

## **Supplementary Information**

### **High performance potassium-sulfur batteries based on sulfurized polyacrylonitrile cathode and polyacrylic acid binder**

Jang-Yeon Hwang,<sup>a</sup> Hee Min Kim,<sup>a</sup> Yang-Kook Sun<sup>\*,a</sup>

<sup>a</sup>Department of Energy Engineering, Hanyang University, Seoul 04763, South Korea

Corresponding author: yksun@hanyang.ac.kr

## **Experimental Method**

### **Synthesis of sulfurized carbonized polyacrylonitrile (SPAN) composite cathode**

Acrylonitrile and 2,2'-Azobis(2-methylpropionitrile) (Sigma-Aldrich, USA) were added to a 1:1 (w/w) solution of acetonitrile (Junsei Chemical Co.) in deionized water. The solution was stirred for 10 min and heated at 80 °C for 2 h to initiate polymerization. After the polymerization was complete, the polymer was filtered using centrifugation and then vacuum dried overnight. The obtained polymer (PAN) was homogeneously mixed with elemental sulfur (PAN:sulfur = 1:4 weight ratio). The PAN and sulfur mixture was converted to the sulfurized polyacrylonitrile (SPAN) powder by conducting calcination at 350 °C for 6 h in argon gas. CPAN was synthesized by conducting calcination of PAN at 350 °C for 6 h in argon gas.

### **Material characterization**

The morphology of the as-prepared PAN and sulfurized PAN powder was observed via scanning electron microscopy (SEM, JSM 6400, Jeol Ltd., Japan). Transmission electron microscopy (TEM, JEM2010, JEOL) was carried out to determine the localized particle morphologies and for EDX mapping. SPAN was analyzed by attenuated total reflection Fourier transform infrared (ATR-FT-IR, Nicolet 6700, Thermo Fisher Scientific, USA). The atomic ratio of SPAN was analyzed with an elemental analyzer (EA, Flash EA 1112, Thermo Fisher Scientific, USA). Thermogravimetric analysis (TGA, TG 209 F3, NETZSCH-Gerätebau GmbH, Germany) was used to observe the change in the weight of sulfur and SPAN. The charge/discharge products of the SPAN composite cathode

at different SOC or DOD in KSBs were analyzed via Raman spectroscopy (Renishaw, United Kingdom). X-ray photoelectron spectroscopy (XPS, PHI5600, Perkin-Elmer, USA) measurements were performed in macro mode (3 mm x 3 mm). For Raman and XPS measurements, the samples were first transferred into a hermetically sealed transfer chamber in a glovebox and then transferred into the XPS machine, preventing exposure to air or water.

