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Improving the electrochemical performance of Lithium–Sulfur batteries using an Nb-Doped TiO_2 additive layer for the chemisorption of lithium polysulfides

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ABSTRACT

This study presents a method to suppress the migration of lithium polysulfides in lithium–sulfur batteries by introducing a dual-layer electrode structure. Herein, unlike conventional methods of mixing the polar additives with sulfur/carbon composites, melted sulfur mixed with mesocarbon microbeads are used as the electrode and covered with an additive layer of Nb-doped TiO_2/graphite composite via two-step blade coating. By doping TiO_2 with Nb, electrical and lithium ion conductivity of TiO_2 can be increased, thereby enhancing the redox reaction kinetics. Most importantly, chemisorption of lithium polysulfides to Nb–TiO_2 can effectively mitigate the shuttle effect, resulting in higher capacity and longer cycle life. The electrode with the Nb–TiO_2 additive layer results in a 1st and 100th cycle specific capacity of 1883 mAh g^{-1} and 894 mAh g^{-1}, respectively, at 0.1 C (1 C = 1675 mAh), indicating enhanced electrochemical performance as compared with that of bare lithium-sulfur batteries. X-ray photoelectron spectroscopy (XPS) study was conducted to investigate the interaction between polysulfides and Nb–TiO_2. The results indicate that the Nb–TiO_2–layered electrode efficiently traps polysulfides on the cathode and improves the rate capability, cycle performance, and specific capacity.

1. Introduction

Recently, given the profound environmental issues associated with fossil-fuel-based transportation, replacing traditional cars with electric vehicles or hybrid electric vehicles has become a global effort. The rapidly increasing demand for high-power sources and energy storage systems has turned lithium–sulfur (Li–S) batteries into a potentially promising energy storage alternative because the active material, sulfur, is low-cost and eco-friendly. In addition, Li–S batteries deliver a high gravimetric capacity of 1675 mAh g^{-1} and a high theoretical specific energy of 2600 Wh kg^{-1} [1]. Although Li–S batteries have many advantages, several critical problems must be solved prior to wider commercial applications. The primary drawbacks include the insulating nature of sulfur (5×10^{-30} S cm^{-1} at 25 °C) [2], large volume expansion (~80%) during the formation of Li_2S, and dissolution of lithium polysulfides (Li_2S_x, $4 \leq x \leq 8$) through the reduction of S_8 or oxidation of short-chain polysulfides in liquid electrolyte, which ultimately leads to the shuttle effect [3], causing low utilization of sulfur, poor Coulombic efficiency, and rapid Li–S battery capacity fading during the charge–discharge process [4,5]. To overcome these obstacles, mesoporous/microporous carbons [6,7], graphene [8], carbon nanotubes [9], and carbon fiber [10] have been used to encapsulate elemental sulfur. Carbon–sulfur composite cathodes enhance the electrical conductivity and the physically confined LiPSs (lithium polysulfides) in the carbon pores or layers. However, polar LiPSs still diffuse out of non-polar carbon after long cycling owing to the lack of chemical interaction between LiPSs and carbon. Hence, incorporating polar metal oxide or sulfides in new cathode designs is a rapidly developing research area [11]. These polar inorganic additives can be classified by the electrical conductivity of conductors (e.g., Ti_4O_7 [12] and Mxene [13]), semiconductors (e.g., TiO_2 [14,15], Nb_2O_5 [16], and FeS_2 [17]), and insulators (e.g., SiO_2 [18], $Mg_{0.6}Ni_{0.4}O$ [19], and Al_2O_3 [20]). These additives provide active sites to absorb LiPSs and enhance surface electrochemical kinetics, effectively reducing the shuttle effect and prolonging the cycle life [21].

