Highly Conductive, High temperature Solid-State Polymer Electrolyte Membranes for Secondary Lithium Ion Batteries

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A conventional wisdom in the design of ‘dream’ polymeric electrolyte membrane (PEM) is to develop a stretchable solid membrane with very high room temperature ionic conductivity in the range of superionic conductivity (> $10^{-3}$ S/cm), electrochemical stability with high operating voltage (> 5 V), thermal stability (> 80 °C), and mechanical sturdiness. Solid polymer electrolyte membranes (PEMs) thus produced are flexible and lightweight with improved safety relative to their liquid counterparts. However, low ionic conductivity of these solid PEMs have greatly hampered their applications in rechargeable lithium-ion batteries. Recently, we have succeeded in preparing solid-state PEM via photopolymerization of a polymer precursor within a single phase window guided by the ternary phase diagram, consisting of a reactive polymer precursor, viz., poly (ethylene glycol diacrylate) (PEGDA), succinonitrile (SCN, solid plasticizer) and lithium bis(trifluoro-methane) sulfonylamide (LiTFSI) salt. SCN was found to serve not only as a plasticizer to the PEGDA network, but also can dissociate (or ionize) the LiTFSI salt and produce lithium ions. More importantly, very high room temperature ionic conductivity on the order of $10^{-3}$ S/cm was achieved in some compositions of the cured PEGDA/SCN/LiTFSI film that reached $10^{-2}$ S/cm at elevated temperatures above 60 °C. These conductivity values are already in the superionic conductor range and significantly higher than most solid PEMs hitherto reported or at least comparable to the liquid electrolyte based Li+ battery containing sizable amount of volatile organic solvents. To our astonishment, the present solid-state PEM can withstand an operation temperature of 140 °C, which exhibits flame retardant properties. In the AC impedance measurement, the 10/70/20 PEGDA/SCN/LiTFSI compositions revealed a very high room-temperature ionic conductivity showing crystal melting ($T_m$) and crystallization ($T_c$) temperatures of SCN plastic crystals during heating/cooling cycles. Cyclic voltammetry measurements of these PEM exhibited excellent electrochemical stability against lithium reference electrode. Half-cell charge/discharge cycling behaviors of these PEM of various compositions were further investigated by using graphite or Li$_4$Ti$_5$O$_{12}$ anode and LiFePO$_4$ cathode. PEGDA/SCN/LiTFSI PEM shows stable cyclic behavior in the half-cell with LiFePO$_4$ cathode, but to a lesser extent with the graphite anode. Urea assisted conductivity enhancement will be discussed.

Supported by NSF-DMR.