



Effect of surface coating on the electrochemical performance of cathode made of sulfur–loaded TiO₂ nanotube arrays



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ABSTRACT

Amorphous phase TiO₂ nanotube (NT) arrays as sulfur reservoir are fabricated by anodization method on Ti plate used as current collector. Properties of the NT arrays before heat-treatment are evaluated with those after heat-treatment for applicability as a reservoir and conductor of sulfur electrode. A reasonably high amount of sulfur is loaded (14.8%) from 30% feed sulfur solution at 160 °C in the candidate NT array chosen as the sulfur reservoir. Three electrodes from the only NT array, the sulfur-loaded NT array with and without coating layer are evaluated on electrochemical performances. The sulfur electrode with coating layer, consisting of super-P and PVdF, exhibits the highest initial and retention capacity in discharge, respectively, of 1547 mAh g⁻¹ and 1085 mAh g⁻¹ up to 100 cycles. Rate capability at various C-rates from 0.1 to 30 C is also found to be exceptionally good.

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1. Introduction

Li-ion batteries used currently in various electronic devices do not possess high energy capacity, sufficient power density and long service life enough to meet the requirements for use in the various devices [1]. These limitations of Li-ion batteries are mainly due to the low capacity of LiCoO₂ (LCO) as a cathode. There are extensive research attempts to explore other materials as substitute to LCO. Among these, sulfur (S) is an attractive candidate for the next generation power sources in Li-S batteries with expected high energy density, low cost and eco-friendliness. S possesses high theoretical capacity of 1675 mAh g⁻¹ and high energy density of 2600 Wh kg⁻¹ [2]. The stated energy density of Li-S cell is thus many times higher than the Li-ion batteries. Yet, there are many problems associated with Li-S battery, such as short cycle life, low cycling efficiency, poor safety and a high self-discharge rate, that

have thwarted its commercialization [2]. S has insulating nature that results in low utilization of the active material. Furthermore, lithium polysulfides (Li₂S_n, 4 < n < 8) are formed as intermediates which dissolve in the electrolyte. The formation of polysulfides results in the loss of the active material and consequent severe capacity fading, but at the same time the dissolution of polysulfides in electrolyte is necessary for the functioning of Li-S battery [3]. Problem of volume expansion of electrodes during the lithiation process also causes fast capacity fading and low safety [4,5]. Hence, the challenges in Li-S battery research and design are to confine sulfur as well as in situ formed polysulfides and to alleviate the 'shuttle phenomenon'. There have been many attempts in this direction and many materials including mesoporous carbon [4,6–10], conducting polymers such as polyaniline (PAN), polypyrrole, and polythiophene [11–13], N-containing and stable structure forming polymers such as polyacrylonitrile [14–16] and metal oxides. Especially, TiO₂ [5,17] have been reported as a conductor, reservoir and support to host and confine in situ formed polysulfides. And, nanotubes (NT) forms of TiO₂ have also been reported as intercalation hosts [18,19]. TiO₂ NTs, are also good candidates for hosting sulfur which can be loaded in their well-defined pore structure and in situ formed polysulfides can also be confined within the pores and not spilled to the surface [17]. Anodization method which

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is convenient to fabricate highly ordered TiO₂ NTs can also be used to tailor their properties to load sulfur [20]. In view of the aforesaid, in the present work, TiO₂ NT arrays synthesized by anodization method were used as a conductor and reservoir for sulfur. Furthermore, amorphous and anatase phases of TiO₂ NTs have been investigated and compared for suitability at sulfur electrode. And, the surface of S-loaded TiO₂ NT was covered by coating the materials, which are sputtered–gold and mixtures of binder (PVdF) with conductor (super-P or AB). These similar enclosed-structure was reported with silicon electrode preventing the secession of active material [21,22]. Li-S cells prepared from the S-loaded TiO₂ NT arrays and surface coating reported in this study exhibited high electrochemical performance and cycle stability.

2. Experimental

2.1. Fabrication of TiO₂ nanotube arrays

TiO₂ nanotubes, NTs, of different diameters were synthesized by using the anodization method and Ti plate (Aldrich Co, 99.7%, T0.25 mm). Electrolyte NH₄F (0.3 M) and ethylene glycol added with distilled-water (H₂O) of 3 vol% were taken in a two–electrode electrochemical cell at 50 V and 30 °C. Time of the reaction was varied from 30 to 300 min to generate different NT arrays. NTs arrays were also subjected to heat–treatment under Ar atmosphere at 450 °C for 4 h in order to change to the anatase phase. TiO₂ NTs before (amorphous) and after (anatase phase) heat-treatment were evaluated as a reservoir for suitability at sulfur electrode. TiO₂ NT array synthesized at 180 min was selected as candidate material for sulfur insertion.

2.2. Electrode fabrication of S-inserted TiO₂ NT arrays

The insertion of sulfur (S, Alfa Aesar Co., 99.5%) into NT arrays selected as stated under the preceding sub-section was carried out with incipient wetness impregnation method using 10, 20 and 30 wt% sulfur solution dissolved in carbon disulfide (CS₂, Aldrich Co., ≥99%) at room temperature. Dissolved S solution was dropped on TiO₂ NT array using a pipette by gravity. For insertion and stability of sulfur, heat-treatment was then carried out with various temperatures of 150, 160, 170, 180 and 190 °C for 1 h. The sulfur–loaded NT array was cleaned in CS₂ solution to remove any surface adsorbed sulfur.

