High-performance nitrogen-doped titania nanowire decorated carbon cloth electrode for lithium-polysulfide batteries

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ABSTRACT

A semi-liquid polysulfide cathode renders a higher sulfur loading for Li-S batteries. However, the aggravated polysulfide shuttle effect and the poor interaction between polysulfide and carbonaceous electrode lower the battery's cycling stability and performance. Here we report a freestanding $N\text{-}TiO_2$ nanowire (NW) decorated carbon cloth electrode for a Li-polysulfide battery, where the nitrogen doping in the formed nanowires allows for a higher electrical conductivity and stronger polysulfide binding ability. Meanwhile, with the facile adsorption of S_4^{2-} and more active sites provided by the nanowire structure, Li_2S precipitation can be improved as well. With the rationally engineered nanostructured polysulfide binding electrode, the battery achieves a remarkably enhanced cycling stability and prolonged discharge capacity ($1210\,mAh\,g^{-1}$, 0.2C and $600\,mAh\,g^{-1}$, 1C), in comparison with the pristine carbon cloth ($890\,mAh\,g^{-1}$, 0.2C and $210\,mAh\,g^{-1}$, 1C). The facile strategy of fabricating conductive and polysulfide binding nanostructure in this work is thus expected to facilitate the design of high-energy sulfur cathode.

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1. Introduction

Beyond the horizon of Li-ion batteries, rechargeable lithium-sulfur (Li-S) batteries nowadays hold the promise of prolonging electric vehicles' mileage. Predominately, the Li-S cathode discharge electrochemistry is the lithiation of S_8 to form Li_2S at the cathode ($S_8 + 16Li^+ + 16e^- \rightarrow 8Li_2S$), with Li stripping occurring at the anode ($Li - e^- \rightarrow Li^+$) [1–9]. Though the high specific capacities of Li anode ($3860\,mAh\,g^{-1}$) and sulfur cathode ($1673\,mAh\,g^{-1}$) render a high theoretical specific energy for the Li-S battery, critical issues arise from the inherent multiple-step cathodic reactions ($S_8 \rightarrow S_8^{2-} \rightarrow S_6^{2-} \rightarrow S_4^{2-} \rightarrow Li_2S$). One is the dissolution of reactive polysulfide anions (so called "shuttle effect"), which can irreversibly passivate the Li anode and shorten the battery's cycle life. The other concerns for the insulating nature of Li_2S ($< 10^{-14}\,S\,cm^{-1}$ RT) as the final discharge product, leading to the necessity to facilitate Li_2S precipitation in the conductive matrix [10–13].

A variety of sulfur cathodes has thus been designed to fulfill the roles of conductive host as well as polysulfide reservoir. The conductive matrix is usually carbon material with different pore scales. One approach is to encapsulate sulfur in the microporous or mesoporous carbon, which confines polysulfides and Li_2S within the pores and thus mitigates the polysulfide shuttle effect [11,14–20]. Though the battery's cycle life can be prolonged, such a confinement strategy meets the challenge of the inferior sulfur loading and requires the use of metallic current collector [5,14]. An alternative approach is to adopt porous current collectors, such as the carbon paper, carbon cloth, CNT paper and graphene sponge, which eliminates the use of metallic current collectors and allows for using energy dense polysulfides (Li_2S_8 or Li_2S_6) as the starting active material [21–35]. A higher areal sulfur loading can be usually attained owing to their more porous structure. However, there are usually loose bindings between non-polar carbon and polysulfides/Li_2S, leading to (i) fast polysulfide dissolution and aggravated side reactions on the Li anode; (ii) the sluggish Li_2S precipitation reaction ($2Li^+ + \frac{1}{4}S_4^{2-} + \frac{3}{2}e^- \rightarrow Li_2S$), and thus a lower utilization of active material [22–24,36–38].

