



Communication

Two-dimensional vermiculite separator for lithium sulfur batteries

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ABSTRACT

Lithium-sulfur batteries have been considered as one of the most promising battery system for their high theoretical energy density. However, the lithium-sulfur batteries suffer from the dissolution and diffusion of polysulfides, which induce parasitic reactions with lithium metal anodes. The safety of lithium-sulfur batteries is also concerned with the risk of dendrite growth on lithium metal anodes. To simultaneously address the challenges in the shuttle effect and safety problems, we demonstrate herein a two-dimensional vermiculite separator. With the assembly of the 2D exfoliated vermiculite sheets, the vermiculite separator can suppress the diffusion of polysulfides across the separator through electrostatic interaction and steric hindrance. Meanwhile, the inorganic sheets with high strength and Young's modulus prevent the penetration of lithium metal dendrite and potentially improve the safety of the system. This work elucidates a promising strategy for safe and stable lithium sulfur batteries, and can also be extended to other electrochemical systems based on metal anodes.

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High-energy-density battery systems have been extensively pursued to catch up with the requirements of portable electronics and electric vehicles [1–6]. Lithium-sulfur (Li-S) battery is endowed by the conversion mechanism with high energy density of 2600 Wh/kg, which is 3–5 times that of conventional Li-ion batteries [7]. Additionally, sulfur is a promising cathode material also due to its natural abundance and environmental benignity. However, the conversion reaction between sulfur and lithium also brings high complexity of the electrochemical system. There are three main technical challenges hindering the practical use of Li-S batteries: the insulating nature of sulfur and lithium sulfides that limits the utilization of active materials, the notorious “shuttle effect” of the polysulfide intermediate product, and the safety concerns raised by potential risk in lithium dendrite penetration [1,8]. Various carbon hosts have been developed as conductive hosts to accommodate sulfur, which is effective in solving the insulating problem and improve the utilization of sulfur [9–12].

The shuttle effect of polysulfide intermediates refers to the dissolution of polysulfides (Li_2S_x , $4 < x < 8$) into the electrolyte and

diffusion across the separator to the anode side, which induces parasitic reactions between polysulfides and lithium metal. The shuttle effect in Li-S batteries results in the loss of active sulfur materials, lowers the coulombic efficiency, and causes the corrosion of lithium metal anode. The strategies in cathode design cannot fully address the shuttle effect yet [13–16].

The modification of a separator is a facile but very effective route in order to suppress the shuttle effect [17–19]. The modification of separator with ion-selective functional layers of Nafion [20], graphene oxides [21], metal-organic frameworks [22] can prevent the diffusion of polysulfide towards anode side. On the other hand, the incorporation of functional layers that can adsorb polysulfides and promote their redox conversion is also effective in mitigating the shuttle of polysulfides [23–26].

Meanwhile, the uneven deposition of lithium at anode side tends to generate lithium dendrites, which is of potential risk on internal short circuit and safety problems [27]. To protect lithium metal anode, several strategies have been proposed focusing on the construction of protective interlayer on lithium surface [28], formation of stable solid electrolyte interface [29–31], the introduction of three-dimensional (3D) conductive hosts [32,33], and the modification of separators for lithium metal anodes [34]. In fact, the separators for lithium sulfur batteries need not only to

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alleviate the shuttle effect caused by polysulfide diffusion, but also to reduce the safety risks of the lithium metal anode.

In this contribution, we proposed a lamellar separator reassembled with exfoliation vermiculites, a type of clay, for Li–S batteries. The vermiculite separator is effective in Li–S batteries in both cathode and anode side. Firstly, the 2D vermiculite flakes are readily assembled to yield a separator structure with the interstitial spaces allowing ion selective transportation [35]. The 2D exfoliated vermiculite sheets are negatively charged to repel the polysulfide anions by electrostatic interaction (Fig. 1a). Meanwhile, the positive equilibrium charges are also presented between the sheets, which enriched positively charged lithium ions after ion exchanging in the interspace of the vermiculite flakes (Fig. 1b). The interlayer space therefore acts as permselective Li-ion transfer channels to avoid the shuttle effect in working Li–S batteries.

The fabrication procedure of vermiculite separator is as follows. The primary mineral of vermiculite was heated at 500 °C for 3 min to make it fully expanded. The thermally-expanded vermiculite was then mechanically sheared to obtain vermiculite powder. As-prepared vermiculite powder was then subjected to a two-step ion-exchange method to replace the interlayer cations with Li ions. 200 mg of vermiculite powder were added into 80 mL saturated sodium chloride (NaCl) solution and heated under 60 °C for 24 h, followed by vacuum filtration and repeated washing with deionized water. The resulting product was re-soaked in 80 mL 2 mol/L lithium chloride (LiCl) solution and heated under 60 °C for additional 24 h, followed by vacuum filtration and repeated washing with deionized water. The Li⁺-exchanged vermiculite was further chemically exfoliated in 30 wt% hydrogen peroxide (H₂O₂) solution for 96 h. The homogeneous dispersion of vermiculite nanosheets was obtained through centrifugation at 5000 revolutions per minute for 10 min. 25 mL of as-obtained vermiculite nano-dispersion was then filtered on a 4 cm-diameter polypropylene (PP) substrate (Celgard 3401). Freestanding vermiculite separator was able to be integrally peeled from the PP matrix while soaking in acetone.

