Supporting Information

K₃SbS₄ as a Potassium Superionic Conductor with Low Activation Energy for K–S Batteries

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Experiment section:

1. Chemicals:

Sb$_2$S$_3$ (Sigma-Aldrich, >99% purity), K$_2$S (STREM, >95% purity), S (Sigma-Aldrich) and WS$_2$ (Sigma-Aldrich) were dried in the chemical drier under vacuum at 150 °C for 2 days before use. Potassium (K) (98%, Sigma-Aldrich) was used directly. Carbon paper (P50, Fuel Cell Store) was dried under vacuum at 120 °C. All the chemicals were stored in an argon-filled glovebox.

2. Synthesis of β-K$_3$SbS$_4$ and K$_3$-xSb$_{1-x}$W$_x$SbS$_4$ (x=0, 0.04, 0.06, 0.08, 0.10 and 0.12):

Herein, we have developed an efficient method to synthesize β-K$_3$SbS$_4$ via a one-step solid-state reaction: 3K$_2$S + Sb$_2$S$_3$ + 2S = 2K$_3$SbS$_4$. To be more specific, 169.86 mg Sb$_2$S$_3$ (0.5 mmol), 171.34 mg K$_2$S (1.575 mmol) and 35.2 mg S (1.1 mmol) were weighted, and hand ground for several minutes with a mortar and pestle. Notably, a 10% excess of S was required due to its evaporation during the tube sealing process, and a 5% excess of K$_2$S was used because of the chemical impurity and the loss of K$_2$S during the synthesis process. The obtained mixture was hot pressed at 200 °C under 400 MPa into a pellet. Since the reactants are moisture-sensitive, the weighing, grinding, and pressing processes were conducted under Ar atmosphere in the glovebox (oxygen level <1.5 ppm; water level <0.5 ppm). The sample pellet was then placed in an alumina tube and sealed in an evacuated quartz tube. Eventually, the pellet was steadily heated at a rate of 2 °C/min to 550 °C, held at this temperature for 12 h, and subsequently cooled naturally to room temperature.

The W-substituted version of K$_3$-xSb$_{1-x}$W$_x$SbS$_4$ (x=0.04, 0.06, 0.08, 0.10 and 0.12) was prepared via the abovementioned reaction by replacing a quantitative amount of Sb$_2$S$_3$ with WS$_2$. Moreover, the mixture pellet was gradually heated at a rate of 2 °C/min to 800 °C, held at this temperature for 24 h, and subsequently cooled naturally to room temperature.

3. Geometrical-topological analyses of β-K$_3$SbS$_4$:

The sites labeled with numbers are Voronoi nodes that have equal distance to the surrounding anions and their calculated coordinates are listed as the ZA sites in Table S1. The radius of these nodes (R$_{sd}$) is larger than that of the mobile cation (K$^+$), ensuring enough space for cation occupancy and acting as voids. K ions have been ignored to compute the largest radius of the free sphere that can pass through the remaining structure formed by framework polyanions (SbS$_4^{3-}$), which is defined as “channel size” and shown in Figure 1b.

The percolation radius of diffusion channels was then quantified, which is crucial for the K ions migration barrier. In general, a migration pathway should satisfy a requirement as: R$_{ad}$$>$$\gamma$ (R$_{cation} + \text{average}$), considering the polarizability of both cations and anions.\[1,2] To be more specific, R$_{ad}$ is the radius of the cross-sectional channel of bottleneck; R$_{cation}$ is the radius of the mobile cation; R$_{average}$ is the average radius of the surrounding atoms, and $\gamma$ is called polarization coefficient in the range of 0.85~0.90. Herein, the channel sizes for all pathways (R$_{ad}$) are larger than 2.748 Å when K cations migrate from one void site to a normal cation position (R$_K^+$=1.52 Å, R$_S^2$ =1.70 Å, $\gamma$=0.85), making cation migration possible and constructing the two-dimensional K ion diffusion network.
4. Fabrication of $K_{2.92}Sb_{0.92}W_{0.08}S_4$ cathode and super-P cathode:

The $K_{2.92}Sb_{0.92}W_{0.08}S_4$ cathode was fabricated by mixing the active material of $K_{2.92}Sb_{0.92}W_{0.08}S_4$ powder, super-P carbon powder (MTI Corporation) and poly(vinylidene fluoride) (PVDF) (Sigma-Aldrich) at a weight ratio of 70:20:10 in N-methylpyrrolidone (NMP) (Sigma-Aldrich) drops. The slurry was ground thoroughly and then pasted onto the carbon paper, followed by drying at 90 °C for 48 h under vacuum. The super-P cathode was fabricated by following the same process, while only super-P carbon powder and PVDF were mixed at a weight ratio of 80:20 in the NMP solvent.

