Reactivation of dead sulphide species in lithium polysulphide flow battery for grid scale energy storage

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Lithium polysulphide batteries have several attractive features including potentially low cost and high energy density for grid energy storage. However, the precipitation of insoluble and irreversible sulphide species on the surface of carbon part and lithium part (called "dead" sulphide species) leads to continuous irreversible capacity loss in high mass loading cells, which still presents a great challenge. To address this problem, herein we propose a strategy to reactivate dead sulphide species by reacting them with cheap sulphur powders under stirring and heating (70 ºC) to recover the cell capacity, and further demonstrate a flow battery system based on above reactivation approach. As a result, ultrahigh mass loading (0.125 g cm^{-3}, 2 g sulphur in a single cell), high volumetric energy density (135 Wh L^{-1}), good cycle life, and high single cell capacity are achieved. The high volumetric energy density indicates its promising application for future grid energy storage.

Introduction

The urgent requirement to develop and integrate renewable energy such as wind and solar into the grid has driven the intense demand for high energy storage systems for grid scale energy storage[1-3]. Electrochemical energy storage, with the benefits of pollution-free operation, high round-trip efficiency, and flexible power, has been regarded as one of the most effective ways to solve the problem of intermittent renewable energy penetration[4]. Commercialized sodium-sulphur (Na-S) batteries have already been implemented for grid applications to regulate peak load and frequency, however, it faces a big safety challenge due to its high working temperature (300-350 $^{\circ}$C)[5]. Its high cost (300 \$ kWh^{-1}) also limits its large scale application[6]. Vanadium redox flow batteries are promising but are still limited by their low energy density (<50 Wh kg^{-1}), relatively high cost and environmental toxicity[7-9]. Other systems such as liquid metal batteries are emerging, is promising but inevitably face the barrier of high working temperature[10].

In order to satisfy future large scale renewable energy storage applications, low cost (<100 \$ kWh^{-1}), high energy density (>100 Wh kg^{-1}), and safe (room temperature operation) electrochemical energy storage systems are urgently needed[6,11]. Lithium-sulphur (Li-S) batteries, with a theoretical energy density of 2600 Wh kg^{-1}, are one of the most promising candidates for next generation rechargeable lithium batteries[12,13]. However, the low electrical conductivity of sulphur/Li$_2$S, deposition of non-soluble and insulating Li$_2$S/Li$_2$S$_2$ on the electrodes, volume change during cycling, and self-discharge and shuttle effect makes it difficult to move towards industrial application[14, 15], especially for high mass loading sulphur electrodes. Many strategies have been proposed to control soluble lithium polysulphides

including the design of various carbon-sulphur cathodes or other architectures to confine sulphur[16-20], exploration of new electrolytes or additives[21, 22], modification of battery configuration[23-24], and protection of the metallic lithium anode[25-27]. Although these strategies can achieve improved electrochemical performance, these issues have still not been entirely solved, and new directions for lithium/sulphur batteries are still in development[28-30].

Our group previously reported on a lithium polysulphides (LPS) semi-liquid flow battery[31], in which liquid polysulphide was used as cathode and metallic lithium as anode, demonstrating high energy density and compatibility with flow battery design (Supplementary Table 1). With the addition of lithium nitrate ($LiNO_3$), a passivation layer will form on the surface of metallic lithium, suppressing parasitic reactions between polysulphide and lithium. No ion-selective membrane was needed thus the cost was reduced. Most of the characterization of the electrochemical performance of LPS batteries were conducted using coin cells, resulting in low mass loading of sulphur, which is not representative of real-world conditions. In the coin cell configuration, it is also difficult to evaluate the full battery performance and not compatible with the semi-liquid flow battery concept.

