The role of surface films during lithiation of amorphous and anatase TiO$_2$ nanotubes

D. Steiner, A. Auer, E. Portenkirchner, J. Kunze-Liebhäuser*

Institute of Physical Chemistry, University of Innsbruck, Innrain 52c, 6020 Innsbruck, Austria

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ABSTRACT

X-ray photoelectron spectroscopy and electrochemical impedance spectroscopy are used to investigate the electrochemical lithiation/delithiation behaviour of self-organized amorphous TiO$_2$ and anatase TiO$_{2-x}$ nanotubes. With proceeding bulk lithiation of the active material, surface films form on both nanotube arrays. Carbonates start forming with the beginning of the phase transitions and are reversibly desorbed upon delithiation, on both materials. LiF is found to mainly influence the lithiation/delithiation properties on amorphous nanotubes due to an important decrease of the surface film resistance and an increase of the surface film capacitance at potentials ≤ 2.0 V, where large amounts of LiF adsorb at the surface. Surface film formation is found to be completely reversible on amorphous nanotubes, while C—O, C=O and fluoride containing adsorbates partially stay adsorbed on anatase nanotubes. The higher reversibility of the surface chemistry on amorphous TiO$_2$ nanotubes is therefore assumed to be essential for the higher rate capability, faster kinetics, and the higher capacity retention observed for amorphous TiO$_2$ materials. This demonstrates that lithiation properties can be substantially altered through changes of the surface chemistry, which can be used to improve kinetics and cycling stability of titania based anode materials in general.

1. Introduction

Electrochemical energy storage in lithium (Li)-ion batteries (LIBs) finds wide use in portable electric devices and is expected to be the key technology for the implementation of electrically powered vehicles. LIBs and next generation LIBs are expected to substantially contribute to balancing the difference between supply and demand of renewable energy sources. Among a large number of electrode materials, TiO$_2$ has important advantages in terms of cost effectiveness, safety and environmental capability [1,2] and is therefore considered an alternative high capacity anode material, especially in its nanostructured form. The use of anodically grown, self-organized TiO$_2$ nanotubes (NTs) supported on Ti [3], which serves as current collector, provides direct one dimensional electron transport and eliminates the need for using conductive carbon to increase the electronic conductivity, which would decrease the electrode's gravimetric capacity. TiO$_2$ with an amorphous or anatase structure has a theoretical capacity of 335 mAh g^{-1}, corresponding to the insertion of one Li per TiO$_2$, associated with a complete reduction of Ti^{4+} to Ti^{3+}; a capacity which is only slightly lower than that of graphite (372 mAh g^{-1}). Its Li insertion potential lies between 1.2 V and 2.0 V vs. Li, which is a potential range where most common organic electrolytes do not show bulk decomposition. The facts that

TiO$_2$ is not combustible and that Li plating during lithiation is unlikely at the given insertion potentials lead to superior safety of the material compared to other anode materials. In bulk, non-nanostructured TiO$_2$ materials, about 0.55 mol Li can be inserted per mole TiO$_2$ at 1.78 V vs. Li/Li$^+$ [4], while nanotextured anatase TiO$_2$ can be fully lithiated forming LiTiO$_2$ [5,6]. TiO$_2$ shows a very low volume change ($< 4\%$) during cycling, which leads to high cycling stability, high rate/low-temperature charge/discharge capability and high thermal stability in both the charged and discharged state.

Especially amorphous TiO$_2$, in both nanoparticle and nanotubular form, has been demonstrated to be a promising and interesting high power and high capacity anode material [7–9], which is ascribed to partly reversible surface lithiation in case of nanoparticle based electrodes [7]. In case of nanotubular electrodes, the high capacity has been shown to be caused by short diffusion paths and improved interfacial characteristics [8], or by self-improvement during cycling due to the electrochemically driven transformation of amorphous TiO$_2$ nanotubes into a face-centered-cubic crystalline phase [9]. Especially the aspect of surface and interface lithiation and the related partial decomposition of the electrolyte can be perfectly studied with surface sensitive methods such as X-ray photoelectron spectroscopy (XPS). XPS has been previously employed to study the solid electrolyte interface (SEI) [10–12].

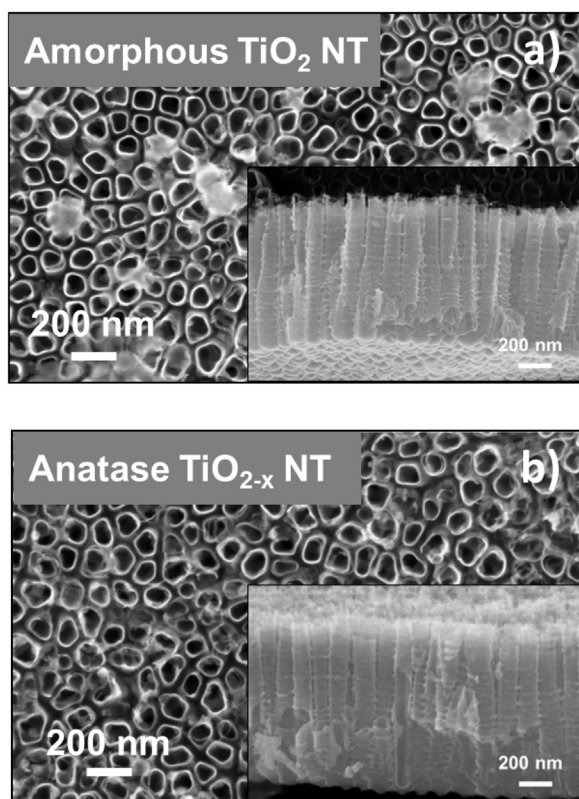**Fig. 1.** SEM images of top and cross-sections of a) amorphous TiO_2 NTs and b) anatase TiO_{2-x} NTs.

