The aim of the work carried out during the three years of PhD and presented in this thesis was devoted to the development of novel SPEs for next-generation, advanced lithium-metal batteries. The research followed a progressive and rational optimization pathway, moving from the formulation of physically blended polymer electrolytes processed through scalable and industrially relevant solvent-free approaches, to the refinement of their properties by crosslinking strategies, plasticizing additives, and, finally, the molecular design of new lithium salts and single-ion conducting polymer architectures. At each stage, the materials were developed with the dual objective of improving the key performance indicators required for practical application, namely ionic conductivity, lithium-ion transport, interfacial compatibility with lithium metal, mechanical and thermal stability, and resistance to anodic oxidation, while also preserving processability and favouring manufacturing routes compatible with large-scale production. As a result, the thesis describes not only the development of increasingly optimized SPE formulations, but also the construction of a coherent materials-design strategy in which each successive step builds on the limitations and insights emerging from the previous one, ultimately contributing to the advancement of safer, higher-energy, and more industrially viable solid-state battery technologies, including operation with high-energy 4V-class cathodes.