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Reversible phase transformation of titania (anatase) nanotubes upon electrochemical lithium-intercalation observed by *ex situ* transmission electron microscopy

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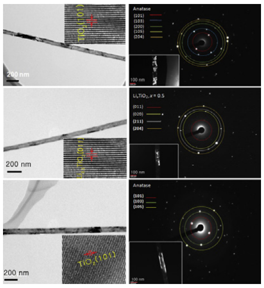
HIGHLIGHTS

- Synthesis of TiO_2 nanotube (NT) array by atomic layer deposition has been reported.
- Li-intercalation in anatase TiO_2 NT curved surface has been investigated by TEM.
- Reversible phase transformation in the NTs was observed in a discharging/charging cycle.
- NTs maintain crystallinity and structural integrity after long cycle run.

GRAPHICAL ABSTRACT



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ABSTRACT

In this article, microstructural changes in anatase titania (TiO_2) nanotubes (NTs) upon electrochemical lithium (Li)-insertion/de-insertion using *ex situ* transmission electron microscopy (TEM) have been reported. TiO_2 NT-arrays have been fabricated by coating the wall of the pores of the nanoporous anodic aluminum oxide (AAO) templates using atomic layer deposition (ALD). Anatase TiO_2 NT-array based anode with the wall thickness of ~ 14 nm shows a reversible discharge capacity of ~ 175 mAh g^{-1} (i.e., Li-concentration (x) of ~ 0.53) in the second discharge cycle. The NTs are structurally intact and maintain their high crystalline quality after many repetitions of charging and discharging. Reversible phase transformations from tetragonal (anatase) to orthorhombic (Li-titanate) polymorphs and back to tetragonal (anatase) in complete discharging/charging cycled TiO_2 NTs are observed *ex situ*. Electrical conductivity of the NTs decreases a bit due to lithiation. Arrays of the anatase TiO_2 NTs as anode in Li-ion secondary batteries show satisfactory cycle response and structural stability even after 50 cycles of charging/discharging.

1. Introduction

Design of new electrode materials for Li-ion secondary battery requires the understanding of microstructural changes and/or phase transformations of the material upon electrochemical reactions associated with Li^+ ions. The electrochemical reaction is further reliant on the texture as well as the size of the electrodes' materials. It has been reported that the reduced dimension significantly improves the storage capacity as well as the reaction kinetics *viz.* rate capability by decreasing the ionic and electronic paths, thus diffusion time ($t = L^2/D$, where L is the diffusion length, D is the diffusion constant). Large surface area of the low-

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dimensional structures further provides a wide contact with the electrolyte which can enhance the lithium-ion flux across the interface and thus the power density as a consequence.

Vertically aligned array of the one-dimensional (1D) nanostructures, for example, nanorods, nanowires, nanotubes (NTs) etc., are known as a class of potential electrode material owing to their large exposed surface area compared to the nanoparticle-based electrode with the same diameter or mass. The space between neighboring 1D nanostructures encourages the diffusion of electrolyte into the inner region of the electrode which improves the specific capacity and durability of the cells. The arrayed 1D structure additionally accommodates strain which arises due to the Li-insertion/de-insertion into/from the structure, along a specific orientation without irregular expansion [1–4]. Among the 1D nanostructures, NTs dominate in term of electrode performance on account of their higher surface area (both the inner and outer surfaces can be exposed to the electrolyte) [5–13]. Axial void space of the NTs also accommodates the volume expansion during Li-intercalation and eliminate the internal stress in the material providing excellent cyclability [2,14]. Moreover, vertically oriented NT arrays are quite significant as electrode materials since all the NTs are directly connected to the current collector which facilitates efficient charge transport without using conductive additives and/or binders.

As a safe and potential anode material for Li-ion battery, TiO_2 has been studied extensively since it has very high chemical stability, low self-discharge rate, low fabrication cost and environmentally benign. Anatase is outstanding owing to its reversible uptake of 0.5 Li per formula unit [15] and fast Li-ion insertion and extraction. Anatase structure consists of four octahedrally coordinated Ti atoms and eight three-fold coordinated oxygen atoms. The structure seems a chain of edge-sharing TiO_6 octahedrons where each Ti^{4+} ion is surrounded by six O^{2-} ions. The empty octahedral and tetrahedral sites in the unit cell are coordinated to host Li^+ upon electrochemical insertion. Since the tetrahedral voids are higher energy sites, only octahedral voids are supposed to take part in Li^+ intercalation. The inserted Li^+ in TiO_2 matrix occupy the interstitial octahedral sites in random fashion, where there are four octahedral sites available per primitive cell. The average overall occupation factor of the octahedral sites is restricted by the Li^+-Li^+ repulsive interactions. Tielens et al. [16] reported that up to $x = 0.25$ Li^+ uptake in the anatase structure, there will be only one octahedral void filled out of four in a primitive cell. The filling factor increases with increase in Li concentration which turns out to be two for $x = 0.5$ and four for $x = 1$ (saturated structure where all the octahedral sites are filled). Upon Li^+ insertion, the tetragonal phase TiO_2 (space group: $I4_1/amd$) undergoes a phase transformation to orthorhombic lithium titanate ($Li_{0.5}TiO_2$, space group: *Imma*) through Li-poor TiO_2 solid solution (space group: $I4_1/amd$) [17,18]. The main redox reaction responsible for the electrochemical activity is the conversion of Ti^{4+}/Ti^{3+} during the discharging process and vice versa during the charging process. The overall Li insertion and de-insertion in/from the TiO_2 can be described as:

