Supporting Information

Tuning the Local-chemistry of the SPAN to Realize the Development of Room-Temperature Sodium-Sulfur Pouch Cells

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Figure S1. FESEM image of SPAN + 400 mg ZnS (a) and corresponding EDS mapping images (b), (c), (d), and (e)



Figure S2. XRD data of Sulfur and SPAN + 400 mg ZnS



Figure S3 TGA data on SPAN and SPAN + 400 mg ZnS



Figure S4. XPS survey spectrum of SPAN and SPAN + 400 mg ZnS

| S. No | Elements | SPAN + ZnS 400 mg (Wt%) | SPAN (Wt %) |
|-------|----------|-------------------------|-------------|
| 1) | Sulfur | 13.1 | 10 |
| 2) | Nitrogen | 2.5 | 61 |
| 3) | Carbon | 15.4 | 23.4 |
| 4) | Zinc | 63 | - |
| 5) | Oxygen | 5.1 | 5.3 |

Table S1. Compositional ratio of SPAN composites based on XPS data



Figure S5. Histogram representation of Zinc, Oxygen, Nitrogen, Carbon and Sulfur in SPAN and SPAN + 400 mg ZnS



Figure S6. XPS spectra of SPAN + 400 mg ZnS (a) C 1s, (b) O 1s (c) Zn 2p and SPAN (d) C 1s, (e) O 1s



Figure S7. CV curves at 0.2 mV s⁻¹ of a) SPAN + 400 mg ZnS and b) SPAN in ether electrolyte.



Figure S8. CV curves at various scan rates ranging from 0.1 to 0.5 mV s⁻¹ of a) SPAN and b) SPAN + 400 mg ZnS in ether electrolyte.



Figure S9. EIS data of SPAN and SPAN + 400 mg ZnS a) before cycling and b) after cycling

| | SPAN | | | | SPAN + 400 mg ZnS | | | | | | | |
|----------------------|-----------|-------------------------|-------|----|-------------------|----------|-----|---------|-----------------|------|------------|------|
| | Bef | ore cyc | ling | Af | ter cycli | ng | Be | fore cy | cling | Af | fter cycli | ng |
| | R1 | R2 | R3 | R1 | R2 | R3 | R1 | R2 | R3 | R1 | R2 | R3 |
| | 10 | 2.41 | 29.66 | 10 | 40.34 | 9.82 | 46 | 2.01 | 12.01 | 1.15 | 23.88 | 8.12 |
| | $m\Omega$ | Ω | Ω | mΩ | Ω | Ω | mΩ | Ω | Ω | Ω | Ω | Ω |
| $R_{ct}=31.9 \Omega$ | | $R_{ct} = 50.16 \Omega$ | | | R _c | t = 14.0 | 2 Ω | R | $L_{ct} = 32$ G | 2 | | |

| Table S2 | Values | obtained | from | EIS | data | fitting |
|----------|--------|----------|------|-----|------|---------|
|----------|--------|----------|------|-----|------|---------|



Figure S10. Voltage profile of SPAN (a), SPAN + 100 mg ZnS (b), SPAN + 200 mg ZnS (c), SPAN SPAN + 400 mg ZnS (d), SPAN +600 mg ZnS (e) in ether electrolyte at 0.14 C.



Figure S11. Voltage profile of SPAN (a), SPAN + 400 mg ZnS (b), composite in ether-based electrolyte.

| Table S3. Pouch | Cell | parameters |
|-----------------|------|------------|
|-----------------|------|------------|

| Electrode size (Anode) | 56 mm*53 mm |
|--------------------------|------------------------|
| Electrode size (Cathode) | 56 mm*43 mm |
| Anode | Sodium metal |
| Anode loading | 15 mg cm ⁻² |
| Cathode | SPAN+ 400 mg ZnS |

| Cathode loading | 4 mg cm ⁻² |
|-------------------|-----------------------|
| Binder | PVDF |
| Current Collector | Al foil |
| Electrolyte | 1M NaOTF in Diglyme |