5. Alternating current (AC) impedance measurements:

The densified pellet of the material was prepared by hot-pressing the solid electrolyte powder at 400 MPa under 150 °C for 1 h. Then the pellet was heated at 400 °C for 1 h to reduce the grain boundary resistance. After the sintering process, the sample pellet was coated with Pt on both sides as blocking electrodes. Since the samples are air sensitive, the temperature-dependent AC impedance measurements were conducted utilizing the home-made airtight and high-temperature adapted Swagelok electrochemical cell setup. The electrochemical resistance (EIS) was measured by applying an AC voltage with an amplitude of 20 mV to the cell and the frequency range is from 1 MHz to 0.01 Hz. The temperature was controlled by a muffle furnace (Thermo Scientific) and was monitored by a digital thermo couple. EIS data was further analyzed by fitting it to an equivalent electrical circuit model through the ZView software.

6. Characterizations:

Powder X-ray diffraction (PXRD) patterns were recorded using an X-ray diffractometer (Bruker D8 Advance, Cu Kα source, 40 kV, 40 mA). The Kapton film was used to protect the air-sensitive samples from air exposure. Synchrotron X-ray diffraction (SXRD) was performed on the Beamline 11 ID-B of the Advanced Photon Source, Argonne National Laboratory, using a wavelength of 0.1173 Å. The powder was sealed in a quartz capillary due to the air sensitivity of the sample. Differential scanning calorimetry (DSC) was used under a dry nitrogen flow. 5-10 mg samples for DSC measurements were sealed in an aluminum hermetic pan in an argon-filled glovebox. The cooling and heating rates were 5 °C/ min. Raman measurements were conducted on a Renishaw inVia microscope with a 633 nm excitation laser and the samples are prestored in a homemade air-free holder. X-ray photoelectron spectroscopy (XPS) spectra were collected on a Kratos Axis Ultra XPS spectrometer using an Al Kα radiation. All the spectra were calibrated with reference to the C-C peak binding energy at 284.8 eV. The curves were fitted using the CasaXPS software with a combined Gaussian-Lorentzian profile after subtracting the background. Scanning electron microscopy (SEM) was performed at an FEI Quanta 200 SEM with an accelerating voltage of 5 kV. Pellet samples were transferred to an air-free SEM holder before SEM observation. UV-vis (Lambda 950 Spectrometer, PerkinElmer) analysis were used to characterize the soluble polysulfide species in DEGDME.
7. Linear sweep voltammetry (LSV) measurements:

The electrochemical window of $K_{2.92}Sb_{0.92}W_{0.08}S_4$ was measured by LSV at the scan rate of 0.1 mV/s. The measurement was performed on the two-electrode cell composed of a K metal reference/counter electrode, $K_{2.92}Sb_{0.92}W_{0.08}S_4$ mixed with 20 wt% super-P carbon as the working electrode, and 1 M KFSI/DME electrolyte. The measurement was carried out within a voltage range of 0.5-4.0 V (vs. $K^+/K$) to avoid the interference of K plating/stripping. Typically, the measurements were conducted by increasing the voltage from the open circuit potential (OCP) to 4.0 V and decreasing the voltage from OCP to 0.5 V in two separate cells. The intrinsic electrolyte window of 1 M KFSI/DME was estimated by using the blank super-P cathode within a voltage range of 0.5-4.5 V (vs. $K^+/K$).

8. Preparation and characterization of potassium polysulfide ($K_2S_5$):

The long-chain potassium polysulfide ($K_2S_5$) was synthesized by mixing commercial short-chain polysulfide of $K_2S_3$ (Acros) and S with a mole ratio of 1:2, and adding the diethylene glycol dimethyl ether (DEGDME, Sigma-Aldrich) solvent, followed by thorough stirring for 30 minutes at room temperature. After reaction, a deep brown solution was formed.

9. Fabrication of the $K_2S_5/K_{2.92}Sb_{0.92}W_{0.08}S_4/K_2S_5$ symmetric cell:

The carbon paper was punched into the desired size (∼0.2 cm$^2$) and soaked into the $K_2S_5$/DEGDME solution. The sintered $K_{2.92}Sb_{0.92}W_{0.08}S_4$ pellet was sandwiched by $K_2S_5$-loaded carbon paper on each side and placed in a home-made Swagelok cell. A compression spring is used to ensure good contact between the carbon paper and the sample pellet.

