An Integrally-designed, Flexible Polysulfide Host for High-performance Lithium-sulfur Batteries with Stabilized Lithium-metal Anode

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Abstract

Fast capacity degradation and low sulfur loading hamper lithium-sulfur batteries from practical application. We present here a flexible and robust paper electrode consisting of carbon nanotubes (CNT) and activated carbon nanofibers (ACNF) loaded with MnO₂ nanosheets to serve as an efficient sulfur host for Li/dissolved polysulfide batteries. This integrally-designed flexible host facilitates high sulfur loading, improves sulfur utilization, and suppresses effectively the parasitic shuttle. Accordingly, the Li/dissolved polysulfide cells with high sulfur loading exhibit a high-rate capacity of 780 mAh g⁻¹ at 2C rate and a high capacity retention of 64% over 300 cycles, demonstrating great promise for practical applications of Li-S batteries. In addition, a stable lithium-metal anode resulting from the suppressed shuttle effect is also proved to contribute significantly to the promising cycling performance.

Keywords: lithium-sulfur batteries, flexible electrodes, polysulfide trapping, manganese dioxide

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1. Introduction

Rapid developments in portable consumer electronics, electric vehicles, and grid energy storage accelerate the demand for high energy density Lithium-ion batteries (LIBs) at an affordable cost [1]. Lithium-sulfur batteries are receiving considerable attention in this regard because their high theoretical specific capacity (1675 mAh g^{-1}) and energy density (2500 Wh kg^{-1}), far exceeding those of current LIBs based on insertion-compound cathodes and anodes [2]. In addition, sulfur has other favorable advantages: it is abundant, inexpensive, and environmentally benign [3]. Despite its promising prospects, several obstacles impede Li-S batteries from commercial application, including (i) the insulating nature of both sulfur and its discharge products ($\text{Li}_2\text{S}/\text{Li}_2\text{S}_2$), which limits the utilization of active material, (ii) the large volumetric change that occur upon cycling, which causes structural damage to the electrode, and (iii) the dissolution of polysulfide intermediates into the liquid electrolyte, which causes a severe shuttle effect and leads to fast capacity fade and lithium-metal corrosion [4].

Many strategies have been developed to improve the conductivity of the cathode and restrict the diffusion of soluble polysulfides. One of the most common approaches for improving the capacity and cyclability is encapsulating sulfur into a carbon matrix through melt-diffusion [5-9]. The carbon matrix provides an interconnected network for fast electron transfer, cavities to accommodate volumetric expansion during cycling, and a physical barrier to block the diffusion and loss of polysulfides [10, 11]. However, the synthesis and processing involved could often be tedious and

time-consuming. Carbon interlayers have been shown to act as an upper current collector for fast electron transport and provide a physical barrier to block the migration of polysulfides, but they introduce additional weight and thereby decrease the overall energy density [12-14]. In addition, the nonpolar nature of carbon dramatically weakens its ability to bind and confine the polar polysulfide species within the cathode during cycling [15].

Recently, compositing polar metal oxides with conductive carbon matrix has been extensively investigated to bond with polysulfide species [13, 16-22]. The combination of physical barrier and chemical binding of polysulfides greatly suppresses the polysulfide shuttle, and endows improved cycle stability. However, the sulfur utilization and rate performance are still low due to the intrinsically poor electrical conductivity of the metal oxides, especially at high sulfur loading ($> 2 \text{ mg cm}^{-2}$) [23-25]. Therefore, it is highly desirable, but still challenging, to achieve high sulfur utilization while effectively suppressing the polysulfide shuttle. Generally, the improved cyclability of Li-S batteries is ascribed to the suppressed polysulfides [26-29]. However, the key role of Li-metal anode hidden behind the suppressed polysulfide shuttle in contributing to the improved cycling stability has seldom been reported. Furthermore, the influence of polysulfide trapping on lithium-metal anode protection is also being largely neglected.

