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ScienceDirect
Journal of Power Sources 159 (2006) 219–222
JOURNAL OF POWER SOURCES
www.elsevier.com/locate/jpowsour

Short communication

Novel TiO_2/C nanocomposites for anode materials of lithium ion batteries

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Abstract

Here we reported an effective method to prepare TiO_2/C core–shell nanocomposites as active anode materials for lithium ion batteries with markedly ameliorated electrochemical performance. At first, a precursor, polyacrylonitrile coated nano-TiO_2 particles, was formed by emulsion polymerization. Then the precursor was heat-treated under argon atmosphere to achieve the nanocomposites. The conductive carbon shell enveloped TiO_2 nanoparticles and suppressed the aggregation of nanoparticles during cycling. Meanwhile, it combined closely with the nanocores, significantly enhanced kinetics of lithium intercalation and de-intercalation and diffusion coefficient of lithium ion. This provides a good way to improve the cycling and kinetics of nanoanode materials.

Keywords: Lithium ion battery; Anode; Core–shell; Nanocomposite; Electrochemical performance

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1. Introduction

Since the commercialization of lithium secondary batteries in the early 1990s, their development has been rapid. Nowadays, improving the preparation technology and electrochemical performance of their electrode materials is a major focus. Recently, nanomaterials for anode of lithium ion batteries stimulated great interest since all of them showed a higher reversible capacity than that of the respective micrometer materials [1–5]. However, there are still some distances for their practical application. The most critical problem is the aggregation of nanoparticles, giving rise to poor cycle performance [6]. Homogeneous dispersion of nanoparticles in a matrix and synthesis of metal-encapsulated spherical hollow carbon were tried to improve cycling behavior. However, neither of the above methods achieved marked progress [7–9].

Titanium dioxide, an insertion host material exhibiting relatively high lithium diffusion, has long been investigated as a positive electrode, later attracted high attention as a negative electrode constructed in combination with a high-voltage cathode like $LiCoO_2$. The application of TiO_2 has been limited by the structure instability to lithium intercalation de-intercalation reaction, giving rise to rapid capacity fading [10,11].

In this work, we used an effective method to synthesize carbon coated titanium oxide nanocomposites as anode materials for lithium ion batteries to enhance their capacity retention. More interestingly, the kinetics of lithium intercalation and de-intercalation was also improved.

2. Experimental

The preparation process is shown as following, different from the reported methods to synthesize core–shell nanocomposites [12]. First, a core–shell shaped TiO_2/polyacrylonitrile (PAN) precursor was synthesized via emulsion polymerization. Then, the precursor was heat-treated to turn into core–shell TiO_2/C nanocomposites. The detail for one experiment is given. OP_9 (1.2 g as surfactant) was dispersed in deionized water (200 ml) to form micelles. Then titanium oxide nanoparticles (2.5 g, Haitai Company, China) were added and sonicated for 30 min to achieve uniform dispersion. The mixture of 2,2′-azobis(isobutyronitrile) (AIBN, 0.015 g as initiator) and acrylonitrile (3.0 g, as monomer) was added for the emulsion polymerization. Degassing was carried out for 1 h under gentle stirring, then the temperature was increased to 60 °C and the mixture was polymerized for 12 h under argon atmosphere to form a core–shell shaped TiO_2/polyacrylonitrile precursor. After drying, the TiO_2/PAN precursor was heat-treated at 800 °C to turn the PAN shell into a carbon one, thus TiO_2/C nanocomposites were synthesized.

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doi:10.1016/j.jpowsour.2006.04.081

Core–shell nanocomposites were identified using a powder X-ray diffractometer with monochromatized Cu Kα radiation. Morphological observation was done by TEM (JEOL JEM 2011).

The two electrode coin-type half-cells were assembled for electrochemical performance evaluation. 85 wt% TiO_2 nanoparticles or TiO_2/C nanocomposites were mixed with 10 wt% acetylene black (AB) as a conductive additive and 5 wt% poly(vinylidene fluoride) as a binder. The mixture slurry was coated on copper foil. After drying, it was cut into small pieces and assembled into coin-type model cells under argon atmosphere in a glove box. These pieces were used as working electrodes, Li metal as the counter electrode, Celgard 2400 as the separator, and 1 mol l^{-1} $LiPF_6$ DEC/EC/DMC (w/w/w = 1/1/1) as the electrolyte. Cycling tests of the coin-type half-cells were performed in the voltage rang of 1.4–2.5 V with a constant current 0.1 mA (0.25 C). Cyclic voltammetry (CV) of TiO_2 and TiO_2/C electrodes were also measured at the range of 1.4–2.5 V at scanning rates of 0.1, 0.2, 0.3, 0.4, and 0.5 mV s^{-1}, respectively.

