Tio$_2$@Sn core–shell nanotubes for fast and high density Li-ion storage material

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ABSTRACT

TiO$_2$@Sn core–shell nanotube material prepared by thermal decomposition of SnCl$_4$ on TiO$_2$ nanotubes at 300 °C has been demonstrated superior Li-ion storage capability of 176 mA h/g even at high current rate of 4000 mA/g (charge and discharge of all TiO$_2$ within 5 min) in spite of using low carbon content (5 wt%). This value corresponds to volumetric energy densities of 317 mA h/cm^3, and its value was 3.5-fold larger than that of the bare TiO$_2$ nanotubes.

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1. Introduction

TiO$_2$ oxide material is typical Li-ion intercalation compound with a volume change <4%, according to the following reaction: TiO$_2$ + xLi$^+$ xe$^-$ ↔ Li$_x$TiO$_2$ ($0 \leqslant x \leqslant 1$), and has bee received much research spotlight for its easy control of particle morphology into nanotubes, nanowires, nanoparticles, etc. [1–9]. In bulk Li$_x$TiO$_2$, x = 0.5 is most consistently reported as the maximum insertion ratio [4]. However, Li surface storage on nanometer-sized particles can be energetically more favorable than bulk insertion. For instance, TiO$_2$-B nanotubes [10] and anatase TiO$_2$ nanotubes [11] can store x > 1 in Li$_x$TiO$_2$. TiO$_2$(B) nanowires and nanotubes can act as an intercalation host for Li-ion in order to render Li ionically and electronically conducting, i.e. as an n-type semiconductor [10,12,13]. However, TiO$_2$ host for Li-ion intercalation has intrinsically low electronic conductivity. Therefore, enhancement of electronic conductivity for the host TiO$_2$ material is also required to decrease the polarization. When conducting additives such as carbon black can be mechanically mixed with the host material in Li-ion battery electrodes, larger amounts of the conducting additives are required to obtain the desirable electronic conductivity. In general, over 10 wt% carbon black was used in order to maintain a high rate performance [1,2,12,13].

Under these strategic concepts, uniform metallic Sn metals are coated onto TiO$_2$ nanotubes in order to overcome the power density of the TiO$_2$ electrode material in this study. A thin Sn coating layer is anticipated to facilitate fast and stable Li-ion pathways and allow smaller amount of conducting-additive carbon for the desired electrochemical performance. The Sn coating TiO$_2$ nanotube with low carbon black content can be investigated in the viewpoint of improvement for the volumetric density at a high current rate of 4000 mA/g, compared to that of the bare TiO$_2$ nanotubes.

2. Experimental section

TiO$_2$ nanotube was synthesized by hydrothermal reaction at 150 °C according to a method previously reported by us [14]. And then for the Sn coating onto the TiO$_2$ nanotube, as-prepared bare TiO$_2$ nanotube was first mixed with 50 g of glyme solvent under Ar atmosphere, and dissolved 3 g of hydrobenzamide at 150 °C under vigorous stirring and 2.4 g of anhydrous SnCl$_4$ was added in this solution, and finally added 5 g of NaBH$_4$, followed by the increasing the temperature at 300 °C for 1 h. After cooling to room temperature, the solution was rinsed with deoxidized water and ethanol for six times, and dried under vacuum at 70 °C for overnight.

Small-angle X-ray scattering (SAXS) measurements were carried out on powder samples of bare TiO$_2$ and TiO$_2$@Sn nanotubes. The scattering intensities were recorded as a function of scattering vector (q) in the range of 0.3–5 nm^{-1}, corresponding to 1.2–21 nm in size. Ti K-edge X-ray absorption spectra (XAS) of the bare TiO$_2$ and TiO$_2$@Sn have been taken on BL$_7$C1 beamline in the storage ring of 2.5 GeV with the ring current of 120–170 mA at Pohang

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light source (PLS) which is the third generation synchrotron radiation source. Soft XAS measurements were performed on U7 beamline in PLS The U7 beamline, which consists of 4.3 m long, 7 cm-period undulator and the variable-included angle plane-grating monochromator, provides the highly brilliant and monochromatic linear-polarized soft X-ray for the high resolution spectroscopy. The electrochemical studies were carried out using the method in Ref. [14], and normally the amount of the electrode materials was 29 mg. The capacity is calculated by the weight of TiO_2 only.

3. Results and discussion

Fig. 1 shows XRD patterns of as-prepared bare TiO_2 nanotube and Sn-coated TiO_2 core–shell type nanotube (TiO_2@Sn). The XRD pattern of bare TiO_2 nanotube shows a mixture of $H_2Ti_2O_5 \times H_2O$ and anatase TiO_2 phases. On the other hand, the Sn coating procedure at 300 °C leads to effective transformation into anatase TiO_2 phase. Thermal dehydration of protonic titanates leads to the predominant formation of anatase or rutile TiO_2 phases, depending on the pretreatment conditions [14–17]. When Sn nanoparticles were coated onto the TiO_2 nanotubes, a tetragonal tin phase with TiO_2 was observed without the formation of SnO_2. ICP-MS analysis confirmed the formation of 20 wt% Sn and 80 wt% TiO_2. When the Sn coating content was decreased to 10 wt%, uncoated TiO_2 parts were observed. Sharp XRD pattern of the Sn phase indicates that metallic Sn on the TiO_2 nanotubes is of a thin film-like form with large crystallites dimension along the parallel tube direction. Same phenomenon to ours was reported in Ti@CNT nanotubes [18].

