Triblock copolymer electrolytes with polymer-in-salt like lithium to oxygen ratios

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Developing new electrolytes is considered as a key to enable advanced cell chemistries based on lithium metal anodes for batteries with increased energy density, which are demanded for efficient energy storage and e-mobility. To guarantee long and stable cycle life, suppression of lithium dendrite growth is one of the crucial properties the electrolyte needs to exhibit. [1] Polymer electrolytes appear as promising candidate, as they offer mechanical stability, compared to liquid electrolytes, [2] and better electrode wetting than solid state electrolytes. Nevertheless, they suffer from insufficient lithium ion conductivity at ambient temperature in exchange for mechanical integrity, as a main throwback. [3]

Block copolymers can be designed to fulfill several requirements at a time, as every block can be used differently. [4] We here report on a poly(isoprene)-block-poly(styrene)-block-poly(ethylene oxide) (ISO) with varying poly(ethylene oxide) (PEO) block sizes, in which ‘polymer-in-salt’ like amounts of bis(trifluoromethane)sulfonimide lithium (LiTFSI) have been dissolved from a tetrahydrofuran (THF) solution.

Optimized ratios show ionic conductivities of 2 mS/cm at 20 °C and a lithium ion transference number of 0.7. We discuss the influence of the 2-D lamellar structure which prevails in the best performing membranes, as well as the PEO block size. Subsequent studies revealed that lithium ions are surrounded by an ordered structure, stabilized not only by ether oxygen of the polymer backbone, but also by remaining, non-removable THF molecules and $TFSI^-$ counter ions, eventually leading to sufficient lithium ion conductivity with low activation barriers in the temperature range of -20 °C to 90 °C.

As further features of interest for application in lithium metal batteries, the mechanical stability and the stability versus lithium metal was investigated. The results validate the studied systems as suitable for extensive cell tests, as the strong poly(styrene) and poly(isoprene) blocks guarantee mechanical integrity while keeping the lamellar microstructure, important for conductivity.

References:
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