Solid Polymer Electrolytes Reinforced With Cellulose Nanofibers For Lithium ion Batteries

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Lithium ion batteries have gained considerable interest and fast growth as rechargeable batteries because of their promising performance in energy storage in portable equipment and future applications in the automotive field. To reach final goals such as high performances, reduction of production and overall device costs and the identification of environmentally friendly materials and production processes, many studies were conducted in the last decade on the principal components of a typical ion lithium battery. The positive, negative electrode and electrolyte are usually studied separately to optimize longevity, safety and capacity of the battery. Solid electrolytes were developed in this perspective to achieve high ionic conductivity, good mechanical properties and thermal stability, other than good processability. A required property is chemical robustness in the presence of the electrodes to achieve the isolation of the electrons and ions transport pathways in the cell and facilitation in the transport of the active ionic species (Li^+) through the electrodes.
Towards this end, previous studies identified a promising ionic conductivity in poly(ethylene oxide) doped with lithium salt system. Subsequent PEO based electrolyte developing was devoted to overcome the poor room-temperature conductivity due to semi-crystallization of the matrix. One of the most successful strategy was the preparation of copolymers with epoxies. Following these examples, the present thesis explored an already studied system: PEO doped with lithium bis (trifluoromethanesulfonyl)imide.
Two different copolymers were investigated: 84:16 and 50:50 monomer ratio. The goal of this project was the enhancement of poor mechanical properties encountered in these copolymers: the composite was reinforced with cellulose nanofibers (CNFs) or cellulose nanocrystals (CNCs). To identify the best system in terms of mechanical properties and ionic conductivity, different concentration of lithium salt and cellulose were incorporated in the composite. Material strength was tested with dynamic mechanical analysis, whereas the ionic conductivity was studied with electrochemical impedance spectroscopy measurements. The best performing composite was then analysed with cyclic voltammetry and galvanostatic cycling to determine the electrochemical stability and the efficiency. The results of this work showed that P(EO-EPI) 84:16 with 10 wt% of CNFs and 4 wt% of LiTSFI system reached a conductivity value of $\sigma \sim 6.4\ 10^{-6}$ S cm^{-1} at room temperature and $\sigma \sim 1.4\ 10^{-4}$ S cm^{-1} at 65 °C, while a storage modulus of more than 30 MPa at room temperatures was determined. This composite showed a good electrochemical stability window, a low resistive SEI and a good dissociation of lithium ions in the electrolyte. For battery application a conductivity of $\sigma \sim 1\ 10^{-4}$ S cm^{-1} at room temperature is suitable. Accordingly, cellulose incorporation needs to be further developed and adapted since it has a negative impact on ionic conductivity.

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