Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Room-temperature rechargeable Na-SO_2 batteries with gel-polymer electrolyte

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Experimental Details

Chemical. The solvent of tetraethylene glycol dimethyl ether (Aladdin) is purified by a reduced pressure distillation method, then it is stored under argon with over freshly activated 4 Å molecular sieves (beads 8-12mesh, *J&K*). Poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) has an molecular weight of ~ 455,000. The fumed silica is hydrophobic and purchased from Sigma-Aldrich. Prior to utilization, the $NaClO_4$ (anhydrous, Alfa Aesar) is dried at 120 °C in a vacuum oven for 12 hours. The preparation of 1 M $NaClO_4$/TEGDME electrolyte is in a glove box with argon (H_2O and $O_2 < 0.1$ ppm). Multi-wall carbon nanotubes (MCNTs) are bought from Cnano Technology Ltd.

Cathode fabrication. The cathodes were prepared by blending MCNTs and polyvinylidene fluoride (PVDF) in N-methyl-2-pyrrolidone (NMP) with a mass ratio of 9 : 1. The obtained slurries were dropped onto a Ni foam (ø10 mm) with a total loading mass of ~0.3 mg cm^{-2}. Then, the as-prepared cathodes were dried at 120 °C for 12 hours at vacuum. The Super P cathodes were prepared vis the same method and consist of 90 wt% Super P and 10 wt% PVDF. The Super P is one traditional conductive carbon used in electrode preparation.

Polymer electrolyte fabrication. The mixture (3.0 g) of PVDF-HFP and Al_2O_3 particles with a mass ratio of 4 wt% is dissolved in acetone (20 mL). This solution is heated in a beaker (50 mL) in water bath at 50 °C with vigorous stirring for 2 h. Then the solution rests for 1 h in this water bath. The resultant solution is spread on an aluminum foil by a graduated blade. The obtained polymer film is dried for 10 h at 100 °C in vacuum. After cooling down to room temperature, the film is soaked into 1 M $NaClO_4$/TEGDME solution for 24 h. Prior to using, the wettish film is slightly dried by a filter paper. Finally, the gel-polymer electrolyte (GPE) possesses the configuration of PVDF-HFP-Al_2O_3/liquid electrolyte.

GPE based Na-SO_2 battery assembly. The GPE based Na-SO_2 batteries are assembled in CR2032 coin type batteries. Each battery is successively assembled by stacking a Na metal anode (ø10 mm), a piece of GPE (ø16 mm), and a MCNTs/Ni foam cathode. The cathode case is drilled 7 holes for SO_2 transfer. The assembled batteries are put in 200 mL glass vessels full of SO_2 gas. Before operation, the batteries rest for 5 h.

Characterization. The powder X-ray diffraction patterns are carried out on a Rigaku MiniFlex600 X-ray diffractometer (Cu $K\alpha$ radiation, λ=1.54 Å). Scanning electron microscopic images are observed in a JEOL JSM-7500F with field emission electron microscope (abstract voltage = 5 kV). Transmission electron microscope (TEM) and high-resolution TEM images are obtained on a Philips Tecnai G2F-20, whose acceleration voltage is 200 kV. The chemical composition of species is detected by energy dispersive spectrometer and X-ray photoelectron spectroscopy (Perkin Elmer PHI 1600 ESCA system). The Raman spectrum signals are collected via a Thermo-Fisher Scientific (532 nm).

Electrochemical test. The galvanostatic discharge/charge tests are taken on a LAND CT2001A instrument. The current density and specific capacity are based on the mass of MCNTs on the cathode. Cyclic voltammograms are carried out on a Parstat 263A workstation (AMTECT Company, USA).

Theoretical specific energy density calculations. The discharge reaction of Na-SO_2 battery can be described as equation (1):

$$2Na + 2SO_2 \leftrightarrow Na_2S_2O_4,\ E_{ocv} \approx 2.80\ V \qquad (1)$$

Where E_{ocv} is the open circuit voltage (OCV) at 25 °C. The theoretical specific energy density of Na-SO_2 battery E_w is calculated via the following equation:

$$E_w = 26800 \times n \times E_{ocv}/M \qquad (2)$$

Where n is the battery reaction electron number (n = 2), M is the molecular weight of $Na_2S_2O_4$ (174.1 g mol^{-1}).

The rough theoretical specific energy density for a Na-SO_2 battery is around 863 Wh kg^{-1}.

