Supporting Information

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

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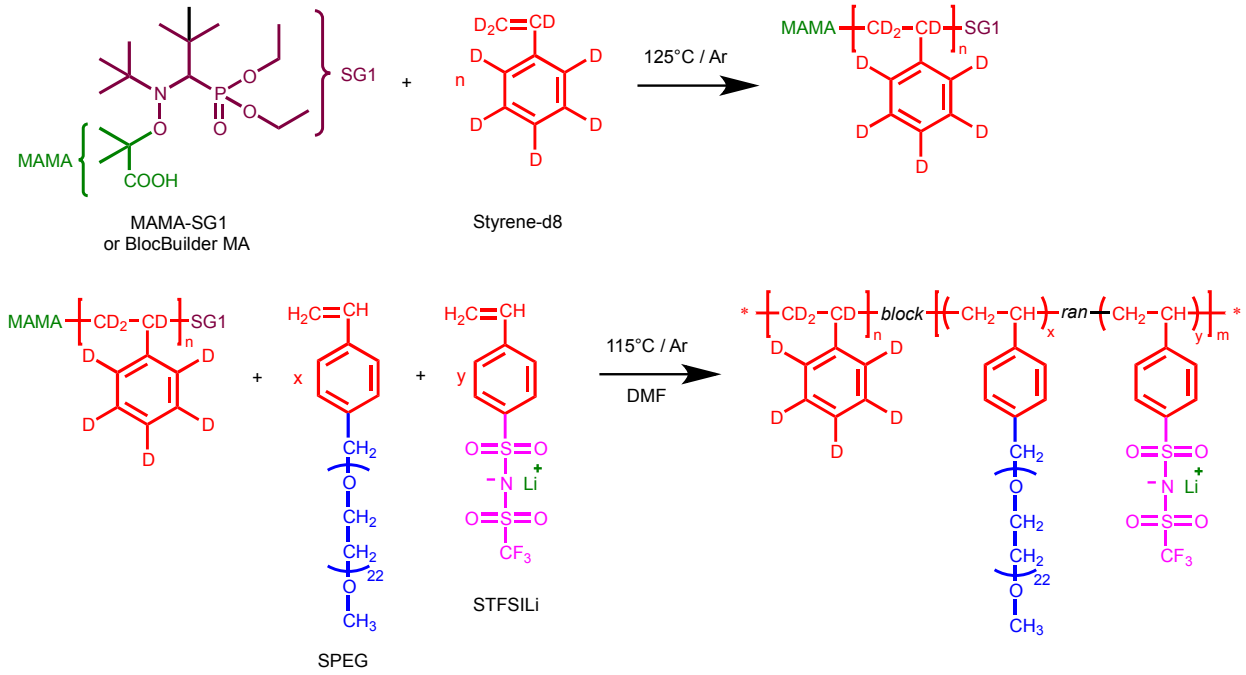
Experimental Section

1. Single-ion diblock copolymer synthesis

Block copolymer was synthesized according to the reaction scheme below:



Monomers synthesis

Lithium 4-styrenesulfonyl (trifluoromethanesulfonyl)imide (STFSILi) was prepared according to the literature (1) with a slight modification. In more detail, the catalyst triethylamine was replaced by potassium carbonate in the second step of the monomer synthesis leading to potassium 4-styrenesulfonyl (trifluoromethanesulfonyl)imide (STFSIK). The STFSILi was then prepared by methathesis of STFSIK with LiBF4 in acetonitrile and the insoluble by-product KBF4 was removed by filtration. The STFSILi was obtained with high purity by removal of the solvent under high vacuum.

4-vinylbenzyl poly(ethylene glycol) methyl ether (SPEG) was synthesized according to the method adopted from the literature (2). SPEG is a macromonomer with a PEG side chain of 1000 $g.mol^{-1}$.