10. Solid K-S cell construction and electrochemical performance evaluation:

As shown in the schematic configuration of the two-compartment cell (Figure S13), a polymer laminated $K_{2.92}Sb_{0.92}W_{0.08}S_4$ was adopted to separate the anode from the cathode. The $K_{2.92}Sb_{0.92}W_{0.08}S_4$ disc with a diameter of 13 mm and a thickness of 0.8 mm was polymer-sealed to a stainless-steel ring. The cathode for the solid K-S cell was constructed by placing one piece of carbon paper into the cavity of the bottom part followed by the addition of 30 μL of as-prepared 0.02 M $K_2S_5$/DEGDME catholyte. The KTFSI (1 M) was added as the supporting salt in the catholyte. A Celgard separator soaked with 30 μL 1 M KFSI/DME anolyte was placed between the metallic K anode and the laminated $K_{2.92}Sb_{0.92}W_{0.08}S_4$ pellet to avoid direct contact.
Table S1. Atomic and voids coordinates obtained from geometrical-topological analyses using ToposPro software.

| Atom | Wyckoff Site | x     | y     | z     |
|------|--------------|-------|-------|-------|
| K1   | 8b           | 0.2232| 0.9699| 0.4886|
| K2   | 4a           | 1     | 0.7007| 0.4808|
| Sb1  | 4a           | 1     | 0.75467| 0.98040|
| S1   | 4a           | 1     | 0.9091| 0.7765|
| S2   | 8b           | 0.1178| 0.7692| 0.15560|
| S3   | 4a           | 1     | 0.571 | 0.8361|
| ZA1  | 8b           | 0.22498| 0.97455| 0.48937|
| ZA2  | 8b           | 0.57920| 0.83682| 0.98662|
| ZA3  | 8b           | 0.73524| 0.06419| 0.38321|
| ZA4  | 8b           | 0.74114| 0.01690| 0.20310|
| ZA5  | 8b           | 0.70299| 0.00698| 0.09035|
Table S2. Rietveld refinement results for the as-prepared $\beta$-K$_3$SbS$_4$.

| Atom | Wyckoff Site | x      | y      | z      | Occupancy | Beq  |
|------|--------------|--------|--------|--------|-----------|------|
| K1   | 8b           | 0.2232 | 0.9699 | 0.4886 | 1         | 7.5(7) |
| K2   | 4a           | 1      | 0.7007 | 0.4808 | 1         | 7.7(11) |
| Sb1  | 4a           | 1      | 0.75467| 0.9804 | 1         | 5.6(4)  |
| S1   | 4a           | 1      | 0.9091 | 0.7765 | 1         | 4.8(11) |
| S2   | 8b           | 0.1778 | 0.7692 | 1.1556 | 1         | 4.3(7)  |
| S3   | 4a           | 1      | 0.571  | 0.8361 | 1         | 4.6(11) |

Space group: Cmc$_2$$_1$  $a$= 10.7306(16) Å, $b$= 11.2788(16) Å, $c$=7.7091(11) Å, $R_{wp}$= 9.12%

Table S3. Rietveld refinement results for the high-temperature phase of $\alpha$-K$_3$SbS$_4$.

| Atom | Wyckoff Site | x      | y      | z      | Occupancy | Beq   |
|------|--------------|--------|--------|--------|-----------|------|
| K1   | 6b           | 0      | 0.5    | 0.5    | 1         | 14.8(3) |
| Sb1  | 2a           | 0      | 0      | 0      | 1         | 3.64(11) |
| S1   | 8c           | 0.178  | 0.178  | 0.178  | 1         | 5.1(2)  |

Space group: I-43m  $a$= 7.84765(14) Å, $R_{wp}$= 5.06%
Table S4. Fitted parameters of the equivalent circuit model for the Nyquist plot of $K_3\text{SbS}_4$ at room temperature.

| Element    | Value                  |
|------------|------------------------|
| $R_s$      | 3 (Ω)                  |
| $R_t$      | $2.7872 \times 10^5$ (Ω) |
| CPEd-T     | $2.6379 \times 10^{-7}$ (F) |
| CPEd-P     | 0.75365                |
| CPEd-T     | $2.686 \times 10^{-10}$ (F) |
| CPEd-P     | 0.78129                |

