Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting information

Aqueous polyethylene oxide-based solid-state electrolyte with high voltage stability for dendrite-free lithium deposition via self-healing electrostatic shield

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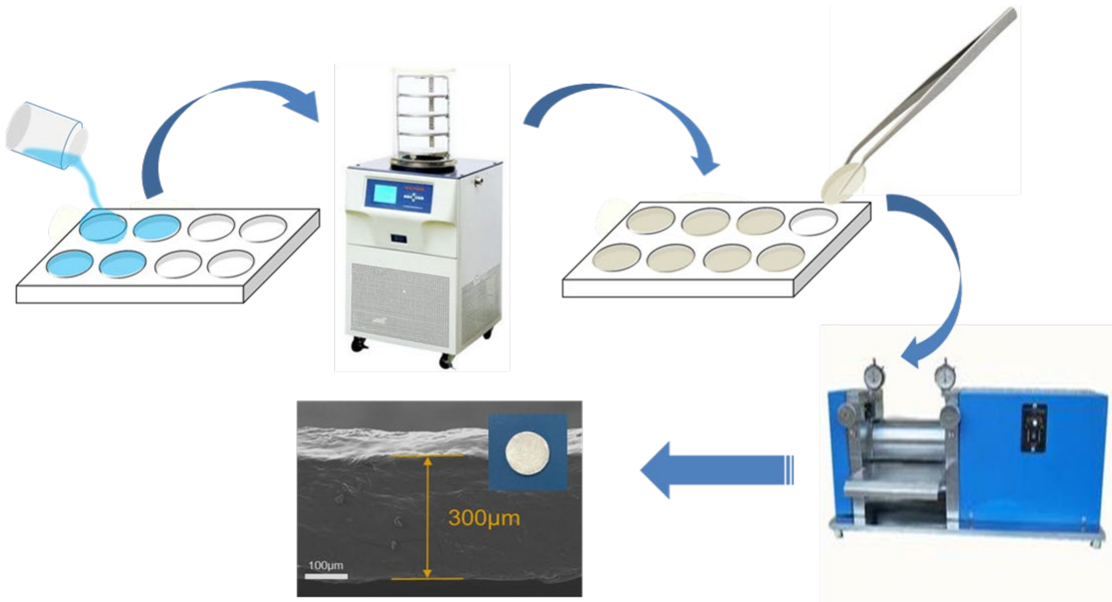

Fig. S1 Preparation process for the BC-PEO-Cs^+ electrolytes.

