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Marine Soler, Celine Barchasz, Vasily Tarnopolskiy, Frédéric Le Cras

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Evaluation of the Chemical Stability of Sulfide Solid Electrolytes with Lithium Metal Using In-Situ, Operando and Post-Mortem Analyses

The high demand for portable energy storage is driving the development of new, more efficient and safer portable energy storage systems. A lithium-sulfur battery is based on a lithium (Li) metal anode and an elemental sulfur cathode. It is a very promising system thanks to the very high theoretical energy density, while sulfur is also an inexpensive, abundant, non-critical and non-toxic raw material. On the other hand, lithium-sulfur batteries with conventional liquid electrolytes suffer from several problems preventing them from being commercialized today. The development of so-called "all-solid-state" lithium-sulfur batteries with the use of a highly conductive solid electrolyte (SE) could resolve some of these difficulties⁽¹⁾. In particular, solid sulfide electrolytes (SSEs) have received increasing interest in recent years due to their promising ionic conductivities around 10^{-2} - 10^{-3} S/cm⁽²⁾ and their ductility. However, while it solves some of the problems associated with liquid electrolytes, the all-solid-state system also presents a number of specific challenges.

One major challenge of the all-solid-state systems is the study and the control of the interfacial issues, in particular of the SE/Li metal anode interface. Indeed, stability issues of the sulfide-based electrolytes with Li metal may be encountered, as being thermodynamically unstable against lithium metal, as well as the possible growth of lithium dendrites through the solid electrolyte separator^(3,4). Since both of these phenomena can severely impact the performance and safety of the battery (poor electrochemical stability of the SE against Li metal leads to decomposition of the SE thus increasing the impedance; growth of lithium dendrites leads to short-circuit of the battery), they must be understood and suppressed.

In this work, we study two sulfide electrolytes: argyrodite-type crystalline $\text{Li}_6\text{PS}_5\text{Cl}$ and glass-ceramic $\text{Li}_7\text{P}_3\text{S}_{11}$. In order to assess and compare their stability against Li metal, Electrochemical Impedance Spectroscopy measurements were carried out over time on symmetric Li/SSE/Li cells. While the impedance is increasing constantly in the case of $\text{Li}_7\text{P}_3\text{S}_{11}$, it remains relatively stable for argyrodite-type SE. In addition, the nature and the morphology of the decomposition products of the two electrolytes in contact with Li metal have been characterized *post mortem* by XPS, ToF-SIMS and SEM analyses, as well as *in-situ* and *operando* using synchrotron radiation to perform X-Ray Diffraction Computed Tomography and Absorption Tomography. We demonstrate that in the case of argyrodite, the decomposition products limit the further reaction of electrolyte with Li metal, whereas they promote the propagation of the decomposition reaction for $\text{Li}_7\text{P}_3\text{S}_{11}$.

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[2] Busche, Martin R. et al. 2016. « *In Situ* Monitoring of Fast Li-Ion Conductor $\text{Li}_7\text{P}_3\text{S}_{11}$ Crystallization Inside a Hot-Press Setup ». *Chemistry of Materials* 28(17): 6152-65.

[3] Wu, Bingbin et al. 2016. « Interfacial Behaviours between Lithium Ion Conductors and Electrode Materials in Various Battery Systems ». *Journal of Materials Chemistry A* 4(40): 15266-80.

[4] Yue, Junpei, Min Yan, Ya-Xia Yin, et Yu-Guo Guo. 2018. « Progress of the Interface Design in All-Solid-State Li-S Batteries ». *Advanced Functional Materials* 28(38): 1707533.