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Communication

# A high-performance energy storage system from sphagnum uptake waste LIBs with negative greenhouse-gas emission

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# ABSTRACT

The ever-growing energy market demands a million tons yield of lithium-ion batteries (LIBs) which contributes to the climate change via huge greenhouse gas (GHG) emission, yet the depleting cathode resources pursuit sustainable production routes. Recycling of the spent LIBs is crucial. Current LIBs recycling utilizes complex process and consumes huge amount of energy. The key question is how to balance the GHG emission and the overall performance of the recycled cathodes. Many techniques have been tried to address the issue, but the GHG-performance dilemma remains to be overcome. Here we provide a route of sphagnum uptake of spent LIBs cathode toward high performance lithium sulfur (Li–S) battery, which may settle the infeasibility of ternary cathode recycling via industrial applicable processes. As-prepared cathode benefits from both chemical stabilization and hierarchical structural encapsulation, hence grants high S ratio (~80%) and good specific capacity (~700 mA h g<sup>-1</sup> after 300 cycles). Eventually, this route realizes an unprecedented negative GHG emission and achieves about 230% specific capacity higher than others.

# 1. Introduction

Since LIBs have been introduced to the public in the early 1990s [1], they have excelled traditional rechargeable batteries (Ni–Cd, Ni-MH, etc) in high specific capacity over a wide range of portable electronics. In the past few years, the booming market of electric vehicles led to an exponentially increased LIBs industry. From 2010 to 2017, the annual production of LIBs have been quadrupled to 1 million tons which led to huge energy input & GHG (greenhouse gas) emission [2]. Significant climate change follows, Greenland ice sheet beats an all-time melt record of 12.5 billion tons in a single day this August [3]. Current research mainly focused on the improvement of LIBs' capacity, cycle life, and safety [4–7]. Yet, it is reported that 95–98% [8,9] of waste LIBs were buried in landfills due to lack of energy-efficient and practical recycling techniques [10–12]. The underestimated issues such as element depletion, waste deflagration, and soil/underground water contamination are unprecedentedly severe (Fig. 1a).

Briefly, LIBs recycling techniques consist of pyrometallurgical/

hydrometallurgical processes for unary cathodes (based on the number of transition metals, e.g. LiCoO<sub>2</sub>, LiFePO<sub>4</sub>) [13]. and ternary cathodes (e. g.  $LiNi_xCo_yMn_zO_2$ ) [14].  $LiCoO_2$  is a well-recycled unary cathode for its high value and low reserve. But it's worth knowing that Li-NCM (Ni, Co, Mn) oxides has become the quickest expanding battery technology among all cathodes (33% share in 2017, estimated 70% in 2025) due to its high capacity and low cost [2]. Current recycling technologies for ternary cathodes consist of two approaches. One of them utilizes multiple separation steps for each ion, therefore the co-extracted impurities will accumulate distinctly [15]. It also makes the products no competitiveness toward pristine materials. The other way directly resynthesizes Li-NCM oxides from leaching solution, but it needs to add large amount of metal to tune the composition. That owes to the different formulas from thousands of manufacturers. So far, no practical technology has been achieved for the recycling of mixed ternary cathode [16]. Therefore, an eco-friendly, GHG-saving, and ternary cathode-processable recycling route is inevitable.

Meanwhile, Li-S batteries was considered as successor of traditional

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Fig. 1. Schematic illustration of (a) element depletion, waste deflagration, and soil/underground water contamination caused by disposal of the spent LIBs, (b) sphagnum uptake Li-NCM ions; calcination form tubular structure with well crystallized Li-NCM oxides; S filtration into the tubular structure to relief the volume expansion of LiPSs plus finely decorated Li-NCM oxides relief the shuttle effect. Red arrows and blue arrows represent the electron/electrolyte flow along/through the tubular structures.