Herein, we present a flexible paper electrode composed of carbon nanotubes (CNT) and activated carbon nanofibers (ACNF) loaded with polar MnO_2 nanosheets as a highly efficient sulfur host for Li/dissolved polysulfide batteries. The ACNFs are

hollow, which provide a large reservoir for liquid polysulfides. The CNTs form a highly conductive network and firmly bind the electrode material together. The MnO₂ nanosheets anchored to ACNF can chemically bind the polar lithium polysulfides and effectively suppress the shuttle effect. As a result, the Li/dissolved polysulfide cells exhibit high rate capacity and superior cycle stability at 0.5C rate over 300 cycles. In addition, we show that the suppressed polysulfide shuttle and the resulting stabilized lithium-metal anode contribute together to the improved cyclability.

2. Experimental

Fabrication of CNT/ACNF@MnO₂ host for polysulfide catholyte: The ACNFs were prepared by activating CNFs with CO₂ at a high temperature, as described previously [30]. The incorporation of MnO₂ nanostructure on the surface of ACNF was achieved by immersing ACNF into a KMnO₄ solution at 65 °C [31, 32]. After 30 min, the intermediate product (ACNF@MnO₂) was collected by vacuum filtration, followed by rinsing with water and isopropanol. Then, a pre-sonicated CNT solution in isopropanol, together with the obtained ACNF@MnO₂, was mixed, dispersed, and filtrated into a flexible CNT/ACNF@MnO₂ paper. Composite papers with higher mass could be obtained by simply increasing the thickness. In this work, different areal masses of ~ 2, 4, and 6 mg cm⁻² were selected for CNT/ACNF@MnO₂ paper to host the polysulfides. For a comparison, CNT/ACNF and ACNF@MnO₂ were also prepared following a similar procedure described above.

Materials Characterization: The morphology and microstructure of the prepared materials were characterized by SEM (FEI Quanta 650) and TEM (JEOL 2010F).

XRD patterns were collected on a Rigaku MiniFlex 600 instrument with Cu K α radiation ($\lambda = 0.154056$ nm) between 10 and 80°. The cycled electrodes were washed with dimethoxyethane (DME) (Acros Organics) and sealed with Kapton film prior to the XRD test. XPS measurements were carried out on a Kratos spectrometer at room temperature with monochromatic Al K α (1486.6 eV) radiation. Raman spectra were recorded with a WITEC Alpha300 S micro Raman system under ambient conditions with a 488 nm laser. TGA was conducted on a TGA 4000 Thermogravimetric Analyzer (Perkin Elmer) under air flow to determine the MnO₂ content.

Preparation of the base electrolyte and polysulfide catholyte: The base electrolyte was 1 M lithium trifluoromethanesulfonate (LiCF₃SO₃) and 0.2 M lithium nitrate (LiNO₃) in a mixture of 1, 3-dioxolane (DOL) and dimethoxy ethane (DME) (1:1 v/v). The polysulfide catholyte was prepared by adding sublimed sulfur (99.5%) and lithium sulfide (Li₂S, 99.9%) in the above base electrolyte to give 6 M sulfur in the form of Li₂S₆ (1 M) in the solution. The solution was then stirred and heated at 70 °C in an Ar-filled glove box for 48 h to produce a brownish-red Li₂S₆ catholyte solution.

Electrochemical measurements: The Li/dissolved polysulfide batteries (2032-type coin cell) were assembled in an Ar-filled glove box. The CNT/ACNF@MnO₂ composite paper was pre-dried at 50 °C under vacuum overnight before being cut into circular disks with an area of 1.13 cm² and areal mass of ~ 2 mg cm⁻². Subsequently, ~ 14 μ L of polysulfide catholyte (1 M Li₂S₆) was dropped onto the CNT/ACNF@MnO₂ paper electrode, corresponding to a sulfur content of ~ 55 wt% and sulfur loading of 2.4 mg cm⁻² in the entire free-standing cathode. For the higher

sulfur loadings of 4.8 and 7.2 mg cm⁻², ~ 28 and 42 μ L of Li₂S₆ solution was added respectively. Before placing the Celgard 2500 separator on top of the electrode, the electrode was allowed to stand for a while to ensure the full absorption of polysulfides. In sequence, the base electrolyte (50 μ L), lithium-metal anode, and nickel foam were added. The assembled cells were galvanostatically charged and discharged with an Arbin battery test station with a cut-off potential of 1.8 – 2.8 V. The capacities were calculated based on the mass of sulfur in the catholyte. CV curves were recorded on a potentiostat (VoltaLab PGZ 402) at various scan rates of 0.1 – 0.5 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) data were collected before and after cycling with an impedance analyzer (Solartron 1260A) in the frequency range of 100 kHz to 10 mHz. For the symmetrical cell, two cycled Li-S cells were first disassembled and then the two Li electrodes were assembled in a symmetrical coin cell (2032-Type) in the glove box.

