Electronic Supplementary Material (ESI) for ChemComm.
This journal is © The Royal Society of Chemistry

Supporting Information

Enabling High-Performance All-Solid-State Hybrid Ion Batteries with a PEO-based Electrolyte

Meng-Xuan Yu,[a] Zhen-Yi Gu,[b] Jin-Zhi Guo,*[b] Chun-Gang Wang,*[a] and Xing-Long Wu*[ab]

[a] Faculty of Chemistry, Northeast Normal University, Changchun, Jilin 130024, P.R. China.

[b] MOE Key Laboratory for UV Light-Emitting Materials and Technology, Northeast Normal University, Changchun, Jilin 130024, P.R. China

Experimental details

Materials

Polyethylene oxide (PEO), M_w=6×10^5 (Aladdin)；Polyethylene glycol (PEG), M_w=2000 (Macklin)；Tetraethyl orthosilicate (TEOS, Beijing Chemical Works) and lithium perchlorate ($LiClO_4$, Shanghai Songjing New Energy Technology Co., Ltd) were used as reactants. Ammonia (Tianjin Xinbote Chemical Co., Ltd.) was used as a reagent to adjust the pH. Lithium metal flakes (Suzhou Dodo Chemical Technology Co., LTD) are with the diameter of 15.6 mm and the thickness of 0.45mm. All the chemicals were used without any purification.

Preparation of SPEs

0.54g TEOS was dissolved in 15 mL deionized water (DI, pH~10.4, adjustment with ammonia), and stirred for 24 h. Then 1.2g PEO and $LiClO_4$ was added into the solution (EO:Li=8:1,10:1,12:1 respectively), PEG of different qualities (0%,15%,20%,25% respectively) was also added into the solution, stirred to mix well. Pour the solution into a PTFE surface dish and kept in vacuum oven at 60°C overnight. The dried material was pressed into a film with a thickness of about 100 μm using a hot press at 60°C.

Electrochemical characterizations

The cathode material NVPOF is synthesized according to the literature.[1]

The NVPOF electrodes were prepared by mixing the slurry with the 65 wt% NVPOF, 25 wt% Acetylene black, 5 wt% SPEs, and 5 wt% CMC in DI water and coated onto the aluminum foil. The average mass loading of NVPOF electrode material in the cells is about 1 mg cm^{-2}. The electrode sheets are dried and hot pressed into a sheet with the SPEs. The CR 2032-type coin cells were assembled in the argonfilled glove box. The metallic lithium tablet was used as the anode. The galvanostatic charge–discharge (GCD) tests of the full cell were performed on the battery testing devices (LAND CT2001A) with the voltage range of 2.0-4.4 V vs. Li^+/Li. The cyclic voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) tests were carried on the VersaStudio electrochemical workstation. All tests are carried out at 60°C, except for the EIS which is tested in the temperature range 30-60 °C

The t_{Li^+} was calculated according to Equation (1).[2]

$$t_{Li^+} = \frac{I_s(\sigma V - I_0 R_0)}{I_0(\sigma V - I_s R_s)} \tag{1}$$

Among them, I_0 is the initial polarization current, R_0 is the initial resistance, I_s is the steady-state current, R_s is the steady-state resistance, and σV is the polarization voltage (σV is 50 mV in this experiment).

The apparent diffusion coefficient D_{app} is calculated according to the Randles-Sevcik equation (2).

$$i_p = 2.69 \times 10^5 n^{3/2} A D_{app}^{1/3} C_0 v^{1/2} \tag{2}$$

Where i_p is the peak current of the oxidation/reduction peak, n is the number of electrons transferred during the Li^+/Na^+ de-/intercalation process (for the V^{4+}/V^{5+} redox pair, n=2), and A is the surface area of the electrode (the electrode with a diameter of 12 mm), C_0 is the concentration of ions in the electrode (0.0077mol cm^{-3}),[3] and v is the scan rate.

