Ultrafine TiO₂ Nanoparticles on Reduced Graphene Oxide as Anode Materials for Lithium Ion Batteries

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Abstract

TiO₂ nanoparticles/reduced graphene oxide (TiO₂/rGO) was prepared by controllable hydrolysis and followed by thermal treatment. First, hydrolysis of titanium isopropoxide formed amorphous titanium hydroxide thin layer on graphene oxide (GO). After annealing at 450 °C under forming gas, amorphous titanium hydroxide layer converted to TiO₂ nanoparticles with particle size of around 5 nm and GO reduced to rGO with enhanced conductivity. TiO₂/rGO was demonstrated as promising anode materials for high performance lithium ion batteries. The high operation potential window of TiO₂ in lithium ion battery can prevent the formation of solid electrolyte interface and subsequently enhance the safety and cycle performance. The high rate and high cycling performance of lithium ion batteries could be ascribed to that the ultrafine TiO₂ nanoparticles provide high active surface area and the strong connection between TiO₂ and high conductive rGO network can enhance the charge transfer.

Keywords: graphene oxide, TiO₂, anode, lithium-ion battery

Introduction

Electrochemical energy storage devices such as Li-ion batteries (LIBs) have been receiving extensive investigation because of their potential applications in electric vehicles [1,2]. However, potential anode materials including transition metal oxides, metal sulfides, and silicon are limited by poor electron transport and slow Li-ion diffusion, which significantly increase the resistance at the interface of electrode/electrolyte under the high charge/discharge rates [3-17]. Therefore, extensive work of improving ion and electron transport in electrodes has carried out to improve the high rate performance [11,12,18,19]. A variety of effective approaches such as conductive coating (e.g., carbon and metal thin layer) [4], conductive additives (e.g., conductive polymers) [18], and defects on the surfaces (e.g., oxygen-deficient TiO_2) [19] have been developed to increase electron and ion transport in the electrode materials. Recently, TiO_2 has been extensively studied as a promising anode for LIBs [20,21]. The structurally stable and low volume change of TiO_2 can avoid Li electrochemical deposition during Li insertion/extraction processes. Besides, the high operation voltage (higher than 1 V) could avoid the formation of lithium dendrites, which decreases the consumption of electrolyte, making TiO_2 more attractive for large scale energy storage.

However, the low electronic conductivity of TiO_2 limits the charge transfer, resulting in its poor performance for LIBs. Combing with conductive materials such as carbon based materials is an effective approach to increase the charge transfer and then increase the battery performance. Recently, the composites

consisting of nanostructure TiO_2 and graphene or reduced graphene oxide have been extensively employed as the electrode materials for the application of LIBs [22-30]. However, the reported composites contain large particle size of TiO_2 (50~100 nm). In this work, ultrafine TiO_2 nanoparticles with sizes of 5 nm were uniformly coated on reduced graphene oxide (TiO_2/rGO) by controllable hydrolysis of titanium isopropoxide. After employing the TiO_2/rGO as an anode for LIBs, the performance for LIBs was significantly improved since the porous structure of rGO provides extra path to lithium ion diffusion and ultrafine TiO_2 nanoparticles provide more active site for lithium insertion/desertion.

Experimental

Synthesis of Graphene Oxide (GO) and TiO_2/rGO : GO was synthesized using the modified Hummer's method [30], and the detailed information about synthetic process can be found in our recent paper [31]. The procedure of TiO_2/rGO is as following: the GO nanosheets were uniformly dispersed in a mixture of 20 ml ethanol and 1 ml water. Diluted titanium isopropoxide ethanol solution was slowly added to the GO nanosheets suspension. Due to the small content of water in the solution, the slow hydrolysis process can prevent the agglomeration of titanium hydroxide. After 4-hour hydrolysis process, the final solution was filtered and then dried in an oven at 60 °C overnight. The resulting amorphous titanium hydroxide and GO nanosheets hybrid was treated at 450 °C for 2 h in forming gas to get TiO_2 nanocrystals and reduced graphene oxide (TiO_2/rGO). For a comparison, larger TiO_2 nanoparticles was prepared by the same hydrolysis process without GO, then mechanically mixed with

rGO nanosheets together, named as M-TiO₂/rGO.

