TiO₂-entrained tubular carbon nanofiber and its electrochemical properties in the rechargeable Na-ion battery system

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Abstract

Well-defined “peapod” nano-carbon structure of TiO_2 nanoparticles entrained tubular carbon nanofiber with nano-gate channels (TNG-TCNF) was first designed and fabricated through the simple low-temperature impregnation of titanium tetrachloride to tubular carbon nanofiber with nano-gate channels (NG-TCNF) for the application as an effective anode material for Na-ion batteries. Many nano-gated channels on the NG-TCNF walls effectively facilitated the deposition of TiO_2 nanoparticles inside its tube. The maximum entrained mass ratio of the TiO_2 nanoparticles in the NG-TCNF was evaluated to 35 wt%. The prepared TiO_2 entrained NG-TCNF exhibited remarkable discharge capacity of 120 mAh/g as anode for Na-ion battery with a relatively stable cycle-ability compared to those of bare TiO_2 , confirming the effective role of gateway for charge/discharge of Na ions.

Keywords: TiO_2 ; Na-ion battery; anode; carbon nanofiber

1. Introduction

High-performance batteries are in high demand in the rapidly developing electric industry. Lithium-ion (Li-ion) batteries currently dominate the market for portable electric devices and electric vehicles due to their high specific energy density and long lifecycle. However, for large-scale energy storage applications, such as smart electric grids, low-cost batteries are required, and sodium-ion (Na-ion) batteries become more attractive because sodium is more abundant than lithium. The high performance requirements, such as high energy density, high rate performance and stability in the Li and Na-ion batteries, are principally related to the electrode materials [1-3]. Graphites are commonly used as the anodic material in commercial Li-ion batteries due to their low and flat potential at discharge, high stability, and safety over a long lifetime [4-6]. However, in Na-ion batteries, graphites are unsuitable for use as an anode because the sodium ions are unable to intercalate into the graphitic material at room temperature [7]. Thus, novel anode material must be developed for Na-ion batteries.

Metal oxides including TiO_2 , Fe_2O_3 and SnO_2 have been suggested as promising anodic materials for Na-ion batteries due to their high theoretical specific capacities [8-10]. Among them, Anatase type titanium oxide (TiO_2) has attracted the most attention due to its high rate performance, small solid electrolyte interphase (SEI) formation and cost competitiveness. However, the intrinsic low electric conductivity and structural instability of anatase type TiO_2 leads to an unsatisfactory discharge capacity and cycle stability, which hinders its further application. Incorporating nanoparticles into a conductive matrix such as graphene or carbon nanotubes (CNTs) has proven an effective strategy for improving the performance of metal oxides, and such composite structures can provide enhanced electric conductivity and protection for loaded materials, qualities that are highly desired in anodes of Li-ion batteries

[11, 12].

We firstly attempted to design and prepare a novel TiO_2 -entrained tubular carbon nanofiber (TNG-TCNF) structure. To prepare the TNG-TCNF, a specially designed tubular carbon nanofiber with nanosized channels on its walls (NG-TCNF) was used as a loading material [13]. The NG-TCNF possesses high electrical conductivity, and its unique structure has been proven useful for entraining TiO_2 nanoparticles inside the tube [14]. The prepared TNG-TCNF was applied to Li-ion and Na-ion batteries to evaluate its anodic performance, reliably demonstrating a large discharge capacity and high rate performance.

2. Experimental

2.1. Sample preparation

The tubular carbon nanofiber with nano-gate channels (NG-TCNF) was fabricated at 685 °C catalytically via chemical vapor decomposition as illustrated in Scheme 1. Fe/Ni alloy (Fe-Ni 6/4 (wt %)) was used as a catalyst with carbon monoxide as a carbon source [13]. The pristine carbon nanofiber was further treated with a 10% HCl solution for 7 days to remove the catalyst. In addition, a commercial CNT (CCNT, JEIOTECH Co. Ltd., South Korea) was used without further purification for comparison.

The TCNF and CCNT were graphitized at 2800 °C for 10 min for TEM observation [13].

