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Enhancement of cycle performance of Li-S batteries by redistribution of sulfur

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Experimental

The cathode slurry was prepared by mortar mixing 50 wt% sulfur (Sigma-Aldrich), 30 wt% conductive carbon black (Super P), and 20 wt% polyvinylidene fluoride (PVDF) polymer binder with *N*-methyl-2-pyrrolidinone as a mixing solvent. The slurry was pasted onto an aluminum current collector through the doctor blade method. After drying overnight at 60 ºC, the resulting slurry-coated aluminum foil was roll-pressed and cut into the required dimensions with a punching machine. The sulfur loading in the cathode disk was around 1 mg cm^{-2}. Electrochemical cell tests were conducted on 2032 coin-type half cells with lithium foil as counter and reference electrode, which were fabricated in an Ar-filled glove box. The electrolyte solution was 1 M lithium bis(trifluoromethanesulfone)imide (LiTFSI) in a mixture of 1,2-dimethoxyethane (DME) and 1,3-dioxolane (DOL) at a 1:1 volume ratio with 0.1 M $LiNO_3$ as an additive. To prepare the dissolved polysulfide catholyte, sublimed sulfur powder and an appropriate amount of lithium sulfide (Alfa Aesar) were added to the appropriate amount of blank electrolyte to render 0.25 M sulfur in the form of Li_2S_6 in the solution. The solution was heated at 45 ºC in an Ar-filled glove box for 18 h.

All electrochemical measurements were made with a WBCS3000 cycler (WonATech, Korea) at room temperature. The C-rate specified in this study was based on the mass and theoretical specific capacity of sulfur (i.e., 1672 mAh g^{-1}). The cells rested for 24 h before the electrochemical test. In a regular cycling test, the cell was galvanostatically charged and discharged in the voltage window of 3.0–1.5 V. The activation cycling consisted of discharging to 2.2 V, and then charging to 3.0 V at 0.05 C. The modified activation cycling was an identical process, except for the fact that the cell was initially charged at 0.2 C to 50 mAh g^{-1}. Scanning photoelectron microscopy measurements were carried out with an 8A1 beamline of the Pohang Light Source (PLS). Electrochemical impedance spectroscopy data were obtained with a Zahner IM6 Impedance Analyzer (Zahner, Germany) from 100 kHz to 10 mHz with an AC voltage amplitude of 5 mV at a 3.0 V voltage of the cell, with the Li metal foil as reference electrode. The data were analyzed using a model circuit derived by the ZView (Scribner Associates, Inc.).

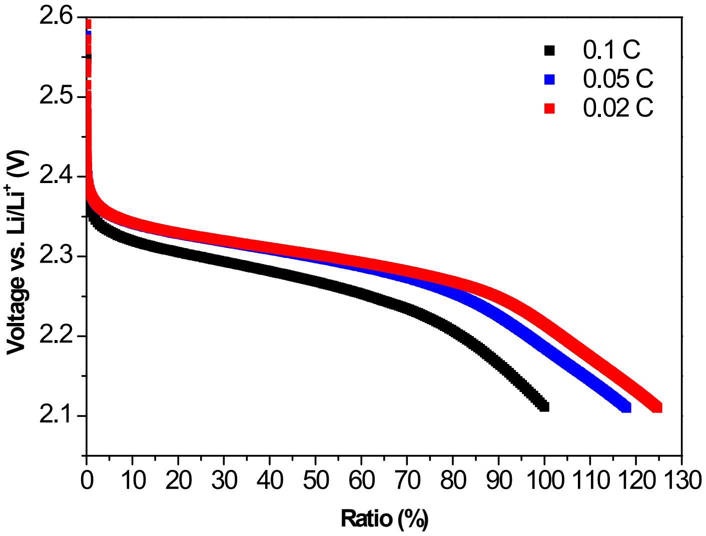


Fig. S1. Comparison of discharge capacities at the first plateau for different C-rates.

