Free-standing TiO₂ nanowire-embedded graphene hybrid membrane for advanced Li/dissolved polysulfide batteries

Guangmin Zhou, Yubao Zhao, Chenxi Zu, and Arumugam Manthiram*

Materials Science and Engineering Program & Texas Materials Institute

The University of Texas at Austin, Austin, TX 78712, USA

Email: manth@austin.utexas.edu

Abstract

The increasing demand for electric vehicles and large-scale smart grids has aroused great interest in developing high energy density storage devices. Lithium-sulfur (Li-S) battery has attracted much attention owing to its high theoretical energy density and abundance, but many challenges such as rapid capacity fade and low sulfur loading and utilization have impeded its practical use. Here, we present a free-standing TiO₂ nanowire/graphene hybrid membrane for Li/dissolved polysulfide batteries with high capacity and long cycling life. Graphene membrane with high electrical conductivity is used as a current collector to effectively reduce the internal resistance in the sulfur cathode and physically immobilise the dissolved lithium polysulfides. The TiO₂ nanowires introduced into the graphene membrane offer a hierarchical composite structure, in which the TiO₂ nanowires not only have strong chemical binding with the lithium polysulfides, but also show a strong catalytic effect for polysulfide reduction and oxidation, promoting a fast redox reaction kinetics with high capacity and low voltage polarization. This hybrid electrode delivers a high specific capacity of 1327 mA h g⁻¹ at 0.2C rate, a Coulombic efficiency approaching 100%, high-rate performance of 850 mA h g⁻¹ at 2C rate, and long cyclic stability with a capacity of 1053 mA h g⁻¹ at 0.2C rate over 200 cycles, demonstrating great prospect for application in high energy Li-S batteries.

Keywords: lithium-sulfur batteries; graphene; TiO₂ nanowire; free-standing membrane; catalytic effect

Introduction

Rechargeable batteries with high specific energy are critical for many applications, such as portable electronic devices, electric vehicles, and grid storage of electricity [1]. Lithium-ion batteries (LIBs) have dominated the energy storage market for decades. However, LIBs cannot satisfy the increasing energy requirements of these applications [2]. In this context, Li-S batteries have attracted much attention due to the high theoretical energy density ($\sim 2500 \text{ W h kg}^{-1}$) and low cost, and are considered as one of the most promising replacements to conventional LIBs as the next-generation high energy secondary batteries [1, 3, 4]. However, many challenges exist with the Li-S battery system, such as the low electrical conductivity of sulfur and its discharge products, low active material utilization, low sulfur loading, poor cycling stability, and self-discharge, which significantly restrict its practical application. Currently, one of the most intractable problems that needs to be addressed to improve the cycling stability is to trap the soluble polysulfides in the cathode and prevent the “shuttle effect” between the cathode and anode [5-7].

To solve these impediments for the development of Li-S batteries, one strategy is to confine the sulfur and polysulfides into porous conductive materials such as a carbon matrix [8] (porous carbon [9-13], carbon nanotubes [14-16] and graphene [17-22]) or some conductive polymers [23, 24]. Up to now, the progress made in these areas has been mainly based on physically trapping the sulfur and polysulfide species. Meanwhile, attention has been paid to using chemical methods to suppress the polysulfide shuttle. For example, functional absorbents are used to suppress “polysulfide shuttling” in Li-S batteries through their chemisorption effect towards polysulfide species. For example, some metal oxides (such

as Al_2O_3 [25], TiO_2 [26], $\text{Mg}_{0.6}\text{Ni}_{0.4}\text{O}$ [27] and La_2O_3 [28]) as absorbents have proven to be highly effective at on-site adsorbing of lithium polysulfides and improving the long-term cyclic ability of Li-S batteries. Besides, surface chemistry of the carbon matrix can play a critical role in chemically adsorbing the sulfur species and controlling the polysulfide dissolution [29-33]. As for the electrolytes and binders, attempts such as using P_2S_5 as an electrolyte additive to form complexes with Li_2S_x ($1 \leq x \leq 8$) and converting the less soluble $\text{Li}_2\text{S}/\text{Li}_2\text{S}_2$ species into highly soluble complexes have been made; these approaches help suppress the polysulfide shuttle effect and passivate the lithium-metal surface [34]. In addition, poly(vinylpyrrolidone) (PVP) binder also exhibits strong interaction with both Li_2S and lithium polysulfides [35]. Nevertheless, neither physical nor chemical methods by their own could completely prevent the polysulfide dissolution. In addition to the polysulfide shuttle, another challenge existing in Li-S batteries is the sluggish redox reaction kinetics, which affects the rate performance of Li-S batteries and leads to gradual capacity loss.

It has been shown that the use of dissolved polysulfides instead of solid sulfur could improve the sulfur utilization, prevent cathode pulverization, facilitate capacity retention, and improve the kinetics of the Li-S redox reaction [36-39]. For example, Zhang et al. assembled a liquid $\text{Li}/\text{Li}_2\text{S}_9$ cell with LiNO_3 additive to passivate lithium anode, enabling a stable reversible capacity of 500 mA h g^{-1} after 100 cycles [36]. Xu et al. proposed a self-healing strategy to mitigate sulfur loss by adjusting the concentration gradient of the polysulfide species at the cathode/electrolyte interface, which was achieved by pre-dissolving lithium polysulfides and LiNO_3 as the lithium salt in the electrolyte [39]. As a result, the cell showed a high capacity of 1450 mA h g^{-1} at C/10, high Coulombic efficiency of nearly 100%, and

excellent cyclic stability. Our group demonstrated a highly reversible Li/dissolved polysulfide cells utilizing a free-standing, interweaved multi-walled carbon nanotube paper as a host electrode [37]. Due to the unique electrode architecture with high active material utilization in the polysulfide electrolyte, a high capacity of 1400 mA h g^{-1} after 50 cycles at C/10 rate was realized. Other lithium/polysulfide cells based on the porous carbon current collector and sandwich cathode structure also verify the advantages of utilizing dissolved polysulfides in Li-S batteries [38, 40, 41].

