the detection limit of XPS. Next to surface analysis and depth profiling, ToF-SIMS analysis was performed on FIB crater sidewalls to verify the results obtained and to identify the individual strengths/weaknesses of the respective type of measurement for this analytical task. Overall, we were able to distinguish between various reaction zones within the composite cathode by imaging mass spectrometry and could provide detailed information on the respective degradation products. Based on this knowledge, we studied the positive effect of a protective coating and were able to correlate the enhanced ASSB cell performance with the reduction of specific degradation products. These results can help to further optimize protection concepts for composite cathodes, which is an essential step on the way to long-term stable ASSBs.

[1] F. Walther et al. *Chem. Mater.* **2019**, *31* (10), 3745–3755.

[2] F. Walther et al. *Chem. Mater.* **2020**, *32* (14), 6123–6136.

[3] F. Walther et al. *Chem. Mater.* **2021**, *33* (6), 2110–2125.

10:20am **SS-MoM3-3 The Effect of Electric Double Layer on Formation of Solid-Electrolyte Interphase in Li Ion Batteries**, Zihua Zhu, C. Wang, PNNL

The solid-electrolyte interphase (SEI) dictates the performance of most Li ion batteries, but the understanding of its formation mechanism is limited by the lack of in situ experimental tools. Recent years, it has been reported that the batteries with more fluorine components in SEI can perform better than the batteries with less fluorine components in SEI. Therefore, an interesting question is how to increase fluorine in SEI. One way is using high concentration electrolytes, in which the anions contain fluorine. The other way is using fluorine-containing electrolytes. In this work, we used unique in situ liquid SIMS to show an electric double layer can form before formation of SEI, even using a high concentration electrolyte. Formation of such an electric double layer repulses anions away from the electrode surface, leading to a fluorine depleted SEI. Therefore, using fluorine-containing electrolytes should be a better idea because electrolyte molecules are neutral and will not be repulsed away from electrode surface after formation of an electric double layer. Such a result strongly supports the recent development of fluorine-containing electrolytes.

10:40am **SS-MoM3-5 Novel Strategy for the Cycling Analysis of Polymer-Based Electrolyte for All-Solid-State Lithium Ion Batteries Using ToF-SIMS**, C. Mawélé Loudy, Université de Pau et des Pays de l'Adour, France; G. Godillot, C. Navarro, ARKEMA France, Groupement de Recherches de Lacq, France; A. Bonnet, ARKEMA France, Usine de Pierre Bénite, France; L. Rubatat, J. Allouche, H. Martinez, Cécile Courrèges, Université de Pau et des Pays de l'Adour, France

Among the wide family of all-solid-state batteries (ASSBs) technology, polymer-based electrolytes have emerged as good candidates for the design of electrolytes for electrical cars and electronic devices.<sup>1</sup>In contrary to liquid electrolytes, polymer-based electrolytes exhibit less reactions with electrodes and are non-flammable. In addition, polymer-based electrolytes are likely to decrease or suppress lithium dendrites growth while maintaining good adhesion properties due to their film-forming properties. However successful comprehension of ASSBs using lithium as anode still requires further study and investigation into the lithium metal-solid electrolyte interface. It is well known that the high reactivity of lithium, the reaction products and the resulting interface when it comes into contact with most solid electrolytes (SEs) can have detrimental effects on cell performance.<sup>2</sup>In this context, Time-of-flight secondary-ion mass spectrometry can be used as a powerful tool to better understand the formation of interface since it can provide chemical information with high resolution in 2D as well as 3D analysis of both the surface and the bulk of the battery.<sup>3</sup>

In fact, depth profiling done on such sample provides information about the stability of the Li-SE interface and the microstructure. In addition to the individual study of the various components of the cell, the bulk and interfaces within the cell can be investigated with more precision when combined with a depth measurement technique such as a chromatic confocal sensor. Additionally, in situ voltage cycling system has been designed in collaboration with Physical Electronics, which will allow the chemical analysis of the battery in its original configuration.

#### References:

1 R. Chen, Q. Li, X. Yu, L. Chen and H. Li, *Chem. Rev.*, **2020**, *120*, 6820–6877.

2 M. Golozar, R. Gauvin and K. Zaghbi, *Inorganics*, **2021**, *9*, 85.

3 S.-K. Otto, L. M. Riegger, T. Fuchs, S. Kayser, P. Schweitzer, S. Burkhardt, A. Henss and J. Janek, *Advanced Materials Interfaces*, **2022**, *9*, 2102387.

