Polymers are Critical to Safer Lithium Ion Batteries: The Case for Polymer Electrolytes

Fascinating World of Invisible Polymers

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Large scale lithium ion battery is expected to play a key role in powering electric cars, as backup power in aircrafts and solar energy storage applications. The intrinsic hazards associated with Lithium Ion batteries hinder their deployment in such applications. Consequently, there is an urgent need for replacing the liquid electrolytes with more stable solid electrolytes. Once again, polymers come to our rescue.

In my previous article (POLYMERS Communiqué, December, 2016 - January, 2017 issue); I addressed the nature of polymer-based separators needed for safer lithium ion batteries. However, one of the most troublesome components in a battery is the liquid electrolyte; typically, a 1:1 mixture of dimethyl carbonate and ethylene carbonate. These are volatile organic liquids which are flammable with high risk of ignition under battery operating conditions. The instability of carbonate-based electrolytes worsens at higher temperatures, resulting in electrolyte decomposition leading to thermal runaways and eventually, catastrophic failure of the battery. The performances of classical Li-ion batteries (LIBs) with non-aqueous liquid electrolytes have made great advances in the past two decades, but the intrinsic instability of liquid electrolytes results in safety issues, and the energy density of the state-of-the-art LIBs cannot satisfy the practical requirements. Large scale lithium ion battery is expected to play a key role in powering electric cars, as backup power in aircrafts and solar energy storage applications. The intrinsic hazards associated with such batteries hinder their deployment in such applications. Consequently, there is an urgent need for replacing the liquid electrolytes with more stable solid electrolytes. Once again, polymers come to our rescue. A study conducted by Toyota Motors, Japan has indicated that an all solid-state lithium ion battery may be

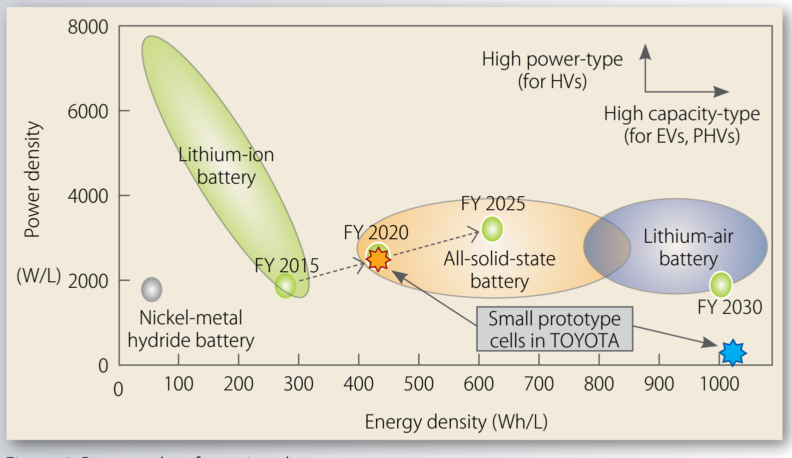

Figure 1: Ragone plots for various battery systems.

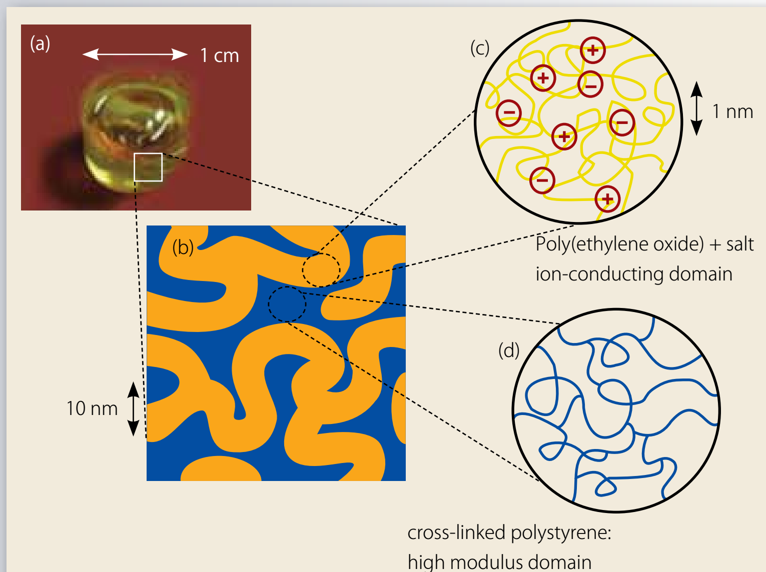

Figure 2: Cross-linked styrene-b-ethylene oxide polymers useful as solid electrolytes.

ready for commercial deployment by 2025 (Refer Figure 1)[1], and polymers could form a large part of these batteries.

