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Titanium Oxide Nanowire Clots with Two Phase Composition as Multi-effect Sulfur Reservoirs for Lithium-Sulfur Batteries

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Lithium sulfur batteries (LSBs) is one of the most promising battery systems for both green energy plants and electric vehicles power sources. High performance sulfur reservoirs have been considered as the most important component for LSBs to protect the soluble lithium polysulfides (LPSs) from shuttling to lithium anode. Herein, a desired titanium oxide nanowire clots (TOCs) with a two phase composition and high effective absorption surface area (270.1 m^2g^{-1}) is developed as the promising LPSs' reservoirs for the accommodation of sulfur and LPSs. Benefitted from the synergistic effect generated from the unique structure of TOCs, the obtained S/TOCs cathode materials exhibit high specific capacity, high coulombic efficiency and excellent cyclic stability at 1C and 2C rate. The corresponding capacity fading rate of each cycle is only ~0.14% and 0.11 % for the LSBs being (dis)charged 1C and 2C, respectively.

Keywords: Lithium sulfur batteries; Titanium oxides; Sulfur reservoirs; Nanowires; Cathode materials;

Lithium sulfur batteries (LSBs), with a much higher theoretical energy density of 2600 Whkg^{-1}, is considered as one of the most promising battery systems for both storing green energy and powering (hybrid) electric vehicles. [1-3] However, coins always have two sides, LSBs also have their own weak points. The insulative nature, the large volume expansion, the "shuttle effect" of the soluble lithium polysulfides (LPSs) from cathode to Li anode during the discharge processes become the big challenges or limitations of LSBs.[4, 5] Therefore, many researchers have paid intensive attention to square up to the challenges mentioned above. Generally, all the related efforts can be sorted into two strategies, namely, to develop advanced sulfur reservoirs to provide enough surface and space to accommodate the large amount of sulfur meanwhile to avoid the escape of dissolved lithium polysulfides out to electrolyte and to create advanced separators to block the shuttle channels for the dissolved LPSs. [6, 7] Especially at a high sulfur loading condition, a systematically strategy should be adopted, including the advanced sulfur reservoir, advanced conductive agent and conductive network construction strategy, as well as advanced separator and electrolyte. Therefore, different types of nanomaterials have been developed as sulfur reservoirs or host to suppress the degradation of sulfur cathode. [3, 8-11] Metal oxides, [12, 13] nitrides, [4, 5, 7] sulfides [14-16] and metal organic compounds [17, 18] have been regards as promising hosts for sulfur, due to their strong chemical absorption capability to LPSs and their much higher tap density than carbon. Moreover, various bulk materials with hierarchical, hollow or porous secondary nanostructures have also been designed to enhance the spatial structure confinement effects to LPSs. [7]

Among them, Ti-based compounds demonstrate excellent sulfur fixation effect due to their high surface adsorption energies (E_{SA}). For example, the E_{SA} of TiO_2 and TiN to Li_2S_4 are ~3.5 and ~2.9 eV, respectively. [7, 19] Therefore, different nanostructured titanium oxides, such as hollow, microboxes, tubular, mesoporous TiO_2, [20-22] and Ti_4O_7 microspheres [23, 24] have been developed as the hosts for immobilizing through chemical bonding and physical trapping of sulfur. TiN sphere and 1-D TiN also have been developed as promising sulfur hosts, since the higher conductivity of TiN than TiO_2. [25-27] Moreover, the twin-born TiO_2-TiN heterostructures demonstrates much improved absorption property to LPSs, comparing to neat TiN and TiO_2 nanostructures. [4] Conductive carbon nanomaterials with high specific surface area have been developed as potential sulfur reservoirs to accommodate sulfur by physical adsorption and/or as conductive additives to enhance the rate capability of LSBs by creating effective three dimensional conductive network. For example, the nano-scale TiO_2 and TiN have also been widely applied to composite with graphene, carbon nanotube, MXene and other materials with a view to form nanostructured reservoirs with both strong chemical bonding and physical absorptions to LPSs. [28, 29] Just recently, we also introduced a sandwiched titanium oxides surface layer made of titanium oxide hybrids of nanowires and nanosheets as multifunctional "wall" to block the shuttle channels through the commercial polypropylene separator for LPSs by synergistic effect of physical blockage and chemical absorption. [6]

