镧掺杂锡酸钡/多壁碳纳米管改性隔膜的制备 及其在锂硫电池中的应用

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摘要:通过将共沉淀法制备的钙钛矿型氧化物镧掺杂锡酸钡(LBSO)与多壁碳纳米管(MCNT)混合均匀,制成浆料,并利用刮涂 法将其涂布在商业隔膜 Celgard 2500(PP)表面构筑阻挡层,获得改性隔膜(LBSO/MCNT/PP)。基于该改性隔膜的锂硫电池在 0.1C下具有高达1 433 mAh·g⁻¹的初始放电比容量,1C时 300次循环后每圈容量衰减率为0.114%;当电流密度提高到 3C时,仍 具有 764 mAh·g⁻¹的放电比容量,表现出优良的倍率性能和循环稳定性,这主要是由于该阻挡层能够有效抑制多硫化物的 穿梭。

关键词: 锂电池; 高储能; 镧掺杂锡酸钡; 穿梭效应; 阻挡层
中图分类号: 0614.33⁺¹
文献标识码: A
文章编号: 1001-4861(2022)07-1433-08
DOI: 10.11862/CJIC.2022.138

La-Doped BaSnO₃/Multi-walled Carbon Nanotube Modified Separator: Synthesis and Application in Lithium-Sulfur Battery

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Abstract: Herein, an interlayer was constructed on the commercial separator Celgard 2500 (PP) by doctor blade coating a mixture slurry of perovskite oxide lanthanum doped barium stannate (LBSO) that was prepared by co-precipitation method and multi-walled carbon nanotubes (MCNT). The as-obtained modified separator was named LBSO/MCNT/PP. The lithium-sulfur battery using the modified separator delivered an initial discharge specific capacity up to 1 433 mAh·g⁻¹ at 0.1C and a capacity decay rate of 0.114% per cycle over 300 cycles at 1C. As the current density was increased to a 3C rate, a discharge specific capacity of 764 mAh·g⁻¹ can still be maintained, showing excellent rate capability and cycling stability, which is ascribed to the effective inhibition of the interlayer towards the shuttle of polysulfides.

Keywords: lithium batteries; high energy storage; lanthanum doped barium stannate; shuttle effect; interlayer

收稿日期:2022-02-01。收修改稿日期:2022-04-29。

国家自然科学基金(No.51972070、52062004)、贵州省科技计划项目重点类型(黔科合基础[2020]1Z042)、贵州省科技支撑项目(黔科合 支撑[2021]一般317)、贵州大学培育项目(贵大培育[2019]01号)和贵州省研究生科研基金立项课题(黔教合YJSCXJH[2020]028)资助。 *通信联系人。E-mail:shaojiao_jing@163.com,xjshao@gzu.edu.cn

0 Introduction

Lithium - ion batteries (LIBs), based on lithium intercalation electrochemistry, have dominated the battery market of portable electronic devices since their successful launch in the 1990s^[1]. Currently, the energy density of LIBs is approaching its upper limit, it is still difficult to satisfy the ever-increasing requirement for high energy density in the field of electric vehicles (EVs) and large-scale smart grids, which urges a lot of researchers to constantly explore advanced battery systems^[2-7]. Lithium - sulfur batteries are one of the most promising candidates for next-generation energy storage devices owing to their high theoretical energy density (2 600 $Wh \cdot kg^{-1}$), high theoretical discharge specific capacity (1 675 mAh \cdot g⁻¹), and low cost of the sulfur cathode. Nevertheless, the practical implementation is largely limited by several challenges including the poor electrical/ionic conductivity of S/Li₂S, the volume variation of S during charge/discharge cycling, and the shuttle effect of lithium polysulfides (LiPSs), which leads to low active sulfur utilization, sluggish electrochemical redox reaction kinetics, and rapid capacity decay^[8].