Figure S1. Raman spectra of as-synthesized $K_3\text{SbS}_4$, $K_{2.96}\text{Sb}_{0.96}\text{W}_{0.04}\text{S}_4$, $K_{2.92}\text{Sb}_{0.92}\text{W}_{0.08}\text{S}_4$ and the corresponding starting materials. Notably, $K_2\text{S}$ does not show any Raman peaks in the range of 250-600 cm$^{-1}$.
Figure S2. Rietveld refinement profiles of SXRD data measured at 400 °C. Black dots and red lines denote the observed and calculated XRD patterns, respectively. The green sticks mark the position of the reflections for K$_3$SbS$_4$. The difference between the observed and calculated patterns is indicated by the grey line. All the peaks match those of cubic K$_3$SbS$_4$, indicating a pure phase of cubic K$_3$SbS$_4$. The inset is the crystal structure of α-K$_3$SbS$_4$ with the unit cell outlined.
Figure S3. Raman spectra of $K_{3-x}Sb_{1-x}W_xS_4$ ($x=0.04, 0.06, 0.08, 0.10$ and $0.12$).
Figure S4. Nyquist plot of K$_{2.92}$Sb$_{0.92}$W$_{0.08}$S$_4$ sample at room temperature, showing the experimental data (black) and the fitting result from the equivalent circuit model (red). $R_s$ is the inner resistance of the set-up (cell + wire); $R_t$ is the total resistance of the electrolyte, including both the bulk resistance and grain boundary resistance; CPE$_{dl}$ is the constant phase element of the blocking electrode-electrolyte interface; CPE$_d$ is the constant phase element of the two blocking electrodes.
Figure S5. Cross-sectional SEM images of the $K_{2.92}Sb_{0.92}W_{0.08}S_4$ pellet after (a) hot press and (b) cold press. It is shown that hot-pressed process can make the pellet more compact with the increased relative density when compared with cold-pressed one. To be more specific, the density of hot-pressed pellet is 2.58 g/cm$^3$ and the relative density is estimated to be 98%. In comparison, the relative density of the cold-pressed pellet is only 89%.
Figure S6. PXRD patterns of K$_{3-x}$Sb$_{1-x}$W$_x$S$_4$ (x=0.04, 0.06, 0.08, 0.10 and 0.12). It is noted that the products contain some impurities when W dopant amount x is larger than 0.08. These structural data suggest that the introduction amount of W$^{6+}$ in K$_{3-x}$Sb$_{1-x}$W$_x$S$_4$ is limited. The formation of impurities may inhibit K ion migration and thus lower the ionic conductivity.
Figure S7. Rietveld refinement profiles of SXRD data for orthorhombic $K_{2.92}Sb_{0.92}W_{0.08}S_4$. Black dots and red lines denote the observed and calculated XRD patterns, respectively. The green sticks mark the position of the reflections for $K_3SbS_4$. The difference between the observed and calculated patterns is indicated by the grey line.
Table S5. Rietveld refinement results for the prepared room-temperature $K_{2.92}Sb_{0.92}W_{0.08}S_4$.

| Atom | Wyckoff Site | x    | y    | z    | Occupancy | Beq   |
|------|--------------|------|------|------|-----------|-------|
| K1   | 8b           | 0.2232 | 0.9699 | 0.4886 | 0.926(4) | 1.0(4) |
| K2   | 4a           | 1    | 0.7007 | 0.4808 | 0.992(5) | 4.7(8) |
| Sb1  | 4a           | 1    | 0.75467 | 0.9804 | 0.919(4) | 1.51(2) |
| W1   | 4a           | 1    | 0.75467 | 0.9804 | 0.079(5) | 20(14) |
| S1   | 4a           | 1    | 0.9091 | 0.7765 | 1        | 2.0(6) |
| S2   | 8b           | 0.1778 | 0.7692 | 1.1556 | 1        | 2.4(5) |
| S3   | 4a           | 1    | 0.571  | 0.8361 | 1        | 1.9(6) |

Table S6. Rietveld refinement results for the cubic $K_{2.92}Sb_{0.92}W_{0.08}S_4$.

