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Supporting Information

Novel safer phosphonate-based gel polymer electrolytes for

sodium-ion batteries with excellent cycling performance

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Table of contents

1. Materials and methodsS2
2. Experimental procedures
3. Cell assembly and Electrochemical measurementsS3
4. CharacterizationS5
4.1 Characterization of TGMAS5
4.2 Characterization of MATEPPS6
4.3 The XRD curve of polymer matrixS8
4.4 FTIR spectra of monomers TFMA, MMA, MATEPP, and the polymer matrix
5. Flammability test procedures
6. The measure method of ionic conductivity
7. The LSV curve of SS/GPE/NaS10
8. The CV curve of SnS ₂ /GPES10
9. The cycling performance of SnS ₂ /GPES11
10. References

1. Materials and methods

Commercial methyl methacrylate (MMA, >99.5%) and trifluoroethyl methacrylate (TFMA, >99.5%) containing double bonds were washed with 10 % NaOH solution to remove the polymerization inhibitor, then washed with water till pH = 7, dried with anhydrous sodium sulfate, and distilled under reduced pressure to obtain the pure monomers. 2,2-Azobisisobutyronitrile (AIBN) was purified by recrystallization from ethanol. The liquid electrolyte containing 1 M NaClO₄ in ethylene carbonate (EC)/propylene carbonate (PC) (1:1 by volume) and 5 wt% fluoroethylene carbonate (FEC) was used. The other chemical reagents and materials were used as supplied.

¹H and ³¹P nuclear magnetic resonance (NMR) spectra were obtained on a Bruker AV 400 NMR spectrometer. HR-MS was recorded on Water Q-Tof Micromass spectrometer. FT-IR spectra were recorded on a Bruker-Alpha spectrometer with KBr pellets. Thermogravimetric analysis (TGA) and differential scanning colorimetry (DSC) of the polymer matrix were performed on Germany STA 409PC thermal analyzer at a heating rate of 10 °C /min under argon atmosphere. The morphologies were observed by scanning electron microscopy (SEM, ZEISS Merlin Compact). Power X-ray diffraction (XRD, X'Pert PRO) using Cu Kα radiation at a scan rate from 5° to 40° at 5° min⁻¹.

2. Experimental procedures



Synthesis of Triethylene glycol monomethacrylate (TGMA): Triethylene glycol (TEG, 34.5 g, 0.230 mol), triethylamine (TEA, 10.12 g, 0.10 mol) and toluene (80 mL) were placed in a round-bottom flask equipped with a mechanical stirrer and an addition funnel. The solution was cooled with an ice-water bath. Then a solution of methacryloylchloride (10.4 g, 0.10 mol) in toluene (20 mL) was added dropwise. The reaction mixture was stirred overnight and allowed to warm to room temperature. The resulting mixture was filtered and the filtrate was concentrated under vacuum. The crude product was obtained and purified by column chromatography to provide

pure TGMA as a colorless liquid (12.2 g, 56%). HR-MS m/z: calcd. for C₁₈H₃₅O₈P, [M+H]⁺ 219.1232, found 219.1228; ¹H NMR (CDCl₃, 400 MHz, ppm) δ: 6.15 (s, 1H, =CH trans), 5.59 (s, 1H, =CH cis), 4.32(t, 2H, -OCH₂), 3.61 (t, 2H, -OCH₂), 3.77-3.68 (m, 8H, -OCH₂), 1.96 (s, 3H, -CH₃); ¹³C NMR (CDCl₃, 100 MHz, ppm) δ: 169.39 (-C=O), 136.09 (-C=CH₂), 125.89 (-C=CH₂), 72.52-61.77 (-OCH₂), 18.32 (-CH₃).