Identifying polysulfide binding material (PBM) is thus critical for improving the battery's performance and has drawn increasing research efforts [11,13,39–47]. Polar metal oxides, such as Al_2O_3, TiO_2 and Ti_4O_7, have been identified to adsorb electron-donating polysulfides on their electron-accepting metal sites by forming Lewis acid-base bonds [48–52]. It is reported that exploring metal

oxides with lithiation potential higher than the sulfur redox reactions, such as δ-MnO$_2$ and V$_2$O$_5$, can facilitate the transformation of polysulfides to Li$_2$S by generating thiosulfate/polythionate redox mediators [41,49,53]. In addition to controlling polysulfide shuttles, with facile adsorption of polysulfides, adding polysulfide binding material can also provide controllable amounts of Li$_2$S nucleation sites, which shows a potential for accelerating Li$_2$S precipitation kinetics [12,49,54–56]. Though promising, a constraining factor is that the majority of PBMs are nonconductive and the absorbed polysulfides need to diffuse to the conductive carbon to undergo further reactions [51]. Enabling conductive polysulfide binding nanostructure that balances surface adsorption and reactions is thus of a notable significance.

To address this issue, an efficient nanostructured carbon cloth electrode is proposed for Li-polysulfide batteries (sulfur loading 4.8 mg cm^{-2}) in this work. Specifically, we synthesized self-supported TiO$_2$ nanowires onto the carbon fiber surface. We show that, with nitrogen doping, the electrical conductivity as well as the polysulfide binding ability of the formed nanowires can be enhanced spontaneously, which facilitate both polysulfide adsorption and Li$_2$S precipitation. As a result, batteries assembled with N-TiO$_2$ nanowire decorated carbon cloth (denoted as N-TiO$_2$ NW @ CC) electrodes show a much more stable cycling performance and a remarkable increase in discharge capacity (1210 mAh g^{-1} at 0.2C and 600 mAh g^{-1} at 1C), much better than the control group of pristine carbon cloth (890 mAh g^{-1} at 0.2C and 210 mAh g^{-1} at 1C).

2. Experimental

2.1. Material preparation

The Li$_2$S$_8$ solution was prepared by dissolving a desired amount of stoichiometric S and Li$_2$S in 1,3-dioxolane (DOL)/1,2-dimethoxyethane (DME) solution (1:1 in volume) with the addition of 1 M LiTFSI and LiNO$_3$ additive (1 wt.%). For the typical preparation of 0.5 M Li$_2$S$_8$ solution, 0.560 g of S and 0.115 g of Li$_2$S were added to 5 mL of DOL/DME (1:1) based electrolyte. The obtained suspension was stirred and heated at 80 °C overnight to yield red-brown Li$_2$S$_8$ solution.

2.2. Preparation of N-TiO$_2$ NW @ carbon cloth

Free-standing TiO$_2$ nanowires were grown directly on carbon cloth by a two-step process [57]. Carbon cloths (6.0 cm × 3.0 cm) were thoroughly rinsed with ethanol, and then dried at room temperature for 12 h. The cleaned carbon cloths were immersed into 0.2 M titanium(IV) chloride aqueous solution for 10 min and blow-dried with compressed air. The dried carbon cloths were further heated on a hotplate in air at 350 °C for 10 min, forming TiO$_2$ nanoparticles on the carbon fiber surface (TiO$_2$ nanoparticle seeded substrate). 18.75 mL of concentrated hydrochloric acid (35%) was diluted with 18.75 mL deionized (DI) water, and mixed with 0.56 mL titanium n-butoxide. This clear solution mixture together with the carbon cloth coated with TiO$_2$ seeds were transferred to a Teflon-lined stainless steel autoclave (50 mL volume). The sealed autoclave was heated in an electric oven at 150 °C for 6 hours, and then cool down slowly at room temperature. A white TiO$_2$ nanowire film was uniformly coated on the carbon cloth surface. The obtained carbon cloth was further annealed in air at 550 °C for 1 hour to stabilize the nanowire structure. The areal loading of TiO$_2$ NW (1.60 ± 0.15 mg cm^{-2}) was determined by measuring the weights of carbon cloths before and after the hydrothermal synthesis.

