Supporting Information

Two-dimensional Nafion Nanoweb Anion-shield for Improved Electrochemical Performances of Lithium Sulfur Batteries

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Experimental

1. Preparation of the sulfur cathode

The sulfur electrode slurry was prepared by mixing sublimed sulfur (60%), carbon black (30%), and PVdf binder (10%) with a planetary mixer. As-prepared slurry was cast onto Al foil with a doctor blade, and then dried in a convection oven at 50 °C for 24 h. To allow for practical utilization and to increase the sulfur mass loading in Li-S batteries, the sulfur electrode slurry was cast with a large thickness. The loading mass of sulfur per unit area was matched to ~2.4 mg cm⁻².

2. Preparation of the Nafion nanoweb solution

To synthesize the Nafion nanoweb, an electro-spinning solution was prepared by the following procedure. 4g of PVP (Mw = 55,000) was dissolved in 6 ml of pure ethanol, and the mixture was magnetically stirred overnight. PVP was used as a supporting material to maintain the Nafion nanoweb structure. A Nafion dispersion solution (Dupont, D2020) was
introduced into the as-prepared PVP-ethanol solution at a ratio of 1 to 1, and magnetically stirred for 24 h.

3. Preparation of Nafion nanoweb-sulfur cathode

For the electro-spinning process, the homogeneously mixed solution was put into a plastic syringe (10 ml) equipped with a SUS needle and then the syringe was loaded on a syringe pump. The as-prepared pure sulfur cathode was placed onto Al foil to directly deposit the Nafion nanoweb above the sulfur cathode. The electro-spinning process was conducted at a feeding rate of 0.5 ml hr\(^{-1}\) under 22 kV for 4 h. After the electro-spinning process was finished, the Nafion nanoweb-sulfur cathode was uniaxially pressed under a pressure of ~ 10 MPa to give a strong adhesion between sulfur cathode and Nafion nanoweb and fabricate the compact Nafion nanoweb structure. After pressing process, the layer of Nafion nanoweb became compact and dense (Figure S1). Finally, the Nafion nanoweb-sulfur cathode was dried in a convection oven at 50 °C overnight in order to eliminate any ethanol remaining in the nanofibers. The Nafion layer-sulfur cathode was prepared by coating the Nafion solution via spin-coating. The same loading mass (~ 0.84 mg cm\(^{-1}\)) for Nafion nanoweb and Nafion layer was coated onto the sulfur cathode in order to directly compare the effect of the structure on the electrochemical performances. The thicknesses of Nafion nanoweb and Nafion layer were 19 μm and 8 μm, respectively.
4. Fabrication of cell
The galvanostatic discharge/charge evaluations, cycling performances, and rate capabilities of each cell were tested by a cell cycle tester TOSCAT 3100 (Toyo Systems, Japan). The working electrodes were fabricated in 2032-type coin cells with Li metal as reference anode electrode. The electrolyte was 1 M lithium bis(trifluoromethanesulphonyl)imide (LiTFSI) in 1,3-dioxolane (DIOX) and 1,2-dimethoxyethane (DME) (v:v=1:1) with lithium nitrate (LiNO$_3$) (1 wt%). The same amount (~80 μl) of electrolyte was used in each cell to directly compare the electrochemical performances of Li-S cells. Each cell was evaluated within the potential window of 1.5-3.0 V.

Characterization
The morphologies of the pure sulfur cathode and Nafion nanoweb were observed by a field emission scanning electron microscope (JSM 4700F). FTIR spectra (FT-IR-4200) were analyzed in the range 2500-1000 cm$^{-1}$ with a FT-IR spectrometer. The EIS of the sulfur cathode, Nafion nanoweb-sulfur cathode, and Nafion layer-sulfur cathode were evaluated by a potentiostat (Autolab PGSTAT 302N) in the frequency range of 100 kHz to 100 mHz with an excitation amplitude of 10 mV. The contact angle measurements were carried out by the
sessile drop method with a digital optical contact angle meter (G-10, Krüss, Germany).
Figure S2 Energy-dispersive X-ray spectroscopy (EDS) mapping of sulfur cathode.

The EDS mapping was performed to check the distribution of sulfur element through the sulfur cathode.
Figure S3 Cross sectional SEM image of Nafion nanoweb-sulfur cathode.

To clearly see the thickness of Nafion nanoweb in Nafion nanoweb-sulfur cathode, the SEM study was performed. The thickness of Nafion nanoweb is around 19 μm.
Figure S4 ζ potential analysis. Average ζ potentials of each sample (PVP nanoweb, Nafion, Nafion nanoweb): (a) Bar graph, (b) zeta potential curve.
Figure S5 SEM analysis. SEM image of Nafion layer-sulfur cathode.

The SEM image clearly shows the compact Nafion layer over the sulfur cathode.
Figure S6 TEM images of PVP nanofiber and Nafion/PVP nanofiber.

For the diffusion test, the PVP nanofiber and Nafion/PVP nanofiber were directly deposited on the separator. To check the nanostructure of PVP nanofiber and Nafion/PVP nanofiber, TEM study was carried out. As shown in Figure S6, the thickness of PVP nanofiber and Nafion/PVP nanofiber are 0.97 μm and 1.04 μm, respectively, and there were no difference in morphology between both samples.
**Figure S7** Electrochemical performance. Comparison study for cycle retention of the Nafion layer-sulfur cathode and the Nafion nanoweb-sulfur cathode after electrochemical stabilization of electrodes (after 3 cycles).
Figure S8 Electrolyte wettability test. Contact angle measurement of each electrode (Nafion layer-sulfur and Nafion nanoweb-sulfur cathode) with a drop of electrolyte.