To better realize the high capacity and high mass loading which are necessary for an industrial set-up, a new battery tank which is suitable for large scale and semi-liquid flow demonstration was designed. During our preliminary high mass loading performance test, we found that the cell capacity was not stable and decayed very quickly. After disassembling the battery tank, it was surprising to find large quantities of insoluble sulphur species deposited on both lithium and cathode (carbon felt) electrodes. These insoluble species result from the low solubility of low order polysulphides like Li_2S_2/Li_2S. As the metallic lithium used in the LPS

battery is in excess compared with the quantity of sulphur, the consumption of metallic lithium

reduces the S/Li ratio and causes precipitation of the insoluble low order polysulphides. These

insoluble sulphide species (Li_2S_x, mainly Li_2S/Li_2S_2), called "dead" sulphide species, are

inactive and cannot contribute capacity in the following cycles. The conversion of soluble high

order polysulphides into insoluble low order polysulphides (dead sulphide species) is the main

cause of fast capacity decay and finally loss of electrochemical activity.

To address the above challenge, herein we propose a method for the reactivation of dead

sulphide species in the cell through stirring and heating them with sulphur at a relatively low

temperature (70 °C). The main idea of reactivation is to use additional cheap sulphur powder

to react with the dead sulphide species in order to recover the lost capacity. By virtue of our

battery tank design, the reactivation process can be implemented without disassembling the

battery. The single cell capacity can reach as high as 0.9 Ah with a corresponding volumetric

energy density of 95 Wh L^{-1} (3 M Li_2S_8), approximately four times higher than that of vanadium

flow battery (25 Wh L^{-1})[6-8]. With high concentration Li_2S_8 (5 M), the volumetric energy density

can reach as high as 135 Wh L^{-1}. It is noted that the energy density and specific energy here are

calculated based on the real cell volume and weight (including polysulphide catholyte, $LiNO_3$

additive, lithium anode, carbon felt, and separator. The theoretical and real energy density

calculation is presented in Supplementary Note 1 and 2. Recipe is shown in Supplementary

Table 2). Excellent performance over 110 cycles was attained with reactivation every 50 cycles,

demonstrating an ultrahigh mass loading of 0.125 g cm^{-3} (2 g sulphur in single cell). To the

best of our knowledge, this is the first time that such high mass loading with stable capacity is

reported for LPS batteries, which is distinctly different from test results derived from coin

cells[30, 31]. To further verify the possibility of its practical use in semi-liquid flow systems for future large scale energy storage, a LPS flow battery system was successfully demonstrated employing our battery tank and reactivation strategy. A capacity of 1 Ah and long cycle life over 300 cycles are achieved with a reactivation tank connected with the battery system through a circulation pump, which gives a new prospect for low cost, high energy density, and stable grid scale energy storage.

Results

LPS battery configuration for reactivation. To address the problem of dead sulphide species deposition on the lithium and carbon electrodes, reactivation *via* heating and stirring at a relatively low temperature (70 $^{\circ}$C) was conducted to recycle the dead sulphide species by reacting them with sulphur powder in order to recover the cell capacity. We hypothesize that such an activation is possible since it is similar to how we prepare polysulphide solution by using Li_2S and S powder mixed in ether solvent at elevated temperature[28, 31]. This approach has two obvious benefits - cheap sulphur powder can be used to increase the capacity while also removing the dead sulphide species from the surface of the electrodes. The process is illustrated in Figure 1a. After prolonged cycling, dead Li_2S_x deposits on both the surface of the lithium foil and the carbon felt. Then the cell was moved to a hot plate with heating and stirring functions (Figure 1b), the stirring rate here was 500 RPM for stable and homogeneously stirring (this rate is variable according to the battery tank size and stirring bar size). The dead sulphide species react with sulphur during heating and stirring and convert to soluble high order polysulphides, like Li_2S_8, Li_2S_6 and Li_2S_4, thus becoming reactivated and increasing the cell capacity. Based on our design, the sulphur added was sufficient for reactivation, and the dead

sulphide species were mainly converted to Li_2S_8, while Li_2S_6 and Li_2S_4 also exist due to the

equilibrium in the electrolyte. It was apparent that coin cell or pouch cell configurations used

in previous research was not suitable for demonstrating the reactivation concept so to verify

the above effect in LPS battery, a new battery configuration was therefore designed for high

mass loading tests. As shown in Figure 1b , a stainless steel tank was made for cell assembly