As illustrated in Figure 1, titanium oxide nanowire clots (TOCs) are developed in this work as the promising candidate sulfur reservoir in order to provide enough space and large the strong chemisorption surface for accommodating sulfur. The as-prepared TOCs are formed by the interconnected nanowires with two phase composition, are developed by following a hydrothermal method assisted ion exchange strategy. The obtained high surface area and porous structure will make TOCs the promising LPSs' reservoirs for the accommodation of sulfur and LPSs. The interconnected structure of nanowires could further boost the charge transfer within TOCs. Therefore, the obtained S/TOCs cathode materials exhibit high specific capacity, high coulombic efficiency and excellent cyclic stability at 1C and 2C rate, benefited from the synergistic effect of the high absorption surface area, strong surface chemical absorption capability and the spatial confinement effect to S and LPSs, as well as the enhanced conductivity, generated from the unique structure of TOCs. The observed electrochemical performance of S/TOCs even better that that of S/TiN nanoparticles clots (TNCs) with a lower sulfur loading.

Here, a modified hydrothermal process was applied to prepare the desired TOCs in a mixed solvent of distilled water and ethylene glycol (Shanghai sihewei Chemical Co., Ltd, $C_2H_6O_2$ >=99.0%) in a volume ratio of 1:1. In a typical process, 0.3 mol sodium hydroxide (Sinopharm Chemical Reagent, sodium hydroxide>=96%) was dissolved into 30 mL distilled water. After 30 min magnetic stirring, a clear sodium hydroxide aqueous solution was obtained. Meanwhile, 6 mmol tetrabutyl titanate (TBT, Shanghai Aladdin Biochemical Technology，TBT>=99.0%) was dissolved into 30 mL ethylene glycol to form 2 molL-1 TBT solution under a magnetic stirring. Subsequently, the as-prepared sodium hydroxide solution was poured into the TBT solution under violently magnetic stirring. 60 mins later, the final mixed solution was transferred and sealed into Teflon-lined stainless steel hydrothermal reactors. Then the sealed reactors were put into a blast drying oven pre-heated to 190 ºC. After hydrothermal reaction for14 h, the reaction product was purified with diluted hydrochloride aqueous solution and washed with distilled water for three times, respectively. Being dried at 60 ºC in a blast drying oven for 24h, and annealing at 550 ºC for 10 under the protection of Ar gas, the desired TOCs were finally obtained and collected for the following application.

In order to obtain the controlled TNCs, the as-prepared TOCs powder were nitridized at 950 ºC for 1 h under the atmosphere of mixed Ar and ammonia gas in a high temperature tube furnace. Finally, the yellow product were collected for the following application.

Subsequently, a two-step melt-diffusion process was conducted to obtain the final S@TOCs and S@TNCs. In the 1st step, sulfur were firstly mixed with TOCs and TNCs in a mass ratio of 4:1 by grinding in an agate mortar, respectively. Then, the ground sulfur containing mixtures was sealed into an Ar gas filled Teflon-lined stainless steel reactor. As follows, the reactor was put in a blast drying oven following by heating at 155 °C for 18 h, which could help sulfur to diffuse to the inner space and surface of nanowire and nanoparticle clots. When the oven was cooled to room temperature, the heat treated mixtures were collected and ground again for the 2nd heating step. During the 2nd step, the collected samples were put into a tube furnace and heat treated at 250 ºC for 30 min with a heating rate of 5 ºCmin^{-1} again, with the aim to remove the sulfur without compositing with TOCs and TNCs. Finally, the desired S@TOCs and S@TNCs were obtained. The controlled sample of S@ Ketjen black composite were prepared by using the same processes with S@TOCs and S@TNCs.