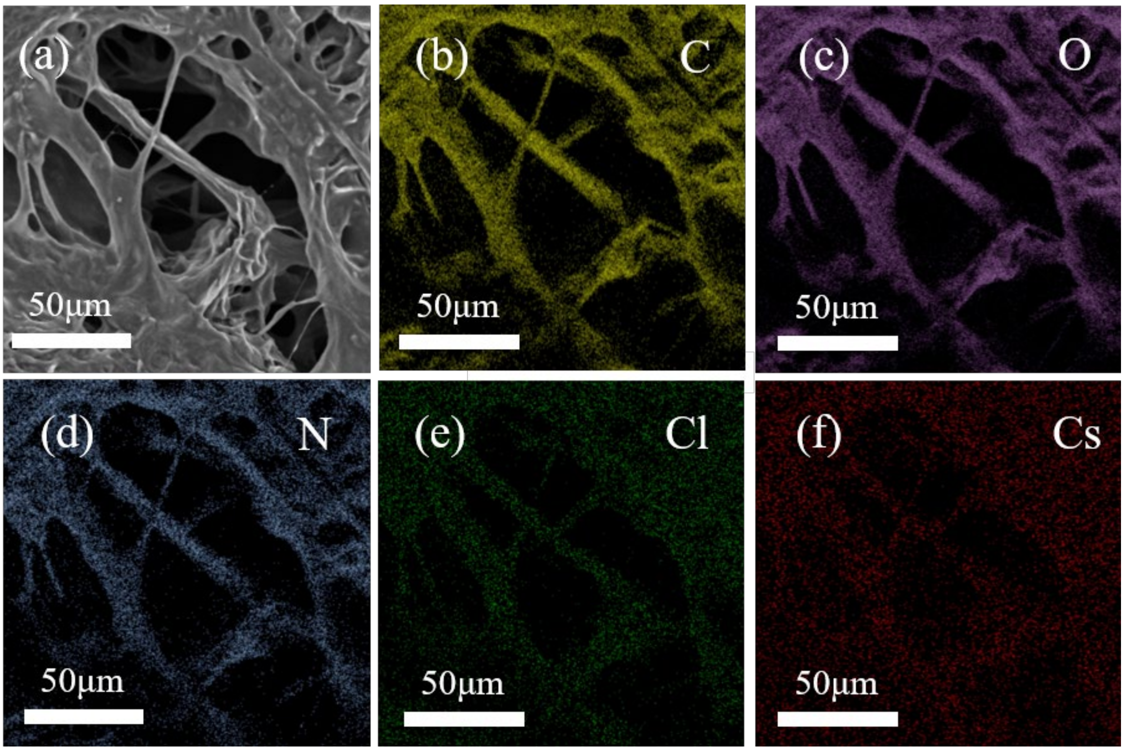

Fig. S2 SEM images of BC-PEO-Cs^+ electrolyte: (a)Cross-sectional morphology, (a) corresponding elemental mappings of (b)C, (c)O, (d)N, (e)Cl, (f)Cs.

The calculation formula of Li transference number is as follows:

$$t_{Li^+} = \frac{I_s(\Delta V - I_0 R_1^0)}{I_0(\Delta V - I_s R_1^s)}$$

where ΔV is the applied voltage (10 mV), I_0 and I_s are the initial current and steady current, respectively, during DC polarization process. R_1^0 and R_1^s are the charge-transfer resistances of Li symmetric cell before and after DC polarization, respectively.