(optical image of different sized tanks in Supplementary Fig. 1). The positive and negative

sides were electrically insulated from one another by a Polytetrafluoroethylene (PTFE) spacer

and the whole battery tank was sealed with a silicone rubber O-ring and a plastic crimp. Lithium

foil was used as the anode and liquid lithium polysulphide solution was selected as catholyte

using carbon felt as the current collector. The lithium foil, wrapped by a separator, was fixed

on the negative bar with a snap joint structure to ensure good electrical contact. The separator

here was used for electrical insulation of the carbon felt current collector from the lithium foil,

which differs from the separator used in specially designed Li-S battery using expensive ion-

selective membranes. The sealing requirement is not strict as the working temperature is low

and no pressure is applied to the container. In contrast, the cost of LPS batteries here will be

largely reduced, making it a good candidate for large scale applications. For reactivation under

stirring and heating condition, a magnetic stir bar was placed on the bottom of the tank. After

configuring the carbon felt and lithium foil, lithium polysulphide (Li_2S_8) solution in 1,3-

dioxolane (DOL)/1,2-dimethoxyethane (DME) was injected into the battery tank. Before

sealing the battery, some additional sulphur powder was added to the bottom of the tank for

future reactivation. As the polysulphide is in its highest order state, the additional sulphur on

the bottom will not turn into soluble polysulphide, and is thus stored in the tank for future

reactivation. The main idea of reactivation is to activate the dead sulphide species (Li_2S_x) on the lithium foil anode and carbon matrix cathode in order to recover its original capacity. When cycling at high mass loading of polysulphide caltholyte, dead sulphide species are easily deposited on the surface of lithium foil, as shown in Figure 1c (left). The dark-red sulphide species is a mixture of Li_2S_x compounds. These insulating species will block ion and electron transport and quickly deteriorate the capacity and stability of the Li-S battery.

After reactivation, as shown in Figure 1c (right), nearly all of the dead sulphide species were removed and the lithium foil surface is refreshed. The reactivation process not only increases the cell capacity, but also reduces the impedance of the battery thus enhancing the cell stability. Based on the outlined new cell configuration design, a high performance LPS battery was achieved.

LPS flow battery with reactivation function was designed based on a new battery configuration. Figure 1d (left) shows a schematic of the LPS flow battery system. The whole energy storage system can be divided into three parts: polysulphide storage tank, heating and stirring tank, and battery tank. The flow battery system can work in two modes: continuous flow working mode and intermittent flow working mode. In the continuous mode, the pump remains on and the polysulphide electrolyte continuously flows through the battery tank. The dead sulphide species on the lithium foil and solid precipitates on the carbon felt current collector can be re-dissolved or reactivated with the flowing polysulphide solution. The stirring and heating tank helps to reactivate the dead sulphide species and solid precipitates. As for the intermittent flow working mode, the pump alternates between the on and off state. After a certain period of cycling, the pump is turned on to initiate the reactivation process and inject

fresh polysulphide solution. Intermittent flow working mode may be more suitable for practical

application as the pump consumes fewer additional electricity.

To further demonstrate the LPS flow battery system, a real system was set up using the

battery tank described above to simulate this mode. As shown in Figure 1d (right), the whole

system includes electrolyte storage tank, battery tank, circulation tube, magnetic circulation

pump, hot plate with stirring function, and load (e.g. bike light). The electrolyte storage tank

was placed on the hot plate and served as the polysulphide reactivation and storage vessel. The

battery tank was assembled with carbon felt, lithium foil, and separator. Fresh and warm

polysulphides can be injected into the battery tank through the pump, and the dead sulphide

species can be reactivated in the storage tank under stirring and heating condition.

Dead sulphide species reacting with sulphur powder. To further confirm the reaction of dead

sulphide species with sulphur powder under stirring and heating condition, sulphide species

evolution experiments were conducted by stirring and heating lithium foil deposited with dead

sulphide species in DOL/DME electrolyte with sulphur powder. As shown in Figure 2a, a bottle

of DOL/DME (1:1) electrolyte with a small amount of sulphur powder (300 mg) added at the

bottom was placed on a hot plate heating at 70 $^{\circ}$C in an argon filled glove box (H_2O<0.1 ppm

and O_2<0.1 ppm). Then the lithium foil with dead sulphide species on the surface was immersed

into the electrolyte. After stirring and heating, the dead sulphide species dissolved into the

electrolyte and the color becomes darker and darker. About 1 h later, the solid dead sulphide