Different sulfur–loaded NT arrays were coated at the top with mixture (Conductor-Binder; CB) layer consisting of a conductor of super-P and a binder of Poly(vinylidene fluoride) (PVdF; Aldrich Co.). In the surface coating process, PVdF was mixed with super-P or AB (acetylene carbon black) in 1–methyl–2–pyrrolidinone (NMP, anhydrous, 99.5%, Aldrich Co.) in the ratio of 1:1:10 wt% (PVdF: super-P or AB: NMP). Finally, all the fabricated electrodes were dried in oven at 80 °C for 24 h. After dry, the weights of coated layers except that of TiO₂ and sulfur were measured by using Thermogravimetric Analyzer (TGA, Q50 of TA instruments co.) with the sensitivity of 0.1 µg. Apart from the electrodes prepared by the coating method as discussed above one electrode was coated with gold (Au) by sputtering (Cressington scientific instruments Co., sputter coater 108). Another one was also fabricated without any layer.

2.3. Characterization of various NT arrays and electrodes

As–prepared and sulfur loaded NT arrays were characterized by recording scanning electron microscopy (SEM) images on field emission scanning electron microscope (FE–SEM, Philips Co. XL30S FEG), X–ray diffraction patterns on (XRD, Bruker Co. DE/D2

PHASER) analysis. S–loaded NT arrays were characterized by recording SEM and also EDS (equipped at FE–SEM) mapping on Oxford INCA system. Thermogravimetric analysis (TGA) was carried out on Q50 of TA instruments Co.

2.4. Electrochemical measurements

Tests for the evaluation of electrochemical properties were performed using a half coin type cell of CR2032(Ø20, T3.2 mm). The S–loaded TiO₂ NT arrays supported electrodes were used directly as the working electrode with or without coating layer and Li metal was used as the counter electrode. The Celgard 2400 membrane was used as the cell separator and the electrolyte (1 M Lithium bis(trifluoromethane sulfonyl) imide; LiTFSI) was dissolved in a mixed solvent comprising of 1,2–dimethoxyethane (DME) and 1,3–dioxolane (DIOX) (1:1 in v/v). The entire cell assemblies were performed in a glove box (KK–021AS, Koreakiyon Co.) filled with pure Ar. Impedance experiments were performed on an electrochemical workstation (VMP3, BioLogic Co.) between 10 mHz and 1 MHz. Galvanostatic charge/discharge and cyclic voltammogram experiments were carried out using a battery test system (WBCS3000L, WonA Tech Co.). Cyclic voltammograms (CV) for electrodes were measured in an electrochemical window from 3.0 to 1.0 V for S–inserted TiO₂ NTs electrode at a scan rate of 0.1 mV s^{–1}. The cycling behaviors were studied at different applied currents of 0.1–30 C–rate in a cut–off voltage range of 1.0–3.0 V.

3. Results and discussion

3.1. Synthesis and characterization of nanotubes arrays

Anodization method was used to synthesize various NT arrays by the variation of time. Variation of time affected the surface morphology as well as pore structure of the NT arrays. FE–SEM images of the top and the cross–sectional view of TiO₂ NT arrays synthesized at different time intervals were recorded at Fig. 1. The pore size and surface morphology of the NT arrays varied as a function of time. NT arrays synthesized at different time intervals within the range of 60–240 min have uniform top view or pore size or structure. The pore size is around 100 nm. However, NT arrays synthesized at 30 min or 300 min have unclear surface and the pore structure is not symmetric. The same can be stated about their cross–sectional view where tube structure is fractured especially at 300 min. Hence, on the basis of sound pore structure and intact morphology, the NT arrays synthesized after 180 min was selected for the further work.

Fig. 2 presents FE–SEM images of the as–prepared TiO₂ NT arrays and after subjecting these to heat–treatment at 450 °C under Ar atmosphere for 4 h. The changes in the pore structure of TiO₂ NTs as a consequence of heat–treatment can also be supported from the FE–SEM images. The pore sizes of NTs before and after heat–treatment were nearly 102 nm and 115 nm, respectively. In other words, pore size was widened after the heat–treatment. The amorphous phase TiO₂ was converted to the anatase phase after the heat–treatment as revealed from their respective XRD patterns as shown in Fig. 2(c). These correspond to Ti (JCPDS card #44–1294), anatase TiO₂ (JCPDS card #21–1272). In the present study of Fig. 2(d), cyclic voltammograms (CV) result of an electrode using anatase phase TiO₂ after heat–treatment presents reaction voltage region similar to that of sulfur. A voltage window between 2.5 and 1.5 V was generated for the anatase TiO₂ NTs. The discharge (oxidation) peak at 1.7 V and charge (reduction) peak at 2.1 V were obtained. On the contrary, the CV of the amorphous phase has flat charge/discharge curves meaning thereby it is hardly react with the Li ion. TiO₂ NT arrays having amorphous phase were selected as

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