Synthesis of deuterated polystyrene macroinitiator MAMA-PS(d)-SG1

Deuterated styrene-d_8 (>98%, Aldrich) was passed through a basic alumina column to remove stabilizer. Typically, purified styrene-d_8 (2.08 g, 1.83 $x10^{-2}$ mol) and MAMA-SG1 as initiator (26.50 mg, 6.89 $x10^{-5}$ mol) were placed in a three-neck flask equipped with a reflux condenser and a magnetic stir bar. Targeted molar mass of deuterated polystyrene (PS(d)) was 30 500 $g.mol^{-1}$. The mixture was purged for 15 min with argon at room temperature to remove oxygen and then immerged in an oil bath preheated at 125°C. The polymerization was stopped after 7 h by quenching the flask in an ice bath. The polymer was purified by precipitation in ethanol, filtered to remove solvents, and dried under vacuum at room temperature to a constant weight. The molecular weights of MAMA-PS(d)-SG1 macroinitiator was determined by size exclusion chromatography (SEC) using tetrahydrofuran as eluent. We obtained a MAMA-PS(d)-SG1 of 26 000 $g.mol^{-1}$ with a dispersity of 1.15.

Synthesis of single-ion diblock copolymer PS(d)-b-P(SPEG-co-STFSILi)

Typically, MAMA-PS(d)-SG1 macroinitiator (385 mg, 1.47 $x10^{-5}$ mol), SPEG (870 mg, 7.71 $x10^{-4}$ mol), STFSILi (270 mg, 8.33 $x10^{-4}$ mol) and 2.3 g of N,N-dimethylformamide (DMF) were charged in in a three-neck flask equipped with a reflux condenser and a magnetic stir bar. The concentration of monomers plus macroinitiator in the mixture was around 40 wt%. Targeted molar mass of random copolymer part was 77 800 $g.mol^{-1}$. Reaction mixture was deoxygenated by bubbling argon for 30 min. The polymerization was carried out at 115°C for 17 h. Monomers

conversion and molecular weights were determined by ^{1}H NMR spectroscopy and LiBr/DMF SEC, respectively. The block copolymer was isolated by precipitation in isopropanol, collected by filtration and dried under vacuum to a constant weight. Monomers conversion was around 83 and 86% for SPEG and STFSILi respectively and the total molar mass of diblock copolymer was around 90 000 g.mol^{-1}.

2. Electrolyte preparation

Solvent casting and hot pressing were used to produce solid electrolyte thin films. The single-ion diblock electrolyte was dissolved in acetone at 10 wt% concentration. After mechanical homogenization, the solution was cast on a Teflon petri dish and evaporated slowly at room temperature during 24 h. The resulting film was further dried by annealing in a vacuum oven during 24 h at 50°C, and then pressed to desired thickness using a hot pressing machine (70°C). Solid electrolyte thin films were finally placed in an argon-filled glove box for at least a week before any experiment. On average, the final solid electrolyte film thickness was around 100 µm.

3. SANS measurements

The SANS experiments were performed using the D22 instrument at the ILL, Grenoble with a neutron wavelength of 6 Å and a wavelength resolution of $\Delta\lambda/\lambda$= 20%. The battery cell was cycled using a constant current provided by a Biologic SP-250 potentiostat. Sample detector distances of 5 and 17.5 m were used, resulting in two q ranges going from 0.003 Å^{-1} to 0.2 Å^{-1} for the 5 m and 0.003 Å^{-1} to 0.06 Å^{-1} for the 17.5 m setting, respectively. Acquisition times were initially set to 5 minutes then changed to 5 x 30 s slices during the 0.5 C cycling experiment. For the 0.7 C cycling experiment, for every beginning of a cycle a trigger pulse was sent from the

potentiostat to the beamline control computer which then started the recording of 5 x 30 s slices of the SANS spectra. Referential scattering patterns of the individual cell components were recorded and transmission corrected by separate transmission measurements (**Figure S1a**). In addition, SANS spectra with extended q range were acquired at the beginning and the end of the beam time, as shown in **Figures S1b** and **S1c.**