To convert TiO$_2$ to nitrogen doped-TiO$_2$ (N-TiO$_2$), the samples were respectively annealed under ammonia atmosphere at temperatures of 700 °C or 800 °C for 1.5 h. The color of the

nanowire film transformed from white to black subsequent to the annealing process.

2.3. Cell assembly and test

One piece of lithium foil (16 mm diameter) was placed onto the bottom Cu cell body. One piece of Celgard (2500) separator (18 diameter) was placed onto the lithium foil, following by the addition of 12 μL DOL/DME electrolyte (1 M LiTFSI and LiNO$_3$ additive (1 wt.%). Subsequently, a piece of hydrophilic carbon cloth (10 mm, 0.79 cm^{-2}) was exploited as the cathode and 30 μL 0.5 M Li$_2$S$_8$ catholyte was uniformly dropped onto the carbon cloth cathode, with a theoretical areal sulfur loading around 4.8 mg cm^{-2} (S → Li2S). The galvanostatic discharge and charge tests were conducted on a battery cycling system (Neware, CT-3008W) at room temperature (298 K).

2.4. Material characterization

The discharged cathodes after cycling were soaked in pure DME for 10 minutes and then dried before SEM observation. JSM-6700F field emission SEM instruments were used for micrograph observation at an acceleration voltage of 5.0 kV. Transmission electron-microscopy (TEM) images of N-TiO$_2$ nanowires were measured by a high-resolution JEOL 2010F TEM system with a LaB$_6$ lament at 200 kV. The samples were dispersed in ethanol, sonicated and dripped onto the regular carbon-coated Cu grids. The crystal phase and composition of the nanowires were analyzed by a Philips high-resolution X-ray diffraction system (XRD, model PW 1825) using a Cu-Ka source operating at 40 keV and a Micro-Raman spectrophotometer (Renishaw RM 3000) at an excitation wavelength of 514 nm.

2.5. Soaking experiment and surface analysis

20 mM Li$_2$S$_4$ solution was also prepared by dissolving a desired amount of stoichiometric S and Li$_2$S in 1,3-dioxolane (DOL)/1,2-dimethoxyethane (DME) solution (1:1 in volume) electrolyte. Commercial TiO$_2$ and TiN powders with similar particle sizes (∼30 nm) were obtained from Sigma-Aldrich. To convert TiO$_2$ to nitrogen doped-TiO$_2$ (N-TiO$_2$), the samples were respectively annealed under ammonia atmosphere at temperatures of 700, 800 °C for 1.5 h. 20 mg sample material (#1-4) were added into 1 mL 20 mM Li$_2$S$_4$ in DOL/DME respectively and the obtained suspensions were rigorously sonicated for 1 h before observation. To prepare the samples for XPS surface analysis, the sample material impregnated with Li$_2$S$_4$ were filtered, dried in the glove box and transferred to the XPS setup in a sealed box to exclude the effects of moisture and oxygen. The X-ray photoelectron spectroscopy (XPS) was performed using a Physical Electronics PHI 5600 multi-technique system equipped with an Al monochromatic X-ray source at a power of 350 W. The binding energy values were all calibrated using the C 1s peak at 285.0 eV.

3. Results and discussion

The carbon cloth (Fig. 1a) was exploited as the current collector in Li-polysulfide batteries, as it renders an excellent liquid absorbence for the semi-liquid cathode and accommodates the volume change induced by the charge/discharge product formation over repeated cycles owing to its robust interwoven structure [22,23,30,58,59]. TiO$_2$, as one of the earliest recognized polysulfide binding material was selected [14,25,32–34]. In the latter section, we demonstrate that by growing one-dimensional TiO$_2$ nanowire on the carbon fiber surface and improving TiO$_2$'s surface properties (nitrogen doping) (Fig. 1b), an enlarged electrode/electrolyte