

Electronic supplementary information

Creating ionic channels in single-ion conducting solid polymer electrolyte by manipulating phase separation structure

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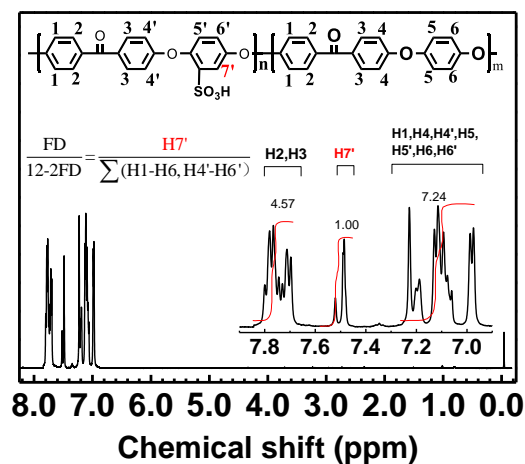


Figure S1 ^1H NMR of SPEEK. #1

The SPEEK used in this study and the SPEEK used in our previous studies were obtained from the same production batch.¹ The degree of functionalization (DF) was calculated by solving the Equation S1.

$$\frac{DF}{12-2DF} = \frac{Area(H7')}{Area(H2, H3) + Area(H1, H4-H6, H4'-H6')} \quad (\text{S1})$$

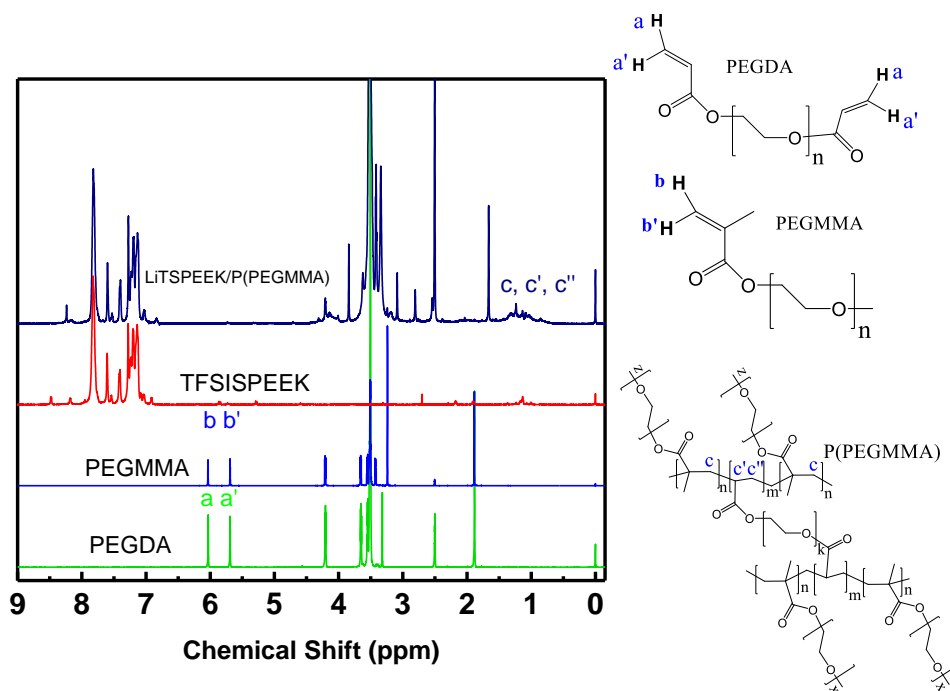


Figure S2 ^1H NMR (DMSO- d_6 as solvent) of PEGDA, PEGMMA, TFSISPEEK and LiTSPEEK/P(PEGMMA).

The peaks at a and a' in Figure S2 relate to the hydrogen atoms of terminal alkenyl groups of PEGDA. The peaks at b and b' in Figure S2 relate to the hydrogen atoms of terminal alkenyl group of PEGMMA. After the *in-situ* polymerization, these peaks disappeared. Meanwhile, a series of new peaks relating to the polyolefin appeared at 0.75-1.5 ppm. This result indicated the vinyl-addition type polymerization, proving the reaction in Scheme 6.

