Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Nitrogen-Containing All-Solid-State Hyperbranched Polymer Electrolyte for Superior Performance Lithium Batteries

Lei Zhang,[b] *Shi Wang,*[a] *Jingyu Li,*[c] *Xu Liu,*[a] *Pingping Chen,*[a] *Tong Zhao,*[c]* *Liaoyun Zhang*[a]*

[a]*School of Chemical Sciences, University of Chinese Academy of Sciences, Beijing 100049, China*

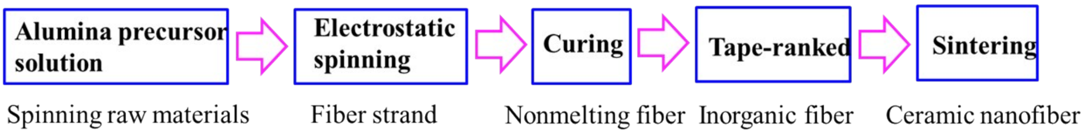
[b]*College of Science, China University of Petroleum-Beijing, Beijing 102249, China*

[c]*Laboratory of Advanced Polymer Materials, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190 , China*

E-mail: zhangly@ucas.ac.cn, tzhao@iccas.ac.cn

Method

Preparation of the ceramic membrane containing the ceramic nanowires via electrostatic spinning



Scheme S1. The preparation route of ceramic membrane containing the ceramic nanowires

Scheme S1 shows the preparation route of ceramic membrane containing the ceramic nanowires. Specifically, the ceramic membrane containing the ceramic nanowires was obtained as follows:

1) The solid alumina precursor (it was provided by *Suzhou tuna new material technology co. LTD*) was melted at 85 ^{o}C. The melt spinning material (4 ml) was spun (the spinning voltage was 10 Kv, the syringe propulsion rate was 50 μL min^{-1}, and the collect silk distance was 25 cm) by portable electrostatic spinning apparatus (PEG-1, *Qingdao junada technology co. LTD*);

2) The as-prepared alumina ceramic nano-fibers precursor is placed in a constant humidity and temperatur chamber. The sample was kept for 10 min at the humidity of 40% and temperature of 35 ^{o}C. Then, the sample was stored at humidity of 85% and temperature of 60 ^{o}C for another 10 min. At last, the curing fiber was obtained;

3) The curing fiber was sintered at 700 ^{o}C for 2 h (the cracking atmosphere was air and the heating rate was 1 ^{o}C min^{-1});

4) To obtain the ceramic film containing the ceramic nanowires, the sample was further sintered at 950 ^{o}C for 1 h (the cracking atmosphere was air and the heating rate was 30 ^{o}C min^{-1}).

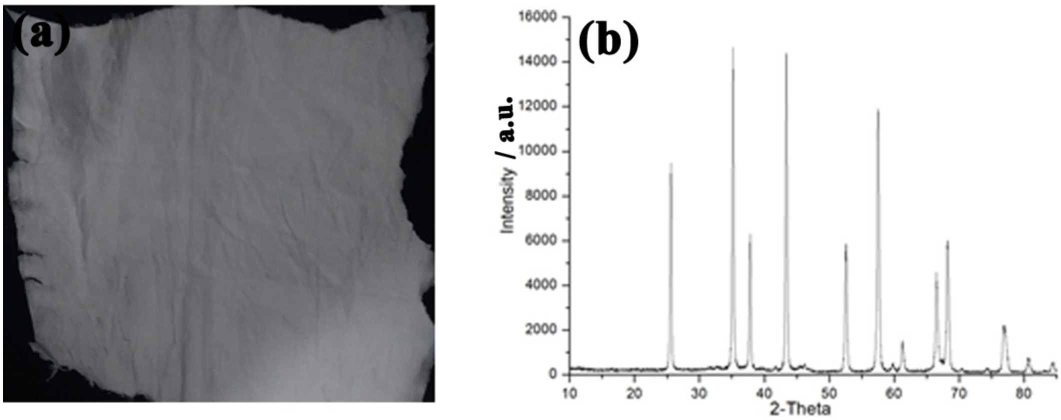


Figure S1. (a) Pictrure of the ceramic membrane containing the ceramic nanowires. (b) XRD.pattern of the ceramic membrane, which indicates that the alumina electrostatic spinning film contains typical α-Al_2O_3 nanowires.

