Supporting Information

Chemical Synthesis of K_2S_2 and K_2S_3 for Probing Electrochemical Mechanisms in K-S Batteries

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1. Experimental section

1.1 Synthesis of K_2S_2, K_2S_3 and K_2S_5

The K_2S_3 were synthesized by the method of precipitation. The K (sigma) and sublime sulfur (Alfa Aesar) were weighted at a mole ratio of 2:3 and added into DME. The K and sulfur were stirred overnight under the protection of argon. The DME was evaporated and the precipitates were collected. The K_2S_2 were synthesized by mixing as-prepared K_2S_3 and K_2S (Sterm Chemical, Inc.) with 1:1 mole ratio and placed in quartz tube. The tube was flame-sealed under vacuum and maintained at 285℃ for 48 h. Then the tube was removed from the furnace and taken into argon filled glove box for collection of K_2S_2. The K_2S_5 were synthesized by mixing as-prepared K_2S_3 and sublime sulfur with 1:2 mole ratio in quartz tube, flame-sealed and maintained at 196 ^oC for 40 h. The K_2S_4 and K_2S_6 were attempted to be synthesized but failed.

1.2 Characterization of potassium polysulfide

K_2S, K_2S_2 and K_2S_3 were characterized by X-ray diffractometer (Bruker D8 Advance, Cu-Kα source, 40 kV, 50 mA). A polymer thermoplastic sealant (3M Company) was applied to seal the XRD holder against the ambient air. UV-vis (Lambda 950 Spectrometer, PerkinElmer) analysis were used to characterize the soluble polysulfide species in DME or electrolytes.

The solubility of K_2S_2 and K_2S_3 in DME were determined by the following experiments: 200 mg K_2S_2 or K_2S_3 was added into 10 mL DME to get a saturated solution and stirred in

room temperature for 12 h. The suspension were filtered by filter (thermos scientific Titan3, 45 μm) to get transparent soluble phase. Then the DME was evaporated and the residues were collected and weighted.

1.3 Synthesis of the 70S/30CNT composites

The cathode materials consist of multiwalled carbon nanotube (Cheap Tubes Inc.) and sulfur, which abbreviated as 70S/30CNT, were fabricated through a melt-diffusion method. In a typical experiment, 0.7g sublimed sulfur and 0.3 g carbon nanotube were weighted and ground homogeneously in a mortar. The mixture was put into a hydrothermal reactor, under the protection of argon. Then, the composites were heated to 160 ℃ at a rate of 50 ℃ min^{-1}. The temperature was maintained for 12 h. The 70S/30CNT composite was obtained after natural cooling.

1.4 Assembly of K-S cells

The Nafion-K^+ membrane was firstly prepared using a previously reported method[1]. To exchange the original cation (H^+) of Nafion to K^+, Nafion 211 membranes (25 um thickness, Dupont) were heated in a 0.5 M KOH solution of dimethylsulfoxide (DMSO) (> 99.99 %, Sigma-Aldrich) and water (volume ratio=1:1) at 60 ℃ for 2 h. The residual solvent and KOH were removed by stirring the membrane in distilled water at 90 ℃ for 2 h. The Nafion-K^+ membrane were dried under vacuum at 100 ℃ overnight and then soaked for 12 h in the battery electrolyte before use.

The potassium bis(fluoroslufonyl)imide (KFSI) (> 99.9 %, water content < 50 ppm, Fluolyte) were dried under high vacuum at 100 ℃ for 48 h prior to use. 1,2-

dimethoxyethane (DME) (BASF) was stored over 3 Å molecular sieves (Sigma-Aldrich). The electrolyte of KFSI/DME (0.5 mr, 0.6 mr) were prepared by mixing KFSI and DME with the salt/solvent mole ratios of 0.5 or 0.6.