Herein, we present the development of a free-standing TiO_2 nanowire-embedded graphene (TiO_2 NW/G) hybrid membrane for Li/dissolved polysulfide batteries with high capacity and long cycle life. Dissolved lithium polysulfide systems were chosen to verify the strategy of integrating physical (nonpolar) and chemical (polar) adsorption materials to constrain polysulfide shuttle. Graphene membrane with high electrical conductivity is used here as the current collector, which can effectively reduce the internal resistance of the sulfur cathode and function as a support to physically immobilize sulfur and the dissolved lithium polysulfides (**Figure 1**). TiO_2 NWs are introduced into the graphene membrane to construct the hierarchical composite structure, in which TiO_2 NWs are used as bifunctional materials that not only have strong chemical binding with lithium polysulfides (**Figure 1**), but also show a strong catalytic effect on polysulfide reduction and oxidation, enabling fast redox reaction kinetics and resulting in high capacity and low voltage polarization.

Figure 1. Schematic illustration of the fabrication of TiO₂ NW/G hybrid membrane and their interaction with lithium polysulfides.

Results and Discussion

TiO₂ NW/G hybrid membrane was prepared by dispersing TiO₂ NWs and graphene in isopropyl alcohol through high-power ultrasonication, followed by vacuum filtration, washing, and drying. The hybrid membrane could then be easily peeled off and used as a free-standing current collector (**Figure 1** and **Figure S1a**). The hybrid membrane is flexible and mechanically robust, which can be bent into arbitrary angles (**Figure S1b**), indicating its potential application as an electrode for flexible energy storage devices.[42] It can be seen from scanning electron microscopy (SEM) micrographs that the graphene membrane shows a rough surface consisting of overlapped graphene sheets (**Figure 2a**). **Figure 2b, c** show the SEM and transmission electron microscopy (TEM) images of the interconnected TiO₂ NWs with a diameter of 50 - 150 nm and a length of several micrometres. The high-resolution TEM (HRTEM) image of a typical TiO₂ NW (**Figure S2a**, marked by a white rectangular dot

in **Figure 2c**) displays the lattice fringes with an inter-planar distance of 0.35 nm, corresponding to the (101) plane of anatase TiO₂ [43]. As shown by the representative SEM and TEM images of the TiO₂ NW/G hybrid (**Figure 2d, e**), TiO₂ NWs were uniformly distributed between or on the surface of graphene sheets. TiO₂ NWs can work as pillars to prevent the overstack of graphene, increasing the accessible surface area for lithium polysulfide absorption. The cross-sectional SEM image of the TiO₂ NW/G hybrid is demonstrated in **Figure 2f**, in which graphene sheets are integrated with embedded TiO₂ NWs (**Figure S2b**) forming an open porous structure with a thickness of ca. 60 μm .

Figure S3a shows the X-ray diffraction (XRD) patterns of the graphene membrane, TiO₂ NWs, and TiO₂ NW/G hybrid. All the identified peaks of TiO₂ NWs can be assigned to the anatase TiO₂ phase (JCPDS card No. 21-1272). The other diffraction peak at $2\theta = 26.2^\circ$ in the hybrid can be assigned to graphene, which also exist for the graphene membrane. Raman spectroscopy was used to characterize the quality of graphene and further verify the coexistence of TiO₂ NWs and graphene in the hybrid. The Raman scattering peaks observed at 398, 518, and 636 cm^{-1} are related to, respectively, the B_{1g}, A_{1g} and E_g vibrational modes of TiO₂ (**Figure S3b**) [44]. The D band at 1363 cm^{-1} corresponds to structural defects and disorders in graphene, and the G band at 1581 cm^{-1} is ascribed to the vibrational mode of sp² carbon [45, 46]. The weak D band and a large intensity ratio of G and D bands suggest the high quality of graphene, which is beneficial for using as a highly conductive support.

Figure 2. (a) SEM image of the surface of graphene membrane, (b) SEM and (c) TEM images of TiO₂ NWs, (d) SEM and (e) TEM images of the TiO₂ NW/G hybrid membrane, and (f) cross-sectional SEM image of the TiO₂ NW/G hybrid membrane.

In order to compare the polysulfide adsorption capability of graphene membrane and TiO₂ NW/G hybrid membrane, UV-visible absorption spectroscopy was used to analyze the concentration variation of Li₂S₆ solution (the same catholyte for battery test but at a lower concentration and without lithium salt) before and after adding graphene membrane or the hybrid membrane. As demonstrated in **Figure 3**, the polysulfide solution showed broad absorption region between 250 and 500 nm, and the characteristic peaks located at approximately 280, 300 and 340 nm can be ascribed to S₆²⁻ species [47, 48]. After absorption for 12 h, it can be clearly observed that the color of the Li₂S₆ solution changes from light yellow to colourless in both vials with graphene and TiO₂ NW/G hybrid membrane (inset of **Figure 3**). However, the peak intensities of the two samples in the absorption spectra are obviously different. Much larger decrease in the absorption peak intensity of the TiO₂ NW/G

hybrid membrane than that of graphene membrane at 280 and 340 nm was identified, indicating the better affinity and strong adsorption of S_6^{2-} species to the TiO_2 NWs.