In case of powder based anatase TiO_2 anodes, early XPS work revealed that bulk lithiation of the active material can be determined through the occurrence of the Ti^{3+} component [13]. In this study, the electrolyte was 0.5 M $LiClO_4$ in acetonitrile which was not water-free. At

present, the main interest in TiO_2 anodes is based on their application in Li-ion batteries with a water free electrolyte [14]. A later XPS study reports on the surface and bulk lithiation of hydrothermally grown TiO_2-B NTs processed into electrodes with a binder and active carbon (TiO_2-B/Kynar/SuperP) [15].

In this paper, we report on an ex situ emersion XPS investigation of surface and bulk lithiation of self-organized anodic titania NTs. We compare the surface chemistry of amorphous TiO_2 and anatase TiO_{2-x} NTs at different lithiation potentials. The XPS results are accompanied by in situ electrochemical impedance spectroscopy (EIS) studies of the same systems. This approach allows for a direct comparison of the evolution of the surface chemistry and of the active material's electrical properties during the reaction with Li. Due to the use of self-organized TiO_2 NTs, the materials employed in this study are free of binder and active carbon which guarantees that the observed surface chemistry is solely caused by reactions of the active material with the electrolyte. The similar morphology allows for a direct comparison of the structural and chemical properties. The reversibility of the lithiation/delithiation cycles is also addressed and found to be remarkably different for amorphous and anatase TiO_2 NTs.

2. Experimental

TiO_2 NTs were grown electrochemically on mechanically polished (4000P SiC grinding paper) Ti disks (99.6%, Advent) by exposing the polished surface (2.54 cm^2) to an electrolyte containing 50 vol% ethylene glycol (99.5%, Merck) in water (18.2 MΩ cm, Milli-Q, Millipore) and 1 wt% NH_4F (99.99%, Merck) and by applying an anodic potential of 20 V for 75 min, after a voltage ramp of 1 V/s. After anodizing, the sample was thoroughly rinsed with deionized water (18.2 MΩ cm, Milli-Q, Millipore) to prevent further etching of the surface. To convert the as-grown amorphous NTs to anatase TiO_{2-x} NTs, they were annealed in Ar at 400 °C. A quartz tube reactor was purged with Ar with a flow of 600 sccm (Messer, 5.0) at room temperature to remove all excess air. The Ar flow was then reduced to 200 sccm. The temperature was gradually increased with a ramp of 10 °C/min^{-1} up to 200 °C, 5 °C/min^{-1}
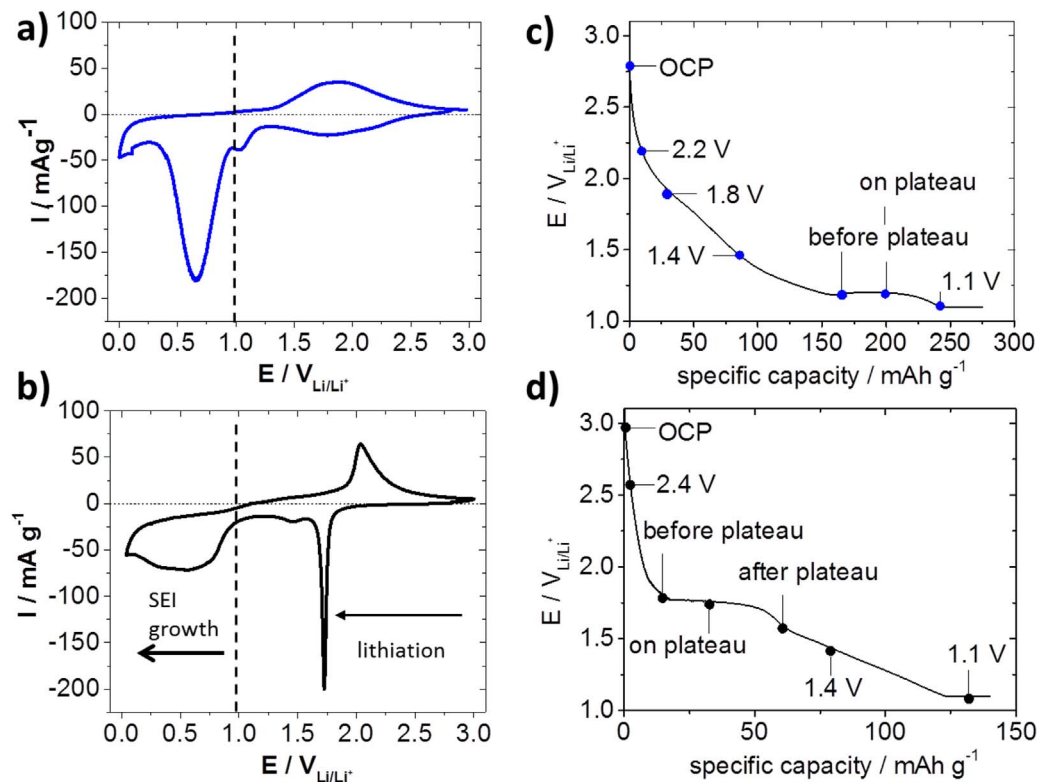

Fig. 2. CVs (1st cycles, 0.05 mV s^{-1}) of a) amorphous TiO_2 and b) anatase TiO_{2-x} NTs. Galvanostatic lithiation (of the pristine samples) of c) amorphous TiO_2 and d) anatase TiO_{2-x} NTs to 1.1 V (C/20) with points marking the positions of ex situ emersion XPS analysis.