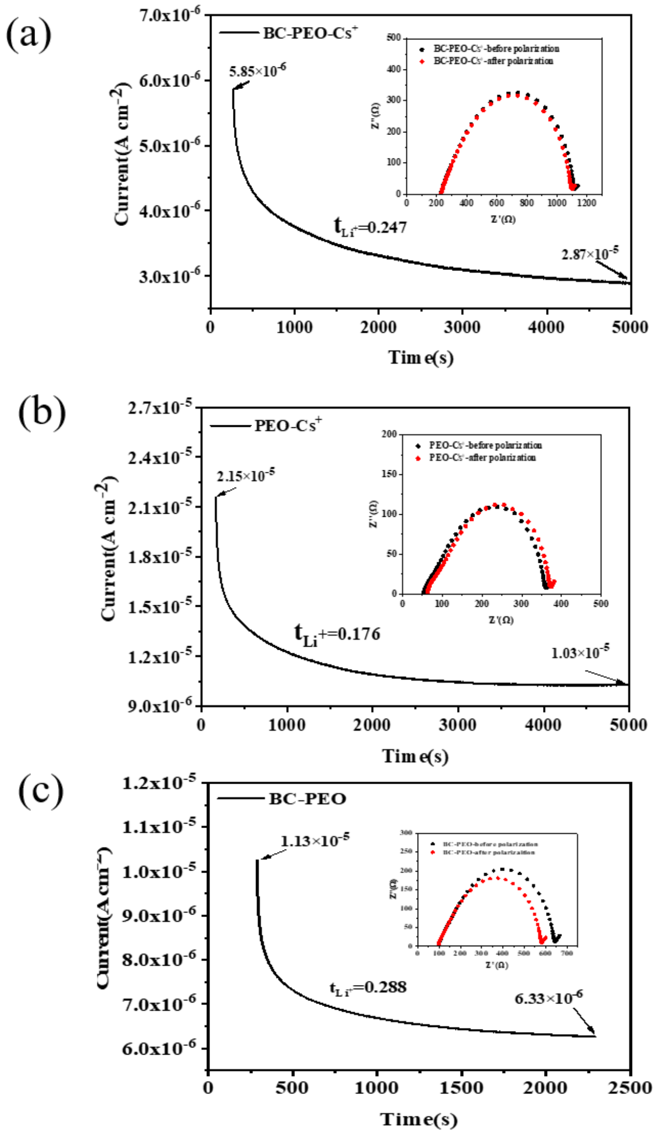

Fig. S3 Li transference number test of (a) BC-PEO-Cs^+、(b) PEO-Cs^+ and (c) BC-PEO electrolyte. (All of the cells are tested at an operating temperature of 60 °C)

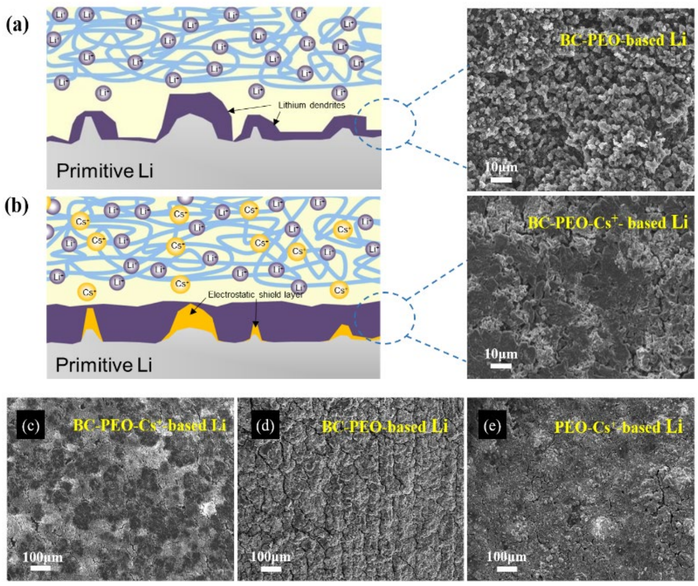

Fig. S4 Mechanism illustration of Li^+ deposition with or without Cs^+ on Li metal. Surface morphologies of Li metal after 1000 h at 0.2 mA cm^{-2} with (a)(d) BC-PEO、(b)(c) BC-PEO-Cs^+ and (e) PEO-Cs^+ electrolyte.

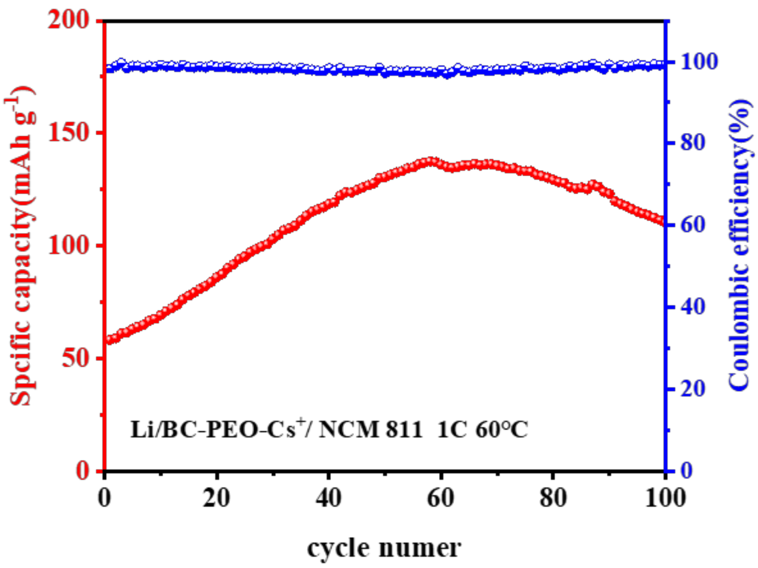

Fig. S5 Cycling performance of Li | BC-PEO-Cs^+ | NCM 811 cell at 1 C. (The cell is tested at an operating temperature of 60 °C)