Figure 3. UV/Vis absorption spectra of lithium polysulfide (Li_2S_6) solution before and after the addition of graphene and TiO_2 NW/G hybrid membrane. Inset is the photograph of sealed vials of a Li_2S_6 /DOL/DME solution after contact with graphene and TiO_2 NW/G hybrid membrane after 12 h.

To demonstrate the catalytic effect and strong affinity of TiO_2 NWs to lithium polysulfides, cyclic voltammetry (CV) and galvanostatic charge-discharge test were performed with Li_2S_6 dissolved in DME/DOL as catholyte and metallic lithium as anode. The typical CV curves of the graphene and TiO_2 NW/G hybrid membrane were obtained in the second cycle over a voltage range from 1.5 to 2.8 V at a scan rate of 0.1 mV s^{-1} , as shown in **Figure 4a**. Both of the electrodes show two cathodic peaks and an anodic peak; the two cathodic peaks can be attributed to the reduction of sulfur (S_8) to long-chain lithium polysulfides at the higher potential and to the formation of short-chain Li_2S_2/Li_2S at the lower potential. When scanning back to 2.8 V, the anodic peak corresponds to the oxidation of

Li₂S/Li₂S₂ to lithium polysulfides and sulfur [8, 14]. It is interesting to note that the reduction peaks with the TiO₂ NW/G hybrid membrane (2.34 and 2.01 V) are at higher potentials than those with the graphene membrane (2.29 and 1.96 V), while the onset reaction and oxidation peaks are at lower potentials (2.26 and 2.44 V vs. 2.32 and 2.52 V), indicating a catalytic effect of TiO₂ NWs on sulfur reduction and Li₂S/Li₂S₂ oxidation with improved redox kinetics [28].

Figure 4b shows the galvanostatic charge/discharge profiles of the Li/dissolved polysulfide cell with graphene and TiO₂ NW/G hybrid membrane electrodes measured at 0.2C (1C=1675 mA g⁻¹) rate. The discharge/charge profiles of TiO₂ NW/G hybrid membrane electrode consist of two well-defined discharge plateaus at 2.35 and 2.07 V and charge plateaus at 2.25 - 2.44 V, which are in agreement with the CV curves. The plateaus are longer and flatter with higher capacity and lower polarization compared to those with the graphene membrane electrode, suggesting a kinetically efficient reaction process. This can be ascribed to the catalytic dissociation/affiliation of S-S bonds with reduced energy barrier enabled by TiO₂ NWs [5, 28]. The discharge/charge plateaus of the TiO₂ NW/G hybrid membrane electrode are well-retained at even higher current densities from 0.3C to 2C. In contrast, the discharge potential is lower and the charge potential is higher with a larger difference between the plateau potentials for the graphene membrane electrode (**Figure S4** and **Figure 4c**). For example, even at a high rate of 2C, the potential difference between the charge and discharge plateaus with the hybrid membrane is 728 mV, much lower than that of graphene membrane (1127 mV), indicating that the introduction of TiO₂ NWs into graphene membrane enables a lower polarization and faster redox reaction kinetics with better reversibility.

In order to demonstrate the rate capability of these membrane electrodes, the current density was changed from 0.2 to 2C, as shown in **Figure 4d**. A high initial discharge capacity of 1270 mA h g⁻¹ was obtained with the TiO₂ NW/G hybrid electrode at 0.2C, and the capacity could be retained at as high as 850 mA h g⁻¹ even at a high rate of 2C, indicating a fast charge/discharge capability. When the total mass including the mass of TiO₂ NW/graphene hybrid is considered, the capacity is still as high as 790 and 527 mA h g⁻¹ at 0.2 and 2C (**Figure 4d**). In contrast, the capacities are 790 and 80 mA h g⁻¹ with the graphene electrode tested under the same conditions. When the current density was tuned back to 0.5C rate, a reversible capacity of 1100 mA h g⁻¹ was achieved with the TiO₂ NW/G hybrid electrode even after the rate capability test, indicative of good rate performance and high cycling stability. **Figure 4e** shows the long-term cyclability of the Li/dissolved polysulfide cell with graphene and TiO₂ NW/G hybrid electrodes. The hybrid electrode demonstrate an excellent cyclic stability and retains a capacity of 1053 mA h g⁻¹ with a Coulombic efficiency above 92 % at a current density of 0.2C for 200 cycles, indicating a suppression of the polysulfide shuttle. In contrast, the capacity of the graphene electrode drops quickly and it retains only 391 mA h g⁻¹ after 200 cycles. The cell with graphene electrode has higher Coulombic efficiency compared to that with the TiO₂ NW/G electrode in the first few cycles, possibly because the LiNO₃ added into the catholyte of the former cell is more easily released from the cathode due to weak confinement and migrate to the anode. LiNO₃ released from the cathode in the cell with graphene electrode will react with the lithium-metal anode, resulting in the formation of a protective surface layer and improvement of Coulombic efficiency in a short-term. The cell with the TiO₂ NW/G electrode has better adsorption ability of lithium

