Synthesis of TiO$_2$ nanoparticles induced by electron beam irradiation and their electrochemical performance as anode materials for Li-ion batteries

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ABSTRACT

We introduce a new synthesis method to prepare small TiO$_2$ nanoparticles with a narrow particle size distribution, which is achieved by electron beam (E-beam) irradiation. The effects of E-beam irradiation on the synthesis of TiO$_2$ nanoparticles and the electrochemical performance of TiO$_2$ nanoparticles as alternative anode materials for Li-ion batteries are investigated. The TiO$_2$ nanoparticles induced by E-beam irradiation present better cycling performance and rate capability than the TiO$_2$ nanoparticles synthesized by normal hydrolysis reaction. The better electrochemical performance is attributed to small particle size and narrow particle size distribution, resulting in the large surface area that provides innumerable reaction sites and short diffusion length for Li$^+$ through TiO$_2$ nanoparticles.

Keywords : TiO$_2$, nanoparticle, electron beam irradiation, anode material, Li-ion battery

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1. Introduction

Titanium oxide (TiO$_2$) has received much attention as the most promising alternative to the conventional graphite anode of Li-ion batteries for hybrid electric vehicle (HEV) and electric vehicle (EV) applications, primarily due to its advantageous material properties, such as enhanced safety, good capacity retention during cycling and non-toxicity [1-2]. Although TiO$_2$ anode exhibits higher operating voltage (~1.7 V vs. Li/Li$^+$) than carbon-based anode (~0.1 V vs. Li/Li$^+$) and it reduces the overall cell voltage accordingly, the high operating voltage of TiO$_2$ anode can prevent the formation of a SEI (solid electrolyte interface) layer under 1 V, which can lead to irreversible capacity loss [3-5]. The performance of TiO$_2$ anode for Li-ion batteries depends strongly on the crystalline phase, the morphology, and the porosity of the structure. Recently, nanostructured TiO$_2$ materials, such as nanoparticles, nanorods, nanowires, and nanotubes have been studied to improve the performance of TiO$_2$ anode, due to their high rate capability, resulting from the large surface area that provides innumerable reaction sites and short diffusion length for Li$^+$ [6].

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Various synthesis methods have been developed for the preparation of TiO$_2$ nanomaterials, such as hydrolysis, sol-gel, hydrothermal reaction, templating, and anodization [4,5,7-9]. The hydrolysis reaction is a very simple method for the synthesis of TiO$_2$ nanoparticles which are more appropriate to use as anode materials of Li-ion batteries, primarily due to their easy mass production and application to slurry process. However, most TiO$_2$ nanoparticles synthesized by the hydrolysis reaction exhibit a wide particle size distribution which is often inhomogeneous with respect to the location inside the electrode and leads to nonuniform electrochemical performance [7]. Herein, we introduce a new synthesis method to prepare the TiO$_2$ nanoparticles of a narrow particle size distribution as well as a homogeneous dispersion throughout the electrode, which can create a large amount of radicals over entire polymer samples [10-12]. In this work, we investigated the effects of E-beam irradiation on the synthesis of TiO$_2$ nanoparticles and their electrochemical performance as alternative anode materials for Li-ion batteries to enhance electrochemical performances because the high density of the E-beam can create a large amount of radicals over entire polymer samples [13-15].

2. Experimental Section

2.1. Material preparation and characterization

To prepare TiO$_2$ nanoparticles by the hydrolysis reaction, titanium (IV) isopropoxide was dissolved in anhydrous ethanol to form titanium (IV) ethoxide of 0.1 M concentration, and then 2 mL deionized (DI) water was added to 60 mL titanium (IV) ethoxide during stirring. After 30 min stirring, the sample was filtered and dried at 100°C for 4 h. In the E-beam irradiation process, 60 mL titanium (IV) ethoxide sealed in a transparent bag with 2 mL DI water was irradiated by E-beam of 2 MeV in energy with exposures of 380 kGy using an ELV-8 (EBTech©) irradiation equipment. The irradiated sample was also filtered and dried at 100°C for 4 h. The final products of each sample were obtained by the thermal treatment at 450°C for 3 h in air using a quartz tube furnace.