PEOs: The Solid Electrolytes

Poly(ethylene oxide)s (PEOs) have been extensively studied as solid electrolytes. PEO can solvate high concentrations of lithium cations and is non-flammable. However, practical conductivity is observed only at elevated temperatures. Additionally, the reduced mobility of lithium ions associated with the polymer chains reduces the overall current carrying capacity of the electrolyte. For fast conduction of lithium ions, the polymer must possess high polymer chain mobility at room temperature, that is, low glass transition temperatures. Furthermore, PEOs have poor mechanical properties which lead to other undesirable effects. For ease of fabrication, the polymer must have reasonable modulus; however, increasing modulus leads to reduced conductivity.

Several well-defined random and block copolymers have been especially designed for use in these applications. They combine, both, structure and functions. A cross-linked block copolymer of styrene and ethylene oxide has been shown to possess useful properties such as high energy density, mechanical stability and good ionic conductivity. The discrete PEO segment provides ion mobility, whereas, the continuous cross-linked domains of polystyrene provide modulus[2] (Refer Figure 2).

Novel block copolymer structures have been designed that are mechanically robust and have ionic conductivities similar to liquid electrolytes. The feature of these polymers are that the positive and negative charges are separated in the block copolymers so that the Lithium ions will not be immobilised by the negatively charges ions[3] (Refer Figure 2).

Recently, efforts have been focused on polymer nanocomposites; especially, nanocomposites of poly(ethylene oxide)s with 2D graphene oxides. Incorporating 1 wt% graphene oxides results in two orders of magnitude increase in ionic conductivity with a 260% increase in tensile strength[4]. Nanocomposites offer another approach to independently tailor ionic conductivity and mechanical properties.

New Class of Fluoropolymer Materials

A new class of fluoropolymer materials useful as solid electrolytes has recently been reported[5]. These polymers are perfluoropolyethers which have been functionally terminated by two methyl carbonate end groups. These polymers possess high thermal stability as shown by the high temperatures at which thermal decomposition begins (212°C) and do not burn. Typical molecular weights of such functional polymers range between 1000 and 4000 g/mol and they possess Tg between -90°C to -120°C. Batteries were fabricated using such polymer electrolytes and they exhibited a capacity of 120 mA.h.g^{-1} compared to 150 mA.h.g^{-1} for a similar battery with conventional liquid electrolytes when the batteries were charged and discharged at an interval of 10 hours. They could be charged and

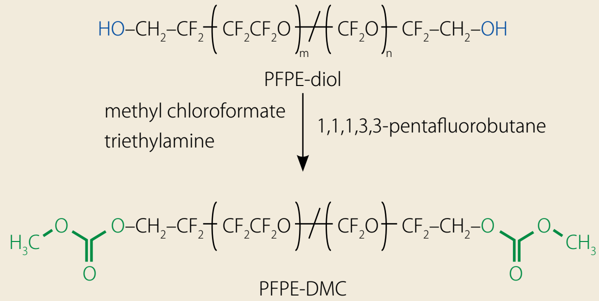

Figure 3 : Synthesis of methyl carbonate end functional perfluoropolyethers (PFPE).

discharged on the time scale of even 8 hours, but with slightly reduced capacities. Such time scale is very relevant for use of lithium ion batteries for backing up of solar energy.

Limitation Addressed by SPEs

A limitation of rechargeable lithium ion batteries arises because most of the ionic current is carried by the anion associated with the lithium cation, the ion that does not participate in energy-producing reactions. Solid polymer electrolytes (SPEs) offer a perfect solution to this problem and to the enhancement of energy density[6]. Traditional SPEs are dual-ion conductors, in which both, cations and anions are mobile and will cause a concentration polarisation leading to poor performance. Single lithium ion (Li-ion) conducting solid polymer electrolytes (SLIC-SPEs), which have anions covalently bonded to the polymer are generally accepted to have advantages over conventional dual-ion conducting SPEs for application in batteries. Single-ion-conducting block copolymer electrolytes, wherein all of the current is carried by the lithium cations, have the potential to dramatically improve battery performance. An example of such a polymer (poly(ethylene oxide)-b-polystyrenesulfonyllithium(trifluoromethylsulfonyl)imide (PEO-b-PSLiTFSI) diblock copolymer)s[7]. These polymers exhibit at low temperatures, an ordered lamellar phase and the 'mobile' lithium ions are trapped in the form of ionic clusters in the glassy polystyrene rich microphase. An increase in temperature results in a transition to a disordered phase. Above this transition temperature, the lithium ions are released from the clusters, and ionic conductivity increases by several orders of magnitude. The ability to design electrolytes, wherein, most of the current is carried by the lithium ions to sequester them in non-conducting domains and release them when necessary, has the potential to enable new strategies for controlling the charge-discharge characteristics of rechargeable lithium batteries.

Once Again

The invisible polymers inside a lithium ion battery will be the key to securing our 'energy future' and provide us an efficient way to use solar energy during the hours, when the sun does not shine as well as ensure an emission-free solution for transportation.

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