



# High performance sulfur graphite full cell for next generation sulfur Li-ion battery

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## HIGHLIGHTS

- Two kinds of sulfur-graphite Li-ion battery have been fabricated.
- High capacity and stable cyclability have achieved in the S Li-ion battery.
- The factor contributes to high performance has been revealed.
- The Li metal free sulfur graphite battery showed advantage over the Li-S cell.
- 10 times scaled-up sulfur graphite battery was assembled with high performance.

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## ABSTRACT

Sulfur (S) Li-ion battery which use the metallic Li free anode is deemed as a promising solution to conquer the hazards originating from Li metal. However, stable cycling performance and low production price of the S Li-ion battery still remain challenging. Here, we propose a S-Li<sub>x</sub>C full cell system by paring a S cathode and a pre-lithiated graphite anode which is cheap and commercially available. It shows stable cycling performance with a capacity around 1300 mAh (g-S)<sup>-1</sup> at 0.2 C-rate and 1000 mAh (g-S)<sup>-1</sup> at 0.5 C-rate. In addition, 0.1% per cycle capacity fading rate with a capacity retention of 880 mAh (g-S)<sup>-1</sup> after 400 cycles at 0.2 C-rate has been achieved. The pre-formed solid electrolyte interphase (SEI) layer on the pre-lithiated graphite anode largely contributes to the high capacity performance. Notably, a 10-times-enlarged scale of S-Li<sub>x</sub>C laminate type full cell has been assembled with high capacity performance (around 1000 mAh (g-S)<sup>-1</sup>) even after high rate cycling.

Sulfur (S), with high theoretical specific capacity of 1672 mAh g<sup>-1</sup> (based on the reaction: S<sub>8</sub> + 16Li<sup>+</sup> + 16e<sup>-</sup> ↔ 8Li<sub>2</sub>S), low price (0.1 \$ kg<sup>-1</sup>) and environmentally friendly, is seemed as the most promising cathode material candidate for next generation high energy storage devices beyond the current commercial Li-ion battery [1–6]. Though the theoretical energy density of Li-S battery, which use Li metal as anode, is about fourfold higher than the LiCoO<sub>2</sub>-graphite based batteries (410 Wh kg<sup>-1</sup>) [7]. There are a few obstacles hindering the application of the Li-S batteries.

The lack of Li-ion in the S cathodes inevitably claim for using the Li metal as anode. However, utilization of Li metal anode raises problems for commercialization. The uneven deposition of Li on Li anode during cycling, which is caused by ununiform solid electrolyte interphase (SEI), will cause the continuous growth of Li dendrite, leading to internal short [1,8,9]. In addition, due to the low melting point of Li metal, it is easily to trigger safety issues like explosion or burst

especially in enlarged scale of Li-S battery in practical use [9]. Li-ion S battery is one of the most promising solution to tackle the hazard triggered by Li metal. Recent years, encouraging progress have been made in making Li-ion S battery systems by applying pre-lithiated electrodes [10,11].

The fully lithiated state lithium sulfide (Li<sub>2</sub>S) which could be synthesized or purchased is considered most as the cathode alternative for S battery [12–15]. A Li<sub>2</sub>S cathode has been used to pair with high theoretical energy density anode, like Sn and Si [16], to assemble the Li<sub>2</sub>S-Sn [17] and Li<sub>2</sub>S-Si [10,18,19] S battery systems, expecting a high energy density ever achieved. However, these S Li-ion full cells suffer from capacity loss, and deliver a depressed cycling performance than the S-Li half cell. The dissolution of polysulfide into electrolyte and the Li-ion consumption due to the unstable SEI formation on Si, Sn anodes are two main factors causing the poor performance [11,20]. Despite the attractive theoretical capacity of Si and Sn, these new type anodes still

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under development [21–24].

Graphite as a commercialized anode is the most stable reservoir for Li-ion intercalation and deintercalation is considered as the most practical anode material for pushing forward the commercialization of S Li-ion battery at this moment. However, lithiated graphite is highly sensitive to electrolyte, especially in ether type electrolyte used in S battery, which will cause low reversible capacity in the graphite anode [25,26]. This has largely prolonged the application of graphite anode in S Li-ion full cell. Until 2016, Li et al. firstly reported the  $\text{Li}_2\text{S}$ -graphite full cell system for S battery by using glyme type electrolyte [27]. While it remains only around  $800 \text{ mAh (g-S)}^{-1}$  discharge capacity in the 1st cycle at  $1/48 \text{ C-rate}$ , which lost half amount of charge capacity. Rapid capacity fading with a fading rate of  $0.4\%$  per cycle is also observed at  $1/12 \text{ C-rate}$ . Recently, Tan et al. reported the  $\text{Li}_2\text{S}@$ graphene-graphite full cell. Attributed by the excellent polysulfide dissolution suppressing ability of graphene, the capacity fading rate decreased to  $0.2\%$  per cycle at  $0.1 \text{ C-rate}$ . However, the discharge capacity shrinks to only  $730 \text{ mAh (g-S)}^{-1}$  in the 1st cycle at  $1/20 \text{ C-rate}$ , which lost  $54.4\%$  charge capacity [28]. Though S Li-ion battery by pairing with various pre-lithiated electrodes has been attempted to obtain better performance, the discharge capacity and capacity retention barely achieved a satisfactory value.