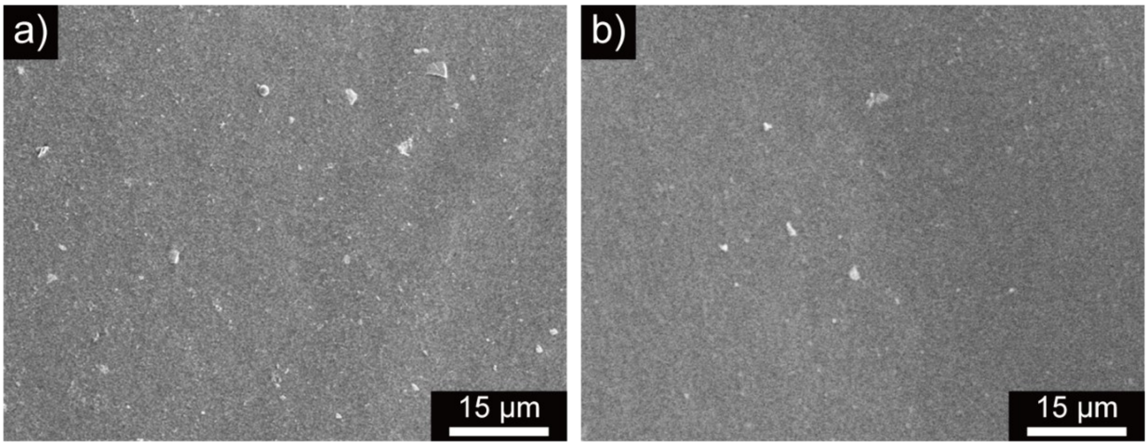

Figure S1 Morphology characterizations of the prepared SPEs. (a) Surface SEM of SPE without PEG. (b) Surface SEM of SPE with 15 wt% PEG.