Scanning electron microscopy (FE-SEM, Hitachi S-4800) was applied to check the morphology of as-prepared TOCs and TNCs. High resolution image and elemental mapping of both products were taken by using transmission electron microscopy (TEM, FEI Talos) at an acceleration voltage of 100 kV. X-ray diffractometer (Bruker D8 Advance A25) using Cu–$K\alpha$ radiation ($\lambda = 1.54051$ Å) were adopted to characterize the crystal structure of the obtained TOCs and TNCs. The X-ray diffraction (XRD) results were recorded from 10 to 80 $^{\circ}$. The applied step size is 0.02 $^{\circ}$. Micromeritics ASAP 2020 automated adsorption apparatus was employed to testing the nitrogen adsorption / desorption isotherms phenomenon of the as-prepared TOCs and TNCs under 77 K. Then, according to the conventional Brunauer–Emmett–Teller (BET) equation, the surface area and the pore structure of the samples can be calculated. The loading of sulfur within the S@TOCs and S@TNCs were estimated by using thermal gravity analyzer of Netzsch STA-449F3.

The S@TOCs, S@TNCs and S@Ketjen black composite cathode was prepared by mixing with 20% acetylene black, and 10% poly (vinylidene difluoride) in N, N-methylprrrolidone as solvent. The electrochemical performance of the as-prepared composite cathodes were measured in CR2032 coin cells. Celgard 2500 membranes was used as separator. The applied electrolyte was 1 M LiTFSI in 1, 2-dimethoxyethane/1, 3 - dioxolane (DOL : DME = 1 : 1 by volume) with 2 % $LiNO_3$. The LSBs were assembled in an Ar-filled glove box with lithium foils as the counter electrodes. The average sulfur loading was about 1.0 mg·cm^{-2}. The applied ratio between electrolyte and mass loading of S within the cathode was ~ 20 μL • mg^{-1}. Galvanostatic charge/discharge performance tests were conducted at different C-rate (1C = 1675 mAh g^{-1}) within a voltage range of 1.7–2.8 V by using the Land CT2001A battery test system. The cut-off voltage window is chosen by referred to references [16, 26-31] and based on the Cyclic voltammetry measurements conducted on a VMP3-Bio-Logic multi-channel potentiostat at a scanning rate of 0.1 mV·s^{-1}. Note that the capacity was based only on the mass of sulfur alone.

During the typical preparation processes of the desired TOCs provided in Figure 1, initially, $Na_2Ti_9O_{19}$ nanowire clots (NTOCs) with a monoclinic structure, as manifested by the XRD pattern given in Figure S1 and illustrated in Figures 1a and 1b, were prepared by using the hydrothermal method described in supplementary information (SI). Subsequently, the as-prepared NTOCs were immersed into and washed with a large amount of HCl aqueous solution to remove most of Na^+ within NTOCs through ion exchange methods. Being further washed with distilled water and dried in a blowing oven, hydrogenated TOCs (HTOCs) were obtained and collected, see Figure 1c. The desired TOCs were successfully prepared after a low temperature annealing, as present in Figure 1d. Then the collected TOCs will be used as reservoirs for sulfur and LPSs, as illustrated in Figures 1e and 1f, respectively.

The morphology and phase structure of the as-prepared products are characterized by using SEM and XRD. The obtained SEM images, whose clarity and the resolution were modified by using the modification function of brightness, color saturation, tone and recolor of Microsoft PowerPoint2013, are shown in Figure 2. Uniform micro-sized clot particles can be observed from the SEM images given in Figures 2a and 2b. The average size of the secondary particles is around 2 μm. It is interesting to further find that all the particles are formed by the interconnected nanowires and nanowire bundles, as demonstrated in Figure 2c. Therefore, the obtained titania products were named as titanium oxide nanowire clots, namely TOCs. The XRD pattern exhibited in Figure 2d indicates that the product obtained being washed the precursor with hydrochloric acid contain two different phase of TiO_2, namely the tetragonal anatase TiO_2 and monclinic TiO_2 (B).