In this study, we made the metallic Li free S Li-ion battery by using the commercialized graphite anode as the counter electrode for the S cathode. The prepared  $\text{S-Li}_x\text{C}$  full cell system, is paired by S and Ketjenblack (KB) composite cathode and pre-lithiated graphite anode as illustrated in Fig. 1a. The  $\text{Li}_2\text{S-C}$  full cell system is assembled by pre-lithiated S/KB composite (S/KB) cathode and graphite anode. The huge decay of capacity in the  $\text{Li}_2\text{S-C}$  full cell reveals the critical role of the S Li-ion battery configuration. Though the graphite anode displays a relatively low theoretical specific capacity of  $372 \text{ mAh (g-graphite)}^{-1}$ , the practical specific capacity achieved in the  $\text{S-Li}_x\text{C}$  full cell system reaches the highest amount up to date, according to our best knowledge. Fig. 1b plots the practical specific capacity of the representative kind of different S Li-ion batteries ever reported. The  $\text{S-LiSi}_x$  full cell and the  $\text{Li}_2\text{S-Si}$  full cell shows around a capacity of  $1100 \text{ mAh (g-S)}^{-1}$  at  $0.2 \text{ C-rate}$  [24, [29]. The  $\text{Li}_2\text{S-C}$  full cell delivers a lower capacity around  $820 \text{ mAh (g-S)}^{-1}$  at  $0.2 \text{ C-rate}$  due to the huge irreversible capacity in the 1st cycle [27]. The  $\text{Li}_2\text{S-Sn}$  displays only  $560 \text{ mAh (g-S)}^{-1}$  at  $0.2 \text{ C-rate}$  [17]. In this work, the fabricated  $\text{S-Li}_x\text{C}$  full cell delivers as high as  $1300 \text{ mAh (g-S)}^{-1}$  at  $0.2 \text{ C-rate}$ . Even in the 10 times scale up laminate type  $\text{S-Li}_x\text{C}$  full cell, stable cyclability with a capacity higher than  $1000 \text{ mAh (g-S)}^{-1}$  can be achieved.

We prepared the S/KB cathode by using the heat treatment process. Through this process, the S can melt and immerse into the nanopores in KB. The S weight ratio in the S/KB composite is around  $49.5\%$  (Fig. S1). By XRD and Raman analysis (Fig. S2) the amorphous structure of the S in the S/KB composite can be confirmed. The high resolution transmission electron microscope (HRTEM) image in Fig. 2a shows the structure of the S/KB composite in which the S fills the nano pore of KB

with a particle size about  $50 \text{ nm}$ . In this case, it is expected to obtain an effective confinement of polysulfide dissolution, which will contribute to the high capacity performance [30]. Fig. 2b shows the structure of  $\text{Li}_2\text{S/KB}$  composites after the pre-lithiation process, thin and amorphous distributed  $\text{Li}_2\text{S/KB}$  composite particles can be observed. From the HRTEM image of the  $\text{Li}_2\text{S/KB}$  composite, the (111) crystal plane of  $\text{Li}_2\text{S}$  with a plane distance of  $0.33 \text{ nm}$  can be observed in the graphitic structured KB particles.