Synthesis of di(2-methacryloyltrioxyethyl)phenylphosphonate (MATEPP): TGMA (13.02 g, 0.06 mol), TEA (6.07 g, 0.06 mol) and toluene (60 mL) were placed in a round-bottom flask equipped with a mechanical stirrer and an addition funnel. The solution was cooled with an ice-water bath. Then a solution of phenylphosphonic dichloride (3.90 g, 0.02 mol) in toluene (10 mL) was added dropwise. The reaction mixture was stirred overnight and allowed to warm to room temperature. The resulting mixture was filtered and the filtrate was washed with saturated NaHCO₃ solution and distilled water for three times, and dried over anhydrous sodium sulfate. Then the volatiles were removed under reduced pressure. The residue was purified by column chromatography to provide pure MATEPP as a colorless liquid (9.90 g, 89%). ¹H NMR (CDCl₃, 400 MHz, ppm) δ: 7.78 (m, 2H), 7.49 (m, 1H), 7.40 (m, 2H), 6.01 (s, 2H, =CH), 5.57 (t, 2H, =CH), 4.19(m, 8H, -OCH₂), 3.66 (t, 8H, -OCH₂), 3.56 (s, 8H, -OCH₂), 1.88 (s, 6H, -CH₃); ¹³C NMR (CDCl₃, 100 MHz, ppm) δ: 167.3 (-C=O), 136.1 (-C=CH₂), 132.5 (-C=CH₂) 131.8 (-C=CH₂), 128.(-C=CH₂), 125.7 (-C=CH₂), 70.5-63.8 (-OCH₂), 18.3 (-CH₃); ³¹P NMR (CDCl₃, 162 MHz, ppm) δ:19.6; IR v/cm⁻¹: 2962, 2875(-CH₂, -CH₃), 1732 (C=O), 1636 (C=C), 1547, 1410 (C=C), 1251 (P=O); HR-MS m/z: calcd. for C₂₆H₃₉O₃₁P, [M+H]⁺ 559.2308, found 559.2311.

3. Cell assembly and Electrochemical measurements

The preparation of electrodes

The Na₃V₂(PO₄)₃ (NVP) cathode was prepared by mixing composited NVP materials, acetylene black and PVDF in a

weight ratio of 8:1:1 to disperse in N-methyl pyrrolidone (NMP) solution. A uniform slurry was obtained after vigorous stirring for 4 h which was then coated onto aluminum foil. The electrode was dried in a vacuum oven at 60 °C for 24 h and 120 °C for 2 h. The mass loading of the NVP active material on the electrode is around 0.85-1 mg cm⁻². And the SnS_2 anode was prepared in the same method with the mass loading is 0.9-1.1 mg cm⁻².

Preparation gel polymer electrolyte films

The gel polymer electrolyte was prepared by in situ radical polymerization. Typically, a precursor solution containing cross-linking agent MATEPP (150 mg, 0.268 mmol, 6.8 wt%), MMA (27 mg, 0.27 mmol, 1.2 wt%), TFMA (45.3 mg, 0.268mmol, 2.0 wt%) and AIBN (1.1 mg) were dissolved in liquid electrolytes (2 g, 90 wt%). The precursor solution was polymerized at 75°C for 40 min to obtain translucent GPE films. All procedures were carried out in an Ar-filled glove box with the concentrations of the moisture and oxygen below 1 ppm.

Cell assembly

The phosphonate-based gel polymer electrolytes coin cells were fabricated by in-situ polymerization. CR2025-type coin cell with Na₃V₂(PO₄)₃ (NVP)as cathode electrode and SnS₂ as anode electrode respectively, glass fiber as separator and sodium foil as anode, then cells were assembled in an Ar-filled glove box. The precursor solution containing 6.8 wt% MATEPP, 1.2 wt% MMA, 2.0 wt% TFMA and AIBN (1% wt%) dissolved in 90 wt% liquid electrolytes was injected into the separator and filled into the cells. Subsequently, the assembled cells were aged for 2 h to ensure the precursor solution to well-wet into the electrodes. Then the cells were heated at 75 °C for 40 min in a vacuum oven to complete polymerization. The electrochemical performances of the gel-polymer electrolyte were tested in CR2025 type coin cells by using NVP as a cathode and sodium foils as the counter electrodes in the glove box (the contents of H₂O and O₂ were both below 1 ppm). The galvanostatic charge-discharge tests were evaluated at a potential range of 2.5-3.9 V (vs Na⁺/Na) and the SnS₂ anode was 0.01-3 V (vs Na⁺/Na) at room temperature using a Land battery test system (LAND CT-2001A, Wuhan, China). In full-cell