LIBs due to its supreme theoretical specific capacity (1675 mA h  $g^{-1}$ ), large reserve, and eco-friendly nature [17,18]. Yet typical Li-S batteries usually provide a low cycled-capacity, which can be attributed to the low columbic efficiency (S agglomeration and insulating S, Li<sub>2</sub>S<sub>2</sub>, Li<sub>2</sub>S), structural instability (~80% volume expansion from S to Li<sub>2</sub>S<sub>2</sub>/Li<sub>2</sub>S), and S-leaking shuttle effect (dissolved LiPSs). To solve these issues, various strategies have been explored by taking the advantages of carbon-based structures such as layer wrapping [19,20], layer-by-layer stacking [21], 3D network [22], nanotube arrays [20], hollow shells [23]/tubes [24], etc. to spatially confine the LiPSs [25]. They can relief the above problems to some extent and increase the S mass-loading by structural confinement. Nevertheless, physically absorption of LiPSs in the pores or slits can only stand for a very limited number of cycling. Owing to the weak interactions between the non-polar carbon surface and polar LiPSs, soluble LiPSs are tend to migrate to the anode, which are causes of the shuttle effect and low utilization of S as well as the low cycle stability. On the other hand, materials with polar-bond were also studied using e.g. graphene oxides (-O) [26], nitrogen-doped graphene [27]/vanadium nitride (-N) [28], sulfides (-S) [29], MOFs [30]/MXenes (-Metal) [31], etc. to bring polar-polar interactions with LiPSs. Moreover, metal oxide hosts such as, V<sub>2</sub>O<sub>5</sub> [32], Fe<sub>2</sub>O<sub>3</sub> [33], Ti<sub>4</sub>O<sub>7</sub> [34], MnO<sub>2</sub> [35], etc. were widely studied since they can form a relatively strong bonding with  $Li^+/S_x^{2-}$  and effectively entrap these species. Generally, the LiPSs trapping was studied in different aspects and neither carbon structure nor the polar binding is adequate separately. Thus, we believe an eco-friendly, energy conserving technique combining unique carbon architectures and relatively high entropy transition-metal-based oxide may enable supreme LiPSs dual-encapsulation and thus largely increase the S mass-loading/ratio and lead to a green future of Li-S batteries.

Targeting both Li-NCM ternary cathode recycling and Li–S batteries advancing, we propose a naturally sphagnum uptake of waste Li-NCM ions loaded with S as novel Li–S battery cathode. This route is energy-&GHG-saving and generally applicable to industrial ternary cathode recycling with high recovery efficiency. As-prepared cathode benefits from both hierarchical structural stabilization and chemical encapsulation, hence grants high S ratio (80% of the mass of active materials, 64% considering the whole electrode), high mass loading, and high specific capacity. Sphagnum moss grows widely (from Finland to south China) with specialties in atmosphere/water quality improvement. As one of the most water-absorbing and metal-accumulating plants, sphagnum can effectively uptake metal ions (Li, Ni, Mn, etc) via its pore-rich structure and then anchor them by an ion-exchange mechanism [36, 37]. It can maintain a tubular scaffold after carbonized as the structural encapsulation to relief the volume expansion, plus the finely decorated Li-NCM oxides can bind with LiPSs to relief the shuttle effect. This naturally uptake route can surprisingly realize negative GHG emission which excels other recycling techniques and achieves 230% higher specific capacity after 300 cycles compared to the top Li-NCM cells to our best knowledge.

# 2. Results and discussions

# 2.1. Metal uptake mechanism of sphagnum

The tubular sphagnum-oxides-sulfur (Sph-Ox-S) composite was cultivated and prepared as shown in Fig. 1b. Sphagnum can effectively absorb and then evaporate water as a purifier. Its metal uptake property is outstanding even in acid environment (pH  $\approx$  4). The interactions of biomass carbon and Li-NCM ions took place uniformly accompanied by sunlight illumination. The metal ions were uptaken and anchored to the biomass carbon via an ion exchange process that was reported elsewhere [37].

$$M^{n+} + n(\mathrm{HX}) \to nH^{+} + (MX_n) \tag{1}$$

Here  $M^{n+}$  are metal ions (Li<sup>+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup>, Mn<sup>2+</sup>), (HX) are the lower pH stronger acid sites, and (MX) represent the anchored meatal ions.

## 2.2. Structural & Elemental characterizations

To better study the unique structures and compositions of sphagnumoxides (Sph-Ox) and Sph-Ox-S, scanning electron microscopy (SEM) images was captured. Fig. 2 shows typical SEM images of the sphagnum cells without (Fig. 2a and b) and with metal uptake (Fig. 2c). The average diameter of the sphagnum cell is around 10  $\mu$ m and the tunnel length is several tens micrometer with respiration pores. This design of nature can accommodate large amount of active materials and allow electron&electrolyte to transport quickly. The carbonization process breaks most of the inner walls along the cell nervure while maintaining the thick external walls with a yield of 25.9%. In general, the tubular carbon-network may simultaneously offer electron transport and ion transport pathways thus enhance the rate performance of the cathode.

