

## Supplementary Information for

# A Membrane-free Lithium/polysulfides Semi-liquid Battery for Large-Scale Energy Storage

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### 1. Energy density calculation

In the calculation,  $E_i = \frac{C_{catholyte,i} C_{Li,i}}{C_{catholyte,i} + C_{Li,i}} V$ ,  $i = M$  or  $V$  for gravimetric and volumetric energy density, respectively.  $V$  is the average voltage of discharge.

The capacity of lithium is set to 2000 mAh g<sup>-1</sup> and 1000 mAh cm<sup>-3</sup>, respectively, to take the low coulomb efficiency of lithium into account.  $C_{catholyte,V} = qmC$ ,  $q$  is the specific capacity for the polysulfide active material based on the mass of sulfur.  $m$  is the molar weight of sulfur, 32 g mol<sup>-1</sup>.  $C$  is the concentration of polysulfide in the unit of mole of sulfur per liter.  $q = 209$  mAh g<sup>-1</sup> for redox reaction between Li<sub>2</sub>S<sub>8</sub> and Li<sub>2</sub>S<sub>4</sub>.  $q = 418$  mAh g<sup>-1</sup> for the range between Li<sub>2</sub>S<sub>4</sub> and sulfur. For example,  $C_{catholyte,V} = 66.9$  mAh cm<sup>-3</sup> for 5 M catholyte and reaction between Li<sub>2</sub>S<sub>8</sub> and sulfur.  $C_{catholyte,m} = C_{catholyte,V} / \rho$ , where  $\rho$  is the density of the catholyte. Our measurement shows that  $\rho = 0.96 + 0.032C$  (g cm<sup>-3</sup>) for the catholyte. The average voltage is 2.30 V based on our experimental data. The specific energy is also plotted as follows.

The volumetric energy density of vanadium flow battery (VFB) is based on that both the concentrations of catholyte and anolyte are 1.7 M. Then both  $C_{catholyte,V}$  and  $C_{anolyte,V}$  are  $96485 \text{ C/mol} \cdot 1.7 \text{ mol/L} = 45.6 \text{ Ah/L}$ . The voltage of VFB is set to 1.3 V and thus the corresponding volumetric energy is 30 Wh/L. The gravimetric energy density is cited from reference.<sup>1</sup>

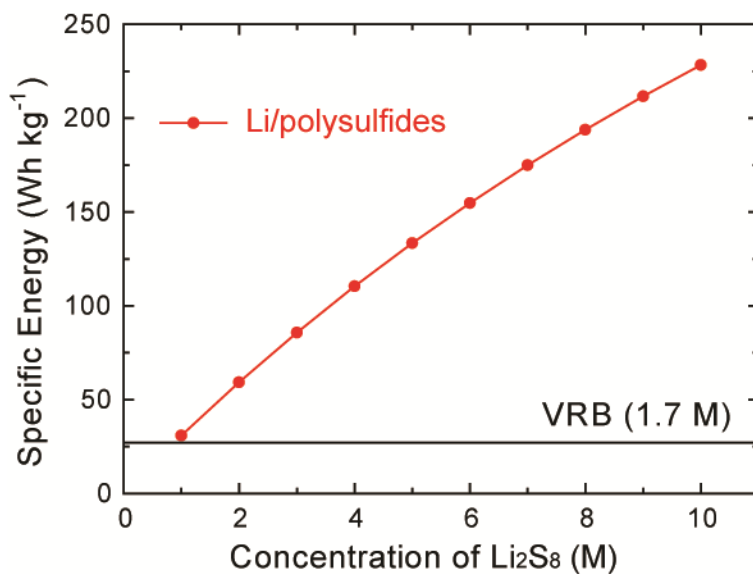


Fig. S1 The specific energy of the Li/PS system with different cycling range. VRB is short for vanadium redox battery. The theoretical specific energy of VRB is considered to be 29 Wh kg<sup>-1</sup> based on literature.<sup>1</sup>