Figure S1 shows the obtained ceramic membrane, which is uniform and free-standing. The XRD pattern of the film is also shown in Figure S1b, which suggests that the alumina electrostatic spinning film contains typical α-Al_2O_3 ceramic nanowires.

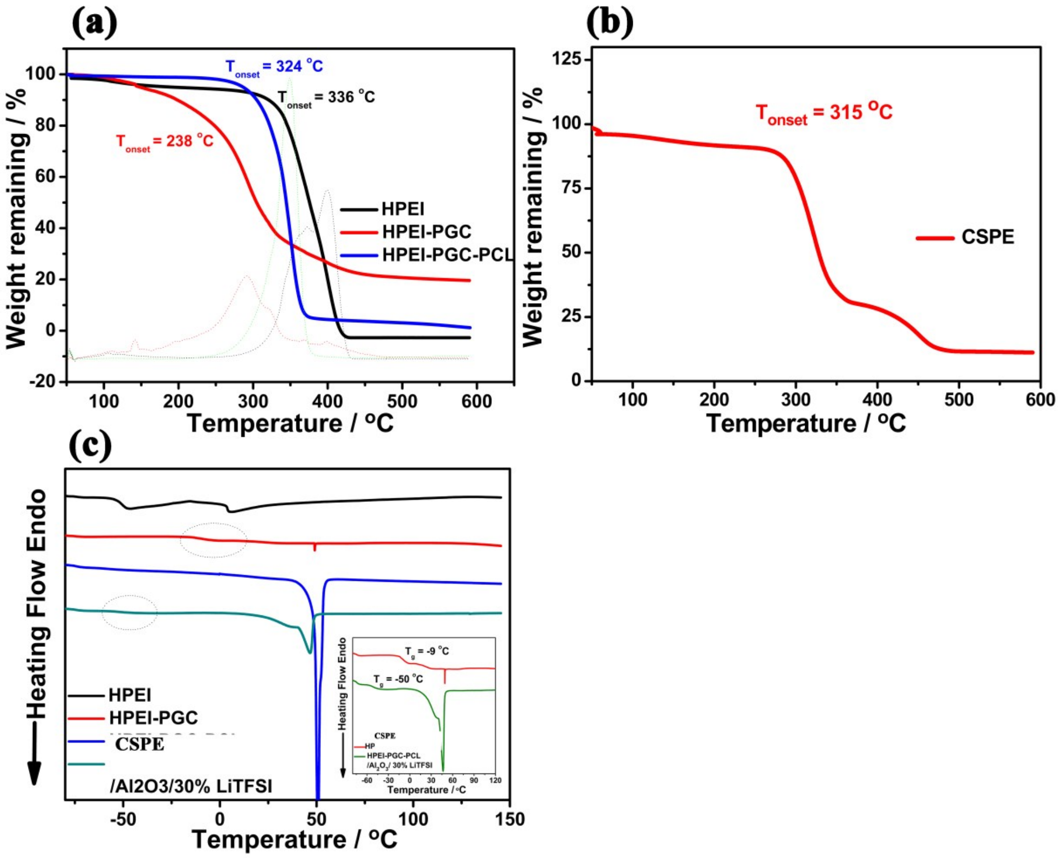


Figure S2. (a) TGA curves of HPEI, HPEI-PGC and HPEI-PGC-PCL, respectively. (b) TGA curves of CSPE. (c) DSC traces (the second heating cycle) presenting the T_g/T_m of the series of hyperbranced polymer and the CSPE.