$$TiO_2 + xLi^+ + xe^- \leftrightarrow Li_xTiO_2 \tag{1}$$

The intercalation properties are reported to be quite different to a large extent from the conventional intercalation kinetics when the size of TiO_2 approaches toward few nanometer and can accept more Li in the structure [19]. It has been reported that particles of 40 nm in diameter can host maximum $x = 0.1$ Li^+ in the structure without forming a new phase and the solubility limit reaches up to $x = 0.22$ for the particle size of 6 nm in diameter [18]. Interestingly, maximum solid solubility limit of Li^+ in the micron-sized/bulk anatase is limited to $x = 0.026$ [20]. Furthermore, the nanoparticles with sizes below 7 nm can host overall lithium concentration $x = 1$ in the structure and completely convert into Li_1TiO_2 with the same space group ($I4_1/amd$) as anatase, but with shifted lattice parameters [21]. With the formation of Li_1TiO_2 ($x = 1$) phase, the structure hosts extra Li compared to the micrometer-sized particles/bulk and the capacity reaches to the theoretical maximum value of ~ 330 mAh g^{-1} for the anatase TiO_2 [21,22]. Micrometer-sized anatase particles form Li-titanate upon lithiation up to maximum obtainable Li concentration depending on the particle size [22] with the expense of anatase phase. Wagemaker et al. [23] reported the formation of both the anatase and Li-titanate domains in a single micrometer sized particle due to lithiation. Wagemaker et al. [22] and van de Krol et al. [24] further reported that the particle size below 120 nm in diameter shows inexistence of two phase equilibrium in a single particle upon lithiation which turns out to be either anatase or Li-titanate phase. For micrometer sized particles, the Li-titanate phase domains grow by the expense of the anatase phase and the two-phase equilibrium between the anatase TiO_2 and orthorhombic Li-titanate phases is maintained by a continuous Li-ion exchange [25]. The micrometer-sized particles, however, can also be transformed to Li_1TiO_2 phase only at the elevated temperature, but not at room temperature because of the poor ionic conductivity of Li_1TiO_2 phase [26,27]. The poor conductivity arises owing to the complete filling up of the octahedral voids by Li-ions. Rahman et al. [28] compared electrochemical performance of TiO_2 NP and NT-based anodes where NP-based anode showed large irreversible capacity and poor capacity retention after several charging/discharging cycles compared to NT-based anode because of the large exposed surface area and short Li^+ diffusion path length in the NTs. Kim et al. [13] further compared electrochemical performance of anatase TiO_2 NT and NR-based anodes which demonstrates higher reversible capacity and capacity retention after large number of cycle run of the NT-based anodes compared to NRs although rate performance of NR-based anode dominates over NTs because of the higher electrode density.

There have been several reports present on the study of the microstructural change in anatase nanoparticles upon electrochemical Li-intercalation using neutron diffraction, *in situ* XRD, NMR and *in situ* Raman spectroscopy, etc. [24,25,29]. Xiang et al. [30] reported the electrochemically driven amorphous to cubic irreversible phase transformation of the TiO_2 NTs. No further work, however, has been reported so far on the study of intercalation mechanism in polycrystalline TiO_2 tubular structures. Li intercalation mechanism in tubular structure and spherical particles has been shown schematically in Fig. 1. In case of polycrystalline NTs, grains are arranged along the length of the NTs which usually appear nonspherical since thickness of the grains are restricted by the wall thickness of the NTs. Elongated grains in the NTs are narrow in the axial direction which gives rise to two variables like NTs' wall thickness and grain diameter in order to express the system unlike only diameter for the nanoparticles. Moreover, there is no report present on the study of reversible Li-intercalation mechanism in crystalline TiO_2 systems (for instance bulk/nanoparticles/one-dimensional structures) using TEM. Ohzuku et al. [31] reported *ex situ* XRD of Li-titanate phase with various degrees of intercalation which demonstrates that Li-titanate phase can be identified separately from anatase diffraction. In this report, *ex situ* TEM study of reversible phase-transformation in anatase TiO_2 nanotubes, fabricated by template-assisted ALD [32], upon Li^+-intercalation have been presented for the first time. The NTs were found to be stable in ambient and also in TEM even under a long time exposure.

2. Results and discussion

Fig. 2 illustrates the electrochemical performances of anatase TiO_2 NT-array based anodes with the average wall thickness of