HR-S/TEM analysis results of TOCs and the elemental mapping analysis results of the final S/TOC composites presented in Figure 3 indicate that TOCs have a hybrid phase composition with a small amount of remained sodium. The atomic sodium content within the obtained titania are less than 10%, well matching with the analysis results of crystal structures. Figure 3a shows a TEM image of a typical as-prepared TOC with a diameter of ~ 100 nm. Firstly, Figure 3b gives an enlarged HRTEM image and the inset FFT pattern for the red square, which is well-indexed in Figure 3c, proving a tetragonal phase of anatase TiO2 in the as-prepared TOCs. In addition, Figure 3d gives another HRTEM image obtained from Figure 3a. The inset FFT pattern for the red square in Figure 3d, corresponding atomic-IFFT image in Figure 3e, and the well-indexed FFT pattern in Figure 3f consistently manifest another monoclinic phase of TiO2 (B), which should be derived from the desodiumized monoclinic $Na_2Ti_9O_{19}$ precursors. However, during the washing process with hydrochloric acid, the sodium ions had not been fully removed, therefore a small amount of sodium ion still was kept in the monoclinic structure of TiO_2 (B).

Furthermore, in this work, TiN clots (TNCs) were also successfully developed as a controlled materials by nitridizing the as-prepared TOCs under ammonia atmosphere at 950 °C. According to the XRD pattern provided in Figure S2a, the as-prepared TNCs is a pure phase osbonite TiN. No other impurity phase can be indexed from the obtained XRD patterns. Figures S2b and S2c present the nitrogen gas isotherm adsorption-desorption (BET) and BJH pore size distribution curves of as-prepared TNCs. Nevertheless, the nitridized TOCs still maintain the clots morphology, the nanowires within the TOCs were converted into TiN nanoparticles after the high temperature thermal treatment, as exhibited in Figures S2d, S2e and S2f. As a result, the specific surface area of the obtained TNCs is only 36.3 m^2g^{-1}, which are much lower than that of 270.1 m^2g^{-1} of TOCs calculated based on the nitrogen gas isotherm adsorption-desorption profile shown in Figure S3a. Furthermore, the average pore volume of TNCs also decrease dramatically from the 0.73 cm^3g^{-1} of TOCs to 0.35 cm^3g^{-1}, meanwhile, the pore size within TNCs increase obviously from 9.4 nm of TOCs to 34 nm, after the nitridization process under 950 °C.

Figure 3g shows the high resolution elemental mapping images of S/TOCs composites. It can be observed that all elements, including S, Ti, O and Na, are uniformly distributed. By mixing all the elements together, we can see that S are homogeneously absorbed on the surface of TiO_2, as the results of the strong chemical interaction between S and TiO_2. Benefited from the much larger BET specific surface area and the stronger chemical absorption capability of TOC, the S loading within the S/TOCs obtained by using the same loading process are 69%, which are much higher than the S loading within TNCs (50%), as present in Figure S3b.