polysulfides, which helps improve the long-term cycling stability and Coulombic efficiency. The cycle stability is better than our previously reported graphene-sulfur (60 wt.% sulfur content) and pure sulfur electrodes, which show rapid initial capacity decay with a capacity retention of around 30% after 100 cycles (**Figure S5**), implying low sulfur utilization with a severe polysulfide dissolution into the electrolyte [5, 29]. These results confirm that the use of dissolved polysulfide catholyte could improve the sulfur utilization and capacity retention. The good rate capability and cyclic stability of the TiO₂ NW/G hybrid electrode can be ascribed to the following: (i) the high electrical conductivity of graphene reduces the internal resistance of the polysulfide cathode; (ii) TiO₂ NWs work as pillars to prevent the stack of graphene, increasing the accessible surface area for lithium polysulfide and electrolyte absorption and shortening the ion-transport distance; (iii) strong adsorption of lithium polysulfides by TiO₂ NWs, inhibiting the polysulfide shuttle; and (iv) catalytic effect of TiO₂ NWs on polysulfides, promoting the reduction and oxidation processes.

Figure 4. (a) CV profiles of the graphene and TiO₂ NW/G hybrid electrodes in the 2nd cycle at a scan rate of 0.1 mV s⁻¹. (b) Galvanostatic charge-discharge profiles of the graphene and TiO₂ NW/G hybrid electrodes at 0.2C rate within a potential window of 1.5 - 2.8 V vs. Li⁺/Li⁰. (c) Comparison of the potential difference between the charge and discharge plateaus at different current densities. (d) Rate performance of the Li/dissolved polysulfide cells with the graphene and TiO₂ NW/G hybrid electrodes at different current densities. The capacity values normalized to the mass of sulfur alone and to the total mass are compared. (e) Cycle stability and Coulombic efficiency of the graphene and TiO₂ NW/G hybrid electrodes at 0.2C rate for 200 cycles.

To further verify the the strong adsorption of TiO_2 NWs on sulfur species, the graphene and TiO_2 NW/G hybrid electrode tested in the Li/dissolved polysulfide cell were disassembled after the 100th charge inside a glovebox. **Figure S6** shows the typical SEM images of the cycled TiO_2 NW/G hybrid and graphene electrodes. Relatively clear and smooth surface of graphene with embedded TiO_2 NWs are observed for the hybrid electrode due to the good catalytic dissociation of lithium polysulfides by TiO_2 (**Figure S6a, b**). In contrast, a thick solid insulating lithium sulfide layer covered on the surface of graphene after repeated reduction/oxidation of dissolved lithium polysulfides is seen with the graphene electrode (**Figure S6c, d**). **Figure S7a** shows the TEM image of the cycled TiO_2 NW/G hybrid electrode (after the 100th discharge), in which the TiO_2 NWs are dispersed on the graphene with attached sulfide species. These species are identified by scanning transmission electron microscope (STEM) and EDS spectra. The sulfides adsorbed on the TiO_2 NWs are brighter, and the EDS spectrum shows much higher sulfur peak intensity compared to the surrounding dark area (**Figure S7b-d**). STEM elemental mapping was used to track the sulfur distribution on the TiO_2 NWs. From the sulfur, titanium, and oxygen elemental distribution images, it is obvious that sulfides are strongly adsorbed on the surface of TiO_2 NWs (**Figure 5**).

Figure 5. (a) STEM analysis of a TiO_2 NW in the hybrid electrode and elemental mapping of (b) sulfur, (c) titanium, and (d) oxygen after cycling.

The above results can further be confirmed by electrochemical impedance spectroscopy (EIS) measurements and lithium anode structural characterization. The Nyquist plots of the graphene and TiO_2 NW/G hybrid electrodes before cycling and after five cycles (charged state) are shown in **Figure S8**. The depressed semicircle in the high-to-medium frequency region can be ascribed to the charge-transfer resistance R_{ct} [45]. The values of R_{ct} for the two fresh cells are similar (**Figures S8a**). After five cycles, the R_{ct} of the TiO_2 NW/G hybrid electrode changes a little while the R_{ct} of the graphene electrode increases significantly, suggesting the cathode passivation by lithium sulfides (**Figure S8b**). On the other hand, to reveal the morphological changes of the lithium anode and thickness of the passivation film after cycling, Li/dissolved polysulfide cells with these two electrodes were detached and studied. The lithium chips were washed using dimethoxyethane (DME) and dried inside

glovebox before the SEM and EDS analyses. It is obvious that the surface of lithium was severely damaged with a higher degree of roughness in the case of graphene electrode, which is caused by side reactions between lithium polysulfides and metallic lithium during cycling (**Figure 6a**). Furthermore, a large amount sulfur-related deposits on lithium surface is observed from the corresponding sulfur elemental mapping characterization (**Figures S9a, b**). In contrast, a relatively dense and smooth surface is found in the case of the TiO₂ NW/G hybrid electrode, suggesting that lithium polysulfides are mostly immobilised in the cathode and less polysulfides diffuse or react with metallic lithium (**Figure 6b** and **Figures S9c, d**). Cross-sectional EDS line scans of the metallic lithium anode are shown in **Figure 6c, d**. The thickness of sulfur signals for the TiO₂ NW/G hybrid electrode-based Li/dissolved polysulfide cell is only 20 μm , significantly lower than that of the graphene-based cell, which penetrates into ca. 80 μm . These results demonstrate that the TiO₂ NW/G hybrid electrode can effectively limit the diffusion of polysulfides into the lithium anode during cycling. Because the polar TiO₂ NWs and nonpolar graphene can strongly bind with, respectively, lithium sulfides and sulfur species [49], the polysulfide shuttle effect and lithium dendrite growth can be suppressed.