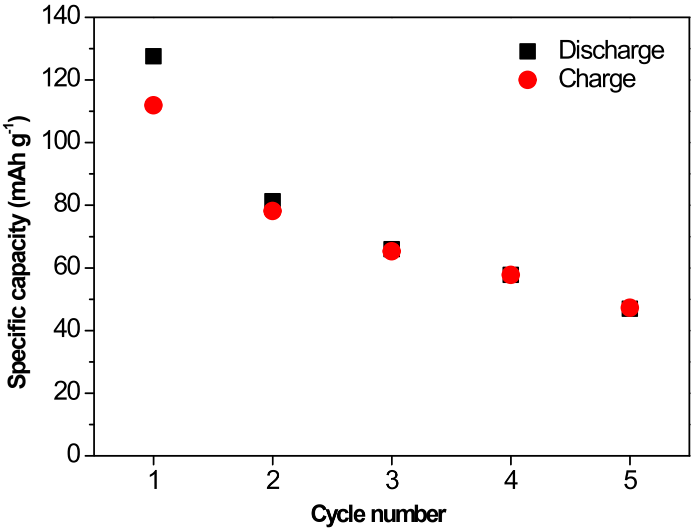


Fig. S2. Charge and discharge specific capacities of activation-cycled cell for the initial 5 cycles. An incomplete charging occurred only at the first cycle. From the irreversible capacity loss, about 15% of sulfur remained in the electrolyte after the first cycle. 20 μL of the electrolyte is present in the each coin cell. The complete utilization of sulfur is almost impossible, as the Nazar group reported.[1] Therefore, we can estimate the sulfur concentration to be as large as 0.23 M.

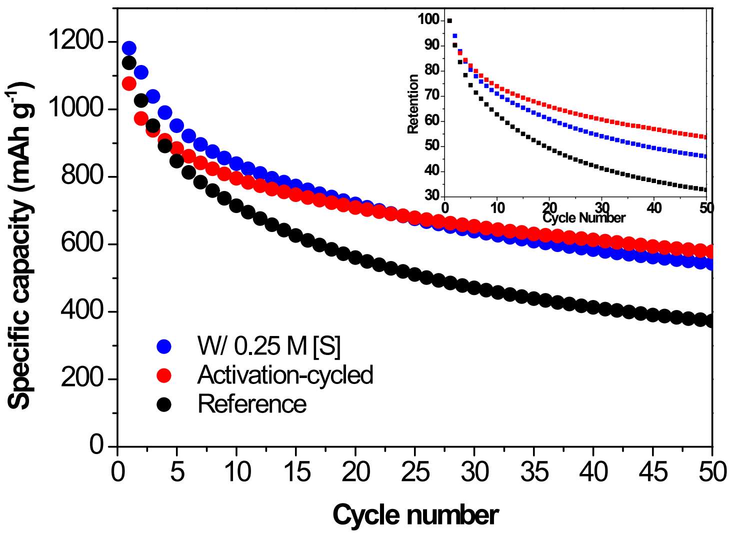


Fig. S3. Cycle life performance of activation-cycled cells (red), cells with 0.25 M (blue), and reference cells (black) at 0.1 C. Inset shows the cycle retention of cells during 50 cycles. The cycle retentions of activation-cycled cell, cell with 0.25 M, and reference cells are 53.7, 46.0, 32.7%, respectively.

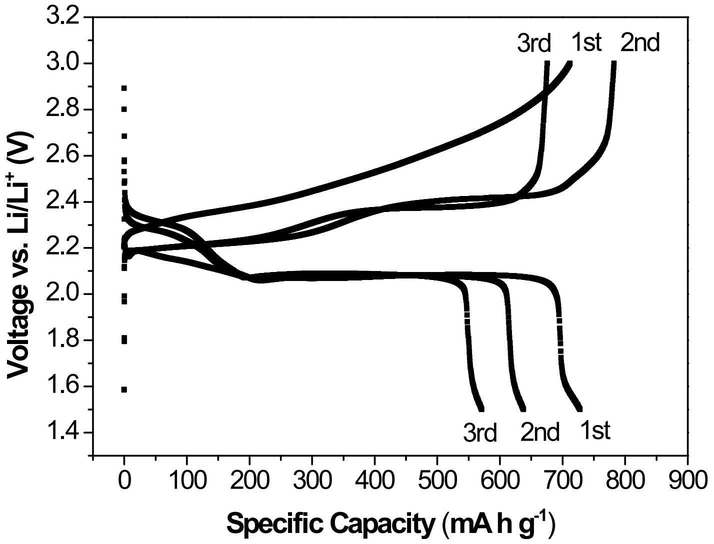
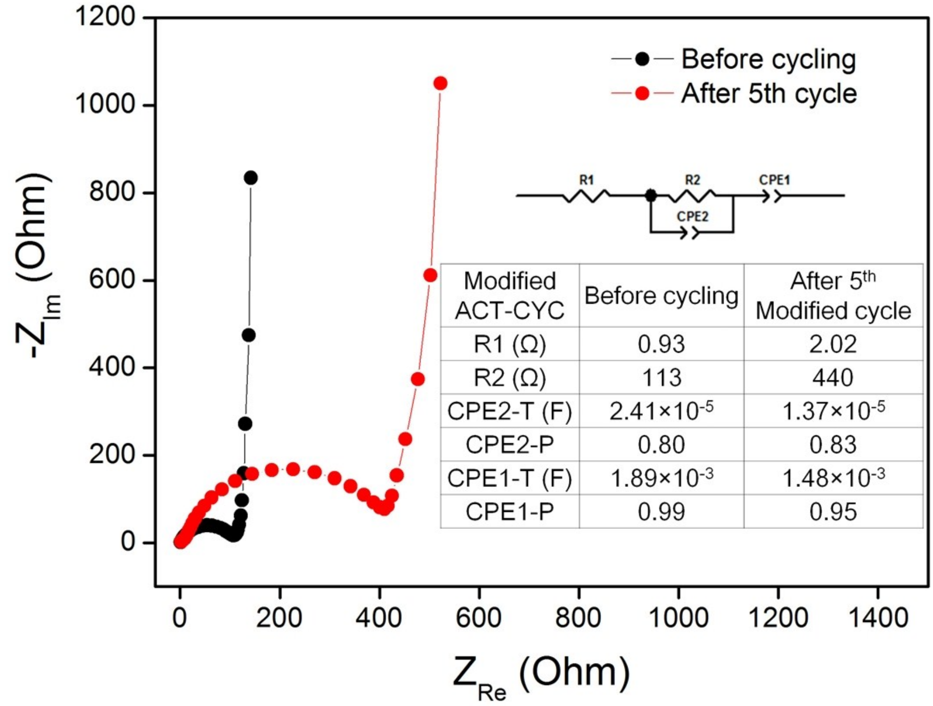


