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Carbon-coated anatase titania as a high rate anode for lithium batteries

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HIGHLIGHTS

- Nanostructured TiO_2 nanorods and nanowires are synthesized via a hydrothermal reaction.
- Carbon coating enhances electric conductivity of nanostructured TiO_2 to ~10^{-1} S cm^{-1}.
- Conducting carbon layer greatly improves electrochemical property of nanostructured TiO_2.

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ABSTRACT

Anatase titania nanorods/nanowires, and TiO_2(B) are synthesized via a hydrothermal reaction of commercial TiO_2 (P-25) in strong alkaline environment. Surfaces of these products are modified by carbon to improve the electrical conductivity through carbonization of pitch as the carbon source at 700 °C for 2 h in an Ar atmosphere. Even after carbon coating, the resultants exhibit the same crystal structure and morphology as confirmed by Rietveld refinement of x-ray diffraction data and transmission electron microscopic observation that the images display thin carbon coating layers on the surfaces of anatase nanorods and nanowires. Although the bare and carbon-coated anatase TiO_2 nanorods exhibit stable cycling performance, the high rate performance is highly dependent on the presence of carbon because of high electrical conductivity, ~10^{-1} S cm^{-1}, enabling Li^+ ion storage even at 30 °C (9.9 A g^{-1}) approximately 100 mAh $(g\text{-}TiO_2)^{-1}$ for the carbon-coated anatase TiO_2 nanorods. Besides, the bare and carbon-coated anatase TiO_2 nanowires show poor electrode performances due to their large particle size and high crystallinity causing Li^+ insertion into the host structure difficult. It is believed that the conducting carbon coating layers greatly improves the electrochemical property through the improved electrical conductivity and shortened diffusion path.

1. Introduction

Lithium-ion batteries (LIBs) are applicable to various electronic devices. In particular, a combination of high power and safety is essential to rechargeable LIBs for energy storage system (ESS), electric vehicles (EVs) and hybrid electric vehicles (HEVs) [1]. Commercial LIBs commonly use graphite as the anode material. The graphite electrode, however, has several disadvantages such as its electrical disconnection, structural deformation and initial loss of capacity [2–4]. To solve the above-mentioned demerits, transition metal oxides have been widely investigated by numerous research groups. Among them, TiO_2 has been paid much attention as anode materials for LIBs because it operates in the voltage range of 1.6–1.9 V vs. Li/Li^+ accompanied by insertion and extraction of Li^+ ion [5]. These characteristics render it a potential anode material for high power lithium ion batteries, avoiding the necessity of a passivation layer at the contact to the liquid electrolyte [5–8].

Interestingly, TiO_2 has various polymorphs such as rutile [9], brookite [10], anatase [11–13], TiO_2(B) [14], etc. Under standard conditions, rutile is the thermodynamically most stable structure of TiO_2, and is also the most common natural form [2]. In particular, anatase phase is capable of electrochemical Li^+ ion storage showing a voltage plateau (1.6–1.9 V vs. Li/Li^+), where the lithium intercalation is controlled by the diffusion of lithium ion. Also, nanostructured anatase TiO_2 are believed as promising materials for

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high rate Li^+ storage because of their large specific surface area and suitable structure for lithium intercalation [1,4,11,15–18]. TiO_2(B) is more open structure than rutile, anatase or brookite, with significant voids and continuous channels that are capable of intercalation [14].

In this work, anatase TiO_2 nanorods/nanowires and TiO_2(B) nanowires are synthesized via a hydrothermal reaction in strong alkaline environment. Also, we attempt to carbon coating on the surface of nanostructured particles to improve their poor electric conductivity. The produced TiO_2 are tested for Li^+ insertion or extraction as high power anode materials.

2. Experimental section

2.1. Synthesis

To obtain nanorods and nanowires-shaped of TiO_2, TiO_2 powders (0.2 g, P-25, Degussa) were dispersed in 10 M NaOH aqueous solution (40 ml), and then transferred to a Teflon-lined stainless steel autoclave (50 ml). The reaction time was set for 11 h for nanorods and 48 h for nanowires at 170 °C [19]. After the hydrothermal reactions the white precipitates were washed by distilled water till pH 7 and were dried at 80 °C overnight in air. The dried powders, presumably $Na_2Ti_3O_7$ nanorods and nanowires, were subject to ion exchange in HCl aqueous solution to yield $H_2Ti_3O_7$ nanorods and nanowires, where the Na/H mole ratio is 0.125. After the ion exchange, the products were rinsed by distilled water again until pH reached neutral and were dried at 80 °C in air. After that, the resultant materials which is $H_2Ti_3O_7$ nanowires were calcined at 450 °C for 4 h and 700 °C for 2 h in air to obtain the TiO_2(B) nanowires and anatase TiO_2 nanowires. Likewise, the other resultant material which is $H_2Ti_3O_7$ nanorods were calcined at 600 °C for 4 h in air to obtain the anatase TiO_2 nanorods. The produced nanorods and nanowires were mixed with an appropriate amount of pitch as a carbon source and were calcined at 700 °C for 2 h in an Ar atmosphere to produce carbon-coated anatase TiO_2 nanorods and nanowires.

