Electronic Supplementary Information (ESI)

A rechargeable metal-free full-liquid sulfur−bromine battery for sustainable energy storage

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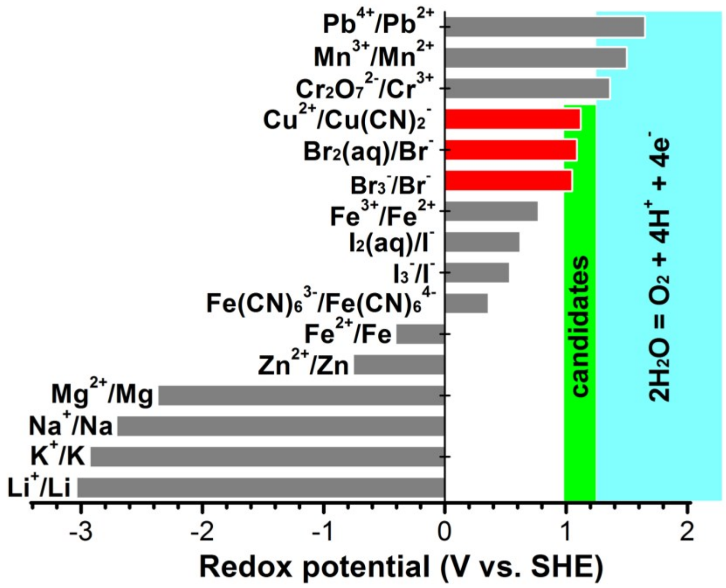

Fig. S1 Redox potential of various reversible redox couples. The ones have a high redox potential above 1 V (vs. SHE) but below the threshold of O_2 evolution by water electrolysis (1.23 V vs. SHE) are within considerations for constructing redox flow batteries to pair sulfur-based anolytes.

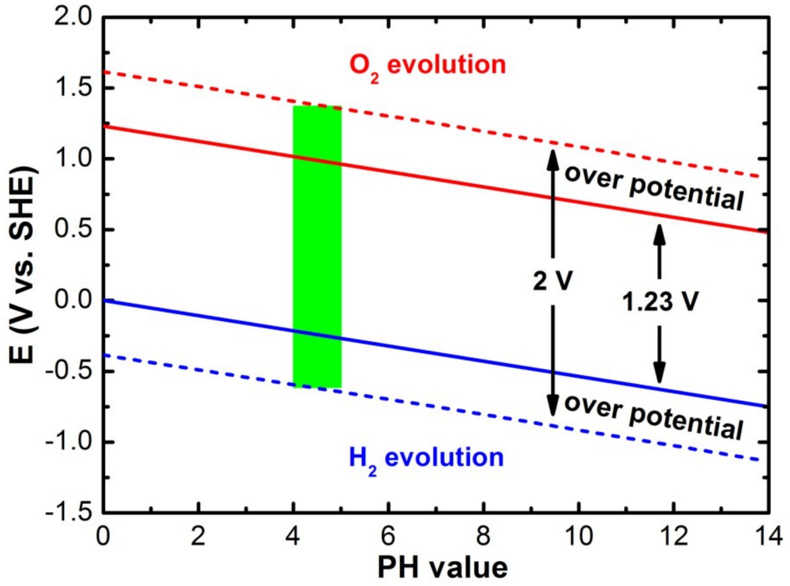

Fig. S2 Stable potential window of H_2O at room temperature. Based on the Nernst equation, the stable electrochemical potentials of aqueous electrolyte solutions at neutral pH should be in the potential window of -0.4–0.83 V (vs. SHE, standard hydrogen electrode). However, water electrolysis would not generally proceed beyond these terminal potentials, as the electrical input must provide the full amount of enthalpy of H_2/O_2 evolution, which broadens the threshold of water electrolysis to ca. 0.75–1.25 V (vs. SHE) or 2.29–4.29 V (vs. Li/Li^+).[1,2] In this work, the pH value of the LiBr-KBr catholyte solutions were tuned into weak acidic, as indicated by the green color.