## 2. Cost of raw materials for the Li/PS system

The prices of raw materials are obtained from [www.metalprices.com](http://www.metalprices.com) and [www.alibaba.com](http://www.alibaba.com). As polysulfide solution can be synthesized through direct reaction between sulfur and lithium, we calculate the cost of sulfur, lithium and solvent required. The specific capacity of lithium is supposed to be 2000 mAh g<sup>-1</sup> to take into account extra lithium needed. The specific capacity of polysulfide is set to 200 mAh g<sup>-1</sup>, For 1 kWh, 330 g lithium and 2.1 kg sulfur are needed; their costs are 22 and 0.6 US dollars, respectively. The total amount of DOL/DME required is 13 kg for a 5 M catholyte

solution and the cost is 20 dollars. So the total price of raw materials is \$45/kWh, which is less than the cost of raw materials in VRB (\$50-110 kWh<sup>-1</sup> for vanadium materials)<sup>2</sup> and much less than the total cost of flow batteries (\$180-250 kWh<sup>-1</sup>).<sup>3</sup>

Regarding to cost per kilowatt, the power density is supposed to be 10 mW cm<sup>-2</sup>, though our data already show capability up to 40 mW cm<sup>-2</sup>, considering that both sides of lithium and carbon electrode can be used for power generation (Fig. 2d in the main text). The cost of carbon substrate is considered as \$100 kg<sup>-1</sup>, which is reasonable based on the cost of multi-walled carbon nanotubes<sup>4</sup> and mass loading of 10 mg cm<sup>-2</sup> for the carbon current collector; thus the cost for carbon electrodes is

$$\$100/\text{kg} \times 10 \text{ mg}/\text{cm}^2 / (10 \text{ mW}/\text{cm}^2) = \$100/\text{kW}$$

The cost of separator is as low as \$1.5 m<sup>-2</sup>.<sup>5</sup> Since the battery could reach 1-2 C rate, the cost of active materials is set to ~\$30 kW<sup>-1</sup>. Consequently the total cost of raw materials per kW is only \$145. The cost per kilowatt in current batteries is over \$1000 for the whole system<sup>6</sup>, which suggests that the material cost is negligible compared to other components in the system.