The cathodes were fabricated by mixing the carbon nanotube/sulfur, K_2S_3, K_2S_2 or K_2S, Super P carbon powder (MTI Corporation) and poly(vinylidenefluoride) (PVDF) (Sigma-Aldrich) at a weight ratio of 70:20:10 in N-methylpyrrolidone (Sigma-Aldrich). The slurry was then pasted onto the Al foil (99.99%, Alfa Aesar) and dried at 60 ℃ for 12 h under vacuum (for carbon nanotube cathode) or room temperature for 48 h under argon protection (for K_2S, K_2S_2, K_2S_3 cathode). The loading weight of sulfur was 1.29 mg (0.478 mg cm^{-2}) per electrode. The loading weight of K_2S_n (n=1,2,3) was 1.0-1.5 mg (1 mg cm^{-2}-0.85 mg cm^{-2}) per electrode. The coin cells were fabricated in Argon-filled glovebox (< 0.5 ppm of H_2O and < 1.0 ppm of O_2) by stacking potassium metal anode (99.5 %, Sigma-Aldrich), trilayer (polypropylene-polyethylene-polypropylene) membrane (25 um thickness, Celgard), Nafion-K^+ membrane, commercial carbon paper (H2315, Freudenberg FCCT SE & Co. KG), cathode electrode and adding 80 uL KFSI-DME (0.5 mr). The electrolyte/sulfur ratio was 62.0 mg uL^{-1}. The commercial carbon paper was used as the upper current collector[2].

The double separators coin cells were fabricated by stacking potassium metal anode, Celgard, Nafion-K^+ membrane, cathode electrode, Celgard, commercial carbon paper.

1.5 Electrochemical measurement of K-S cells

Galvanostatic charge and discharge tests and galvanostatic intermittent titration

technique (GITT) tests were carried out using a MTI battery analyzer (BST8-WA) within the voltage range of 1.2-3.0 V (vs K^+/K).

1.6 Chemical reactivity of KSFI salt

The chemical stability of KFSI salt is studied by the following experiments and NMR. (1) The KFSI salt was mixed with the methanol-D. (2) The KFSI and K_2S_3 were dissolved in DME. (3) The KFSI salt (82 mg) was mixed with K_2S_3 (32.5 mg) in DME solvent (2.5 mL), 18-Crown-6 (200 mg) was added to promote the dissolution of K_2S_3 (mole ration of KFSI/K_2S_3/18C6=1/0.5/2). The results are summarized in Figure S2.

NMR 19F NMR were carried out on a 400 MHz NMR spectrometer (Bruker, Avance III) after mixing 50 uL soluble phase mentioned above into 450 uL MethonalD (99.9 atom % D, Sigma-Aldrich).

Reference:

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Table S1. Electrochemical performance of reported K-S batteries

Cathode materials	Electrolyte	Capacity/ mAh g^{-1}	Discharge plateaus/V	Discharge product
polyaniline coated ordered mesoporous carbon/sulfur [3]	1 M $KClO_4$ /TEGDME	512.7	1.8, 1.66	K_2S_3
Catholyte: 1.5 M KTFSI or KPF_6 /tetraglyme /$K_2S_{1.52}$[4]	β''-Al_2O_3 solid electrolyte	402	2.1	K_2S_2, K_2S_3
3-dimensional freestanding carbon nanotube+ K_2S_x catholyte[5]	0.5 M KTFSI /DEGDME	400	2.1, 1.8	K_2S_3
Sulfur-carbon nanotube fiber[6]	1 M KCF_3SO_3 /TEGDME	1144	1.95, 1.4	K_2S

Table S2. Theoretical capacities of sulfur battery

Discharge	Number of electrons involved in	Theoretical capacity

products	charge transfer per sulfur (e^-)	(mAh g^{-1})
K_2S_6	1/3	279.2
K_2S_5	2/5	335.0
K_2S_4	1/2	418.8
K_2S_3	2/3	558.3
K_2S_2	1	837.5
K_2S	2	1675.0

The theoretical discharge capacities are calculated according to the equation C=nF/3.6M, where n is the number of electrons involved in the charge transfer, F is the Faraday constant, M is the formula weight of sulfur.