In the past few decades, great efforts have been devoted to addressing the above-mentioned issues. For example, designing S cathode^[9-10], synthesizing novel electrolytes and constructing functional interlayers^[5,11-12]. Among them, introducing an interlayer between the separator and active electrodes is believed to be a promising way to suppress the notorious shuttle effect of LiPSs. In addition, the interlayer could also regulate the uniform deposition of Li ions on the lithium metal anode, which plays a certain role in addressing the lithium dendrite issue^[13-14]. It is reported that perovskite oxide (BaTiO₃)^[15] can form strong chemical interaction with LiPSs through metal - sulfur bonds, which is critical for effective inhibition of the polysulfide shuttle. While, the low electronic conductivity $(3.10 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1})$ and mobility $(2 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1})$ of BaTiO₃^[16] are disadvantageous to the fast electron and ion transport, which impairs the rate capability and specific capacity. Hence, it is essential to improve the conductivity of perovskite oxide. Zhao et al.^[17] designed a kind of BaTiO₃ with defects as an additive in the cathode. The defects endowed $BaTiO_3$ with improved electronic conductivity, which promoted redox reaction kinetics. Recently, it is found that La-doped $BaSnO_3$ (LBSO) exhibited an unusually high electrical mobility of 320 cm²·V⁻¹·s⁻¹ at room temperature^[18-19].

Herein, the perovskite-type LBSO prepared by the co-precipitation method was mixed with multi-walled carbon nanotubes (MCNT). As - obtained LBSO/MCNT slurry was coated on a commercial Celgard 2500 separator (PP) by the doctor blading method, leading to a modified separator (denoted by LBSO/MCNT/PP). The Li-S battery using LBSO/MCNT/PP delivered a high initial discharge specific capacity of 1 433 mAh \cdot g⁻¹ at 0.1C and a low - capacity decay rate of 0.114% per cycle over 300 cycles at 1C. A high discharge specific capacity of 764 mAh·g⁻¹ can still be maintained even at a high rate of 3C, which is attributed to the cooperative effect of MCNT and LBSO in the LBSO/MCNT interlayer. The high electronically-conductive MCNT could act as the secondary current collector that promotes the electron transport and improves the kinetic reaction process^[20], while the strong polarity and structural defects enhance the chemical adsorption between LBSO and LiPSs, which contributes to inhibiting the polysulfide shuttle and increases the S utilization. Intrinsically, the interlayer can also form a physical barrier to block the shuttle of LiPSs.

1 Experimental

1.1 Synthesis of LBSO

La(NO₃)₃·6H₂O (0.5 mmol), BaCl₂·2H₂O (9.5 mmol), SnCl₄·5H₂O (10 mmol), and C₆H₈O₇ (5 mmol) were dissolved in H₂O₂ aqueous solution (170 mL, 30%) with constant stirring at 50 °C. After it became transparent, ammonia solution (25% - 28%) was dropwise added into the solution until the pH reached 10. Then the solution became turbid together with precipitation of white substance. Followed by stirring for 60 min, the white substance was firstly rinsed using distilled water and ethanol and then dried in an oven at 50 °C for 24 h. After that, the dried solid was calcined at 900 °C for 3 h in the air, which finally leads to LBSO.

1.2 Preparation of the S/MCNT cathode

Typically, a mixture of MCNT and S with a mass ratio of 3:7 was ground and heated at 155 °C for 12 h. Then, 80% of S/MCNT, 10% of MCNT, and 10% polyvinylidene difluoride (PVDF) were mixed in *N*-methyl-2-pyrrolidone (NMP) to form a slurry. Then, such slurry was coated on a carbon-coated aluminum foil and vacuum-dried at 60 °C for 10 h. The areal mass loading of S was calculated to be 1.0-1.4 mg • cm⁻².

1.3 Preparation of the LBSO/MCNT and MCNT electrode

To further evaluate the electrochemical stability of LBSO, 80% of LBSO, 10% of MCNT, and 10% PVDF were mixed in NMP to form a slurry. Then, such slurry was coated on a carbon - coated aluminum foil and vacuum - dried at 60 °C for 10 h. For comparison, MCNT (90%) was also mixed with a binder (10%) in NMP to form the electrode. They were then assembled in a cell with Li metal as the anode.

