Supplementary information

Dual-Functional Polymer Coating on Lithium Anode for Suppressing Dendrite Growth and Polysulfide Shuttling in Li–S Batteries

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Experimental

Preparation of polymer protected Li metal anodes: Li metal foil (300-μm thick) supported on a 16-mm-diameter stainless steel disk was used as a pristine anode. Dried Nafion was obtained by evaporating the solvent of the Nafion® perfluorinated resin solution (5%, Sigma-Aldrich) in a convection oven at 50 °C for 2 hr and further drying under vacuum at 50 °C for 12 hr. 2.5 wt% dried Nafion was dissolved in N,N-dimethylacetamide (DMAc, 99%, Acros) by magnetic stirring on a hotplate at 100 °C for 2 hr in an Ar-filled glovebox. The PVDF coating solution was prepared by dissolving 2.5 wt% PVDF (HSV 900, Kynar) powder in DMAc at ambient temperature. Mixing equal mass quantities Nafion solution and PVDF solution gave a 2.5 wt% Nafion/PVDF polymer blend solution (1.25 wt% Nafion and 1.25 wt% PVDF in DMAc). The polymer coated Li metal anodes were prepared by cast coating the Li metal anode disks with the corresponding polymer solution. The coatings were dried on a hotplate at 65 °C for 30 min and vacuumed at 25 °C for overnight. The polymer loading of each coating layer was controlled to be approximately 200 μg cm^{-2}. The moisture and O_2 level in the glovebox were maintained below 1 ppm during the coating process.

Preparation of S/C nanocomposite cathode: Elemental sulfur (99.98%, Aldrich) and porous activated carbon (Pearl 2000, 99.9%, Cabot) were dispersed in N-Methyl-2-pyrrolidone (NMP, 99%, Taiwan Maxwave) in a mass ratio of 3:1:60 by magnetic stirring for 90 min and sonication for 30 min. When the mixture was heated on a hotplate at 180 °C and wrapped with a heat preserving jacket for another 90 min, the low-viscous molten sulfur infiltrated the activated carbon. The S/C nanocomposite was collected by vacuum filtration and further drying under vacuum at 50 °C for 12 hr. The resulting sulfur contents of the S/C nanocomposite was determined to be 75 wt% by thermogravimetric analysis. To prepare the cathode, a homogeneous slurry comprising 70 wt% of S/C nanocomposite, 15 wt% of conductive additive (KS6, TIMCAL) and 15 wt% of binder (PVdF-HSV 900, Kynar) in N-Methyl-2-pyrrolidone (NMP, 99%, Taiwan Maxwave) was cast coated onto a KS6 coated aluminum foil and vacuum dried at 50 °C for 12 hr. The areal sulfur loading was approximately 0.7 mg cm^{-2}.

Electrochemical measurements: Electrochemical characterizations were carried out using CR2032-type coin cells with Asahi 16-μm separator. A pair of Li metal anodes (either both pristine or both modified with the same coating) were used in symmetric cells. The symmetric cells were galvanostatically cycled at a current density of 1.1 mA cm^{-2} for 1 h during each half cycle. The performance at various current densities from 0.11 to 11 mA cm^{-2} was investigated with a fixed areal capacity of 1.1 mAh cm^{-2}. The performance of symmetric cells were measured using a battery tester (Maccor/Series 4000) The electrochemical impedance spectra (EIS) were collected at open circuit potential (OCP) after 0th, 10th and 100th cycle using an frequency analyzer (Metrohm Autolab/PGSTAT30) in a frequency range from 100 kHz to 10 mHz with an amplitude of 10 mV. In Li-S cells, pristine Li foil and polymer modified Li metal anodes were used as the anode for the Li-S cells respectively. The electrolyte was composed of 1 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, 99.95%, Sigma-Aldrich) in a 1:1 (v/v) mixture of

1,3-dioxolane (DOL, 99.8%, Sigma-Aldrich) and 1,2-dimethoxyethane (DME, 99.5%, Sigma-Aldrich). The coin cells were fabricated in an Ar-filled glove box with moisture and oxygen level below 1 ppm. The Li-S cells were cycled between 1.5 to 3.0 V at 1 C rate (1.672 A g^{-1}) at room temperature using a battery tester (AcuTech/BAT-70). The rate performance was measured in the same operating conditions but with various current densities ranging from 0.1 to 10 C (0.1672 to 16.72 A g^{-1}). The leakage current was measured at 2.4, 2.3, 2.25, and 2.18 V after 5 h of a step change in voltage.

