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 (ESS) 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 “charged 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 carbones, 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...
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]:

\[(n \times C_0) Li_2S_n + 2Li \rightarrow nLi_2S_{n-1}\] (A chemical redox) (1)

\[(n \times C_0) Li_2S_n + 2Li^+ + 2e^- \rightarrow nLi_2S_{n-1}\] (An electrochemical reduction) (2)

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, SnO₂ 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 SnO₂ anode is a combination of conversion and alloying mechanisms [26,27]. SnO₂ is electrochemically reduced to Sn during the primary discharge process, and simultaneously forms Li₂O scaffold which buffers the subsequent volumetric change of Sn [28]. Then the Sn particles in the Li₂O 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,
SnO$_2$ also shows advantage of anti-oxidation, easy to synthesis and low cost, beneficial to be a suitable anode candidate for LISB [29,31]. In this work, based on our previous work [32–34], we adopted monodispersed SnO$_2$ particles as an active material, graphene as two-dimensional conductive network and carboxymethyl cellulose (CMC) as a binder to fabricate a robust stable anode with a stable SEI in ether-based electrolyte. Moreover, a compatible pentaerythritol tetraacrylate (PETEA)-based gel polymer electrolyte (GPE) for both anode and cathode is exploited to assemble a novel lithium-ion sulfur polymer battery (LISPB) system to suppress the diffusion of polysulfides. This unique design of LISPB spontaneously mitigates the safety hazards and maintains the high energy density, addressing the demanding concerns for full cells with sulfur-based cathodes.

2. Results and discussion

2.1. Stability characterization of SnO$_2$ anodes in ether-based electrolyte

To attain a robust SnO$_2$ anode in ether-based electrolyte (1 M bis(trifluoromethane) sulfonamide lithium (LiTFSI) in 1,2-dioxolane (DOL)/dimethoxymethane (DME) (1:1 by volume) with 1 wt% LiNO$_3$), conductive additive and binder have to be firstly investigated. Because the strong size dependence for lithiation of individual nanoparticles, SnO$_2$ particles with a corresponding particle diameter of ~150 nm are adopted as the anode material [35]. The SnO$_2$ is fabricated by a simple hydrothermal method followed by a thermal treatment in air [31]. As shown in Fig. 1a and Fig. S1, the obtained SnO$_2$ particles are porous monodisperse secondary nanospheres (150 nm) that consist of much smaller SnO$_2$ primary nanoparticles (20 nm). The high resolution transmission electron microscopy (HR-TEM, the inset of Fig. 1) image shows an interplanar spacing of about 3.35 Å, corresponding to the (110) plane of SnO$_2$ [36]. During electrochemical test process, it is interesting to find that the conductive additive and binder play important roles for the anode stability in ether-based electrolyte. As a conductive additive, graphene possesses larger aspect ratios and higher surface area than traditional carbon black, providing an excellent conductive matrix with good mechanical flexibility to accommodate the volumetric changes of SnO$_2$ during charge/discharge cycles, while the graphene can provide extra capacity for unique lithiation property [28,32,37]. The LISB using graphene as conductive additive exhibits a much enhanced electrochemical performance compared with that using traditional Super-P (Fig. 1c). Binders, including typical non-aqueous (polyvinylidene fluoride (PVDF)), aqueous (poly acrylic acid (PAA)), brittle polymer (carboxymethyl cellulose (CMC)) and conductive polymer binders (polystyrenesulfonate doped poly (3, 4-ethylenedioxythiophene) (PEDOT: PSS)) are chosen to carry out the stability test. The specific capacity of SnO$_2$-graphene-binder electrode is calculated based on the whole mass of electrochemically active material (including SnO$_2$ and graphene, Fig. S2). For the initial Coulombic efficiency of SnO$_2$ half cells with different binders, 46.7%, 56.9%, 64.1% and 66.1% were achieved with binders of PVDF, PAA, CMC and PEDOT: PSS, respectively. It is seen that cells with CMC and PEDOT:PSS as binders show higher initial Coulombic efficiency than PVDF and PAA. Such higher Coulombic efficiency of anode is beneficial to the utilization of the limited lithium ions in full cells. After rate and cycling test as shown in Fig. 1c, it is apparently seen that the SnO$_2$ anode with CMC binder achieves the most satisfactory electrochemical performance, which displays superior high rate capability with a reversible capacity of ~440.1 mA h g$^{-1}$ at 5 C and the capacity subsequently retains at ~746.3 mA h g$^{-1}$ after 140 cycles at 0.3 C. The corresponding charge/discharge profiles of SnO$_2$ cell employing CMC binder are shown in Fig. 1b, which present much improved capacity and decreased polarization compared with cell with PVDF binder (Fig. S3). The initial surface morphologies of the pristine SnO$_2$ anode with PVDF and CMC binder are shown in Fig. S4. After cycling, obvious cracks caused by continuous breakdown/reconstruction of SEI are found on the anode with PVDF binder, while surface of electrode with CMC binder maintains relatively robust and intact (Fig. 1d and e). The improvement of cycle life when using CMC binder is mainly attributed to the high polymer mechanical modulus values of CMC and the strong binding between the ether and ester functional groups on the polymers and the surface oxide on the SnO$_2$ particles [38,39]. To recap, the good power and retention capability of the SnO$_2$ electrode in ether-based electrolyte can be attributed to a combined function of uniformly distributed particles, highly conductive and stretchable graphene matrix as well as cumulative effects of brittle CMC binder.

