WO₃ nanowire/carbon nanotube interlayer as a chemical adsorption mediator for high-performance lithium-sulfur batteries

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Figure S1. (a) SEM images of CNT interlayer with EDS mapping images of carbon, tungsten, oxygen. (b) Isotherm profiles and (c) pore size distributions of WNW.
**Figure S2.** (a) Cycling performance and (b) voltage profiles of a lithium-sulfur cell without an interlayer.
Figure S3. Cyclic voltammetry curves of the lithium-sulfur cells with a (a) WNW/CNT interlayer and (b) CNT interlayer, respectively, at different scan rates.
Figure S4. (a) Cycling performances of the interlayers without sulfur electrodes. (b) CV profiles of WNW (1.5–3.8 V).
Table S1 Comparison of overall electrochemical performances previously reported lithium-sulfur batteries incorporating different types of interlayer or functional separators.

| Samples                     | Sulfur content in cathode (%) | Overall S content (%) | Sulfur loading (mg cm$^{-2}$) | Specific capacity (mAh g$^{-1}$)(s) | Cycle number | Capacity fading rate (%/cycle) | Rate capability | Reference |
|-----------------------------|-------------------------------|-----------------------|-------------------------------|--------------------------------------|--------------|---------------------------------|-----------------|-----------|
| CNF-T interlayer            | 60                            | 42.5                  | 0.8                           | 1328 (0.2 C)                         | 500          | 0.121                           | 1091 (0.1 C)    | [S1]      |
|                             |                               |                       |                               |                                      |              |                                 | 940 (0.3 C)     |           |
|                             |                               |                       |                               |                                      |              |                                 | 820 (0.5 C)     |           |
|                             |                               |                       |                               |                                      |              |                                 | 740 (1 C)       |           |
|                             |                               |                       |                               |                                      |              |                                 | 620 (2 C)       |           |
| PANiNF/CNT separator        | 60                            | 59.7                  | 1.4                           | 1020 (0.2 C)                         | 100          | 0.3                             | 1020 (0.2 C)    | [S2]      |
|                             |                               |                       |                               |                                      |              |                                 | 867 (0.5 C)     |           |
|                             |                               |                       |                               |                                      |              |                                 | 791 (1 C)       |           |
| Glass fiber/CNT interlayer  | 70                            | 56.6                  | 1.6                           | 1111.7 (0.2 C)                       | 230          | 0.12                            | 1260 (0.1 C)    | [S3]      |
|                             |                               |                       |                               |                                      |              |                                 | 1150 (0.2 C)    |           |
|                             |                               |                       |                               |                                      |              |                                 | 1070 (0.5 C)    |           |
|                             |                               |                       |                               |                                      |              |                                 | 1000 (1 C)      |           |
| Material Description                              | Temperature (°C) | Voltage (V) | Current Density (C) | Resistance (Ω) | Thickness (µm) | Ref. |
|-------------------------------------------------|-----------------|-------------|--------------------|----------------|---------------|------|
| Self-assembled CNT interlayer                   | 80              | 52.6        | 3.0                | 851 (0.5 C)    | 100           | 0.042| [S4] |
| Graphene/PP/Al₂O₃ separator                    | 60              | 45.1        | 2.4                | 1068 (0.2 C)   | 100           | 0.25 | [S5] |
| Ti₃C₂ nanosheet/glass fiber separator            | 70              | 59.0        | 1.9                | 820 (0.3 C)    | 100           | 0.12 | [S6] |

**Self-assembled CNT interlayer**

- Temperature: 80°C
- Voltage: 52.6 V
- Current Density: 3.0 C
- Resistance: 851 Ω
- Thickness: 100 µm
- Resistance at various C rates:
  - 0.5 C: 670 Ω
  - 0.9 C: 600 Ω
  - 1.2 C: 530 Ω
  - 1.8 C: 450 Ω

**Graphene/PP/Al₂O₃ separator**

- Temperature: 60°C
- Voltage: 45.1 V
- Current Density: 2.4 C
- Resistance: 1068 Ω
- Thickness: 100 µm
- Resistance at various C rates:
  - 0.2 C: 1060 Ω
  - 0.5 C: 950 Ω
  - 1 C: 870 Ω
  - 2 C: 780 Ω

