Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information for

A lithium/polysulfide semi-solid rechargeable flow battery with high output performance

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Experimental Section

Blank electrolyte (BE) with 1 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and 0.1 M $LiNO_3$ in a solvent mixture of DME/DOL (v/v, 1:1) was purchased from Novolyte Technologies (Suzhou). To prepare polysulfide catholytes, stoichiometric amounts of lithium sulfide (Li_2S, 99.9%, Alfa Aeser) and sulfur powder were mixed in proper volume of BE in an argon-filled glove box. The mixture was then stirred at 50 °C overnight to obtain polysulfide catholytes with moderate viscosity in the form of 0.05 M, 0.1 M, 0.2 M Li_2S_8 and 0.2 M Li_2S_6.

To prepare working electrodes, 0.6 g acetylene black and 0.1 g polyvinylidenefluoride (PVDF) were mixed together and dispersing in N-methylpyrrolidone (NMP) overnight to prepare a slurry. The slurry was then cast onto aluminium current collectors and drying at 65 °C under flowing air. After the organic solvent was evaporated, the electrode film was punched out and further dried in a vacuum oven at 65 °C for 24h.

A laboratory lithium/semi-solid polysulfide flow cell was constructed using lithium plates as anode and lithium polysulfide solution as catholyte employing carbon electrode (1 cm × 2 cm, 30 um thick) as cathode with polysulfide solution continually flowing through the two electrodes to avoid large concentration polarization. While a type of Swagelok-type cells was used with carbon cathodes in circular disks with 15 mm diameter, lithium foil as anode and Celgard 2300 as separator. All the cells were assembled in argon-filled glove box and the metal lithium had been pre-passivated by soaking in the BE for 24 hours before use.

Characterizations

The morphology of the lithium and carbon cathodes was investigated using a Hitachi SU8010 high resolution field emission scanning electron microscope (SEM) equipped with an energy-dispersive X-ray spectroscope (EDS) attachment. The pre-passivated lithium was washed with pure DME to remove the lithium salts on the surface while the cathodes after cycling were washed and soaked in DME for 24 hours before characterization. A box with argon filled was used to protect lithium during the transfer process before test. The UV–visible absorption spectroscopy (UV) of the polysulfide catholytes was performed on a TU-1901 spectrophotometer using BE as the reference. Both the catholytes and the BE were diluted with DME to reach the necessary detection limit before the UV tests.

Galvanostatic cycling of the cells was conducted using a CT2001A battery cycler (Land, Wuhan). The polarization curves of four types of lithium polysulfide catholytes were performed on a VMP3 (Biologic, France) electrochemical workstation around the open-circuit voltage. Cyclic voltammetry (CV) tests and electrochemical impedance spectroscopy (EIS) were performed using a classical two-electrode Swagelok-type cell on a VMP3 electrochemical workstation with a scan rate of 0.1 mV s^{-1} at 2.5-2.2 V and an amplitude of 5 mV from 100 kHz to 10 mHz, respectively. The obtained impedance data were analyzed using EC-Lab V10.37 software. All experiments were conducted at room temperature.

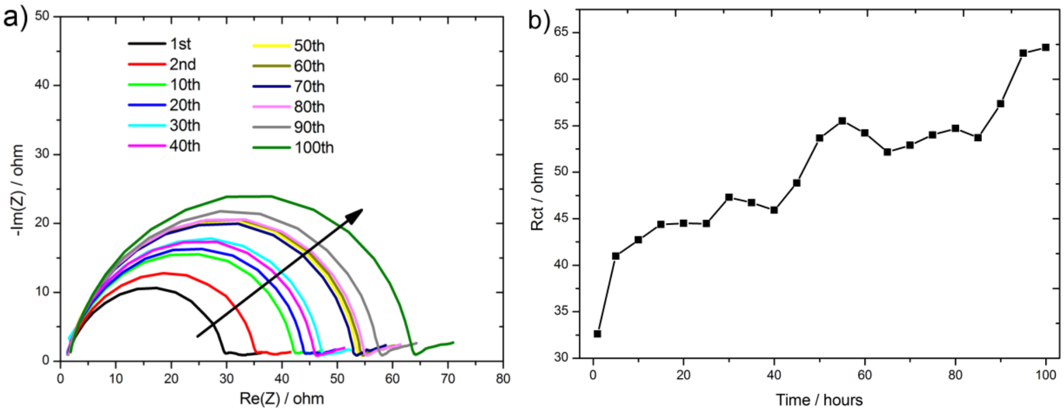

Figure S1. EIS measurements for monitoring the SEI growth using a Li/Li symmetric cell in BE. a) The EIS spectra of the resistance of the surface layer with BE recorded at OCV at 15 mins time intervals for 100 times. b) The passivation resistance on the Li electrode during the storage.