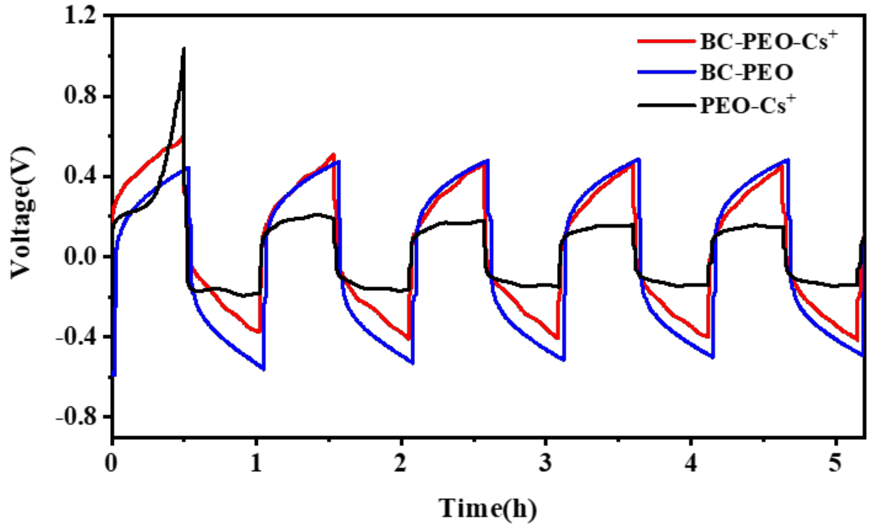

Fig. S6 The initial cycling stability of Li-Li symmetrical cells assembled with ASSEs at 0.2 mA cm^{-2}.

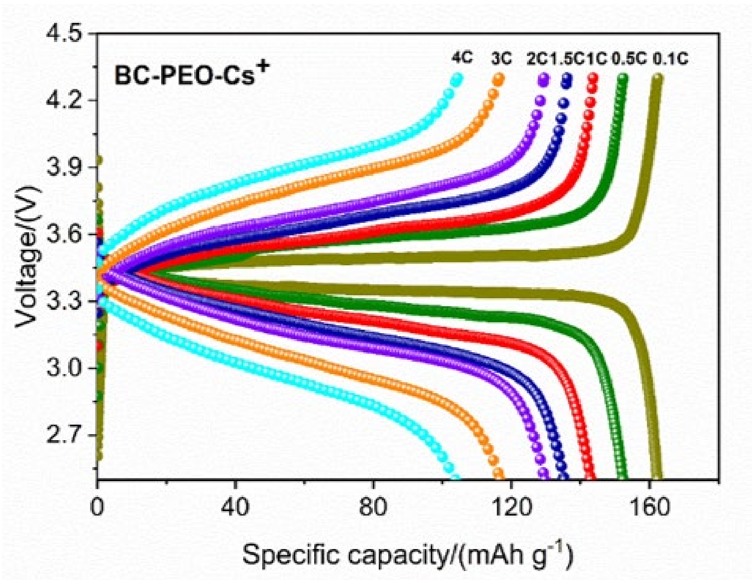

Fig. S7 Charge-discharge profiles of the Li | BC-PEO-Cs^+ | $LiFePO_4$ cells at various C-rate from 0.1 to 4 C. (All of the cells are tested at an operating temperature of 60 °C)