The XRD pattern of pristine optimized SnO$_2$ electrode is shown in Fig. 2a, which is in well consistent with the JCPDS standard (Card no. 41-1445) and can be indexed to the tetragonal structure of SnO$_2$ with the space group Fd3m [40]. The lithiated SnO$_2$ electrode was prepared for the assembling requirement of LISB. After lithiation, the crystalline phase structure was transformed to an amorphous structure, meanwhile the thickness of anode expanded from 35 μm to 50 μm, which are in good accordance with previous reports (Fig. 2a and b) [41–43]. After preparing the lithiated anode, optically transparent model cells are assembled in a glove box to illustrate the compatibility between lithiated SnO$_2$, sulfur electrode and different electrolytes. The cathode is prepared by mixing 80 wt% sulfur@CMK-3 composites, 10 wt% carbon black and 10 wt% poly vinyl pyrrolidone (PVP), the anode is lithiated SnO$_2$ electrode and the electrolyte is ether-based liquid electrolyte (LE)/pentaerythritol tetraacrylate (PETEA)-based GPE. The obtained SnO$_2$/GPE transparent cell is discharged from the open circuit potential (2.8 V, 0 h) to 0.01 V (8 h) at 0.1 mV s$^{-1}$. As seen from Fig. 2c, the LE changed from colorless to bright yellow after only 1 h discharge, which indicates the polysulfides concentration reaches the maximum value. At the end of discharge state (8 h), the color of LE still maintained intermediate yellow, demonstrating that most dissolved polysulfides cannot be cyclically utilized. This phenomenon exactly verifies the concern that the dissolution of polysulfides and the loss of active materials is still inevitable issues in LISBs. In a recent study, we proposed a PETEA-based gel polymer electrolyte (GPE) with an extremely high ionic conductivity ($1.13 \times 10^{-2}$ S cm$^{-1}$) for Li-S batteries, achieving an excellent compatibility with sulfur cathode and successfully inhibiting the diffusion of polysulfides [33]. For comparison, SnO$_2$/GPE/S optical transparent cell is in-situ assembled with the replacement of LE to GPE and the schematical configurations of LISPB is shown in Fig. 2d. Consequently, the color of GPE keeps pure white during the whole discharge process, which proves that the integrated LISPB system distinctly suppress the detrimental side reactions of polysulfides and possesses untapped potentials for cycle life enhancement. The reduced shuttle effect can be attributed to the appropriate polysulfides interaction ability of the ester functional groups and the reasonable geometric design of GPE [33].