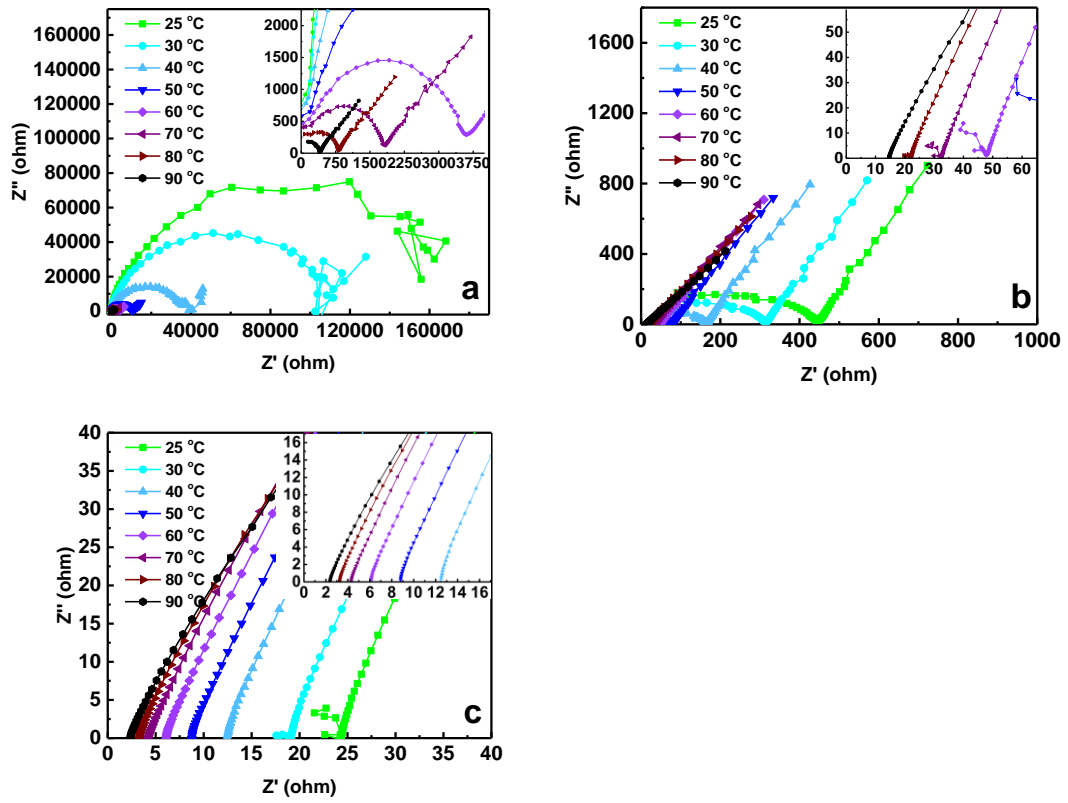


Figure S3 Nyquist plots of membranes: (a) LiTSPEEK; (b) LiTSPEEK/P(PEGMMA);
(c) LiTSPEEK/P(PEGMMA)/PC.

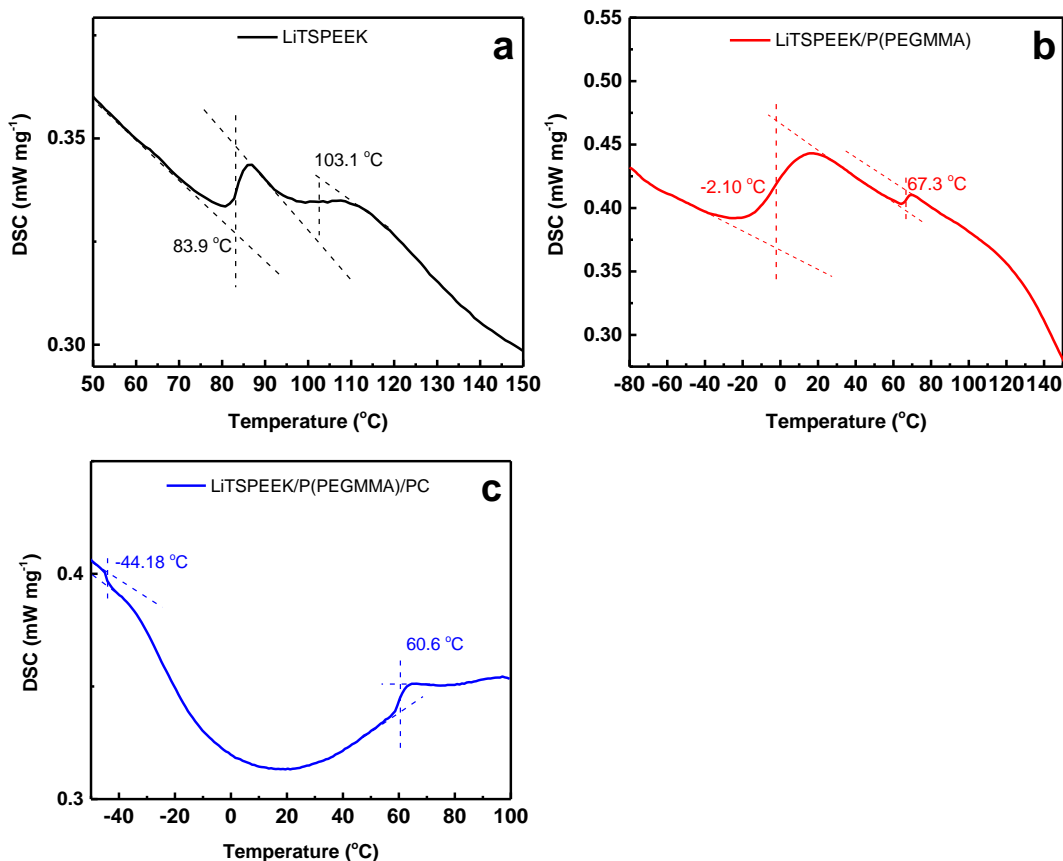


Figure. S4 DSC curves of (a) LiTSPEEK; (b) LiTSPEEK/P(PEGMMA); (c) LiTSPEEK/P(PEGMMA)/PC.

