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An efficient Li$_2$S-based lithium-ion sulfur battery realized by a bifunctional electrolyte additive

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ABSTRACT

Previous investigations have shown that high-energy lithium-ion sulfur batteries could be directly assembled with lithium sulfide (Li$_2$S) cathode and a non-lithium anode. However, the existing lithium-ion sulfur battery suffers from the multistep sophisticated preparation process, high activation potential and also polysulfides corrosion to the anode. In this work, we propose and prepare a facile and feasible Li$_2$S-based lithium-ion sulfur battery system, which is enabled by a bifunctional electrolyte additive. At first, Li$_2$S particles were loaded on the low-cost carbonized commercial wipes by a solution-based infiltration method. Interestingly, for the first time, it is found that the well-designed indium triiodide (InI$_3$) electrolyte additive not only performed as a cathodic redox mediator, reducing the activation potential of Li$_2$S cathode, but also resulted in a passivation layer, preventing the anode from corrosion due to the shuttle effect. The obtained SnO$_2$/Li$_2$S full cell exhibits a stable electrochemical performance (983, 878, 746 and 675 mA h/g at 0.2, 0.4, 0.8, and 1.5 C, 647 mA h/g after 200 cycles at 0.5 C). Moreover, the manageable amount of lithium ions and the voltage cooperation between the cathode and anode in the full cell rendered the battery with a strong recovery ability against the abusive conditions test, such as over-charge, over-discharge and short-circuit, showing a great potential for practical use.

1. Introduction

Much attention has been devoted recently to rechargeable lithium-sulfur (Li-S) batteries because of their much higher energy density compared with traditional lithium-ion (Li-ion) batteries [1–3]. The theoretical specific energy density of Li-S battery can reach ~ 2600 W h/kg, which fulfill the requirement of the future electric vehicles (EVs) and distributed-grid energy storage system (EES) [4]. However, the shuttle effect in Li-S batteries, which is the side deposition of the polysulfides, greatly deteriorates the state-of-art electrochemical performance of Li-S batteries [5,6]. In addition, the safety concerns associated with the metallic lithium (Li) anode such as dendritic growth and inherent chemical reactivity have long prevented the Li-S battery from practical application [7–9]. Therefore, in the real battery design, replacing Li anode with other high capacity non-lithium anode is considered to be an advisable choice [9–12]. Whereas, due to the need for complex and dangerous pre-lithiation steps for the anode with highly active Li powders, this technique raises serious safety concern [13–16].

In this regard, compared to the pre-lithiated anode, a lithium sulfide (Li$_2$S) cathode is more favorable [17–19]. Moreover, the advantages of Li$_2$S, such as abundance, non-toxicity and environmental benignity, further facilitate it to be the promising cathode for next-generation lithium-ion sulfur (Li-ion sulfur) batteries [17,19].

It is reported that the commercial Li$_2$S particles are usually micro-sized, even after ball-milling [18]. When used as the active material, the large Li$_2$S particle size and the coarse Li$_2$S/carbon interface usually lead to a harsh activation process and a lower utilization ratio [19]. Research efforts have thus been directed to lower the activation over-potential by reducing the Li$_2$S particle size, enhancing the Li$_2$S/carbon binding and exploring appropriate redox mediators to facilitate the charge transfer process [20–22]. In general, there are two strategies for preparing Li$_2$S electrode. One approach is to synthesize coated Li$_2$S particles. The carbon and conductive polymer coated Li$_2$S nanoparticles have been reported, but the sophisticated synthetic routes and the strict atmosphere protection are rather difficult for scaled-up production [23–30]. To address this problem, a facile approach is proposed to
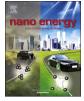
impregnate Li_2S particles into conductive carbon substrate via the drop coating method, which eliminates the multiple transfer processes [29]. Such a drop-coating method usually allows for a high mass loading Li_2S electrode (> 2 mg cm^{-2}) [20,22,31–33]. To guarantee a lower activation potential, phosphorus pentasulfide (P_2S_5) [34], ammonium iodide (NH_4I) [35], lithium iodide (LiI) [36], benzo peryleneimide (BPI) [37], polysulfides [38] and other redox mediators [21,39] have been proposed for use in such Li_2S electrodes. Though effective for lowering the charge over-potential, just like polysulfides, these mobile and corrosive redox mediators can lead to the degradation of Li anode [21,40].

