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Study of transport mechanisms of lithium in hybrid electrolytes for solid-state batteries

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Abstract: Topic: NRG – Energy, Environment and Sustainability

The next generation of lithium-ion batteries needs to have better electrochemical performances and to be intrinsically safer. The replacement of liquid electrolytes by solid-state electrolytes can lead to higher specific or volumetric energy density, and to obtain more thermally stable batteries.[1] Hybrid solid-state electrolytes, i.e. a dispersion of ceramic particles in a polymer matrix, could be a solution.[2] The goal is to combine advantages of different materials: the easy implementation from conducting polymer that also offer good interfaces with the electrodes and the high ionic conductivity of ceramics. This study aims at estimating lithium diffusion coefficients in these hybrid materials by providing information about lithium diffusion paths. It will lead to a better understanding of lithium transport phenomena in the bulk and at interfaces.

Methodologies based on characterisations of lithium isotopes (⁷Li, ⁶Li) are developed. ⁶Li-rich materials are used to label the lithium ions of a specific material to be able to differentiate these lithium ions from others. Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) and ^{6/7}Li solid-state Nuclear Magnetic Resonance spectroscopy (ssNMR) can distinguish between isotopes. That is why they are used to track the diffusion of lithium ions. ToF-SIMS and ssNMR analyses are complementary. On one hand, ToF-SIMS is a surface analysis, which gives local micrometric information on the molecular fragments, and a ratio of the lithium isotopes can be calculated. On the other hand, ssNMR analyses provide global information on lithium ions environment and quantitative experiments can lead to calculate isotopes concentrations.

The first studied configuration is composed of a ceramic pellet sandwiched within two layers of a polymer containing a lithium salt. Such design simplifies the study of interfaces by using ToF-SIMS. The chosen materials are a garnet-type ceramic, Li_{6,4}La₃Zr_{1,4}Ta_{0,6}O₁₂ (LLZTO) and a well-known polymer, poly(ethylene oxide) (PEO) containing lithium bis(trifluoromethylsulphonyl)imide (LiTFSI) as the lithium salt.[3] To study spontaneous isotopic exchange between materials, a ⁶Li-metal foil is put into contact with either the polymer membrane or the ceramic. Then, these systems are heated at 60°C during different contact times. Numerical simulations consider experimental parameters and process them to develop models to predict the electrochemical responses of the studied composite solid electrolytes.

By using ToF-SIMS analysis, the evolution of the relative isotopic abundance has been measured. ⁶Li⁺ ions diffuse from the ⁶Li-metal foil up to thousands of micrometres into the material. They diffuse faster in the ceramic than in the polymer membrane: 70 μm.h⁻¹ in the ceramic vs. 50 μm.h⁻¹ in the membrane. ssNMR allows to differentiate lithium ions from the ceramic or from the polymer and quantitative experiments have been carried out. Under an electric field, the favourite diffusion paths of lithium will be analysed in the hybrid electrolyte.

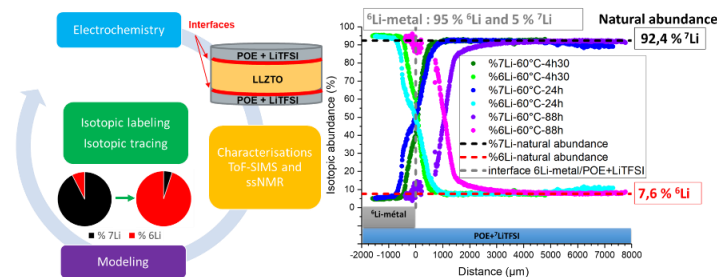


Figure 1: Methodologies for analysing and understanding the behaviour of ⁶Li-enriched materials.

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