Glass transition temperatures (T_g s) of materials were measured using DSC tests, as shown in Figure S2. LiTSPEEK exhibited high T_g s of 83.9 and 103.1 °C (Figure. S4a), corresponding to the conducting phases consisting of lithium salt groups (Li^+TFSI) and the uncharged phases consisting of semi-crystalline PEEK backbones, respectively. The T_g s of LiTSPEEK are lower than other PEEK based polymers (such as SPEEK), which is caused by a fact that the plasticizing effect of TFSI can decrease the degree of crystallinity of polymers.^{2, 3} For LiTSPEEK/P(PEGMMA), the uncharged phases mainly consist of the incorporated P(PEGMMA), which is branched and of low crystallinity. Thus the T_g of uncharged phases decreases to 67.3 °C. Meanwhile the PEO segments of P(PEGMMA) can insert into the conducting phases, which act as

“solvent” to dissociate the lithium salt groups and disturb the conducting phases. The Tg of conducting phases significantly decreased to -2.1 °C (Figure. S4b). PC, as a micromolecule plasticizer, can significantly disturb the segments of polymers, and dissolve the lithium salts. As a result, the Tgs of conducting phases decreased to -44.8 °C. However, the crosslinking effect of uncharged phases prevents the polymer matrixes from excessively swelling and disintegration. the Tgs of uncharged phases just slightly decrease to 60.6 °C. The low Tgs of conducting phases indicate the reinforced mobility of polymer chains, which are beneficial to the transport of lithium ions. The moderate Tgs of uncharged phases indicate fair mechanical stability, which can support the membrane to achieve the free-standing.

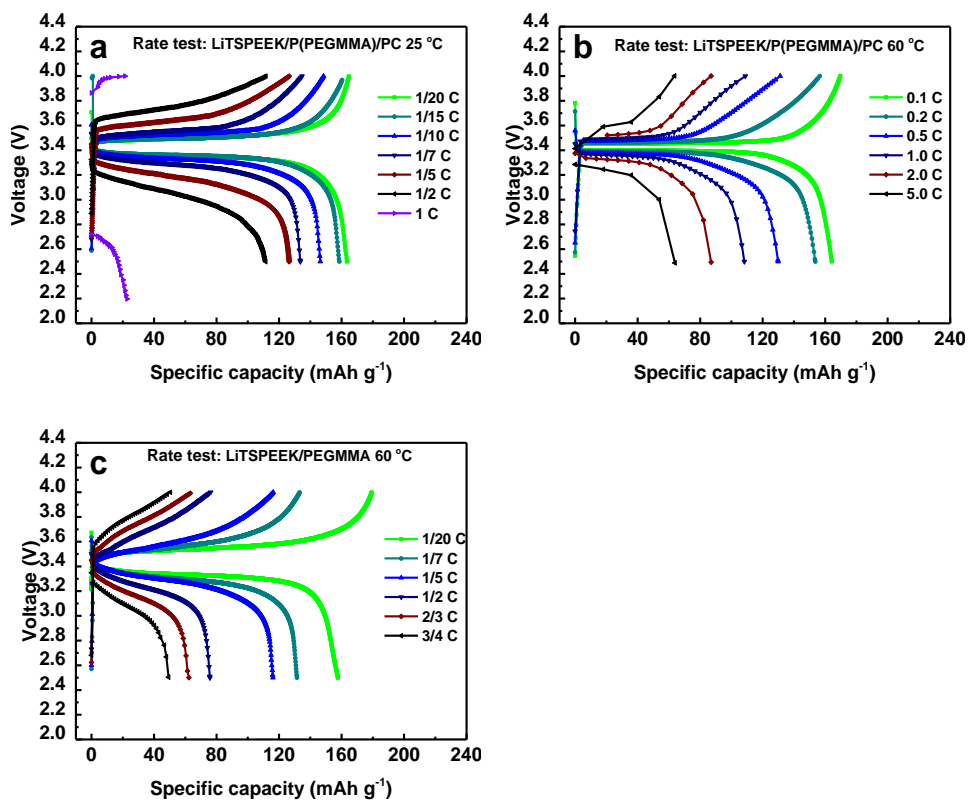


Figure S5 Specific discharge capacity-voltage profile curves of (a) LIB with LiTSPEEK/P(PEGMMA)/PC at 25 °C; (b) LIB with LiTSPEEK/P(PEGMMA)/PC at 60 °C; (c) all solid-state LIB with LiTSPEEK/P(PEGMMA) at 60 °C.

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2. J. Zhang, X. Zang, H. Wen, T. Dong, J. Chai, Y. Li, B. Chen, J. Zhao, S. Dong and J. Ma, *J. Mater. Chem. A*, 2017, **5**.
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