

Performances' enhancement ensured by the addition of filler in PVDF-HFP-based electrolytes for lithium metal batteries

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To win the energetic challenges of the future, it is mandatory to invest in technologies able to grant better employment of alternatives to fossil fuels. Electric vehicles and renewable energies request energy storage devices able to deliver higher specific capacity and energy density. Although metallic lithium-based rechargeable batteries could ensure these characteristics, their employment is still in the research stage as it is necessary to overcome some issues, the first and foremost the uncontrolled dendritic growth. A possible solution is to replace commercial liquid electrolytes with solid-state electrolytes (SSEs) constituting a physical barrier, opposing mechanically to the dendrites' continuous growth; also, the dispersion of inert filler inside the SSEs could be employed in order to additionally increase the mechanical reinforcement.

The project here developed is based on the synthesis of PVdF-HFP-based nanocomposite electrolyte membranes through a simple and cost-effective solvent casting method, dispersing the polymer, which forms the matrix, lithium bis(fluorosulfonyl)imide (LiFSI) and a new functionalized filler in a binary solvent mixture (DMF:THF) [1]. Novel hybrid nanoparticles (NPs) were synthesized by grafting short chains of poly(ethylene glycol) (PEG_x) with different molecular weights ($x=750, 5000 \text{ g mol}^{-1}$) on silica, that was previously synthesized and functionalized with APTES molecules [2]. The NPs mechanically reinforce the solid electrolyte to inhibit the dendritic growth and reduce crystallinity to raise the ionic conductivity, which is also achieved through the coordination of Li⁺ performed by ethers groups on PEG_x chains; at the same time, polymers grafted on silica NPs promote the obtaining of homogeneous systems by increasing the degree of compatibility between the polymeric matrix of the electrolyte and inorganic filler. The obtained nanocomposite membranes (~150 μm), previously characterized through NMR and SEM-EDX, were first tested to determine their ionic conductivity, then in symmetric lithium cells subjected to increasing current densities: this confirmed that nanocomposite electrolytes can withstand metal deposition during stripping and plating analysis, differently from the membrane without dispersed filler. In particular, the most promising sample (realized dispersing 5 wt% of SiO₂@PEG₇₅₀) registered 0.1 mS cm⁻¹ at room temperature and more than 250 hours of stripping and plating analysis. This encouraging result opens to the possibility to test this SSE also in LMB with LiFePO₄ as cathodic material, to verify its behaviour in real working conditions.

Overall the nanocomposite PVdF-HFP membranes are able to provide adequate mechanical reinforcement against dendrite perforation, excellent chemical and electrochemical stability, good ionic conductivity, and promising electrochemical performances; at the same time, they solve the problems of toxicity and leakages that make liquid electrolytes commonly used in commercial batteries unsafe.

References

- [1] Zhang et al. *Adv. Mater.* **2019**, 31, 1806082
- [2] Mezzomo et al. *Electrochim. Acta* **2022**, 411, 140060