

# Abstract

LIBs have a central role in our daily lives for their widespread use in smart mobile devices, electric vehicles, and large-scale energy storage from renewables. The technology seems to be mature in terms of energy and power density, reliability and cyclability; unfortunately, this is still not enough to satisfy the always growing demand and voracious energy needs by our modern, global society. Indeed, there is an ever-increasing demand for batteries, especially from the automotive field, with greatly enhanced energy and power density (fast performance upon discharging and charging). Moreover, the legislation is forcing car manufacturers to sizeably reduce CO<sub>2</sub> emissions of their vehicles. This burden has driven the effort of the research community to focus on new propulsion concepts with rechargeable batteries at their core. In this context, the need for advanced batteries is evident and urgent, thus revolutionizing the market by combining high-voltage cathode materials (HVCMs), high-capacity anodes and innovative solid-state electrolytes (SSEs). The stringent requests of European legislation along with technological progress led to the discovery of several LIB configurations involving innovative electrodes and electrolytes. In the past years, tremendous research efforts have been focused on the development of safer electrolytes to replace current toxic and flammable organic carbonate solvents. Following the discovery of ion conductivity in poly(ethylene oxide) (PEO) with alkali metal salts, the use of solid polymer electrolytes (SPEs) gathered much attention, which resulted in sizeable developments towards its practical application. Among the wide variety of SPEs, single ion-conducting polymer electrolytes (SICPEs) are currently at the forefront of the research by the scientific community because of their promising prospects of targeting high energy density at high current rate due to the transference number close to unity. In addition, the tunability of the macromolecular structure in the polymer network by means of controlled polymerization and monomer selection allows easy control over the final SICPE properties, which may be finely tuned and optimized depending on the final envisaged application.

Considering the abovementioned scenario, the research efforts in the three years of Ph.D. course were focused on developing innovative SICPE networks with easily tuneable properties obtained by exploring the combination of different monomers with different chemical characteristics. Various copolymers with Li<sup>+</sup> single ion conducting features were prepared in order to investigate several aspects, mainly including the use of polycarbonate to increase the oxidative stability of the SICPE, the effects of phase separation on SICPE electrochemical and mechanical properties and the advantages resulting from the development of novel ionic monomers. All the samples were fully characterized from the chemical-physical and electrochemical viewpoints to evaluate their promising prospects for application in next-generation solid-state Li metal batteries. The initial research efforts were mainly dedicated to address at the limited electrochemical stability of ethylene oxide-based polymer electrolyte by preparing a SICPE comprising carbonate-based polymer backbone. The dual ROP-RAFT polymerization technique allowed the preparation of polymers composed by different blocks with different polarity (partially immiscible), resulting in block copolymers with well-defined morphology. The ROP investigation on trimethylene carbonate was fundamental for the preparation of a carbonate-based macro-RAFT agent, which was further used for the preparation of the ionic block, by means of controlled RAFT polymerization of PEGM and lithium ILM. Noteworthy, limiting the amount of -EO- units to solely those contained in the ionic block, the novel carbonate-based SICPE showed enhanced resistance towards high oxidation potential (~5 V vs Li<sup>+</sup>/Li at 70 °C).

Indeed, while maintaining sufficient ionic conductivity and high lithium-ion transference number (0.91), the material exhibited a much higher complex viscosity than poly(LiM<sub>m-r</sub>-PEGM<sub>k</sub>) in a wide range of temperature, demonstrating enhanced solid-like character and limiting the lithium dendrite growth. The improved electrochemical stability of the polymer electrolyte was nonetheless demonstrated by galvanostatic cycling in Li-metal cells assembled with high voltage NMC-based cathodes at 70 °C, showing excellent performances in terms of high specific capacity output, stability, and reversible cycling even up to 4.8 V vs Li<sup>+</sup>/Li.

Successively, the phase separation phenomena in block copolymers and its related benefits on SICPE properties was in depth investigated by improving the control over polymerizations. Different single-ion conducting block copolymers (A-b-B), possessing a Li-ion conducting block and an incompatible poly(2-phenylethyl methacrylate) block providing mechanical strength, were successfully prepared by controlled RAFT polymerization. The incompatibility of different blocks resulted in phase segregation, also demonstrating that, by working on the polymerization parameters, it is possible to obtain two types of morphologies: perpendicular hexagonally packed cylinders (HPC) and perpendicular lamellae. Noteworthy, the ionic conductivity in such poly[(LiM<sub>17-r</sub>-PEGM<sub>86</sub>)-b-PhEtM<sub>131</sub>] ( $\sim 3.6 \times 10^{-7}$  S cm<sup>-1</sup> at 25 °C) almost approached the conductivity of initial ionic A-blocks ( $4.1 \times 10^{-7}$  S cm<sup>-1</sup> at 25 °C) despite the significant decrease in the concentration of mobile charges. It was found that cylindrical morphology results in the decrease in ionic conductivity, while the lamellar samples exhibit conductivity comparable to the parent ionic A-blocks. Such results were attributed to the formation of the nano-sized channels with high concentration of Li cations responsible for ionic conductivity and poly(PhEtM) based phase accounting for toughness. Moreover, the novel block copolymers showed an improved viscoelastic performance in comparison with parent poly[LiM<sub>17-r</sub>-PEGM<sub>86</sub>] copolymer. Indeed, the proof-of-concept lab-scale truly-solid-state Li-metal cells with Li/poly[(LiM<sub>17-r</sub>-PEGM<sub>86</sub>)-b-PhEtM<sub>131</sub>]/LiFePO<sub>4</sub> configuration provided excellent performances in terms of high specific capacity output, stability and reversible cycling at 70 °C, delivering > 130 mAh g<sup>-1</sup> after more than 75 cycles at C/20 rate with a capacity retention of 86.67 %.

Finally, following the target of trying to improve the ionic conductivity of truly solid-state SICPEs, a novel Li monomer (ILM53) was synthesized and successfully applied for the preparation of new set of SICPEs. Noteworthy, the addition of several -EO- units into the main monomer chain of ILM resulted in the obtainment of a transparent oil-like material. The direct polymerization of ILM53 results in homopolymer (PIL53) with improved ionic conductivity ( $9.2 \times 10^{-8}$  S cm<sup>-1</sup> at 25 °C) in comparison with the polyLiMTFSI previously characterized ( $1.1 \times 10^{-12}$  S cm<sup>-1</sup> at 25 °C). The beneficial effect of the elongated -EO- chains terminated with anchored TFSI anion moieties was also demonstrated upon characterization of copolymers (coPIL1-3) prepared by copolymerization of ILM53 and PEGM. The best sample, namely coPIL2, showed ionic conductivity values of  $3.0 \times 10^{-6}$  and  $3.8 \times 10^{-5}$  S cm<sup>-1</sup> at 25 and 70 °C, respectively, along with relatively high viscoelastic behaviour. It allowed for the fabrication of a solid-state Li metal lab-scale cell with LFP-based cathode able to stably operate for more than 200 cycles at relatively high current rate (C/5), without any observable signs of short circuits and/or dendrite growth. Optimisation is still in progress, particularly to achieve prolonged cycling at ambient conditions, but this is a remarkable result for a truly solid-state electrolyte, at the level of the best literature results so far, which paves the way for the development of the next-generation of high-performing Li-metal cells conceived for practical application mainly in the electric transportation field.