2.2. Characterization

The crystalline phase of the products was characterized by powder x-ray diffraction (XRD, Rint-2000, Rigaku) using Cu-Kα radiation. The XRD data were obtained with a step size of 0.03° and a count time of 5s. The collected intensity data from the XRD were analyzed by the Rietveld refinement program Fullprof 2002 [20]. The particle morphologies of the produced powders were observed by scanning electron microscopy (SEM, S-4700, Hitachi) and transmission electron microscopy (TEM, JEM-3010, JEOL).

2.3. Electrochemical properties

For electrode fabrication, the synthesized powders were separately mixed with Super-P and Ketjen black (1:1 in weight) as conducting materials and polyvinylidene fluoride (8:1:1 in weight) in *N*-methylpyrrolidinon. The obtained slurry was coated onto Cu foil and roll-pressed. The electrodes were vacuum dried overnight at 80 °C prior to use. The typical amount of loaded active material was typically 3 mg cm^{-2}. Charge-discharge tests were done using R2032 type coin cells having Li metal as the counter electrode. The electrolyte solutions were 1 M $LiPF_6$ in a mixture of ethylene carbonate - dimethyl carbonate (1:1 in volume). The cells were cycled between 1 V and 2.5 V from 50 mA g^{-1} to 9.9 A g^{-1} at 25 °C.

3. Results and discussion

According to our previous report [19], the formation of anatase nanorods and nanowires is greatly dependent on reaction time under the hydrothermal environment, so that longer reaction leads to the formation of nanowires through merging of smaller nanorods. The starting TiO_2 particles dissolve in the NaOH solution during the hydrothermal reaction that breaks the Ti–O bond from TiO_2. This leads to immediate formation of low crystalline $Na_2Ti_3O_7$ lamellar sheet. Since the bond strength of Na–O is weaker than that of Ti–O in the lamellar sheet [21,22], the weaker Na–O bonds, thereby, are likely to be readily broken during the high-pressure hydrothermal reaction. This may split the surface of the lamellar sheets and induce formation of whisker-like nanorods in the nanosheet. The reaction further progresses toward the center of the nanosheets, which are then completely transformed to nanorods as shown in Fig. 1a.

Anatase structured TiO_2 is synthesized through the above-mentioned process. Produced powders, anatase nanorods (ANR) and carbon-coated anatase nanorods (C-ANR), are observed by transmission electron microscopy (TEM). The ANR exhibits rod-shaped particles lengthened to tens of nanometers with thickness of 5–10 nm (Fig. 1a and b), and the morphology does not change even after the carbon coating, carbonized from pitch, at 700 °C for 2 h in an Ar atmosphere (Fig. 1c and d). TEM image displays that carbon layers present on the surfaces of nanorods (Fig. 1e), while the surface is smooth for the carbon-free ANR without sediment of carbon (Fig. 1b). In addition, the coating layers are found to be uniform and thin (approximately 1–3 nm). Produced carbon from pitch is also observed by TEM (inset of Fig. 1e), since the carbon layer was originated from the carbonization of pitch. Produced carbon exhibits plate-like particles with amorphous or low crystallinity as confirmed in electron diffraction. The presence of carbon layer is further confirmed in Raman spectrum (Fig. 2b), namely, appearance of two bands at 1347 cm^{-1} and 1591 cm^{-1} of which the latter is due to the C=C symmetrical vibration that results from the formation of crystalline π-bond sp^3 character after the carbonization. The content of carbon is approximately 2.9 wt. % as analyzed by CHN analyzer and the resulting electric conductivity measured by a 4-probe method is 1.8×10^{-1} S cm^{-1}, whereas that of the carbon-free ANR is approximately 6.9×10^{-6} S cm^{-1}.

Rietveld refinements are performed for x-ray diffraction (XRD) data of ANR (Fig. 1c) and C-ANR (Fig. 1f) based on the space group of $I4_1/amd$ tetragonal structure. The results show that the observed patterns coincide with the calculated ones, meaning formation of anatase structure for both ANR (*R*wp: 11.8%) and C-ANR (*R*wp: 12.5%). The formation of pure anatase is also proved in the Raman data that presents a typical spectrum of anatase phase (Fig. 2a). The broadened XRD peaks indicate that both ANR and C-ANR have low crystallinity because the clear peak separation of (103), (004), and (112) peaks around 38° (2θ) is not observed, which would be affected by the smaller particle size. Though synthesis of anatase TiO_2 nanorods is successful, it is not possible to produce TiO_2–B nanorods because the phase is metastable so that our method spontaneously leads to formation of anatase phase during dehydration process as we previously reported [19]. Crystal structure does not vary before and after the carbon coating as confirmed in the lattice parameters calculated from the Rietveld refinement (ANR: a = b: 3.7882(4) Å, c = 9.5115(9) Å, C-ANR: a = b: 3.7887(5) Å, c = 9.5115 (9) Å). Indeed, oxygen chemistry is highly sensitive in TiO_2 system, since even a tiny amount of oxygen vacancy ($TiO_{2\text{-}x}$, $x > 0.001$) can induce the spontaneous structural transformation to Magn'eli form (TiO_{2-x}, $x > 0.001$ [23]), which can no longer be described as defective titanium dioxide, but as a different compound with a new crystallographic structure. The present carbon