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Titanium oxide nanofibers attached to zinc oxide nanobranches as a novel nanostructure for lithium ion batteries applications

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In this study, the performance of titanium oxide to be used as an anode in lithium ion batteries has been improved by producing this oxide in nanofibrous form and outgrowing zinc oxide nanobranches around the titanium oxide nanofibers obtained. First, electrospinning of a colloidal solution consisting of titanium isopropoxide/poly(vinyl acetate) zinc nanoparticles has been achieved to produce polymeric nanofibers embedding solid nanoparticles. Calcination of the electrospun nanofibers mats obtained in air at 600 °C produced TiO₂ nanofibers containing ZnO nanoparticles; ZnO-doped TiO₂ nanofibers. The ZnO nanoparticles formed have been exploited as seeds to outgrow ZnO branches around the TiO₂ nanofibers using a hydrothermal technique. As an anode in a lithium ion battery, the prepared nanostructure exhibited a high rate capacity of 1232 mAhg^{-1} . Considering the distinct physiochemical characteristics of TiO₂ the proposed nanostructure might open an avenue for TiO₂ to be used for high energy density lithium-ion batteries with higher performances.

Key words: Titanium oxide, Zinc oxide, Lithium ion batteries, Electrospinning.

Introduction

A major challenge for modern societies is energy storage. Lithium ion batteries offer a promising solution to the energy storage dilemma, with their inherently high volumetric, gravimetric energy density, high working voltage and low self-discharge rate. The next generation of lithium ion batteries will require safer and less costly electrodes [1, 2]. Earlier, materials for the anode for lithium ion batteries have rarely been studied. A number of transition metal oxides have been proposed as anode materials. For instance, it has been shown that metal oxide nanoparticles of Co, Ni, Mn, Cu and Fe show capacities of around 700 mAh/g [3, 4]. Titanium dioxide (TiO₂) is a functional material that has potential applications for use as catalytic devices, solar cells and optoelectronic devices [5]. TiO₂ can be produced in various forms such as anatase, rutile, brookite, TiO₂ B (bronze), TiO₂R (ramsdellite), TiO₂H (hollandite) TiO₂II (columbite) and TiO_2III (baddeleyite). However, TiO_2 in the anatase form is considered the most electroactive Li-insertion host among these TiO₂ polymorphs [6]. Titanium oxide particularly in the anatase form has been used as an anode material for lithium ion batteries with a low production cost and high

Nanostructured materials as an anode in lithium-ion batteries stimulate great interest since they demonstrate a better improvement in electrochemical properties than that of the respective micrometre materials because they provide a large contact area between the electrolyte and electrode

capacity [7, 8, 9], however its capacity is still unsatisfactory. Therefore, much research is going on to modify TiO_2 to

improve its efficiency as an anode to exploit the other intre-

sting physiochemical characteristics of this semiconductor.

and a shorter diffusion path for Li ions and electrode and a shorter diffusion path for Li ions and electrons [10, 11]. Among the reported nanostructures, one dimensional (1D) nanostructures revealed distinct results, for instance TiO₂ nanorods exhibit acceptable performance [12] due to the axial ratio impact. Actually, the axial ratio has a distinct effect since manganese nanofibers gave excellent performance as these nanofibers have very high axial ratio [13].

Moreover, modification of TiO_2 nanomaterials with other semiconducrors could affect the charge transfer properties between TiO_2 and external systems [14] which might have a positive effect on lithium batteries performance. Zinc oxide (ZnO) is an excellent semiconducting material with extraordinary physical and chemical stability; moreover, it is a large band gap semiconductor. Therefore, it has received world wide attention because of its wide application in solar cells, semiconductor lasers, surface acoustic wave devices and secondary batteries [15]. ZnO is a potential candidate in the field of light emitting diodes, varistors,

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gas sensors, photocatalysts, solar cell electrodes [16-22]. Compared with transition metal oxides pure zinc oxide has been rarely used as an anode material in lithium ion batteries. The reason for the poor performance is believed to be because of the low electronic conductivity, the large volume change during the lithium insertion-extraction process and poor cycleability. However, ZnO nanostructures have given a good performance [23]. Accordingly, the main aim of this study was incorporation of ZnO in TiO₂ in novel 1D nanostructures to exploit both parameters affecting the performance of titania.

In this study, we introduce a TiO_2 -ZnO 1D hierarchical nanostructure composed of TiO_2 (anatase) nanofibers with ZnO branches attached to the main nanofibers. This novel morphology was obtained by first producing TiO_2 nanofibers via an electrospinning process, and then a hydro-thermal treatment was achieved to outgrow ZnO branches. The new nanostructure strongly modifies the performance of titanium oxide as an anode in a lithium ion battery.