Although intensive efforts have been paid in the preparation of Li_2S electrodes, a suitable non-lithium anode with high capacity and electrochemical stability, which is crucial for achieving high specific energy density, has rarely been demonstrated to pair with the Li_2S-based cathode [10,41–43]. Though the Si or SnO_2 anode can storage lithium in a rather safe approach that eliminates Li dendrite growth, under the corrosive electrolyte environment containing polysulfides, such anodes usually suffer from fast degradation as the side reactions between polysulfides and stored Li atoms can still occur in a rapid manner [16,38,44]. In our recent work [45], we proposed that indium triiodide (InI_3) could be used as an electrolyte additive in a semi-liquid Li-polyiodide battery to protect the lithium metal from the corrosion of polyiodide. Based on the theoretical investigations, it can be deduced that the pre-deposited Li-In layer, allowing for facile Li$^+$ transport and the Li stripping/plating beneath its shield. Furthermore, the function of InI_3 electrolyte additive may further extend to non-lithium anode in Li-ion sulfur batteries. Therefore, to demonstrate an efficient Li-ion sulfur configuration, the facile activation of Li_2S electrode and protection of the non-lithium anode need to be realized spontaneously.

In this regard, we propose and prepare a facile and feasible Li_2S-based Li-ion sulfur battery configuration, which is activated by a bifunctional InI_3 electrolyte additive. Li_2S particles were uniformly loaded on the low-cost carbonized wipes with a solution-based infiltration method. InI_3 additive in electrolyte not only functionalized as a cathodic redox mediator to activate the Li_2S cathode, but also pre-covered the surface of the anode with a passivation layer to inhibit the corrosion due to shuttle effect. The obtained SnO_2/Li_2S cell present high specific capacities of 983, 878, 746 and 675 mAh/g at 0.2, 0.4, 0.8, and 1.5 C respectively and maintains at 647 mAh/g after 200 cycles at 0.5 C. Most importantly, the SnO_2/Li_2S Li-ion sulfur battery shows a strong recovery ability in the abusive conditions of over-charge, over-discharge and short-circuit due to the controllable Li ions and separated potentials of both electrodes in the full cell.

2. Results and discussion

2.1. Preparation of the Li_2S cathode with a solution-based infiltration method

Based on previous papers [20,22,31–33], we exploited the carbonized wipes as the conductive substrate for the impregnation of Li_2S particles due to its extremely excellent liquid absorbance (74 μL cm^{-2}). Its light-weight freestanding, flexible and robust nature are very suitable for use in the Li_2S electrode to buffer the volume change induced by the charge/discharge product formation. Fig. 1a presents the surface morphology of the carbonized commercial wipes, which displays interwoven structure with band-like carbon belt. The carbon matrix still maintains the flexible and freestanding property as shown in the inset of Fig. 1a after heat treatment and demonstrates sufficient mechanical strength to resist the bending force. The Li_2S particles were loaded by a solution-based infiltration method by repeatedly adding the Li_2S solution into the carbonized wipes (detailed preparation process is shown in experimental section). Due to the excellent liquid absorbency, the carbonized wipes allows for a high mass loading of Li_2S ($\sim$ 2.4 mg cm^{-2}). As shown in Fig. 1b, Li_2S particles with a diameter of $\sim$ 400 nm were uniformly anchored on the surface of every single carbon

belt. The close contact between Li_2S particles and carbon matrix enabled the sufficient utilization of the active material [46]. Moreover, the freestanding nature of the Li_2S paper cathode facilitates the fabrication of the flexible device for further research [47].