Material Characterizations: The morphology of the electrode surface were examined via scanning electron microscopy (SEM; JEOL JSM-5310). The cycled electrodes were washed with DME and dried in a vacuum chamber for overnight. The SEM samples were prepared in a glove box and transferred to the SEM chamber using an Ar-filled desiccator. Swelling of the polymers (Nafion®, Nafion®/PVDF and PVDF) was measured in a glass-cell with inner thickness and width of 0.5 and 8 mm respectively. Cu foils (0.65 cm in diameter and 15 μm in thickness) loaded with 7 mg polymers were submerged in 1 M LiTFSI electrolyte for 72 h in separate glass-cells. 20 μL of polysulfide containing electrolyte (0.05 M Li$_2$S$_8$ &1 M LiTFSI in 1:1 DOL/DME) was injected into the glass-cells to trace the edge of the swollen polymers.
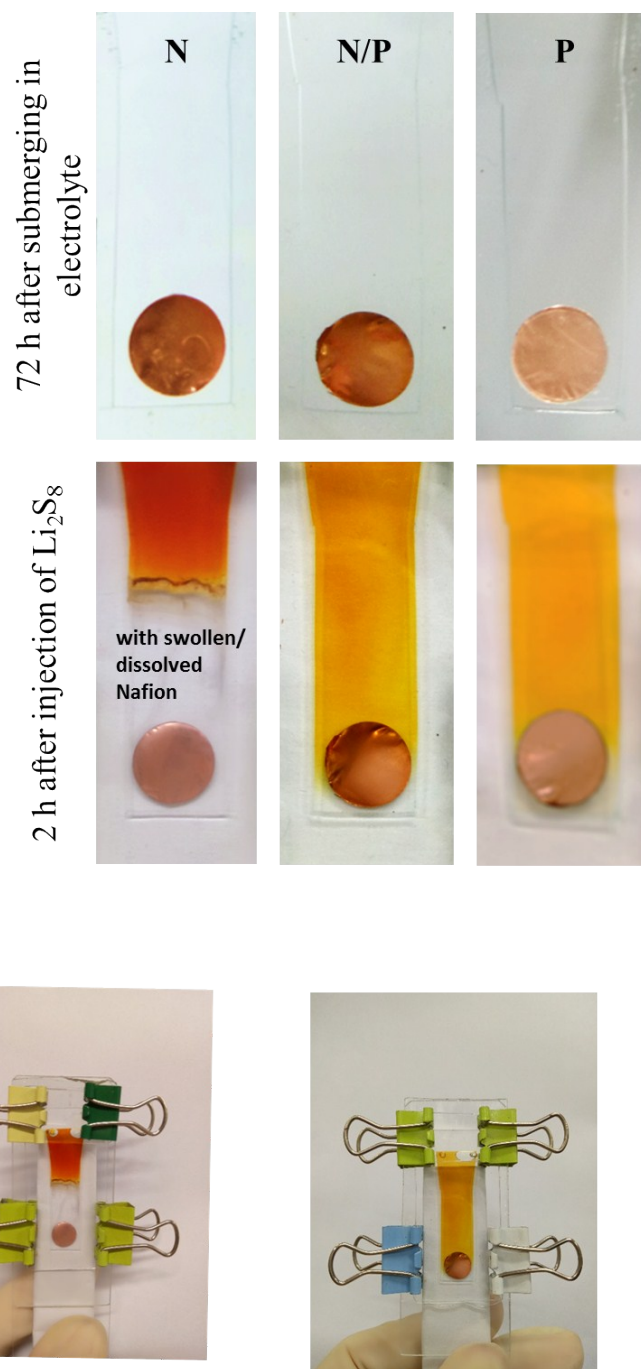
Supporting figures

Figure S1. Swelling test for the Nafion® (N), Nafion®/PVDF (N/P), and PVDF (P) polymers in the designated electrolyte of 1 M LiTFSI in a 1:1 (v/v) in DOL/DME.
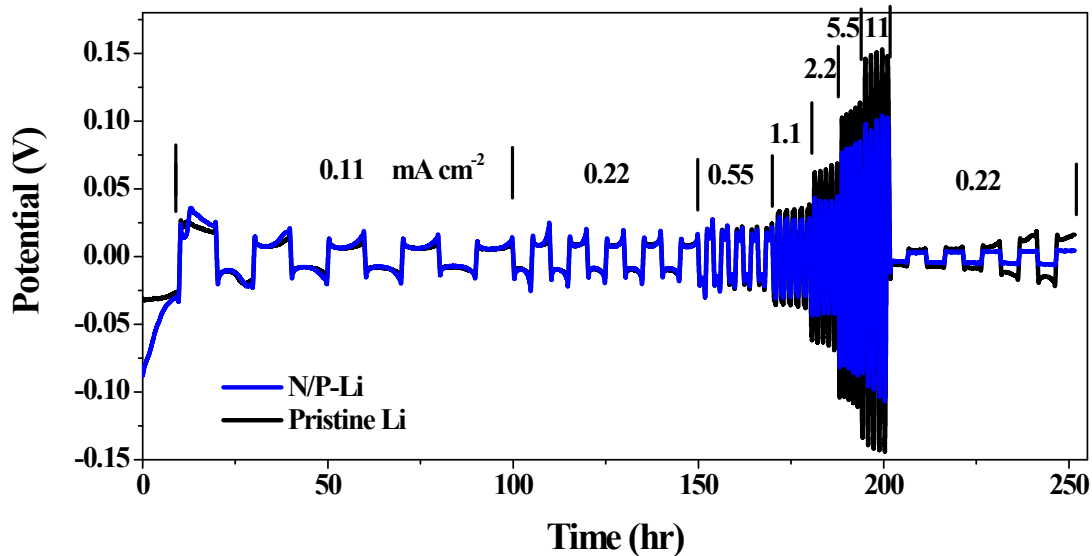
Figure S2. Overpotential profiles of symmetric cells employing either N/P-Li (blue line) or pristine Li (black line) electrodes during galvanostatic cycles at various current densities ranging from 0.11 to 11 mA cm^{-2} with fixed areal capacity of 1.1 mAh cm^{-2}.
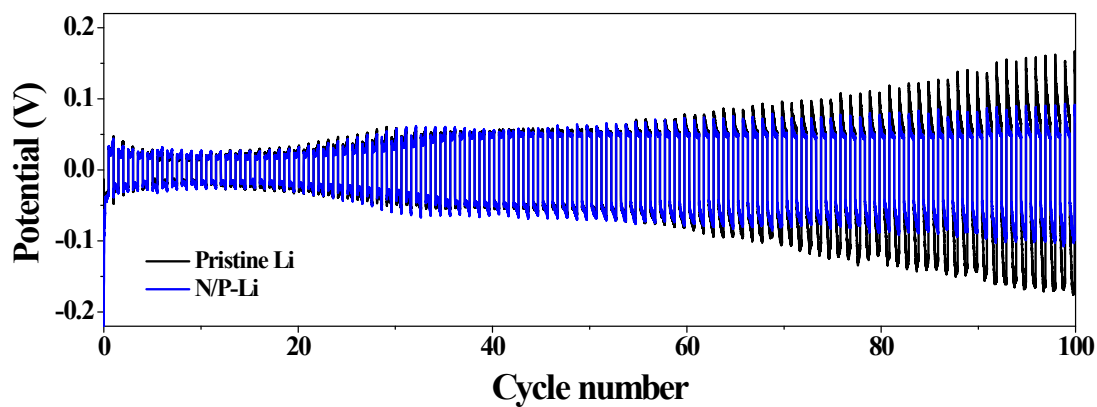