### **Electrochemical measurements**

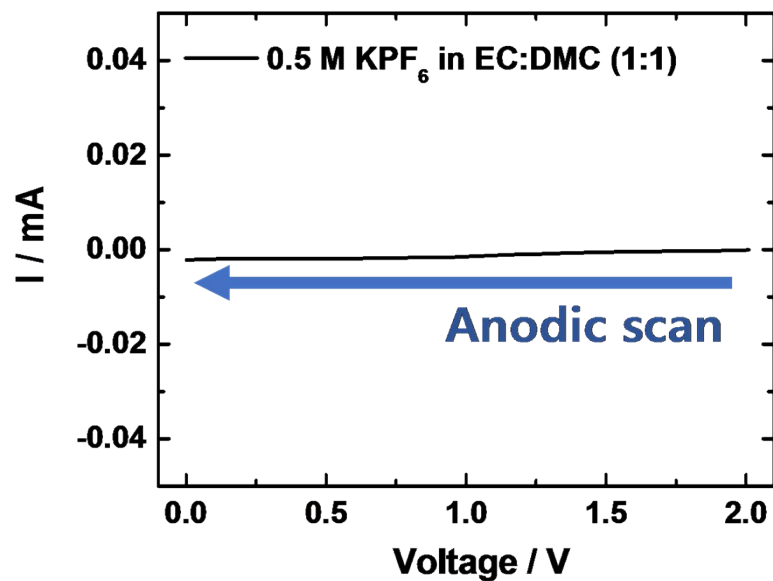
Electrochemical testing was performed in a CR2032 coin-type cell using potassium metal as the anode for half-cell tests. The SPAN and CPAN electrodes were fabricated by blending the as-synthesized cathode material (80 wt.%), carbon black (10 wt.%), and binder (10 wt.%). The resulting slurry was applied to an aluminum foil and dried at 60 °C for 12h in a vacuum oven. The fabricated cathode and the potassium metal anode were separated using a glass filter separator (ADANTEC, USA) to prevent short circuiting. Electrochemical characterization was conducted using a 2032 coin-type cell in a 0.5 M KPF<sub>6</sub> solution in ethylene carbonate and dimethyl carbonate (50:50 by volume). All cells were prepared in an argon-filled dry box. The cells were typically cycled in constant current mode at 0.5 C-rate with various discharge cut-off voltages (0.1, 0.3, 1.0–3.0 V versus K/K<sup>+</sup>). The specific capacity was calculated based on the weight of sulfur. Electrochemical impedance spectroscopy was performed using a multichannel potentiostat (Bio-Logic, VMP3) over the frequency range of 1 MHz to 1 Hz. Linear sweep voltammetry (LSV) and cyclic voltammetry (CV) was also performed using a multichannel potentiostat (Bio-Logic, VMP3).

**Table S1.** Elemental analysis result of polyacrylonitrile (PAN) and sulfurized polyacrylonitrile (SPAN).

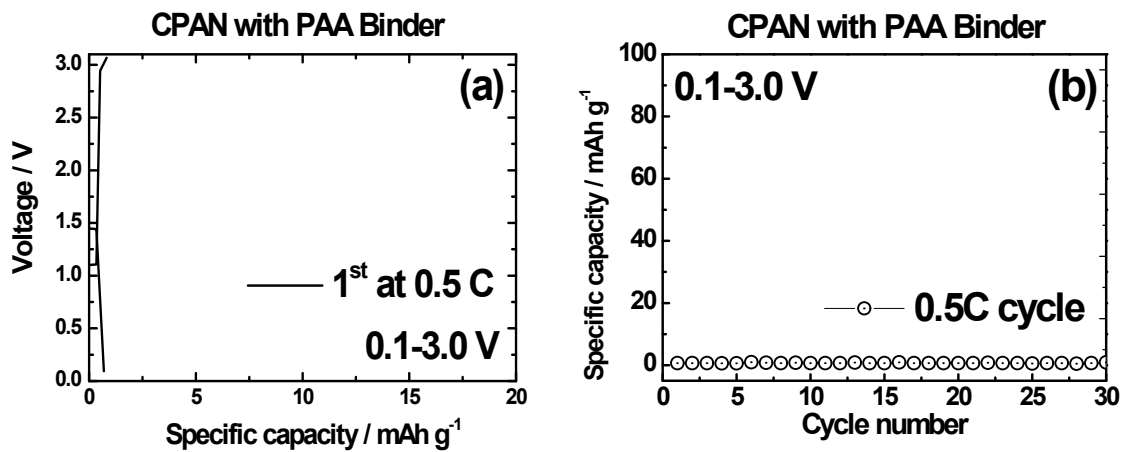
(wt.%)	C	H	N	S
PAN	68.1	6.0	26.9	0
SPAN	40.9	0.8	12.9	45.5

**Table S2.** FT-IR peak information of SPAN.

Peak (cm <sup>-1</sup> )	Information
1549	C=C Asymmetric stretch
1502	C=C Symmetric stretch
1431	C=N Asymmetric stretch
1363	C–C Deformation
1250	C=N Symmetric stretch
943	Ring Breath (side-chain containing S–S)
804	Ring Breath (main-chain hexahydric-ring)
671	C–S stretch
513	S–S stretch



**Fig. S1** Linear sweep voltammetry (LSV) using a 0.5M KPF<sub>6</sub> solution in EC : DMC = 1 : 1 in the voltage range of OCV – 0.1 V. The LSV measurement was performed under two electrode geometry (K-metal/0.5M KPF<sub>6</sub> in EC:DMC electrolyte/SUS) by using coin-type cell.

