Supporting Information

Approaching the Voltage and Energy Density Limits of Potassium-Selenium Battery Chemistry in a Concentrated Ether-Based Electrolyte

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Experimental Section

Materials

Selenium powders were purchased from Aladdin Chemical and used as received. CMK-3 powders were purchased from Nanjing XFNANO Materials Technology. CNTs were synthesized by chemical vapor deposition at 815 °C using an iron catalyst and acetylene gas precursor as described previously and treated by partial oxidation using nitric acid before use. Specifically, CNTs (60 mg) and concentrated nitric acid (7 mL) were placed in a 25 mL Teflon-line autoclave and heated to 150 °C for 24 hours. After cooling to room temperature, CNTs were washed with deionized water for several times and collected by filtration.

Preparation of CNTs/CMK-3/Se electrode

CMK-3 powders (20 mg), CNTs (5 mg), and polyvinylpyrrolidone (3 mg) were dispersed in ethanol (50 mL) by sonication for 2 hours. The mixture was then collected by filtration (with a Nylon 6 filter membrane with a pore size of 0.45 μm). After rinsing with water, the CNTs/CMK-3 film was peeled off and cut to circular disks with a diameter of 7 mm. CNTs/CMK-3/Se (CCSe) electrodes with varying Se contents were obtained through a
melt-diffusion strategy. Specifically, Se powders and CNTs/CMK-3 were placed in a quartz tube (12 mm in diameter) which was subsequently vacuum-sealed and heated at 600 °C for 5 hours before cooling to room temperature naturally. The Se contents in the composite cathodes were determined by two methods: (1) subtracting the weight of blank CNTs/CMK-3 from the composites and (2) thermogravimetric analysis (TGA), which give consistent results. The Se contents in CCSe are 35 wt%, 51 wt%, and 72 wt% with areal mass loadings of ~1.0, 2.1, and 5.0 mg Se cm⁻², respectively. A higher Se mass loading of 2.8 mg cm⁻² in the same Se content of 35 wt% was obtained by increasing the thickness of the composite films. For the control experiments, CNTs/CMK-3/S (CCS) composite electrodes with an S content of 35 wt% were prepared with a similar process (commercial sulfur powders and CNTs/CMK-3 were heated in a vacuum-sealed quartz tube at 300 °C for 5 hours).

Characterization

The morphology, energy-dispersive X-ray analysis (EDX) and elemental mapping were characterized by field emission scanning electron microscopy (SEM, JSU-8010). Elemental mappings for the fresh CCSe electrode and cycled electrodes were characterized by Phenom ProX SEM and JSU-8010 SEM, respectively. X-ray diffraction (XRD) patterns were recorded on an Ultima IV diffractometer with Cu Kα radiation. N₂ sorption isotherms were measured at 77 K on the analyzer (Quantachrome autosorb-iQ2). The specific surface areas and the pore size distributions were calculated using Brunauer-Emmett-Teller (BET) model and density function theory (DFT) model, respectively. Thermogravimetric analysis (TGA) was conducted on Netzsch STA449F3 with a heating rate of 10 °C min⁻¹ in nitrogen. X-ray photoelectron spectroscopy (XPS) measurements were performed on ESCALAB 250Xi instrument. UV–visible (UV-vis) absorption measurements were conducted on Perkin–Elmer Lambda 950. For Raman spectra analysis, electrolytes were sealed in quartz cuvettes in glove-box and Raman spectra were recorded on LabRam HR Evol using 532 nm excitation. The
ionic conductivity of electrolyte was measured by electrochemical impedance spectroscopy (EIS) using two symmetric titanium foil electrodes, and calculated using Equation (1):\(^2\)

\[
\sigma = \frac{d}{R*S} \tag{1}
\]

where \(d\), \(S\) represent the distance, surface area of the electrodes, and \(R\) represents the solution resistance.

