Supporting Information

A Hierarchical Carbonized Paper with Controllable thickness as a Modulable Interlayer

System for High Performance Li-S Batteries

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CK interlayer fabrication: The cost-effective carbonized Kimwipes[®] papers were prepared by a time-effective carbonization route. To the best of our knowledge, the CK interlayer with various layer modules is the most inexpensive interlayer substrate and also has a light weight. The Kimwipes[®] paper was folded into layers and directly carbonized for 2 h at 800 °C with a heating rate of 2 °C min⁻¹ in a tube furnace under flowing argon. After carbonization, the multilayer CK paper forms a free-standing carbon thin film with a size of around 2.0 cm × 6.0 cm. The size was limited by the diameter of the tube furnace. The CK paper was cut into circular discs (12 mm in diameter) with various thicknesses as the interlayer. The CK paper offers two major advantages. First, the CK paper was prepared by a facile and low-cost production method, avoiding any kind of complex multistep processes, acid/alkali treatments, hard template processes, and extra chemical additives. Second, it is noteworthy to emphasize that the CK paper has a light weight of as low as 0.23 mg cm⁻² and can be easily prepared from single layer to multilayer. The light weight and controllable modular manufacture are not so easy to be fulfilled by other carbon interlayers. Most importantly, this layered structure

provides benefits for us, foe the first time, to investigate the thickness effect and analyze the interception mechanism of each layer in the interlayer.

Sulfur cathode preparation: The active material slurry contains 60 wt. % precipitated sulfur, 20 wt. % Super P, and 20 wt. % polyvinylidene fluoride (PVDF, Kureha) in an N-methyl-2-pyrolidone (NMP) solution. The slurry was continuously stirred for 2 days to form a viscous paste. Then, the well-mixed active material slurry was tape-casted onto an aluminum foil current collector and dried for 24 h at 50 °C in an air oven. As a result, the pure sulfur cathode has the sulfur content of 60 wt. % and sulfur loading of 1.1 mg cm⁻².

Cell assembly: The sulfur cathodes were dried in a vacuum oven for one hour at 50 °C before cell assembly. The electrolyte contained 1.85 M LiCF₃SO₃ salt (Acros Organics) and 0.1 M LiNO₃ salt (Acros Organics) in a 1:1 volume ratio of 1, 2-Dimethoxyethane (DME; Acros Organics) and 1, 3-Dioxolane (DOL; Acros Organics). The CR2032-type coin cells were assembled with the sulfur cathode, CK paper, polypropylene separator (Celgard), lithium foil anode, and a nickel foam spacer. The inserted CK paper was fully immersed into the electrolyte. The assembled CR2032-type Li-S cells were allowed to rest for 30 minutes at 25 °C before collecting the electrochemical data.

Material characterization and microanalysis: The nitrogen adsorption-desorption isotherms were measured at -196 °C with an automated gas sorption analyzer (AutoSorb iQ2, Quantachrome Instruments). The surface area of the CK paper was calculated by the Brunner-Emmett-Teller (BET) method. The microstructure of the CK paper and the morphological changes of the CK paper modules before and after cycling were observed with a scanning electron microscope (SEM) (JEOL JSM 5610) and a field emission scanning electron microscope (FE-SEM) (FEI Quanta 650 SEM). Both SEMs are equipped with energy

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dispersive spectrometers (EDS) for collecting elemental signals and mapping. The cycled cells were opened inside an argon-filled glove box for retrieving the cycled CK paper. The cycled CK paper was cut by a razor blade for cross-sectional SEM observations and further separated one layer after another for the surface SEM investigation. All samples were stored in an argon-filled sealed vessel prior to analyses.

Electrochemical characterization: The electrochemical impedance spectroscopy data were obtained with an impedance analyzer (SI 1260/SI 1287, Solartron) between 1 MHz and 100 mHz with an AC voltage amplitude of 5 mV. The cyclic voltammogram plots were recorded with a universal potentiostat (VoltaLab PGZ 402, Radiometer Analytical) at a scan rate of 0.1 mV s⁻¹ in the voltage window of 1.8 - 2.8 V. The discharge/charge voltage profiles and cyclability data were collected with a programmable battery cycler (Arbin Instruments). The cells were first discharged to 1.8 V and then charged to 2.8 V for a full cycle at a wide range of cycling rates from C/10 to 2C. The cycling rates are based on the mass and theoretical capacity of sulfur (1C = 1675 mA g⁻¹). The complete electrochemical cycling performance and polysulfide diffusion effect was investigated at C/5 rate. The cycle lives were investigated at C/2 to 2C rates. The capacities of the upper discharge plateau of the cells were captured from the data points in the discharge curves.

