

Abstract

Imidazolium-based Block Copolymers as Solid-State Separators for Alkaline Fuel Cells and Lithium Ion Batteries

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In this study, polymerized ionic liquid (PIL) diblock copolymers were explored as solid-state polymer separators as an anion exchange membrane (AEM) for alkaline fuel cells AFCs and as a solid polymer electrolyte (SPE) for lithium-ion batteries. Polymerized ionic liquid (PIL) block copolymers are a distinct set of block copolymers that combine the properties of both ionic liquids (*e.g.*, high conductivity, high electrochemical stability) and block copolymers (*e.g.*, self-assembly into various nanostructures), which provides the opportunity to design highly conductive robust solid-state electrolytes that can be tuned for various applications including AFCs and lithium-ion batteries *via* simple anion exchange.

A series of bromide conducting PIL diblock copolymers with an undecyl alkyl side chain between the polymer backbone and the imidazolium moiety were first synthesized at various compositions comprising of a PIL component and a non-ionic component. Synthesis was achieved by post-functionalization from its non-ionic precursor PIL diblock copolymer, which was synthesized *via* the reverse addition fragmentation chain transfer (RAFT) technique. This PIL diblock copolymer with long alkyl side chains resulted in flexible, transparent films with high mechanical strength and high bromide ion conductivity. The conductivity of the PIL diblock copolymer was three times higher than its analogous PIL homopolymer and an order of magnitude higher than a similar PIL diblock copolymer with shorter alkyl side chain length,

which was due to the microphase separated morphology, more specifically, water/ion clusters within the PIL microdomains in the hydrated state. Due to the high conductivity and mechanical robustness of this novel PIL block copolymer, its application as both the ionomer and AEM in an AFC was investigated *via* anion exchange to hydroxide (OH^-), where a maximum power density of 29.3 mW cm^{-1} (60 °C with H_2/O_2 at 25 psig (172 kPa) backpressure) was achieved. Rotating disk electrode (RDE) experiments determined the interfacial resistance imposed during cell assembly between the AEM, catalyst, and ionomer was a factor in fuel cell performance. Further RDE studies investigated the electrochemical stability of the PIL block copolymer ionomer under applied potentials, where it was determined that potential cycling increased the degradation compared to constant voltage or open circuit voltage studies.

The PIL diblock copolymer was then anion exchanged to the bis(trifluoromethane)sulfonamide (TFSI) anion form and imbibed with a lithium salt and ionic liquid solution for use as a SPE in lithium-ion batteries resulting in a maximum discharge capacity of 112 mAh g^{-1} at 0.1 C with a Coulombic efficiency greater than 94% over 100 cycles. PIL block copolymers have promising mechanical properties and transport properties (*i.e.*, ion conductivity) in both the hydrated (hydrophilic anions; Br^- , OH^-) and dry (hydrophobic anions; TFSI) states resulting in highly conductive, chemically/thermally stable, and mechanically robust solid-state polymer separators for use as AEMs in AFCs and as SPEs in lithium-ion batteries