Besides the microscopy of carbon-network, energy-dispersive X-ray spectroscopy (EDS) mappings were also acquired to reveal the distribution of Ni, Co, Mn, and S elements. Different from other methods in synthesizing hybrid metal oxides, the naturally uptake cultivated a precursor with evenly distributed Li, Ni, Co, and Mn ions which is energy-free. Fig. 2c–f shows the SEM and EDS mapping of the welldistributed Li-NCM oxides after calcination. The size of oxides ranges



**Fig. 2.** Physical characterization of the synthesized Sph-Ox and Sph-Ox-S: (a–b) SEM images at different magnifications, (c–f) SEM image of Sph-Ox and corresponding EDS mapping on elements Ni, Co, and Mn, (g–j) XPS spectra of the above element plus Li, (k–m) SEM image of the sample after loaded S and EDS mapping, (n) XRD pattern of the composite. Scale bars:  $20 \,\mu m$  (a),  $5 \,\mu m$  (b),  $8 \,\mu m$  (c–f), and  $10 \,\mu m$  (k–m).

from ten to a hundred nanometers. The morphologies of illuminationassisted uptake Sph-Ox shows sharp contrast to the dipped sample which proves its advantage (well-distribution vs. agglomeration in Fig. S1). S was dispersed in the cell tunnel in order to accommodate the volume change as expected (Fig. 21). The element presence and oxidation states of Ni, Co, and Mn were also analyzed by X-ray photoelectron spectroscopy (XPS). The data were processed (details in SI) and assigned using the C 1s peak (Fig. S2) as calibration. The binding energies of Li, Ni, Co, and Mn at 55.5, 779.8, 642.0 and 854.2 eV, are corresponding to  $\text{Li}^+$ , Ni<sup>2+</sup>, Co<sup>3+</sup>, and Mn<sup>4+</sup>, respectively. The Li 1s (Fig. 2c) peaks at 54.2 and 55.5 eV agrees well with the reported data for metallic lithium and the formation of Li<sup>+</sup> [38]. For Mn, Ni, and Co, containing multiplet peaks, their 2p peaks were fitted with 2:1 area ratio between the  $2p_{3/2}$  and  $2p_{1/2}$ . Fig. 2h–j shows the Ni, Co, Mn  $2p_{3/2}/2p_{1/2}$  spin orbit doublet components. It is noticeable that two dominant peaks of Ni 2p locate at 854.4 and 871.5 eV (with spin-orbital splitting of ~17.1 eV), which



**Fig. 3.** (a) CV of the Sph-Ox-S composite of the first ten cycles at a scan rate of  $0.1 \text{ mV s}^{-1}$  within 1.6-2.8 V versus Li/Li<sup>+</sup>. (b) Galvanostatic charge–discharge profiles at 0.2C for up to 40 cycles. (c) Cycling performance and Coulombic efficiency of the composite and control at 0.2C for 300 cycles. (d) Nyquist plots of the Sph-Ox-S electrodes at different cycles from 100 kHz to 0.01 Hz.

represent the Ni<sup>2+</sup> cations [39]. While the two less dominant shake-up peaks can be assigned to Ni<sup>2+</sup> at 860.7 and 879 eV. Meanwhile, the lower doublet components at 856.1, 862.4, 873.5, and 881.3 eV show the higher oxidation state of Ni<sup>3+</sup>. Different from Ni, the 2p spectrum of Co has only one pair of major peaks at 780.1 and 795.0 eV, representing  $2p_{3/2}$  and  $2p_{1/2}$  with a spin-orbital splitting of 14.9 eV. Two weak peaks at 781.6 and 796.5 eV can be assigned to Co<sup>4+</sup> to confirmed its coexistence. Note that there is a shake-up satellite peak at 789.6 eV, which indicates the coexistence of  $Co^{3+}$  cations [40]. Similarly, the major pair peaks of Mn located at 642.3 eV  $(2p_{3/2})$  and 653.5 eV  $(2p_{1/2})$  has a separation of 11.4 eV, which correspond to Mn<sup>4+</sup> cation. More than that, the lower oxidation state of  $Mn^{3+}$  also exists (644.3 and 655.1 eV) plus a small Auger peak at 648.1 eV. The XPS results about S (Fig. S3) and Li-NCM oxides (Fig. 2g) are consistent with the standard PDF card. The strong characteristic peaks indicate highly crystalline S and LiNi<sub>0.33-</sub> Co<sub>0.33</sub>Mn<sub>0.33</sub>O<sub>2</sub> were formed. To sum up, the tubular carbon backbones and the well-distributed oxides were studied. They may accommodate the volume expansion and may provide large reactive sites for the complex Li-S electrochemical reactions.