Figure 6. SEM images of the lithium surface after 100 cycles in the (a) graphene electrode and (b) TiO₂ NW/G hybrid electrode. Cross-sectional EDS line scans (for sulfur) of the lithium metal after 100 cycles with the (c) graphene electrode and (d) TiO₂ NW/G hybrid electrode.

The binding between lithium polysulfides and TiO₂ NWs was characterized by Fourier transformation infrared spectroscopy (FTIR). Structural information of the graphene, TiO₂ NWs, and TiO₂ NW/G hybrid before and after cycling was analyzed in the 900 - 400 cm⁻¹ wavelength region. Li₂S_x sample was used as reference and it was prepared by drying Li₂S₆ solution at 50 °C in an Ar-filled glove box overnight. Before cycling, the graphene shows no signal in this area while TiO₂ NW/G hybrid shows peaks at 460 and 812 cm⁻¹ that are derived from the stretching vibration of TiO₂ [50], similar to pure TiO₂ NWs (**Figure S10 a-c**). After

cycling in the Li/dissolved polysulfide cell, two characteristic peaks at 496 and 650 cm^{-1} emerge in the graphene and TiO_2 NW/G hybrid electrodes, corresponding to, respectively, S-S and Li-S bonds [26, 51]. This is in agreement with the Li_2S_x spectrum (**Figure 7a-c**). Moreover, it is worth to note that a new peak appearing at 522 cm^{-1} is ascribed to the interaction between lithium polysulfides and TiO_2 forming an S-Ti-O band, which is consistent with a previous report [26]. Raman characterization was used to delineate the interaction between TiO_2 and polysulfides. Raman spectra of Li_2S_x , TiO_2 NW/G/ Li_2S_x and TiO_2 NW/G are shown in **Figure S11**. The D and G bands of graphene in TiO_2 NW/G/ Li_2S_x are located at the same position as that in TiO_2 NW/G, while the B_{1g} , A_{1g} and E_g vibrational modes of TiO_2 shift to a lower frequency by 8-9 cm^{-1} and the vibrational mode of Li_2S_x shifts to a higher frequency, indicating the interaction between TiO_2 and polysulfides.[26]

The interaction between lithium polysulfides and TiO_2 NWs was confirmed by X-ray photoelectron spectroscopy (XPS) analysis. All the peak positions for analysis were calibrated using C 1s peak at 284.6 eV. High-resolution S 2p XPS spectra are shown in **Figure 7d** and **e**; the samples were charged to the 2.3 V plateau before characterization. The corresponding compositional analysis on sulfur species are summarized in **Table S1** and **S2**. A Gaussian-Lorentzian fit to the S 2p spectrum of the graphene electrode was performed. Three different doublet peaks with an energy separation of 1.2 eV at 160.0/161.2, 161.5/162.7 and 163.0/164.2 eV (**Figure 7d**) are observed, corresponding to, respectively, Li_2S and terminal (S_T) and bridging sulfur (S_B) of polysulfides [41, 52]. Relative to the graphene electrode, the TiO_2 NW/G hybrid electrode exhibits higher binding energies with a shift of 0.8 - 0.9 eV for the corresponding three doublet peaks, which evidence the strong

interaction between the terminal/bridging sulfur and TiO₂ NWs (**Figure 7e**). This conclusion is in agreement with the recently proposed mechanism that electron transfers from the sulfur atoms to the electropositive titanium and/or oxygen vacancies, resulting in the shift of binding energy [52]. It is possible that the Li₂S peak position changes due to the variation of the chemical environment. For example, Li₂S peak at 160.0 eV shifts to 161.7 eV after adding LiNO₃ to the DOL-Li₂S₆ system [51]. Moreover, from the sulfur compositional analysis, it can be clearly seen that the content of the remaining Li₂S in the TiO₂ NW/G hybrid electrode (43.3 wt %) is much lower compared to that of the graphene electrode (64 wt %), which further confirms the catalytic effect of TiO₂ NWs facilitating the conversion of Li₂S. Therefore, the TiO₂ NWs embedded in the graphene can act as strong adsorbents to restrict the lithium polysulfide dissolution/diffusion and improve the utilization efficiency of polysulfides, thus promoting the electrochemical performance of Li/dissolved polysulfide batteries.

Figure 7. FTIR spectra of (a) Li₂S_x, (b) graphene/Li₂S_x and (c) TiO₂ NW/G/Li₂S_x after cycling. S 2p XPS spectra of (d) graphene and (e) TiO₂ NW/G hybrid electrodes after cycling.

charging to the plateau (2.3 V).

Conclusion

In summary, we have developed a free-standing TiO₂ NW/G hybrid membrane for high performance Li/dissolved polysulfide batteries. The physical confinement from graphene and chemical binding between lithium polysulfides and the TiO₂ NWs have been combined to prevent sulfur loss during discharge/charge processes. Graphene not only serves as a current collector, but also helps immobilize the dissolved lithium polysulfides. On the other hand, TiO₂ NWs chemically trap the lithium polysulfides within the cathode, preventing them from dissolving into the electrolyte and subsequently diffusing into and reacting with the lithium-metal anode. Moreover, the TiO₂ NWs exhibit a strong catalytic effect on promoting the polysulfide redox reaction kinetics. As a result, a high specific capacity, high-rate performance and long cyclic stability have been achieved. The work reported herein demonstrates the successful use of new strategy for designing high performance Li/dissolved polysulfide batteries by integrating physical (nonpolar) and chemical (polar) adsorption materials.