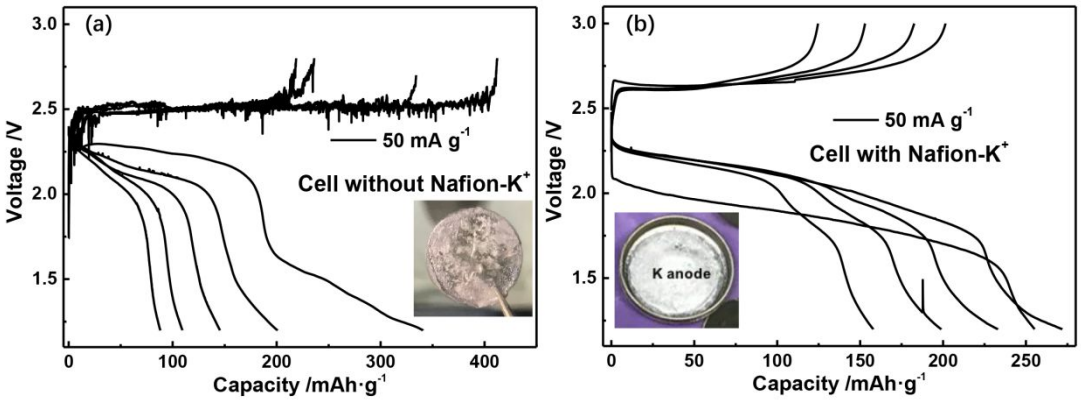

Figure S1. Galvanostatic profile of cell without Nafion-K^+ (a) or with Nafion-K^+ (b), Inset: the K anode after cycling.

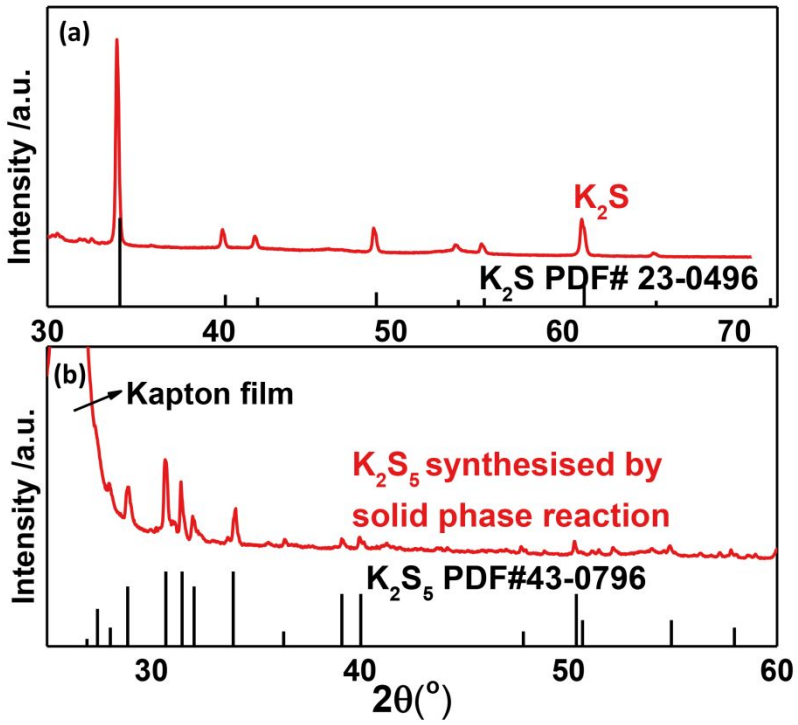

Figure S2. XRD characterization of commercially available K_2S (a) and as-prepared K_2S_5 (b).

NMR was used to investigate the side reaction between the K_2S_3 and KFSI-DME, the 18C6 was used to coordinate KF that could be generated by the side reaction between the KFSI and K_2S_3. The amount of 18C6 was designed to be enough to coordinate all the K species, so the KF can be released into the solution and detected by NMR[7].