Supporting figures



Figure S1 Morphology of the CK paper: (a) comparison between the Kimwipes[®] paper and the CK paper, (b) excellent flexibility of the CK paper, (c) CK paper after bending, and (d) cycled CK paper. Figure S1a shows the textile architecture of the Kimwipes[®] paper and the carbonized long fiber network of the CK paper, which evidences that the morphology of the Kimwipes[®] was well retained in the CKs. Figure S1b and S1c demonstrate the excellent flexibility and high mechanical strength of the CK paper. The CK paper module includes 6 layers of CK paper. Figure S1d indicates that the CK paper possesses high flexibility and resistance to crushing to remain its complete thin film morphology during cell assembly/cycling and to tolerate the volume changes of the active material during cycling.



Figure S2 Electrolyte absorption tests of the Kimwipes[®] and the CK paper with various number of layers. Figure S2 demonstrates that the high water absorptivity of Kimwipes[®] (68 μ L cm⁻²) endows the CK paper with a similarly excellent electrolyte absorptivity (74 μ L cm⁻²), which is essential for absorbing the electrolyte that may contain the dissolved polysulfides.



Figure S3 (a) Electrochemical discharge/charge curves of the Li-S cell with the conventional cell configuration at C/5 rate. (b) Variation of the capacity in the upper plateau with cycling (the conventional cell configuration is marked as black and the cell employing the 6-layer CK paper module is marked as red). Figure S3a shows the typical severe capacity fade and plateau shrinkage that is commonly associated with the conventional sulfur cathodes. Figure S3b demonstrates that a simple configuration modification by inserting the CK paper significantly enhances both the stability and utilization of the upper plateau discharge capacity.



Figure S4 Electrochemical properties of the CK interlayer with the 3-layer module: (a) cyclability of the cells at various C-rates, (b) discharge/charge curves, (c) variation of the capacity in the upper plateau region with cycling (the conventional cell configuration is marked as black and the cell utilizing the CK paper module is marked as red). The cells employing the 3-layer module also shows the outstanding cycling performance.



Figure S5 High magnification SEM/EDS and elemental mapping microanalyses of the CK interlayer with 6-layer module: (a) 1st layer, (b) 2nd layer, (c) 3rd layer, (d) 4th layer, (e) 5th layer, and (f) 6th layer. The combination of Figure S5 and Figure 3 strongly evidences the interception mechanism of the 6-layer CK paper module. The CK paper that is close to the sulfur cathode shows obvious active material precipitation on the surface of the carbon fibers and also displays strong sulfur signal in the elemental mapping results. On the other hand, the CK paper that is close to the separator shows no significant active material coverage and displays weak sulfur signal on the elemental mapping results. The carbon signals are all strong, indicating that the covered sulfur could be easily reactivated in subsequent cycles.



Figure S6 Low magnification cross-sectional SEM and elemental mapping microanalysis of the CK interlayer. The sulfur cathode is on the left side. As a result, from left to right, the SEM shows an increasing porous gradient and the elemental mapping displays a decreasing sulfur concentration gradient. This phenomenon is because a higher amount of the trapped active material was stored in the first one to four CK interlayers, which well supports the results in Fig. 3.



Figure S7 Cross-sectional SEM microanalysis of the CK interlayer with 6-layer modules: (a) 1st and 2nd layers, (b) 3rd and 4th layers, and (c) 5th and 6th layers. Fig. S7a shows the 1st and 2nd CK paper layers closest to the sulfur cathode, which are characterized by trapped active material visible in the SEM images and a strong sulfur signal in the elemental mapping results. Fig. S7b shows the 3rd and 4th CK paper layers, showing weaker sulfur signals than those in the 1st and 2nd CK layers. Fig. S7c shows the 5th and 6th CK layers, displaying even weaker sulfur signals and the most porous structure. This decreasing sulfur concentration gradient reconfirms the statement of Figure 3 that the initial one to four CK layers intercept most of the migrating polysulfides.