A Li/Li symmetric cell in blank electrolyte (BE) was used to monitor the impedance change during storage. Some selected EIS cycles are displayed in Figure S1a and the passivation resistance of the Li electrode is fitted and plotted in Figure S1b. Note that the impedance can be considered to be the combined result of the passivation resistance on both sides of the symmetric lithium electrode, which, however, could make it easier to observe the SEI growth. Upon aging, the impedance of the cells gradually increased and did not show any obvious decline tendency within 100 h, indicating the formation and growth of a passivation layer or SEI on the Li electrode, which is in good agreement with previous observations.[1, 2]

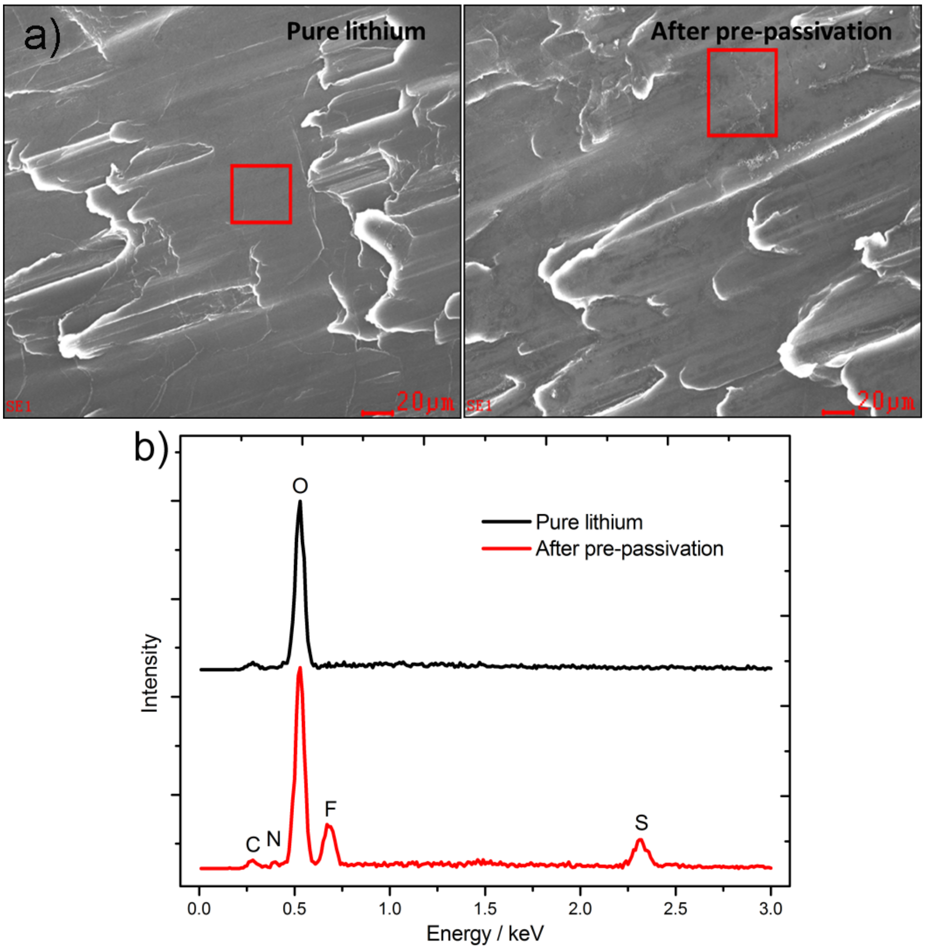

Figure S2. (a) SEM and (b) EDS characterizations of the lithium surface with and without pre-passivation in BE for 24 h. The lithium after passivation was washed with DME for three times to remove lithium salts on the surface before test.