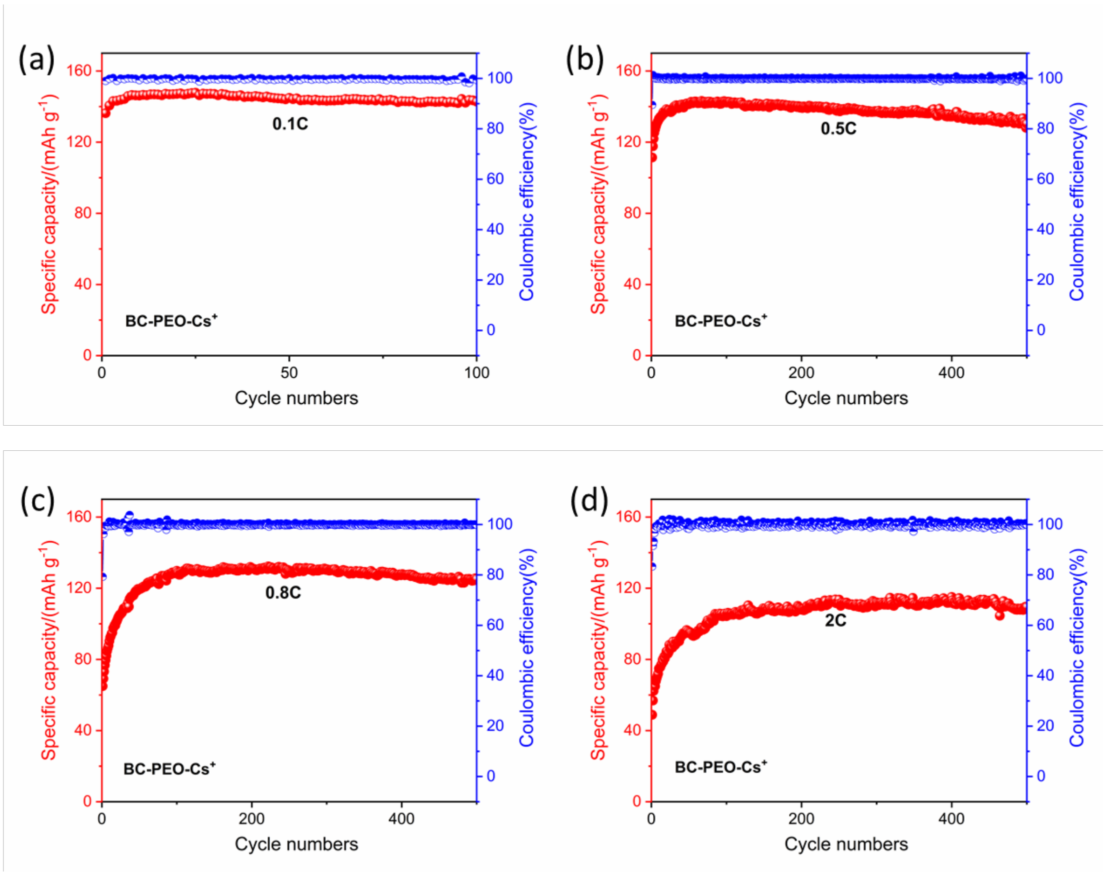

Fig. S8 Cycling performance of Li | BC-PEO-Cs^+ | $LiFePO_4$ cells at 0.1 C, 0.5 C, 0.8C, 2 C. (All of the cells are tested at an operating temperature of 60 °C)