species were nearly all dissolved and the electrolyte becomes dark red. Then the lithium foil

was taken out and washed with DOL to remove liquid polysulphide on the surface. No obvious

solid precipitates are observed in the electrolyte solution (Figure 2a, 60 min). Figure 2b shows

the optical image of lithium before and after reaction with sulphur powder. It is clear that nearly

all the dead sulphide species were removed and the surface is refreshed and shining. The

lithium foil remains intact and no obvious corrosion or deformation is noted. Further evidence

is provided when lithium foil was immersed in high concentration polysulphide solution for a

long time (the lithium foil used in this experiment was taken from a battery running for almost

4 months) and the morphology remains unchanged (Figure 2b). Figure 2c shows the Raman

measurement of lithium foil before and after reactivation. It demonstrates that there are

Li_2S_2/Li_2S and Li_2S_x (2<x<4) species[32] on the surface of the lithium foil before reactivation.

After 1 h of heating and stirring, almost all of the species are reactivated and dissolved to form

polysulphide solution. Only the lithium signal is detected after reactivation indicating the

surface is very clean. To confirm the activity of lithium foil after reactivation, coin cells were

assembled using reactivated lithium foil as anode and fresh lithium polysulphide electrolyte (5

M) as catholyte. At a current density of 2 mA cm^{-2}, a high area capacity of 4 mAh cm^{-2} was

measured even after 600 cycles (Figure 2d). Voltage profiles show the standard

discharge/charge process (Figure 2e). Coin cells were also assembled using the newly dissolved

lithium polysulphide electrolyte (from reaction of dead sulphide species with sulphur) as

catholyte and fresh lithium foil as anode. The stable electrochemical performance

(Supplementary Fig. 2) of the coin cell confirms the activity of the obtained lithium

polysulphide solution. Stirring is very important during the reactivation process. In the

procedure for preparing the polysulphide solution, both stirring and heating are necessary for

the formation of a uniform solution. In our case, as the dead sulphide species are deposited on

the surface of lithium foil, stirring can increase the reaction rate and effective contact area

between dead sulphide species and sulphur powder. Based on our experiment, the process can

be completed very quickly, requiring less than an hour.

Another experiment was conducted to verify the stirring and heating function. Three vials

were prepared with Li_2S and S powders (1:7, mass ratio, Supplementary Fig. 3). Vial 1 was

neither heated nor stirred, vial 2 was only stirred while vial 3 was both heated (70 ^oC) and

stirred. One hour later, almost all the sulphur powder in vial 3 reacted to form soluble Li_2S_8. In

sharp contrast, vial 1 and 2 still contain a large quantity of solid powder at the bottom of the

vial. Even after 48 h, the Li_2S has not completely reacted with S. Stirring can accelerate the

reaction but heating is essential in forming a uniform solution. This demonstrates that the

heating and stirring process in the battery tank plays an important role in reactivation, which

cannot be realized in coin cells or pouch cells. It is noted that this process engineering is

compatible with large scale energy storage station construction.

Characterization of dead sulphide species. In order to understand the mechanisms for

capacity improvement during the reactivation process, we carried out X-ray photoelectron

spectroscopy (XPS) and scanning electron microscopy (SEM) measurements of lithium foil

and carbon felt before and after reactivation. Before reactivation, the battery was cycled for 50

cycles and was stopped at the end of the discharge process (2.06 V). The high-resolution S 2p

region spectra are shown in Figure 3(a-d), corresponding to the surface species on the lithium

foil and carbon felt before and after reactivation. All the binding energies were calibrated with

respect to the C1s peak at 284.6 eV. Spin-orbit coupling gives rise to a doublet in the S 2p peak

