

Novel Nitrile-Bearing Polymer Electrolytes for Solid-State Lithium Batteries

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In state-of-the-art lithium ion batteries, energy dense anodes and cathodes are separated by tens of micrometers and are infiltrated with flammable, aprotic liquid electrolytes. Solid state batteries that utilize nonflammable solid lithium ion conductors are being developed as safer alternatives, but significant material challenges remain. Polymer electrolytes are an important class of solid electrolytes due to their processability and low cost; they are used in composite solid-state cathodes to effectively wet the active material surface and provide effective transport throughout the electrode porosity. However, archetypical polymer electrolyte compositions based on the ethylene oxide-bearing structural units are limited by relatively low oxidative stability of approximately 4V vs. Li/Li⁺. For high voltage cathodes, oxidatively stable yet conductive materials are required. Polyacrylonitrile (PAN) has high oxidative stability, but Li⁺ transport is limited in PAN due to its semicrystalline nature and high glass transition temperature ($T_g > 95^\circ\text{C}$). In this study, hydrogenated poly(acrylonitrile_x-co-butadiene_y) (HNBR, $T_g = -19^\circ\text{C}$) was investigated as a novel polymer electrolyte composition. The copolymer contains acrylonitrile units to solvate lithium cations, but the chain mobility is enhanced (T_g is reduced) and crystallinity is inhibited through the incorporation of butane residues in the polymer backbone. The objective of this study was to characterize the essential physical, chemical, and electrochemical properties of HNBR mixed with lithium salt in order to assess the practical utility of this material in solid state lithium ion batteries.

Polymer electrolyte films consisting of HNBR and bis(trifluoromethane)sulfonimide lithium salt (LiTFSI) were prepared by solution casting in a controlled inert N₂ environment. Through analysis of a nitrile stretch band at 2235 cm⁻¹, Fourier transform infrared spectroscopy (FTIR) of the films revealed that the HNBR interacts strongly with the Li⁺ cations, effectively solvating the salt. Large concentrations of salt were soluble in HNBR, down to a N/Li ratio of 5. Glass transition temperatures of the polymer electrolytes were shown to be 2 – 6°C higher than in pure HNBR, which was attributed to Li⁺ cations being complexed by multiple nitrile functional groups. Significant crystallinity was not observed, and the resulting films were highly flexible – capable of 200% tensile strain without fracturing. Lithium ion conductivities of HNBR reached 1x10⁻⁷ S/cm at 20°C, which is comparable to conventional PEO-LiTFSI compositions and three to four orders of magnitude more conductive than dry polymer electrolytes based on polyacrylonitrile. The electrochemical stability of HNBR electrolyte was measured with linear sweep voltammetry and compared with corresponding PAN-based electrolytes. It showed that HNBR electrolytes can withstand oxidation potential >5V. These results suggest that HNBR is a potential matrix for oxidatively stable, fully solid electrolyte (liquid/plasticizer-free) for lithium batteries.

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