The morphology of TiO$_2$ nanoparticles was characterized by scanning electron microscopy (SEM, JEOL, JSM-7000), and the crystal structure was confirmed by X-ray diffraction (XRD, Bruker AXS, D8 ADVANCE). The particle size distribution of samples was measured by particle size analyzer (PSA, NANOPHOSX, NX0046) with photon cross-correlation spectroscopy from 1 nm to 10 µm, and the Brunauer-Emmett-Teller (BET) surface area analysis was performed using a surface area analyzer (BET, BEL Japan Inc., BELSORP-max).

2.2 Cell fabrication and electrochemical analysis

To fabricate electrode, a mixture of 80 wt% of each TiO$_2$ active material and 10 wt% acetylene black was added to N-methyl-2-pyrrolidene (NMP) solvent containing 10 wt% polyvinylidene fluoride (PVdF). This slurry was pasted onto an Al foil substrate and dried at 120°C for 4 h in a vacuum oven. The dried electrodes were pressed and punched into a disc shape with a diameter of 1.6 cm. The loading level and electrode density of all electrodes were about 2.0 mg cm$^{-2}$ and 1.0 g cc$^{-1}$. The electrochemical properties of the prepared electrodes were evaluated using 2016 coin-type cells that were assembled in an argon-filled glove box. A polypropylene separator soaked with a liquid electrolyte (Panax Etec©) of 1 M LiPF$_6$ dissolved in a 1:1:1 volume ratio of ethylene carbonate (EC), ethyl methyl carbonate (EMC), and dimethyl carbonate (DMC) was placed between the electrode and a Li metal foil in the cell.

The charge-discharge characteristics of the fabricated cells were measured with a battery cycler (WBCS3000, Won-A Tech©). For the activation of the cells, the cells were charged in a constant current (CC)-constant voltage (CV) mode at 0.2 C (1 C = 200 mA g$^{-1}$) until 1.0 V of 0.01 C cut-off, and discharged in a constant current (CC) mode at 0.2 C until 3.0 V for the first two cycles. From the 3$^{rd}$ cycle onward, the cells were galvanostatically charged in the CC-CV mode and discharged in the CC mode at various current densities between 1.0 and 3.0 V (vs. Li/Li$^+$) for the cycling performance and rate capability tests.

3. Results and Discussion

Fig. 1 shows the SEM images of the hydrolysis synthesized TiO$_2$ nanoparticles and the E-beam irra-
Synthesis of TiO$_2$ nanoparticles induced by electron beam irradiation and their electrochemical performance as anode.

All samples were composed of nano-sized primary particles and secondary particles of micro-size, which were formed by aggregation of the primary particles. The hydrolysis TiO$_2$ sample showed a wide size distribution. The primary particles of hydrolysis TiO$_2$ presented a fine size of 100~500 nm, but they were easily agglomerated by the attractive force between individual particles due to their fine size. The agglomerated primary particles were further aggregated to the secondary particles with 5~10 $\mu$m size. On the other hand, the primary and secondary particles of E-beam TiO$_2$ showed not only narrower particle size distribution, but also smaller particle size than that of hydrolysis TiO$_2$. Although the primary particles of E-beam TiO$_2$ presented finer particle size of 100~200 nm, their agglomeration was suppressed by the E-beam irradiation, resulting in smaller secondary particles of 0.5~1 $\mu$m. Resultingly, the BET specific surface area of E-beam TiO$_2$ (25.6 m$^2$ g$^{-1}$) was larger than that of hydrolysis TiO$_2$ (10.6 m$^2$ g$^{-1}$).

