Supporting Information

The Effect of Polymeric Binders in the Sulfur Cathode on the Cycling Performance for Lithium-Sulfur Batteries

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Experimental

Material Characterization

The crystalline phase of the electrodes was identified by X-ray diffraction (XRD). The morphology and surface chemistry of the electrodes were characterized using a scanning electron microscope (SEM) and an energy dispersive X-ray (EDX) analysis. Adhesion strength of the electrodes was measured by a peeling test using the Instron Tensiometer. In this test, the coating layer of the electrodes was first attached onto a glass substrate using a double-sided scotch tape with a size of 2.5 x 5 cm^2, and then it was pulled off at a speed of 5 cm/min. Raman spectra and maps of the S cathodes were measured by confocal Raman spectroscopy (Ramanforce, Nanophoton). Laser of 532 nm wavelength with 1 mW was probed during the measurement of Raman spectra. Raman spectra were obtained using x50 objective lens (Nikon, NA=0.8).

Electrode Preparation

All sulfur cathodes were composed of 70 wt.% active materials (sulfur powder, 100 mesh, Sigma-Aldrich), 20 wt.% carbon black (Timcal), and 10 wt.% binder (PVdF or SBR/CMC). The SBR (Zeon) and CMC (Dai-ichi Kogyo Seiyaku) with weight ratio of 1:1 binder was used in the SBR/CMC mixture binder. SBR was used as purchased form of an aqueous emulsion solution and CMC was added to act as the thixotropic agent. The slurry for the sulfur cathode with a SBR/CMC binder was prepared by thoroughly mixing the components with deionized water by a planetary centrifugal mixer. The slurry for the sulfur cathode with a PVdF (Arkema) binder was prepared by the same method but with solid components dissolved in NMP. Sulfur cathodes were prepared by casting the slurry onto the Al foil and then being dried at 120℃ for

4 h in a vacuum oven overnight. Finally, the dried electrodes were calendared using the roll press before being punched. The electrochemical performances of the sulfur cathodes, SBR/CMC- and PVdF-based cathode, were investigated using 2032 coin-type cells assembled in an Ar-filled glove box. Li metal and 1 M lithium bis(trifluoromethane sulfonyl)imide ($LiN(SO_2CF_3)_2$, LiTFSI) dissolved in a 1:1 volume ratio of tetraethylene glycol dimethyl ether (TEGDME) and 1,3-dioxolane (DIOX) with the 0.1 M lithium nitrate ($LiNO_3$) additive were used as a counter electrode and an electrolyte, respectively, in the coin cells. An electrolyte/Sulfur ratio was 20 μL mg^{-1}. Since the sulfur loading was 2.5 mg cm^{-2}, 50 μL electrolyte was added in the coin cell.

Electrochemical Property Measurement

The charge/discharge characteristics of the cells were measured with a battery cycler (WBCS3000). While cells were charged in the constant current and constant voltage (CC-CV) mode (0.2, 0.5, 1, 2, 5, 10, and 20 C rate (assuming 1 C = 1675 mA g^{-1}) charging to 2.65 V (vs. Li^+/Li) and then holding 2.65 V until current decrease to 0.01 C), the discharge process was performed in a constant current mode (CC) (0.2 C rate discharging to 1.5 V). The electrochemical impedance spectroscopy (EIS) measurements were carried out using FRA2 and PGSTAT20 system over the frequency range from 100 kHz to 0.01 Hz. The electrical conductivity of the electrodes was measured using the four-point probe DC method.