Experimental Section

TiO₂ NW synthesis:

TiO₂ NWs were prepared as reported previously [43]. Briefly, Degussa P25 TiO₂ (1.5 g) was dispersed in NaOH solution (80 mL, 5 M). The mixture was stirred for 10 minutes and then sealed in a 100 mL Teflon-lined stainless steel autoclave for a hydrothermal reaction at 200 °C for 24 h. After the reaction, the white precipitate was transferred into HCl solution (250

mL) with a concentration of 10 % (v/v) and magnetically stirred for 10 h, followed by washing with deionized water several times until the pH of the filtrate became neutral. The precipitate was then dried and calcined at 700 °C in air for 3 h to obtain the final product of fluffy TiO₂ NWs.

Preparation of TiO₂ NW/G hybrid membrane:

The graphene powder was obtained using previously reported methods [5]. To obtain the TiO₂ NW/G hybrid membrane, graphene powder (17 mg) and TiO₂ NWs (3 mg) were dispersed in isopropyl alcohol (50 mL) by high-power ultrasonication for 0.5 h and vacuum filtered through a nylon membrane with a pore size of 0.44 μm. After washing with de-ionized water and ethanol, followed by drying at 50 °C for 30 min, the hybrid membrane could be easily peeled from the filter surface and used as a freestanding current collector. For the preparation of the graphene membrane, graphene powder (20 mg) was directly dispersed in isopropyl alcohol and the membrane was obtained following a similar procedure described above for the TiO₂ NW/G hybrid membrane.

Materials Characterization:

Microstructural observations were performed on a FEI Quanta 650 SEM operated at 20 kV. EDS was used for collecting elemental signals and mapping. TEM and STEM were performed with a JEOL 2010F field emission TEM at 200 kV. XRD patterns were collected with a Philips X-ray diffractometer with Cu Kα radiation between 10 and 80° at a scan rate of 0.04° s⁻¹. UV-visible absorption spectroscopy analysis was performed to evaluate the polysulfide adsorption capability of graphene membrane and TiO₂ NW/G hybrid membrane. 4 mg each of graphene membrane and TiO₂ NW/G hybrid membrane were separately added into two sealed vials of Li₂S₆ solution (4 mL each, 0.03 mmol L⁻¹), and the remaining Li₂S₆

solution (8 mL) without adding anything was used as a control. After absorption for 12 h, the UV-visible absorption spectra of these solutions were collected with a Cary 5000 spectrophotometer with baseline correction (Varian). XPS analysis was performed on a Kratos Analytical spectrometer at room temperature with monochromatic AlK α (1486.6 eV) radiation. Raman spectra were collected with a 488 nm laser under ambient conditions with a WITEC Alpha300 S micro-Raman system at room temperature. FTIR spectra were obtained with a Thermoscientific Nicolet iS5 FT-IR Spectrometer. The samples were made with KBr-pellets and the obtained spectra were normalized using OMNIC Spectra software.

Preparation of electrolyte and polysulfide catholyte:

The blank electrolyte was prepared by dissolving an appropriate amount of lithium trifluoromethanesulfonate (LiCF₃SO₃, 98%, Acros Organics, 1 M) and lithium nitrate (LiNO₃, 99+%, Acros Organics, 0.1 M) in 1,2-dimethoxyethane (DME, 99+%, Acros Organics) and 1,3-dioxolane (DOL, 99.5%, Acros Organics) (1:1 by volume). The polysulfide catholyte was prepared by chemically reacting sublimed sulfur (99.5%, Fisher Scientific) and an appropriate amount of lithium sulfide (Li₂S, 99.9%, Acros Organics) in the blank electrolyte to form Li₂S₆ (0.5 M) in the solution. The solution was then stirred at 50 °C in an Ar-filled glove box overnight to produce a brownish-red Li₂S₆ catholyte solution.

Electrochemical Measurements:

Li/dissolved polysulfide cells (CR2032 coin cells) were assembled in an Ar-filled glove box. The graphene and TiO₂ NW/G hybrid membranes were cut and shaped into a rectangular plate with an area of 0.9 cm² and were used as the current collectors. 30 μ L of polysulfide catholyte was added into each of the graphene membrane and TiO₂ NW/G hybrid membrane electrodes, corresponding to a sulfur loading of 3.2 mg cm⁻² and a sulfur content of 62 wt. % in the whole cathode. The Celgard 2400 separator was then placed on the top of the

membrane electrode followed by adding 30 μL of the blank electrolyte. Finally, the lithium-metal foil anode was placed on the separator as the anode. An Arbin battery cycler was used to perform the galvanostatic cycling measurements between 1.5 - 2.8 V (*vs.* Li/Li^+) at room temperature. The current density set for tests was referred to the mass of sulfur in the cathode and was varied from 0.2C to 2C. The cyclic voltammetry (CV) profiles were measured with a VoltaLab PGZ 402 Potentiostat at a scan rate of 0.1 mV s^{-1} between 1.5 and 2.8 V. Electrochemical impedance spectroscopy (EIS) measurements were performed with a Solartron Impedance Analyzer (Solartron 1260 A) in the frequency range of 1 MHz to 0.1 Hz with an AC voltage amplitude of 5 mV at the open-circuit potential. For the cycled samples, the cycled cells were disassembled inside an Ar-filled glove box and the electrodes were washed with DME solvent to remove the lithium salt and dried inside the glovebox at room temperature before analysis.