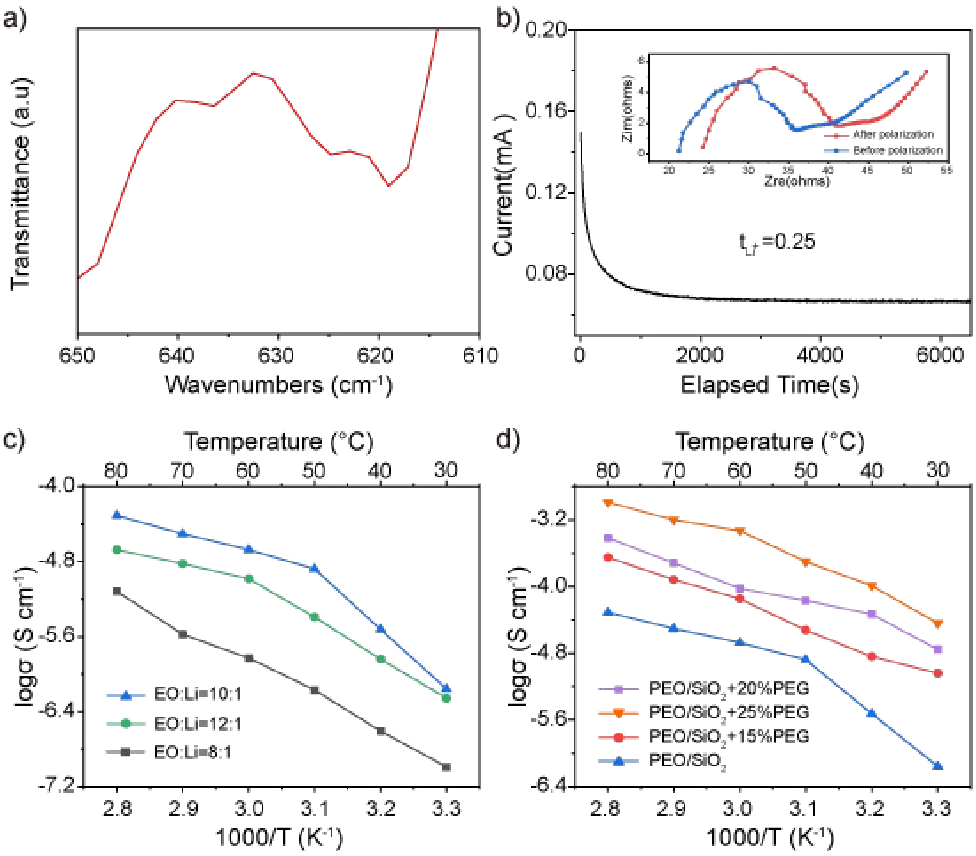

Figure S2 (a) FTIR with wave numbers in the range 610-650 cm^{-1}, where the peak at 624 cm^{-1} is attributed to dissociated ClO_4^-. (b) Chronoamperometry curve of Li//PEO/SiO2 //Li at 60 °C at 10 mV. Inset is the impedance before and after polarization. (c) Ionic conductivity of the SPE with different EO: Li^+. (d) Ionic conductivity of the SPE with different PEG content.

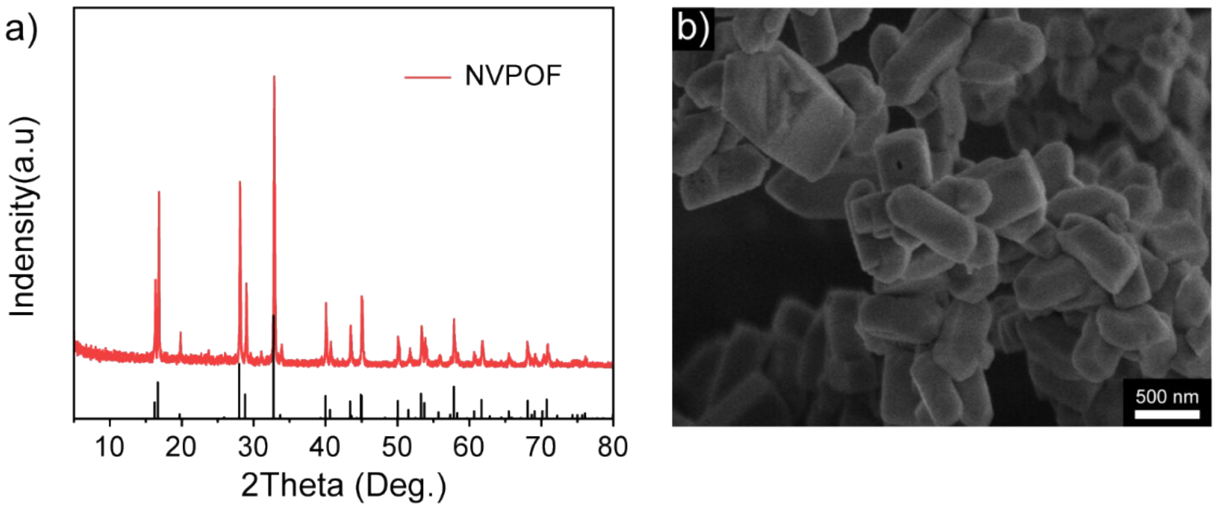

Figure S3 Structure and morphology characterizations of the prepared NVPOF cathode material. (a) XRD results of NVPOF compared to standard PDF. (b) SEM image of NVPOF

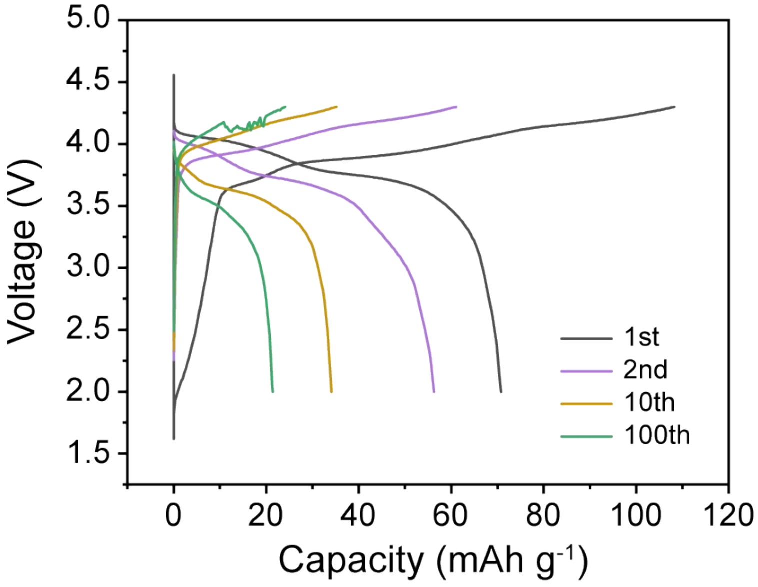

Figure S4 Charge/discharge curve of HLNIBs using PEO/SiO_2 as the electrolyte.