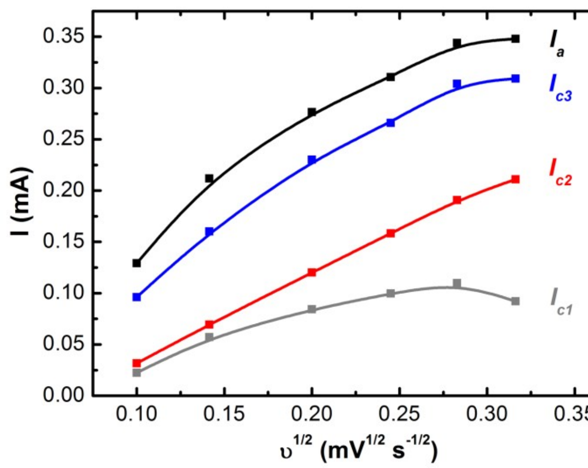

Fig. S3 Relationship between the cathodic and anodic peak currents (I) and the square root of the sweep rates (υ) .

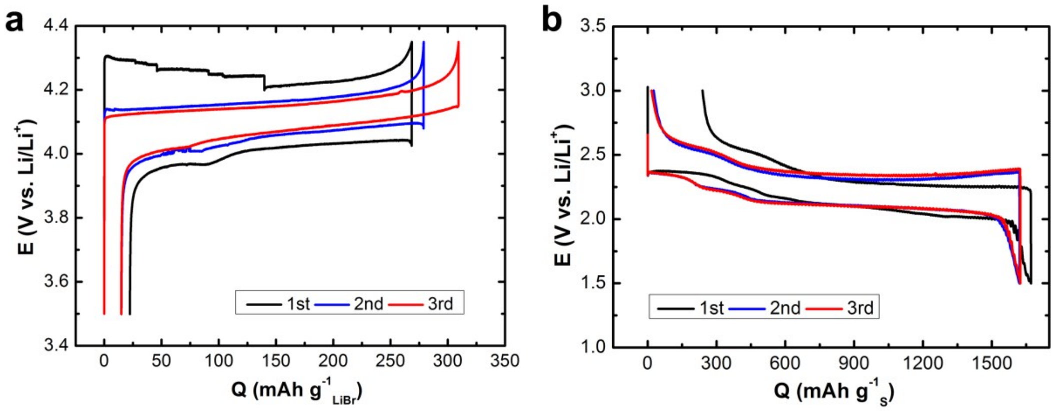

Fig. S4 Galvanostatic charge–discharge profiles of (a) Li–LiBr and (b) Li–S half cells for the initial 3 cycles at 0.02 mA cm^{-2}. The Li–LiBr half cell with an aqueous solution in presence of 0.3 M LiBr and 1 M KBr, and the Li–S half cells with a THF solution containing 0.1 M S and 1 M $LiClO_4$. Both of the counter/reference anode is metallic Li.

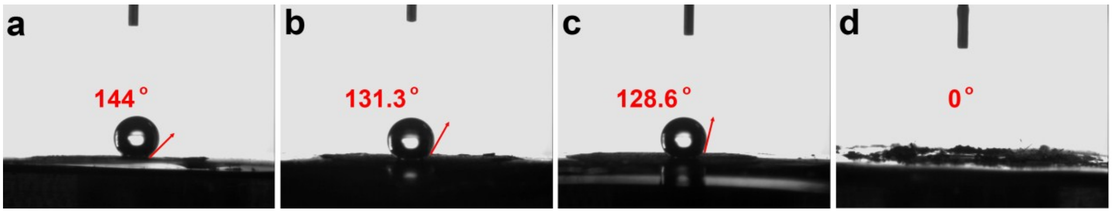

Fig. S5 Contact angle of catholyte and anolyte with the carbon current collectors. (a) Catholyte with the pristine carbon current collector. (b) Catholyte with the carbon current collector after the 1st cycle. (c) Catholyte with the carbon current collector after 5 cycles. (d) Anolyte with the pristine carbon current collector. The images were taken when the electrolyte solution in contact with the carbon surface for 120 s.