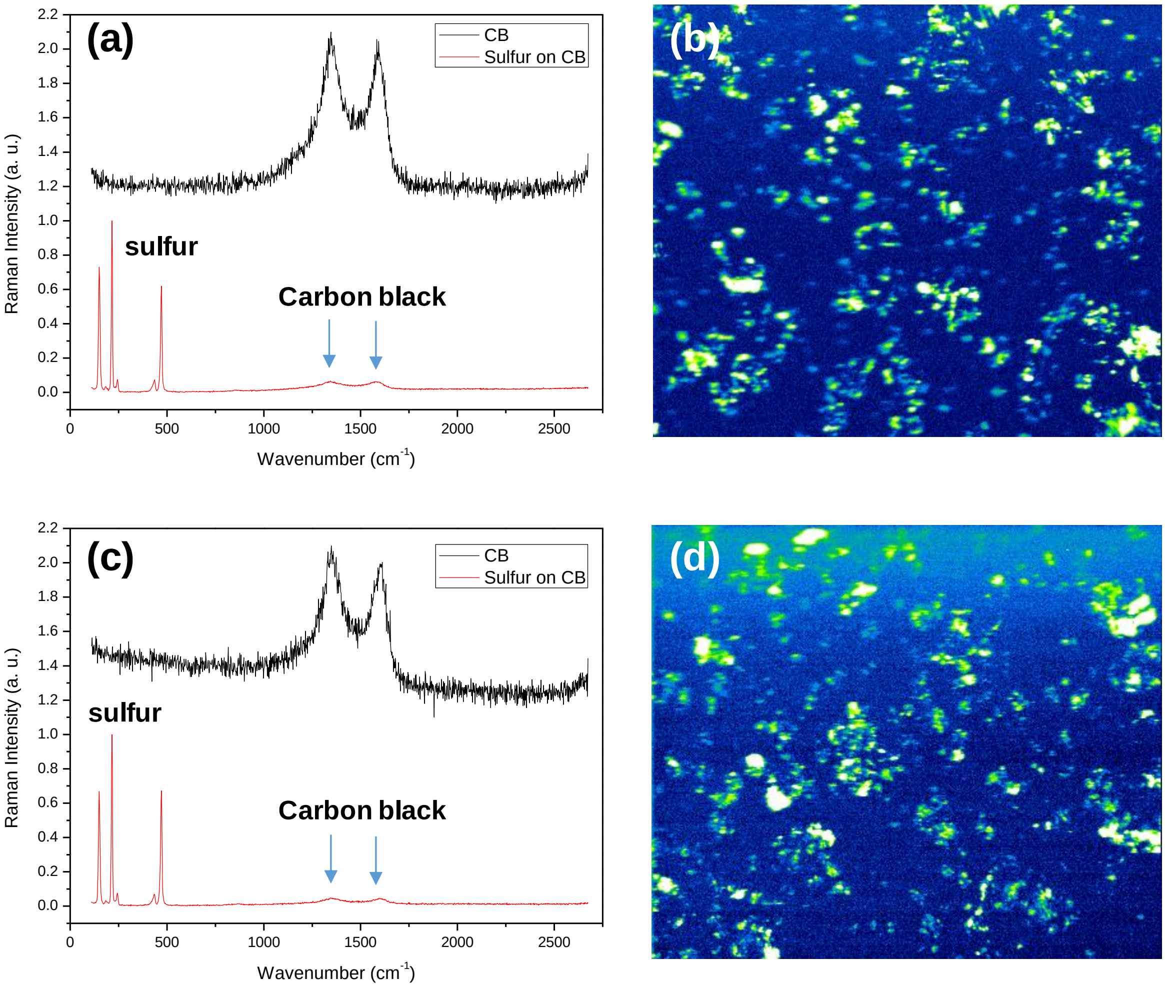


Fig. S1. Raman spectra of (a) SBR/CMC- and (c) PVdF-based electrodes. Only Raman feature of sulfur and carbon black could be identified. Elemental Raman mappings of (b) SBR/CMC- and (d) PVdF-based electrodes are also presented. Sulfur (green) and carbon black (blue) are homogeneously distributed on the electrode surface.