2.2. Electrochemical measurements of SnO$_2$/LE/S and SnO$_2$/GPE/S full cells

Fig. 3 compares the electrochemical performances from 0.01 to 3 V of SnO$_2$/LE/S and SnO$_2$/GPE/S in coin cells. The first cycle was activated at a current density of 0.05 C (based on the weight of sulfur, 1 C=1675 mA g$^{-1}$). For the SnO$_2$/LE/S cell, the initial discharge capacity of 1311.5 mA h g$^{-1}$ is not completely reversed during the following charge process, mainly due to the formation
of interfacial passivation layer and initial dissolution of the polysulfides; the corresponding Coulombic efficiency is 86.3% (defined as the discharge capacity per the charge capacity). The SnO2/GPE/S cell shows a first cycle Coulombic efficiency of 87.5%, higher than that of SnO2/LE/S cell, mainly due to the inhibition of dissolution of polysulfides. Generally, during the following cycles, a overall higher Coulombic efficiency (\%\text{C}) are achieved for the SnO2/GPE/S cell, which benefits cyclic utilization of limited lithium ions in Li-ion-S batteries. Meantime, it is clear that the SnO2/GPE/S cell shows a remarkably better rate performance than the SnO2/LE/S cell. The specific discharge capacities of the SnO2/GPE/S at 0.1, 0.3, 0.5, 1, 3 and 5 C are 954.69, 889.3, 824.9, 750.3, 666.9 and 608.2 mA h g\(^{-1}\), respectively. When the C-rate is switched back from 5 to 0.1 C again (Fig. 2a), the original capacity of SnO2/GPE/S is largely recovered, reflecting that the SnO2/GPE/S cell is highly reversible and the active material could be recycled. While for the SnO2/LE/S cell, the capacity of 0.1 C return test cannot be recovered to original level, proving an irreversible loss of active materials in LiSB, consistently with the result of optical transparent cells (Fig. 2c). The corresponding different rate charge/discharge curves

Fig. 2. XRD patterns (a) and cross-sectional morphologies (b) of pristine SnO2 electrode and prelithiated SnO2 electrode; visual observation of polysulfides diffusion in SnO2/LE/S and SnO2/GPE/S transparent cells (c); Schematical configurations of LISPB (d).

Fig. 3. Electrochemical performances of SnO2/LE/S and SnO2/GPE/S batteries: rate performances and the corresponding Coulombic efficiencies of the SnO2/LE/S cell and SnO2/GPE/S cell from 0.1 to 5 C (the current density of 1 C is 1675 mA g\(^{-1}\)) (a); typical charge/discharge voltage curves of SnO2/GPE/S cell at various C-rates (b); cycling performances of SnO2/LE/S cell and SnO2/GPE/S cell at 0.3 C (c) and 1 C (d). Specific capacity values are calculated based on the mass of sulfur.
of SnO2/GPE/S and SnO2/LE/S cells are shown in Figs. 3b and S5. It is clearly seen that the SnO2/GPE/S cell shows higher capacity and slower decay rate than the SnO2/LE/S cell under different current densities. The long cycling performances of the SnO2/LE/S and SnO2/GPE/S cell under high and low current densities are presented in Fig. 3c and d. SnO2/GPE/S cell can deliver a discharge capacity of 755.7 mA h g\(^{-1}\) after 300 cycles at 0.3 C with a capacity retention of 83.3% (Fig. 2c). In sharp contrast, the corresponding retention for the S/LE/Li cell is only 49.1%. Similarly, the SnO2/GPE/S cell also exhibits an obvious enhanced cycling performance at high current density. It can be seen from Fig. 2d that the SnO2/GPE/S cell achieves a discharge capacity of 653.5 mA h g\(^{-1}\) (a capacity retention of 82.1%) after 500 cycles at 1 C. However, the S/LE/Li cell delivers a low discharge capacity of only 386.3 mA h g\(^{-1}\) after 500 cycles. The LISPB performs the superior electrochemical performance with the simplest optimization method, which is of great significance to the development of low-cost, high-energy storage systems (A comparisons of the configuration and cycling performance with recent LISBs are shown in Table 1).

