

21st International Conference on Solid State Ionics

Highlights of the latest developments in solid-state batteries for energy storage

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Introduction

The 21st International Conference on Solid State Ionics (SSI-21) was held in Padova, Italy, from 18th to 23rd June, 2017. The conference saw ~1300 people attend over the six days, covering four macro areas:

- energy and environment
- communication and robotics
- biological systems and life sciences
- fundamental theory.

The energy and environment macro area saw 30 topics including: beyond lithium-ion batteries, advanced lithium and sodium batteries, solid-state batteries (SSB), redox-flow batteries, polymeric batteries, solid oxide fuel cells and many others. The attendance was truly international with a significant proportion of attendees travelling from academic institutions outside Europe. A few companies were also in attendance, predominantly from the USA and Japan.

This review will focus on the recent advancements presented in the field of SSB. This topic was the largest of those on offer within the energy and environment macro area and was well attended over the six days. The talks covered herein have been grouped by topic and include:

- solid-state electrolytes
- analytical techniques for SSB
- all-solid-state Li-ion batteries (ASSLiB).

Solid-State Electrolytes

The garnet-type group of solid-state electrolytes (SSEs) were a focus of numerous talks with two sessions dedicated to the $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) ceramic. S. Uhlenbruck (Jülich Research Centre, Germany) opened one of the sessions with an overview of the recent developments in the field. He mentioned that the discrepancy in many reported conductivity results could in some part be explained by preventable sample aging. LLZO is known to react with water and carbon dioxide to form lithium carbonate and Uhlenbruck showed that samples stored in an argon box were still affected by the ppm levels of water present, leading to carbonate formation and depletion of lithium at the electrolyte surface. Uhlenbruck also showed that the cycle life of LLZO-based SSB could be enhanced when a gold nano-layer was deposited at the electrolyte/Li-metal interface.

The development of LLZO electrolytes was discussed further by A. Aguadero (Imperial College London, UK) with her work on aluminium/gallium doped LLZO; these elements are known to stabilise the favourable, highly Li-ion conducting cubic phase. Focused ion beam secondary ion mass spectrometry (FIB-SIMS) was used to locate the position of the dopant within the LLZO electrolyte, with Al found concentrated at the particle grain boundaries. Aguadero suggested the possibility of different dendrite formation mechanisms for Al and Ga doped samples when used with Li-metal anodes. She linked this difference in mechanism to the inhomogeneity of cation distribution leading to uneven polarisation in the electrolyte. The mechanism of lithium dendrite growth through solid electrolytes, in particular LLZO, was further discussed by B. Sheldon (Brown University, USA). He argued that dendritic growth does not

necessarily require grain boundary pathways to propagate. Instead, he proposed that dendritic growth is in fact caused by surface imperfections. Large surface flaws allow Li penetration beyond the crack into the bulk crystal, driven by strain energy release at the dendrite tip. He is continuing his work towards a general model for dendrite growth in SSEs with more results soon to be published.

In addition to garnet-based electrolytes, sulfide electrolytes featured heavily throughout the week. A notable speaker was R. Kanno (Tokyo Institute of Technology, Japan), one of the initiators of research into highly conductive sulfide based $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ (LGPS) electrolytes. Kanno presented his recent work on overcoming the electrochemical stability limitations of these SSEs through element substitution. Although substitution of silicon with oxygen was found to decrease the conductivity performance, higher electrochemical stability was also indicated. Other sulfide systems were tested by Kanno with the metal removed; the idea being that the removal of the metallic elements would increase their stability towards Li-metal anodes. Both showed good coulombic efficiency so were believed to be more electrochemically stable than their germanium containing counterparts.

Alternatives to garnet and sulfide based electrolytes were also discussed in the SSE sessions. One such electrolyte was the Li salt/ C_{60} polymeric electrolyte presented by D. Pontiroli (Università di Parma, Italy).

The lithium sits in pseudo-octahedral sites causing polymerisation of the C_{60} as shown in **Figure 1**. Due to the high electrical conductivity of the polymer, its use as an electrolyte for all-solid-state Li-ion batteries was limited, however Pontiroli *et al.* showed that the ionic and electronic conductivities may originate from different causes. This suggests that it could be possible to shut off the electrical conductivity whilst maintaining the high Li-ion conductivity of the polymer.

A nano-composite electrolyte comprised of an insulating matrix of silica particles and lithium salts was presented by P. M. Vereecken (University of Leuven, Belgium). These systems work by the selective adsorption of the salts at the insulating particle surface, leading to an accumulation of vacancies at the interface and higher conductivities. The ionic liquid and lithium salt (ILE) system discussed was shown to reach conductivities approaching 1 mS cm^{-1} , rivalling conventional liquid organic electrolytes.