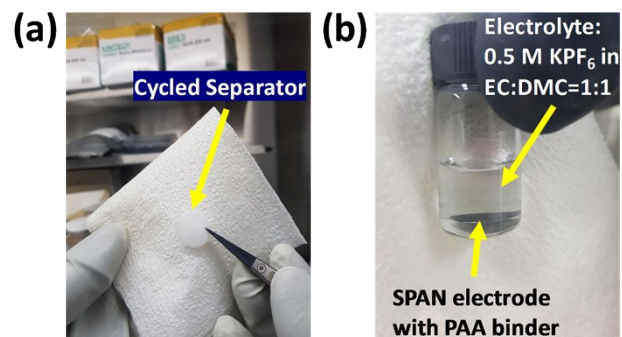


**Fig. S2** (a) Initial charge–discharge curves and (b) cycling life of CPAN electrode with PAA binder test at 0.5 C-rate in the voltage range of 0.1–3.0 V.

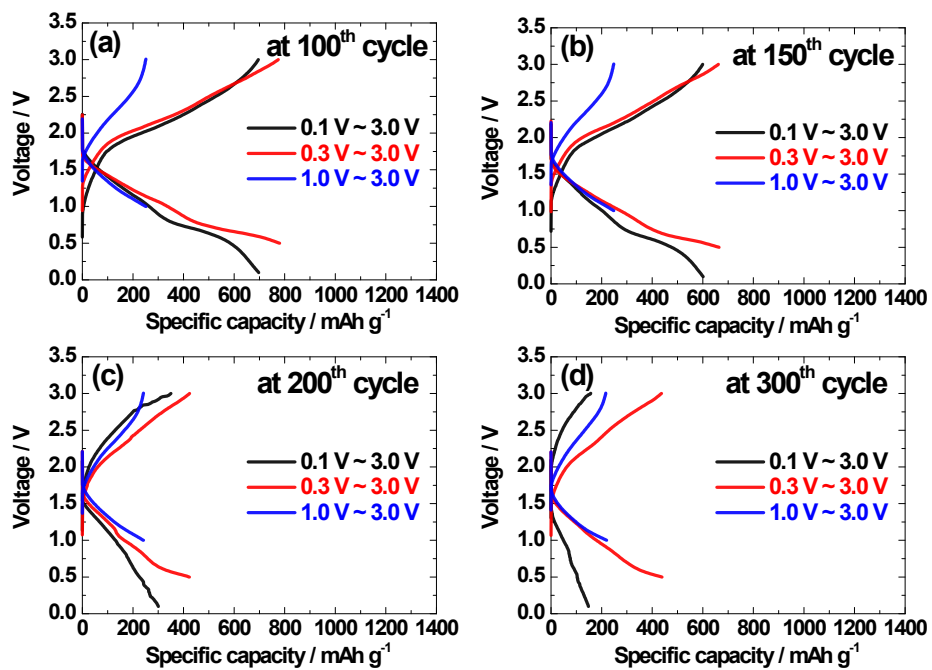
**Table S3.** Raman shifts ( $\text{cm}^{-1}$ ) and assignments for SPAN.

Assignments	Raman peak ( $\text{cm}^{-1}$ )
C-S in plane bending	298–308
C-S deformation	370–378
S-S	460





**Fig. S3** Digital photographs: (a) cycled separator collected from K/SPAN electrode with PAA binder cell, (b) 0.5M  $\text{KPF}_6$  in EC:DMC electrolyte solution with SPAN electrode.