The TiO_2 was entrained into the TCNFs and incorporated to CCNTs through the impregnation of Ti^{4+} ions using an aqueous 1 M TiCl_4 solution at room temperature. To facilitate the deposition of the Ti^{4+} ions into the TiO_2 particles, the solution pH was carefully controlled at

approximately 2 by adding a suitable quantity of NaOH to the solution. Scheme 2 depicts the process for fabricating the loaded TiO₂.

2.2 Characterization of the as-prepared samples

The mass ratio of TiO₂ in the products was evaluated via thermogravimetric analysis (TGA, Shimadzu, Japan) in air. Transmission electron microscopy (TEM, JEOL JEM-2100F, operated at 200 kV) was employed to observe the product structures. Small quantities of NG-TCNF, CCNT, Graphitized NG-TCNF (GNG-TCNF), Graphitized CCNT (GCCNT), TNG-TCNF (TiO₂ entrained NG-TCNF), and T-CCNT (TiO₂-incorporated CCNT) were suspended in n-butanol, and the suspension was dropped onto a thin amorphous carbon-coated copper grid, then dried in air to allow TEM imaging. The crystallographic properties of the products were confirmed via X-ray powder diffractometry (CuK α , Ultima-III, Rigaku, Japan).

The anode performance was evaluated by assembling the materials into CR2032 coin-type cells. Styrene-butadiene rubber (SBR, trade name BM-400B, ZEON, Japan) and carboxymethyl cellulose (CMC) were used as the binder and thickening agent, respectively (anode material: Ketjen black: SBR: CMC = 75:5:14:6, wt %). The slurry mixture was coated onto copper foil (18- μ m-thick), dried at 120°C under vacuum for 12 h, pressed using a roll-type mill under 100 MPa and cut into discs (12 mm in diameter and approximately 40- μ m-thick). The coin-type cells were assembled in an Ar-filled glove box using a polyethylene film (16- μ m-thick) as a separator. 1 M NaClO₄ in ethylene carbonate (EC) / dimethyl carbonate (DMC) (1:1 vol%, Ube Kosan, Japan) was used as the electrolyte and Na metal was used as the counter electrode. The electrochemical measurements were obtained by

charging at a constant current/constant voltage and discharging at a constant current (CCCV-CC) with a current density of 35 mA/g in the potential range of 0–3.0 V at room temperature (Toscat-3100, Toyo System, Japan).

3. Results and discussion

3.1 Preparation and structural feature of tubular carbon nanofiber with nano-gate channels

The TEM images of the pristine and GNG-TCNFs and GCCNTs are exhibited in Figure 1 and 2. Both the NG-TCNF and CCNT clearly displayed hollow channels (inside the tubes) with average outer diameters of 40 and 20 nm and inner diameters of 14 and 10 nm, respectively. In most case, the NG-TCNF tubes are not straight throughout their length but bend slightly, indicating surface-modulated structures. The inner diameter of one NG-TCNF tube varies from 7.2-16.2 nm with a pseudo-periodicity of 40-60 nm [13], although its outer diameter appears nearly identical. The metal particles embedded in the tube display an obvious elongation as indicated by the arrows in the images. Such elongation is generally irregular with several steps along the tube axis. The TEM image (Figure 1(d)) reveals lattice-resolved graphene layers that are oriented parallel to the tube axis, but exhibit a local dislocation within the bending region, indicating that the graphene layers are not always straight as explained in our previous work [13].

The structural stabilities of the NG-TCNF and CCNT were evaluated using high-temperature graphitization. The GNG-TCNF also exhibits hollow channels and stepwise sidewalls (Figure 2). The TEM images in Figures 1 and 2 depict the pristine and graphitized NG-TCNFs within

planar facets in a dislocated graphite-like stack constructed with polygonal shaped units and nanosized channels crossing the walls like nano-gates. The nano-gates and thus the polygonal shape become more distinct after with graphitization. These results indicate that these NG-TCNFs have a polygonal cross section not a circular one as in the CCNTs [13].