Acknowledgements

This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under award number DE-SC0005397. We thank Profs. H.-M. Cheng and F. Li for providing the graphene.

References

- [1] P.G. Bruce, S.A. Freunberger, L.J. Hardwick, J.-M. Tarascon, *Nat. Mater.*, 11 (2012) 19-29.
- [2] R.V. Noorden, *Nature* 507 (2014) 26-28.
- [3] Y. Yang, G. Zheng, Y. Cui, *Chem. Soc. Rev.*, 42 (2013) 3018-3032.
- [4] A. Manthiram, Y. Fu, Y.-S. Su, *Acc. Chem. Res.*, 46 (2012) 1125-1134.
- [5] G.M. Zhou, S. Pei, L. Li, D.-W. Wang, S. Wang, K. Huang, L.-C. Yin, F. Li, H.-M. Cheng, *Adv. Mater.*, 26 (2014) 625-631.
- [6] S. Evers, L.F. Nazar, *Acc. Chem. Res.*, 46 (2013) 1135-1143.
- [7] A. Manthiram, Y. Fu, S.-H. Chung, C. Zu, Y.-S. Su, *Chem. Rev.*, (2014) DOI: 10.1021/cr500062v.
- [8] D.-W. Wang, Q. Zeng, G.M. Zhou, L. Yin, F. Li, H.-M. Cheng, I.R. Gentle, G.Q.M. Lu, *J. Mater. Chem. A*, 1 (2013) 9382-9394.
- [9] X.L. Ji, K.T. Lee, L.F. Nazar, *Nat. Mater.*, 8 (2009) 500-506.
- [10] D.-W. Wang, G.M. Zhou, F. Li, K.-H. Wu, G.M. Lu, H.-M. Cheng, I. Gentle, *Phys. Chem. Chem. Phys.*, 14 (2012) 8703-8710.
- [11] J. Schuster, G. He, B. Mandlmeier, T. Yim, K.T. Lee, T. Bein, L.F. Nazar, *Angew. Chem. Int. Ed.*, 51 (2012) 3591-3595.
- [12] C. Zhang, H.B. Wu, C. Yuan, Z. Guo, X.W. Lou, *Angew. Chem. Int. Ed.*, 51 (2012) 9456-9456.
- [13] Z. Li, Y. Jiang, L. Yuan, Z. Yi, C. Wu, Y. Liu, P. Strasser, Y. Huang, *ACS Nano*, 8 (2014) 9295-9303.
- [14] G.M. Zhou, D.-W. Wang, F. Li, P.-X. Hou, L. Yin, C. Liu, G.Q. Lu, I.R. Gentle, H.-M. Cheng, *Energy Environ. Sci.*, 5 (2012) 8901-8906.
- [15] S. Moon, Y.H. Jung, W.K. Jung, D.S. Jung, J.W. Choi, D.K. Kim, *Adv. Mater.*, 25 (2013) 6547-6553.
- [16] X.-B. Cheng, J.-Q. Huang, Q. Zhang, H.-J. Peng, M.-Q. Zhao, F. Wei, *Nano Energy*, 4 (2014) 65-72.
- [17] H.L. Wang, Y. Yang, Y.Y. Liang, J.T. Robinson, Y.G. Li, A. Jackson, Y. Cui, H.J. Dai, *Nano Lett.*, 11 (2011) 2644-2647.
- [18] W. Lv, Z. Li, G. Zhou, J.-J. Shao, D. Kong, X. Zheng, B. Li, F. Li, F. Kang, Q.-H. Yang, *Adv. Funct. Mater.*, 24 (2014) 3456-3463.
- [19] M.-Q. Zhao, Q. Zhang, J.-Q. Huang, G.-L. Tian, J.-Q. Nie, H.-J. Peng, F. Wei, *Nat. Commun.*, 5 (2014) 3410.
- [20] C. Zhang, W. Lv, W. Zhang, X. Zheng, M.-B. Wu, W. Wei, Y. Tao, Z. Li, Q.-H. Yang, *Adv. Energy Mater.*, 4 (2014) 1301565.
- [21] G.M. Zhou, L. Li, C. Ma, S. Wang, Y. Shi, N. Koratkar, W. Ren, F. Li, H.-M. Cheng, *Nano Energy*, 11 (2015) 356-365.
- [22] J.-Q. Huang, X.-F. Liu, Q. Zhang, C.-M. Chen, M.-Q. Zhao, S.-M. Zhang, W. Zhu, W.-Z. Qian, F. Wei, *Nano Energy*, 2 (2013) 314-321.
- [23] Y. Fu, A. Manthiram, *J. Phys. Chem. C*, 116 (2012) 8910-8915.
- [24] Y. Yang, G.H. Yu, J.J. Cha, H. Wu, M. Vosgueritchian, Y. Yao, Z.A. Bao, Y. Cui, *ACS Nano*, 5 (2011) 9187-9193.

