Experimental report

22/12/2017

Proposal: **9-11-1821** **Council:** 10/2016

Title: In operando SANS study of single-ion copolymer electrolytes for Li-metal battery

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: polysyrene-block-polyethylene oxide

Instrument	Requested days	Allocated days	From	To
D22	3	2	01/02/2017	03/02/2017

Abstract:

Multifunctional single-ion block copolymer electrolytes (BCEs) based on polyanionic block copolymers comprising polystyrene segments were successfully prepared at our lab. With a lithium-ion transport number close to unity, these BCEs showed excellent mechanical properties and an electrochemical stability window spanning 5V versus Li+/Li0. A prototype battery using this polyelectrolyte outperforms a conventional battery based on a polymer electrolyte especially at high temperatures. Using SAXS measurements, nanoscale structured polyanionic-BCE has been proved. The proposed SANS experiment aims at investigating the evolved morphological modification of this solid-state electrolytes as well as the electrode-electrolyte interface stability during galvanostatic charge/discharge cycling in Li/electrolyte/ LiFePO4 cell at two different temperatures. The in situ SANS investigation along with the measured battery performance at different discharge/charge rates will also provide important information on possible formation of oriented 1D-ion conductive polymeric materials.

In operando SANS study of single-ion copolymer electrolytes for Li-metal battery
(Proposal 9-11-1821)

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Lithium-ion batteries are the most popular energy storage system not only for electrical devices like laptops, cameras or mobile-phones, but also for electric vehicles. These batteries have a high power to weight ratio, a good cycle lifetime, low self-discharge rates and no memory effect. Usually lithium-salts in aprotic organic solvents are used as electrolytes, but these liquid electrolytes render the system thermally and electrochemically unstable. To overcome these problems, solid state polymer electrolyte membranes (PEMs) are alternatively employed. The PEMs are less volatile and allow the fabrication of batteries in various shapes and configurations. For instance, diblock copolymer (DBC) electrolytes have been recently attracted a prime interest as ion-conducting membranes. The lithium-ion-doped polystyrene-block-polyethylene oxide (PS-b-PEO) DBC electrolyte has been proved as an advantageous membrane over the polyethylene (PEO) homopolymer, because 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. Previous studies have reported that nanostructured lithium-ion containing DBCs exhibit nearly two order of magnitude higher ionic conductivity than typical PEO homopolymer electrolytes. We investigated the ionic conductivity in relation to the morphology of lithium-doped high-molecular-weight PS-b-PEO DBC films using both SAXS/WAXS and AC-impedance spectroscopy. In two separate experiments, the membranes were sandwiched between two mica windows or between two metal electrodes for SAXS/WAXS and conductivity measurements, respectively. We approved that the ionic conductivity is enhanced by the PEO amorphorization and the formation of nanostructured membrane upon Li-ion doping. In other words, well-ordered nanostructured membrane may offer an oriented chain packing around Li ions that facilitates the Li-ion mobility in DBC electrolyte systems. It has been assumed that the effect of the applied voltage during conductivity measurement is negligible at all employed temperatures. This assumption can be acceptable for the small AC voltage applied used for conductivity measurements. For real applications, however, higher voltage during many charge/discharge cycles can affect the initially established morphologies of the DBC membrane, especially at elevated temperatures. Additionally, the interface between the electrode and PEM is an important parameter. It has been demonstrated that the lithium electrode has a strong tendency to form high-surface area microstructures upon repeated charge/discharge cycles; these structure can readily grow into filaments that can penetrate the membrane, causing an electrical short/local heating and then fires or even explosions. During the charge/discharge cycles, the “mossy” lithium structures are known to be initially formed, leading to a large surface area for electrolyte reduction and the build-up of a resistive solid-electrolyte interphase (SEI) which reduces cell performance and leads to a rapid cell failure. Thus, only in situ SANS investigation during lithium stripping/plating experiments can give deeper insights on the Li-electrode/DBC interface stability.

The carbon-coated $LiFePO_4$ active materials were used to formulate lithium/SPE/cathode batteries through lamination processes which were sealed in coffee bags. Batteries were cycled using a Solartron 1470 multi-potentiostat. In situ SANS data were collected while the charge/discharge (0.5 h) experiments were performed over five different charge/discharge rates (C/8, C/4, C/2, 1C, and 2C). The SANS experiment monitored the potential concomitant morphological changes of the SPE and possible formation of a stable passivation layer at the PSE-cathode interface. The special synthesized DBC P(STFSILi)-b-PEO-b-P(STFSILi) was prepared with the corresponding deuterated P(STFSILi)-d block in our lab at CNRS. According to the contrast factor calculations, the employed electrode/electrolyte assembly (Li/SPE/LiFePO4) inside a pouch cell provided the necessary contrast between both PEO-h and P(STFSILi)-d blocks as well as between electrolyte and cathode. The temperature of the battery samples was controlled using a bulky heat-conducting metal cylinder.

Unique advantage of the neutron experiment as compared to synchrotron radiation experiments was to possibility of acquiring all the evolved nanoscale morphology within an operational real battery cell during several charge/discharge cycles nondestructively, without neither to disassemble the electrolyte/working electrodes nor to otherwise disturb the cell assembly.

Meanwhile the data were analyzed and published in: ACS Energy Lett. 2018, 3, 1-6.

ACS Energy Letters

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In Operando Small-Angle Neutron Scattering Study of Single-Ion Copolymer Electrolyte for Li-Metal Batteries

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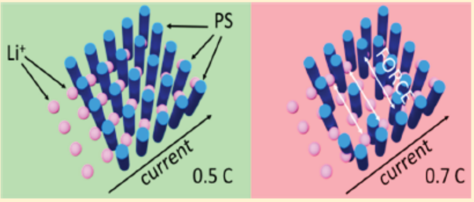
Supporting Information



ABSTRACT: To enable a renewable energy future, electrochemical energy storage remains as one of the main challenges of today's society. Lithium-ion batteries have been shown to be of great potential in that respect, but they still suffer from safety instabilities arising from the use of flammable liquid electrolytes. Solid electrolytes are an interesting alternative that provide the required safety properties. We introduce a highly stable solid single-ion diblock copolymer electrolyte poly(deuterated styrene)-*block*-poly(poly(ethylene glycol) methyl ether styrene-*co*-lithium styrene sulfonyl(trifluoromethane sulfonyl)imide), denoted PS(d)-*b*-P(SPEG-*co*-STFSILi). Lithium metal batteries based on PS(d)-*b*-P(SPEG-*co*-STFSILi) are probed in operando with small-angle neutron scattering in order to investigate their suitability as safe batteries using lithium metal anodes. We compare cell operation when cycling at 0.5 C at 80 °C to 0.7 C at 90 °C, which represent severe working conditions for the battery. More than 200 cycles are performed, showing the inflation of the ionic pathways through cycling at 0.7 C, whereas at 0.5 C and 80 °C, battery performance and morphology remain unchanged.