The actual specific energy density calculation is based on the mass of MCNTs and discharge product. The mass of MCNT and discharge product can be calculated using the following equation:

$$m = m_{MCNT} + \frac{C \times m_{MCNT}}{K} \qquad (3)$$

Where m_{MCNT} (300 µg cm^{-2} × 0.785 cm^2) is the mass of MCNT, C (5000 m Ah g^{-1}) is the specific capacity for the active material (m_{MCNT}) on cathode, K is the theoretical specific capacity (308 mA h g^{-1}) based on $Na_2S_2O_4$. The calculated total mass of MCNTs (0.236 mg) and discharge product (3.823 mg) is 4.059 mg.

The practical energy density is obtained by the following equation:

$$E = \frac{C \times m_{MCNT}}{m} \times V \qquad (4)$$

Where V (2.63 V) is the average discharge voltage of GPE based Na–SO_2 batteries. E = 763 Wh Kg^{-1}.

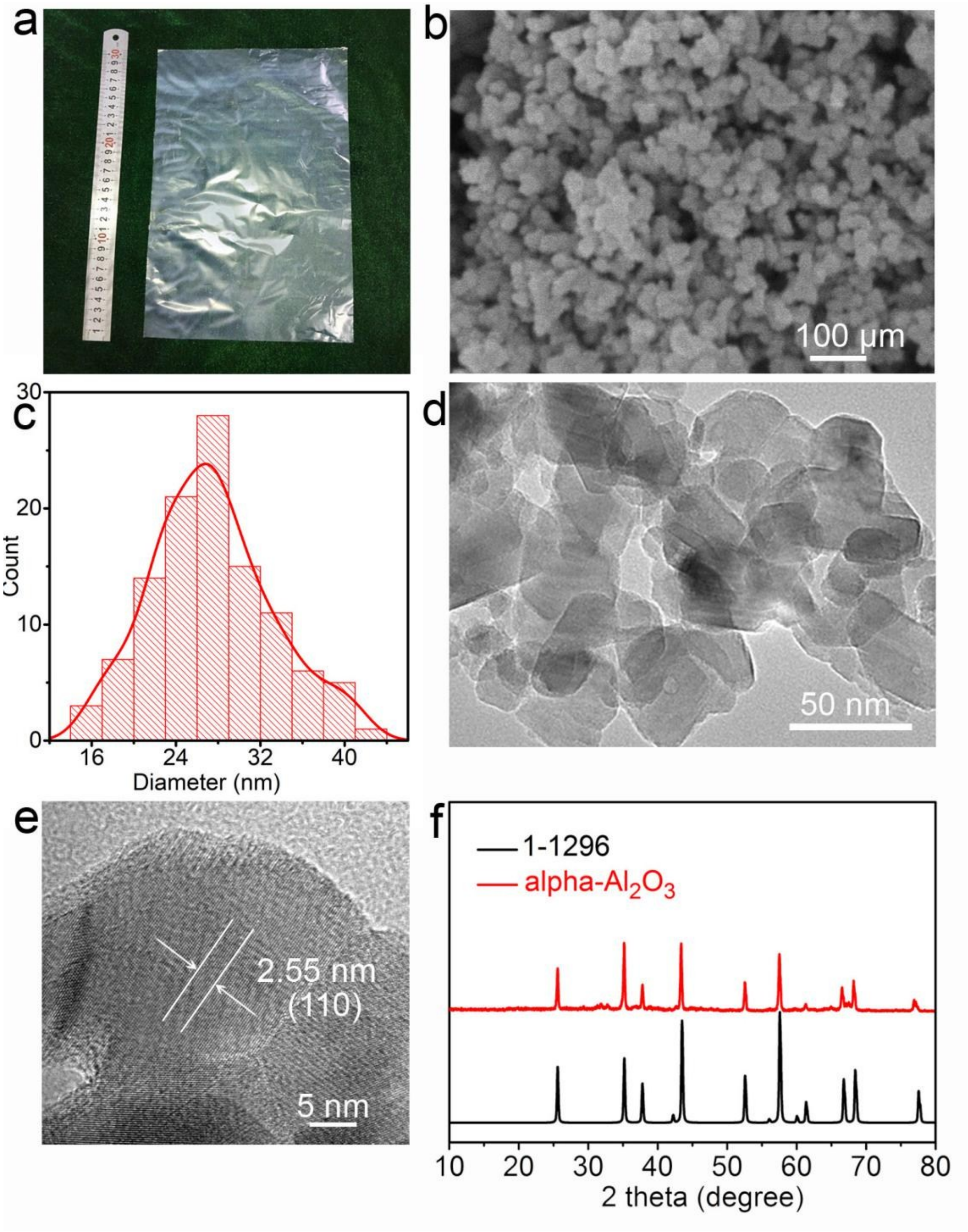

Fig. S1 (a) A photo graph of GPE matrix. (b) A SEM image and (c) a size distribution of Al_2O_3 fillers. (d) TEM and (e) HRTEM images of nanosized Al_2O_3 with an average diameter of 28~30 nm. (f) XRD of the nanosized alpha-Al_2O_3.