- [25] Y.J. Choi, B.S. Jung, D.J. Lee, J.H. Jeong, K.W. Kim, H.J. Ahn, K.K. Cho, H.B. Gu, *Phys Scripta*, T129 (2007) 62-65.
- [26] S. Evers, T. Yim, L.F. Nazar, *J. Phys. Chem. C*, 116 (2012) 19653-19658.
- [27] Y. Zhang, Y. Zhao, A. Yermukhambetova, Z. Bakenov, P. Chen, *J. Mater. Chem. A*, 1 (2013) 295-301.
- [28] F. Sun, J. Wang, D. Long, W. Qiao, L. Ling, C. Lv, R. Cai, *J. Mater. Chem. A*, 1 (2013) 13283-13289.
- [29] G.M. Zhou, L.-C. Yin, D.-W. Wang, L. Li, S. Pei, I.R. Gentle, F. Li, H.-M. Cheng, *ACS Nano*, 7 (2013) 5367-5375.
- [30] C.X. Zu, A. Manthiram, *Adv. Energy Mater.*, 3 (2013) 1008-1012.
- [31] J. Song, T. Xu, M.L. Gordin, P. Zhu, D. Lv, Y.-B. Jiang, Y. Chen, Y. Duan, D. Wang, *Adv. Funct. Mater.*, 24 (2014) 1243-1250.
- [32] F. Sun, J. Wang, H. Chen, W. Li, W. Qiao, D. Long, L. Ling, *ACS Appl. Mater. Interfaces*, 5 (2013) 5630-5638.
- [33] X.G. Sun, X.Q. Wang, R.T. Mayes, S. Dai, *ChemSusChem*, 5 (2012) 2079-2085.
- [34] Z. Lin, Z. Liu, W. Fu, N.J. Dudney, C. Liang, *Adv. Funct. Mater.*, 23 (2013) 1064-1069.
- [35] Z.W. Seh, Q. Zhang, W. Li, G. Zheng, H. Yao, Y. Cui, *Chem. Sci.*, 4 (2013) 3673-3677.
- [36] S.S. Zhang, *Electrochim. Acta*, 70 (2012) 344-348.
- [37] Y. Fu, Y.-S. Su, A. Manthiram, *Angew. Chem. Int. Ed.*, 52 (2013) 6930-6935.
- [38] C. Zu, A. Manthiram, *Adv. Energy Mater.*, (2014) DOI: 10.1002/aenm.201400897.
- [39] R. Xu, I. Belharouak, J.C.M. Li, X. Zhang, I. Bloom, J. Bareño, *Adv. Energy Mater.*, 3 (2013) 833-838.
- [40] S.-H. Chung, A. Manthiram, *Adv. Mater.*, 26 (2014) 1360-1365.
- [41] C. Zu, Y. Fu, A. Manthiram, *J. Mater. Chem. A*, 1 (2013) 10362-10367.
- [42] G. Zhou, F. Li, H.-M. Cheng, *Energy Environ. Sci.*, 7 (2014) 1307-1338.
- [43] Y. Zhao, Q. Chen, F. Pan, H. Li, G.Q. Xu, W. Chen, *Chem.-Eur. J.*, (2014) DOI: 10.1002/chem.201400120.
- [44] J. Pan, X. Wu, L.Z. Wang, G. Liu, G.Q. Lub, H.M. Cheng, *Chem. Commun.*, 47 (2011) 8361-8363.
- [45] G.M. Zhou, D.-W. Wang, L.-C. Yin, N. Li, F. Li, H.-M. Cheng, *ACS Nano*, 6 (2012) 3214-3223.
- [46] Z.S. Wu, W.C. Ren, L. Xu, F. Li, H.M. Cheng, *ACS Nano*, 5 (2011) 5463-5471.
- [47] C. Barchasz, F. Molton, C. Duboc, J.C. Lepretre, S. Patoux, F. Alloin, *Anal. Chem.*, 84 (2012) 3973-3980.
- [48] K. Han, J. Shen, S. Hao, H. Ye, C. Wolverton, M.C. Kung, H.H. Kung, *ChemSusChem*, 7 (2014) 2545-2553.
- [49] H. Yao, G. Zheng, P.-C. Hsu, D. Kong, J.J. Cha, W. Li, Z.W. Seh, M.T. McDowell, K. Yan, Z. Liang, V.K. Narasimhan, Y. Cui, *Nat. Commun.*, 5 (2014) 3943.
- [50] R. Nakamura, Y. Nakato, *J. Am. Chem. Soc.*, 126 (2004) 1290-1298.
- [51] D. Aurbach, E. Pollak, R. Elazari, G. Salitra, C.S. Kelley, J. Affinito, *J. Electrochem. Soc.*, 156 (2009) A694-A702.
- [52] Q. Pang, D. Kundu, M. Cuisinier, L.F. Nazar, *Nat. Commun.*, 5 (2014) 4759.

Curriculum Vitae

Guangmin Zhou is a postdoctoral research fellow at the Texas Materials Institute of the University of Texas at Austin. He received his Ph.D. in Materials Science in 2014 at Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences. His research interests mainly focus on the design, synthesis, and applications of carbon-based materials for lithium-sulfur batteries and lithium-ion batteries.

Yubao Zhao is a postdoctoral research fellow at the Texas Materials Institute of the University of Texas at Austin. He received his Ph.D. degree at the Institute of Chemistry, Chinese Academy of Sciences in 2012. His research interests are in nanomaterials design and synthesis for energy storage and conversion.

Chenxi Zu received her B. Eng. degree from the Department of Materials Science and Engineering at Beihang University in 2011. She is currently a Ph.D. candidate in the Materials Science and Engineering Graduate Program at the University of Texas at Austin. Her research is focused on high energy-density Li-S batteries, surface/interface studies, and metallic anode protection.

Arumugam Manthiram is the holder of the Cockrell Family Regents Chair in Engineering and the Director of the Texas Materials Institute and the Materials Science and Engineering Program. His research interests are in the area of rechargeable batteries, fuel cells, and solar cells, including novel synthesis approaches for nanomaterials and nanocomposites.