1.4 Preparation of the interlayer

LBSO, MCNT, and PVDF with a mass ratio of 8:1: 1 were dispersed in NMP to form a homogeneous slurry that was then coated on a Celgard 2500 separator (PP) by the doctor blading method. After that, the modified separator was dried at 60 °C overnight in a vacuum and punched into discs with a diameter of 16 mm, leading to LBSO/MCNT-modified separator (denoted by LBSO/ MCNT/PP). In a control experiment, the mixture slurry of MCNT and PVDF with a mass ratio of 9:1, as well as that of LBSO and PVDF with a mass ratio of 9:1 were respectively coated on the PP, leading to MCNTmodified (denoted by MCNT/PP) and LBSO-modified (denoted by LBSO/PP) separators. In these modified separators, the areal mass loading of the interlayer materials was kept to be about 0.9 mg·cm⁻².

1.5 Testing and characterizations

Standard CR2032 coin batteries were assembled in an Ar-filled glovebox based on the modified separators by using lithium foil as the anode, and 1.0 mol·L⁻¹ dilithium (trifluoromethane sulfonyl imide) imide (LiTFSI) in a DOL/DME (DOL=1,3-dioxolane, DME=1, 2-dimethoxyethane) solution (1:1, V/V) with 2.0% LiNO₃ as the electrolyte (electrolyte/S ratio of 25:1). Electrochemical impedance spectroscopy (EIS) in the scan frequency range of 10 mHz to 1 000 kHz and cyclic voltammetry (CV) were conducted on a CHI604e electrochemical workstation, and the cyclic stability and galvanostatic charge-discharge (GCD) behavior of the batteries were investigated by the Neware battery test system (CT-4008-5V 10 mA). X-ray diffraction (XRD, Empyrean) with Cu K α radiation (40 kV, 40 mA, λ = 0.154 nm, 2θ =10° - 80°) was used to characterize the crystal structure of the sample. Scanning electron microscopy (SEM, ZEISS GeminiSEM300) was used to observe the micro-morphology of the sample at 0.02-30 kV. UV-Vis spectra were recorded using a MAPADA UV-6300 spectrometer.

2 Results and discussion

The XRD pattern of as-synthesized LBSO (Fig.1) shows six diffraction peaks located at 30.7° , 37.8° , 43.9° , 54.5° , 63.9° , and 72.5° , being assigned to the (110), (111), (200), (211), (220), and (310) crystalline planes of LBSO, respectively, which is consistent with the standard profile of LBSO^[21] (PDF No.15-0780).



Fig.1 XRD pattern of as-obtained LBSO

Fig. 2a, 2b shows that as-fabricated LBSO particles had uniform size. To further study the elemental distribution, EDS (energy-dispersive X-ray spectroscopy) was used to perform. As shown in Fig. 2c, four elements including La, Sn, Ba and O evenly distribute in the LBSO particles, which indicates the successful doping of element La.

A cross-sectional SEM image shows that the thickness of the LBSO/MCNT interlayer was about 21.61 μ m. To investigate the adsorption ability of LBSO towards LiPSs, a static adsorption test was conducted.



Fig.2 SEM images (a, b) and EDS mappings (c) of LBSO

As displayed in the inset of Fig.3b, although there was no obvious change in three samples after reacting 48 h, the UV-Vis spectra (Fig.3b) show that the intensities of the solutions with MCNT and LBSO were lower than that of blank Li_2S_6 solution, and the solution with LBSO displayed the weakest characteristic adsorption peaks at 263.9 and 314.8 nm that are assigned to S_6^{2-} , which indicates the favorable chemical interaction between the interlayer materials and the LiPSs. To further evaluate the electrochemical stability of the LBSO, a mixture slurry of LBSO, MCNT, and PVDF with a weight ratio of 8:1:1 was prepared in NMP to prepare the cathode, and then a cell was assembled by using Li metal as the anode and 1.0 mol· L^{-1} LiTFSI in a DOL/ DME solution (1:1, V/V) with 2.0% LiNO₃ as the electrolyte. For comparison, MCNT and PVDF were also mixed with a ratio of 9:1 in NMP to form the electrode. As shown in Fig. 3c, 3d, there was no redox peak for both the two cells within a potential range of 1.7 to 2.8 V in the CV curves at 0.1 mV \cdot s⁻¹, indicating the electrochemical stability of LBSO^[22].