Coin cell type lithium sulfur batteries (LSBs) were assembled by using S/TOCs, S/TNCs and S/Kejten black (KJB) composites as cathode in an Ar gas filled grove box. The electrochemical measurements results are shown in Figure 4 and S4, which further manifest that the special phase composition and nanostructure could effectively enhance the sulfur fixation capability of TOCs. As exhibited in Figure 4a, the LSBs using S/TOCs composite as cathode can deliver discharge capacities of 1163, 971, 761, 634, 533 and 430 mAh g^{-1} at the C-rate of 0.1C, 0.2C, 0.5C, 1C, 1.5C and 2C, respectively. The observed rate capability are much better than LSBs using S/TNCs and S/KJB as cathode, as demonstrated in Figure S4a and S4b. The specific capacity differences among LSBs using S/TOCs, S/TNCs and S/KJB as cathode become more obvious as the charge/discharge current density increases. The low inner resistance should be responsible for the observed outstanding rate capability, as indicated by the electrochemical impedance spectroscopy (EIS) given in Figure 4b and S4c. Figure S4d shows the typical cyclic voltammetry (CV) curves of LSBs using S/TOCs, and S/TNCs as cathode. However, the S/TNCs cathode exhibits a larger polarity than that of S/TOCs cathode, which is consistent with the results observed from EIS testing results. Above electrochemical testing results clearly prove that the TOCs can be a more promising sulfur reservoir due to the higher specific surface area and the lower charge transfer resistance resulted from the interconnected TiO_2 network. Although TiN should be theoretically more conductive than TiO_2, the TNCs formed by the fused TiN nanoparticles shows larger charge transfer resistance comparing to TOCs. Furthermore, the LSBs using S/TOCs composite as cathode also displayed an excellent cyclic stability. As present in Figure 4c, the LSBs using S/TOCs composite as cathode can still provide capacities of 427.6 and 404.5 mAh g^{-1} at C-rates of 1C and 2 C after 200 cycles, respectively. The corresponding capacity fading rate of each cycle is only ~0.14% and 0.11 % for the LSBs being (dis)charged 1C and 2C, respectively. The excellent cyclic stability should be ascribed to the enhanced chemical absorption to LPSs by the hybrid phase composition of anatase and beta TiO_2. As reported by Yang, et al, hybrid Anatase/Rutile nanodots-embedded covalent organic frameworks showed complementary polysulfide adsorption capability. [19] However, The initial several cycles at small current density face a capacity fade. As reported by S. Risse et al, [32] the majority of Li/S cells exhibit a sharp decay in electrochemical capacity at the beginning of the cycling process. This process has been attributed to the film formation of e.g. a SEI layer or an electrode passivation layer during the early cycling periods. Formation of these films are caused by electrolyte decomposition and unwanted side reactions of the polysulfide or lithium-ions in the vicinity of both electrodes' surfaces. After all available electrode surfaces are coated, this reaction stops. The dissolution of bulk sulfur without infiltrating into the TiO_2 nanowire clots could also be one of the probable reasons. Therefore, in order to reduce the initial capacity decay, it is very important to make sure the sulfur infiltration quality, especially to decrease the residual bulk sulfur. Additionally, the introduction of advanced separator or interlayer to further suppress the shuttle effect of soluble lithium polysulfide, meanwhile to decrease the formation of dead sulfur on the lithium anode surface. Advanced electrolyte is also required to form a stable SEI film on both anode and cathode.

In conclusion, a hydrothermal method assisted ion exchange strategy has been applied in this work to prepare the desired TOCs. The obtained TOCs demonstrate a high effective absorption surface area (270.1 m^2g^{-1}). The interconnected structure of nanowires could further boost the charge transfer within TOCs. The two phase composition further make the interconnected nanowires showed an enhanced surface chemical absorption capability to sulfur and polysulfides, as graphically illustrated in Figure 1f. Therefore, the synergistic effect generated from the unique structure of TOCs make TOCs the promising LPSs' reservoirs for the accommodation of sulfur and LPSs. The obtained S/TOCs cathode materials exhibit high specific capacity, high coulombic efficiency and excellent cyclic stability at 1C and 2C rate. the LSBs using S/TOCs composite as cathode can deliver discharge capacities of 1163, 971, 634 and 430 mAh g^{-1} at the C-rate of 0.1C, 0.2C, 1C and 2C, respectively. The corresponding capacity fading rate of each cycle is only ~0.14% and 0.11 % for the LSBs being (dis)charged 1C and 2C, respectively. Above observations prove that TOCs could be a promising sulfur reservoir for LSBs, however, additional work should be done in future work to construct a 3D conductive network to make it maintain the same energy storage performance at much higher sulfur loading.

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