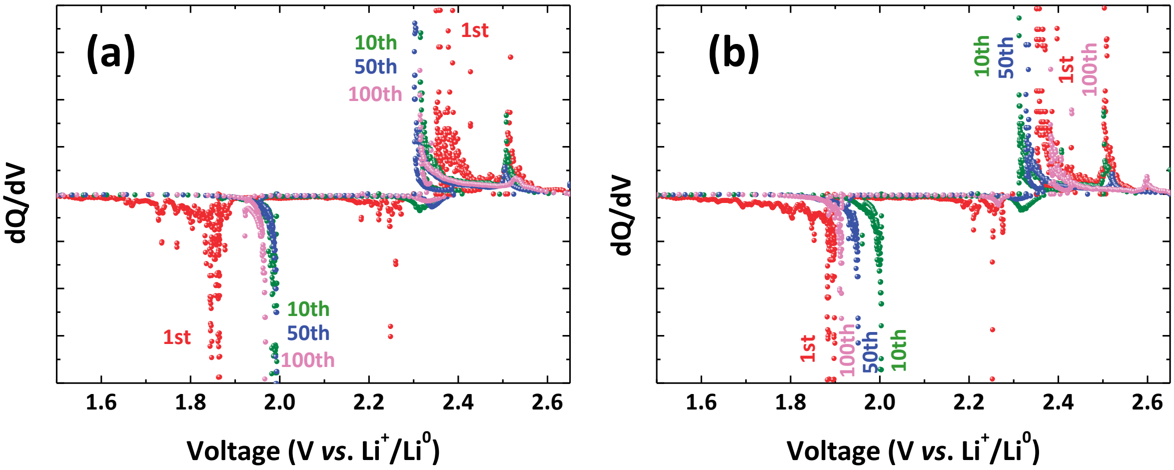


Fig. S2. Plots of differential capacity derived from capacity vs. voltage curves (Figure 4). (a) The SBR/CMC-based cathode showed negligible change in the polarization after the initial cycle while increase of the polarization was observed in (b) the PVdF-based cathode during extended cycles.

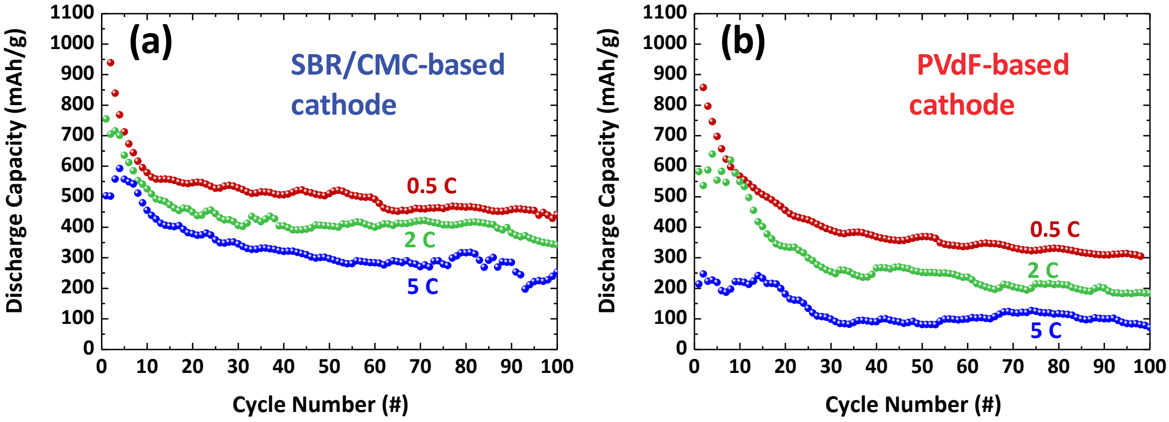


Fig. S3. Cycle retention of (a) SBR/CMC- and (b) PVdF-based cathodes for 100 cycles at the cycling rate of the 0.5, 2, and 5 C rate. In any current rate, the SBR/CMC-based cathode exhibited enhanced cycle retention.

