Hybrid Ionogels and Self-Healing Electrolytes: Innovative Solutions for Safer Lithium Metal Batteries

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Lithium-ion batteries (LIBs) emerged in the past three decades as reliable and efficient energy storage devices. LIBs powered the revolution of portable electronics, allowing the construction of lightweight, miniaturized and affordable technologies, such as smartphones, tablets, and laptops that have become indispensable to modern life. Recently, in response to the worsening of the current climatic crisis, a strict decarbonisation path has been undertaken by numerous institutions driving the urgent need for alternatives to oil-fuelled internal combustion engines (ICEs). In this scenario, LIBs have been employed for new applications, including electric vehicles (EVs), stationary energy storage devices and micromobility solutions. However, despite significant advancement, LIBs are still failing to meet market requirements, offering lower energy/power density compared to traditional ICEs. Furthermore, this technology is reaching its theoretical limits, necessitating the development of next-generation alternatives.

Metallic lithium is considered a valuable anode material due to its extremely high theoretical capacity and low redox potential. Lithium metal batteries (LMBs) represent a potential alternative technology for future high-performance batteries. Nevertheless, the use of metallic lithium is hampered by its high reactivity, leading to challenges such as dendrite formation, interface degradation, and the generation of dead lithium. Conventional electrolytes can no longer be used for LMBs necessitating the development of advanced electrolytes, not only offering a physical barrier between the electrodes but actively increasing the safety.

In this dissertation three distinct polymer electrolytes were investigated as a suitable tool for safer LMBs. The first study focused on a polymeric backbone impregnated with a high ionic liquid (IL) content, obtained by chemically crosslinking the polymer precursors in the presence of the liquid phase. Despite the reduced amount of polymer, the obtained ionogel (IG) was self-standing and mechanically robust. However, to enhance electrochemical performance and oxidation stability, alumina nanoparticles (Al_2O_3 NPs) were incorporated into the polymer electrolyte. This inorganic filler promoted faster Li^+ kinetics by favouring lithium salt dissociation and anion coordination. The synergy of IL and Al_2O_3 NPs induced a promising flame resistance capability and high thermal stability, significantly increasing battery safety.

The second work, based on the same polymer matrix previously discussed, focused on the insertion of the garnet active filler $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$ (LLZTO). The active filler, owning the ability to conduct the lithium cation, was functionalised with an organosilane to improve the compatibility with the organic matrix and remove the resistive surface layer. The functionalisation resulted in an optimal dispersion of the filler within the polymer electrolyte, inducing outstanding cycling performances both in symmetric and half-cell configurations. The combination of inorganic filler and IL was the key to the development of IGs with high thermal stability and wide electrochemical stability window (ESW).

The third study applied a different approach to increasing the safety of LMBs. A self-healing polymer electrolyte was prepared using a catalyst/initiator-free polymerization performed in water. The capacity to recover from damages was given by the presence of disulfide bonds capable of re-forming upon exposure to heat. The insertion of functionalised and bare Al_2O_3 NPs was also investigated to increase the electrochemical performances. The self-healing capabilities were tested both outside and inside the cell, comparing the pristine polymer electrolyte to formulations containing Al_2O_3 NPs.

These investigations demonstrate the potential of innovative polymer electrolyte designs to address safety and performance challenges in LMBs, paving the way for their deployment in next-generation energy storage technologies.