The NG-TCNF and CCNT structures after TiO_2 entrainment / incorporation are presented in Figure 3. The TiO_2 nanoparticles can be successfully entrained into the NG-TCNF, whereas a separate phase containing TiO_2 nanoparticles and CCNT can only be obtained when using CCNT as the loading material. A comparison of the structural differences between the NG-TCNF and CCNT provides several explanations for the different mechanism by which the TiO_2 is deposited in these two processes.

According to Figures 1 and 2, the NG-TCNF has a larger inner diameter and higher surface roughness, and possesses lots of nano-gate channels on its walls which are absent from the CCNT, which was schematically depicted in Figure 4.

3.2 The entrainment of TiO_2 nanoparticles into the tube of NG-TCNF

For impregnation with the Ti^{4+} in solution, the nucleation of TiO_2 can be either homogeneous or heterogeneous, depending on the structural factors of the foreign species. **Generally, heterogeneous nucleation takes place more easily because the foreign species can act as nucleation substrates for the formation and growth of crystalline particles, eliminating the need to create new surface-sites.** However, to achieve heterogeneous nucleation, high-energy sites are required for the crystal nucleation [15]. CCNT has smooth surfaces both inside and outside the tube. These surfaces are chemically inert due to their graphitic nature and can

therefore not act as heterogeneous nucleation sites for the TiO_2 . Thus, only homogeneous nucleation can occur with TiO_2 when CCNT is used as a loading material, which leads to a separate product phase. The NG-TCNF has several advantages over CCNT as a loading material: the nano-gates on the walls and the relatively large inner diameter can simplify the diffusion of Ti^{4+} into the tube, and the dislocated graphite-like stacking can create numerous high-energy sites that allow the heterogeneous nucleation of TiO_2 inside the tube and its further growth into nanoparticles. Therefore, a well-defined “peapod” structure can be obtained when TiO_2 nanoparticles are incorporated into NG-TCNF tubes. The mass ratios of the TiO_2 nanoparticles in the NG-TCNF was evaluated via TGA and found to be 35 wt%, respectively. Considering the high electric conductivity and mechanical stability of NG-TCNF, such structure is expected to enhance the performance of the TiO_2 when used as an electrode material in Na-ion battery.

Figure 5 provides the XRD results for samples. According to the XRD results, Titania of the bare TiO_2 and TNG-TCNF were clearly confirmed as anatase types of TiO_2 .

3.3 Electrochemical properties of TNG-TCNF as an anode material in Na-ion battery

The charge-discharge profiles and cycle-ability of bare TiO_2 , NG-TCNF and TNG-TCNF in the Na-ion battery system were illustrated provided in Figure 6.

TNG-TCNF showed much higher capacities than the bare TiO_2 (average particle size: 100 nm, not shown) possibly due to the nanosized TiO_2 particles distributed throughout the carbon matrix. The smaller particle size can create additional insertion sites for the Na-ion, and the existence of NG-TCNF can enhance the overall electrode conductivity, which can facilitate

the rapid electric and ion transport properties.

To investigate the effects of different carbon loading materials on the performance of TiO₂ in a battery, the discharge capacity of the TiO₂ nanoparticles in the TNG-TCNF was calculated using following Equation.

$$C_{\text{calc, TiO}_2} = \frac{(C_{\text{TiO}_2\text{-carbon}} - C_{\text{carbon}}(1 - R_{\text{TiO}_2}))}{R_{\text{TiO}_2}}$$

List of symbols

$C_{\text{calc, TiO}_2}$	Calculated discharge capacity [mAh/g]
$C_{\text{TiO}_2\text{-carbon}}$	Discharge capacity of TNG-TCNF [mAh/g]
C_{carbon}	Converted discharge capacity of NG-TCNF [mAh/g]
R_{TiO_2}	Content percentage of TiO ₂ [wt.%]

The discharge capacities of the Na-ion battery anodes consisting of bare TiO₂, NG-TCNF and TNG-TCNF were determined to be 78, 45 and 120 mAh/g, respectively (Figure 6 (a)). The composite material exhibits improved performance.