To estimate the practical application of the interlayers, the electrochemical test was carried out on the cells using these interlayer - modified separators. As shown in Fig.4a, two pairs of redox peaks correspond to the multistep reaction mechanism appearing in the lithium-sulfur batteries with LBSO/MCNT/PP separator. The cathodic peaks (2.31 and 2.03 V) are ascribed to the multistep conversion from S to long-chain LiPSs and then to short-chain Li₂S₂/Li₂S^[23]. The subsequent anodic peaks at 2.30 and 2.36 V are related to the reversible reaction of insulating Li₂S₂/Li₂S to S^[24]. Moreover, the battery using LBSO/MCNT/PP showed smaller potential polarization (ΔE) of 356 mV than those using pristine PP (420 mV), MCNT/PP (380 mV), and LBSO/ PP (520 mV), demonstrating the excellent redox conversion kinetics of LBSO/MCNT/PP, which is attributed to the cooperative effects of high electronic conducting MCNT and strong chemical affinity of LBSO to LiPSs^[25-26]. Fig.4b illustrates the GCD curves of the batteries in the first cycle at 0.1C. The two discharge plateaus and one charging plateau in the GCD curves are consistent with the redox peaks in the CV curves. LBSO/MCNT/PP delivered a high initial discharge specific capacity of 1 433 mAh \cdot g⁻¹ at 0.1C. The $Q_{\rm I}/Q_{\rm H}$ ($Q_{\rm L}$: lower potential plateau discharge specific capacity, $Q_{\rm H}$: upper potential plateau discharge specific capacity) of the cell using LBSO/MCNT/PP were larger than those using other interlayers, indicating that LBSO/MCNT/ PP enables higher S utilization. In the GCD profiles of the cells using PP, MCNT/PP, and LBSO/PP, the beginning point of the second plateau had an obvious poten-



Fig.3 (a) Cross-sectional SEM image of the LBSO/MCNT-modified separator; (b) UV-Vis spectra of the blank $\rm Li_2S_6$ solution (green line) and solutions with LBSO (earth yellow line) or MCNT (blue line); CV curves of the MCNT-based (c) and the LBSO/MCNT-based (d) cells at 0.1 mV \cdot s⁻¹



Fig.4 (a) CV curves at 0.1 mV·s⁻¹, (b) GCD curves at 0.1C, (c) Nyquist plots, and (d) rate performance of the batteries using LBSO/MCNT/PP, MCNT/PP, PP, and LBSO/PP; GCD curves of the cells with LBSO/MCNT/PP (e), MCNT/PP (f), PP (g), and LBSO/PP (h) at different rates; (i) Cycling performance of these cells at 1C