((2p$_{1/2}$−2p$_{3/2}$)) separated by 1.18 eV with a 2/1 intensity ratio[33]. Signal from Bis(trifluoromethane) sulfonimide lithium salt (LITFSI) in the electrolyte can be observed on both lithium and carbon felt (S 2p$_{3/2}$ at 169.4 eV) due to the electrolyte precipitate trapped on the rough surfaces[34, 35]. Additional 2p$_{3/2}$ peaks at 167 eV are assigned to the degradation product of Bis(trifluoromethane) sulfonimide (TFSI), which forms a solid-electrolyte interphase (SEI) on the electrode[28, 33]. The presence of soluble polysulphide (Li$_2$S$_x$) can be verified from peaks at ~162 eV and 164 eV, together with Li$_2$S$_2$/Li$_2$S peaks at 160 eV and 158.3 eV[36]. The non-soluble species generated from the reduction of longer-chain polysulphide[37] will cause a loss of reversible capacity in the following cycles of the polysulphide catholyte. After the reactivation process, the Li$_2$S$_2$/Li$_2$S signal diminishes on both the Li (Figure 3a, b) and carbon electrodes (Figure 3c, d), indicating the dead sulphide species have dissolved and reacted back into the catholyte. Additional differences between lithium foil and carbon felt before and after reactivation can be found in the C1s spectra (Supplementary Fig. 4, 5). The polysulphide (Li$_2$S$_x$) signal was largely reduced after reactivation, which are mainly due to the SEI component changing. The SEM images of Li foil and carbon felt before/after activation, in Figure 3(e-h) validate this smoothing effect. In sum, the heating process can reactivate the sulphur species that precipitated on both anode and cathode and increase the accessible surface area on the cathode current collector, ultimately improving the cell capacity.

Electrochemical performance. After effective reactivation, our LPS battery shows excellent electrochemical performance. As demonstrated in Figure 4a, at a high current density of 5 mA cm^{-2}, a high single cell capacity of 0.9 Ah was achieved (recipe can be seen in Supplementary

Table 2, additional 0.4 g sulphur powder was added for reactivation). Previous reports of LPS

battery using coin cells demonstrate a capacity of just 1-3 mAh, which is two orders lower than

our results. Even though the cell capacity decays due to the formation of dead sulphide species,

leading to irreversible capacity, the capacity can be immediately recovered to a higher value

after reactivation which was conducted every 50 cycles under stirring and heating at 70 °C. The

increased capacity comes from the newly formed soluble polysulphide and it can recover as

much as 50% of the lost capacity. Even after 110 cycles, the battery tank still retains a high

capacity of 0.7 Ah, which clearly confirms that reactivation can improve the performance of

LPS batteries. Not only can the dead sulphide species on the metallic lithium anode be

reactivated, but also those on the carbon felt cathode. Even though the voltage window was

controlled between 2.06-2.8 V, some Li_2S/Li_2S_2 species are inevitably formed as the

disproportionation reaction occurs. Reactivation of these species increases the overall cell

capacity, while simultaneously enhancing the conductivity of the carbon felt. We further test

the LPS flow system with reactivation equipment as shown in Figure 1d. The LPS flow battery

system can be charged and discharged normally at a current of 200 mA in the constant capacity

cycling mode (Supplementary Fig. 6 and Supplementary Movie 1). Reactivation induced by

turning the pump on (intermittent flowing mode) was conducted when the capacity decayed,

as demonstrated in Figure 4b. After reactivation, the flow battery system can run for another

hundred cycles. Fresh and warm polysulphide was injected into battery tank from the

reactivation tank, which helps react with the dead sulphide species and increase the capacity.

On the other hand, old polysulphide was circulated into the reactivation tank for further

reactivation, thus turning into fresh polysulphide with high activity. Recipe of LPS flow system

can be seen in Supplementary Table 3, 4.

Discussion

The new setup, which is similar to the industrial standard, can significantly increase both the energy density and the mass loading. Figure 4c shows the energy density at different current densities. Even at a high current density of 9 mA cm^{-2}, the specific and volumetric energy can still reach 82 Wh kg^{-1} and 80 Wh L^{-1}, much higher than our previous results (72 Wh L^{-1}) measured in a coin cell configuration with relatively low mass loading and low current density (1.5 mA cm^{-2}). Since dead sulphide species lower the electronic and ionic conductivity, the reactivation process decreases the charge transfer resistance, which is supported by the Nyquist plot obtained from electrochemical impedance spectroscopy (EIS). Figure 4d shows EIS result of LPS battery before and after reactivation (lithium foil anode, 3 M Li$_2$S$_8$ as initial catholyte, and carbon felt as cathode current collector). The Equivalent circuit diagram of LPS battery, which was fitted well with the experimental result, was shown in the inset of Figure 4d. Before reactivation, the value of R1 which represents the interfacial impedance of lithium was 1.321 Ω, which was reduce to 0.52 Ω after reactivation. The surface kinetics of activated lithium foil is much faster than the lithium foil pre-activation. The EIS measurement provides strong evidence for the improvement of electrochemical stability through reactivation (Figure 4d, and Supplementary Fig. 7). Figure 4e shows the voltage profiles with single cell capacity before and after reactivation. In the 51st cycle, the cell capacity increases by about 50% compared with that of the 50th cycle. The discharge profile in the 60th cycle is almost the same as in the 50th cycle, meaning there is almost no capacity decay during the following cycles. It is noted that

