Supporting Information

Novel Flame Retardant Rigid Spirocyclic Biphosphate Based

Copolymer Gel Electrolyte for Sodium Ion Battery with Excellent

High-temperature Performance

Jinyun Zheng^{a,*}, Yiwan Yang^a, Wenjie Li^a, Xiangming Feng^a, Weihua Chen^{a,*}, Yufen Zhao^{a,b}

^a Green Catalysis Center, and College of Chemistry, Zhengzhou University, Zhengzhou 450001, PR

China

^b Institute of Drug Discovery Technology, Ningbo University, Ningbo, 315211, P R China

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1. Materials and Methods

Pentaerythritol, 2-hydroxyethyl acrylate, ethyl acrylate, trifluoroethyl methacrylate, 2,2azobisisobutyronitrile and perylene-3,4,9,10-tetracarboxylic di-imide were purchased from Shanghai Aladdin Bio-chem Technology Co. LTD. Phosphorus oxychloride and acryloyl chloride were purchased from Shanghai SAAN Chemical Technology Co., Ltd. Glass fibre was purchased from Henan Huanyu Group Co., Ltd. Liquid electrolyte containing 1 M NaClO₄ in ethylene carbonate/propylene carbonate (EC/PC, 1:1 by volume) and 5 wt.% fluoroethylene carbonate was purchased from DoDoChem. PVDF was supplied from Arkema SA. Super P was purchased from Brilliant Chemical Co., Ltd. Tianjin. Other chemical reagents, solvents and materials were used as supplied.

NMR spectra were obtained on a Bruker AV 400 NMR spectrometer with the CDCl₃ as solvent. FT-IR spectra were performed on a PerkinElmer spectrometer. HR-MS was recorded on Water Q-TOF Micromass spectrometer. The morphologies were observed by scanning electron microscopy (SEM, ZEISS Merlin Compact). Powder X-ray diffraction (XRD, X'Pert PRO) used Cu Kα radiation at a scan rate from 10° to 90° at 10° min⁻¹. Thermogravimetric analysis (TGA) and differential thermal gravity (DTG) were recorded on Germany STA 409PC thermal analyzer at a heating rate of 10 °C min⁻¹ under argon atmosphere. The mechanical property of GPE and LE separators were evaluated by stretching testing machine (ELECTRONIC UNIVERSAL TESTING MACHINE, UTM2203). The theoretical simulation was used with the program of Gaussian 09.

2. Electrochemical measurements

Alternating current (AC) impedance curves was used with CHI 604E electrochemical workstation to carry out onto Na/GPE/Na cell. Changes in current over time curves was used with CHI 604E electrochemical workstation at the applied potentiostatic of 20 mV and polarization time of 1000 s, which is the Na/GPE/Na cell. Linear-sweep voltammetry (LSV) was used with CHI 600E electrochemical workstation to carry out onto the stainless-steel (SS) as working electrode and sodium mental as reference and counter electrodes between 2.0 V and 6.0 V (vs. Na/Na⁺) at the scan rate of 1.0 mV s⁻¹, which is the SS/GPE/Na cell. Sodium plating-stripping galvanostatic cycling curves was used with battery test system (Neware CT-4008, Shenzhen, China) at a constant current density of 0.1 mA cm⁻², which is the Na/GPE/Na cell. Cyclic voltammetry (CV) was tested using CHI 604E electrochemical workstation over the voltage range from 2.5 V to 4.0 V (vs. Na/Na⁺) with Na₃V₂(PO₄)₃

as the working electrode and sodium metal was used as the counter electrode at a scan rate of 0.1 mV s⁻¹. The galvanostatic charge-discharge tests were evaluated at a potential range of 2.5-4.0 V (vs. Na/Na⁺) using a battery test system (Neware CT-4008, Shenzhen, China).

3. Characterization of SPDPA







Fig. S5 The HR-MS spectrum of SPDPA

4. Separation and purification of the polymer matrix from GPE

To separate and purify the polymer matrix from the GPE, the GPE was mashed into pieces and washed with ethyl alcohol, then the mixture was ultrasound for 3 h, the procedures were repeated for three times, subsequently stirred hard for 2 days to separate the white precipitates, followed by a

vacuum drying at 80 °C. The obtained precipitates were washed used deionized water for 2 days to further remove the residual ions. The precipitates were then vacuum-dried at 80 °C again to obtain the polymer matrix.

