

Multifunctional Binder-Electrolyte for Use in Lithium Battery Cathodes

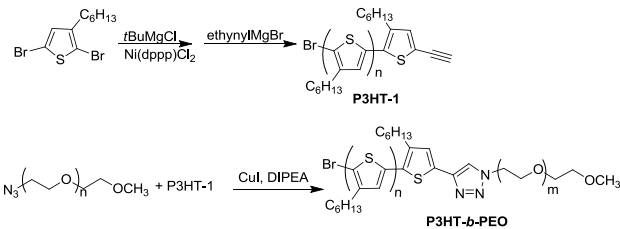
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Traditional lithium-ion batteries contain several non-energy-producing components: (1) a liquid electrolyte to transport ions between the electrodes, (2) a polymeric separator to prevent contact between the electrodes, (3) an inactive polymer that binds the active particles in the electrodes, (4) an electronic conductor such as carbon to conduct electrons within the electrode, and (5) current collectors that deliver electrons to the external circuit. These non-energy producing components account for roughly 50% of the mass of a weight of a lithium battery. Significant improvements are possible if high voltage cathodes can be used or if the anode can be substituted to an alloy/intermetallic or Li metal.

The redox reactions giving rise to the energy obtained at the electrodes of batteries require transport of both ions and electrons to the active centers. This brings significant complications not only because it requires that the active centers be located at the junctions of conduction pathways, but also because the materials that transport ions and electrons are vastly different. Ions are usually transported in aqueous or organic salt solutions, while crystalline solids, such as metals and semiconductors, usually transport electronic charges. Conjugated polymers such as poly(3-hexylthiophene) (P3HT) have been used extensively as the active material in various electronic devices. This report describes the synthesis and performance of a polymeric binder that simultaneously delivers both lithium ions and electronic charge to active centers that performs all the support functions needed in the electrodes.



Scheme 1. Synthesis of multifunctional binder-electrolyte: poly(3-hexylthiophene)-b-poly(ethylene oxide).

Our system uses a block copolymer, poly(3-hexylthiophene)-b-poly(ethylene oxide).¹ The P3HT-rich microphase conducts electronic charge while the PEO-rich microphase conducts ionic charge after the addition of lithium salts. All our studies were conducted using lithium bis(trifluoromethane sulfone)imide (LiTFSI) as the lithium ion source. A combination of ac and dc impedance measurements was used to determine the electronic and ionic conductivity of our samples.² The ionic conductivities of P3HT-PEO/LiTFSI mixtures are lower than those of mixtures of PEO homopolymer and LiTFSI, in agreement with published data obtained from other block copolymer/salt mixtures.

Cathode films were fabricated by mixing P3HT-b-PEO, LiTFSI with the active material, LiFePO₄ as the only other component. Two different cathode

compositions were used, containing 50- and 70-weight percent of the active material. All-solid lithium batteries were then assembled in a sandwich cell configuration, using solid polymer electrolyte/separator and lithium foil as anode. These batteries were cycled at 90°C from 3.8V to 2.5V at a current density of 20 $\mu\text{A}/\text{cm}^2$. Specific capacities were thus obtained and were seen to be approaching the theoretical limit for LiFePO₄ batteries.⁹ Specific power and energy were also calculated using different current densities during charge-discharge cycles.

Both ionic and electronic charges are transported simultaneously in the present block copolymer system, as determined by a combination of ac impedance spectroscopy and dc measurements. Using the P3HT-b-PEO polymer as binder material in a lithium battery cathode showed specific capacities that are within experimental error of the theoretical capacity of the battery. The ability of P3HT-PEO to serve all of the transport and binding functions required in a lithium battery electrode is thus demonstrated.

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References

¹ A. E. Javier, S. N. Patel, D. T. Hallinan, V. Srinivasan, N. P. Balsara, *Angew. Chem. Int. Ed.* 2011, **50**, 9848.
² S. N. Patel, A. E. Javier, G. M. Stone, S. A. Mullin, N. P. Balsara, *ACS Nano*, 2012, **6**(2), 1589.