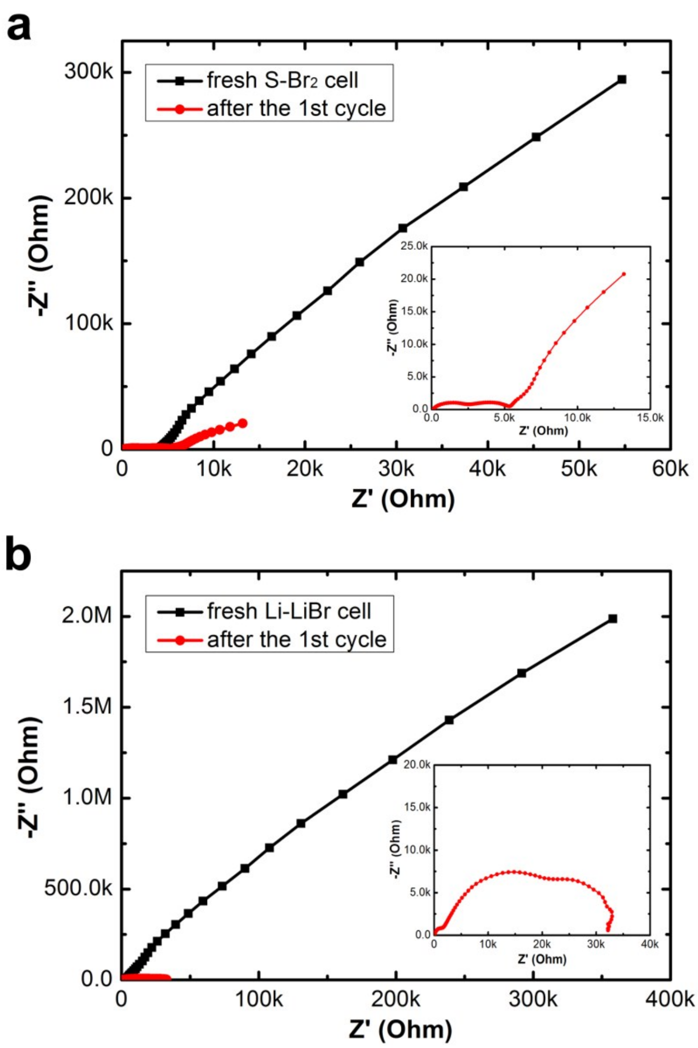

Fig. S6 Nyquist plots of the as-assembled fresh (a) S–Br_2 full cell and (b) Li–LiBr half cell (black) and the cells after the initial charge–discharge cycle (red). The insets are the zoomed-in view of Nyquist plots from cycled cells.

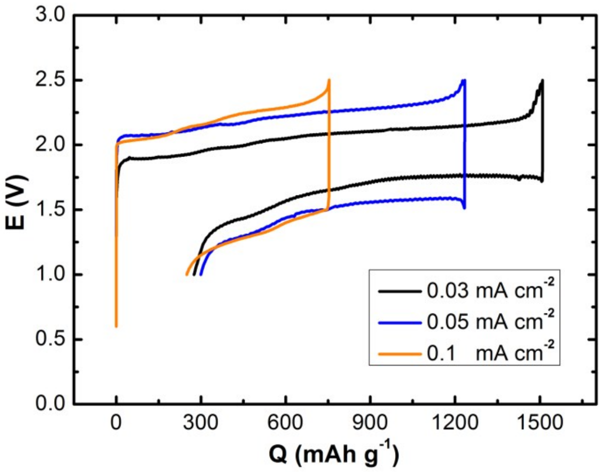

Fig. S7 Galvanostatic charge–discharge profiles of S–Br_2 cells on the 1st cycle at various current densities of 0.03, 0.05 and 0.1 mA cm^{-2}.