Materials Characterization and Electrochemical Test: The crystal structure of TiO₂/rGO was determined by X-ray diffraction (XRD, Rigaku Miniex-II with Cu K α (1.5406 Å) radiation, 30 kV/15 mA). The morphology and particle size of TiO₂ were characterized by a transmission electron microscope (TEM) (JEOL, model JEM-2100) operating at 200 kV. Thermogravimetric analysis (TGA) and was used to determine the mass content of rGO in the TiO₂/rGO composite. The surface area and pore size distribution were characterized by a Micromeritics ASAP 2050 using the standard N₂ adsorption and desorption isotherm measurements at 77 K. For LIB test, the uniform N-methyl-2-pyrrolidinone slurry consisting of active materials (85 wt%), carbon black (10 wt%) and polyvinylidene fluoride binder (5 wt%) was casted on the copper foil to form the working electrode. The as-prepared working electrode was dried in a vacuum oven to evaporate the NMP solvent. The loading weight for the working electrode was around 1 mg. A mixture of 1 M LiPF₆ in ethylene carbonate – dimethyl carbonate (1: 1 by volume) was used as the electrolyte. CR-2032 coin cells consist of the as-prepared working electrode, separator, and lithium foil. Cell assembly was carried out in an argon-filled glovebox where the concentration of oxygen is below 1 ppm. The galvanostatic charge/discharge test at different current densities and cycle performance at 20 C (1 C = 168 mA h/g) were performed by a land battery testing system at the potential window of 1–3 V (vs. Li⁺/Li). Cyclic

voltammetry (CV) was recorded by Princeton Applied Research Versa STAT4 electrochemical workstation at a range of 1–3 V (vs. Li^+/Li).

Results and Discussion

After controllable hydrolysis process and following heat treatment, TiO_2 nanoparticles with particle size of around 5 nm were uniformly deposited on rGO sheets. Interestingly, porous rGO network could be observed, as shown in **Figure 1a** and **1b**.

Figure 1. TEM images of TiO_2/rGO at different magnifications.

Figure 2 shows the typical XRD pattern of TiO_2/rGO . Only peaks corresponding to pure anatase phase (JCPDS 84–1285) and no observable peaks from a secondary phase were observed. However, the specific peak corresponding to graphite character around 26 degree (2θ) was not observed in TiO_2/rGO due to the possible overlap between the (002) peak of graphite carbon and the (101) peak of anatase TiO_2 phase.

The mass ratio of rGO in the composite is around 26.8 wt.%, as shown in **Figure 2b**.

Figure 2. XRD pattern of TiO_2/rGO and (b) TGA profile for TiO_2/rGO .

Figure 3. (a) Nitrogen adsorption/desorption profile of TiO_2/rGO and (b) pore width distribution.

The nitrogen adsorption/desorption profile of TiO_2/rGO is displayed in **Figure 3a**, indicating BET surface area of $141 \text{ m}^2 \text{g}^{-1}$. The pore width distribution curve (**Figure 3b**) shows that the TiO_2/rGO mainly contains 15, 30, and 500 nm pores, consistent with TEM images.

The space between TiO_2 nanocrystals and porous network of rGO will provide extra diffusion path for ion transport and increase the contact area between electrode

and electrolyte, resulting in enhanced ion and charge transfer. The rGO also provides the enhanced conductive network for charge transfer during charge/discharge processes, especially for high rate battery test. Therefore, it is expected that the material with ultrafine nanoparticles and conductive porous rGO network should deliver a high rate performance and durability for LIB. **Figure 4a** shows the typical CV profile of TiO₂/rGO anode and the control sample in the voltage window of 1–3 V at a scan rate of 0.1 mV s⁻¹. The CV behavior of these two samples is almost the same. The redox peaks at 1.7 V at anodic scan and 1.9 V at cathodic scan are corresponding to the changing valence state of Ti⁴⁺/Ti³⁺, which is associated with Li ion insertion/extraction processes into TiO₂ during charge and discharge processes. The CV behavior of TiO₂/rGO anode is consistent with that of previously reported on TiO₂ based nanostructured anodes [23]. **Figure 4b** shows typical discharge/charge profiles for TiO₂/rGO anode at 0.5 C (1 C = 168 mA·h g⁻¹). The charging plateaus at 1.9 V and the discharging plateau at 1.7 V are consistent with the redox peaks (1.9 V at cathodic scan and 1.7 V at anodic scan) in the CV result. The initial discharge and charge capacities are 260 and 235 mA·h g⁻¹, respectively. The capacity of TiO₂/rGO at 0.5 C is comparable to those previously reported for TiO₂ based anodes for LIBs [7]. **Figure 4c** shows the rate performance of TiO₂/rGO, M-TiO₂/rGO (control sample) and pure TiO₂. The performance of TiO₂ nanoparticles is comparable with M-TiO₂/rGO. Compared with M-TiO₂/rGO and pure TiO₂, a much better rate performance was obtained for TiO₂/rGO because of the enhanced electronic and ion conductivity, thanks from the porous rGO network and ultrafine TiO₂ nanoparticles.