### 3. The electrochemical voltage profile of Li/PS cell without LiNO<sub>3</sub>

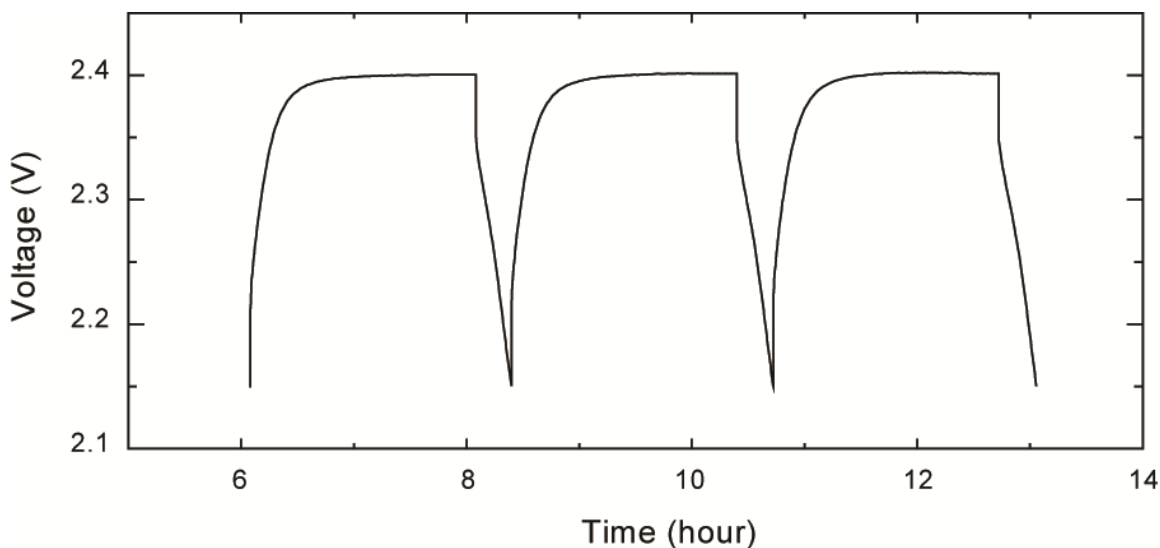


Fig. S2 The voltage profile of typical cycles of a 30  $\mu\text{L}$  5 M  $\text{Li}_2\text{S}_8$  solution at a 0.8 C rate. The cell cannot be fully charged due to strong shuttle effect. As a result, two hours is used as the time cut-off for charging, corresponding to 1045  $\text{mAh g}^{-1}$ . The discharge time is about 0.3 hour and thus the coulomb efficiency is only 15%.

#### 4. Effects of different factors on cycle life and coulomb efficiency

To understand how different factors affect the cycle life and coulomb efficiency of the Li/PS system, we perform a survey on various parameters: concentration of  $\text{Li}_2\text{S}_8$  (2.5 M vs. 5 M), concentration of  $\text{LiNO}_3$  (1 wt% vs. 2.5 wt%), current rate (0.4 C vs. 0.8 C) and volume of catholyte (20  $\mu\text{L}$  vs. 35  $\mu\text{L}$ ). The four parameters generate 16 combinations and all conditions are tested. As a result, in the statistics in Fig. 4, other factors are not fixed along with the parameter studied. However, the three statistically significant parameters shown in Fig. 4 are all further confirmed by at least four pairs of samples whose other parameters are all the same.

#### 5. Self Discharge

In the self discharge test, 25  $\mu\text{L}$  5 M catholyte with 2.5 wt%  $\text{LiNO}_3$  is used. The current rate is 0.8 C. The cell is first cycled for 20 times. Then it is rested at the end of charge for seven days and discharged at the same current rate as previous cycling. The result is shown in Fig. S4. The open circuit voltage drops by only 28 mV from 2.404 V at 0.5 day to 2.376 V at the end of the seventh day. The following discharge capacity is 162  $\text{mAh g}^{-1}$ , which is 55% of the previous discharge (294  $\text{mAh g}^{-1}$ ). This indicates that 45% capacity is lost in seven-day resting, or 6.5% loss per day.

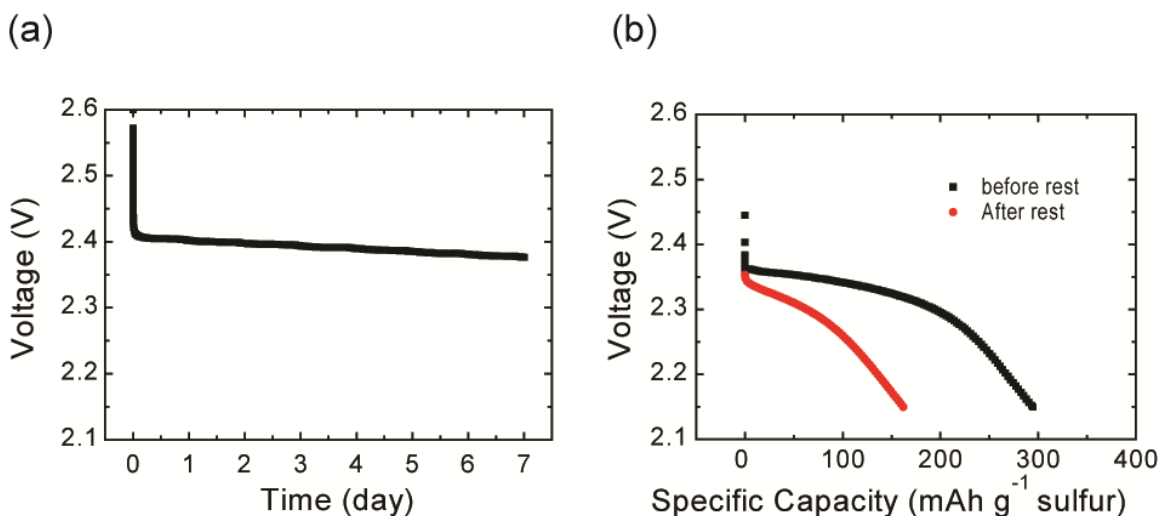


Fig. S3 (a) The voltage change of a PS/Li cell during rest. (b) The discharge voltage profile before and after rest.