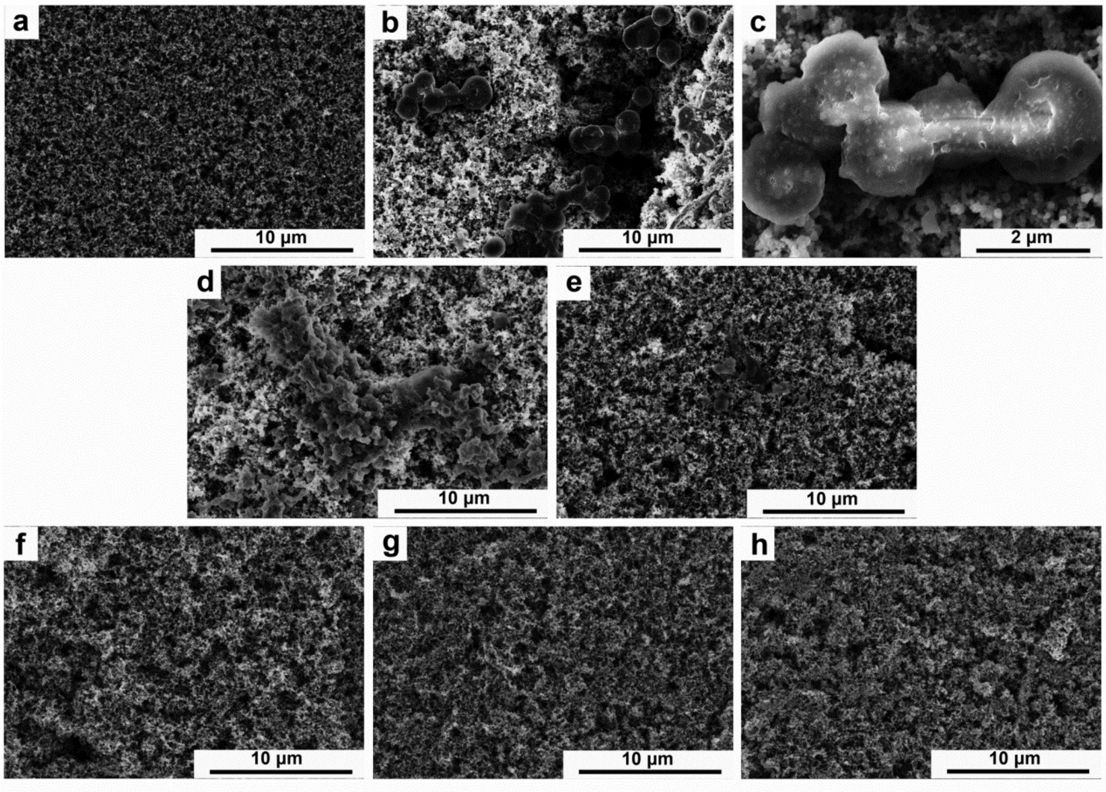

Fig. S8 SEM images of carbon current collectors for (b–e) anolytes and (f–h) catholytes. (a) Pristine carbon film. (b, c, f) After the first charge. (d, g) After the first discharge. (e, h) After the 5th discharge.