13

the single cell reactivation process can be completed in about 2 h (Supplementary Fig. 8).

Figure 4f shows the voltage profiles with single cell capacity and volumetric energy density at different concentrations of Li_2S_8. As expected, with increasing concentration, cell capacity and volumetric energy also increase. At 5 M concentration, a high energy density of 135 Wh L^{-1} was attained when employing activated carbon felt (using NaOH as an activation agent) as a current collector with high surface area. The mass loading of each concentration is very high. About 1-2.6 g sulphur element (sulphur and sulphur in Li_2S) was used per single battery (Supplementary Table 5, 6). Compared with other battery technologies designed or used for grid scale energy storage[38, 39], LPS batteries demonstrate obvious advantages in energy density. The volumetric energy density is four times higher than that of vanadium redox flow battery, and two times higher than lead acid battery (Figure 4g), making it a promising candidate for future large scale energy storage applications.

A long cycle life, high capacity, and high energy density LPS battery was achieved by introducing a method for reactivation of dead sulphide species. It is noted that the battery tank design makes it very easy to assemble and disassemble. The replacement of lithium or adding sulphur is also operable in engineering practice (Supplementary Note 3, 4). The very low price of sulphur as a raw material makes it cost-effective for future large scale storage for renewable energies like wind and solar. The energy cost was reduced to a low value (<100 \$ kWh^{-1}) (calculated based on Supplementary Table 7 and Supplementary Note 5, not including heating cost for reactivation). Through cost analysis, it can be seen that the cost of LITFSI contributes about half of the total cost (Supplementary Fig. 9). Low concentration LITFSI or cheaper alternative salts may reduce the energy cost to a much lower value (<50 \$ kWh^{-1}). This work

successfully demonstrates the possibility of using our LPS battery for practical engineering

application in grid energy storage.

Method

Assembly of single LPS battery. 1.4 g sulphur powder and 0.28 g lithium sulphide were mixed in 16 ml DOL/DME (1:1) electrolyte in a 20 ml vial, followed by addition of 0.5 g $LiNO_3$ and 1.5 g LITFSI. The $LiNO_3$ and LITFSI were heated at 110 $^\circ$C for two days before use. Then the solution was heated and stirred at 70 $^\circ$C for 6 h to generate 3 M Li_2S_8 solution. Carbon felt was placed on the bottom of the negative part of the battery tank. Before use, the carbon felt was heated at 60 $^\circ$C in a vacuum oven for two days. Then a magnetic stir bar and 0.4 g of sulphur powder were placed on the bottom of the tank. Lithium foil was fixed onto the negative bar with a snap joint structure to ensure good electrical contact and then wrapped with commercial separator (Celgard 2250). Lithium foil was set into the center of the carbon felt and Li_2S_8 solution was injected into the battery tank. Finally, the battery tank was sealed with a plastic crimp. There is a specially designed PTFE spacer between the positive part and negative part to insulate them from one another.

Characterization. The electronic environment of the samples were investigated through XPS (Phi5000 VersaProbe, Ulvac-Phi) with Al Kα radiation. All samples were sealed in a vacuum transfer chamber in the glove box and then transferred into the XPS equipment for measurement. Raman was conducted through the Horiba Scientific LabRAM HR Evolution Spectrometer. The wavelength of laser is 532 nm and the power is 5 mW.