Small-angle X-ray scattering (SAXS) experiment has been carried out to investigate averaged overall structure of nanotubes. Overall array repeating distances of the bare TiO_2 and TiO_2@Sn nanotubes, calculated from Bragg equation, have been estimated as 6.65 and 6.84 nm, respectively, which correspond to 7.68 and 7.90 nm of center-to-center distance of nanotubes. Therefore, the introduction of Sn layer on the TiO_2 nanotube surface almost retains array structure of nanotubes unchanged, while the array distance is increased by 2.2 Å, indicating a successful coating of Sn layer on TiO_2 nanotube. Brunauer–Emmett–Teller (BET) measurement of the coated sample was 210 m²/g, compared to uncoated one (213 m²/g). This value is quite reasonable because Sn coating at 300 °C led to removal of H_2O molecules from the uncoated sam-

ple. It has been reported that BET surface area of the dehydrated TiO_2 nanotubes showed 239 m²/g [14]. In addition, such a large BET surface area after coating indicates the highly defective Sn coating layer.

Fig. 2 shows TEM images of as-prepared bare TiO_2 nanotube and the core–shell TiO_2@Sn nanotube. After coating with Sn, its surface morphology appears to change completely, and lattice images confirms the lattice fringe of (2 0 0) plane corresponding to the *d* spacing distance of 2.91 Å of the tetragonal metallic Sn phase. As can be seen in the TEM image for the local-area selected nanotube, the tube diameter increases from 8.5 to 12 nm after Sn coating, implying that the Sn coating thickness is ∼1.8 nm. The mismatched values of the coating thickness estimated from SAXS and TEM results from following facts: while the TEM reveals a detailed local morphology of nanotubes, the SAXS technique presents an overall averaged structure within relatively large sampling area, ∼500 × 800 μm², in this study.

Fig. 3 shows Ti K-edge XANES (X-ray absorption near edge spectra) spectra and Fourier transformed magnitude (FT) of the k^3-weighted EXAFS (extended X-ray absorption fine structure) spectra for both bare TiO_2 and TiO_2@Sn nanotubes. The XANES spectra of the nanotubes show quite different pre-edge peak features compared to those of the bulk TiO_2 (Fig. 3a). Compared to the bulk TiO_2, a higher peak A_2 at the both bare TiO_2 and TiO_2@Sn nanotubes indicates that relative higher local structural distortion and lower coordination exists due to the oxygen vacancies that result from the smaller particle size and higher surface to volume ratio. This leads to surface distortions and the surface defective sites. For the TiO_2@Sn, the peak A_2 becomes effectively weaker than the bare TiO_2 nanotube. It can be considered that the metallic Sn covers the TiO_x unit associated with the defective surface, which is opened to free volume space in the bare TiO_2 nanotube. The local structural environment of TiO_x unit in the interface region then becomes relatively stable. Fig. 3c shows radial distribution function (RDF) around the Ti ion of the nanotubes, compared to those of bulk TiO_2 reference materials. For the TiO_2@Sn, a new shoulder FT peak occurs at ∼3.1 Å, which corresponds to the third FT peak of rutile-type TiO_2 (Ti–O–Ti binding pair in the corner-sharing TiO_6 octahedra). This indicates that a minor rutile phase exists in the TiO_2@Sn nanotube. During the Sn coating process of the anatase-like TiO_2 nanotube, Sn atoms can be adsorbed onto distorted
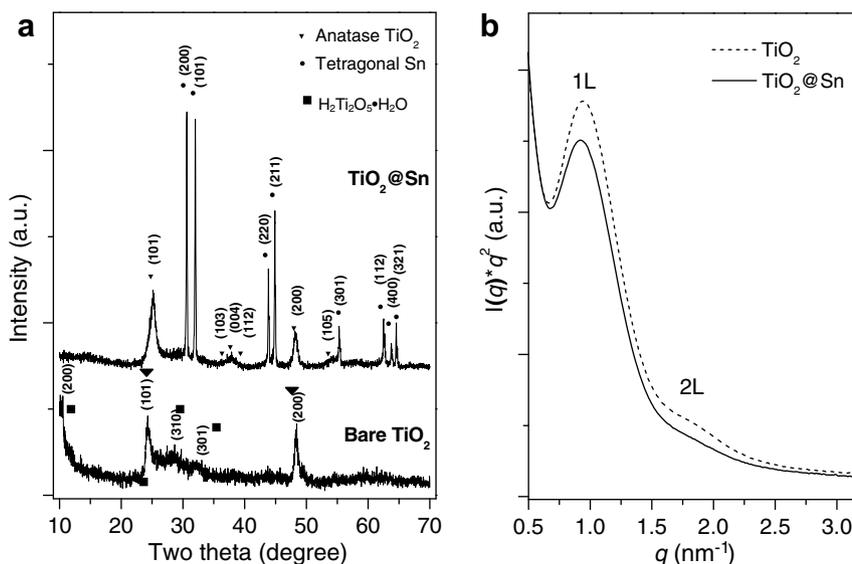
Fig. 1. (a) XRD patterns of the TiO_2 nanotubes prepared at 150 °C, and TiO_2@Sn core–shell nanotube powders. (b) Azimuthally averaged Lorentz corrected SAXS intensity measured from the TiO_2 and TiO_2@Sn nanotubes.