| Atom | Wyckoff Site | x    | y    | z    | Occupancy | Beq   |
|------|--------------|------|------|------|-----------|-------|
| K1   | 6b           | 0    | 0.5  | 0.5  | 0.979(12) | 13.7(4) |
| Sb1  | 2a           | 0    | 0    | 0    | 0.921(4) | 3.3(4) |
| S1   | 8c           | 0.178 | 0.178 | 0.178 | 1        | 5.0(3) |
| W1   | 2a           | 0    | 0    | 0    | 0.079(6) | 1.8(5) |
Figure S8. DSC data of $K_{2.92}Sb_{0.92}W_{0.08}S_4$ collected at a heating rate of 5 °C min$^{-1}$ in a flow of dry nitrogen gas.
Figure S9. Rietveld refinement profiles of SXRD data for cubic $K_{2.92}Sb_{0.92}W_{0.08}S_4$ measured at 400 °C. Black dots and red lines denote the observed and calculated XRD patterns, respectively. The green sticks mark the position of the reflections for $K_3SbS_4$. The difference between the observed and calculated patterns is indicated by the grey line.
Figure S10. LSV curve of the K/1 M KFSI-DME/super-P at 20 °C at the scan rate of 0.1 mV/s. In the light blue region, the current density is below 10 μA cm⁻².
Figure S11. PXRD pattern of the commercial short-chain polysulfide. The as-received polysulfide powder match well with the crystalline \( \text{K}_2\text{S}_3 \).
**Figure S12.** UV-vis spectrum of long-chain potassium polysulfide (K₂S₅) in DEGDME. Inset: image of K₂S₅ dissolved in DEGDME. For UV-vis analysis, the S₅²⁻ was observed as the absorption peak at 317 nm. S₅²⁻ then disproportionated into S₄²⁻ (446 nm) and S₆²⁻, which later generated S₃⁻ (617 nm).
Figure S13. (a) The sequential 100 voltage profiles of the K$_2$S$_5$/K$_{2.92}$Sb$_{0.92}$W$_{0.08}$S$_8$/K$_2$S$_5$ symmetric cell at 20 °C with the current density of 5 $\mu$A cm$^{-2}$, 10 $\mu$A cm$^{-2}$ and 25 $\mu$A cm$^{-2}$. (b) Typical voltage profiles of the room-temperature (20 °C) K$_2$S$_5$/K$_{2.92}$Sb$_{0.92}$W$_{0.08}$S$_8$/K$_2$S$_5$ symmetric cell performed at a current density of 5 $\mu$A cm$^{-2}$, 10 $\mu$A cm$^{-2}$, 25 $\mu$A cm$^{-2}$, 50 $\mu$A cm$^{-2}$, and 0.1 mA cm$^{-2}$. 
Figure S14. The configuration of two-compartment K-S cell in which a polymer-laminated $K_{2.92}Sb_{0.92}W_{0.08}S_4$ was adopted to separate the anode part from the cathode part.
**Figure S15.** Ex-situ Raman spectra of the cathodes: 1st discharge (I, black line), 1st charge (II, red line), 2nd discharge (III, blue line), and 2nd charge (IV, purple line).
Figure S16. Cycling performance and coulombic efficiencies of solid K-S cell at a current density of 260 mA g⁻¹ sulfur. The specific capacities are calculated based on the mass of sulfur.
Figure S17. (a) Raman spectrum and (b) XPS spectrum of 1st full discharged cathode after aging for 1 week. Two peaks centered at 161.7 eV and 163.2 eV could be assigned to the S 2p_{3/2} peak of terminal (S_{T}^{-1}) and bridging (S_{B}^{0}) sulfur of polysulfide species, respectively. Peaks located above 169 eV are mainly derived from the sulfate compound which is the main component of the SEI layer.\textsuperscript{[4–6]}
Scheme S1. Schematics of reaction mechanism for K-S batteries during cycling. Here, the abbreviation “DC” represents the discharging procedure and “C” represents the charging process.
Figure S18. (a) XPS spectra of the S 2p region on the cycled K metal anode surface of the solid K-S cell after 672 h operation. Inset is the optical image of the cycled K anode. (b) XPS spectra of the S 2p region on the K metal anode of the K-S cell without solid electrolyte after the initial cycle. Inset is the digital photograph of K anode with a dark brown color after cycling. The thick red lines represent the fitted results.
Figure S19. Typical voltage profile of the initial discharge and charge of K-S cell in 1 m KTFSI/DME without solid electrolyte. The current density is 260 mA g\(^{-1}\)\text{_{sulfur}}. The cell exhibits a typical endless charge behavior due to the polysulfide shuttling phenomenon.
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