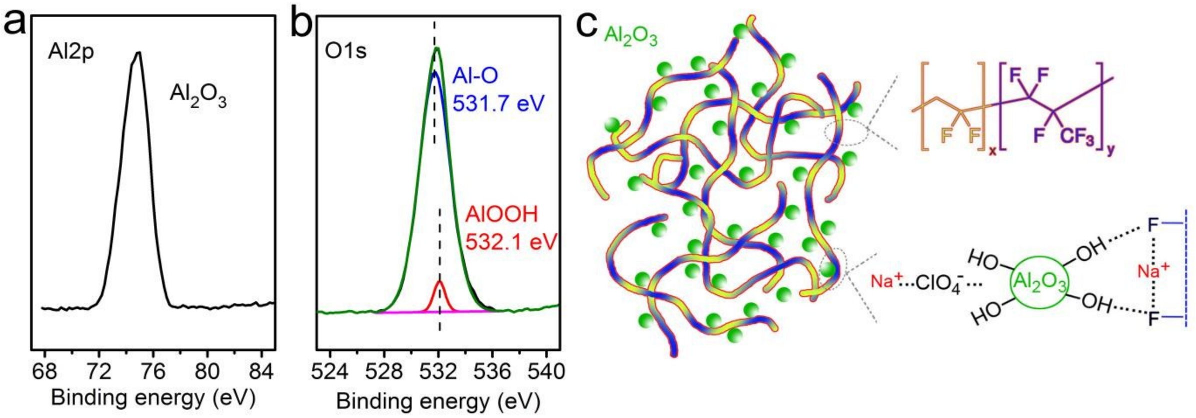

Fig. S2 XPS and Na-ion transporting mechanism. (a) XPS of Al2p in Al_2O_3. (b) XPS of O1s in Al_2O_3. (c) Na-ion transporting mechanism of the composite polymer electrolyte of PVDF-HFP-Al_2O_3/$NaClO_4$-NaI-tetraglyme.

According to previous reports, the -OH groups on the Al_2O_3 fillers' surface belong to the Lewis acid groups and may quite likely compete with the Lewis–acid Li^+ for the formation of complexes with the polymer chains, as well as with the anions (ClO_4^-) of the added $LiClO_4$ salt in the polymer electrolyte.[1,2] These interactions could increase the ionic conductivity of polymer electrolyte. Now that the $NaClO_4$ is similar to $LiClO_4$, the -OH groups on the surface of Al_2O_3 fillers also would compete with the cations (Na^+) and anions (ClO_4^-) from the added $NaClO_4$ salt in our polymer electrolyte.

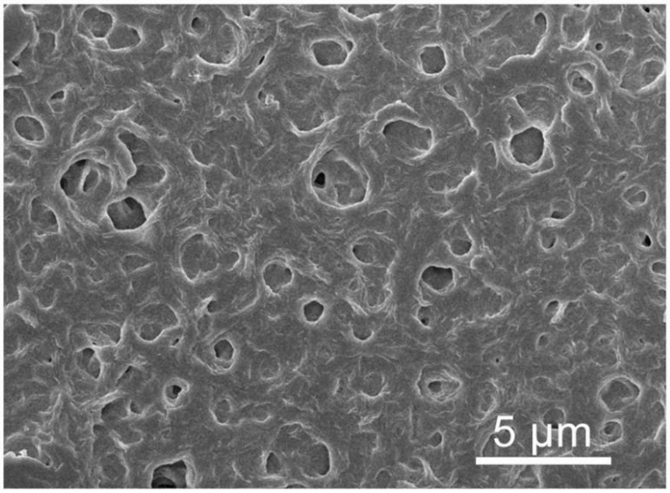

Fig. S3 A SEM image of the GPE before soaking in LE.