![Figure 4](image)

**Fig. 4.** CVs of SnO2/LE/S (a) and SnO2/GPE/S (b) cells at a scan rate of 0.1 mV s\(^{-1}\); EIS plots of SnO2/LE/S (c) and SnO2/GPE/S (d) fresh cells, cells after 1 cycle and 300 cycles (f). Impedances are measured at fully charged state (3 V).
(2.437 V) and anodic (1.411 V) peak gap as well as steady peak current, suggesting the decreased polarization and consistency of LISPB. Electrochemical impedance spectroscopy (EIS) is used to evaluate the interfacial resistance and reversibility of full cells. The EISs of the battery with LE and GPE after different cycles are simulated using an equivalent circuit shown in inset of Fig. S6 meanwhile the simulation results are summarized in Table 2. As can be seen from Fig. S6, the experimental and simulated spectra are matched quite well. The high-frequency and medium-frequency semicircles are attributed to the SEI film resistance ($R_f$) and charge transfer resistance ($R_{ct}$), respectively. The incline at low frequency corresponds to the lithium-diffusion process within the electrode [46,47]. It is seen from Table 2 that the $R_b$ and $R_f$ of SnO$_2$/GPE/S cell are higher than those of SnO$_2$/LE/S mainly due to the lower ionic conductivity of GPE (1.13 x 10$^{-2}$ S cm$^{-1}$ at 25 °C) than LE (1.19 x 10$^{-2}$ S cm$^{-1}$ at 25 °C) and the PETEA-based polymer matrix with higher resistance that pre-covers the electrode surface, respectively. However, the cell with GPE exhibits an obviously smaller increase in $R_f$ after 300 cycles (from 15.19 Ω to 16.36 Ω) compared with SnO$_2$/LE/S cell (from 6.11 to 14.84 Ω), demonstrating stable interfaces between electrodes and electrolyte layer which maintaining integrity against the dissolution and reprecipitation of polysulfides during the charge/discharge process. Such stable interfaces contribute to the remarkably improved performance of SnO$_2$/GPE/S cell.

2.3. Surface characterization of SnO$_2$ anodes in SnO$_2$/LE/S and SnO$_2$/GPE/S

To intuitively verify the proposed concern about polysulfides diffusion and deposition, field emission scanning electron microscope (FE-SEM) and X-ray photoelectron spectroscopy (XPS) are used to examine the surface morphology and constitution of SnO$_2$ anodes obtained from the cycled SnO$_2$/LE/S and SnO$_2$/GPE/S. The batteries were disassembled under full-discharge conditions (0.01 V) in order to exclude the anode lithiation effect. It is seen from Fig. 5a that the morphology of SnO$_2$ anode from SnO$_2$/LE/S shows an uneven surface and the sulfur content determined by energy dispersive spectrometer (EDS) is 4.86 wt%, demonstrating a serious deposition of sulfur-species, and further confirming the increasing impedance from EIS plots (Fig. 4c). For the SnO$_2$ anode from SnO$_2$/GPE/S cell, as expected, a smooth surface with relatively low sulfur content (0.42 wt%) proves the side effect of sulfur-species has been much inhibited (Fig. 5b). The clean anodic SEI is critical for performance optimization, because it acts as a passive layer between the electrolyte and electrode that allows facile transport of ions but avoids extra resistance caused by upright contact. As shown in Fig. 5c, d and e, XPS is used to identify the surface constituent of SnO$_2$ anode after dissembling from SnO$_2$/LE/S and SnO$_2$/GPE/S after cycles, respectively. The Sn 3d and O 1s

**Table 2**

Summary of EIS simulation results from Fig. 4c and d.

