

# Redox-active cathode interphase formation in solid-state batteries probed by *in situ* XPS

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Environmental concerns and the growing fraction of renewable energy in our energy grid drive the development of electric vehicles with high-energy batteries. However, within the next few years, “conventional” lithium ion batteries (LIBs) will reach their performance limits.<sup>1</sup> Coming closer to these performance limits, safety concerns grow. Therefore, all-solid-state batteries (SSB) without liquid electrolyte are now studied intensively as reliable and safer alternative of lithium ion batteries. Instead of the commonly employed carbonate-based liquid electrolytes, SSBs contain a consolidated polycrystalline or glass-ceramic solid as the separator.

In particular, lithium thiophosphate-based solid electrolytes like  $\text{Li}_3\text{PS}_4$ ,  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  or  $\text{Li}_7\text{P}_3\text{S}_{11}$  are studied extensively, as they combine favorable mechanical properties with high ionic conductivities. However, when employed in an SSB, the performance is limited by chemo-mechanical shape changes of the electrode material and interfacial side-reactions.<sup>2</sup> Especially the latter represents a detrimental factor for capacity retention because of the growing overvoltage of the resistive layer. Despite their undeniable importance for the cell performance, the underlying interfacial side reactions between thiophosphates and cathode active materials are not yet understood well.

In this work, we explore the effect of the upper voltage limit on solid-state batteries using NCM-811 as cathode active material and  $\beta$ - $\text{Li}_3\text{PS}_4$  as SE.<sup>3</sup> We observe the formation of a redox-active resistive layer in the solid electrolyte, which impedes the conductivity depending on the state-of-charge of the battery. By the means of electrochemical impedance spectroscopy as well as depth profiling with X-ray photoelectron spectroscopy we find a nanometer-thick passivation layer at the current collector and decomposition products within the cathode composite. In addition, we employ an *in situ* electrochemical experiment during X-ray photoelectron spectroscopy and show that the solid electrolyte is redox-active and undergoes local structural changes at the cathode/solid electrolyte interface in solid-state batteries.

Based on the conducted experiments, we propose a redox reaction scheme for the conversion of the  $\text{Li}_3\text{PS}_4$  solid electrolyte during oxidation and reduction. The presented structures match well with the binding environments found in XPS analysis. The presented data underline the importance of the solid electrolyte redox-activity at the interfaces, for  $\text{Li}_3\text{PS}_4$  i.e. polymerization and possible formation of the presumed structural moieties  $\text{Li}_4\text{P}_2\text{S}_8$ ,  $\text{Li}_4\text{P}_2\text{S}_7$  and  $\text{Li}_2\text{P}_2\text{S}_6$ .

## References:

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