Electrochemical measurement. The LPS battery was tested with a Biologic EC-Lab Electrochemistry instrument between 2.06 V and 2.8 V. The applied current varies from 20 to 200 mA. EIS was conducted with frequency range of 100 kHz to 0.1 Hz, at the sinus amplitude of 5 mV.

Assemble of LPS flow battery system. The demonstration LPS flow battery system was made with two battery tanks (one for the battery and one for polysulphide storage). The two tanks were connected through a 6 mm stainless steel tube. A magnetic circulation pump was connected to the two tanks. The battery tank assembly was the same as the above battery, and the electrolyte tank was injected with about 48 mL of polysulphide solution. The storage tank was placed on a hot plate for reactivation.

Data availability. The data that support the findings of this study are available from the authors on reasonable request.

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Author contributions

Y.C. conceived the project. Y.J. and G.M.Z. assembled the batteries and performed the battery tests. F.F.S., J.Z., K.L. and Y.Y.L performed the characterization. All authors analyzed the data and contributed to the discussion. Y.J., G.M.Z., F.F.S. and Y.C. wrote the manuscript.

Additional information

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11 **Figure 1 | Schematic and optical image of reactivation of LPS battery using stirring and

12 heating method.** (**a**) Schematic of the reactivation process by reaction of sulphur particles with

13 dead sulphide species under stirring and heating condition. (**b**) Design of LPS battery tank with

14 reactivation function on a stirring and heating hot plate. (A magnetic stir bar was placed at the

15 bottom of battery tank for stirring and additional sulphur powder was placed on the bottom

16 before sealing). (**c**) Optical image of lithium foil before and after reactivation (heating and

17 stirring at 70 °C for 3 h). Dead sulphide species are shown on the surface of lithium foil marked

18 by the outlined yellow area (before reactivation, after 50 cycles). After reactivation, almost all

19 of the dead sulphide species disappeared. (scale bar, 2 cm) (**d**) Schematic drawing of LPS flow

20 battery system for future grid energy storage. (**e**) Optical image of LPS flow battery system

21 (with the function of reactivation) demonstration based on above schematic drawing.

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24 **Figure 2 | Dead sulphide species reaction with sulphur particles.** (**a**) Optical images of dead

25 sulphide species on the surface of lithium foil after reaction with sulphur particles in

26 DOL/DME electrolyte under stirring and heating (70 °C) condition to form polysulphides after

27 0 minute, 5 minute, 10 minute, and 60 minute. (**b**) Optical images of lithium foil before and

28 after dead sulphide species reaction with sulphur particles. (scale bar, 2 cm) (**c**) Raman

29 measurement of lithium foil before and after dead sulphide species reaction with sulphur

30 particles. (**d**) Electrochemical performance of lithium foil (after reactivation) with 5 M LPS

31 catholyte. (**e**) Voltage profiles of lithium foil (after reactivation) with 5 M LPS catholyte.

Figure 3 | Characterization of dead sulphide species. (a-d) XPS analysis before and after reactivation: (**a, b**) lithium foil, (**c, d**) carbon felt. S_{2p} spectra are presented, including peak deconvolution and assignments. (**e-h**) SEM images before and after reactivation: (**e,f**) lithium foil (scale bar, 100 μm), (**g,h**) carbon felt (scale bar, 50 μm).

Figure 4 | Electrochemical characterization of LPS battery. (a) Cell capacity and coulombic efficiency of single LPS battery during 110 cycles (reactivation was conducted every 50 cycles). (**b**) Constant capacity cycling of LPS flow battery system (recipe of LPS flow battery system can be seen in Supplementary Table 5, 6). The charge capacity is set to 1000 mAh and the discharge cut-off voltage is set to 2.06 V. (**c**) Gravimetric and volumetric energy density at different current densities. (**d**) EIS measurement of LPS battery before and after reactivation (Inset Equivalent circuit diagram of LPS battery). (**e**) Voltage profiles and the corresponding cell capacity before and after reactivation. (**f**) Voltage profiles and their corresponding cell capacity and volumetric energy density for different concentrations of Li_2S_8. (2 M & 3 M with pure carbon felt and 5 M with activated carbon felt, which has higher surface area for active materials trapping, as the current collector). (**g**) Gravimetric and volumetric energy density comparison between different batteries designed and used for grid application