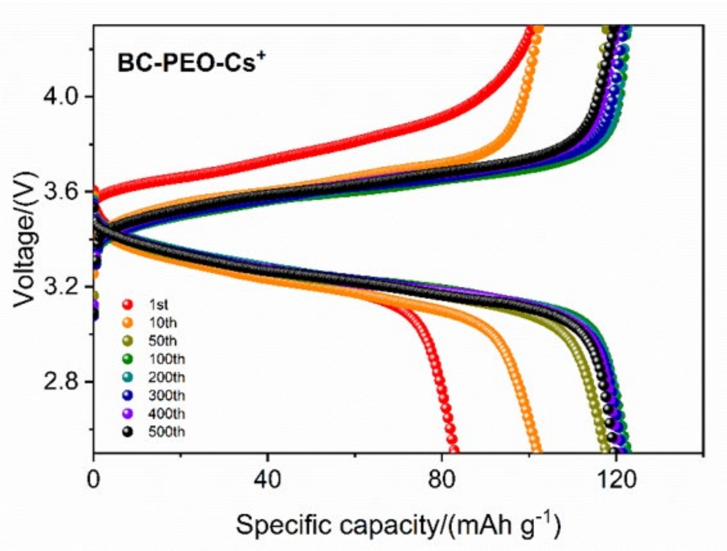

Fig. S9 Charge-discharge profiles of Li | BC-PEO-Cs^+ | $LiFePO_4$ cell at 1 C. (The cell is tested at an operating temperature of 60 °C).

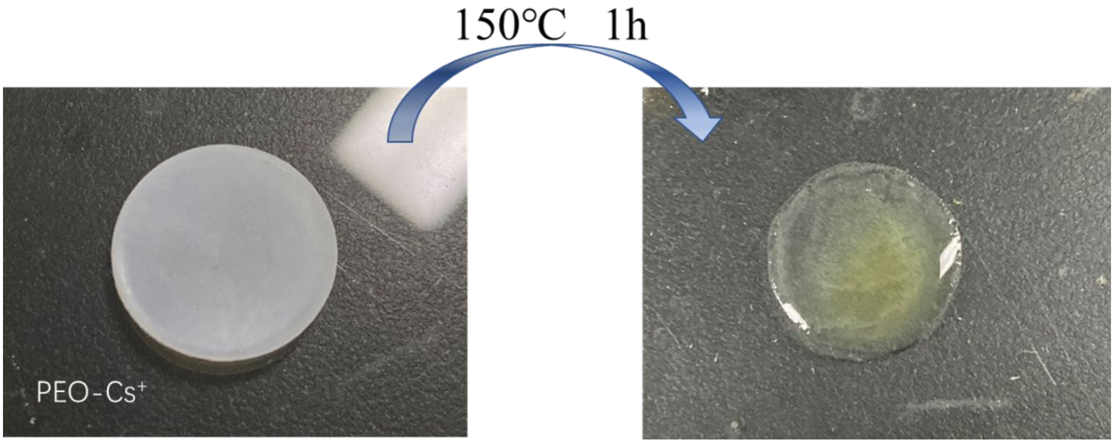

Fig S10. Thermal properties of PEO-Cs^+ electrolyte exposed at 150°C for 1 h.

Table.S1 Electrochemical performances comparison of Li-metal cells with all-solid-state electrolytes

Li-metal cells with all-solid-state electrolytes	Electrochemical performance	Reference
SiO_2-areogel-reinforced CPE-based Li-metal all-solid-state cell	110 mAh·g^{-1}, 0.5 C, room temperature	1
LLTO-(PEO-FEC) CSSE-based $LiFePO_4$-Li cell	115 mAh·g^{-1}, 0.5C, 50 ℃ 86 mAh·g^{-1}, 0.5 C, 35 ℃	2
Li/PEO-Cs^+/$LiFePO_4$ cell	120 mAh·g^{-1}, 0.5 C, 60 ℃	3
solid-polymer-electrolyte-based $LiFePO_4$-Li cell	134 mAh·g^{-1}, 0.2 C, 60 ℃ 101.7 mAh·g^{-1}, 0.5 C, 60 ℃	4
Li/BC-PEO-Cs^+/$LiFePO_4$ cell	**142 mAh·g^{-1}, 0.5 C, 60 ℃** **100 mAh·g^{-1}, 2 C, 60℃**	**This work**

Reference

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2. H. Li, W. Liu, X. Yang, J. Xiao, Y. Li, L. Sun, X. Ren, P. Zhang and H. Mi, *Chem. Eng. J.*, 2020, **408**, 127254.

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