11:00am **SS-MoM3-7 Investigation of the Li<sup>+</sup>/H<sup>+</sup> Exchange Process on Washed Cathode Active Material Using ToF-SIMS**, Anja Henss, Justus-Liebig University, Heinrich Buff Ring 17, Germany

Energy transition and increasing electrification of transport are placing ever higher demands on the performance of lithium-ion batteries (LIB). For this reason, intensive research and development is being carried out for high-performance and competitive LIBs. <sup>1</sup>

[file:///E:/JLUbox/Reisen/SIMS%20Minneapolis/Abstract\_AH.docx#\_ENREF\_1] High-voltage, nickel-rich cathode active materials (CAMs) are particularly promising for electromobility, but their performance is highly dependent on the processing steps. In industry, CAMs are washed immediately after synthesis, which has several advantages: Removal of surface contaminants, prevention of gelation of slurries and reduced gas formation during cycling when surface species react off. However, washing also brings disadvantages: thermal stability seems to decrease, which is related to Ni content, and nickel-containing NCMs seem to be particularly affected. In addition, cycle performance seems to change and capacity deteriorates.<sup>2</sup>

[file:///E:/JLUbox/Reisen/SIMS%20Minneapolis/Abstract\_AH.docx#\_ENREF\_2] Unfortunately, current mechanistic understanding is relatively limited; we know that protons are deposited in near-surface layers during washing or high relative humidity, and lithium leaves the material to form LiOH. However, it is unknown how many protons are exchanged, what the kinetics of this process is, and how it can be controlled.

Therefore, we performed a comprehensive ToF-SIMS study to localize the protons in the NCM and to investigate the kinetics of the Li<sup>+</sup>/H<sup>+</sup> exchange process. For this purpose, in a first step single crystalline NCM particles were synthesized (in micrometer range) and washed in D<sub>2</sub>O for different time periods. The washed and unwashed NCM particles were pressed onto Al foil and investigated by FIB-SIMS. Therefore, a FIB crater was prepared at a small angle and subsequently analyzed by SIMS. In the sample with the longest washing time, an increased signal intensity of deuterated fragments could be localized in the outer regions of the particles. In addition, a 2D model system with a thin layer of NCM deposited on MgO substrate was used to study the kinetics of the exchange process. The results are discussed in context with other characterization techniques that

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show the structural change induced by washing and electrochemical performance data.

1. J. Janek and W.G. Zeier: A solid future for battery development. *Nature Energy***1**, 1167 (2016).

2. D. Pritzl et al: Washing of nickel-rich cathode materials for lithium-ion batteries: towards a mechanistic understanding. *Journal of The Electrochemical Society***166**, A4056 (2019)

11:20am **SS-MoM3-9 In Situ Investigation of Lithium Metal–Solid Electrolyte Anode Interfaces with ToF-SIMS**, *Svenja-Katharina Otto*, L. Riegger, Justus-Liebig-Universität Giessen, Germany; S. Kayser, IONTOF GmbH, Germany; A. Henss, J. Janek, Justus-Liebig-Universität Giessen, Germany

Solid-state batteries (SSB) with lithium metal anodes (LMAs) are explored as a promising approach for next-generation batteries with high energy densities. However, the implementation faces severe challenges partly caused by the high reactivity of lithium metal. Most electrolyte materials are unstable in direct contact with the LMA and interphases which are detrimental for the battery properties form. In order to overcome interphase formation, exact knowledge about the forming reaction products and their microstructure is needed.

In this context, we studied lithium |solid electrolyte (Li|SE) interfaces with ToF-SIMS to complement the commonly used X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM) characterization.[1] In situ electrochemical deposition or lithium vapor deposition are used to prepare the interfaces. Classification of the interface type and characterization of the 3D structure of the formed interphases are possible by depth profiling through micrometer-thick lithium layers on the SE substrate. We combine ToF-SIMS with complementary XPS analyses to confirm the structural information and with atomic force microscopy (AFM) to obtain roughness and thickness information. As an example, the thickness of the forming  $\text{Li}_2\text{S}$ -rich interphase layer between the argyrodite-type LPSCl and lithium is determined. In addition, the influence of different in situ preparation methods of the Li|SE contact is investigated.[1] Also, we show the characterization of recently developed materials like the  $\text{Li}_7\text{SiPS}_8$  ( $\text{LiSiPS}$ ) solid electrolyte.[2]

[1] Svenja-K. Otto et al. *Adv. Mater. Interfaces* **2022**, doi.org/10.1002/admi.202102387.

[2] Luise M. Riegger et al. *Chem. Mater.* **2022**, doi.org/10.1021/acs.chemmater.1c04302.

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