#### 2.3. Electrochemical measurements

To prove the above assumptions, the electrochemical properties of the electrodes were evaluated. Coin-cell battery was assembled with high S content of 79.8 wt% (Fig. S4). Fig. 3a shows the first 10 cycles of cyclic voltammetry (CV) with two cathodic peaks located at 2.29 and 1.94 V. The former peak corresponds to the formation of long-chain LiPSs (Li<sub>2</sub>S<sub>x</sub>, x = 4–8) and the later one is for the conversion of long-chain to short-chain LiPSs (Li<sub>2</sub>S<sub>2</sub>, Li<sub>2</sub>S) [41]. Two slightly separated anodic peaks at 2.37 and 2.42 V correspond to the reverse conversion from polysulfides to Li<sub>2</sub>S<sub>8</sub> [42]. [43] Sph-Ox-S enables slightly reduction in voltage polarization of 32, 38, and 18 mV for peak I–III in comparison with (Fig. S5). The discharge peaks of Sph-Ox-S are more prominent and the Sph-S charge peaks are overlapped, which indicates favorable Li

bonds are formed and prompt the reaction kinetics [44].

Moreover, it is found that the curves shift from the initial scan by a voltage gap around 0.02 V and the later curves show high stability in shape and size. To reveal the cause of instability of the initial cycle, galvanostatic charge-discharge was performed at 0.2C (Fig. 3b). The discharging curve consists of a steep and a flat plateau while the charging curve has a slightly inclined and a flat plateau, which is consistent with the two distinct discharge peaks and two partially overlapping anodic peaks of CV. However, it is worthy of mention that there is a V-shape over potential (up to 0.23 V) in the flat plateau during early cycles (1st to 10th). Similar result was observed in a S filled hollow tubular composite at increasing discharge rates. This is probably due to the S chunk which filled in the tubes/pores which hindered the Li<sup>+</sup>-S reaction on the surface [45]. Yet after several activation cycles, the as-synthesized LiPSs were effectively captured by the Li-NCM oxides for their high binding energy (Fig. 5), plus the hollow structure can restrain the loss of LiPSs and alleviate S expansion. Since the S and LiPSs were confined by the Li-NCM to form an equilibrium, the charge-discharge plateau was eventually stabilized and a high capacity system with long cyclic performance was achieved.

In the cycling test of Sph-Ox-S and the Sph-S without Li-NCM oxides (Fig. 3c), a relatively low initial discharge capacity of 880 mA h g<sup>-1</sup> and poor columbic efficiency of 77% was delivered, which agrees with the above discussion. After the activation cycles, the specific capacity recovered quickly to 1040 mA h g<sup>-1</sup> with columbic efficiency of almost 100% at 0.2 C at high mass loading of  $3.4 \text{ mg cm}^{-2}$  (with electrolyte/sulfur ratio of  $12 \,\mu\text{L mg}^{-1}$ ). The cell still maintains a discharge capacity of ~700 mA h g<sup>-1</sup> after 300 cycles, indicating a long cycling stability with 0.1% capacity loss per cycle. In comparison, while the control group can also deliver high specific capacity and columbic efficiency in the beginning, there is significant shuttle effect which is severely undermining the cycling performance without the protective Li-NCM oxides. Capacity quickly drops to less than 300 mA h g<sup>-1</sup> after 300 cycles. Unlike the smooth profile of Sph-S, a slightly rough curve was

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shown probably due to the strong binding between Li-NCM oxides and LiPSs [46,47].