The passivation layer was further examined by energy-dispersive X-ray spectroscopy. The EDS results reveal that a passivation layer containing C, N, F, S may generate on the lithium surface after pre-passivation in BE. As observed by Doron Aurbach,[1] $LiNO_3$ can probably reduce to LiN_xO_y on lithium. And the formation of ROLi and HCO_2Li species and species containing C-F, S-O and S=O are due to the reduction of DOL and LiTFSI, respectively. All the species generated can act as a barrier to protect lithium from the possible reduction in polysulfide species solutions and thus remarkably improve the coulombic efficiency.[1, 3]

Equations:

Polysulfide can be also obtained through the reaction of elemental sulfur and lithium sulfide ($Li_2S + (x\text{-}1)\ S \rightarrow Li_2S_x$). It is obviously a redox reaction. However, except the redox reaction, as the Gibbs free-energy of each polysulfide anion is so close that there are also a series of reversible disproportionation reactions.[4, 5] Some of the reversible disproportionation reactions are shown below.

$$4\ Li_2S_8 \longleftrightarrow 4\ Li_2S_6 + S_8 \qquad (1)$$

$$2\ Li_2S_8 \longleftrightarrow 2\ Li_2S_4 + S_8 \qquad (2)$$

$$3\ Li_2S_4 \longleftrightarrow 2\ Li_2S_3 + Li_2S_6 \qquad (3)$$

When the cell is under charge or discharge, the new product like S_8 or Li_2S would destroy the former chemical equilibriums in the catholyte solution. The polysulfides can react with S_8 or Li_2S (Eq. (4) and (5)) and reach new steady state through a series of reversible disproportionation reactions (Eq. (1)-(3)).

$$2\ Li_2S + 5\ Li_2S_8 \rightarrow 7\ Li_2S_6 \qquad (4)$$

$$S_8 + Li_2S \rightarrow Li_2S_x\ (\text{e.g. } Li_2S_8,\ Li_2S_6) \qquad (5)$$

The disproportionation reactions can be summarized as follows:

$$8\ Li_2S_x \longleftrightarrow 8\ Li_2S_y + (x\text{-}y)\ S_8 \qquad (6)$$

$$Li_2S_x \longleftrightarrow Li_2S_{x+y} + Li_2S_{x\text{-}y} \qquad (7)$$

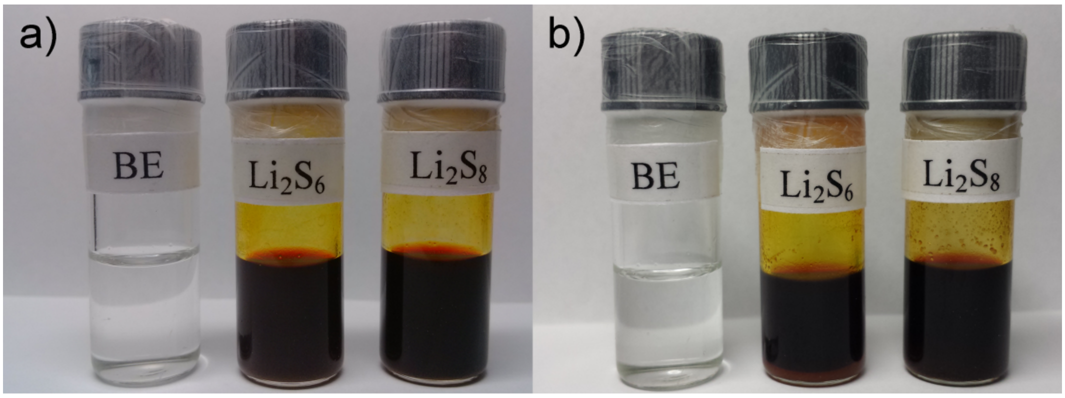

Figure S3. The photographs of blank electrolyte, 0.2 M Li_2S_6 and Li_2S_8 a) before storage test, b) after storing for 3 months.