Previous studies have reported that Nb-doped TiO_2 has many electrochemical applications [22]. Nb–TiO_2 is selected as the

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absorbent to anchor LiPSs owing to relatively high electrical and better lithium ion conductivity as compared to other semiconductors [23,24]. Additionally, Nb–TiO_2 participates in the electrochemical reaction, thereby providing additional capacity for the Li–S battery. Here, instead of mixing metal oxide additives with sulfur and carbon, a dual-layer cathode is developed with an Nb–TiO_2 coating on an MCMB–sulfur layer via the doctor-blading technique. The Nb–TiO_2 layer acts as a protective layer that physically and chemically prevents LiPSs from dissolving directly into the electrolyte. Moreover, Nb–TiO_2 layer renders a pathway for lithium ions to diffuse into the cathode. Nb–TiO_2 was synthesized to fabricate dual-layer Li–S cathodes, and the electrochemical behaviors were studied in detail. Furthermore, lithium ion diffusivity was analyzed using AC impedance, and chemisorption was analyzed via X-ray photoelectron spectroscopy (XPS).

2. Experimental

2.1. Preparation of materials

The MCMB–sulfur composites were prepared by mixing and melting sulfur (95% purity, SHOWA KAKO) and MCMB at 155 °C for 5 h in a sealed glass bottle. Nb–TiO_2 was synthesized according to procedures reported elsewhere [25], $Nb_{0.15}Ti_{0.85}O_2$ (NTO15) was selected for this study.

2.2. Preparation of cathodes

The pristine cathodes abbreviated as MCMB/S were prepared by mixing 80 wt% MCMB–sulfur composite powder, 10 wt% Super P, and 10 wt% polyethylene oxide/polyvinylpyrrolidone (PEO/PVP) in DI water to form a slurry that was cast on aluminum foil via doctor blading. On the other hand, the slurry of 80 wt% NTO15s, 10 wt% graphite, and 10 wt% PEO/PVP was cast on the MCMB/S cathodes to construct the dual-layer structure. The dual-layer cathodes were abbreviated as MCMB/S/NTO15. All electrodes were dried for 24 h at 40 °C in a vacuum oven.

2.3. Preparation of XPS samples

To investigate the interaction between NTO15s and LiPSs, Li_2S_8 was selected as the representative. A 20 mM Li_2S_8 solution was prepared by dissolving dry sulfur powder and Li_2S in a molar ratio of 7:1 in anhydrous tetrahydrofuran (THF) at 55 °C in a glove box. After stirring for 48 h, the Li_2S_8 solution with a red–brown color was obtained. The solvent was dried out in a vacuum oven, and the resulting solid was heated at 130 °C in a glove box to remove any residual solvent to produce Li_2S_8 powder. 50 mg NTO15s were added to 5 mL Li_2S_8 solution and stirred for 48 h to obtain the NTO15/Li_2S_8 solution. Then, the precipitated product was dried under vacuum to obtain NTO15/Li_2S_8 powder for XPS analysis.

2.4. Characterization

X-ray diffraction (XRD) patterns were measured on a Bruker D2-phaser using Cu-Kα radiation ($\lambda = 1.5418$ Å) at 30 kV. Sample morphology was analyzed via field-emission scanning electron microscopy (FE-SEM, JEOL JSM-7600F) equipped with energy-dispersive spectroscopy (EDX). High-resolution XPS (HR-XPS) performed with a ULVAC PHI Quantera SXM spectrometer with a monochromatic Al-Kα X-ray source was used to investigate the interaction between NTO15s and LiPSs. The XPS spectra were fitted using Gaussian–Lorentzian functions and a Shirley-type background; C 1s peak at 285.0 eV was used to calibrate the spectra.