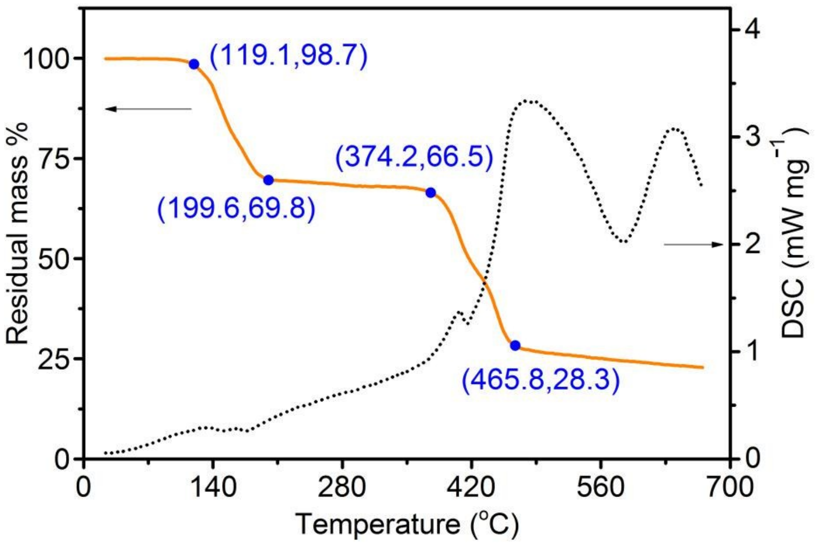

Fig. S4 Thermal gravity analysis and DSC curves of GPE.

According to the thermal gravity analysis (TGA) and differential scanning calorimetry (DSC), the GPE of PVDF-HFP-Al_2O_3/$NaClO_4$-NaI-tetraglyme experienced two mass loss processes during temperature ranges of 119.1 °C to 199.6 °C and 374.2 °C to 465.8 °C. Two temperature ranges correspond to the evaporation of TEGDME and decomposition of PVDF-HFP, respectively. After TEGDME volatilization at 199.6 °C, the residual mass is 69.8%, suggesting that only 30.2% of the GPE is liquid electrolyte.

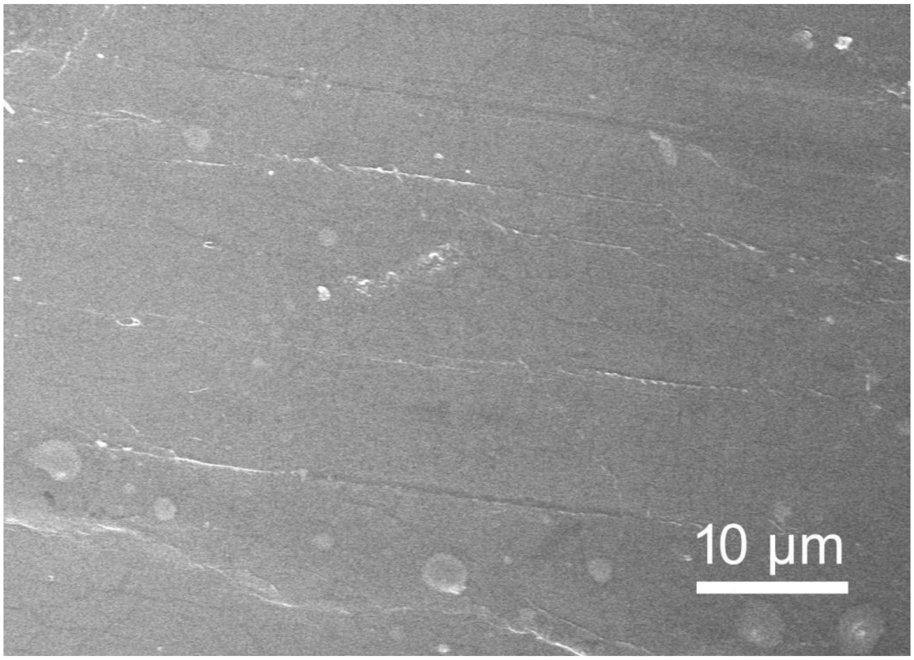

Fig. S5 A SEM image of the pristine Na anode.