To compare the self-discharge rate with other system, we convert the self-discharge rate to permeation rate, which describes how fast active species is consumed at the interface between two electrodes. In flow battery, the diffusion of active species (e.g. V<sup>2+</sup>) across the ion-selective membrane is the major reason for self discharge and permeation rate is used to evaluate the performance of the membrane and self-discharge rate. In tests of permeation rate, a membrane is sandwiched between two reservoirs where the right one is filled with the species to study while the left one does not contain the species to study.<sup>7</sup> Permeation rate ( $P$ ) is defined based on the following equation:

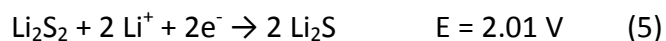
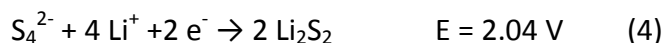
$$V_R \frac{dC_R(t)}{dt} = AP[C_L(t) - C_R(t)]$$

where  $C_L$  and  $C_R$  are the concentration of studied species on the left and right side of the membrane, respectively.  $A$  is the area the membrane.  $V_R$  is the volume of right reservoir with species to study. In other word, permeation rate equals to the ratio of permeability to the thickness of membrane.

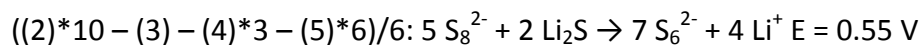
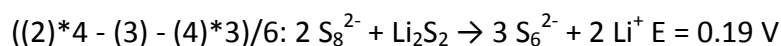
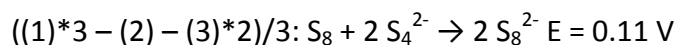
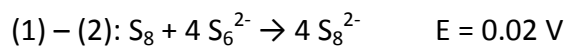
The typical permeation rate of Nafion membrane is  $5 \times 10^{-5} \text{ cm min}^{-1}$ , as permeability of Nafion is  $10^{-6} \text{ cm}^2 \text{ min}^{-1}$  and its thickness is  $175 \text{ }\mu\text{m}$ .<sup>7</sup> For the Li/PS system, parameters in the self-discharge test described above are used, and the corresponding permeation rate  $P$  is around  $10^{-6} \text{ cm min}^{-1}$ , about two orders of magnitude smaller than the Nafion membrane. This indicates that the self-discharge rate in Li/PS system is much less than that in the vanadium system. Such result also demonstrates the high quality of the passivation layer.

## 6. Calculations on thermodynamics of reactions between polysulfides

To analyze the stability of less soluble  $\text{Li}_2\text{S}_4$  phase and insoluble  $\text{Li}_2\text{S}_2$  and  $\text{Li}_2\text{S}$  phases in the catholyte, we calculate the Gibbs free energy for various reactions. The thermodynamic data are obtained from previous work:<sup>8</sup>



All potentials are versus  $\text{Li/Li}^+$ . The Gibbs free energies of following reactions could be calculated based on data above:



In the four reactions above,  $E = -\Delta G/2F$ , where  $F$  is 96485 C/mol, the Faraday constant. As a result, less soluble  $\text{Li}_2\text{S}_4$  phase and insoluble  $\text{Li}_2\text{S}_2$  and  $\text{Li}_2\text{S}$  phases are thermodynamically unstable in the catholyte. These species can be dissolved through chemical reaction with  $\text{Li}_2\text{S}_8$  and sulfur formed in charge. This indicates that the solubility issue is not the same as that in vanadium flow battery, where precipitate cannot be chemically consumed. Consequently this issue should have much less effect on the flowing capability of the system.

We also notice that the voltage for reaction (4) and (5) is considered to be higher (2.18 V) in other reports,<sup>9</sup> but  $\Delta G$  for reactions above is still negative.

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