2.5. Electrochemical measurements

Electrochemical studies were conducted in 2230-type coin cells in an Ar-filled glove box ($O_2 < 0.1$ ppm; $H_2O < 0.1$ ppm) using lithium foil as the counter electrode. The sulfur fraction in MCMB was determined to be 46.8 wt% via thermogravimetric analysis (TGA). The sulfur content in the MCMB/S/NTO15 was calculated using an average pristine electrode weight of 1.2–1.3 mg. The electrolyte was a solution of lithium bis(trifluoromethanesulfonyl) imide (1 M) in 1:1 v/v 1,2-dimethoxyethane (DME) and 1,3-dioxolane (DOL) containing $LiNO_3$ (1 wt%). The cells were charged and discharged using an Arbin battery tester, and cycled between 1.6 and 2.6 V (vs. Li/Li^+) at 25 °C ± 0.1 °C. Electrochemical impedance spectroscopy (EIS) measurements were carried out over the frequency range of 100 to 0.01 kHz at 2.15 V. The ac impedance and CV measurements were obtained using an Ametek 263A electrochemical workstation.

3. Results and discussion

3.1. Cathode characterization

Fig. 1a shows the morphology of NTO15s synthesized via the hydrothermal method, which are hollow spherical nanoparticles with a mesoporous surface. Fig. 1b presents the XRD pattern of NTO15s. As Compared to the spectrum of anatase TiO_2, the XRD pattern of NTO15s shifts to lower angles, suggesting that TiO_2 is doped with Nb atoms, resulting in lattice expansion ($Nb^{5+} = 0.64$ Å, $Ti^{4+} = 0.61$ Å), as reported in literature [25,27]. Based on the XRD pattern of NTO15s, a small trace of rutile TiO_2 is found in NTO15s.

Fig. 2a presents the structure of the cell with the MCMB/S/NTO15, comprising an Al foil, an MCMB–sulfur layer, and an NTO15 layer. The SEM images in Fig. 2b and c shows that the MCMB/S/NTO15 is covered by NTO15s over the entire surface of the MCMB–sulfur layer. Furthermore, EDS mapping results presented in Fig. 2d clearly show that some NTO15s interfuse with the sulfur-rich layer. The same binder and solvent are used in each layer, suggesting that NTO15s possibly penetrate the MCMB–sulfur layer during the casting and drying process. Therefore, NTO15s can form a thin protective layer and additives for MCMB/S-layer. Furthermore, the binder could rebind these two layers together to provide better contact.

3.2. Interaction between NTO15s and the lithium polysulfide

The reaction between NTO15s and LiPS was examined by XPS. L_2S_8 was prepared by combining sulfur powder with Li_2S and chosen as the LiPS representative. Fig. 3a and b presents the Ti 2p spectra of NTO15s before and after stirring with L_2S_8. A small shift (−0.2 eV) to a lower binding energy in the Ti 2p spectrum of NTO15s/L_2S_8, and a lower Ti^{3+} oxidation state are observed. The same phenomenon is observed in the Nb 3d spectrum (Fig. 3d), which shifts to a lower binding energy as compared to the NTO15s spectrum (Fig. 3c). The peak of Nb^{4+} is evaluated at 206.5 ($3d_{5/2}$) and 209.3 eV ($3d_{3/2}$) in the NTO15s/L_2S_8 spectrum. As shown in Fig. 3e, the S 2p spectrum of Li_2S_8 exhibits two $2p_{3/2}$ peaks at 161.1 and 163.0 eV referred to terminal (S_T^{-1}) and bridge sulfur (S_B^0). A 3:1 ratio between these two $2p_{3/2}$ peaks is consistent with the Li_2S_8 composition. In the S 2P spectrum (Fig. 3f), post stirring with NTO15s, S_T^{-1} and S_B^0 move to 161.8 and 163.4 eV, respectively, indicating a shift (+0.7 eV; +0.4 eV) to a higher binding energy. The XPS study represents oxygen atoms binding with Nb or Ti, which may oxidize sulfur atoms in Li_2S_8 and form S–O bonds. The replacement of lower electronegativity sulfur results in the shifting peaks [26]. Based on Tao et al.'s DFT calculations [27], LiPSs tend to