Analytical Techniques for Solid-State Batteries

A number of new techniques aimed at probing the structure/performance relationship in both SSEs and SSB were presented across the week. S. Taibl (Vienna University of Technology, Austria) presented her work on the spatially resolved electrochemical

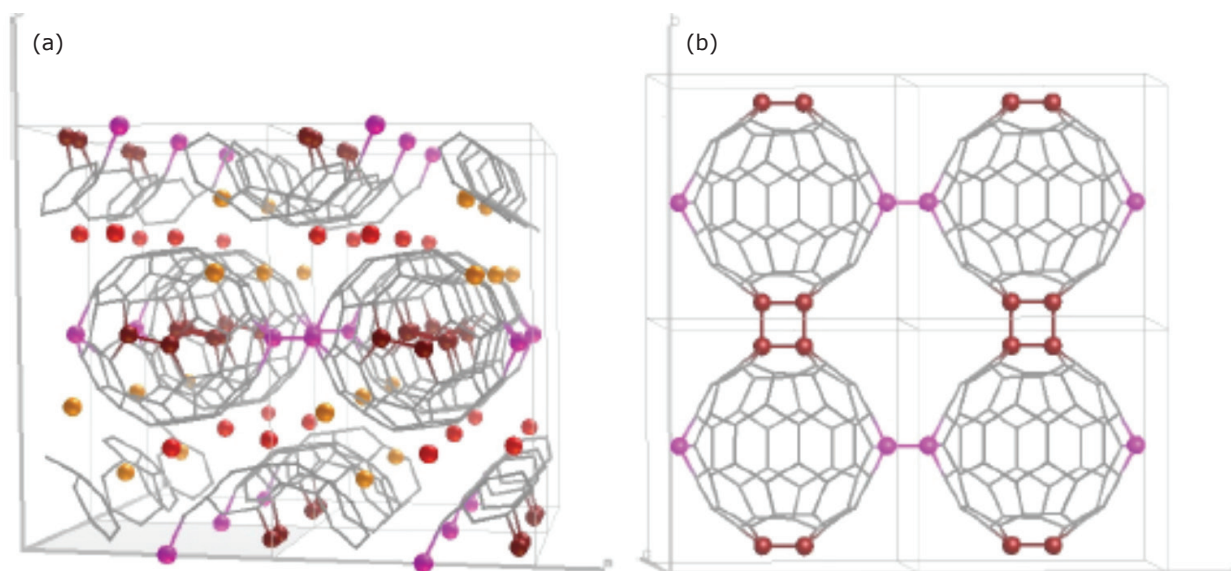


Fig. 1. (a) Structure of Li_4C_{60} as obtained from geometry optimisation, in the space group $I_{2/m}$. Grey sticks are carbon bonds, magenta and brown spheres are carbon atoms involved in the covalent intermolecular bonds: [2+2] bridges and single bonds respectively. Red and yellow spheres represent Li_T and Li_O respectively; (b) view along the \vec{c} axis of one polymeric plane (the Li ions have been omitted for clarity) (Reprinted with permission from (1) Copyright 2015 by the American Physical Society)

characterisation of SSEs. Conventional impedance spectroscopy uses macro-electrodes to probe diffusion within the bulk of the SSE. Here, Taibl *et al.* used individually accessible micro-electrodes, deposited by lithography, to electrochemically map the conductivity of the sample surface. This electrochemical map was combined with elemental mapping obtained through laser ablation inductive coupled plasma mass spectrometry (LA-ICP-MS) to correlate the Al and lanthanum surface concentration with Li-ion conductivity.

A look at combinatory techniques to probe SSB during operating was delivered by K. Yamamoto (Japan Fine Ceramics Center, Japan). The talk highlighted his recent work on the study of SSB by transmission electron microscopy (TEM). The systems presented were interesting in that the anode is formed *in situ* from the SSE. The SSE is reduced to form a $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{TiO}_2-\text{P}_2\text{O}_5$ -based electrode (2) and was followed by *ex situ* spatially resolved electron emission loss spectroscopy (SR-EELS) to resolve the electronic structural changes occurring. This was correlated with *in situ* electron holography (EH) experiments to correlate the electronic structural changes occurring to the Ti/O in the lithium titanium aluminium phosphate

material, with the Li distribution during charge/discharge. Advances in probing the structure of more conventional electrode systems were discussed by J. Joos (Institute for Applied Materials (IAM-WET), Karlsruhe Institute of Technology (KIT), Germany). His talk gave an update on their model development for correlating bulk X-ray tomography with TEM three-dimensional (3D) laser ablation; the concept behind this model is to use the high resolution data from small areas of sample analysed by TEM 3D laser ablation and apply this to the comparatively fast and non-destructive X-ray tomography of the bulk sample. Joos *et al.* showed how such a method could allow the voids within the electrode ink to be calculated, and hence inform on the particle distribution required to minimise void space and maximise performance.