Cycling test under 0.1C rate was also performed to show the advantages of the Sph-Ox-S electrode (Figs. S6a and b). Overwhelm the 33% capacity retention of the control after 100 cycles, a high specific capacity of  $1320 \text{ mA h g}^{-1}$  with 68% capacity retention was achieved. Rate capability of the Sph-Ox-S cathode was tested by increasing the charge/discharge current density from 0.1 to 1C and then back to 0.5C every five cycles (Fig. S7). The discharge capacities at 0.1, 0.2, 0.5, and 1C  $(1C = 1675 \text{ mA g}^{-1})$  are 1335, 1050, 705, and 420 mA h g<sup>-1</sup>, respectively, which indicating an overall decent performance. Note that the Li-NCM oxides without S loading has a charge plateau around 3.62 V (Fig. S8) which is far off the charge-discharge window (1.7 V-2.7 V). The Li<sup>+</sup> insertion brings charge capacity to some extent, yet the capacity retention is as low as 62%, indicating a poor cyclic performance. Furthermore, the specific capacity of Sph-Ox under same condition is only  $63 \,\text{mA} \,\text{hg}^{-1}$  (account for 1.19% capacity of the whole electrode) with rapidly decrease (Fig. S9) and thus its contribution is out of account

The stable tubular structure also realizes fast electro-transfer kinetics by providing a conductive network. This is further supported by the electrochemical impedance spectroscopy (EIS) Nyquist plot after different charge-discharge cycles in Fig. 3d (inset is the magnified curves). The plot of fresh cell clearly starts with a single dot in the higher frequency over 10 kHz, which represents the resistance of electrolyte about 2.2  $\Omega$  (R<sub>e</sub> in the proposed equivalent circuit model [48], Fig. S10). In high frequency region, there is an obvious semicircle related to the interphase resistance, which simulates the process of electron transfer from the current collector to Sph-Ox (R<sub>int</sub>//CPE<sub>int</sub>). As to the middle frequency, a flat semicircle shows in the fresh cell correlates to the

charge-transfer resistance, which reflects the electrochemical processes between the Li-NCM oxide/S and the LiPSs/electrolyte ( $R_{ct}$ //CPE<sub>dl</sub>). In Fig. 3d inset,  $R_{int}$ //CPE<sub>int</sub> decreased from 10.1 to 6.4  $\Omega$  and the semicircle of  $R_{ct}$ //CPE<sub>dl</sub> become unapparent after 10 cycles. These findings agree well with the CV and charge-discharge analysis due to the fact that deeply embedded S was not fully participated in the formation of LiPSs. Therefore, the resistance from current collector to surface was reduced due to the transformation from bulk S to LiPSs. More than that,  $R_{ct}$ //CPE<sub>dl</sub> is nearly diminished since the affinitive binding between Sph-Ox and LiPSs after the initial activation cycling. In the low frequency, the plots end with inclined lines, which is similar to previous result [49]. Overall, the long-cycling performance suggests the volume expansion was accommodated by the carbon-backbones and the embedded Li-NCM oxide nanoparticles shows significant relief toward LiPSs shuttling.

# 2.4. Chemical & Physical dual-encapsulation of LiPSs

To further study the chemical encapsulation of Li-NCM nanoparticles, the reactions of Sph-Ox and LiPSs were studied via XPS measurement of S 2p peaks of the initial and 10th discharge (Fig. 4a and b). Li<sub>2</sub>S<sub>4</sub> was used as the representative polysulfide (preparation in SI). The S 2p doublet  $2p_{3/2}$  and  $2p_{1/2}$  peaks were fit using equal full width at half maximum (FWHM), with a 2:1 area ratio. Only the  $S2p_{3/2}/2p_{1/2}$  spin orbit component with lower binding energies are discussed. There are 4 sets of doublet peaks with binding energy at 162.7, 164.2, 168.2, and 169.4 eV in the highly resolved XPS spectrum of the electrode after initial discharge. The corresponding peaks of the cycled electrode shift to lower positions at 162.7, 164.2, 167.8, and 168.7 eV. Based on analysis of the previous publications [35,50–52], the I peaks can be



**Fig. 4.** High-resolution XPS S 2p spectra of Sph-Ox-S (a) after initial discharge, (b) after 10 cycles of charge-discharge, (c–f) Contact angle of the electrolyte on the surface of Sph, Sph-S, Sph-Ox, and Sph-Ox-S, (g) Ex situ adsorption test of pure Li<sub>2</sub>S<sub>4</sub>, Li<sub>2</sub>S<sub>4</sub>+Sph, and Li<sub>2</sub>S<sub>4</sub>+Sph-Ox, (h,i) BJH adsorption plot of pore volume vs. width of the Sph and Sph-Ox.