tial dip (marked by a red arrow) is attributed to the concentration polarization, which is disadvantageous to the fast Li⁺ transport because the dissolved LiPSs increased the viscosity of electrolyte^[27-28]. On the contrary, the potential dip in the GCD profile of the battery using LBSO/MCNT/PP was negligible. EIS spectra of these cells were also compared. The Nyquist plots (Fig. 4c) display that the batteries have semicircles at the high-frequency range, corresponding to the charge transfer resistance (R_{ct}) . The battery using LBSO/ MCNT/PP has lower $R_{\rm et}$ (37.09 Ω) than those using the pristine PP (53.66 Ω), LBSO/PP (78.52 Ω), and MCNT/ PP (46.84 Ω), which was attributed to the fast electron transfer paths provided by MCNT/LBSO interlayer, which is beneficial for promoting the redox conversion of Li_2S_n . The rate performance of the cells was further evaluated at different rates from 0.2C to 3C (Fig. 4d). LBSO/MCNT/PP delivered the discharge specific capacities of 1 204, 1 015, 902, 815, and 764 mAh·g⁻¹ at 0.2C, 0.5C, 1C, 2C and 3C, respectively. When the current density was switched back to 0.2C, a discharge capacity of 1 071 mAh \cdot g⁻¹ can be recovered, corresponding to a capacity retaining rate of 89%. In contrast, the remaining capacities of the cells using MCNT/PP, PP, and LBSO/PP displayed much poor rate performance, showing the capacity retaining rate of 73%, 72%, and 74%, respectively. Fig.4e-4h presents the discharging-charging curves of the cells at different rates. With the increase of the current density, LBSO/ MCNT/PP showed the highest discharge specific capacities, implying the excellent redox reaction kinetics^[29], which is attributed to the adsorption ability of the interlayer material towards LiPSs, as well as the high electronic conductivity endowed by MCNT. To investigate the long cycling stability of the batteries, the batteries were tested at 1C (Fig.4i). For LBSO/MCNT/PP, the initial specific capacity was 861 mAh \cdot g⁻¹ at 1C with a capacity decay rate of 0.114% per cycle over 300 cycles, which is much lower than those using MCNT/ PP (0.218%), LBSO/PP (0.157%), and pristine PP (0.164%). Although the discharging specific capacity of the cell using LBSO/MCNT/PP was superior to others, obvious capacity decay was still observed. It is proposed that LBSO/MCNT can't completely suppress the shuttle of LiPSs due to the absence of a catalyst that can't effectively realize the instant LiPSs conversion.

Fig. 5 presents the first three CV curves of the cells. The cell with LBSO/MCNT/PP showed better -



Fig.5 CV curves of the batteries with LBSO/MCNT/PP (a), MCNT/PP (b), PP (c), and LBSO/PP (d) in first three cycles

overlapped CV curves (Fig. 5a) than those (Fig. 5b-5d) using MCNT/PP, PP, and LBSO/PP, indicating that the LBSO/MCNT endows the cell with excellent capacity reversibility^[30].

In addition, the electrochemical performance of the cell using LBSO/MCNT as the interlayer was also compared with those of many previously reported lithium-sulfur batteries using other perovskites as the interlayer materials. Table 1 shows that the LBSO/MCNT host has a high discharge specific capacity and low capacity decay rate as the result of its effective suppression ability towards the polysulfide shuttle.

 Table 1
 Electrochemical performance comparison of this work with previously-reported literatures using other perovskites as the interlayer materials

Interlayer material	Initial discharge capacity / (mAh•g ⁻¹)	Cycle	Capacity retention / (mAh•g ⁻¹)	Rate capacity / (mAh•g ⁻¹)	Fading rate per cycle / %	Ref.
LBSO/MCNT	1 433(0.1C)	300	565(1C)	764(3C)	0.114(1C)	This work
MWCNT-BTO	1 388.6(0.1C)	100	—	455(3C)	0.145(1C)	[31]
BTO/C	—	200	—	—	0.122(0.2C)	[15]
rGO/BTO@CNF	1 452.3(0.1C)	200	865	672(3C)	0.2(0.3C)	[32]

3 Conclusions

Herein, an interlayer LBSO/MCNT/PP was prepared by coating LBSO/MCNT mixture slurry on a PP. The MCNT acts as the upper current collector to further improve the utilization rate of S species. Also, the polar LBSO provides strong chemical interaction with LiPSs, further enhancing the inhibition of the polysulfide shuttle. Consequently, the cooperative effect of MCNT and LBSO improved the overall electrochemical performance of the lithium-sulfur batteries. Specifically, the battery using LBSO/MCNT/PP delivered a high initial discharge capacity of 1 433 mAh·g⁻¹ at 0.1C together with S utilization reaching 85.6% and showed an initial discharge capacity of 860.8 mAh·g⁻¹ at 1C with the capacity decay rate of 0.114% per cycle over 300 cycles. When the current density was increased to 3C, the cell still has a discharge capacity of 764 mAh. g⁻¹. Overall, this work presents the LBSO/MCNT interlayer exhibits an obvious suppression effect for the polysulfide shuttle by taking advantage of both physical blocking and chemical adsorption, demonstrating that LBSO/MCNT is promising as the interlayer materials for suppressing the polysulfide shuttle.

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