3. Results and Discussion

The flexible CNT/ACNF/MnO₂ paper electrode was fabricated through a facile vacuum filtration method (**Figure 1**). In brief, MnO₂ nanosheets were first grown on to the ACNF *via* a bath deposition, and then the ACNF/MnO₂ composite and CNT were vacuum-filtrated into a hybrid film of CNT/ACNF/MnO₂. For a comparison, CNT/ACNF film was also prepared without MnO₂ deposition. In the CNT/ACNF/MnO₂ host, liquid polysulfides can be uniformly distributed and trapped by the strong surface bonding with MnO₂ nanosheets. Trace amounts of lithium polysulfides diffused out of the cathode, and LiNO₃ was used as an electrolyte

additive to facilitate the formation of a uniform passivation layer on the lithium-foil anode and prevent Li corrosion and electrolyte depletion [33, 34]. Without the assistance of MnO_2 , the CNT/ACNF host cannot effectively block polysulfides from migrating to the anode, which leads to the formation of a thick passivation layer on the corroded Li metal.

ACNF possesses a smooth surface, a diameter of ~ 100 nm, and a length of up to several micrometers. The hollow structure provides an ideal reservoir to accommodate polysulfides (Figure S1). Together with CNT, a hybrid CNT/ACNF membrane was prepared with vacuum-filtration (Figure S2). Scanning electron microscopy (SEM) images (**Figure 2** a and b) show that the ACNF and CNT are well intertwined. The entangled network facilitates electron transfer and provides large interspaces to accommodate diverse materials, including the active materials. MnO_2 covers the entire surface of the ACNF, and the CNT/ACNF@ MnO_2 paper is formed after immersing CNT/ACNF in KMnO_4 solution for only 30 min, making the ACNF surface much rougher (Figure 2c and d). The transmission electron microscopy (TEM) images reveal more clearly the MnO_2 distribution and microstructure. Figure 2e shows that MnO_2 coats the external surface of the ACNF and also grows inside the hollow ACNF. Furthermore, the deposited MnO_2 is actually a two-dimensional lamellar structure (Figure 2f), which could facilitate the adsorption of polysulfides. The elemental maps show that MnO_2 is homogeneously deposited and distributed throughout the ACNF (Figure 2h). In addition, the ACNF@ MnO_2 entangles well with CNT (Figure 2g). CNT provide a highly conductive, mechanically robust structure

that enables efficient sulfur utilization. Figure 2i-k shows that the CNT/ACNF/MnO₂ composite is approximately 70 μm thick and exhibits excellent flexibility; it can be readily rolled and folded without cracks. In contrast, the ACNF/MnO₂ without CNT is very brittle and fractures easily under a small bending angle (Figure S3). The flexibility and mechanical robustness indicate its potential application for flexible energy storage devices.

The X-ray photoelectron spectroscopy (XPS) survey spectrum (**Figure 3a**) confirms the presence of Mn, C, and O elements in the CNT/ACNF/MnO₂ paper. The high-resolution Mn 2p spectrum (Figure 3b) shows two peaks located at 642.2 eV (Mn 2p_{3/2}) and 653.8 eV (Mn 2p_{1/2}), with a spin orbit coupling separation of 11.6 eV, which is consistent with the previous reports on MnO₂ [35]. The 4.8 eV peak separation for Mn 3s and the calculated Mn valence of +3.6 further confirm that MnO₂ is the dominant constituent (Figure S4) [36]. The presence of pure MnO₂ is further verified by Raman spectroscopy (Figure S5) and X-ray diffraction (XRD) analyses (Figure 3c), which show that the birnessite-type MnO₂ (JCPDS 42-1317) is formed after immersing carbon into KMnO₄ solution at an elevated temperature. The weak, broad peaks indicate poor crystallinity, which is in accordance with the previous reports on MnO₂ nanosheets prepared by reducing KMnO₄ with carbon [37, 38]. MnO₂ nanosheets in the birnessite phase help constrain the polysulfides within the hollow carbon fibers, and promote a fast redox reaction kinetics [39]. However, too much MnO₂ in the cathode would compromise the overall energy density since MnO₂ suffers from low conductivity and contributes negligibly to the capacity of Li-S

batteries [40]. Therefore, we limited the reaction time to control the amount of as-grown MnO₂. Thermogravimetric analysis (TGA) reveals that the MnO₂ content in the composite is approximately 9.7 wt% (Figure 3d).