assigned to short-chain LiPSs and the II peaks are mainly from pure S. Since the electropositive Sph-Ox can induce a polarization of the electrons away from S atoms to the oxides-LiPSs interface, the initial response of I and II peaks are more predominant due to incomplete reaction and the disproportionation of intermediate LiPSs [53]. On the contrary, based on the decreased peaks intensities, cycled electrode shows good interaction between Sph-Ox and LiPSs plus a small ratio of unreacted S & short-chain LiPSs. The III and IV peaks between 167 and 170 eV represent S in [SO<sub>3</sub>]<sup>2–</sup> and [SO<sub>4</sub>]<sup>2–</sup> ions, respectively. Moreover, their shift to lower energy suggesting an increased density of electron clouds from S which is consist with previous discussion.

To directly demonstrate the physical interactions between the Sph-Ox and LiPSs, contact angle (CA) of typical electrolyte on the surface of pure sphagnum, Sph-S, Sph-Ox, and Sph-Ox-S were measured (Fig. 4c-f). It is obvious that CA of the above surface decreased from  $32.3^{\circ}$  to  $37.2^{\circ}$ – $4.5^{\circ}$  and  $7.2^{\circ}$ , respectively, which indicates the Li-NCM oxides can largely improve the permeability with electrolyte at the interface. More than above, visually Li<sub>2</sub>S<sub>4</sub> absorbing test was run on the same surface area of pure sphagnum and Sph-Ox. In Fig. 4g, the Sph-Ox can rapidly absorb most of the Li<sub>2</sub>S<sub>4</sub> in 30 min while the sphagnum shows no sign of absorption even after 6 h. Corresponding electrodes were analyzed by surface area test with BJH and BET calculation. In the BJH pore volume vs. pore width curve, the carbonized sphagnum mainly consists micro-pores below 0.5 nm (Fig. 4h and i). However, the oxides decorated sphagnum shows increasing micro-pores which is created by the NO<sub>x</sub> decomposition and meso-pores from oxides particles based on our presumption. The pore-structure modification based on the absorption-desorption curves (Fig. S11) refined the interface contact even more with an increased specific surface area at  $444 \text{ m}^2 \text{ g}^{-1}$ . This hierarchical porous structure ensures highly efficient electrochemical reaction on the surface of well-distributed Li-NCM nanoparticles to promise exceptional LiPSs encapsulation performance.

#### 2.5. Computational calculations

To fundamentally study the chemical LiPSs encapsulation of the relatively high entropy Li-NCM nanoparticles [54], density functional theory (DFT) calculations was performed. The interaction of various LiPSs from Li<sub>2</sub>S<sub>8</sub> to Li<sub>2</sub>S with the Li-NCM (001) surface and S<sub>8</sub> (001) surface as control were investigated [55]. The bonding energies ( $E_{bind}$ ) of LiPSs with Sph-Ox were calculated as equation (2) (details in



Fig. 5. Computational calculation of binding energies of  $Li_2S_8$ ,  $Li_2S_6$ ,  $Li_2S_4$ ,  $Li_2S_2$ , and  $Li_2S$  onto the surface of Li-NCM oxide.

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**Fig. 6.** Processes with GHG emission (CO<sub>2</sub>, in terms of energy consumption) of regular LIBs recycling routes and ours.