The chemical equilibrium of Eq. (6) is affected by the temperature and concentration of polysulfide solution and high temperature and high PS concentration favor Eq. (6) moving backward (left side).[6] As shown in Fig. S3, after 3 months, yellow sulfur precipitated at the bottom of 0.2 M Li_2S_6 and can be treated by a high temperature or improve the concentration to obtain homogeneous solution. While 0.2 M Li_2S_8 remained unchanged only with little sulfur precipitated on the bottle's wall above the solution, which can be ascribed to the loss of solvent.

$$8\ Li_2S_x \longleftrightarrow 8\ Li_2S_y + (x\text{-}y)\ S_8 \quad (6)$$

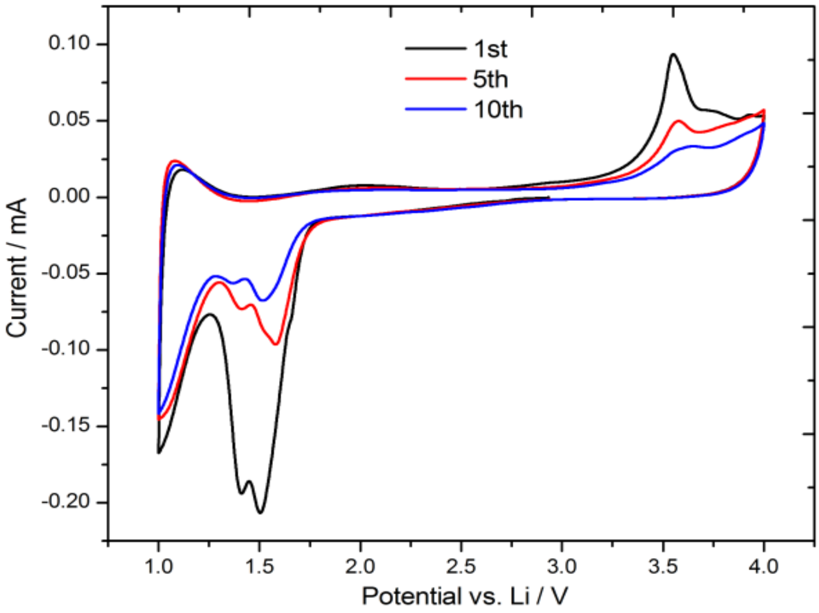

Figure S4. Cyclic voltammograms of blank electrolyte cycled on carbon cathode by scanning at 0.1mV s^{-1} between 1.0 and 4.0 V.

The appropriate working potential window of the blank electrolyte was investigated by CV tests on carbon cathode (Figure S4). The results show clearly that the electrochemical window should be limited between 1.8 V and 3.2 V. In addition, the declining peaks appeared at 1.5 V should be ascribed to the irreversible reduction of $LiNO_3$ on carbon surface.[3]

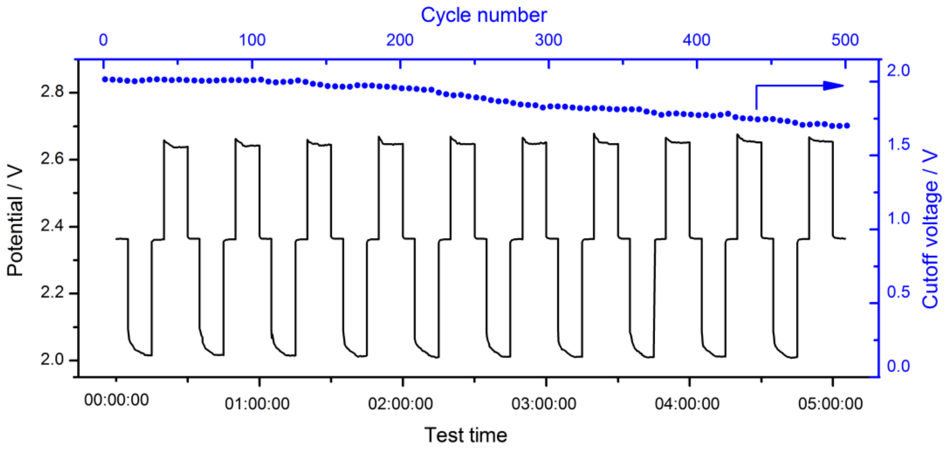

Figure S5. The voltage profiles and cutoff voltage using 0.2 M Li_2S_8 catholyte cycling at 2.5 mA cm^{-2} for 500 times. The cell was cycling with the limit of the charge and discharge time (10 minutes for charge and discharge, respectively).

To show clearly, only first 10 cycles of the voltage profiles are displayed above. The charge and discharge profiles do not show any obvious changes and the cutoff voltage remains stable with the limit of the charge and discharge time. However, after about 100 cycles, the cutoff voltages begin to decline slightly with the increase of the cycle number. The decline of cutoff voltages should be mainly attributed to the constant growth of the passivation layer on the Li electrode, which is in accord with the observation as shown in Figure S1b.

References

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