Figures 6 (b) compared the cycling behaviors of the bare TiO₂, NG-TCNF and TNG-TCNF electrodes. Both bare TiO₂ and NG-TCNF showed gentle capacity fading until 50th cycles. On the other hand, TNG-TCNF composite showed sudden drop of initial capacity within 10th cycles, and then its capacity fading became gentle. However, its discharge capacity after 50th cycles was much larger than the others. This steep change on the initial capacity fading of TNG-TCNF composite would be originated from complicated factors of bare TiO₂ and NG-TCNF relating with poor electronic conductivity and SEI formation, respectively.

Fig. 7 showed the Nyquist plots for the bare TiO₂, NG-TCNF and TNG-TCNF electrode

materials. The diameter of the semicircle correlating with the charge-transfer resistance was much smaller for NG-TCNF which meant the higher conductivity than that of the bare TiO_2 in high frequency region. The sloping line at the low frequency reflects the ionic diffusion of Na ions in the bulk materials [16-18]. The slope of bare TiO_2 with poor electronic conductivity was gentle. On the other hand, the slope of TCNF was steep. From these impedance results, TNG-TCNF also showed improved electrochemical performance compared to the bare TiO_2 . Especially, TNG-TCNF, even though its TiO_2 nanoparticles existed at inside of tube of NG-TCNF, it could be proved to have higher charge/discharge capacity and smaller ionic diffusion resistance, meaning that the nano-gate channels of NG-TCNF with high electric conductivity was very effective as a gateway for insertion/desertion of Na ions as well as a conducting and diffusion pathway for transfer of electron and ion.

4. Conclusion

(1) A special “peapod” structure in which TiO_2 nanoparticles are entrained in the inner spaces of NG-TCNFs was successfully fabricated through a low-temperature impregnation process using NG-TCNF as the loading material.

(2) The maximum entrained mass ratio of the TiO_2 nanoparticles in the NG-TCNF was evaluated to 35 wt%. The prepared TiO_2 entrained NG-TCNF exhibited remarkable discharge capacity of 120 mAh/g as anode for Na-ion battery with a relatively stable cycle-ability compared to those of bare TiO_2 , confirming the effective role of gateway for charge/discharge of Na ions.

(3) NG-TCNF was confirmed as a good loading material for TiO_2 , capable of facilitating the diffusion and heterogeneous nucleation of the Ti^{4+} into the nanotube.

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Figure captions

Scheme 1. NG-TCNF manufacturing process.

Scheme 2. TiO₂ nanoparticle incorporation / entrainment processes to CCNT / NG-TCNF.

Figure 1. TEM images of pristine CCNT and NG-TCNF samples.

(a), (b): TEM images of CCNT; (c), (d): TEM images of NG-TCNF

Figure 2. TEM images of graphitized CCNT and NG-TCNF samples.

(a), (b): TEM images of graphitized CCNT; (c), (d): TEM images of graphitized NG-TCNF

Figure 3. TEM and EDX images of TiO₂ incorporated CCNT and TiO₂ entrained NG-TCNF samples.

(a), (b), (c): TiO₂ incorporated CCNT; (d), (e), (f): TiO₂ entrained TNG-TCNF

Figure 4. Schematic pictures of TiO₂ nanoparticle incorporation / entrainment mechanisms to CCNT / NG-TCNF samples.

(a) TiO₂ incorporation model to CCNT, (b) TiO₂ entrainment model to NG-TCNF

Figure 5. X-ray diffraction profiles of bare TiO₂, NG-TCNF and TNG-TCNF samples.

Figure 6. Electrochemical performances of bare TiO₂, NG-TCNF and TNG-TCNF samples in the Na-ion battery system

(a) Charge–discharge profiles in 1st cycle, (b) Cycle-abilities.

Figure 7. Nyquist plots for the bare TiO₂, NG-TCNF and TNG-TCNF samples.

Scheme 1.

Scheme 2

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.

Figure 7.