experimental section).<sup>50</sup>

$$E_{bind}(Li_2S_x) = E(Li_2S_x / M) - E(Li_2S_x) - E(M)$$
<sup>(2)</sup>

Ebind is the binding energy corresponds to a stable substrate-adsorbate system. M represents the Li-NCM or S8 which correlates to the Li2Sx/Li-NCM or Li<sub>2</sub>S<sub>x</sub>/S<sub>8</sub> interactions, respectively. Since the more negative E<sub>bind</sub> values indicate more favorable adsorption and stronger bond formation, the absolute values of E<sub>bind</sub> (equals to -E<sub>bind</sub>) were discussed instead of E<sub>bind</sub> for clarity. Fig. 5 shows the geometrical configurations of the most stable states of each substrate-adsorbate systems and the plot of corresponding binding energies. The early stage long-chain LiPSs show very low  $-E_{bind}$  (Li<sub>2</sub>S<sub>8</sub> = 0.17 eV, Li<sub>2</sub>S<sub>6</sub> = 0.13 eV) on the surface of S<sub>8</sub>. The weak adsorption is mainly originated from interactions between the terminal S atoms from the opened S<sub>8</sub> ring and the Li. As the lithiation preceding, the Li<sub>2</sub>S<sub>4</sub>, Li<sub>2</sub>S<sub>2</sub>, and Li<sub>2</sub>S show increasing -E<sub>bind</sub> from 0.41 eV to 0.8 eV. It is due to the short-chain LiPSs have strong interactions with S<sub>8</sub>. On the other hand, the Li<sub>2</sub>S<sub>8</sub> and Li<sub>2</sub>S<sub>6</sub> are absorbed on the surface of Li-NCM with -E<sub>bind</sub> of 1.45 and 1.92 eV, respectively. They are around 10 times higher than that of -E<sub>bind</sub> (Li<sub>2</sub>S<sub>x</sub>/S<sub>8</sub>) for the double interactions of S = O and Li–O chemical bonds. When S is fully lithiated to Li<sub>2</sub>S, it leads to even higher binding energy at 3.47 eV. That owes to the tendency of LiPSs to decompose and form new S=O and Li-O bonds on the Li-NCM surface. This further demonstrates that the soluble short-chain LiPSs tend to be absorbed on the surface of Li-NCM oxides imbedded in the micro-/meso-pores instead of the bulk S. Moreover, fundamental study shows the optimal binding energy for LiPSs absorption is around 2.0 eV [56]. This computation result agrees well with the electrochemical tests and XPS analysis that Li-NCM oxides can efficiently anchors the Li<sub>2</sub>S<sub>v</sub> to relief the dissolve/shuttle effect by forming strong bonds.

# 2.6. Environmental analysis

High energy-consuming industries contribute to the imbalance of current ecosystems. In analyzing their impact, modern environmentology emphasizes the GHG emission instead of the energy consumed. Therefore, it is reasonable to convert energy to GHG (on the basis of CO<sub>2</sub>) [57,58]. Fig. 6 shows the comparison of routes of regular

LIBs recycling and our technique (data processing details in SI). In current recycling, the extra filtration and precipitation processes will increase the GHG emission. Moreover, it is required the addition of valuable metal ions in order to balance the ratio. However, the loaded S has high reserve and only emit 8% compare to the metal from the aspect of GHG. Among the flow chart, the high-temperature calcination is one of the most energy-intensive step. The calcination parameters employed by previous methods cost 230% energy compare to ours [59-66]. Furthermore, our technique utilizes photosynthesis of sphagnum to fixate  $CO_2$  and uptake Li-NCM ions naturally. Studies shows that  $1 \text{ m}^2$ sphagnum moss can consume 1810 g CO<sub>2</sub> per year in average [67,68]. That is a remarkable positiveness for GHG reduction. Eventually, our eco-friendly recycling technique only produces about 33% of the GHG compare to other techniques. Considering the CO<sub>2</sub> fixation, our route may achieve a total -0.25 kg CO<sub>2</sub> -eq per kg cathode while exhibiting a specific capacity 230% higher compare to one of the best Li-NCM ternary cathode (560 vs.170 mA h  $g^{-1}$ , considering the cathode mass without binder and additives) after 300 charge-discharge cycles.

## 3. Conclusions

In summary, a facial spent LIBs recycling technique has been demonstrated for rational design of hierarchical porous strictures. It can overcome the problems of ternary LIBs recycling and then exploit them for Li-S battery enhancing. As-prepared cathode can both structurally accommodate the volume expansion and chemically relief the shuttle effect. Overall, our technique cost only 33% energy intensity and produces cell with 230% higher specific capacitance compare to other LIBs recycling methods. The areal capacity of our cell also excels other works based on biomass precursors including S content and number of cycles (Fig. S15). Considering the carbon fixation of sphagnum, this route may achieve negative GHG emission which shows superiority in the longterm climate change. This study establishes an applicable route which may replace current LIBs recycling techniques with negative GHG emission. Furthermore, this route may be applied to the synthesis of high entropy transition-metal-based oxide in diverse technologies including batteries, supercapacitors, fuel cells, and catalysis.

#### Declaration of competing interest

There are no conflicts to declare.

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# Appendix A. Supplementary data

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