The thermal properties of the series topological polymers were further evaluated based on TGA (Figure S2a and b) and DSC (Figure S2c). As shown in Figure S2a, HPEI has a T_{onset} of 336 °C. However, the T_{onset} decreases to 238 °C after attatching PGC segmetns onto the core of HPEI, which likely because the hydrogen-bond interaction between N and H atom is destroyed in some extent. Meanwhile, the T_{onset} increases to 324 °C for HPEI-PGC-PCL due to further increased molecular weight. Therefore, the hyperhranched polymer electrolyte matrix shows very good thermal stability. In addition, the TGA curve of CSPE is also shown in Figure S2b, it is seen that the T_{onset} of the CSPE can still reach 315 °C, which is very close to the T_{onset} of the corresponding SPE. However, there is some weight loss from 50-200 °C, which can be attributed to the evolution of absorbed water since the LiTFSI is rather sensitive to water.[S1, S2] The DSC curves of the series of the polymer are presented in Figure S2c. Compared with the T_g (-51 ^{o}C) of HPEI, HPEI-PGC has a much higher T_g of -9 ^{o}C, which likely because PGC segments are more rigid than PEI segments and the ability of the segments to move is reduced. A much high melting peak at 51 ^{o}C is observed on the DSC curve of HPEI-PGC-PCL due to the characteristic of easy crystallization of PCL segments. Addition of lithium salt (LiTFSI) causes the obvious decreasing of the melting peak.

