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Phases hybriding and graphene-like TiO_2 for high-performance Na-ion batteries

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ABSTRACT

Rational design and controllable synthesis of TiO_2 based materials with unique microstructure and excellent electrochemical performance for Na-ion batteries have been imperative requirement at present. In our work, TiO_2 with graphene-like (TiO_2-GL) structure has been synthesized from P25 (commercial TiO_2 with phases hybriding) by skillful controlled hydrothermal synthesis conditions. As a result the obtained TiO_2-GL still possesses hybrid phases, and delivered high reversible capacity, fantastic cycling performance and superior rate capability for Na-ion battery system. When discharged for 100 cycles at current density of 100 mA g^{-1}, the TiO_2-GL shows a reversible capacity of about 150 mAh g^{-1}. Even when the current density is increased to 500 mA g^{-1}, a very stable and extraordinarily high reversible capacity of 100 mAh g^{-1} can be delivered. Obviously, the excellent performance are owing to the synergistic effect of hybrid phases and graphene-like structure.

1. Introduction

Lithium-ion batteries (LIBs) are widely used in consumer electronics and are also growing in popularity for electric vehicles and aerospace applications. The study for LIBs have also caused widely concern and achieved great achievements [1–8]. According to statistics, consumption of lithium doubled during the decade through 2012 and continues to grow at a rapid rate. However, the lithium content in the earth is very limited, only 0.006 wt% [9]. So, looking for a better energy materials is very urgent and necessary [10–13].

As a promising alternative to rechargeable LIBs, sodium ion batteries (SIBs) has drawn increasing attention owing to their lower cost, environmentally friendly, excellent recharge ability and higher security [14–16]. Recently, SIBs have gained increased recognition as intriguing candidates for next-generation large-scale energy storage systems [17–20], which attributed to the uniform distribution and 2.64 wt% elemental abundance in the earth's crust [21]. It should be noted that the low energy density of SIBs needs to be improved to meet the requirement of grid energy storage [22–24]. Furthermore, the development of sodium ion battery anode material is still a great challenge, because only a very limited amount of Na can be intercalation/deintercalation into graphite and Na ions could hardly form staged intercalation compounds with graphite [25,26]. So, there is still a long way to go towards the commercial realization of SIBs, which would be economic, safe, and durable [27]. Resent years, Ti-based compounds have been extensively studied as anode materials in energy-storage applications due to their low volume expansion and stable cycling performance [28–33]. Especially, TiO_2 has been of great concern in electrochemical energy storage field, because it has several phase structures, such as rutile, anatase, brookite, hollandite [34] and metastable monoclinic phase [35]. For example, using ultrafine nanocrystalline anatase or rutile, the Li insertion host can efficiently enhance the lithium storage capacity even at high discharge-change current densities [36,37]. In addition, the phases hybriding of TiO_2 has recently aroused much attention for improving the capacities of the electrode materials. Because the synergistic effect can efficiently enhance the lithium storage capacity even at high discharge-change current densities [38].

In this manuscript, we controlled hydrothermal synthesis conditions to obtain hybriding phases (anatase/rutile) TiO_2 with graphene-like structure, which demonstrated high reversible capacity (above 150 mAh g^{-1} after 100 cycles at current of 100 mA g^{-1} in voltage range of 0.005–3.0 V), good cycling rate capability performance (100 mAh g^{-1} at 500 mA g^{-1} for 100 cycles) for SIBs. Such excellent electrochemical performance is much superior to the commercial TiO_2, proving that the TiO_2-GL is a promising candidate

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as anode material for SIBs.

2. Experimental section

2.1. TiO_2-GL synthesis

All reagents were analytical purity, and purchased from Aladdin Chemical Reagents Company without further purification. In a typical procedure, 5 M NaOH aqueous solution (30 ml) was prepared in a beaker and then 0.2 g of TiO_2 was added into the solution. After being stirred for 30 min, the mixture was transferred into the Telfon-lined stainless steel autoclave. The autoclave was sealed and heated at 160 °C for 12 h, and then cooled to room temperature naturally. The as-synthesized product was washed several times with distilled water and ethanol before 120 °C vacuum drying.

2.2. Characterization

X-ray diffraction (XRD) analysis was performed with a Bruker D8 advanced X-ray diffractometer equipped with Cu Kα radiation (λ = 1.5418 Å). Diffraction datas were collected by step scanning over an angular range of 10–80° with a step width of 0.02° (35 kV, 30 mA). A scanning electron microscope (SEM, Hitachi, S-3000N) were used to investigate the morphology and size of the samples. The high-resolution transmission electron microscopy (HRTEM) images and the selected area electron diffraction (SAED) patterns were taken on a JEM-2100 transmission electron microscope with the accelerating voltage of 200 kV.