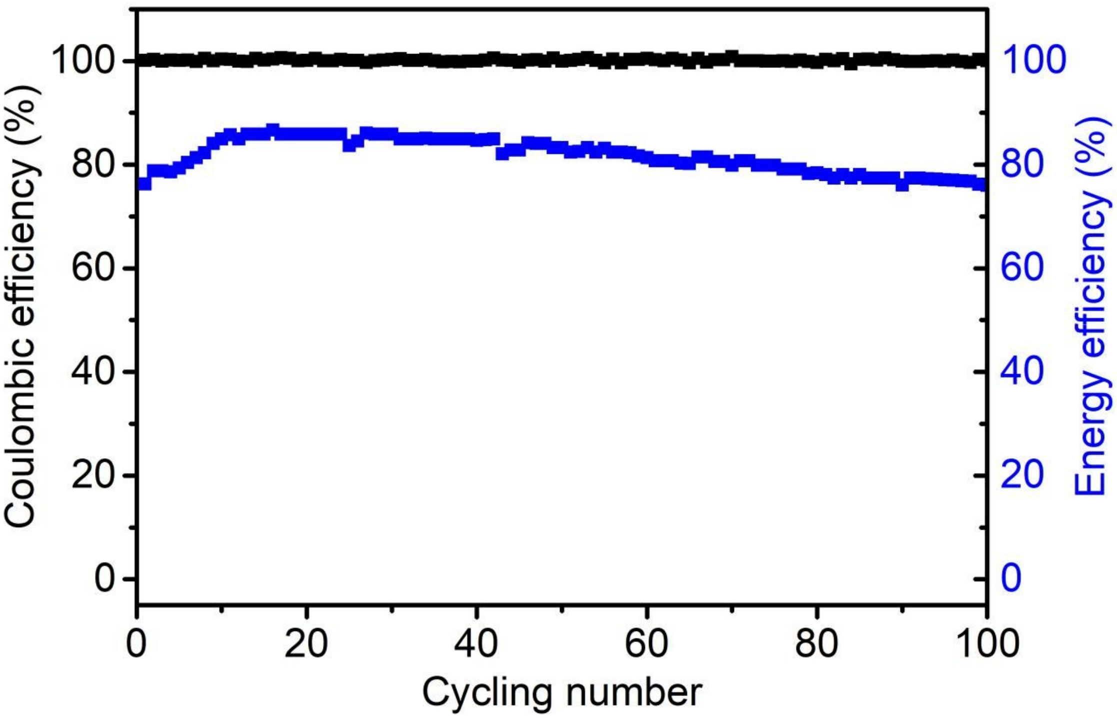

Fig. S6 Coulombic efficiencies and the energy efficiencies of GPE-based Na-SO_2 batteries as a function of cycle number. Rate: 200 mA g^{-1}. The fixed capacity is 1000 mA h g^{-1}.

During the cycling process, nearly 100% Coulombic efficiencies were obtained. The energy efficiency increased from 76.3% to 85.0% in the first 10 cycles and kept stable in the following 40 cycles at between 83.3% and 86.0%, and gradually decreased in the last 50 cycles from 82.4% to 76.0%.

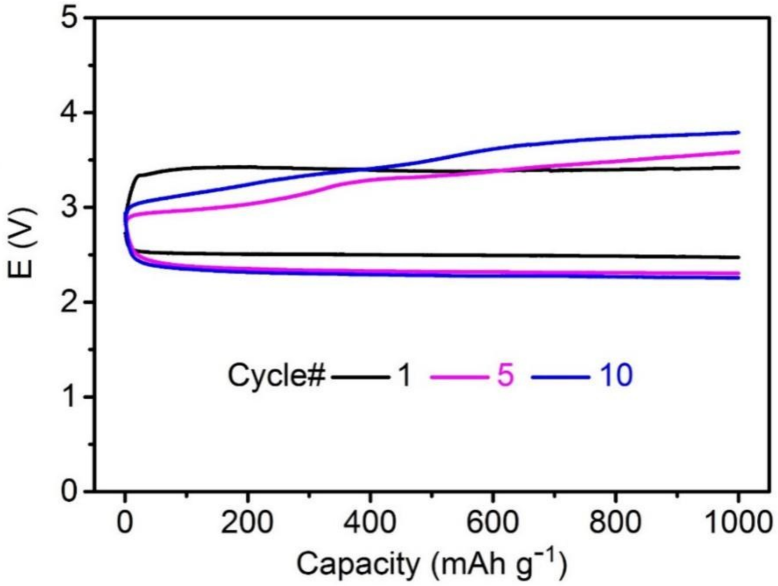

Fig. S7 Discharge/charge profiles of GPE based Na-SO_2 batteries without NaI addition. Rate: 100 mA g^{-1}.