**Electrochemical measurements**

The CR 2032 coin-type batteries were assembled using potassium metals (a small piece of K metal chunk was pressed into a film on a stainless steel spacer) as both anode and counter electrode and glass fiber membranes (Whatman GF/F) as separators in an argon-filled glove-box (Vigor, \(\text{H}_2\text{O} < 0.1 \text{ ppm, O}_2 < 0.1 \text{ ppm}\)). For the electrolyte preparation, potassium bis(trifluoromethylsulfonyl)imide (KTFSI, DoDoChem) was dried under vacuum at 100 °C for 48 hours to remove residual water. KTFSI dissolved in diethylene glycol dimethyl ether (DEGDME, DoDoChem) was used as the electrolyte. 1 wt% vacuum-dried KNO\(_3\) (100 °C for 48 hours) was subsequently added into the above electrolytes. The electrolyte/electrode ratio is fixed at \(\sim\)80 \(\mu\)L mg\(^{-1}\) in each cell. Galvanostatic discharge/charge tests were conducted on a LANHE system in a voltage range of 1.2 - 3.0 V (vs K/K\(^+\)). The energy density was determined by integrating the discharge voltage vs specific capacity curve. The energy density contribution solely from Se is calculated to be 1204 Wh kg\(^{-1}\) - 111 Wh kg\(^{-1}\) \times (65%/35%) = 998 Wh kg\(_{\text{Se}}\)\(^{-1}\) (1204 Wh kg\(^{-1}\) and 111 Wh kg\(^{-1}\) correspond to energy contributions from the composite cathode and CNTs/CMK-3, respectively. 65% and 35% are the mass contents of CNTs/CMK-3 and Se in the composite electrodes, respectively). And, the energy density is calculated to be 1204 Wh kg\(^{-1}\) \times 35% = 421 Wh kg\(^{-1}\) based on the composite cathode. Electrochemical impedance spectroscopy (EIS) measurements were taken on a Bio-Logic (SP-300) electrochemical workstation, with a frequency range from 100 kHz to 10 mHz and
an amplitude of 10 mV. For the transparent K-Se batteries, the potassium metals were loaded on titanium foils.

**Ex-situ characterization**

For ex-situ XRD, XPS, and UV-vis absorption analyses, the K-Se batteries at certain charge/discharge states were disassembled in argon-filled glove-box. For XPS characterization, the Se electrodes were sealed in a glass vessel and transferred into XPS equipment under Ar protection. For ex-situ XRD, the electrodes were kept in the glove-box for 30 minutes to evaporate the solvent and then sealed with Kapton tapes (~35 μm in thickness) for protection. For UV-vis absorption measurement, each discharged cathode was immersed in 3 mL DEGDME solvent, and the collected solution was sealed in a quartz cuvette and immediately removed from the glove-box for measurement.

**DFT Calculations**

The structures of \( \text{K}_2\text{Se}_x \) and \( \text{K}_2\text{S}_x \) were optimized based on density functional theory (DFT). The first-principles calculations were carried out using CASTEP.\(^5\) The generalized gradient approximation (GGA) exchanged-correlation functional by the Perdew-Burke-Ernzerhof (PBE) form\(^6\) was formulated, with cutoff energy set to 500 eV and convergence parameters for energy and force set to \( 10^{-5} \) eV and \(-0.03\) eV/Å, respectively. \( 2 \times 2 \times 3 \) and \( 2 \times 2 \times 2 \) k-point meshes were used for Brillouin zone summations for \( \text{K}_2\text{Se}_x \) and \( \text{K}_2\text{S}_x \), respectively. All the electronic properties were performed by the screened hybrid functional of Heyd, Scuseria, and Ernzerhof (HSE06) for a more accurate description of the electronic structure than GGA functional.\(^5,6\) The electrochemical voltages were calculated for \( \text{K}_2\text{Se}_x \) structures in accordance with Equation (2):

\[
E = \frac{[E_{\text{total}}(\text{K}_2\text{Se}_x) - E_{\text{total}}(\text{K}) - xE_{\text{total}}(\text{Se})]}{x} \quad (2)
\]

where \( x \) refers to the number of potassium transferred, \( E_{\text{total}}(\text{K}_2\text{Se}_x) \), \( E_{\text{total}}(\text{K}) \), \( E_{\text{total}}(\text{Se}) \) refer to the total energy of \( \text{K}_2\text{Se}_x \), K, and Se, respectively.
References

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Table S1. Fitted charge-transfer resistance ($R_{ct}$) of K-Se batteries with 1, 3, 5 M electrolytes.

|          | 1 M [Ω] | 3 M [Ω] | 5 M [Ω] |
|----------|---------|---------|---------|
| Initial  | 1050    | 1363    | 1627    |
| 1st cycle| 2646    | 3641    | 1683    |
| 2nd cycle| 4723    | 3372    | 1182    |
| 3rd cycle| 7023    | 4829    | 1374    |
Fig. S1. TGA curves of CCSe composites with a) 35 wt% and b) 71.5 wt% Se.

Fig. S2. Voltage profiles of CNTs/CMK-3 at a rate of 7.3 mA g\(^{-1}\) in 5 M electrolyte.
Fig. S3. Long-term Cycling performance of the K-Se batteries at 0.2 C and Se mass loadings of 1.0 and 2.8 mg cm$^2$. Solid and empty squares represent the discharge and charge capacities, respectively.
Fig. S4. Band structures of a-e) Se and f-j) S species from DFT calculations.