**Fig. S4** Charge-discharge curves at different discharge cut-off voltage: at (a) 100<sup>th</sup> cycle, (b) 150<sup>th</sup> cycle, (c) 200<sup>th</sup> cycle (d) 300<sup>th</sup> cycle.

**Table S4.** Comparison of electrochemical performances with reported potassium–sulfur batteries.

	Cathode	S-loading level (electrode)	S contents (electrode)	Electrolyte	Voltage range	Discharge capacity	Cycle life
Ref S1.	PANI@CMK- 3/sulfur composite	-	31 wt. %	1.0 M KClO <sub>4</sub> in TEGDME	1.2–2.4 V	524 mAh g <sup>-1(s)</sup> (50 mA g <sup>-1</sup> )	63% (50 cycles)
Ref S2.	Polysulfide catholyte (MWCNT paper)	0.56 mg cm <sup>-2</sup>	30 wt. %	0.5 M KTFSl, 0.05 M K <sub>2</sub> S <sub>x</sub> in DEGDME	1.2–2.4 V	400 mAh g <sup>-1(s)</sup> (55.8 mA g <sup>-1</sup> )	94% (20 cycles)
Ref S3.	Sulfurized polyacrylonitrile	0.38 mg cm <sup>-2</sup>	30 wt. %	0.8 M KPF <sub>6</sub> in EC:DEC (1:1)	0.8–2.9 V	710 mAh g <sup>-1(s)</sup> (328.8 mA g <sup>-1</sup> )	54% (100 cycles)
This Work	Sulfurized polyacrylonitrile	0.8 mg cm <sup>-2</sup>	36 wt. %	0.5 M KPF <sub>6</sub> in EC:DMC (1:1)	0.1–3.0 V	1045 mAh g <sup>-1(s)</sup> (838.5 mA g <sup>-1</sup> )	95% (100 cycles)
		1.5 mg cm <sup>-2</sup>			1.0–3.0 V	330 mAh g <sup>-1(s)</sup> (838.5 mA g <sup>-1</sup> )	75% (500 cycles)

Ref S1. Q. Zhao, Y. Hu, K. Zhang, J. Chen. *Inorg. Chem.*, 2014, **53**, 9000–9005.

Ref S2. J.-Y. Hwang, H. M. Kim, C. S. Yoon, Y.-K. Sun. *ACS Energy Lett.*, 2018, **3**, 540–541.

Ref S3. Y. Liu, W. Wang, J. Wang, Y. Zhang, Y. Zhu, Y. Chen, L. Fu, Y. Wu. *Chem. Commun.*, 2018, **54**, 2288–2291.

**Table S5.** Comparison of gravimetric energy density of K-S battery based on theoretical and practical values.

**Gravimetric energy density (theoretical value based on weight of sulfur)**

Cathode	Theoretical Capacity	Average Voltage	Theoretical Energy Density
Sulfur (*)	1675 mAh g <sup>-1</sup>	1.5 V	2512.5 Wh kg <sup>-1</sup>
SPAN (&)	1675 mAh g <sup>-1</sup>	1.1 V	1842.5 Wh kg <sup>-1</sup>

**Gravimetric energy density (practical value based on weight of sulfur and electrode)**

Cathode	Practical Capacity	Average Voltage	Practical Energy Density
Sulfur (*)	512.7 mAh g <sup>-1(s)</sup>	1.5 V	769.05 Wh kg <sup>-1(s)</sup>
			238.4 Wh kg <sup>-1(electrode)</sup>
SPAN (&)	1050 mAh g <sup>-1(s)</sup>	1.1 V	1155 Wh kg <sup>-1(s)</sup>
			378 Wh kg <sup>-1(electrode)</sup>

References

\*: Chen et al., Inorg. Chem. 2014, 53, 9000-9005 (S contents in electrode: 31 %),

&: This work (S contents in electrode: 36 %).