To demonstrate the advantages of MnO₂ in absorbing polysulfides, we compared the cycle and rate performances of the Li/dissolved polysulfide cells containing a CNT/ACNF@MnO₂ host with those employing a CNT/ACNF host. It's worth noting that the CNT/ACNF@MnO₂ host contributes negligibly to the capacity in the voltage range of 1.8 – 2.8 V (Figure S6). As shown in **Figure 4a**, the CNT/ACNF@MnO₂ electrodes with a sulfur loading of 2.4 mg cm⁻² deliver an initial capacity of 1022 mA h g⁻¹ at 0.2C rate and maintain a stable cyclability of 927 mA h g⁻¹ after 100 cycles, with nearly 100% Coulombic efficiency. In contrast, the capacity of the CNT/ACNF electrode declines rapidly and only retains a capacity of 545 mA h g⁻¹ after 100 cycles, even though the initial capacity is almost the same as that of CNT/ACNF@MnO₂. Furthermore, the electrode with MnO₂ exhibits higher capacity for all C rates (0.2C and 2C rates). As shown in Figure 4b, the CNT/ACNF@MnO₂ electrode exhibits excellent rate capability and high capacities of 1045, 1000, 955, 911, 878, and 773 mAh g⁻¹ at, respectively, 0.2C, 0.3C, 0.5C, 0.8C, 1C, and 2C rates. **More importantly, the capacity recovers to ~ 915 mAh g⁻¹ when the rate returns to 0.5C rate, corresponding to an areal capacity of 313 mAh cm⁻³, which is comparable to or higher than those reported previously [29, 41].** The significant enhancement in capacity and rate capability can be attributed to the effective localization of polysulfides by MnO₂, which was further verified by visual observation (Figure S7).

CNT in the CNT/ACNF/MnO₂ hybrid electrode also play a key role in improving the performances. The ACNF/MnO₂ electrode without CNT suffers from poor rate capability due to slow electron and ion transport (Figure S8).

Figure 4c shows the representative charge and discharge voltage profiles of cells with the CNT/ACNF/MnO₂ electrodes. The curves all display clear voltage plateau for the charge and discharge processes that are consistent with the typical cyclic voltammogram (CV) of Li-S cells (Figure S9) [42, 43]. The discharge plateaus correspond to the reduction of elemental sulfur to high-order polysulfides and then to Li₂S/Li₂S₂, while the charge plateaus represent the reverse process (Figure S10) [44]. In addition, these cells show low polarization. For example, the cell displays a long, flat discharge plateau at 0.2C rate with a voltage gap of only 0.18 V. Even at a high rate of 2C, the voltage gap is no more than 0.6 V, and the discharge plateau is still flat and remains above 1.9 V. These values are among the best reported results for Li-S batteries [45]. CV analyses at various scan rates were carried out to determine the lithium-ion diffusion coefficient. As plotted in Figure 4d and Figure S11, the linear relationship between I_p and $v^{0.5}$ indicate a diffusion-controlled process. The diffusion coefficient is calculated to be D_{Li}^+ (A, cathodic peak at 2.3 V) = $4.81 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$, D_{Li}^+ (C1, cathodic peak at 2.0 V) = $6.42 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$, and D_{Li}^+ (C2, cathodic peak at 2.35 V) = $7.41 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$. The average D_{Li}^+ values for the cells with MnO₂ are similar to those employing a regular host electrode, suggesting that the MnO₂ does not affect the diffusion of lithium ions [46, 47]. Meanwhile, the presence of trace amount of MnO₂ does not significantly increase the host electrode resistance since the