Experimental

Titanium (1V) isopropoxide (Ti(Iso), 98.0 assay) was purchased from Junsei Co. Ltd., Japan. Poly (vinyl acetate) (PVAc, MW = 500,000 g/mol) and N,N-dimethylformamide (DMF, 99.5 assay) were obtained from Aldrich USA and Showa Co. Japan, respectively. Zinc powder, bis hexamethylene triamine (BHT), zinc nitrate hexahydrate (ZNH) and acetic acid (99.7 assay) were obtained from Showa, Co. Japan. All these materials were used without any further purification.

Preparation of ZnO-doped TiO₂ nanofibers

Generally, the electrospun solution is either a polymer(s) dissolved in a proper solvent or a metallic precursor/ polymer solution. The distinct feature of these solutions is that they have to be completely miscible. In other words, in the case of adding metallic precursor, it should be soluble in a suitable solvent since it has to hydrolyze and polycondensate in the final precursor/polymer mixture to form the gel network. However, in this study, we have utilized a different strategy to produce TiO2 nanofibers containing ZnO seeds; a colloidal solution containing Ti(Iso), PVAc and zinc powder (particle size < 50 nm) was electrospun. Electrospinning of the colloidal solution was achieved as follow: 5 g of PVAc solution was made by dissolving PVAc granules in DMF solvent at room temperature with vigorous stirring, the polymer content in the final solution was 14 wt%. The prepared polymer solution was mixed with 5 g of Ti(Iso) and a few drops of acetic acid were added untill the solution became transparent. Later on, 0.1 g of zinc powder was added to the polymeric solution. The mixture was stirred for 10 minutes, so a colloid was obtained. A high voltage power supply (CPS-60 K02V1, Chungpa EMT Co., Republic of Korea) was used as a source of the electric field. The colloid was supplied through a plastic syringe attached to a capillary tip. A copper wire originating from a positive electrode (anode) connected with a copper pin was inserted into the colloid and a negative electrode (cathode) was attached to a metallic collector covered with a polyethylene sheet. Briefly, the colloid was electrospun at 6 kV voltage and 15 cm working distance (the distance between the needle tip and the collector). The nanofiber mats formed were initially dried for 24 h at 80 °C under vacuum and then calcined in air atmosphere at 600 °C for 1 h with a heating rate of 5 °C minute⁻¹.

Fabrication of ZnO outgrowths

ZnO outgrowths were fabricated by a solution based hydrothermal method introduced [24]. The calcined nanofibers were treated with two chemicals bis-hexamethylene triamine and zinc nitrate hexahydrate to grow the outgrowths. Typically, 1.076 g of bis-hexamethylene triamine was dissolved in 50 g of water. In another bottle 1.487 g of zinc nitrate hexahydrate were dissolved in 50 g of water. To the latter, 10 mg of the calcined nanofibers were added and vigorously stirred for 4 h. The two solutions were well mixed and placed in a teflon crucible inside an autoclave. The later was made of stainless steel with a height of 15 cm and diameter of 7 cm. The autoclave was maintained at 150 °C for 1 h and then naturally cooled to room temperature. The product obtained was filtered off, washed several times with distilled water and dried at 60 °C for 12 h for further analysis.

Characterization

Surface morphology of nanofibers was studied by a JEOL JSM-5900 scanning electron microscope, JEOL Ltd., Japan and a field-emission scanning electron microscope equipped with EDX (FE-SEM, Hitachi S-7400, Japan). The phase and crystallinity were characterized using a Rigaku X-ray diffractometer (Rigaku Co, Japan) with Cu Ka $(\lambda = 1.54056 \text{ Å})$ radiation over a range of 20 angles from 20 to 80°. High resolution images and selected area electron diffraction patterns were observed by a JEOL JEM 2010 transmission electron microscope (TEM) operating at 200 kV, JEOL Ltd., Japan. Galvanostatic charge-discharge profiles were made on a computer-controlled battery testing unit (BTS 2004, Japan). Composite titanium oxide-zinc oxide nanostructure electrodes were prepared by blade coating a slurry of 90 wt% pyrolytic carbon, 8 wt% poly (vinylidene fluoride), and 2 wt% carbon black dispersed in N-methyl-2-pyrrolidine on a copper foil. This was dried at 110 °C in an air oven and punched out as circular sheets. The prepared electrodes were coupled with an electrolyte of 1 M LiPF₆ in a 1:1 (v/v) mixture of EC-DMC (1:1 by volume) and coin cells were assembled in an argon-filled glove box (OMNI-LAB system). The lithium foil was employed as counter and reference electrodes and the composite zinc oxide-titanium oxide electrode was employed as a working electrode. The lithium insertion electrochemical performance of the composite electrodes were examined on a computercontrolled battery-testing unit (BTS 2004, Japan) between 3.000 and 0.002 V.