In Derjaguin-Landau-Verwey-Overbeek (DLVO) theory, the agglomeration and stability of particle dispersions are determined by the sum of the attractive and repulsive forces between individual particles. And the attractive force is due to the van der Waals force [16]. To overcome the van der Waals force and suppress the agglomeration between individual particles, the electrostatic repulsive forces caused by high surface charge, thicker double layer, and steric forces have to be applied to individual particles [16]. Typically, when the agglomerated nanoparticles are added to a liquid, they can be separated by overcoming the weaker attractive force in several ways, whereas the aggregated nanoparticles cannot be separated. It is believed that the weaker attractive force between the agglomerated primary particles of TiO$_2$ nanoparticles was easily broken by the E-beam irradiation. The E-beam irradiation through H$_2$O contributes to the ionization/excitation of H$_2$O molecules forming a number of transient species and stable products [17,18]. Among all species generated during H$_2$O radiolysis, hydroxyl radicals (\*OH) are the most reactive with the TiO$_2$ surface, as a very strong oxidizing agent [19]. It is reported that the \*OH induced by H$_2$O radiolysis contribute to the formation of hydroxyl (OH$^-$) groups, which increase the charge and wettability of the TiO$_2$ surface [17,19,20]. Therefore, it is evident that the E-beam irradiation on TiO$_2$ nanoparticles with H$_2$O suppressed the agglomeration between individual TiO$_2$ nanoparticles, leading to smaller primary and secondary particles with narrower size distribution.

Fig. 1. SEM images of (a-b) the hydrolysis synthesized TiO$_2$ nanoparticles and (c-d) the E-beam irradiated TiO$_2$ nanoparticles.
Fig. 2 exhibits the particle size distribution of the hydrolysis synthesized TiO$_2$ nanoparticles and the E-beam irradiated TiO$_2$ nanoparticles. The E-beam TiO$_2$ presented not only narrower particle size distribution, but also smaller particle size than that of the hydrolysis TiO$_2$. Although the average E-beam TiO$_2$ particle size (noted as D50) was 202.73 nm, smaller than that of the hydrolysis TiO$_2$ (489.84 nm), the smallest particle size (noted as D10) of E-beam TiO$_2$ (178.07 nm) was slightly bigger than that of hydrolysis TiO$_2$ (100.17 nm). It is reported that the E-beam irradiation increased the diffusivity of atoms by several orders of magnitude compared to that in the thermal treatment step during synthesis. The precipitation of nanoparticles occurs not only at distinctly lower temperatures, but also at considerably higher rates in the irradiation process [10,12]. This demonstrates that the E-beam irradiation can lead to a fast grain growth of the primary TiO$_2$ nanoparticles, resulting in a bigger smallest particle size. However, subsequent grain growth of the primary TiO$_2$ nanoparticles was suppressed during the E-beam irradiation, because the diffusion of atoms for the growth of TiO$_2$ nanoparticles was inhibited by the separation of individual TiO$_2$ nanoparticles. Thus its average particles size is smaller than that of the hydrolysis sample.

Fig. 3 presents the XRD patterns of the hydrolysis synthesized TiO$_2$ nanoparticles and the E-beam irradiated TiO$_2$ nanoparticles. The crystallographic structures of both samples had been confirmed to be the tetragonal anatase phase (JCPDS card no. 21-1272, S.G.: I41/amd). Although the peak position of both samples corresponded well, the peak width of E-beam TiO$_2$ was slightly wider than that of hydrolysis TiO$_2$ for all peaks. This demonstrates that the E-beam TiO$_2$ had smaller the crystallite size than the hydrolysis TiO$_2$. The crystallite size, which is different than the particle size could be estimated by a full width at half maximum (FWHM) of XRD peaks using the Scherrer equation [21]. The crystallite size of the E-beam TiO$_2$ and hydrolysis TiO$_2$ was 23.4 and 29.1 nm for (101) peak, and 19.1 and 24.0 nm for (200) peak, respectively. It is expected that the E-beam TiO$_2$ with smaller crystallite size would be favorable for the diffusion of Li$^+$ through TiO$_2$ nanoparticles, resulting in a better electrochemical performance.