Figure S3. Overpotential profiles of symmetric cells employing either N/P-Li (blue) or pristine Li (black) electrodes during galvanostatic cycles at a current density of 1.1 mA cm^{-2} with the presence of 0.05 M Li$_2$S$_8$ in the electrolyte (1 M LiTFSI in 1:1 DOL/DME).
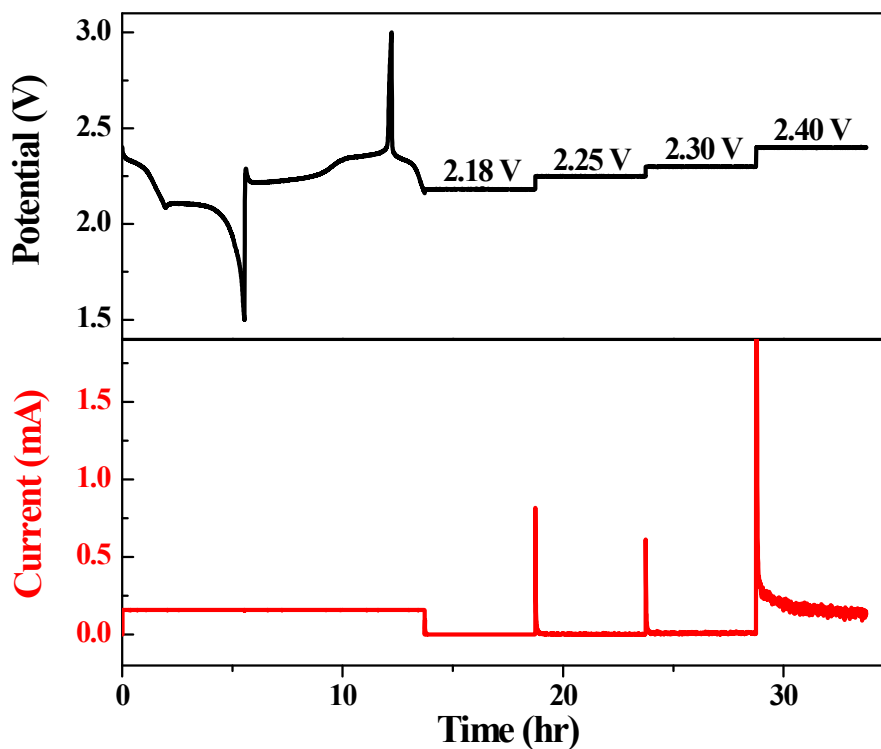
Figure S4. Leakage current measurements for a Li-S cell with pristine Li anode. After 1 formation cycle at 0.1 C (0.1672 A g^{-1} sulfur), the cell was discharged to 2.18 V at 0.1 C and held at constant voltages of 2.18, 2.25, 2.30, and 2.40 V for 5 h respectively. The intake current must equal to the leaked current in order to maintain the cell at a specific voltage. An instantly large current was required for a step change in voltage, while the equilibrium current represented the leakage current due to self-discharging. Similarly, the leakage current values for Li-S cells employing N-Li and N/P-Li anodes were determined and summarized in Figure 3d.