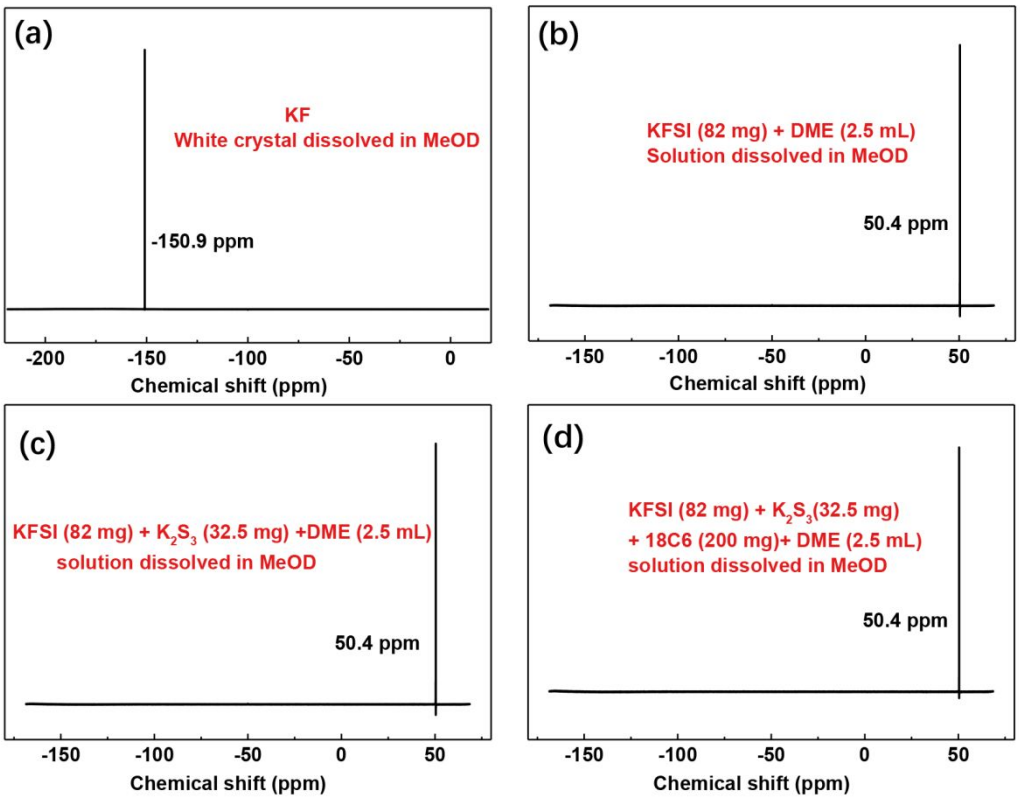

Figure S3. The 19F NMR spectrum of (a) KF dissolved in MeOD, (b) pure 0.5 M KFSI-DME electrolyte, (c) supernatant from mixture of K_2S_3 and KFSI-DME electrolyte, (d) supernatant from mixture of K_2S_3, 18C6 and 0.5 M KFSI-DME electrolyte.

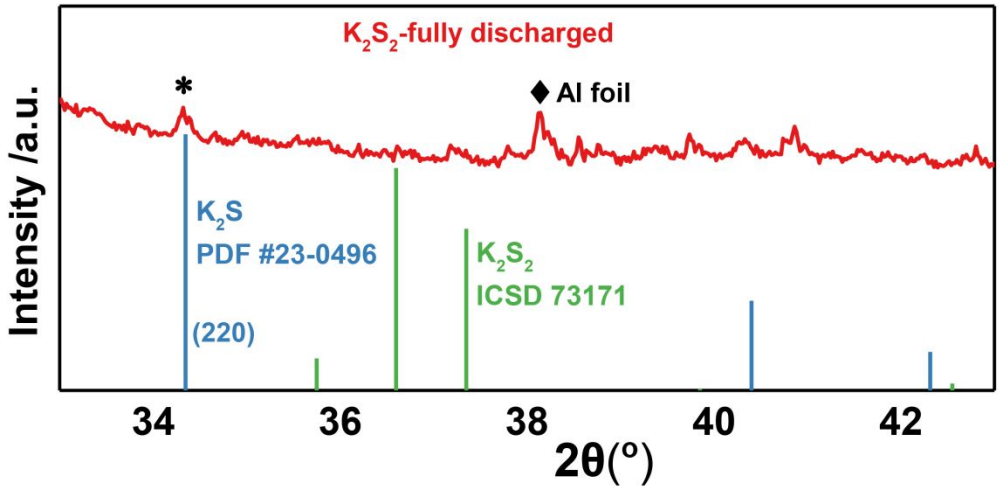

Figure S4. XRD characterization of fully discharged K_2S_2 cathode, the star and diamond indicate the peaks of K_2S_2 and Al foil (current collector).