MECHANOCHEMICAL SYNTHESIS OF Li-BASED IONIC CONDUCTORS FOR ALL-SOLID-STATE BATTERIES

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Inorganic All-solid-state batteries (ASSBs) have recently gained great interest as next-generation energy storage systems due to their potentially better safety and higher energy density compared to the current lithium-ion batteries with organic liquid electrolytes [1,2,3,4]. The development of these batteries is based, on the one hand, on the exploration of electrolyte conductors with high ionic conductivity (10^{-3} $S.cm^{-1}$) and high voltage windows and, on the other hand, on the optimization of the interfaces between electrolyte and active materials at the positive and negative electrodes.

The use of mechanical milling has proved effective to address these two challenges[5].

Major research efforts have been undertaken to optimize inorganic solid electrolytes (SEs) including sulfides, oxides, polymers and halides. Among them, sulfides and halides are more promising owing to their high ionic conductivities, their plasticity enabling good contact with electrode materials and suitable integration conditions in All-Solid-State batteries systems conditions, in particular compared to oxide electrolytes. However, oxides exhibit higher stability in the ambient condition.
The electrolytes synthesis can be performed by solid-state and solvent based reactions, as well as through mechanochemical synthesis by ball milling.
In the case of oxides, the solid-state reaction, where the precursors are simply mixed, calcinated and sintered, is a common synthesis to obtain polycrystalline ceramics. Easy to scale-up, it is considered the most suitable for mass production but a critical process is to obtain homogeneous mixture of raw material powders and ball-milling has been widely used to achieve this step.
In the case of sulfides and halides, ball milling is a promising route for upscaling processes, since the synthesis without many additives and/or solvent is reproducible, the absence of toxic solvents yielding, in addition, a more sustainable approach. This physical synthesis technique also enables the stabilization of metastable phases that cannot be achieved at high temperature, and the formation of glassy and glass-ceramic solid electrolytes obtained previously by costly melt-quenching route.

The presentation will make a review, mostly of the mechanochemical synthesis of solid electrolytes but also, the input of ball milling for the preparation of cathode composites in Li-ion solid state batteries.

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