Analysis has also been conducted to study the pre-lithiation process in graphite anode. The morphology of the graphite anode shows almost no change after the pre-lithiation process (Fig. S3). Fig. 2d shows the XRD patterns of the graphite anode before and after pre-lithiation. The Cu substrate shows high (200) peaks at  $51^\circ$ . The (002) plane carbon peak at  $26^\circ$  should be assigned to both the graphite peak and the acetylene black (AB) in the graphite anode. The  $\text{Li}_x\text{C}$  anode after pre-lithiation of graphite anode exhibits the obvious decreased peak of carbon (002) crystal plane indicating the lithiation of graphite. Since the open circuit voltage (OCV) of the graphite anode after the pre-lithiation process decreased to  $0.09 \text{ V}$ , it is definitely to say that the residue of carbon peak is supposed to be originate from AB in the anode. From the enlarged XRD pattern inside Fig. 2d indicating the newly formed phase of  $\text{Li}_x\text{C}$ . Fig. 2f showed the C1s X-ray photoelectron spectroscopy (XPS) spectra of the graphite anode after pre-lithiation. The peak was deconvoluted into the peaks at  $288.6 \text{ eV}$ ,  $286.6 \text{ eV}$ ,  $284.9 \text{ eV}$ , and  $283.3 \text{ eV}$ . The peaks at  $288.6 \text{ eV}$ ,  $286.6 \text{ eV}$  and  $284.9 \text{ eV}$  are assigned to the C=O bonding, C-O bonding and C-C bonding respectively. The distinguished peak at  $283.3 \text{ eV}$  is assigned to the Li-C bond. Therefore, the pre-lithiation of graphite anode was confirmed. The OCV value of  $0.09 \text{ V}$  and the initial voltage profile of the pre-lithiated graphite anode ( $\text{Li}_x\text{C}$ ) illustrated in Fig. 3a manifest the electrochemically fully lithiated state of graphite. The  $\text{S-Li}_x\text{C}$  full cell assembled by  $\text{Li}_x\text{C}$  anode and the S/KB cathode showed an OCV of  $2.2 \text{ V}$ , while the OCV of the S/KB half cell was  $2.3 \text{ V}$ . After fully discharged to  $1.0 \text{ V}$ , the XPS was used to analyze the active material in both electrodes. The S2p peak composed of two satellite peaks, S2p1/2 peak and S2p3/2 peak. After the discharge process, the S peak in the S2p XPS spectra disappeared with the appearance of the  $\text{Li}_2\text{S}$  peak in the S cathode (Fig. 2e), implying the fully discharged state of the S cathode. The S2p3/2 peak at  $167.4 \text{ eV}$  originated from the LITFSI residue in the electrolyte. The disappearance of the Li-C peak in Fig. 2f after discharge indicated the fully delithiated stage of the graphite anode.

Two available S-C full cell systems,  $\text{Li}_2\text{S-C}$  full cell and  $\text{S-Li}_x\text{C}$  full cell, are assembled after the appropriate pre-lithiation process. The 1st charge-discharge curves of the  $\text{S-Li}_x\text{C}$  full cell and  $\text{Li}_2\text{S-C}$  full cell are exhibited in Fig. 3b. The  $\text{Li}_2\text{S-C}$  full cell appears  $50.9\%$  capacity loss after the 1st discharge process, while the irreversible capacity in the 1st cycle in the  $\text{S-Li}_x\text{C}$  full cell almost decreased to  $0\%$ . Fig. 3a illustrates the 1st charge discharge curve of the graphite half cell (C-Li) and the pre-lithiated graphite half cell ( $\text{Li}_x\text{C-Li}$ ) respectively, from which the C-Li half cell shows  $28.5\%$  irreversible capacity loss in the 1st charge

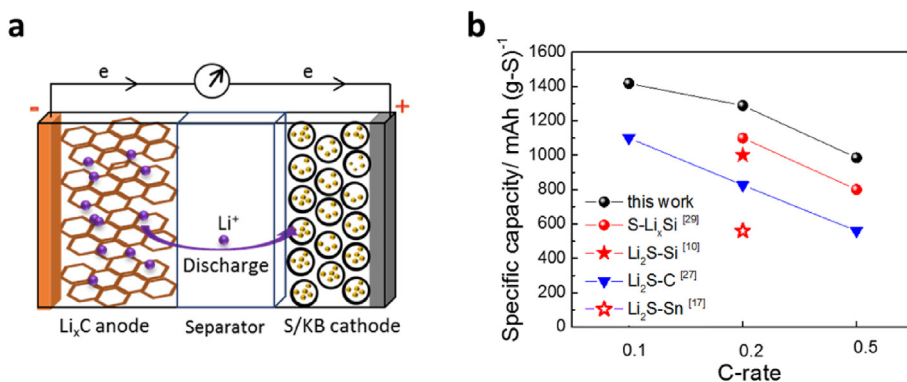


Fig. 1. Schematic of the structure of the  $\text{S-Li}_x\text{C}$  battery and specific capacity comparison of different S Li-ion battery systems. (a) Schematic diagram of the structure of the supposed  $\text{S-Li}_x\text{C}$  full cell system. (b) Comparison of the specific capacity achieved in different S Li-ion battery systems. The weight loading of S in the cathode is  $1 \text{ mg cm}^{-2}$ .

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