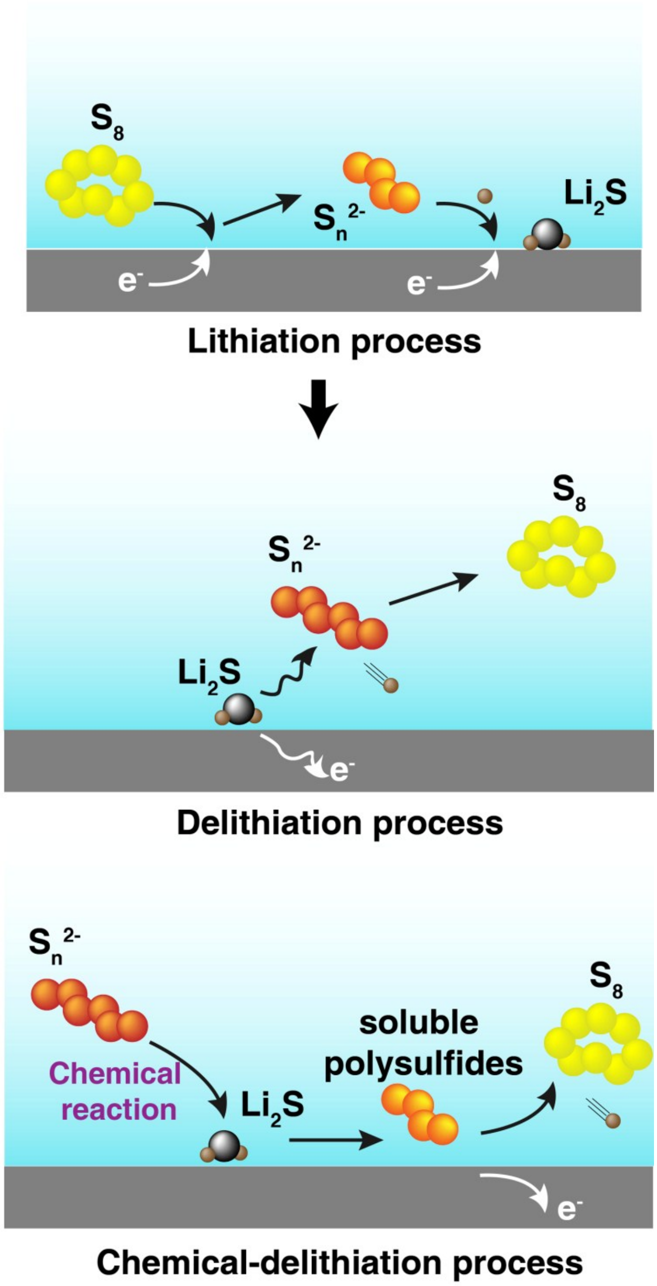

Fig. S9 Illustration of the electrochemical and chemical delithiation process of Li_2S. Except the direct electrochemical delithiation of Li_2S, the Li_2S can also be oxidized by the liquid intermediate products (e.g., long-chain polysulfides) to soluble short-chain polysulfides through chemical reactions.

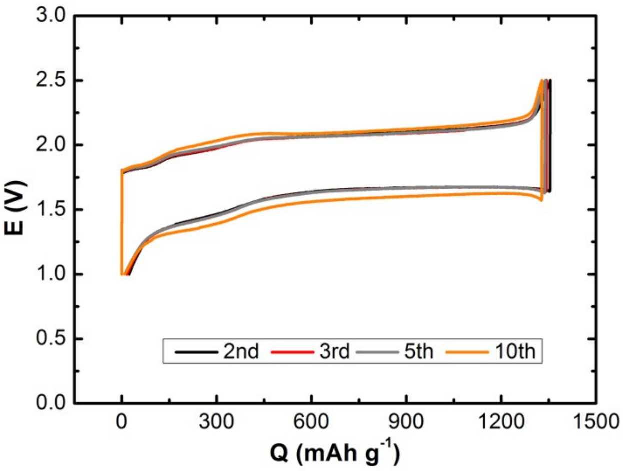

Fig. S10 Charge–discharge curves of a S–Br_2 battery for repeated cycles with a current density of 0.1 mA cm^{-2} at 30 ^{o}C.

