High grain boundary density $Li_4Ti_5O_{12}$/anatase-TiO_2 nanocomposites as anode material for Li-ion batteries

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ABSTRACT

$Li_4Ti_5O_{12}$/TiO_2 nanocomposites are synthesized by a sol-gel method. The size of $Li_4Ti_5O_{12}$ and TiO_2 particles is of 4–5 and 7–10 nm, respectively. The obtained materials are characterized by XRD, SEM, HRTEM and BET. Ion mobility of the composites and their performance as anode materials for lithium-ion batteries are studied. According to the conductivity and ^7Li NMR data, Li^+ mobility is much higher in the $Li_4Ti_5O_{12}$/TiO_2 nanocomposites as compared with that in pure $Li_4Ti_5O_{12}$. For $Li_4Ti_5O_{12}$/TiO_2 nanocomposites, marked changes in the charge–discharge curves are observed; charge–discharge rate and effective capacity at a high cycling rate are shown to increase. During the first cycle, charge capacity of these materials surpasses the theoretical capacity of $Li_4Ti_5O_{12}$. However, this parameter decreases sharply with cycling, whereas the discharge capacity remains almost unchanged. This phenomenon is attributed to the solid electrolyte interphase formation due to a partial electrolyte reduction on the $Li_4Ti_5O_{12}$/TiO_2 composite surface.

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1. Introduction

Lithium-ion batteries (LIBs) have been widely used as energy storage sources for portable electronic devices and large-scale applications in electric vehicles due to their high energy density and reliability [1]. In recent years, lithium titanate $Li_4Ti_5O_{12}$ has been developed as a very promising electrode material [2–5], which allows intercalation of three lithium ions per formula unit with a theoretical capacity of 175 mAh g^{-1}:

$$Li_4Ti_5O_{12} + 3e^- + 3Li^+ = Li_7Ti_5O_{12} \qquad (1)$$

Charge and discharge processes in $Li_4Ti_5O_{12}$ take place in a two-phase system via transformation between a spinel structure of $Li_4Ti_5O_{12}$ and a rock-salt type structure of $Li_7Ti_5O_{12}$ determining a flat potential plateau of 1.55 V (vs. Li^+/Li) [6]. Moreover, changes in its cubic unit cell parameter are very small (from 8.3595 to 8.3538 Å [7]), thus providing an excellent cycling stability and reversibility of this material. At the same time, electron and ion conductivity of $Li_4Ti_5O_{12}$ is rather low (10^{-13} S cm^{-1}) [8].

A promising approach to improve the performance of electrode materials is concerned with the use of nanosized materials [9–11]. For example, dramatic changes (by 3–4 times) in the unit cell

volume of silicon- and tin-based materials during lithium intercalation/deintercalation prevent their practical application [10,12] because their structure breaks down. However, as the particle size decreases, the material becomes more stable [13]. The use of nanoparticles provides the decrease in Li ions diffusion pathway, thereby yielding better electrode kinetics and an enhanced current-rate capability. Generally, as compared with micronsized lithium titanate, nanosized $Li_4Ti_5O_{12}$ were reported to have increased capacities with good rate capability [2].

Electrode materials for oxide-based LIBs are often prepared by the solid state method. The advantages of the sol–gel route are associated with the use of lower synthesis temperatures. However, even in this case, a final calcination temperature for the preparation of single-phase samples should be rather high. As the synthesis temperature is decreased, nanocomposites with smaller particles are formed. Moreover, such systems can provide a higher diffusion over multiple interfaces and a shorter diffusion pathway. For this purpose, carbon coating of the electrode materials is often used. Electronically conductive phase improves the electrical contact between active materials and enables an increased transfer of Li-ions and electrons at interfaces [10,14].

Another approach is concerned with the formation of composites with oxides such as SiO_2, TiO_2, etc. This leads to the sorption of mobile ions at grain boundary interfaces and formation of a highly conductive Debye layer with high defect concentration yielding in ionic conductivity improvement [15–17]. Moreover,

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anatase TiO_2 can contribute some electrochemical capacity to the composite electrode. The electrochemical performance of $Li_4Ti_5O_{12}$–TiO_2 nanocomposites as anode material has been reported by some researchers [18–21]. The composite $Li_4Ti_5O_{12}$–anatase TiO_2 synthesized by hydrothermal route with thiourea [18] and ethylene glycol [19] show better rate capability than pure $Li_4Ti_5O_{12}$. Rahman et al. synthesized $Li_4Ti_5O_{12}$–TiO_2 nanocomposite via molten salt precipitation method [20], which yields good electrochemical performance. The $Li_4Ti_5O_{12}/TiO_2/Li_3PO_4$ nano-forest composite layer obtained from a layer of self organized TiO_2/Li_3PO_4 nanotube shows electrochemical capacity about $70\,\mu Ah\,cm^{-2}$ at the first cycle and good cycling behavior [21]. Nevertheless, most of methods need some special instruments or a relatively high processing temperature, so that the production of nanocrystalline, high grain boundary density, dual phase $Li_4Ti_5O_{12}$-TiO_2 is difficult and inconvenient.

In this work, a simple route for the synthesis of $Li_4Ti_5O_{12}/$anatase-TiO_2 nanocomposites is reported. Due to the *in situ* composite formation, lithium titanate and anatase-TiO_2 can be homogeneously mixed with each other, thus yielding a material with improved electrochemical properties in comparison with the single-phase $Li_4Ti_5O_{12}$ or anatase-TiO_2. To the best our knowledge nanocomposites with such low particle size have not been reported yet. Structural characteristics and electrochemical properties of $Li_4Ti_5O_{12}/$anatase-TiO_2 nanocomposites and pristine $Li_4Ti_5O_{12}$ were evaluated and compared. The synthesized nanocomposite exhibits high reversible capacity and good cycling performance, which indicates promising applications as anode materials for high-rate Li-ion batteries.