<table>
<thead>
<tr>
<th>Battery type</th>
<th>SnO$_2$/LE/S</th>
<th>SnO$_2$/GPE/S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cycle number</td>
<td>$R_b$ (Ω)</td>
<td>$R_f$ (Ω)</td>
</tr>
<tr>
<td>Fresh cell</td>
<td>4.81</td>
<td>3.82</td>
</tr>
<tr>
<td>After 1 cycles</td>
<td>4.37</td>
<td>6.11</td>
</tr>
<tr>
<td>After 300 cycles</td>
<td>5.99</td>
<td>14.84</td>
</tr>
</tbody>
</table>

**Fig. 5.** Morphology and constitution characterizations of SnO$_2$ anodes obtained from cycled SnO$_2$/LE/S and SnO$_2$/GPE/S cells: surface morphologies of SnO$_2$ anodes obtained from cycled SnO$_2$/LE/S (a) and SnO$_2$/GPE/S (b) cells; Sn 3d (c), O 1s (d) and S 2p (e) XPS spectra for SnO$_2$ anodes obtained from cycled SnO$_2$/LE/S and SnO$_2$/GPE/S cells.
spectra characterizes the phase change of active material from SnO2 to Sn and Li2O, including Sn–O (496 eV and 487.5 eV) to Sn (494.5 eV and 463.2 eV) and Sn–O (530.1 eV) to Li–O (531.8 eV) [48–50]. This phenomenon reveals a total phase transformation and a formation of scaffold. Moreover, the S 2p spectrum shows two peaks at 165.9 and 162.1 eV assigned to sulfur signals from Li2S–SO3 and sulfite (Li2S), which deposits on the surface of anodic SEI [51–53]. The sulfur signals from SnO2/LE/S shows obvious stronger peak density, indicating the side deposition of sulfur species on SnO2/LE/S is much more severe than SnO2/GPE/S. In brief, the LISPB presents to be a much more promising and stable candidate for the inhibition effect of the GPE layer.

3. Conclusions

To conclude, we have devised a novel lithium ion sulfur polymer battery (LISPB), which not only allows the replacement of the lithium metal with the SnO2 anode, but also suppresses the shuttle effect by an acrylate-based electrolyte. In the LISPB, the configuration of the SnO2 electrode in the ether-based electrolyte was carefully optimized via applying graphene as conductive additives and CMC as the binder. Acrylate-based GPE was used to further constrain the dissolution and diffusion of polysulfides. The LISPB shows the superior electrochemical performance with the most efficient method. A robust and smooth anodic SEI was proved to be an important issue in the LISPB, which can reflect the stability of the whole system from two aspects: (i) the anodic cracks caused by volumetric change of anode materials is effectively buffered, and (ii) the continuous electrochemical deposition of polysulfides is much inhibited. This full battery design solves the safety hazards of lithium metal and simultaneously restrains shuttle effect in sulfur-based batteries, meanwhile the facile in-situ fabrication method accomplishes the production design for sulfur-based power sources in future electric vehicles.

4. Experimental section

4.1. Synthesis of SnO2 particles and preparation of electrodes

The SnO2 particles were obtained by hydrothermal method. 12.67 g glucose was firstly dissolved in 100 mL H2O and subsequently 5.61 g potassium stannate (K2SnO3) was added to the solution with continuous stirring. Then the solution was transferred into a 150 mL Teflon-lined stainless steel autoclave after ultrasonic dispersion for 1 h and heated at 180 °C for 4 h. The prepared precipitate was washed by filtration with water and ethanol, and then dried at 80 °C overnight to obtain the original SnO2. After that, original SnO2 was heated at 550 °C for 4 h to obtain porous SnO2 particles. Graphene was synthesized from natural graphite flake by the modified Hummers method [54] and was thermal reduced at 900 °C under the protection of argon atmosphere. An anodic slurry consisting of 0.35 g porous SnO2 particles, 0.1 g conductive additives and 0.05 g binder were then prepared. The slurry was pasted on the copper current collector and dried in vacuum at 80 °C for 24 h to form SnO2 electrode. The overall mass loading of the active material on the electrode is about 3 mg cm−2 (including ~2.35 mg cm−2 SnO2 and ~0.65 mg cm−2 graphene).