**Ti₃C₂ nanosheet/glass fiber separator**

- Temperature: 70°C
- Voltage: 59.0 V
- Current Density: 1.9 C
- Resistance: 820 Ω
- Thickness: 100 µm
- Resistance at various C rates:
  - 0.3 C: 886 Ω
  - 0.45 C: 716 Ω
  - 0.6 C: 589 Ω
  - 0.9 C: 530 Ω
  - 1.2 C: 476 Ω
| Interlayer Type                  | Percentage | Thickness (µm) | Thermal Conductivity (W/mK) | Flexibility (°C) | Reference |
|---------------------------------|------------|----------------|-----------------------------|------------------|-----------|
| SRGO/glass fiber interlayer     | 53.3       | 50.6-51.2      | 1.2-1.5                     | 1320 (0.5 C)     | [S7]      |
|                                 |            |                |                             | 250              |           |
|                                 |            |                |                             | 0.18             |           |
|                                 |            |                |                             | 1240 (0.2 C)     |           |
|                                 |            |                |                             | 1019 (0.5 C)     |           |
|                                 |            |                |                             | 866 (1 C)        |           |
|                                 |            |                |                             | 673 (2 C)        |           |
|                                 |            |                |                             | 550 (3 C)        |           |
|                                 |            |                |                             | 471 (4 C)        |           |
| PAA-SWNT interlayer             | 65         | 54.3           | 2.7                         | 770 (1 C)        | [S8]      |
|                                 |            |                |                             | 200              |           |
|                                 |            |                |                             | 0.13             |           |
|                                 |            |                |                             | 1117 (0.1 C)     |           |
|                                 |            |                |                             | 860 (0.2 C)      |           |
|                                 |            |                |                             | 740 (0.5 C)      |           |
|                                 |            |                |                             | 640 (1 C)        |           |
|                                 |            |                |                             | 592 (2 C)        |           |
| MoS₂/graphene interlayer        | 60         | 43.6-48.0      | 0.8-1.2                      | 840 (0.6 C)      | [S9]      |
|                                 |            |                |                             | 200              |           |
|                                 |            |                |                             | 0.13             |           |
|                                 |            |                |                             | 850 (0.3 C)      |           |
|                                 |            |                |                             | 770 (0.6 C)      |           |
|                                 |            |                |                             | 701 (1.2 C)      |           |
|                                 |            |                |                             | 600 (1.8 C)      |           |
| N-doped conductive interlayer   | 75         | 50.0           | 3.0                          | 990 (0.2 C)      | [S10]     |
|                                 |            |                |                             | 200              |           |
|                                 |            |                |                             | 0.24             |           |
|                                 |            |                |                             | 1295 (0.1 C)     |           |
|                                 |            |                |                             | 990 (0.2 C)      |           |
|                                 |            |                |                             | 750 (0.5 C)      |           |
| Interlayer Type                              | T (°C) | T (°C) | V (g/cm³) | T (°C) | V (g/cm³) | T (°C) | V (g/cm³) | T (°C) | V (g/cm³) | T (°C) | V (g/cm³) | Notes  |
|---------------------------------------------|--------|--------|-----------|--------|-----------|--------|-----------|--------|-----------|--------|-----------|--------|
| Graphene/CNT aerogels interlayer            | 50     | 48.0   | 2.46      | 1128   | (0.5 C)   | 100    | 0.25      | 1286   | (0.2 C)   | 990    | (0.5 C)   |        |
|                                             |        |        |           |        |           |        |           |        |           |        |           | [S11]  |
|                                             |        |        |           |        |           |        |           |        |           |        |           |        |
| P-doped C microtube textile interlayer      | 60     | 36.3-37.2 | 2.9-3.1   | 788    | (1 C)     | 100    | 0.07      | 1220   | (0.1 C)   | 1040   | (0.2 C)   |        |
|                                             |        |        |           |        |           |        |           |        |           |        |           | [S12]  |
|                                             |        |        |           |        |           |        |           |        |           |        |           |        |
| WNW/CNT interlayer                          | 70     | 48.0   | 3.0       | 1225   | (0.5 C)   | 300    | 0.11      | 1558   | (0.1 C)   | 1281   | (0.2 C)   |        |
|                                             |        |        |           |        |           |        |           |        |           |        |           |        |
| This work                                   |        |        |           |        |           |        |           |        |           |        |           |        |
References