Fig. 4 shows the charge-discharge curves for the first two cycles of the hydrolysis synthesized TiO$_2$ nanoparticles and the E-beam irradiated TiO$_2$ nanoparticles. All samples presented almost the same voltage profile during the charge-discharge. At the first cycle, the discharge capacity and coulombic efficiency of hydrolysis TiO$_2$ and E-beam TiO$_2$ were 197.67 mAh g$^{-1}$ and 85.75%, and 198.36 mAh g$^{-1}$ and 86.14%, respectively. And at the 2nd cycle, the E-beam TiO$_2$ also exhibited slightly bigger discharge capacity (194.74 mAh g$^{-1}$) and higher coulombic efficiency.
Synthesis of TiO$_2$ nanoparticles induced by electron beam irradiation and their electrochemical performance as anode (97.65%) than those of hydrolysis TiO$_2$ (193.60 mAh g$^{-1}$ and 97.52%). The better electrochemical performance of E-beam TiO$_2$ was demonstrated well in the cycling performance and rate capability tests, as presented in Fig. 5 and 6. In spite of the similarity in the crystallinity and initial discharge capacity at 0.2 C (the first cycle) of both samples, there are notable differences in the initial discharge capacity at 0.5 C (the 3$^{rd}$ cycle) and capacity retention capability. After 50 cycles, the E-beam TiO$_2$ exhibited higher discharge capacity of 148.50 mAh g$^{-1}$, corresponding to 77.97% of its initial discharge capacity at 0.5 C (the 3$^{rd}$ cycle), whereas the hydrolysis TiO$_2$ showed lower discharge capacity of 123.55 mAh g$^{-1}$, corresponding to 67.35% of its initial discharge capacity at 0.5 C (the 3$^{rd}$ cycle). This indicates that the insertion/extraction of Li$^+$ into/from the E-beam TiO$_2$ was preferable to that into/from the hydrolysis TiO$_2$.

The rate capability, in common with the cycling performance, of E-beam TiO$_2$ was superior to that of hydrolysis TiO$_2$. There was no significant difference between both samples at relatively low current density (< 0.2 C). However, an abrupt decrease in the discharge capacity of hydrolysis TiO$_2$ was observed with an increase in the current density (> 0.5 C), which indicates that the insertion/extraction of Li$^+$ into/from the hydrolysis TiO$_2$ was kinetically limited at a relatively high current density. At the high current density of 10 C, the discharge capacity (100.99 mAh g$^{-1}$ = 50.74%) of E-beam TiO$_2$ was much higher than that of hydrolysis TiO$_2$ (61.92 mAh g$^{-1}$ = 31.60%). The better electrochemical performance of E-beam TiO$_2$ than that of hydrolysis TiO$_2$ was attributed to smaller particle size and narrower particle size distribution, resulting in the large surface area that provided innumerable reaction sites and short diffusion length for Li$^+$ through TiO$_2$ nanoparticles. The homogeneous arrangement of E-beam TiO$_2$ nanoparticles also contributed to improvement of the electrical contact between individual TiO$_2$ nanoparticles and acetylene black in the electrode, which led to better electrochemical performance of E-beam TiO$_2$ than that of hydrolysis TiO$_2$.

4. Conclusions

The effects of E-beam irradiation on the synthesis of TiO$_2$ nanoparticles and their the electrochemical performance as alternative anode materials for Li-ion batteries are investigated and compared with that of TiO$_2$ nanoparticles synthesized by normal hydrolysis
reaction. All samples were composed of nano-sized primary particles and micro-sized secondary particles which were formed by aggregation of the primary particles. The E-beam irradiation on TiO$_2$ nanoparticles suppressed the agglomeration between individual TiO$_2$ nanoparticles, resulting in a smaller particle and crystallite size with a narrower size distribution. These features of E-beam irradiated TiO$_2$ nanoparticles contributed to not only a larger surface area that provided innumerable reaction sites and short diffusion length for Li$^+$ through TiO$_2$ nanoparticles, but also improvement of the electrical contact between individual TiO$_2$ nanoparticles and acetylene black in the electrode. Therefore, the TiO$_2$ nanoparticles induced by E-beam irradiation present better cycling performance and rate capability than the TiO$_2$ nanoparticles synthesized by normal hydrolysis reaction.

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