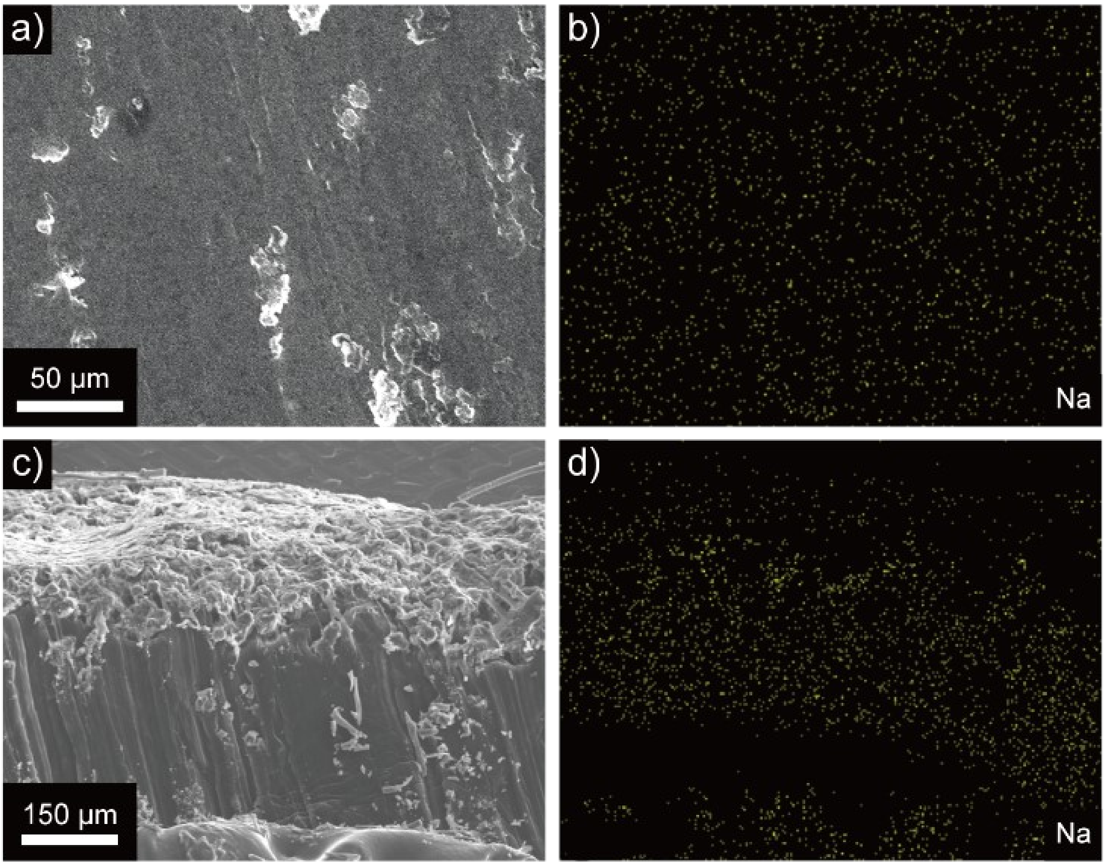

Figure S5 Plane and Cross-sectional SEM images of Li-metal anode and corresponding elemental mapping after 100 charge-discharge cycles. (a) and (b) Plane SEM and mapping images of Li-metal after 100 charge-discharge cycles at 0.1C. (c) and (d) Cross-sectional SEM and mapping images of Li-metal after 100 charge-discharge cycles at 0.1C.

