Experimental report

14/11/2016

Proposal: **9-11-1804**

Council: 4/2016

Title: In situ SANS investigation of block copolymer electrolyte under lithium stripping/platting cycling

Research area: Soft condensed matter

This proposal is a new proposal

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Samples:
polymer
lithium

Instrument	Requested days	Allocated days	From	To
D22	2	2	26/09/2016	28/09/2016

Abstract:

For lithium-ion battery, nanostructured lithium-ion-doped polystyrene-block-polyethylene oxide (PS-b-PEO) diblock copolymer electrolyte has been proved as an advantageous membrane over the polyethylene (PEO) homopolymer. The conductive PEO block has the ability to solvate lithium ions, while the glassy polystyrene (PS) block offers a mechanically stable membrane, especially at elevated temperatures. Owing to possible morphological modification of the electrolyte and dendrite formation on the surface of the lithium metal anode, failure of a battery is a fast process. The proposed SANS experiment aims at investigating the evolved morphological modification of lithium-ion containing DBC electrolyte as well as the electrode-electrolyte interface stability during galvanostatic charge and discharge cycling in Li/membrane/Li cell at different temperatures. The in situ SANS investigation along with the measured resistance of the cell will provide important information on the electrolyte structure-property relationship as well as on the possible rapid battery failure mechanisms.

In situ SANS investigation of block copolymer electrolyte under lithium stripping/platting cycling

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Lithium ion batteries offer high energy densities as well as high discharge potential and low self discharge which makes them the most promising battery system. In order to overcome safety concerns, solid polymer electrolytes are essential. Polyethylene oxide (PEO) has been extensively investigated as a solid-state polymer electrolyte due to its high alkali metal conductive properties. To further improve the mechanical/thermal stability of PEO while maintaining good conductivity, polystyrene-*block*-polyethylene oxide PS-*b*-PEO diblock copolymer (DBC) have been recently investigated [1-3]. The lithium-ion-doped DBC electrolyte has been proved as an advantageous electrolyte over the polyethylene oxide (PEO) homopolymer, because the conductive PEO block has the ability to solvate lithium ions, while the glassy polystyrene (PS) block offers a mechanically/thermal stable membrane, especially at elevated temperatures. In this report, the structure of the Li-ion containing solid-state PS-*b*-PEO DBC electrolyte was investigated during lithium ion stripping/platting cycling. The aim of this study is to explore the evolved morphological modification of Li-ion containing DBC electrolyte as well as the electrode-electrolyte interface stability during galvanostatic cycling. The nanostructured Li-ion/DBC electrolyte (300 μm) film were sandwiched between two non-blocking lithium electrodes via solution casting process. Time-resolved (10 s) in situ SANS measurements were performed at D22 beamline (ILL) during lithium stripping/platting cycling. The impedance spectroscopy measurement was also acquired at the end of each galvanostatic cycle, obtaining the resistance of the cell. The time of complete charge/discharge cycles was set at about 12 minutes. To enable a significant contrast to our electrolyte a PSd-*b*-PEO DBC with a deuterated PS block (PSd), protonated PEO block was employed. As indicated from scattering rings in the SANS 2D scattering patterns (Fig. 1), the solid-state Li-ion/DBC ([Li]/[EO] = 0.1) successfully provided adequate contrast to the nanostructured Li-ion/DBC electrolyte. The SANS 1D profiles are plotted in Fig. 2. From Fig. 2 the cylindrical structure of the as-prepared Li-ion/DBC electrolyte is indicated. At both 20 and 35°C, the SANS investigation did not show any significant morphological changes during lithium stripping/platting cycles (Fig. 2; the 35°C plots are only shown). A stable morphology showing no structural modification up to >15 cycles is observed. These results indicates that the nanostructured morphology survive possible degradation during operation.

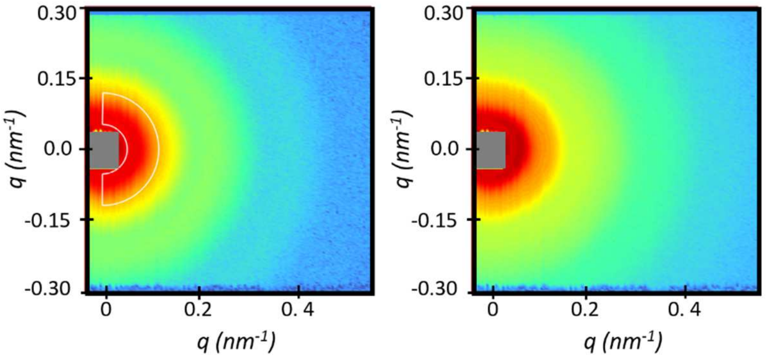

Fig. 1 SANS 2D scattering patterns of Li-salt containing DBC hybrid electrolyte sandwiched between two thin lithium electrodes at 20 ℃ (left) and 85 ℃ (right).