assembling, firstly, the SnS₂ anode in a sodium half-cell with the gel polymer electrolyte was activated by galvanostatic of 0.1 A/g between 0.01 and 3 V for 2 cycles, and then was used for assembling the sodium-ion full-cell SnS₂/Na₃V₂(PO₄)₃ with the gel polymer electrolyte. The mass loading of the Na₃V₂(PO₄)₃ cathode was about 1 mg cm⁻², and the mass loading of the SnS₂ anode was about 0.34 mg cm⁻² in full cell. The sodium-ion full-cell SnS₂/Na₃V₂(PO₄)₃ was cycled in the voltage window of 0.5–3.0 V instrument on a Land galvanostatic charge/discharge.

AC impedance cure was obtained by using CHI 604e electrochemical workstation between a frequency range from 100 kHz to 10 mHz. 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 1.0 V and 6.0 V (vs Na⁺/Na) at a scan rate of 1.0 mV S⁻¹, that is SS/GPE/Na. The electrolyte contact angle of polymeric precursor solution containing glass fiber was determined by a contact angle measurement instrument (Dataphysics OCA20).

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.

4. Characterization

4.1 Characterization of TGMA

S5



Fig. S1. (a) ¹H NMR, (b) ¹³C NMR (c) HR-MS spectra of TGMA

4.2 Characterization of MATEPP





Fig. S2· (a) ¹H NMR, (b) ¹³C NMR, (c) ³¹P NMR spectra of MATEPP, (d) HR-MS of MATEPP, (e) The stack ³¹P

NMR spectrum of MATEPP in liquid electrolyte and pure MATEPP.



4.3 The XRD curve of polymer matrix

Fig. S3 The XRD curve of the polymer matrix.



4.4 FTIR spectra of monomers TFMA, MMA, MATEPP, and the polymer matrix

Fig. S4 FTIR spectra of TFMA, MMA, MATEPP, and the polymer matrix.

5 Flammability test procedures

The different content of flame retardant additive MATEPP (2.5, 5.0, 7.5, 10, 12.5 wt%) was dissolved in the liquid electrolyte. The self-extinguishing time measurements and the linear flame propagation rate were measured according to the literature report¹.

Percentage MATEPP /wt%	0	2.5	5	7.5	10	12.5
Self-extinguishing time/s	28	26	23	17	14	12
Flammable propagation/mm s ⁻¹	7.14	6.92	5.97	4.02	3.26	3.05

Table S1 The SET and flammable propagation rate

6 The measure method of ionic conductivity

The ionic conductivity (σ) of the GPE was determined by electrochemical 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 (SI). The ionic conductivity (σ) was obtained based on Equation (1).

$\sigma = I/(R \times S)$

(1).

where I is the thickness of GPE (cm), R is the bulk gel electrolyte resistance (Ω) that was determined by EIS, and S is

the area of the stainless-steel electrodes (cm²).



Fig. S5 The electrochemical impedance spectroscopy of the SS/Liquid electrolyte/SS and SS/GPE/SS cells

at room temperature.

7. The LSV curve of SS/GPE/Na



Fig. S6 The LSV curve of SS/GPE/Na at the scan sweep 0.1 mV/s from -1 V to 6 V.

8. The CV curve of SnS₂/GPE



Fig. S7 The CV curve of SnS_2/GPE at the scan sweep 0.1 mV/s from 0 V to 3 V.

9. The cycling performance of SnS₂/GPE



Fig. S8 Cycling performances for the SnS₂/GPE/Na: a) Cycling performance at a constant current density

of 1 A/g. b) Galvanostatic charge/discharge profile of 1 A/g.

10. References

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