Standard CR2025 coin-type cells were employed for the evaluation of vermiculite separator for Li–S cells. The assembly process was carried out in an Ar-filled glove box with O₂ and H₂O content blow 1 ppm. The ether-based electrolyte of 1 mol/L LiTFSI-1:1 DOL/DME was utilized in this work. To standardize, equal electrolyte of 25 μL/mg_S was added in a cell. The S powder (54 wt%), carbon nanotubes (36 wt%) and poly(vinylidene fluoride) binder (10 wt%) are dispersed in *N*-methylpyrrolidone solvent. The cathodes were prepared by a doctor blade method with an areal weight loading of 1.1 mg/cm² to 1.3 mg/cm². All the Li–S batteries were cycled in the voltage range of 1.7 V to 2.8 V.

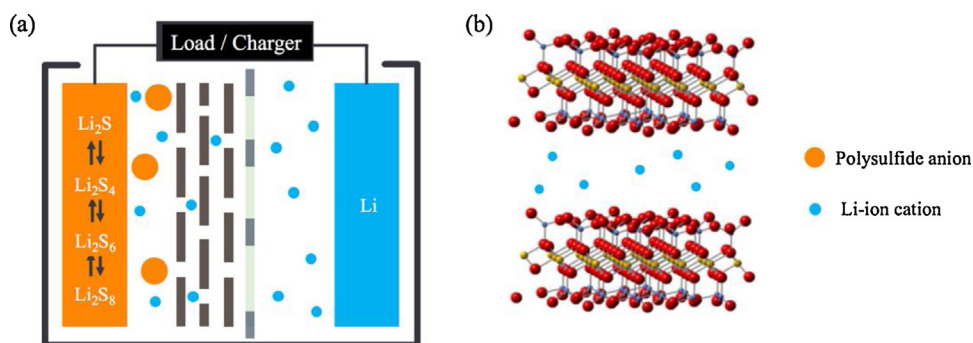


Fig. 1. (a) Schematic of exfoliated vermiculite separator in lithium-sulfur battery, which can effectively repel the polysulfide anions and mitigate the “shuttle effect”. (b) The structure of vermiculite sheets with enriched interlayer lithium cations as transfer channels.

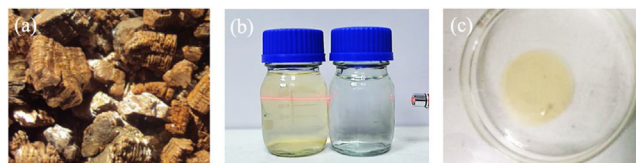


Fig. 2. (a) Optical morphology of vermiculite minerals; (b) laser irradiation experiments with solution containing exfoliated vermiculite sheets (left) and deionized water (right); (c) optical image of assembled freestanding vermiculite separator through facile vacuum filtration.

Vermiculites are typical clay minerals widely applied in cushion materials, nanocomposite reinforcement, and for the generation of paper-like materials. The vermiculite particles are of two-dimensional structures (Fig. 2a), which are composed of silicate layers of vermiculite and inter-lamellar water molecules associated with metallic cations. Due to the presence of interlayer water between the silicate lamellae, the vermiculite is intended to expand vigorously when rapidly heated at a high temperature, and can be partially peeled off by mechanical exfoliation into micron-sized sheets easily. Furthermore, hydrogen peroxide expansion method was employed to ensure the high dispersibility of vermiculite silicate sheets, which can be indicated by the significant Tindal effect of the vermiculite sheet dispersion with deionized water as dispersant during the laser irradiation experiment (Fig. 2b). In this work, the vermiculite nanosheets are subjected to an ion-exchange process in LiCl solution to enrich lithium ions in the inter-lamellar structures for rapid lithium ion transportation. The dispersed vermiculite nanosheets were then reassembled into a freestanding membrane via a vacuum filtration technique. The thin vermiculite separator is transparent and flexible (Fig. 2c).

After vacuum filtration, the vermiculite nanosheets dispersed in solution were well reassembled into a lamellar structure. Based on the scanning electron microscopy (SEM) observation at the cross section of the as-obtained vermiculite separator, layer-by-layer vermiculite silicate sheets with densely stacked morphology are observed with a thickness of about 10 μm (Fig. 3a). The thickness of vermiculite separator is highly tuneable by regulating the amount of the vermiculite dispersion to be filtered. The vermiculite silicate nanosheets, which are commonly several tens of nanometers thick, are observed under SEM as well (Fig. 3b). The vermiculite nanosheets with average sizes of about several tens of microns are assembled into a uniform and dense separator (Fig. 3c). X-ray diffraction (XRD) pattern further indicated that the vermiculite sheets stacked are of uniform size with the interlayer cations fully replaced by Li ions as there was only a single broad peak can be observed. Such a compactly stacking structure

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