2.3. Electrochemical measurement

The electrodes were prepared by dispersing 80 wt% active material, 10 wt% conductivity carbon black, and 10 wt% polyvinylidene fluoride (PVDF) in N-methyl-2-pyrrolidone (NMP, C_5H_9NO, Sigma-Aldrich, 99.5%). The well-mixed homogenous mixture was coated on a copper foil using a doctor blade. After being dried in a oven for 12 h made into an electrode plate. Then, the coin-type cells (size: 2025) were assembled in the argon-filled glove box (Mikrouna, Super 1200/750) with the concentrations of moisture and oxygen below 1 ppm. Na metal was applied as anode, and the separator was glass fiber (GF/D) from Whatman. The electrolyte was 1 M sodium perchlorate ($NaClO_4$, Sigma-Aldrich, ≥99%) dissolved in a mixture of ethylene carbonate (EC, $C_3H_4O_3$, Sigma-Aldrich, 99%) and propylene carbonate (PC, $C_4H_6O_3$, sigma-Aldrich, 99.7%) in a volume ratio of 1:1. The galvanostatic charge/discharge cycling was performed using LAND-CT2001A multichannel galvanostat (Wuhan, China) in the voltage range of 0.005–3.0 V (vs. Na^+/Li) at room temperature. The cyclic voltammetry (CV) measurements were carried out in the voltage window 0–2.8 V at a scan rate of 0.2 mV/s by electrochemical workstation (CHI660D, Chenhua Co., Shanghai, China) at room temperature.

3. Results and discussion

Fig. 1 shows the XRD patterns of commercial P25 and TiO_2-GL. The strong and sharp diffraction peaks reflect the as-synthesized products and P25 are all well crystallized and homogenous orientation. The XRD patterns indicate that all the diffraction peaks of TiO_2-GL composite are in good agreement with the raw P25. All the diffraction peaks can be well indexed as the anatase phase TiO_2 (JCPDS card No: 21-1272 with the cell parameters of a = 3.785 Å, c = 9.513 Å) mixed with a small amount of rutile phase TiO_2 (JCPDS card No: 21-1276 with cell constants of a = 4.593 Å, c = 2.959 Å). At the same time, the significant enhancement of almost every diffraction peak could be observed in the TiO_2-GL pattern in

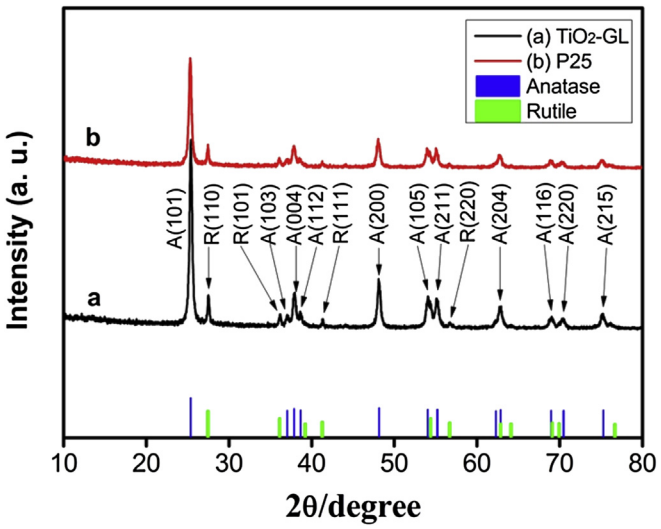

Fig. 1. XRD patterns of (a) P25 and (b) TiO_2-GL.

relation to P25, which indicated that the TiO_2-GL possesses better crystallization. Furthermore, the (101) crystal plane of anatase phase TiO_2 diffraction peak intensity was significantly enhanced compared to the standard XRD pattern of JCPDS card, indicating that the sample has a strong preferential orientation growth trend.

The morphology and structure of P25 and the as-prepared TiO_2-GL are investigated by SEM and TEM. Fig. 2a and b show the typical panoramic SEM image of the P25, indicating the presence a lot of irregular microparticles. From the SEM image of Fig. 2c, we found that the as-prepared TiO_2-GL showing film-like structure, and with the typical thickness of about several nanometers. After further amplification, graphene-like structure is clearly observed (Fig. 2d). It must be noted that the graphene-like structure can be fully in contact with the electrolyte and shorten the Na^+ transport path, which may result in good electrochemical storage performance.

To further detect the crystallinity and internal homogeneity, we get more detailed information on the structure and local atomic composition of the TiO_2-GL by high-resolution TEM (HRTEM). Fig. 2e shows a representative HRTEM image of TiO_2-GL. The measured interplanar distance is 0.236 and 0.323 nm, which are corresponding to the (004) plane of anatase phase and (110) plane of rutile phase, respectively. The SAED pattern in Fig. 2f exhibits diffraction rings of the A (004), A (200) and R (110) indicating alternated anatase and rutile nanodomains in the whole film structure. In fact, the co-existence of the anatase and rutile phases in the same particle is commonly observed in other study [38]. On one hand, such graphene-like morphology with hybrid crystal structure can provide higher specific surface areas and more active sites for the Na^+ insertion/extraction and elevate the Na^+ storage properties. On the other hand, each film is formed by crystalline structures (mixture of anatase and rutile) of TiO_2, which are a stable host for the Na^+ insertion/extraction reaction and facilitate charge transportation the electrode/electrolyte interface.

CV measurements were conducted to confirm the electrochemical reaction of P25 and TiO_2-GL between 0 and 2.8 V vs. Na/Na^+ with a scan rate of 0.2 mV s^{-1}, the results are shown in Fig. 3. It could be observed that for both P25 and TiO_2-GL, the currents in the initial cathodic scans were higher than subsequent sweeps, indicating the occurrence of irreversible decomposition of the electrolyte and formation of solid electrolyte interface (SEI) film during the first cycle. Similar results have been reported by other researchers [39]. Particularly, an intense irreversible peak can be