baseline charge-transfer resistance (R_{ct}) of the two fresh cells are almost the same (Figure S12). The R_{ct} of the cell with MnO_2 decreases after cycling, reflecting the redistribution of the active material on MnO_2 and the carbon matrix. In contrast, the R_{ct} of the cell without MnO_2 increases significantly. This may be ascribed to the severe shuttle effect and the formation of a thick, insulating passivation layer on the Li anode [48]. The CNT/ACNF@ MnO_2 host electrode also possesses excellent cycle stability during long-term cycling at 0.5C rate. As shown in Figure 4e, the reversible capacity remains stable and eventually stabilizes at 618 mAh^{-1} after 300 cycles, with an average capacity loss of 0.11% per cycle. The Coulombic efficiency is approximately 98% after 300 cycles, indicating that most polysulfides are trapped in the cathode side by MnO_2 .

To further explore the feasibility of the composite host for high sulfur loading, we prepared thicker electrodes by increasing the thickness of the filter-fabricated paper electrode. In this way, the sulfur loading could be further increased from 2.4 to 4.8 and even to 7.2 mg cm^{-2} as the thickness of host electrode increases. **Figure 5a** and **b** show the galvanostatic charge/discharge curves of the CNT/ACNF@ MnO_2 electrode with sulfur loadings of 4.8 and 7.2 mg cm^{-2} at 0.2 - 2C rates. The two thick electrodes with high sulfur loadings display well-defined discharge/charge plateaus and low overpotential, suggesting good conductivity and full electrolyte wetting. The higher voltage gaps of the thicker electrode (S loading: 7.2 mg cm^{-2}) are ascribed to the increased concentration polarization of polysulfides in the cathode. These cells also exhibit high sulfur utilization with good cyclability at various rates. As shown in

Figure 5c, the electrode with 4.8 mg cm^{-2} sulfur delivers high capacities of 826, 740, and 627 mAh g^{-1} , respectively, at 0.2C, 0.5C, and 1C rates. Even with a high loading of 7.2 mg cm^{-2} , the cell displays reversible capacities of as high as 765, 648, and 483 mAh g^{-1} at, respectively, 2.4, 6, and 12 mA cm^{-2} , corresponding to areal capacities of 5.5, 4.6 and 3.5 mAh cm^{-2} . **Considering the thickness of the electrode, the calculated volumetric capacity at 2.4 mA cm^{-2} is around 262 mAh cm^{-3} .**

The thick electrodes with high sulfur loading also show good capacity retention (Figure 5d). At 0.5C rate, the electrodes with sulfur loadings of 4.8 and 7.2 mg cm^{-2} retain 87% and 76% of their original capacity after 100 cycles. These results are comparable to or better than those with similar sulfur loadings [7, 49-51]. The integrated design of the CNT/ACNF@MnO₂ electrode offers excellent electrode conductivity and space to accommodate polysulfides and efficiently traps the polysulfides within the cathode.

This hypothesis is also supported by the postmortem studies of the surface morphology of the cycled Li-metal anode. **Figure 6a–e** shows the fresh Li foil and cycled Li foil disassembled from cells employing the CNT/ACNF and CNT/ACNF@MnO₂ electrodes. Compared to the fresh Li foil (Figure 6a), the cycled Li from a cell employing a CNT/ACNF electrode (Figure 6b and c) exhibits a rough surface with lots of aggregated particles, which is caused by a severe corrosion of lithium metal by the polysulfides during extended cycling. In contrast, the cycled Li from cells employing the CNT/ACNF@ MnO₂ exhibits a relatively smooth and dense surface (Figure 6d and e), implying that the polysulfides are effectively immobilized