At higher temperatures, 65 and 85°C while cycling (Fig. 2), however, an extended inter-domain spacing is initially observed during the first cycle indicating some structural changes. This structural modifications cannot ultimately explain the measured high conductivity enhancement (data are not shown) of the electrolyte at these elevated temperatures. Following the first cycle at higher temperatures (> 50 °C), the morphology again did not show any further changes neither in the form of a phase-transformation nor in the inter-domain distance. The structure does not seem severely penalized upon an operational high temperature half-cell battery, even at an extended cycling time of one hour. The increase of domain spacing *D* and enhancement of the conductivity of the electrolyte may be attributed to an increase of Li-ion solubilization and concomitant PEO chain mobility enhancement at the elevated temperatures.

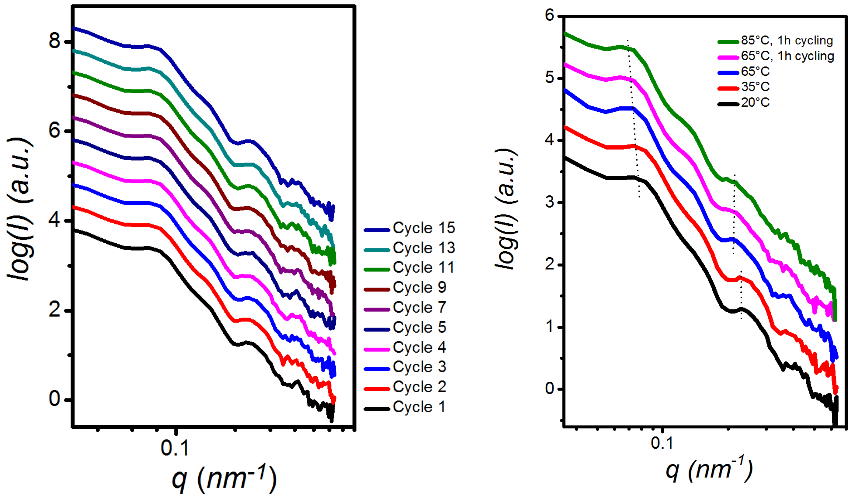

Fig. 2. *SANS 1D profiles of Li-ion/DBC hybrid electrolyte, (left) during various lithium stripping/platting cycles at 20°C, (right) at different temperatures. The data are vertically offset for clarity.*

An exciting observation is that the level of domain alignment achieved following the increase of the temperature while cycling (Fig. 3). The possible migration of the lithium ions during the galvanostatic process seems to open pathways between the two electrodes so that at high enough temperatures the domain re-orientation is favored. The absence of any new scattering features and a stable nano-scale morphology strongly implies that the possible dendrite growth is highly suppressed by the current solid-state electrolyte. Currently, further analyses of these results is in progress and a manuscript preparation will follow to include all these interesting results.

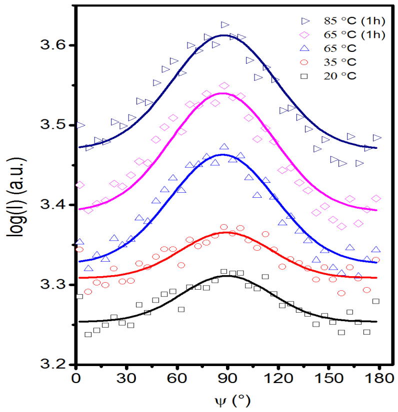

Fig. 3 Azimuthal SANS intensity profiles corresponding to the reciprocal space vector of the main interference maximum between 0.053-0.119 nm^{-1}. The solid lines are fits of the data with Gaussian functions. The curves are vertically offset for clarity.

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[2] W. S. Young; Kuan, W. F.; Epps, T. H., *J Polym Sci Pol Phys* **2014,** 52, 1-16.
[3] I. Gunkel; Thurn-Albrecht, T., *Macromolecules* **2012,** 45, 283-291.