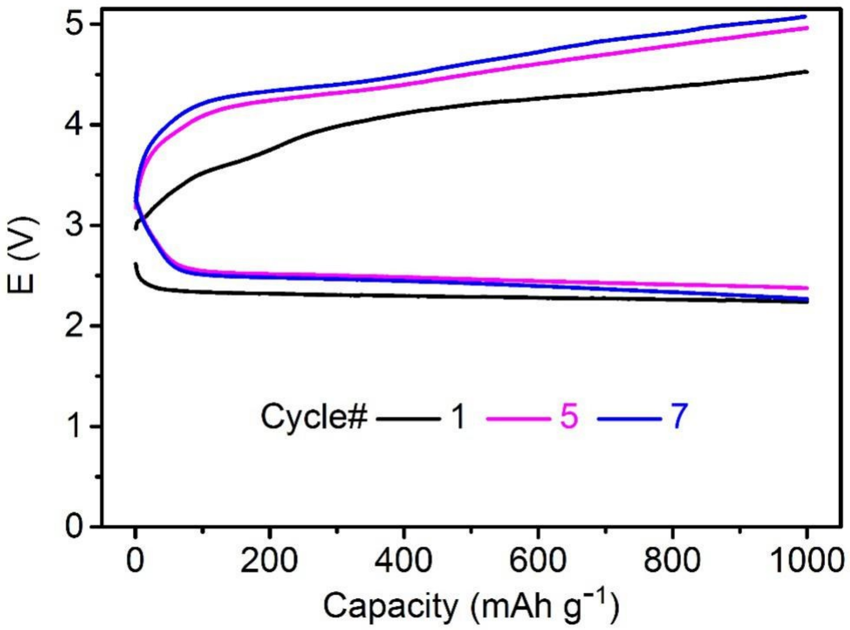

Fig. S8 Discharge/charge profiles of the GPE based Na-SO_2 batteries without NaI addition. Rate: 200 mA g^{-1}.

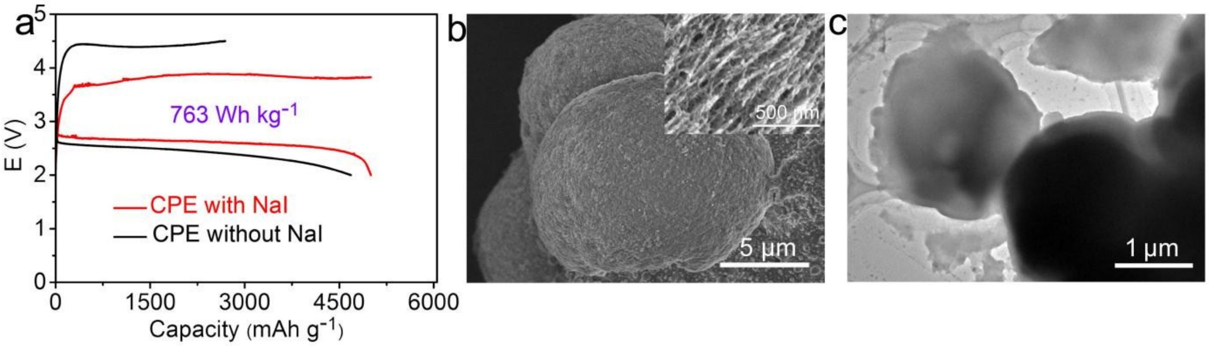

Fig. S9 Full discharge/charge profiles and corresponding SEM images. (a) Full discharge/charge profiles at 200 mA g^{-1}. (b) SEM images of a discharged cathode with a capacity of 5000 mA h g^{-1}. The inset SEM image is a detailed view. (c) TEM image of the discharge product.