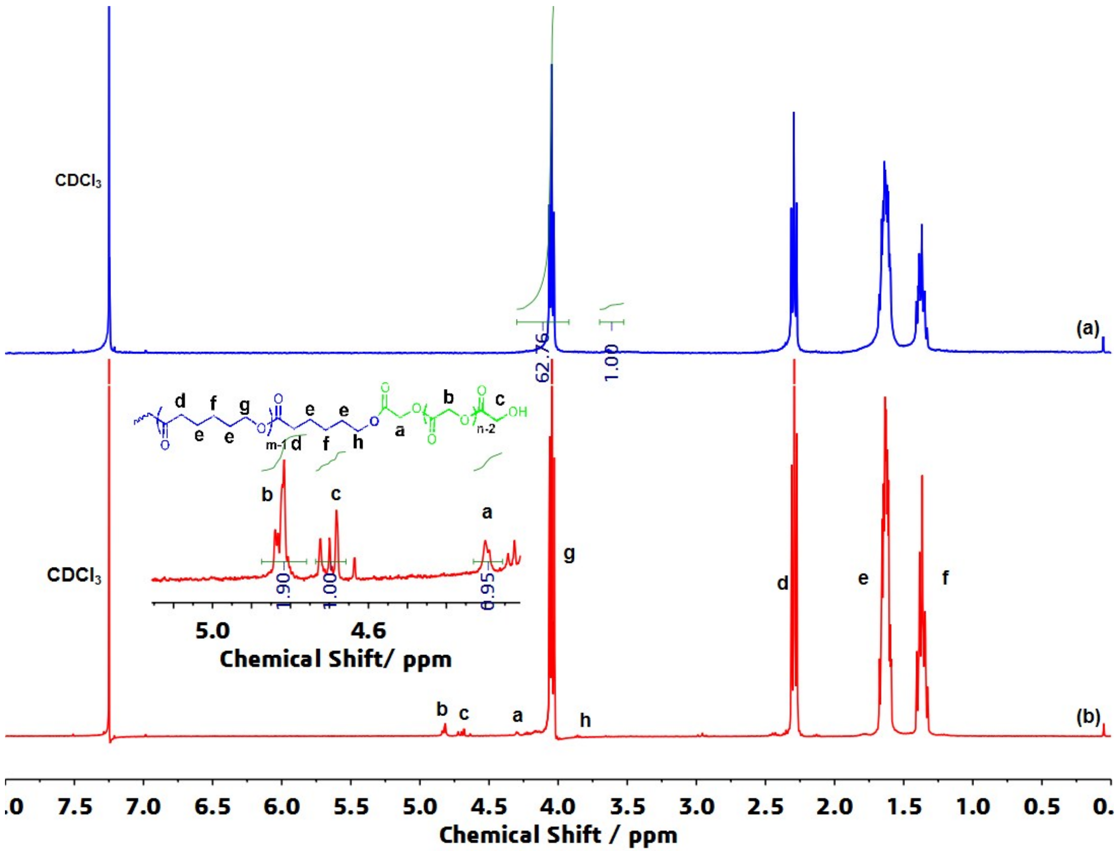


Figure S3. (a) ^{1}H NMR of PCL. (b) ^{1}H NMR of PCL-PGC

PCL was synthesized using CL as monomer and Sn(Oct)$_2$ as the catalyst. Typically, CL (5 mL), DMF (5 mL) and Sn(Oct)$_2$ (40 mg, 0.099 mol) were added in a dry round-bottom flask under N$_2$ atmosphere. The mixture was stirred at 130 °C for 24. Pure PCL was obtained after the sample was washed by methanol and dried at 50 °C under vacuum for 24 h. the ^{1}H NMR of the PCL is presented in Figure S2a. According the ^{1}H NMR, the DP of PCL is calculated ($DP_{PCL} = 63$).

The terminal hydroxyl of PCL can initiate the ring opening polymerization of GC. In a typically experiment, PCL (1.96 g), GC (0.5 g), Sn(Oct)$_2$ (30 mg) and DMF 5 mL was added in a dry round-bottom flask under N$_2$ atmosphere. The mixture was stirred at 140 °C for 24 h. After the reaction, the sample was washed by methanol for 3 times and dried under vacuum at 50 °C for 24 h. The ^{1}H NMR of PCL-PGC is shown in Figure S2b. Compared with the ^{1}H NMR of PCL, new peaks appears from 4.2 to 4.8 ppm, which belongs to the PGC segment.

According to the integrated intensity of peak b, c and a. the DP of PGC can be obtained ($DP_{PGC} = 4$).

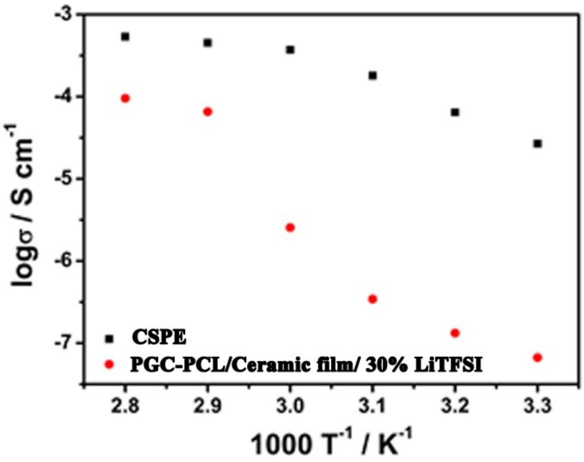


Figure S4. (a) Comparison of ionic conductivity of CSPE and PGC-PCL/30% LiTFSI/ceramic film from 30 to 80 °C.

Table S1. The related parameters of E_a and T_o, which is obtained by a nonlinear least-squares fitting regression on the experimental data.

Models	E_a (kJ mol^{-1})	T_o (K)
VTF	4.16	173.15
Arrhenius	34.53	/

Table S2. The related parameters and t^+ of the CSPE membrane.

Samples	R_{lo} (Ω)	R_{ls} (Ω)	I_o (μA)	I_s (μA)	t_{Li}^+
CSPE	115	159	31.6	19.3	0.57

References

(S1) Zhang, J.; Ma, C.; Xia, Q.; Liu, J.; Ding, Z.; Xu, M.; Chen, L.; Wei, W. Composite electrolyte membranes incorporating viscous copolymers with cellulose for high performance lithium-ion batteries. *J. Membrane Sci.* **2016,** *497*, 259-269.

(S2) Ueno, M.; Imanishi, N.; Hanai, K.; Kobayashi, T.; Hirano, A.; Yamamoto, O.; Takeda, Y. Electrochemical properties of cross-linked polymer electrolyte by electron beam irradiation and application to lithium ion batteries. *J. Power Sources* **2011,** *196*, 4756-4761.