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Study of the electrode/electrolytes interfaces in lithium-rich sulfide all-solid-state lithium batteries

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Lithium-ion battery is the most effective electrochemical storage technology in terms of energy density nowadays. However, it is believed that the performances of this technology are close to their theoretical limits. Developing all-solid-state batteries in which the liquid electrolyte is replaced by a solid could be a way to overcome these limits. Firstly, the use of an organic liquid electrolyte is a safety issue due to the risk of thermal runaway and limits the operating temperature window of the system. Secondly, the use of a solid separator could block dendrites propagation and allows for the use of metallic lithium as an anode. The removal of the liquid electrolyte could also allow the manufacturing of thick cathodes if proper industrial processes are developed. Both perspectives may lead to a significant increase in energy density at the battery level¹.

However, few solid electrolytes are considered viable because of insufficient ionic conductivities ($<10^{-3}$ S.cm⁻¹). Among them, polymers have an easy processability and sufficient ionic conductivities when heated (~70°C). Sulphide electrolytes and especially argyrodite Li₆PS₅Cl are promising due to their high ionic conductivity (~2 mS.cm⁻¹), low density, ability to be processed near room temperature and relatively cheap material price. However, with both type of electrolytes, traditional oxide cathode materials such as NMC leads to a decomposition of the electrolyte at the interface and a quick decay of the electrochemical performances². Thus, their usage requires using a coating layer that complicates the system manufacturing and may decrease the performance of the system.

In order to develop a system with decent energy density and without using a coating layer, Li-rich layered Li_{1,2}Ti_{0,8}S₂ (LTS) will be here studied as a cathode material in an all-solid-state cell LTS||Argyrodite||Li⁰. LTS has shown promising performances in liquid electrolyte cells with a reversible capacity of 250mAh.g⁻¹ after 20 cycles

due to the redox processes involving both Ti and S, low polarisation (<0,1V) and an operating voltage comprised between 2-2,8 V vs Li⁺/Li³ which may be compatible with argyrodite.

Thus, the LTS/Argyrodite interface has been studied during the cycling process of an all-solid-state battery in this work. Interfaces issues in solid-state battery could be classified in two categories: mechanical problems leading to contact loss between particles and chemical problems leading to interphase formation⁴.

At first, the chemical reactivity of argyrodite towards LTS has been studied via X-Ray Photoelectron Spectroscopy (XPS) on a composite electrode. The formation of an interphase between the two materials when contacted has been shown. Lithium/argyrodite reactivity has also been described via *in-situ* lithium plating and XPS analysis.

To correctly study interfaces in solid-state cells, optimisation of the formulation and operating conditions had to be done. In this regard, several experimental parameters have been optimised such as electrolyte/carbon/active material ratios and assembling/operating pressures. For a better understanding of each parameter influence, a model active material, TiS₂, has been used for this part of the study.

At last, the evolution of the LTS/Argyrodite interphase has been studied with *ex situ* and *in situ* XPS. The morphological changes occurring during cycling have been characterized via the coupling of SEM, Auger spectroscopy and X-ray tomography.

References:

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