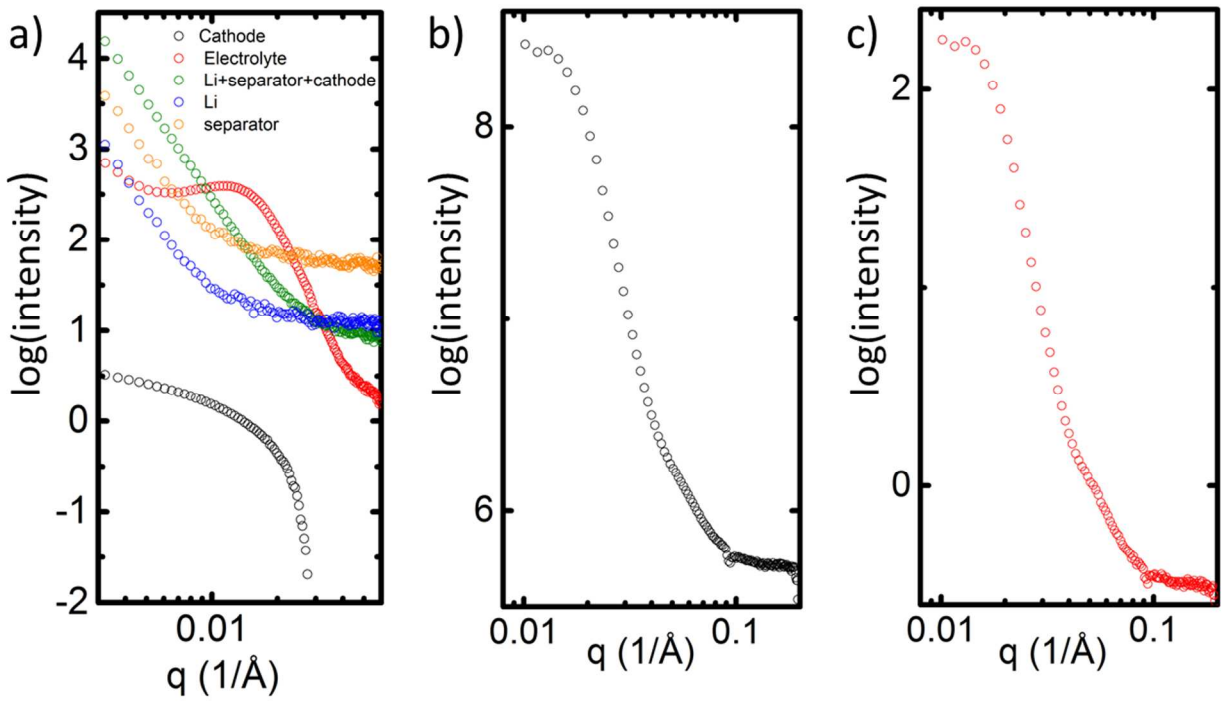


Figure S1: (a) Radial SANS profiles of the individual battery components: Cathode (black), electrolyte (red), Li+separator+cathode (empty cell) (green), lithium anode (blue), separator (orange). Radial SANS profile of the cell (b) before and (c) after cycling with extended q range.

4. SANS data treatment

SANS data were corrected using the GRASP[3] software package. The empty cell reference was subtracted from for every single frame (**Figure S1a**, green) by denoting it as background. Differential images were extracted in the same fashion, routing the first frame of the experiment

as the background to subtract. Radial profiles of the corrected and subtracted images were then achieved by averaging the spectra one by one.

5. SANS modelling

The radial SANS profiles were modeled using the SASfit[4] software. In the model, hexagonally packed cylinders were used, where a cylindrical contribution corresponded to the form and a hexagonal lattice to the structure factor. A Gaussian size distribution of cylinder radii was assumed.

References

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(2) Zhao, B.; Li, D.; Hua, F.; Green, D. R. Synthesis of thermosensitive water-soluble polystyrenics with pendant methoxyoligo(ethylene glycol) groups by nitroxide-mediated radical Polymerization, *Macromolecules* **2005,** *38*, 9509-9517.

(3) *Dewhurst C GRASP: graphical reduction and analysis SANS program for Matlab' http://www.ill.fr/lss/grasp/ (Institut Laue-Langevin 2001-2006)*

(4) Breßler, I.; Kohlbrecher, J.; Thünemann, A.F. SASfit: a tool for small-angle scattering data analysis using a library of analytical expressions. *J. Appl. Cryst.* **2015**, *48*, 1587-1598.