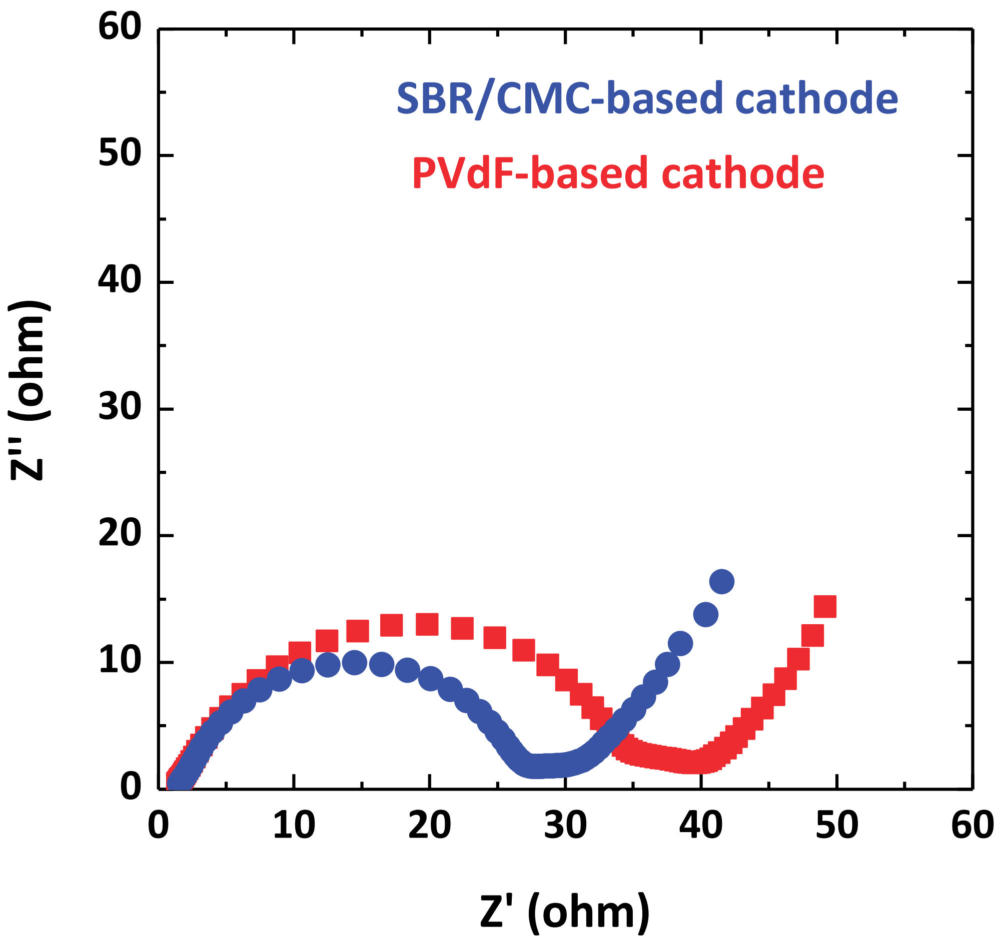
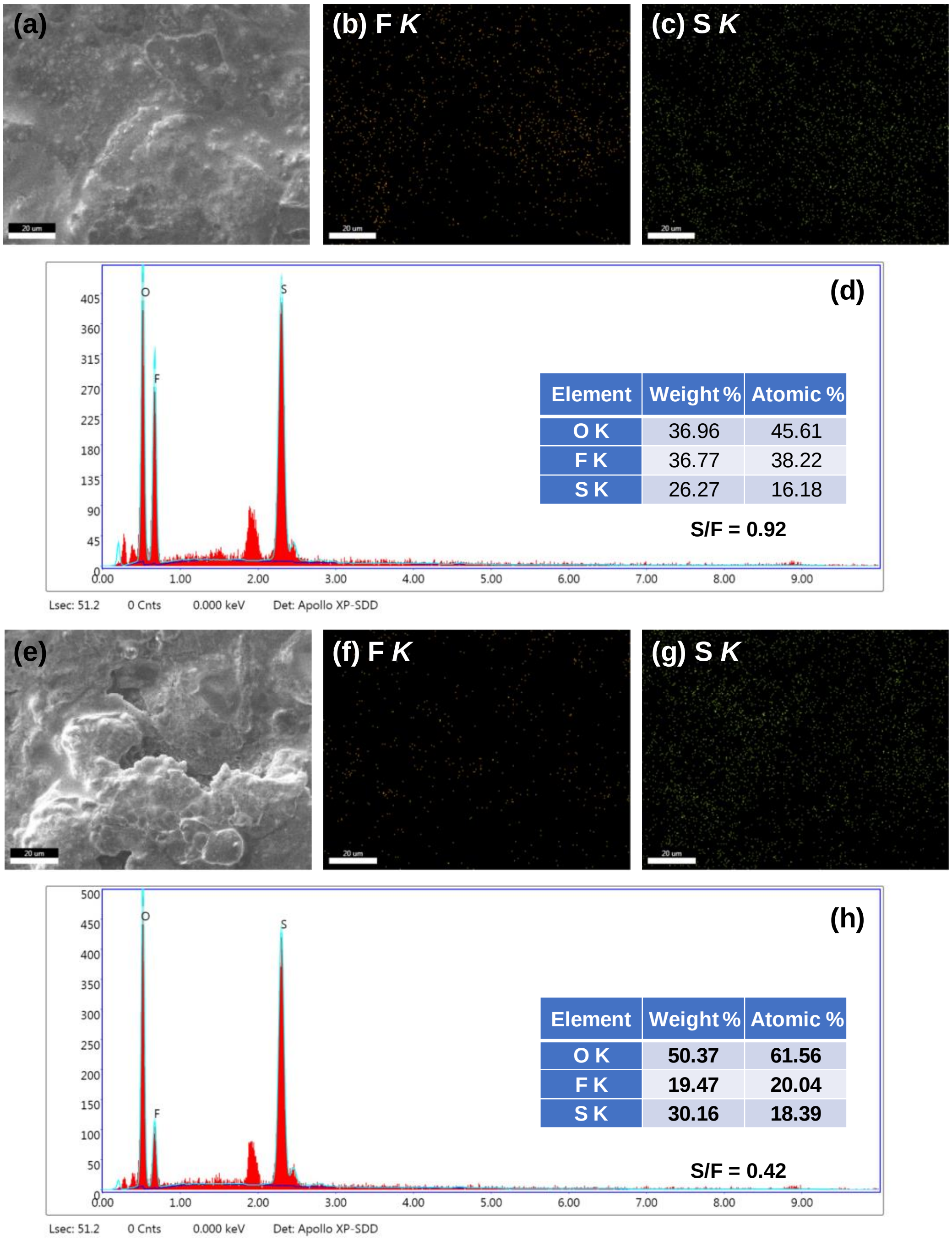


Fig. S4. Electrochemical impedance spectra were recorded from both (a) SBR/CMC- and (b) PVdF-based electrodes. The SBR/CMC-based cathode revealed less charge transfer resistance after the 10th cycle.



Element	Weight %	Atomic %
O K	36.96	45.61
F K	36.77	38.22
S K	26.27	16.18

S/F = 0.92

Element	Weight %	Atomic %
O K	**50.37**	**61.56**
F K	**19.47**	**20.04**
S K	**30.16**	**18.39**

S/F = 0.42

Fig. S5. (a) The SEM image, corresponding EDS mappings of (b) F and (c) S, and (d) EDS spectra with element ratio from the Li anode matched with the PVdF-based electrode. (e) The SEM image, corresponding EDS mappings of (f) F and (g) S, and (h) EDS spectra with element ratio from the Li anode matched with the SBR/CMC-based electrode are also presented. Li metal anodes were harvested after 30 cycles. Scale bars show 20 micrometers.