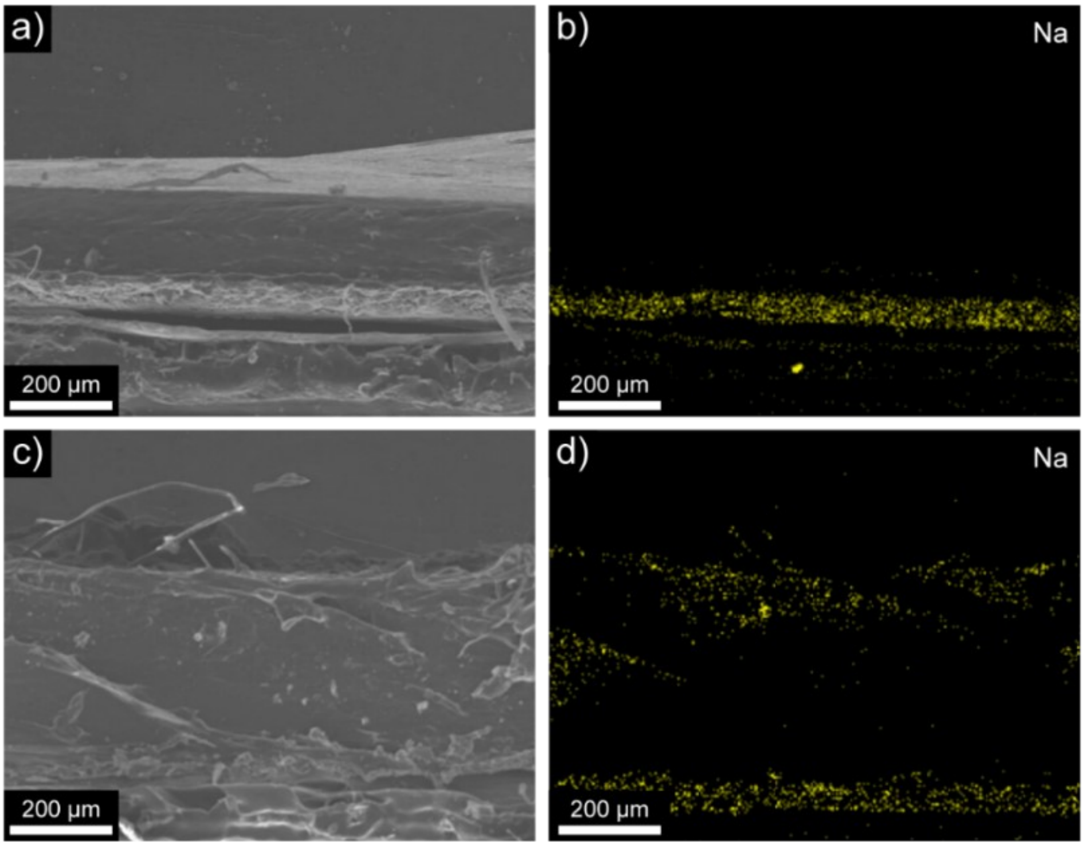

Figure S6 Cross-sectional SEM images of SPEs and corresponding elemental mapping. (a) and (b) SEM and mapping image of a cross-section of a cathode/SPE composite film after resting in a cell at 60°C at the same time. (c) and (d) SEM and mapping of a cross-section of a cathode/SPE composite film after 100 cycles of charge and discharge

References:

1. J. Z. Guo, P. F. Wang, X. L. Wu, X. H. Zhang, Q. Yan, H. Chen, J. P. Zhang and Y. G. Guo, *Adv. Mater*, 2017, **29**, 1701968.
2. K. Tang, X. Yu, J. Sun, H. Li and X. Huang, *Electrochim. Acta*, 2011, **56**, 4869-4875.
3. J. Z. Guo, A. B. Yang, Z. Y. Gu, X. L. Wu, W. L. Pang, Q. L. Ning, W. H. Li, J. P. Zhang and Z. M. Su, *ACS Appl. Mater. Interfaces*, 2018, **10**, 17903-17910.