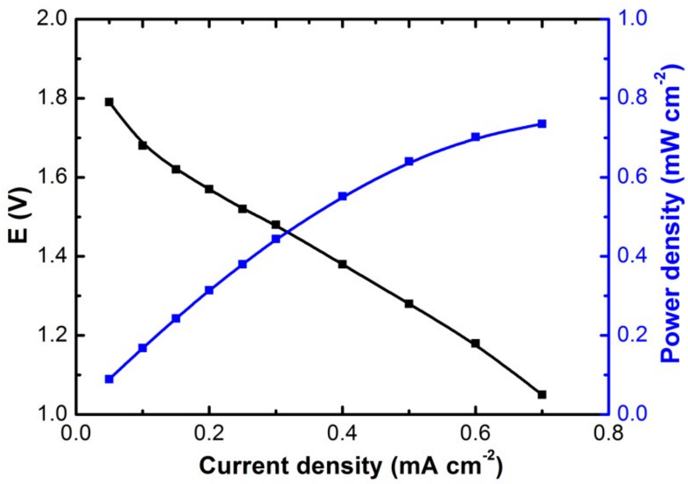

Fig. S11 Polarization curve (black) and corresponding specific power density (blue) of S–Br_2 battery. The operation temperature is 30 ^{o}C. The power density was calculated from the midpoint discharge voltage at 50% depth of discharge at the respective current density in voltage range of 1.0–2.5 V. Presently, a wider cut-off voltage was not applied due to the consideration of potential issues such as the O_2 and H_2 evolution of aqueous catholyte.

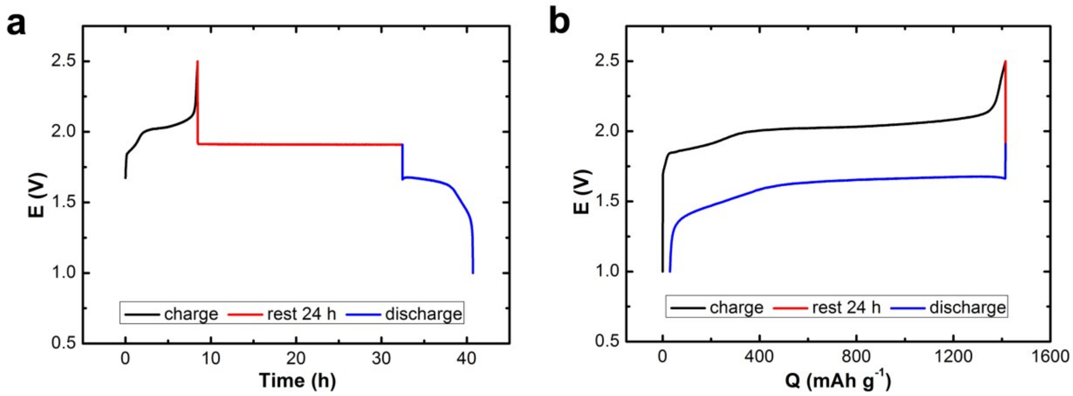

Fig. S12 Self-discharge behavior of S–Br_2 battery. (a) Charge–rest–discharge curves as a function of time. (b) The corresponding galvanostatic profiles as a function of specific capacity. The operation temperature is 30 ^{o}C.

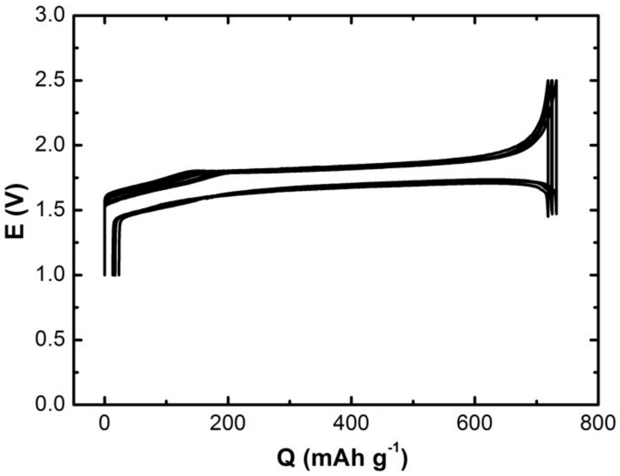

Fig. S13 Galvanostatic charge–discharge profiles of S–Br_2 battery with a high concentration of polysulfides. The aqueous catholyte solution containing 3 M LiBr and 2 M KBr. The anolyte is a THF solution in presence of 1/8 M Li_2S_8 and 1 M $LiClO_4$. The current density is 0.05 mA cm^{-2}.

References

1. L. Chen, Z. Guo, Y. Xia and Y. Wang, *Chem. Commun.* 2013, **49**, 2204–2206.
2. Y. Zhao, Y. Ding, J. Song, J. B. Goodenough and G. Yu, *Energy Environ. Sci.* 2014, **7**, 1990–1995.