5. The XRD curve of polymer matrix



Fig. S6 The XRD curve of polymer matrix

6. The measure method of ionic conductivity and ion transference number

The ionic conductivity (σ) of the GPE and liquid electrolyte was determined by electrochemical AC impedance spectroscopy experiments in a symmetric cell with the GPE sandwiched between two stainless-steel electrodes with AC amplitude of 5 mV from 100 kHz to 0.01 Hz. The ionic conductivity (σ) was obtained based on equation (1).

$$\sigma = L/(R \times S) \tag{1}$$

where L is the thickness of GF with GPE and liquid electrolyte (cm), R is the bulk gel electrolyte resistance (Ω) that was determined by electrochemical impedance spectroscopy (EIS), and S is the area of the stainless-steel electrodes (cm²).

The type of symmetric Na/GPE/Na coin cell was also assembled to characterize the transference number of sodium ions. The Na⁺ transference number is obtained based on EIS and potentiostatic polarization method. The transfer number (t_{+}) for the sodium cation can be given by the Bruce-Vincent-Evans (BVE) equation (2).

$$t_{+}=I_{s}(\Delta V-I_{0}R_{0})/I_{0}(\Delta V-I_{s}R_{s})$$
(2)

where I_0 and I_s are the initial and steady current, respectively; R_0 and R_s are the resistances before and after polarization, respectively; ΔV is the applied potentiostatic of 20 mV.¹

Table S1 lonic conductivity of gel polymer electrolyte and liquid electrolyte at different temperatures

| | | | Temperature (°C) | | | | |
|-------|--------------|-----|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| | | | 25 | 30 | 40 | 50 | 60 |
| lonic | conductivity | GPE | 2.49×10 ⁻³ | 2.70×10 ⁻³ | 3.52×10 ⁻³ | 4.11×10 ⁻³ | 4.96×10 ⁻³ |

| (S/cm) | LE | 3.23×10 ⁻³ | 3.47×10 ⁻³ | 3.53×10 ⁻³ | 4.04×10 ⁻³ | 5.40×10 ⁻³ |
|--------|----|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| | | | | | | |



Fig. S7 Ionic conductivity of liquid electrolyte at different temperatures (298–333 K) The Arrhenius equation is $\sigma = Aexp \ (-\frac{E_a}{RT})$ (3)

Where σ is the ionic conductivity, A is the pre-exponential factor, T is the test temperature, R is the Boltzmann constant of 8.314×10^{-3} kJ·mol⁻¹·K⁻¹.

7. Flammability test procedures

The preparation of liquid electrolyte with flame retardant: The liquid electrolyte solutions containing different concentrations of flame retardant additive with 0.0, 5.0, 10.0, 15.0, 20.0 wt% ratios were prepared by mixed SPDPA with liquid electrolyte (1 mol L⁻¹ NaClO₄ in EC/PC, 1:1 by volume, and 5 wt.% FEC). The SET measurements method was based on the reference published by our research group². **The burning video of separators:**

The burning video of GPE separator.mp4

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The burning video of LE separator.mp4

8. The stress-strain behavior of GPE and LE



Fig. S8 Stress-strain curves of the GPE and LE

9. The theoretical simulation



Fig. S9 a) The adsorption energies of different number of Na⁺ coordinated by SPDPA; b) The electrostatic surface potential (ESP) of SPDPA coordination of sodium ions before and after.

10. The electrochemical characterization of NVP/Na cells



Fig. S10 CV curves of the first three cycles of NVP cathode with GPE.



Fig. S11 Different cycles charge/ discharge curves of the LE cell



Fig. S12 Galvanostatic charge/discharge profile of the LE cell at different current densities

| | Capacity retention (rt.) | | | | |
|---|--------------------------|--------------|-------------|--|--|
| | 500 cycles | 1000 cyclels | 1600 cycles | | |
| This work | 94.3% | 90.0% | 81.4% | | |
| Previous work | 89.6% | 81.6% | - | | |
| (J Membr. Sci. 2019, 583, 163-170) | | | | | |
| Previous work | 85.5% | - | - | | |
| (J. Mater. Chem. A, 2018, 6, 6559-6564) | | | | | |

Table S2 The property comparison of different GPEs



Fig. S13 The charge/discharge curves of the LE cell at 60 °C.

11. The electrochemical characterization of PTCDI/Na cells



Fig. S14 Cycling performances of the PTCDI/Na cells. a) The charge/discharge curves of the GPE cell; b) The charge/discharge curves of the LE cell; c) Cycling performances.

References

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- 2. J. Zheng, X. Li, Y. Yu, X. Feng and Y. Zhao, J. Therm. Anal. Calorim., 2004, 117, 319-324.