Abstract

All solid state lithium batteries are a promising prospect in the field of energy storage devices providing high energy density and safety. Presently, the rechargeable lithium battery technology stands at the pinnacle of the energy storage sector for powering a wide range of green technologies used in daily life. Besides the use of high capacity and high voltage cathode materials, the use of lithium metal as anode is considered advantageous in lithium batteries because of its high theoretical specific capacity, low density and the lowest electrochemical potential (−3.04 V vs. standard hydrogen electrode). Generally, lithium batteries suffer from various shortcomings associated with the electrochemical operation and design limitations which often get accelerated when lithium metal anode is used. Firstly, the conventional liquid electrolytes used in lithium batteries are predominantly based on a mixture of lithium salt in organic solvents that are highly toxic, flammable, and volatile with a narrow electrochemical stability window, and prone to liquid leakage. The uncontrolled dendrite growth on lithium metal surface in lithium batteries using liquid electrolytes brings additional safety issues, such as internal short circuits, thermal runaway, and, even causes explosion. "Solid state" batteries seek to resolve these limitations of current lithium battery technology by eliminating the need for a liquid electrolyte and replacing it with solid state electrolytes. Solid polymer electrolytes based on polymeric materials can promote safe and reliable solid state lithium batteries with several advantages like high flexibility, lightweight, good chemical stability, safety, and easy fabrication. The traditional solid polymer electrolytes suffer from reduced ionic conductivity due to the semi-crystalline nature of the polymers employed, as a result plasticizer addition or other modifications are required to reduce crystallinity and improve the ionic conductivity. A balanced solution for fabricating solid polymer electrolytes can involve ionic liquids as plasticizers with improved ionic conductivity and crosslinking or incorporation of fibrous frameworks as reinforcements. The prime objective of this research work is the synthesis and application of ionic liquid based solid polymer electrolyte systems for solid state lithium batteries. For this purpose, cage-like 1,4-Diazabicyclo [2.2.2] octane (DABCO) was selected to synthesize novel ionic liquids. In this thesis, attempts have been made to achieve excellent electrochemical performance of true solid state lithium batteries via the development of solid polymer electrolytes based on ionic liquids and poly(ionic liquids), that have remained relatively unexplored as lithium battery electrolytes.

Firstly, a simple solvent-free melt-diffusion method is presented to fabricate a free-standing solid electrolyte. A porous polymer host is infiltrated with a binary mixture composed of mono-quaternized DABCO based ionic liquid and a lithium salt. Next, DABCO is used to prepare backbone poly(ionic liquids) or ionenes with cationic moieties tethered to the backbone separated by oxyethylene spacers (-CH_2CH_2O-). The effect of spacer length on the electrochemical performance is investigated. Moreover, binary mixtures of the prepared ionene oligomers and lithium salt are used to coat poly(acrylonitrile) based electrospun fibrous mat to fabricate the flexible fibre reinforced solid polymer electrolytes. In this case, the soft ionene improves the interfacial contact and the cell operation in absence of any micro-wetting. In continuation to the previous work, a unique one-step fabrication approach is also tried where an all solid state polymer electrolyte is fabricated by uniaxial electrospinning of poly(acrylonitrile) blended with ionene oligomer and doped with lithium salt. Following heat-treatment, the ionene oligomer flows out of and around the nanofibers, closing the pores of the nanofibrous mat forming all solid state polymer electrolytes reinforced by fibrous framework. Therefore, to incorporate electrolyte in the fibrous mat an extra step involving coating or melt-diffusion gets eliminated in this case. Compared to the coating process this one step process can achieve greater mechanical strength and ionic conductivity. Lastly, DABCO is further used to synthesize cationic monomers with $TFSI^-$ and FSI^- anions to form a semi-interpenetrating network-based polymer matrix that is incorporated within an electrospun fibrous poly(acrylonitrile) network. A two-fold reinforcement effect is achieved collectively from the semi-interpenetrating structure and the three-dimensional fibrous network. Further, a dual anion synergy is demonstrated by the formation of an ion conductive inorganic rich solid electrolyte interface layer when both $TFSI^-$ and FSI^-anions are present. The fibre reinforced solid polymer electrolyte can remain stable at high temperatures of 150°C while the traditional polyolefin based commercial separator shrinks at such high temperature. The fabricated solid polymer electrolytes here in each case shows good electrochemical performance when evaluated in lithium metal batteries with high voltage cathodes like $LiFePO_4$ (LFP) and $LiNi_xMn_yCo_{1-x-y}O_2$ (NMC) or high-capacity sulfur/carbon cathodes in lithium sulfur batteries.

The knowledge from textile and fibre engineering proved to be valuable in designing flexible lithium batteries with the fabricated fibre reinforced solid polymer electrolytes that are shown to operate under bent, folded or cut states. In summary, this work can provide inspiring ways to fabricate flexible batteries that can be integrated to power next generation wearable technologies.