

A highly-safe lithium-ion sulfur polymer battery with SnO₂ anode and acrylate-based gel polymer electrolyte

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ABSTRACT

Safety is a prime concern associated with the use of metallic lithium in high-capacity Li-S batteries. Recent studies have shown that replacing lithium metal with other high performance anodes and assembling as lithium-ion sulfur battery (LISB) are effective methods to enhance the safety coefficient of the battery. However, the volume expansion of anodic active materials and gradual thickening of solid electrolyte interface (SEI) on the anode, as well as the ever-existing detrimental shuttle effect of sulfur cathode still limit the performance of LISBs. In this work, we propose and prepare a lithium-ion sulfur polymer battery (LISPB) that employs a stable SnO₂ anode and a bi-functional gel polymer electrolyte (GPE). We demonstrate that graphene and carboxymethyl cellulose (CMC) are able to form a robust anode structure and simultaneously maintain a stable SEI in ether-based electrolyte, while the acrylate-based GPE immobilizes the polysulfides and protects the anodic SEI from side deposition reactions. The LISPB renders a superior high rate capability (608.2 mA h g⁻¹ at 5 C), while maintaining excellent retention at both high and low current densities (83.3% after 300 cycles at 0.3 C and 82.1% after 500 cycles at 1 C). This novel and simple LISPB system represents a significant advancement of high-safety sulfur-based batteries.

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1. Introduction

Lithium-sulfur (Li-S) battery based on a multi-electron chemical reaction has shown great energy density potential to evolve energy storage systems (EES) and boosted the endurance mileage of next-generation electric vehicles (EV) [1–6]. Nevertheless, the safety concerns associated with the metallic lithium anode such as dendritic growth and intrinsically chemical reactivity have long prevented the Li-S battery from becoming a reality. For this reason, the lithium-ion sulfur battery (LISB) that replaces the metallic lithium with other anode materials shows an attractive perspective to enhance the battery safety coefficient [7]. LISB can be assembled by applying the Li-alloying technique to the anode or cathode, resulting in pairs including unalloyed anodes to lithium sulfide (Li₂S) cathode (“discharged state”) or Li-alloying anodes to sulfur cathode (“charged state”) [8,9]. However, the sensitivity to

moisture confines the broad application of the Li₂S cathode, leading to a sluggish progress for the pair of “discharged state”. Hence, the “charged state” LISB exhibits great potential for high-safety and high-performance sulfur-based battery.

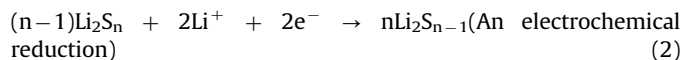
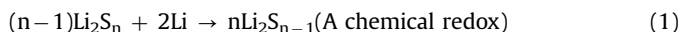
Though possessing above merits, LISB still faces tremendous challenges for practical applications. Firstly, the commercialized graphite-based intercalation-type anode materials are limited by their relatively low theoretical specific capacity (372 mA h g⁻¹) [10]. Therefore, high capacity non-lithium anode materials such as B [11], Si [7] and Sn [12] were attempted to pair with the sulfur cathodes and assemble as LISBs. Unexpectedly, the huge volumetric expansion of these anode materials during charging/discharging process results in a great loss in anodic active materials and a rapid fading during cycling. Moreover, the complex synthetic routes of these anode materials and the massive electrochemically inert carbon as conductive additives in the anode further restrained the implementation of above anodes. Secondly, ether-based electrolyte systems are considered as a better option for LISB compared with carbonate-based electrolytes, because polysulfides is verified to react with carbonates, which generates a different anodic solid electrolyte interface (SEI) compared with anode in ether-based electrolytes [13–16]. In addition, solvents can greatly influence both the morphology, composition and robustness of the

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SEI layer. On the other hand, the properties of the SEI layer is critical to anode performance since it acts as a passivation layer that allows a facile transport of ions and simultaneously buffer the volumetric change [16]. The shortage of compatible comprehension between anode and ether-based electrolyte (especially different SEI formation mechanisms) leads to fast capacity decay and short cycle life for the LIBs. Finally, the constraint that ever-existing in sulfur-based battery, during the discharge process solid-state sulfur would be reduced to the long-chain polysulfides, dissolving into the electrolyte and diffusing across the separator [17,18]. The intermediate polysulfides could parasitize and passivate the anode through direct chemical reaction and electrochemical reduction according to Eq. (1) and (2) (so called shuttle effect) [19–21]:



The above-mentioned disadvantages of vulnerable anodes, together with the shuttle effect, result in a massive loss of power and active materials and deteriorating the whole system [22]. Among the non-lithium anodes, SnO_2 has presented a more promising capability than Si, Sn and other high capacity anode materials due to its unique multiple lithiation mechanisms with formation of volumetric buffer scaffold [23–25]. Precise in-situ studies proved that the lithiation of SnO_2 anode is a combination of conversion and alloying mechanisms [26,27]. SnO_2 is electrochemically reduced to Sn during the primary discharge process, and simultaneously forms Li_2O scaffold which buffers the subsequent volumetric change of Sn [28]. Then the Sn particles in the Li_2O framework could totally embed 4.4 Li^+ ions and exhibit a high theoretical specific capacity of 782 mA h g^{-1} [29,30]. In addition,