The initial discharge capacity at a low current density of 0.5 C was around 260 mA·h g⁻¹, the capacity at the same current density reached to around 230 mA·h g⁻¹ after repeating cycles. As expected, the reversible capacity of TiO₂/rGO decreases with increasing the current densities from 230 mA·h g⁻¹ at 0.5 C to 200 mA·h g⁻¹ at 2 C, 171 mA·h g⁻¹ at 5 C, 128 mA·h g⁻¹ at 10 C and 83 mA·h g⁻¹ at 20 C, respectively. Nevertheless, when the current density returns to 2 C, the capacity practically recovers to 200 mA·h g⁻¹ with the retention rate of as high as 100%. However, for the pure TiO₂ and the control sample with mixture of TiO₂ and rGO, the capacities are lower than those of TiO₂/rGO at all the current densities. For example, the M-TiO₂/rGO sample delivered a lower capacity of ~150 mA·h g⁻¹ at low current density of 0.5 C and 20 mA·h g⁻¹ at 20 C, respectively (**Figure 4c**). The poor contact between TiO₂ and rGO in M-TiO₂/rGO results in poor electron and ion transfer. These results demonstrated that our TiO₂/rGO exhibited excellent rate performance and cycle stability.

Figure 4d shows the cycling performance of TiO₂/rGO at high current density of 20 C and the corresponding Coulombic efficiency (CE). As we can see that only limited capacity loss after 100 cycles could be observed and the discharge capacity delivered as high as 79 mA·h g⁻¹ after 100 cycles while maintaining CE nearly 100%. The high surface area of ultrafine TiO₂ nanoparticles, strong connection between TiO₂ and rGO, porous rGO network and enhanced conductivity of rGO significantly increase the charge transfer and ion diffusion, resulting in its high rate and high cycle performance.

Figure 4. (a) CV curve of TiO_2/rGO and the control sample $\text{M-TiO}_2/\text{rGO}$ at low scan rate of 0.1 mV s^{-1} ; (b) galvanostatic discharge/charge profiles of TiO_2/rGO at 0.5 C; (c) rate capability of TiO_2/rGO , $\text{M-TiO}_2/\text{rGO}$, and TiO_2 at different current densities from 0.5 to 20 C; and (d) cycling performance of TiO_2/rGO at 20 C and corresponding Coulombic efficiency.

To characterize the charge transfer resistance for different samples, the electrochemical impedance measurement for the TiO_2/rGO , control sample and pure TiO_2 were performed. The impedance spectra are shown in **Figure 5**. Depressed

semi-cycles at high frequencies could be observed at the Nyquist plots for all three samples. Considering that the fabrication of electrolyte and electrode are similar, the resistance including transfer and ohmic resistance should be related to the high frequency semicircle. It can be estimated that the resistivity of the cells is 165, 130 and 68 ohms for the pure TiO_2 , control sample and TiO_2/rGO . Therefore, the enhanced high charge rate performance for TiO_2/rGO can be ascribed to the increased conductivity and charge transfer of the composite.

Figure 5. Electrochemical impedance spectra of the TiO_2/rGO , control sample, and pure TiO_2 .

Conclusion

TiO_2 nanoparticles with size of 5 nm were uniformly coating on rGO sheets by controllable hydrolysis and thermal treatment in forming gas. The high rate and high

cycling performance of TiO₂/rGO for LIBs could be ascribed to the ultrafine TiO₂ nanoparticles with large surface area and high conductive rGO network. Porous structure of rGO can increase the contact area between electrolyte and the electrodes, enhance the ion diffusion during the charge/discharge processes under high current density.

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