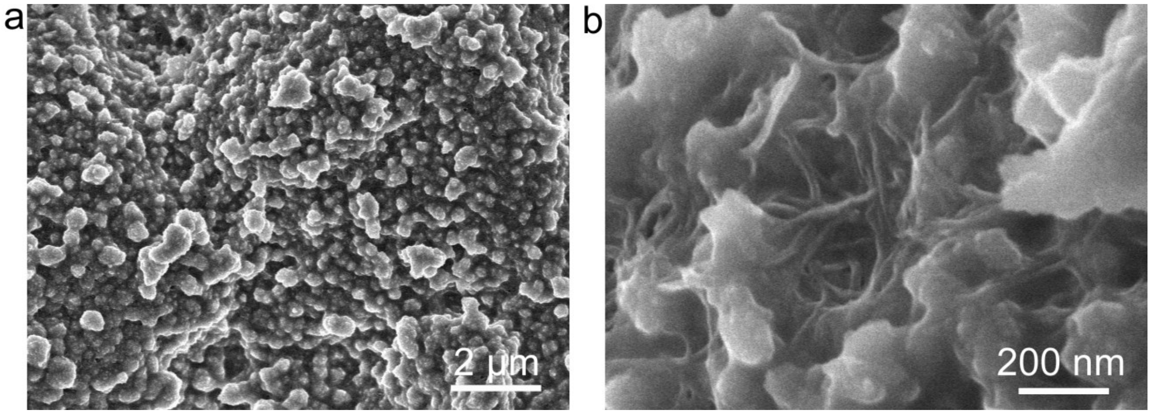

Fig. S10 SEM images of discharge products beneath large spherical products with 5000 mA h g^{-1}.

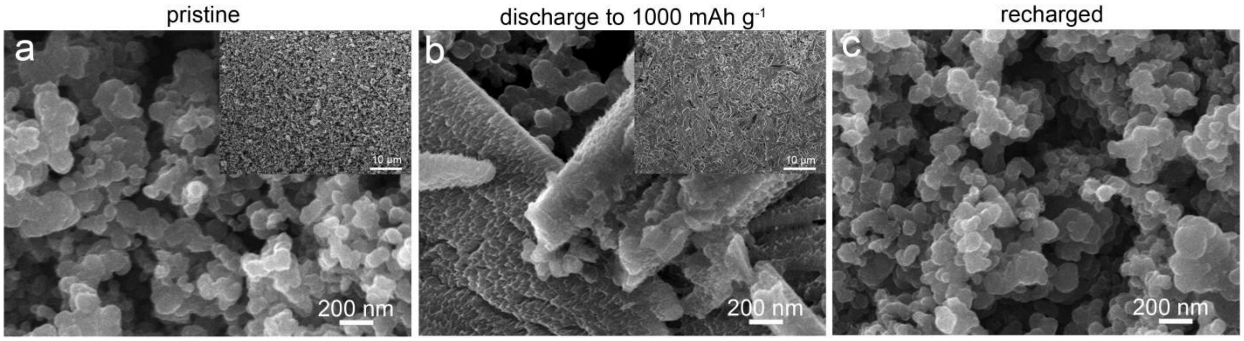

Fig. S11 SEM images of a super P cathode at different states. (a) Pristine state. (b) Discharged state with a capacity of 1000 mAh g^{-1}. (c) Recharged state.

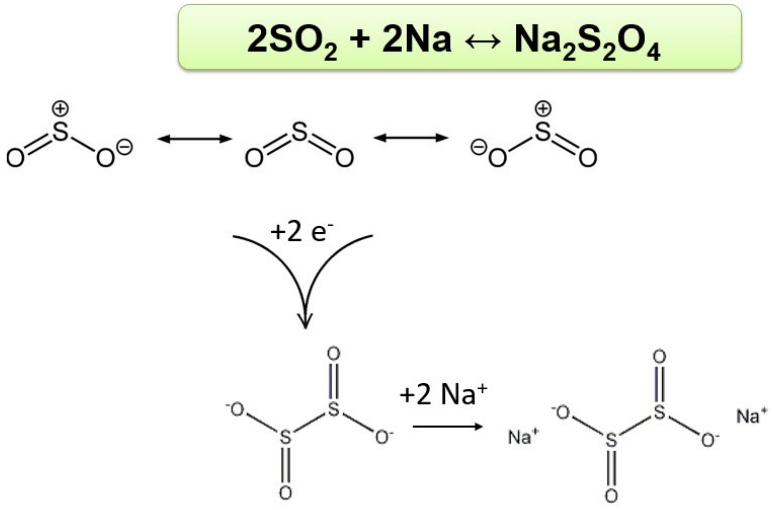

Fig. S12 A possible reaction mechanism of $Na_2S_2O_4$ formation.

