Supporting Information

for

In situ cross-linked gel polymer electrolyte membranes with excellent thermal stability for lithium ion batteries

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Scheme S1. Synthesis strategy of the PS-PEO-PS triblock copolymer by ATRP.



Figure S1. ¹H NMR spectra of (a) Br-PEO-Br macroinitiator, (b) PS-PEO-PS triblock copolymer (taking SES-22 as an example).

Samples	Copolymer 1	Copolymer 2	Copolymer 3	Copolymer 4	Copolymer 5
M _{n,total*} (g mol ⁻¹)	11687	13826	22652	36855	61265

Table S1 Molecular weights of PS-PEO-PS block copolymers.

 $M_{n,total*}$ was obtained from GPC.



Figure S2. FT-IR spectra of pure PEO, Br-PEO-Br macroinitiator, PS-PEO-PS triblock copolymer and PVDF/PS-PEO-PS precursor polymer (taking Copolymer 2 as an example).



Figure S3. DSC curves of membranes of PVDF, CPE-1, CPE-2, CPE-3, CPE-4 and CPE-5.

Table S2. Porosities of precursor membranes and cross-linked membranes of CPE-1, CPE-2, CPE-3, CPE-4 and CPE-5, respectively.

Samples	Porosity of precursor membranes	Porosity of cross-linked membranes
CPE-1	62.6%	63.7%
CPE-2	62.3%	64.4%
CPE-3	60.8%	63.6%
CPE-4	56.7%	58.3%
CPE-5	44.1%	49.8%



Figure S4. TGA curves of membranes of PVDF, CPE-1, CPE-2, CPE-3, CPE-4 and CPE-5 from room temperature to $600 \,^{\circ}$ C.



Figure S5. Porosities of pure PVDF membrane under heat treatment at different temperature from 120 °C to 300 °C.



Figure S6. Surface morphology images of the cross-linked membranes of (a) CPE-1, (b) CPE-2, (c) CPE-3, (d) CPE-4 and (e) CPE-5 after the heat treatment at 300 °C.



Figure S7. Cross-section images of the cross-linked membranes of (a) CPE-1, (b) CPE-2, (c) CPE-3, (d) CPE-4 and (e) CPE-5 after the heat treatment at 300 °C



Figure S8. Charge-discharge curves of the cells assembled with (a) PVDF, (b) CPE-1, (c) CPE-2, (d) CPE-3, (e) CPE-4 and (f) CPE-5 at the rate of 0.1 C.



Figure S9. Initial charge-discharge curves of the cells assembled with (a) PVDF, (b) CPE-1, (c) CPE-2, (d) CPE-3, (e) CPE-4 and (f) CPE-5 at varied C rates.