Fig. S4. Charge and discharge profiles of a Li_2S electrode for initial three cycles (0.1 C).



Modified ACT-CYC	Before cycling	After 5^{th} Modified cycle
R1 (Ω)	0.93	2.02
R2 (Ω)	113	440
CPE2-T (F)	2.41×10^{-5}	1.37×10^{-5}
CPE2-P	0.80	0.83
CPE1-T (F)	1.89×10^{-3}	1.48×10^{-3}
CPE1-P	0.99	0.95

Fig. S5. Nyquist plots of modified activation-cycles. Inset shows the fitting results of EIS.

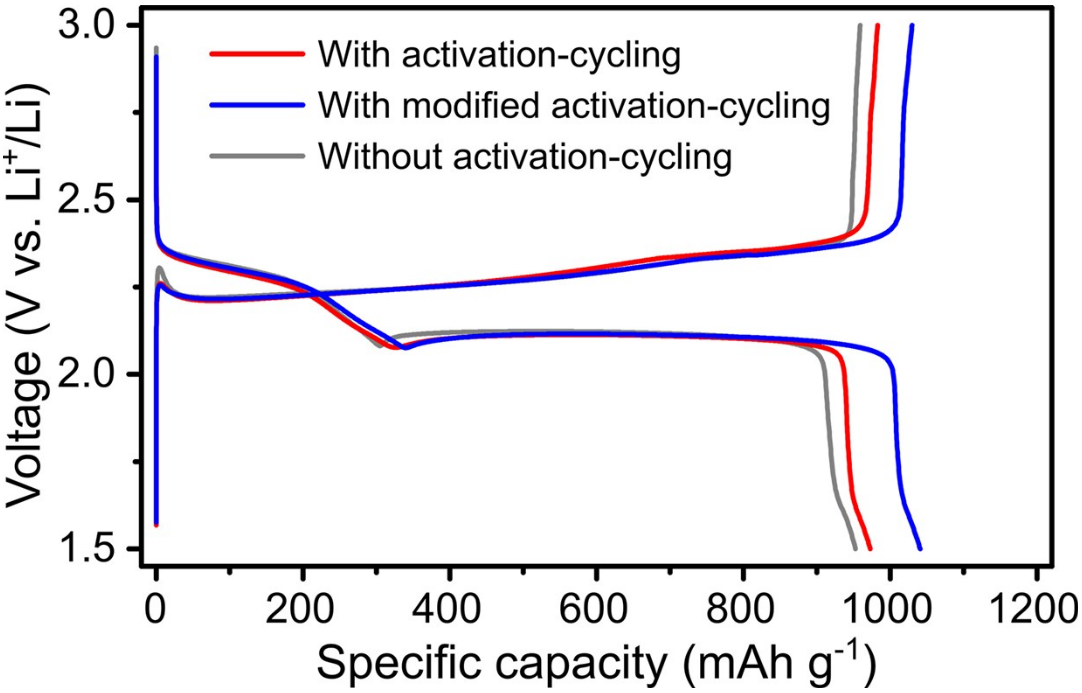


Fig. S6. Charge and discharge curves of reference, activation-cycled and modified activation-cycled cells for the second cycle.

Reference

1. M. Cuisinier, P.-E. Cabelguen, S. Evers, G. He, M. Kolbeck, A. Garsuch, T. Bolin, M. Balasubramanian and L. F. Nazar, *J. Phys. Chem. Lett.*, 2013, **4**, 3227.