Case Report

Electrospun Titania Oxide Nanofibers Coupled Zinc Oxide Nanobranches as a Novel Nanostructure for Lithium Ion Batteries Applications

Muzafar A. Kanjwal,1 Nasser A. M. Barakat,2 Faheem A. Sheikh,2 and Hak Yong Kim2

1Department of Polymer Nano Science and Technology, Chonbuk National University, Jeonju 561-756, Korea
2Organic Materials and Fibers Engineering, Chonbuk National University, Jeonju 561-756, Korea

Address correspondence to Hak Yong Kim, khy@chonbuk.ac.kr

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Abstract First, electrospinning of colloidal solution consisting of titanium isopropoxide/poly(vinyl acetate) zinc nanoparticles has been achieved to produce polymeric nanofibers embedding solid nanoparticles. Calcination of the obtained electrospun nanofiber mats in air at 600 °C has been revealed to produce TiO2 nanofibers containing ZnO nanoparticles; ZnO-doped TiO2 nanofibers. The formed ZnO nanoparticles have been exploited as seeds to outgrow ZnO branches around the TiO2 nanofibers using a hydrothermal technique. As anode in lithium ion battery, the prepared nanostructure exhibited a high rate capacity of 1232 mAhg–1.

Keywords titanium oxide; zinc oxide; lithium ion batteries; electrospinning

1 Introduction

Lithium ion batteries offer promising solutions 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 the lithium ion batteries will require safer and less costly electrodes [6, 7]. Earlier, the materials as anode for lithium ion batteries are rarely studied. A number of transition metal oxides have been proposed as anodes. 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 to be used as catalytic devices, solar cells and optoelectronic devices [8]. TiO2 can be produced in various forms such as anatase, rutile, brookite, TiO2 B (bronze), TiO2 R (ramsdellite), TiO2 H (hollandite), TiO2 II (columbite) and TiO2 III (baddeleyite). However, TiO2 in anatase form is considered the most electroactive Li-insertion host among these TiO2 polymorphs [9]. Titanium oxide particularly in anatase phase has been used as an anode material for lithium ion batteries with low production cost and high capacity [1,2,5], however its capacity is still unsatisfactory. Therefore, much research is going on to modify the TiO2 to improve its efficiency as anode to exploit the other interesting physiochemical characteristics of this marvel semiconductor.

2 Preparation of ZnO-doped TiO2 nanofibers

Generally, the electrospun solution is either 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 solution. In other words, in a case of adding metallic precursor, it should be soluble in a suitable solvent since it has to hydrolyze and polycondense in the final precursor/polymer mixture to form the gel network.

3 Fabrication of ZnO outgrowths

The calcined nanofibers were treated with two chemicals: bis-hexamethylene triamine and zinc nitrate hexahydrate for growing 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 latter 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 obtained product was filtered off, washed several times by distilled water and dried at 60 °C for 12 h for further analysis.

4 Results and discussions

Figures 1A and 1B illustrate the SEM image in low and high magnifications, respectively, for the obtained product.
by the hydrothermal treatment process. As it can be clearly seen, dots like outgrowths are spread all over the surface of nanofibers. To observe these spots, we invoked FE-SEM analysis to get clear information. Figures 1C shows the resulted FE-SEM image. As the utilized hydrothermal process has been reported to synthesize zinc oxide nanorods, the formed branches from TiO₂ are ZnO outgrowths as supported by XRD.

XRD is a reliable technique to investigate the nature of any crystalline compounds. A typical XRD pattern of the obtained nanofibers after both of calcination and hydrothermal treatment processes is presented in Figure 2. As shown in the pattern (A) which refers to the calcined nanofibers, anatase phase of titanium oxide has been obtained. Existence of strong crystalline peaks at 2θ values of 25.2°, 37.80°, 48.049°, 53.890°, 55.060°, 62.119° and 75.029° corresponding 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 value of 31.66°, 34.22°, 36.16°, 47.86°, 56.52°, 62.66°, 67.86°, and 68.96° corresponding 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 noteworthy mentioning that some peaks corresponding to ZnO could be seen in pattern (A), however, these peaks have a small intensity. Therefore, we can say that the calcined nanofibers contain ZnO in a trace amount and/or presence of this oxide in the form of dispersed nanoparticles. This finding supports the FE SEM results indicate that the calcined nanofibers do have zinc oxide.

4.1 Lithium ion battery study

Figure 3 shows the galvanostatic charge-discharge curves for the prepared TiO₂-ZnO nanostructure. The first lithium insertion capacity of 1232 mAh g⁻¹ has been observed which is far ahead of the previous literatures about pristine TiO₂ (∼350 mAh g⁻¹). Nanostructured TiO₂ is the best choice for lithium battery anodes not only due to a low voltage insertion host for Li, but also for a fast Li insertion/extraction host. The need of a passivation layer at the contact to the liquid electrolyte has been ruled out due to the potential characteristics of TiO₂ nanofibers. 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 overall charge neutrality. The high capacity of the prepared nanofibers was attributed to the high surface-to-volume ratio, shorter length transportation of electronic as well as lithium ions and the increased area of the electrode/electrolyte interface. Reaction kinetics was
enhanced due to the aforementioned advantages of titanium oxide nanofibers and the increment of the reaction kinetics has become responsible for the increased cell capacity, better capacity retention and high charge/discharge rates. Though the titanium oxide nanofibers provide various advantages, it leads to a greater vulnerability due to the attack by the electrolyte which prolonged the lithium insertion/extraction process. It suppresses the corrosion of current collectors and anodic breakdown of the electrolyte solution which provides the high stability.

5 Conclusion

Electrospinning of zinc powder/Ti(Iso)/PVAc colloid can be successfully achieved. Calcination of the electrospun mats results in a complete elimination of the polymer and producing titanium oxide nanofibers doped with zinc oxide nanoparticles in a good morphology. The spread zinc oxide nanoparticles in the surface of the titanium oxide nanofibers can be utilized as seeds to hydrothermally synthesize zinc oxide nanobranches around the main nanofibers. Overall, this study introduced a considerable solution to overcome the drawbacks constraining utilizing the titanium oxide nanostructure in lithium ion batteries.

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References