2.2. Electrochemical performance of Li/Li_2S and SnO_2/Li_2S batteries

In this section, to investigate the effective role of InI_3 additive in activating Li_2S cathode, we assembled the Li/Li_2S half cells employing Li anode, Li_2S cathode and ether-based electrolyte (1 M LiTFSI in DOL/DME with 1 wt% $LiNO_3$) with 150 mM LiI or 50 mM InI_3 additive. Meanwhile, Li/Li_2S and Li/Li_2S_x cells with standard ether-based electrolyte were assembled as a control group. Firstly, the rate and cycling tests of the Li/Li_2S batteries and Li/Li_2S_x batteries with standard electrolyte are shown in Fig. S2. It can be seen both of the batteries that show unsatisfactory electrochemical performance, displaying poor rate capability and the capacity subsequently retains at $\sim$ 400 mA h g^{-1} after only 40 cycles at 0.2 C. While the capacity of Li/Li_2S_x battery is higher than the Li/Li_2S battery, even both of them are assembled with standard ether-based electrolyte and similar sulfur loading. Hence, without redox mediator in the electrolyte, the Li_2S particles as the starting active material cannot be fully activated to contribute the whole capacity, due to the large Li_2S particle size and coarse Li_2S/carbon interphase. However, for the Li/Li_2S_x battery, the liquid polysulfides as starting active materials can be uniformly distributed in the electrode and exhibit benign reaction kinetics, resulting in a higher active material utilization ratio. Fig. 2a presents the first activation curves of the Li/Li_2S cells employing ether-based electrolyte with 50 mM InI_3 and 150 mM LiI additive under the current density of 0.05 C (the current density of 1 C is 1166 mA/g). Along with the function of InI_3 additive or LiI additive, the Li/Li_2S cell shows a lower activation potential of $\sim$ 2.45 V, but the battery with LiI additive presents lower initial coulombic efficiency, which is attributed to the side reactions between polysulfides/polyiodide and lithium metal. In order to testify the chemical oxidizability of iodide/triiodide redox mediator, we dispersed 0.767 mg Li_2S powders into the DOL/DME electrolyte via sonication and further added 5 mL InI_3, LiI or LiI_3 solution (2.5 mM). Simply after 30-min rest at the room temperature, those sediment Li_2S powders were found to be dissolved only in the LiI_3 solution. As can be confirmed in the UV–vis spectra in Fig. S1, two absorption peaks around 295 and 366 nm, representing I_3^- species, disappear with the formation of Li_2S_4 and Li_2S_6 species [40,48]. The peak representing Li_2S_6 is found to emerge at around 470 and 350 nm, while S_4^{2-} at 420 and 320 nm [40,48]. The oxidative I_3^- resulted from the I^-, efficiently transforms the outmost surface of Li_2S particles into soluble polysulfides, and the resultant polysulfides could inversely promote the activation reactions, leading to a much decreased charge over-potential [38]. In this regard, the roles of I^-/I_3^- redox couple in facilitating the charging process of Li_2S electrode is substantial. After the Li_2S particles are oxidized into dissolved polysulfides, the carbon matrix (with specific surface area of $\sim$ 300 m^2/g) could physically immobilize the polysulfides between the belt layers and efficiently benefit the following precipitation of sulfur particles [49,50]. The repeated dissolution/precipitation can be confined within every single layer of the carbonized wipes.

On the other hand, in terms of anode protection, we compare the InI_3 and LiI electrolyte additive in the standard electrolyte (1 M LiTFSI in DOL/DME with 1 wt% $LiNO_3$). As shown in Fig. 2b, the Li_2S battery with 150 mM LiI redox mediator still shows quick capacity decay rate and poor rate capability, which is in consistent with previous work [21]. In fact, when iodide is oxidized into polyiodide, irreversible anode degradation will happen due to the side reaction between Li metal and polyiodide [40]. Meanwhile, as shown in Fig. S3a, the surface of the lithium metal in the cycled Li_2S battery with LiI additive has been severely damaged by the deposited Li_2S particles. In contrast, the performance of the Li/Li_2S cell employing ether-based electrolyte with 50 mM InI_3 additive at various rates from 0.2 to 1.5 C is shown in