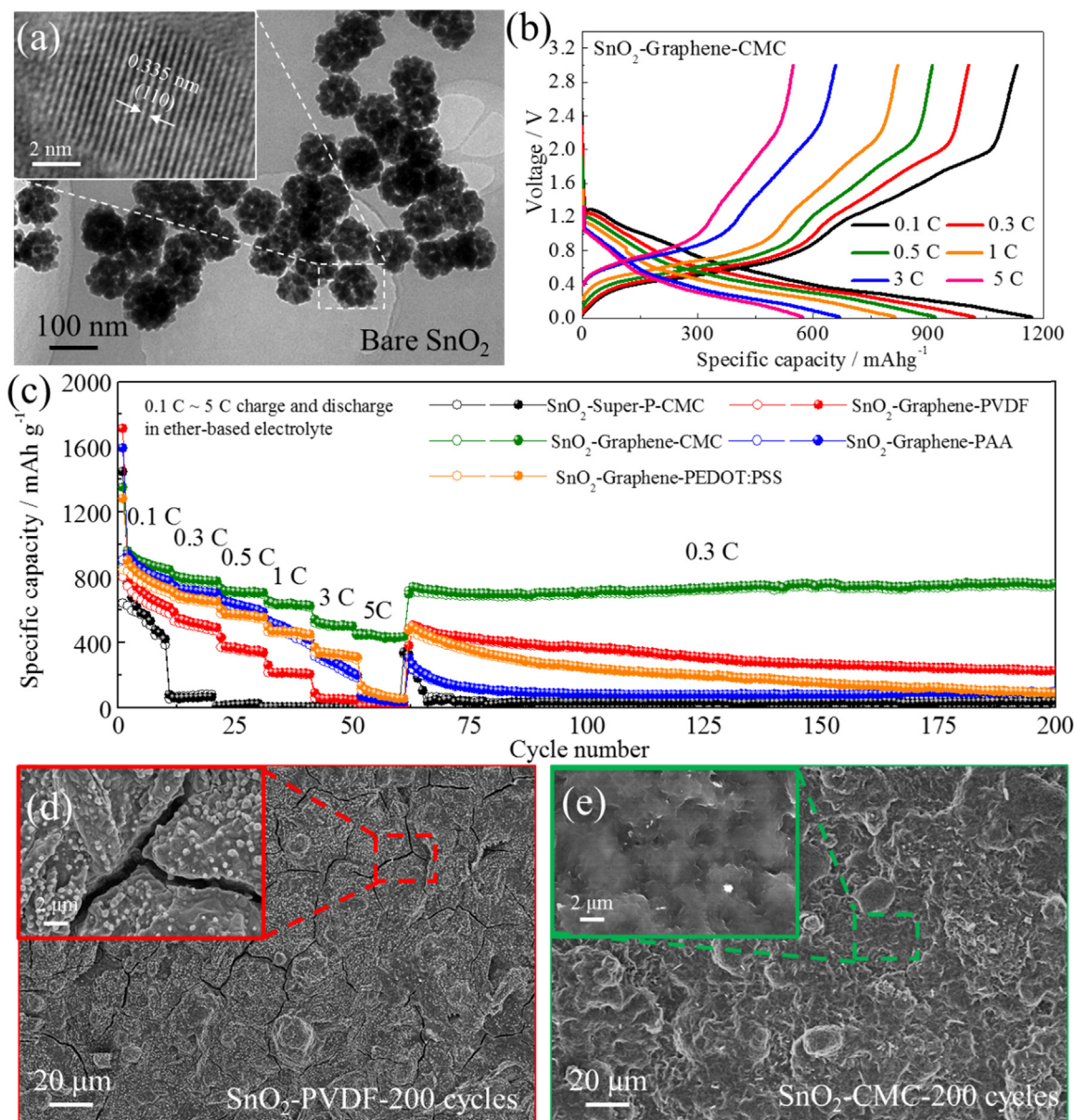


Fig. 1. Morphologies and electrochemical characterization of SnO_2 particles and electrodes: HR-TEM images of the pristine SnO_2 particles (the crystal lattice is shown in inset) (a); typical charge/discharge voltage curves of $\text{SnO}_2/\text{LE}/\text{Li}$ cell at various C-rates with CMC binder (b); rate performances from 0.1 to 5 C and following cycling performances at 0.3 C of the $\text{SnO}_2/\text{LE}/\text{Li}$ cell with different binders and conductive additives (the current density of 1 C is 782 mA g^{-1}) (c); morphologies of SnO_2 electrodes after 200 cycles with PVDF (d) or CMC (e) as binders, respectively. Specific capacity values are calculated based on the total mass of active material (including SnO_2 and graphene).

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