3. Results and discussion

3.1. Characterization of the nanocomposites

Fig. 1a is the TEM micrograph of the precursor TiO_2/PAN. It shows that titanium oxide nanoparticles were coated with PAN shell. The TEM micrograph of the TiO_2/C core–shell nanocomposite is shown in Fig. 1b, which presents a clear core–shell structure in which the core combines more closely with the carbon shell in comparison with that synthesized by another way [9].

The X-ray diffraction of TiO_2/C nanocomposites confirms that the titania cores of the nanocomposite are in the form of rutile. By changing the ratio of TiO_2 and the monomer and the experimental conditions such as the amount of surfactant and the initiator, the thickness of carbon shell and the number of nanoparticles of TiO_2 in the shell could be adjusted.

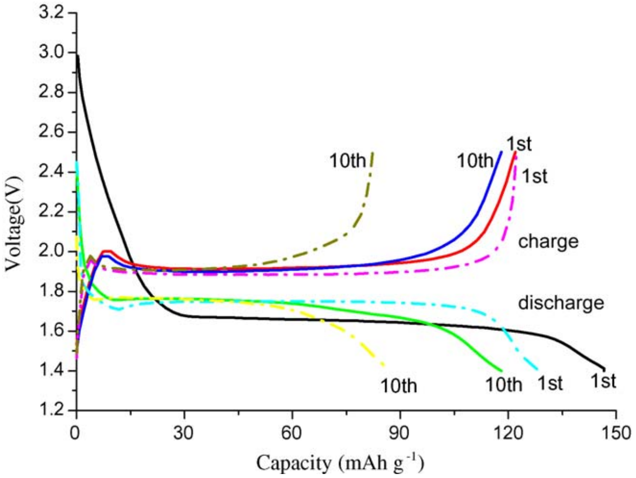
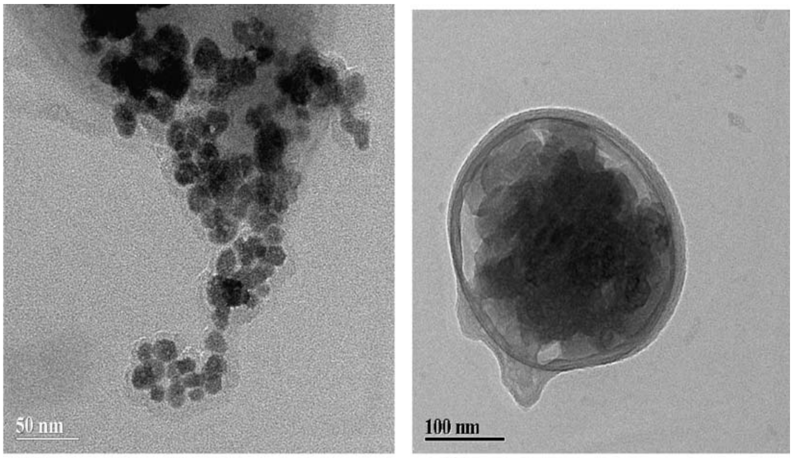


Fig. 2. Discharge and charge profiles of TiO_2 nanoparticles and TiO_2/C core–shell nanocomposite at a constant current density of 0.25 C between 1.4 and 2.5 V (solid line: TiO_2/C; dashed line: TiO_2).

3.2. Discharge and charge performance

The discharge and charge curves of TiO_2 and TiO_2/C (87/13, w/w) electrodes in 1 mol l^{-1} $LiPF_6$ DEC/EC/DMC (w/w/w = 1/1/1) are illustrated in Fig. 2. The charge and discharge capacity of carbon shell in TiO_2/C nanoparticles could be ignored since the intercalation voltage of lithium ion into the prepared amorphous carbon material is below 0.8 V [13,14]. The anode of TiO_2 nanoparticles showed a rapid capacity fading and retained only 67.5% of the original capacity after 10 cycles. It is well known that nanoparticles have a very high surface energy and can easily agglomerate. Even at room temperature, the dispersion of nanoparticles needs quite some time for ultrasonication. In the case of cycling, lithium intercalation and de-intercalation will enhance the aggregation tendency of nanoparticles and worse and worse cycling behavior was achieved [3].

In the case of TiO_2/C nanocomposite, after 10 cycles, the charge capacity still remained 96.7% (i.e., 118 mAh g^{-1} titania) of its original capacity (i.e., 122 mAh g^{-1} titania), which



(a) (b)

Fig. 1. TEM micrographs of TiO_2/polyacrylonitrile (a) and TiO_2/C (b) core–shell nanoparticles.