S1. Liang, G.; Wu, J.; Qin, X.; Liu, M.; Li, Q.; He, Y. B.; Kim, J. K.; Li, B.; Kang, F., Ultrafine TiO$_2$ Decorated Carbon Nanofibers as Multifunctional Interlayer for High-Performance Lithium-Sulfur Battery. *ACS Appl. Mater. Interfaces* 2016, 8, 23105-23113.

S2. Chang, C.-H.; Chung, S.-H.; Manthiram, A., Ultra-lightweight PANiNF/MWCNT-functionalized separators with synergistic suppression of polysulfide migration for Li-S batteries with pure sulfur cathodes. *J. Mater. Chem. A* 2015, 3, 18829-18834.

S3. Lee, C. L.; Kim, I. D., A hierarchical carbon nanotube-loaded glass-filter composite paper interlayer with outstanding electrolyte uptake properties for high-performance lithium-sulphur batteries. *Nanoscale* 2015, 7, 10362-10367.

S4. Kim, H. M.; Hwang, J. Y.; Manthiram, A.; Sun, Y.-K., High-Performance Lithium-Sulfur Batteries with a Self-Assembled Multiwall Carbon Nanotube Interlayer and a Robust Electrode-Electrolyte Interface. *ACS Appl. Mater. Interfaces* 2016, 8, 983-987.

S5. Song, R.; Fang, R.; Wen, L.; Shi, Y.; Wang, S.; Li, F., A trilayer separator with dual function for high performance lithium–sulfur batteries. *J. Power sources* 2016, 301, 179-186.

S6. Lin, C.; Zhang, W.; Wang, L.; Wang, Z.; Zhao, W.; Duan, W.; Zhao, Z.; Liu, B.; Jin, J., A few-layered TiC nanosheet/glass fiber composite separator as a lithium polysulphide reservoir for high-performance lithium–sulfur batteries. *J. Mater. Chem. A* 2016, 4, 5993-5998.

S7. Lu, Y.; Gu, S.; Guo, J.; Rui, K.; Chen, C.; Zhang, S.; Jin, J.; Yang, J.; Wen, Z., Sulfonic Groups Originated Dual-Functional Interlayer for High Performance Lithium-Sulfur Battery. *ACS Appl. Mater. Interfaces* 2017, 9, 14878-14888.

S8. Kim, J. H.; Seo, J.; Choi, J.; Shin, D.; Carter, M.; Jeon, Y.; Wang, C.; Hu, L.; Paik, U., Synergistic Ultrathin Functional Polymer-Coated Carbon Nanotube Interlayer for High Performance Lithium-Sulfur Batteries. *ACS Appl. Mater. Interfaces* 2016, 8, 20092-20099.

S9. Guo, P.; Liu, D.; Liu, Z.; Shang, X.; Liu, Q.; He, D., Dual functional MoS$_2$/graphene interlayer as an efficient polysulfide barrier for advanced lithium-sulfur batteries. *Electrochim. Acta* 2017, 256, 28-36.

S10. Chang, C.-H.; Chung, S.-H.; Manthiram, A., Transforming waste newspapers into nitrogen-doped conducting interlayers for advanced Li–S batteries. *Sustainable Energy Fuels* 2017, 1, 444-449.

S11. Shi, H.; Zhao, X.; Wu, Z.-S.; Dong, Y.; Lu, P.; Chen, J.; Ren, W.; Cheng, H.-M.; Bao, X., Free-standing integrated cathode derived from 3D graphene/carbon nanotube aerogels serving as binder-free sulfur host and interlayer for ultrahigh volumetric-energy-density lithium sulfur batteries. *Nano Energy* 2019, 60, 743-751.

S12. Zheng, B.; Yu, L.; Li, N.; Xi, J., Efficiently immobilizing and converting polysulfide by a phosphorus doped carbon microtube textile interlayer for high-performance lithium-sulfur batteries. *Electrochim. Acta* 2020, 345, 136186.