2. Experimental

2.1. Synthesis

$Li_4Ti_5O_{12}/$anatase-TiO_2 nanocomposites were prepared by a simple sol–gel method. As starting materials, the stoichiometric amounts of lithium carbonate and tetrabutyl titanate were used. Citric acid solution in minimal amounts of water was added to the mixture of tetrabutyl titanate and lithium carbonate. The molar ratio of citric acid to titanium was 4:1. The obtained gel was dried at 373 K and then ground completely. The obtained precursor was calcined for 5 h in air at different temperatures from 673 to 1073 K in order to estimate the optimum temperature of synthesis for nanocomposites.

2.2. Material characterization

Structure of the samples was examined by the X-ray powder diffraction (XRPD) using a Rigaku D/MAX 2200 diffractometer (CuKα radiation). Data processing was performed using the Rigaku Application Data Processing software package. The morphology and particle size were characterized by scanning electron microscopy (SEM, Carl Zeiss NVision 40 station) and high resolution transmission electron microscopy (HRTEM, JEM-2100) combined with selected area electron diffraction (SAED). Static ^{7}Li NMR spectra were obtained using a Bruker MSL-300 spectrometer at 116.6 MHz. Chemical shifts were given relative to 0.1 M LiCl. The Brunauer–Emmett–Teller (BET) measurements were performed on a surface area analyzer (Micrometrics ASAP 2020) to examine nitrogen absorption–desorption behavior and specific surface area of the sample.

2.3. Electrochemical characterization

Conductivity measurements were performed on an IPU-p.62 impedance analyzer in a frequency range from 10 Hz to 2 MHz. The impedance data were collected on round pellets (pressure 2×10^8 Pa) with painted silver electrodes in the temperature range of 298–773 K using the two-probe method. Ionic conductivity was calculated as the difference between total and electronic conductivity.

Electrochemical tests were performed in the hermetically sealed three-electrode cells with a metallic lithium counter and reference electrodes. Electrode paste was prepared by a thorough mixing of $Li_4Ti_5O_{12}/$anatase-TiO_2 nanocomposites or $Li_4Ti_5O_{12}$ as an active material, conductive carbon black, and polyvinylidene-fluoride binder dissolved in anhydrous *N*-methyl-2-pyrrolidinone. The electrode paste was applied on the stainless steel gauze (current collector) as a 10–$15\,mg\,cm^{-2}$ layer. The resultant electrode was pressed at $1000\,kg\,cm^{-2}$ and vacuum-dried at 393 K for 8 h. The cells were assembled in a glove box under an argon atmosphere with a humidity level below 10 ppm. The electrolyte was 1 M $LiPF_6$ in ethylene carbonate, diethyl carbonate and dimethyl carbonate mixture (EC:DC:DMC = 1:1:1 v/v). Water content was <20 ppm. A nonwoven polypropylene separator was placed between the electrodes. Electrochemical cycling of the cells was performed over the potential range of 13 V using a ZRU 50 mA–10 V charge–discharge system (LLC NTTs Buster, Russia). The tests were performed in a galvanostatic mode at current densities of 20–$3200\,mA\,g^{-1}$. Cycling voltammorgrams (CV) were obtained using an EL-2 potentiostate (designed and fabricated in the Frumkin Institute of Physical Chemistry and Electrochemistry RAS). The scan rates were varied from 0.1 to $1.0\,mV\,s^{-1}$.

3. Results and discussion

3.1. Structure and morphology characterization

Fig. 1 shows the X-ray powder diffraction patterns of the composite precursors calcined at different temperatures. Formation of $Li_4Ti_5O_{12}$ and anatase-TiO_2 begins at 673 K (Fig. 1a). Broad peaks of $Li_4Ti_5O_{12}$ obtained at 673 K indicate the small size of the particles. The crystallite size of lithium titanate estimated from the Debye–Scherrer equation is about 4–5 nm, while that of anatase-TiO_2 is of 7–10 nm (Table 1). As the calcination temperature increases, the peaks in the XRPD patterns become sharper and demonstrate further crystallization and simultaneous growth of particles in both phases. The reflections of anatase-TiO_2 obtained at 773 K can be indexed in tetragonal system (space group I41/amd) with the unit cell parameters $a = 3.784(4)$ Å, $c = 9.4959(9)$ Å. Above 873 K anatase-TiO_2 is transferred into a more stable rutile phase
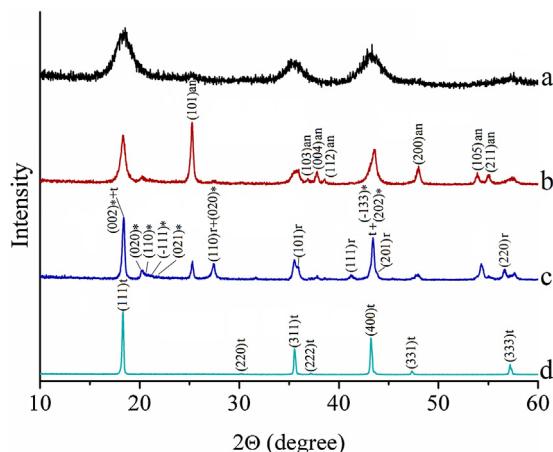

Fig. 1. X-ray powder diffraction patterns of the composite precursors calcined at 673 (a), 773 (b), 873 (c), and 1073 (d) K. The Miller indexes are shown for anatase-TiO_2 (an), rutile-TiO_2 (r), Li_2TiO_3 (*), $Li_4Ti_5O_{12}$ (t).