Results and Discussions

Fig. 1A and 1B show the SEM images of the dried zinc powder-titanium isopropoxide/poly (vinyl acetate) (Zn-Ti(iso)/PVAc) nanofibers at low and high magnifications. As can be clearly seen, smooth and continuous nanofibers are formed by electrospinning of the prepared colloid. It is clear from these figures that addition of zinc powder has not affected the morphology of the nanofibers as the zinc nanoparticles-free solution revealed nanofibers mats with a good morphology; the regular shape and absence of beads are quite clear from these SEM images. The small size of the zinc nanoparticles utilized compared with the PVAc nanofibers resulted in imprisoning all the nanoparticles inside the nanofibers. Fig. 1C and 1D show SEM images of the Zn-Ti(Iso)/PVAc nanofiber mats at low and high magnifications after calcination at 600 °C for 1 h. Calcination of the electrospun nanofiber mats obtained results in a sharp decrease in the average diameter of the nanofibers obtained compared to the original ones. The reduction in the nanofiber diameters can be explained by the removal of the polymer by calcination at high temperature. To ensure that the added zinc particles have been oxidized and not evaporated since the utilized calcination temperature is higher than the melting point of zinc metal (~420 °C), FE-SEM EDX analysis was utilized; the results are presented in Fig. 2. As shown in this figure, zinc metal can be detected which means that the TiO₂ nanofibers prepared contain ZnO nanoparticles which were exploited as seeds to outgrow the ZnO branches.

The nanofibers obtained after calcination were allowed to undergo a hydrothermal process according to the above mentioned procedure to produce zinc oxide outgrowths on the titanium oxide nanofiber. Figs. 3A and 3B give SEM images at low and high magnification, respectively for the product obtained by the hydrothermal treatment process. As



Fig. 1. SEM images of the dried Zn-Ti(iso)/PVAc at low and high magnifications; (A and B), and after calcination at 600 °C for 1 h; (C and D).



Fig. 2. EDX results for the calcined nanofibers.



Fig. 3. SEM; (A and B) and FE-SEM; (C) images of hydrothermally-treated nanofibers.

can be clearly seen, dot like outgrowths are spread all over the surface of the nanofibers. To image these spots, we used FE-SEM analysis to get clear information. Fig. 3C shows the resulting FE-SEM image. As the hydrothermal process utilized has been reported to synthesize zinc oxide nanorods [24], we can say that the newly apparent branches on the prepared TiO₂ nanofibers are ZnO outgrowing branches.

XRD is a reliable technique to investigate the nature of any crystalline compounds. Typical XRD patterns of the nanofibers obtained after both the calcination and hydrothermal treatment processes are presented in Fig. 4. As shown in pattern (A) which refers to the calcined nanofibers, the anatase phase of titanium oxide has been obtained. The existence of strong crystalline peaks at 2θ values of 25.2° . 37.800°, 48.049°, 53.890°, 55.060°, 62.119°, and 75.029° correspond to the crystal planes of (101), (004), (200), (105), (211), (213), and (215) indicates the formation of anatase titanium dioxide (JCPDS card No 21-1272). In addition to these peaks, other peaks were created due to the hydrothermal treatment process as shown in the pattern (B). The newly apparent peaks at 2θ values of 31.66° . 34.22°, 36.16°, 47.86°, 56.52°, 62.66°, 67.8°, and 68.96° correspond to the crystal planes of (100), (002), (101), (102), (110), (103), (112), and (201) confirm the formation of zinc oxide (JCPDS card No 36-1451). It is worth mentioning that, some peaks corresponding to ZnO could be seen in



Fig. 4. Typical XRD pattern of calcined nanofibers; (spectra A) and the nanofibers obtained after the heat treatment process (spectra B).

pattern (A), however, these peaks have a small intensity. Therefore, one can say that the calcined nanofibers contain ZnO as a trace amount and/or the presence of this oxide in the form of dispersed nanoparticles. This finding supports the FE SEM results indicating that the calcined nanofibers do contain zinc oxide.