All-Solid-State Lithium-Ion Batteries

E. Wachsman (University of Maryland, USA) opened the first ASSLiB session, presenting an overview of different techniques for improving the performance of garnet-based ASSLiBs. An Al-nanolayer coating at the Li-metal anode/SSE interface (Figure 2) was shown to permit wetting of the SSE by the

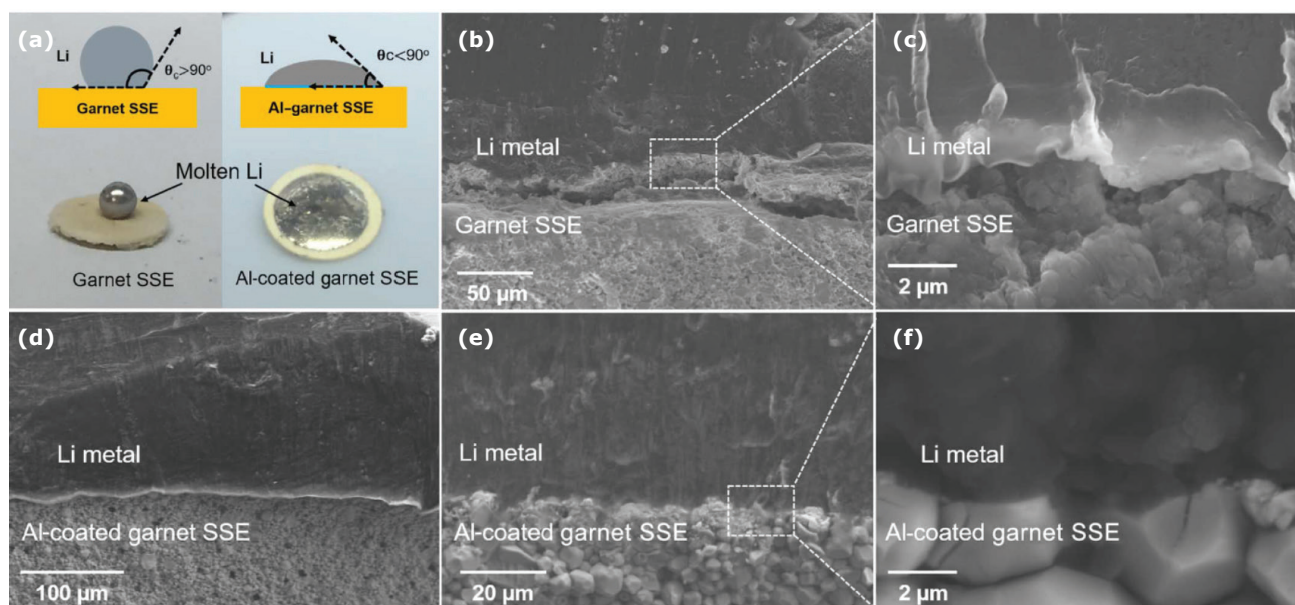


Fig. 2. Wetting behaviour and interfacial morphology characterisation of Li/garnet SSE and Li/Al-coated garnet SSE: (a) wetting behaviour of molten Li with garnet SSE and Al-coated garnet SSE. The inset is a schematic showing the contact angles of a molten Li droplet wetting the surface of both uncoated and Al-coated garnet SSEs. Improved Li wettability is demonstrated after Al-coating the garnet surface; (b) and (c) SEM images of Li/garnet SSE, showing the poor Li wettability of uncoated garnet; (d) to (f) SEM images of Li/Al-garnet SSE-Al exhibiting superior Li wettability with Al-coated garnet (Reprinted from (3) © The Authors, some rights reserved; exclusive licensee American Association for the Advancement of Science. Distributed under a Creative Commons Attribution Non Commercial License 4.0 (CC BY-NC))

Li-metal and reduce the contact resistance significantly. Wachsman also presented a method for fabricating flexible solid-state conductive membranes; this consisted of a polymer matrix and 3D ceramic network formed by electrospinning a garnet salt and polyvinylpyrrolidone (PVP) polymer. This polymer-ceramic composite possessed a conductivity of $2.5 \times 10^{-4} \text{ S cm}^{-1}$ and suppressed dendrite formation over 300 h at 0.5 mA cm^{-2} when fabricated with a Li-anode. These types of flexible polymer-ceramics were shown to be compatible with scalable tape-casting processes and were reported by Wachsman to achieve current densities of up to 3 mA cm^{-2} .

The final ASSLiB session was opened by E. Ivers-Tiffée (KIT, Germany). She presented a modelling approach to predict the structure required for LGPS-based batteries to compete with conventional Li-ion batteries. The model indicated that it was possible to match Li-ion in terms of power and energy density for bulk-type ASSLiB systems, with an electrolyte thickness of $1 \mu\text{m}$. Ivers-Tiffée discussed how this model could be applied to other systems, such as garnet-based ASSLiBs, to help direct battery design and achieve systems that can compete with conventional Li-ion technologies.

Conclusions

The conference was well attended by the international community covering all aspects of solid-state ionics. Within the battery macro-area, particular emphasis was put on research into SSB. All aspects of academic research in the field were represented including electrolyte development, interfacial studies and routes for ASSLiB fabrication. The presentations were of high quality and audience interaction with the speakers was both frequent and impactful.

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The Reviewer



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