Table S4. Na–S battery systems based on different sulfur composites

| S. | Cathodes | Electrolyte | Initial | Final | Capacity | Cycle | Ref. |
|----|---------------------------------------|-----------------------|---------------------------------|------------------------|-----------|-------|------|
| no | | | capacity | capacity | decay | life | |
| 1) | HPCM/S | 1 M NaOTF | 617 mA h g ⁻ | 311 mA | - | 60 | 1 |
| | composite | in diglyme | ¹ (0.7 C) | h g ⁻¹ (0.7 | | | |
| | | | | C) | | | |
| 2) | Polysulfide | 1 M NaOTF | 755 mAh | 755 mA | - | 200 | 2 |
| | catholyte in | in diglyme | g-1 | h g-1 | | | |
| | rGO-CNT- | | (0.2 C) | (0.2 C) | | | |
| | CMC | | | | | | |
| | sponge | | | | | | |
| 3) | CS90-rGO | 1 M | 542 mA h g ⁻ | 335 mA | 0.76% per | 50 | 3 |
| | | NaClO ₄ + | 1 (0.2 A g ⁻¹) | h g ⁻¹ (0.2 | cycle | | |
| | | 0.2 M | | A g ⁻¹) | | | |
| | | NaNO ₃ in | | | | | |
| | | tetraglyme | | | | | |
| 4) | (S@iMCHS | 1.0 M | 418.75 mAh | 292 mAh | - | 200 | 4 |
| |) | NaClO ₄ in | g^{-1} | g ⁻¹ | | | |
| | | PC: EC | (0.2 A g^{-1}) | (0.2 A g- | | | |
| | | (1:1, v/v) | | 1) | | | |
| | | with 5 wt. | | | | | |
| | | % FEC of | | | | | |
| | | additive | | | | | |
| 5) | c-PANS NF | 0.8 M | 796 mAh/g- | 219 | - | 500 | 5 |
| | | NaClO ₄ in | 1 | mAh/g ⁻¹ | | | |
| | | EC: DEC | (0.1 C) | (1 C) | | | |
| 6) | S _{0.6} Se _{0.4} @C | 1 M | 417 mAh g ⁻ | 375 mAh | - | 100 | 6 |
| | NFs | NaClO ₄ in | 1 | g ⁻¹ | | | |
| | | EC: PC | (0.1 A g^{-1}) | 0.1 A g ⁻ | | | |
| | | (1:1, v/v)) | | 1) | | | |
| 7) | SeS-PAN | 1.0 M | 721 mAh g ⁻ | 550 mAh | - | 150 | 7 |
| | particles | NaClO ₄ in | 1 (0.2 A g ⁻¹) | g-1 | | | |
| | | EC: DEC: | | (0.2 A g- | | | |
| | | PC (1:1:1, | | 1) | | | |

| | | v/v) with | | | | | |
|-----|--|-----------------------|---------------------------------------|-----------------------|---------------------|------|----|
| | | 5.0 vol. % | | | | | |
| | | FEC | | | | | |
| 8) | Sulfurized | 1 M of | 342 mAh g- | 266 mAh | - | 200 | |
| | polyacrylon | NaPF ₆ in | 1 | g-1 | | | |
| | itrile | EC: DEC | (0.1 C) | (0.1 C) | | | 8 |
| | nanofiber | (1:1, v/v) | | | | | |
| | (SPAN) | | | | | | |
| | web | | | | | | |
| 9) | Multi- | 1 M NaOTF | 523 mAh g ⁻ | 437 mAh | - | 100 | |
| | channel | in diglyme | ¹ (0.1 A g ⁻¹) | g ⁻¹ (0.1 | | | 9 |
| | sulfurized | | | A g ⁻¹) | | | |
| | polyacrylon | | | | | | |
| | itrile | | | | | | |
| 10) | H-SPAN | 1.0 M | 599.2 mAh | 717 mAh | - | 200 | 10 |
| | | NaClO4 in | g-1 | g-1 | | | |
| | | EC: PC | (0.05 C) | (0.1 C) | | | |
| | | (1:1, v/v) | | | | | |
| 11) | Te _{0.04} S _{0.96} @ | 1 M | 503 mA h | 463 mA | 0.015% | 600 | 11 |
| | pPAN | NaClO ₄ in | g-1 | h g-1 | decay per | | |
| | | EC: DMC | (0.5 A g ⁻¹) | (0.5 A g ⁻ | cycle | | |
| | | (1:1, v:v) | | 1) | | | |
| | | with 10% | | | | | |
| | | FEC | | | | | |
| 12) | Se _{0.08} S _{0.92} @ | 1.0 M | 1185 mA h | 770 mA | 0.045% | 500 | 12 |
| | pPAN | NaClO ₄ in | g-1 | h g-1 | decay per | | |
| | | PC: EC | (0.4 A g ⁻¹) | (0.4 A g ⁻ | cycle | | |
| | | (1: 1, v/v) | | 1) | | | |
| | | | | | | | |
| 13) | SPAN@ | 1 M | 1100 mAh | 400 | 0.13 mAh | 1000 | 13 |
| | TiO ₂ | NaClO ₄ | g ⁻¹ | mAh g ⁻¹ | g ⁻¹ per | | |
| | | in EC: PC | (0.2 C) | (0.2 C) | cycle | | |
| | | (1:1, v:v) | | | | | |

| 14) | SPAN@ | 1 M | 500 mAh | 227 | 0.07 % | 450 | Our |
|-----|-----------|----------|-------------|---------------------|-----------|-----|------|
| | ZnS | NaOTF in | g -1 | mAh g ⁻¹ | decay | | work |
| | composite | diglyme | (1 C) | (1 C) | per cycle | | |

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