It is well known that transmission electron microscope analysis (TEM) can be utilized to differentiate between the crystalline and amorphous structures of materials. Fig. 5 shows TEM and high resolution TEM (HRTEM) images of the hydrothermally-treated nanofibers which are consistent with the FESEM images in morphology. As shown in Fig. 5A there are small outgrowths obtained everywhere on the main nanofiber. The upper inset in Fig. 5A shows the (SAED) pattern of the main TiO₂ nanofiber, which indicates good crystallinity of the synthesized material. The lower inset in Fig. 5A shows the SAED pattern of ZnO branch, where good crystallinity can be observed as well. Fig. 5B shows a HR TEM image for a part of a main TiO₂ nanofiber, existence of the atomic planes in a parallel form reveal excellent crystallinity. The inverse fast Fourier transformation (FFT) image (the inset) also confirms the good crystallinity in accordance with HRTEM and SAED results. Fig. 5C shows a high-resolution TEM image of ZnO outgrowths. The synthesized ZnO nanobranches do have a good crystalline structure; the same result can be concluded from the inverse fast Fourier transformation (FFT) image (the corresponding inset). Overall the TEM results reveal the production of titanium oxide nanofibers with well developed ZnO outgrowths; both titanium oxide and zinc oxide have good crystallinity.

In order to confirm that the observed nanobranchs are composed of pure zinc oxide, TEMEDX analysis has been invoked. The analysis has been performed at two different points as shown in Fig. 6. As shown in this figure and its corresponding panels, there is a large difference in the intensity of titanium and zinc signals at the two chosen points. Therefore, one can say that the chosen area in Fig. 6A contains a maximum titanium content. However, Fig. 6B represents an almost titanium-free point as the titanium



Fig. 5. TEM; (A) and high resolution TEM (HRTEM); (B and C) images of the hydrothermally-treated nanofibers. The upper and lower insets in figure A show the SAED pattern of TiO_2 and ZnO counterparts, respectively. The insets in figures C and D demonstrate the corresponding fast Fourier transformation pattern.



Fig. 6. TEM-EDX results for a part form the main nanofiber; (A) and another at an outgrowing branch created by the hydrothermal treatment process; (B).

peak is almost absent and an intense zinc peak is present. Therefore one can say that the ZnO branches produced by the hydrothermal method are titanium-free. Considering that the electron beam in the TEMEDX analysis had specific width which was more than the titanium oxide nanofiber size, the small atomic percentage of titanium in Fig. 6B might be explained as coming from a small part of bordering titanium dioxide nanofiber.

Lithium ion battery study

Fig. 7 shows the galvanostatic charge-discharge curves for the TiO₂-ZnO nanostructures prepared. A first lithium insertion capacity of 1232 mAh g⁻¹ has been observed which is far ahead of the previous literature about pristine TiO₂ (~350 mAh g⁻¹) [12, 25]. Nanostructured TiO₂ is the best choice for lithium battery anodes not only due to a



Fig. 7. The galvanostatic charge-discharge curves for the TiO_2 -ZnO nanostructure prepared.

low voltage insertion host for Li, but also because of a fast Li insertion/extraction host. The need for a passivation layer at the contact to the liquid electrolyte has been ruled out due to the potential characteristics of TiO₂ nanofibers. Among the various forms, the anatase phase is more stable despite of its surface tension. The high ability of the anatase TiO₂ structure to accommodate charges in the form of H⁺ and Li⁺ ions promoted the higher capacity values of the nanostructures. By the utilization of an electric field as a driving force on the anatase TiO2 electrodes lithium ions can be inserted and extracted, which is referred as an intercalation. Titanium oxides nanofibers provide more sites for lithium ion intercalation/de-intercalation which dramatically increased the capacity values. The insertion of positively charged ions has been balanced with an uptake of electrons to preserve the overall charge neutrality. The high capacity of the prepared nanofibers is attributed to the high surfaceto-volume ratio, shorter distance transportation of electrons as well as lithium ions and the increased area of the electrode/ electrolyte interface. Reaction kinetics were enhanced due to the aforementioned advantages of titanium oxide nanofibers and the increment of the reaction kinetics was responsible for the increased cell capacity, better capacity retention and high charge/discharge rates. Although titanium oxide nanofibers provide various advantages, this lead to a greater vulnerability due to attack by the electrolyte which prolongs the lithium insertion/extraction process. This was effectively cured by the zinc oxide branches which were effectively attached on the titanium oxide nanofibers. This suppress the corrosion of current collectors and anodic breakdown of the electrolyte solution which provides a high stability.

Conclusions

Electrospinning of a zinc powder/Ti(Iso)/PVAc colloid can be successfully achieved. Calcination of the electrospun mats results in complete elimination of the polymer and produces titanium oxide nanofibers doped with zinc oxide nanoparticles in a good morphology. The spread of zinc oxide nanoparticles on the surface of the titanium oxide nanofibers can be utilized as seeds to hydrothermally synthesize zinc oxide nanobranches around the main nanofibers. The newly proposed nanostructure revealed good behavior when it was exploited as an anode in a lithium ion battery. Overall, this study has introduced a considerable solution to overcome the drawbacks constraining the use of titanium oxide nanostructures in lithium ion batteries.

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