by MnO_2 . XRD analysis of the cycled Li foils (Figure 6f) indicates that fewer sulfur-related species are present on the foils cycled in cells with MnO_2 than that in cells without MnO_2 , further confirming the reduced polysulfide shuttle in the presence of MnO_2 . Liquid polysulfides can easily diffuse into the anode and severely corrode the Li-metal anode during repeated cycling. However, trace amounts of polysulfides that diffuse into the anode side can help form a protective layer on the Li surface that alleviates Li corrosion and minimizes electrolyte decomposition [33]. To evaluate the effect of Li protection more directly, we assembled two cycled Li foils collected from the cells with MnO_2 into a symmetrical coin cell (Figure 6g). For a comparison, a symmetrical cell with cycled Li foils from cells without MnO_2 was also tested. Figure 6h illustrates the charge/discharge voltage profiles of the Li symmetric cells at 1 mA cm^{-2} , which show the effect of the protection layer. The capacity is 3 mAh cm^{-2} for both charge and discharge. The symmetric cell with the cycled Li from a MnO_2 -containing cell displays a low and stable overpotential for 400 h, which is ascribed to Li metal anode surface protection by the stable and uniform passivation film and the consequent suppressed electrolyte consumption [52]. In contrast, the cycled Li foils from cells without MnO_2 are more porous and have a much larger surface area, which could greatly facilitate the soaking of electrolyte. The voltage hysteresis increases and eventually transforms into random oscillations as the electrolyte continuously corrodes the lithium metal.

4. Conclusion

In summary, we have demonstrated the effectiveness of an integrally-designed

CNT/ACNF@MnO₂ host for lithium polysulfide cathodes. In this advanced design, hollow ACNFs serve as a reservoir for dissolved polysulfides and enable high sulfur loading, while CNTs act as a conductive network to enhance sulfur utilization and mechanical stability for the highly-flexible electrode. MnO₂ is easily grown onto the CNT/ACNF scaffold and it chemically binds with polysulfides to effectively suppress them from diffusing out of the cathode. This advanced design enables high sulfur loadings from 2.4 to 7.2 mg cm⁻² with high rate capability, low polarization, and superior cycling performance at high current densities. Additionally, we reveal that trace amounts of lithium polysulfides diffused out of the cathode act as an electrolyte additive to protect the lithium-metal anode and thus efficiently prevent further Li-metal corrosion and electrolyte depletion. Our results show that the integrated electrode design holds great promise in developing flexible and high energy density Li-S batteries.

Appendix A: Supplementary material

Supplementary data associated with this article can be found in the online version.

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Figure Captions:

Figure 1. Schematic illustration of the flexible CNT/ACNF@MnO₂ electrode synthesis and the advantages of the CNT/ACNF@MnO₂ host over CNT/ACNF in suppressing the shuttle effect and protecting the Li-metal anode.

Figure 2. (a, b) SEM images of the CNT/ACNF paper. (c, d) SEM, (d–f) TEM, (h) elemental mapping, (i) cross-sectional view, and (j, k) digital images of the CNT/ACNF@MnO₂ paper.

Figure 3. (a) Survey XPS and (c) high-resolution Mn 2p spectra of the CNT/ACNF@MnO₂ paper. c) XRD patterns of CNT/ACNF and CNT/ACNF@MnO₂ paper. (d) TGA curves of CNT/ACNF@MnO₂ in air with a heating rate of 10 °C min⁻¹.

Figure 4. (a) Cycling performances and (b) rate capability of the Li/dissolved polysulfide cells with CNT/ACNF and CNT/ACNF@MnO₂ host electrodes. (c) Voltage profiles at various C rates, (d) CV curves at different scan rates, and (e) cycling performance at 0.5C rate over 300 cycles of the cells with the CNT/ACNF@MnO₂ electrodes. Here, the volumetric capacity is calculated based on the volume of the CNT/ACNF@MnO₂ host.

Figure 5. Electrochemical performance of cells employing CNT/ACNF@MnO₂ electrode with sulfur loadings of 4.8 and 7.2 mg cm⁻²: voltage profiles of cells with sulfur loadings of (a) 4.8 mg cm⁻² and (b) 7.2 mg cm⁻² at various C rates, (c) rate capability, and (d) cycling performances at 0.5C rate.

Figure 6. (a) SEM image of a fresh Li foil before cycling. SEM images of the cycled Li foils in the cells with (b, c) CNT/ACNF and (d, e) CNT/ACNF@MnO₂ composite electrode. (f) Comparison of the XRD patterns of the cycled Li foils with and without MnO₂ in the cathode. (g) Schematic of the symmetrical cell design. (h) Comparison of the voltage profiles of the Li symmetric cells employing the cycled Li from disassembled cells with the two composite electrodes: the current density of the Li plating/stripping process was set at 1 mA cm⁻² and each half-cycle lasted for 3 h.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6