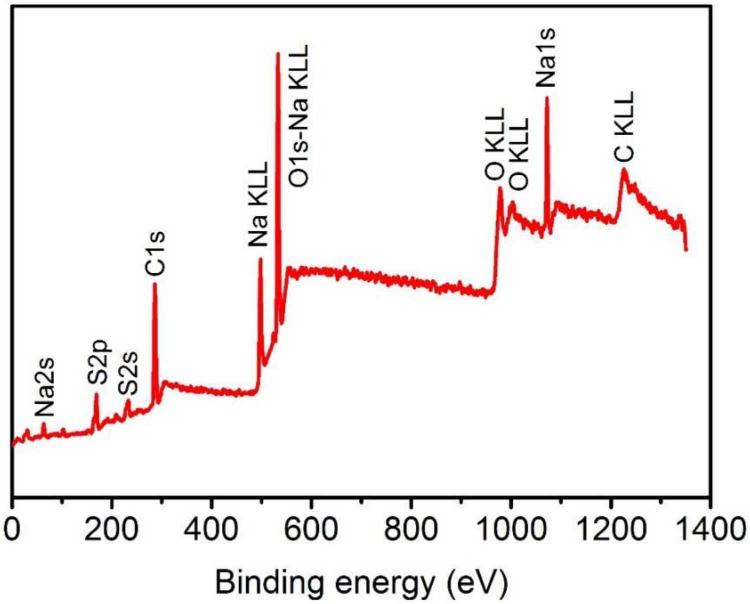

Fig. S13 Overall XPS spectra of the discharge products.

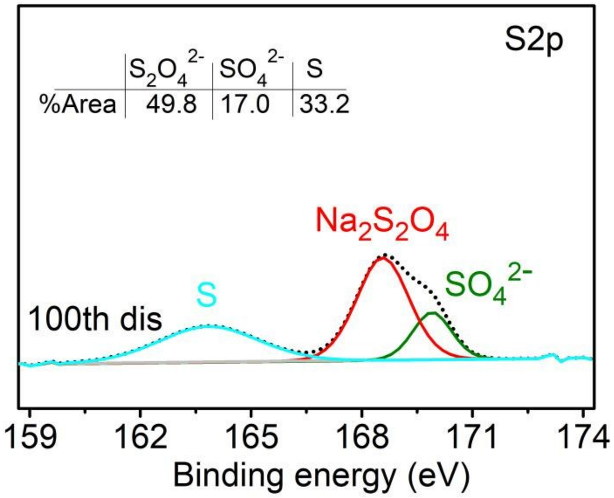

Fig. S14 S2p XPS of the 100th discharged cathode. The ratio between Na_2SO_4 and $Na_2S_2O_4$ after the 100th discharge is around 1 : 2.9.

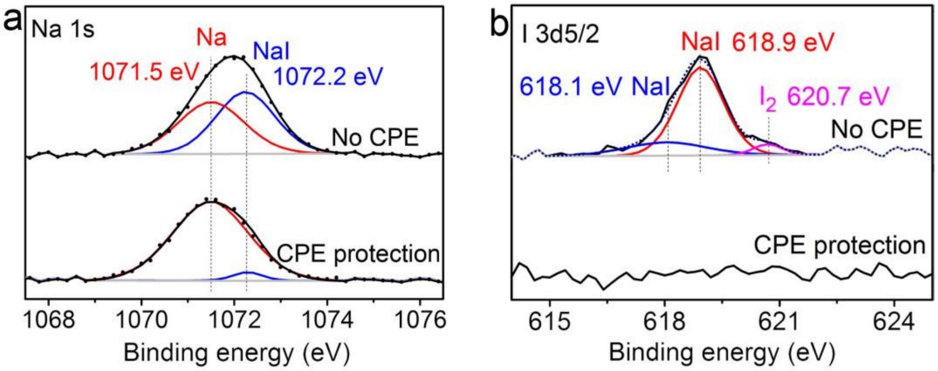

Fig. S15 XPS of Na anodes with and without a GPE protection, (a) Na 1s, (b) I 3d5/2. The Na anodes are tested after charging in batteries for 5 h at 50 mA g^{-1}.

Table S1 The content of each S-containing species in discharge products

	$Na_2S_2O_4$	SO_4^{2-}	S
1st discharge	56.2%	14.8%	29.0%
2nd discharge	53.8%	15.7%	30.6%

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2. F. Croce, L. Persi, B. Scrosati, F. Serraino-Fiory, E. Plichta, M.A. Hendrickson, *Electrochim. Acta*, 2001, **46**, 2457–2461.