The S@CMK-3 nanocomposite was prepared following a melt-diffusion strategy. 0.25 g CMK-3 (XF Nano, Nanjing) and 0.75 g nano sulfur powder (Dk Nano technology, Beijing) were ground, and then heated to 155 °C for 10 h under the protection of argon. The S@CMK-3 electrode was prepared by mixing 80 wt% S@CMK-3 powder, 10 wt% Super P and 10 wt% PVd in a N-Methyl-2-pyrrolidone (NMP) solvent dispersant and then coating the cathodic slurry on carbon-coated aluminum foil and drying at 60 °C for 24 h. The mass loading of the sulfur active material on the electrode is about 2 mg cm−2.

XRD patterns were recorded using an X-ray diffraction measurement at a scan rate of 5° min−1 (XRD, Rigaku D/max 2500/PC using CuKα radiation with k = 1.5418 Å). A field emission scanning electron microscope (FE-SEM, HITACHI54800) at 100 kV and a high-resolution transmission electron microscopy (HR-TEM, FEI TECNAIG2 F30) at 300 kV were carried out to investigate the morphology of the anodes.

4.2. Electrochemical performance measurements

CR2032-type coin cells were assembled in an Ar-filled glove box. The SnO2/GPE/S coin cells were fabricated in-situ by the direct polymerization. The cells comprised sulfur cathode, a commercial separator, and SnO2 anode. The morphology of lithium powders used in our experiment is shown in Fig. S8, which possess a spherical structure with a diameter of 20–40 μm. Lithium powders that required to fully prelithiate the SnO2 anode (~1.2 mg cm−2 for each anode) were sprayed on the anode surface. Then a mechanical pressure of around 5 MPa was applied on the anode to ensure a close contact between the lithium metal and SnO2 anode. Then the precursor solution containing 1.5 wt% PETA and 0.1 wt% AIBN dissolved in 1 M LiTFSI/DOL: DME (1:1 by volume) with 1 wt% LiNO3 electrolyte was injected into the commercial separator and filled into the cells. To ensure the accuracy of experiment, the sulfur/electrolyte ratio in each cell is uniformly set as ~50 g L−1. Subsequently, the assembled cells were aged for 2 h to ensure the precursor solution well-wetted into the electrodes. The cells were then heated at 70 °C for 2 h in a vacuum oven to make the complete polymerization of monomers, and further aged for 2 days at room temperature to ensure a fully lithiation of SnO2 anode. The SnO2/LE/Li was assembled according to the same procedure except the adoption of traditional LE (1 M LiTFSI/DOL: DME (1:1 by volume) with 1 wt% LiNO3) replacing GPE precursor. The assembled full cells were cycled at various charge/discharge rates between 0.01 and 3 V on a Land 2001 A battery testing system at 25 °C. Cyclic voltammograms (CVs) of the assembled polymer full cells were tested using a VMP3 electrochemical working station (Bio Logic Science Instruments, France) at a scanning rate of 0.1 mV s−1. Electrochemical impedance spectrum (EIS) of cells at full-charge state was examined using the VMP3 multichannel electrochemical station in the frequency range of 10−2 to 105 Hz by applying a 5 mV-ac oscillation.

The full cells after designated cyclic tests were transferred into the glove box and assembled for further examination. Their anodes were repeatedly rinsed with DME and vacuum dried at 50 °C for 6 h to remove the residual solvent. X-ray photoelectron spectroscopy (XPS) measurements were conducted on a Physical Electronics PHI5802 instrument using an X-rays magnesium anode (monochromatic Ka X-rays at 1253.6 eV) as the source. C 1s region was used as references and set at 284.8 eV.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.nanoen.2016.08.033.
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