A NEW PARADIGM TOWARDS ADVANCED Li-BASED BATTERIES: A TRUE POLYMERIC APPROACH

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Introduction

In the last decades, the development of reliable and high performing electrolytes for the next generation of lithium-based batteries has been a major challenge for the scientific community and the industry. Solid polymer electrolytes (SPEs) have been intensively studied since their intrinsic enhanced safety. Ideally, SPEs should display both high lithium transference number \( (t_{Li^+}) \) and ionic conductivity. Practically, strategies for increasing \( t_{Li^+} \) often result in low ionic conductivity and vice versa. To date, the development of SPEs showing both \( t_{Li^+} \) approaching unity, and high ionic conductivity at ambient temperature remains a major intriguing and challenging task.

Considering such a scenario, the research work during this Ph.D. career has been focused on the development of novel polymer electrolytes for applications in lithium-based batteries.

Results and discussions

Initially limited to portable consumer electronics, the field of lithium ion batteries (LIBs) is rapidly expanding toward performance-demanding applications such as electric vehicles and load levelling of electric grids. The success of LIBs is owed to high energy density, lightweight, rapid charge/discharge, and long lifetime. However, safety issues deriving from the use of flammable liquid organic electrolytes are at present one of the major drawbacks of this technology. Solid polymer electrolytes (SPEs), representing a lithium salt associated with a polar neutral polymer or with an ion-conducting polymer matrix have been proposed to replace liquid electrolytes in LIBs. Among other benefits, SPEs offer inherent thermal stability, nonflammability and good mechanical stability. Moreover, they do not require liquid electrolyte confinement and, therefore, enable the production of flexible and thinner batteries. Despite the mentioned advantages, the intrinsic low ionic conductivity of polymer electrolytes have precluded their use in real devices so far, and significant research efforts are still required to address this open issue.

Considering such a scenario, the research work during this Ph.D. career has been focused on the development of novel high-performance polymer electrolytes for applications in LIBs. The goal has been pursued exploiting a series of smart engineering strategies and synthetic pathways. All of the newly designed materials were characterized in terms of their physicochemical and electrochemical properties, and their performance evaluated in lab-scale lithium cell prototypes.

In the first part of this Ph.D. work, UV-induced crosslinking has demonstrated to be a versatile tool for preparing different families of quasi-solid polymer electrolytes based on polyethylene oxide (PEO). In the past decades, this polymer has been intensively studied since its ability to complex and transport alkali metal cations. At ambient temperature, the ionic conductivity of lithium salt complexes in PEO is limited by the semicristalline domains, and ion conduction is limited to the amorphous phase. Recently, combinations of high molecular weight PEO, lithium salts and low molecular weight plasticizer have been explored as polymer based electrolyte. Despite an increase of ionic conductivity, the mechanical stability of the composite was poor when the content of plasticizer exceeded a certain limit. In this thesis a solution to this problem was proposed: highly conductive PEO based polymer electrolytes were prepared via UV induced crosslinking in the presence of a lithium salt (lithium bis(trifluoromethanesulfonyl) imide, LiTFSI) and various high boiling point liquid plasticizers. A room
temperature ionic liquid, namely 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide (EMITFSI) was used in the former case,[1] whereas tetraethylene glycol dimethyl ether (TEGDME) was employed in the latter.[2] In both systems, ionic conductivity substantially increased upon incorporation of the plasticizer (up to $10^{-4}$ S cm$^{-1}$ at 25 °C). Noteworthy, the obtained crosslinking assured the mechanical properties to be well retained despite the high plasticizer content (up to 45% wt). Moreover, the prepared SPE showed outstanding characteristics in terms of thermal stability (>170 °C) and electrochemical stability window (>4.5 V in both cases). Finally, the prepared materials were successfully tested in lithium cells prototypes. An in situ polymerization method was developed to obtain an improved interfacial adhesion between the polymer electrolyte and the cells electrodes. Lab-scale lithium cells were assembled and tested up to hundred cycles of full charge and discharge, showing excellent performance at different operating temperatures and applied current rates.

Given the promising prospect of the developed materials, along with the easiness of the proposed process, the newly developed preparation method has led to an international patent.[3]

In the course of the Ph.D. work, the attention was also focused on single-ion conducting polymer electrolytes. In typical SPE, most of the ionic current is carried by the anion of the lithium salt, corresponding to a lithium transference number ($t_{Li^+}$) ranging from 0.1-0.4. Consequently, only 10-40% of the ionic current is useful to the lithium-ion cell chemistry and strong salt concentration gradients are established during battery operation with deleterious effects on performance and battery lifetime. High transference number polymer electrolytes were proposed to reduce significantly concentration polarization. This new class of materials is composed of negatively charged polymer backbones having lithium-ion counter ions. Since anionic moieties are covalently bonded to the polymer backbone, lithium ions are the only mobile ionic species, thus preventing polarization phenomena. A specifically developed anionic monomer, namely lithium 1-[3-(methacryloxy) propylsulfonyl]-1(trifluoromethanesulfonyl)imide (LiMTFSI), was synthesized and used to prepare the single-ion conducting polymer electrolytes. Different macromolecular architectures were prepared: random or block copolymers with poly(ethylene glycol) methyl ether methacrylate and crosslinked networks with poly(ethylene glycol) dimethacrylate.

All the proposed systems showed lithium transference number approaching the unity. For comparison, previously described SPEs based on EMITFSI and TEGDME showed $t_{Li^+}$ of 0.17 and 0.32, respectively. Remarkably, the electrochemical stability window of both proposed systems exceeded 4.5 V. Moreover, by changing the polyelectrolyte microstructure, it was also possible to tailor the ion conductivity of the proposed SPEs. In particular, single-ion block SPE exhibited ionic conductivity values as high as $10^{-5}$ S cm$^{-1}$ at 55 °C; and prolonged cycling in prototype lithium cells was demonstrated at 70 °C.[4] The ionic conductivity of single-ion crosslinked networks was substantially enhanced (up to $8.6 \times 10^{-5}$ S cm$^{-1}$ at 20 °C) by the incorporation of propylene carbonate as liquid plasticizer. The obtained gel electrolytes were tested in lab-scale lithium cells, which showed outstanding performance in terms of rate capability (up to 5C and 1C current rates respectively at 70 °C and ambient temperature) and cycling stability upon prolonged cycling (more than 3 months of uninterrupted testing), outperforming the current reports on single-ion conducting systems.[5]

In conclusion, the strategies presented in this PhD work in terms of performance optimization of different polymer electrolytes, as well as the engineering and synthetic procedures suggested will optimistically represent reliable solutions for the scientific community for the development of the next-generation of safe, cost-effective and environmentally friendly lithium-ion as well as lithium metal batteries.

References: