



Electrochemical behavior of anodically obtained titania nanotubes in organic carbonate and ionic liquid based Li ion containing electrolytes



S. Ivanov^{a,*}, L. Cheng^a, H. Wulfmeier^b, D. Albrecht^b, H. Fritze^b, A. Bund^a

^a Ilmenau University of Technology, Department of Electrochemistry and Electroplating, Gustav-Kirchhoff-Straße 6, D-98693 Ilmenau, Germany

^b Clausthal University of Technology, Institute of Energy Research and Physical Technologies, Am Stollen 19 B, D-38640 Goslar, Germany

ARTICLE INFO

Article history:

Received 31 December 2012

Received in revised form 2 April 2013

Accepted 18 April 2013

Available online 29 April 2013

Keywords:

TiO₂

Li ion battery

Ionic liquid

Anodization

Self-organized TiO₂ nanotubes

ABSTRACT

Amorphous and anatase TiO₂ nanotube layers were synthesized by means of Ti foil anodic oxidation performed in ethylene glycol based electrolyte containing fluoride ions. A typical surface structure of TiO₂ nanotubular layer, well aligned nanotubes with inner diameter of 70–100 nm and wall thickness of about 10–15 nm was obtained. Both amorphous and converted to anatase nanotube layers were mechanically stable and well adherent to the Ti current collector.

The nanostructured Ti/TiO₂ layers were tested as a current collector – anode material system for Li-ion intercalation in 1 M LiPF₆ ethylene carbonate/dimethyl carbonate (EC:DMC) and in 1-butyl-1-methyl pyrrolidinium is (trifluoromethyl) sulfonylimide ([BMP][TFSI]) containing 1 M Li[TFSI]. The potential window of [BMP][TFSI] measured on Ti current collector remains not considerably influenced by addition of Li[TFSI]. The type of electrolyte does not influence the voltammetric behavior of the amorphous TiO₂ nanotube layers, whereas in case of anatase there is a definite inhibition of the Li intercalation in 1 M Li[TFSI] [BMP][TFSI], expressed by increasing the peak-to-peak voltage difference between the Li insertion and de-insertion processes. The observed phenomenon is discussed in terms of viscosity difference between both electrolytes.

TiO₂ nanotube structures displayed a stable galvanostatic cycling, reaching the theoretical capacity of TiO₂ structure and high current efficiencies in both Li ion containing media.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Titania (TiO₂) has been intensely investigated as a potential anode material for lithium-ion batteries [1–11]. It was concluded that because of its good electrochemical stability, high operating voltage, low cost and environmental compatibility TiO₂ has a promising future in Li-ion battery technology. A high number of reports pointed out that by introducing TiO₂ the risk of battery overcharging is reduced, avoiding the growth of metallic Li dendrites during the Li ion insertion into the anode and corresponding thermal runaway of the battery [7,9]. Furthermore, the initial irreversible capacity due to formation of the solid-electrolyte interfacial layer (SEI) can be significantly suppressed due to the high operating potential of TiO₂ [7]. Under these circumstances, the intensity of the total Li ion exchange at high charge/discharge currents will be enhanced since the diffusion limitations through a thick very resistive SEI are diminished. In order to preserve a high battery voltage when titania anode is applied, different possibilities to combine TiO₂ with high potential cathode materials are available [12,13].

A variety of different approaches has been directed toward minimizing the slow electrochemical kinetic of TiO₂ related to its low conductivity and improving the anode capacity. Studies performed in the recent years suggest that useful direction for Li ion mobility enhancement is the nanostructuring of the active materials in the process of their fabrication [8,9,11]. In the particular case of TiO₂ one lately introduced method is Ti anodization, performed in fluoride containing media [7–11,14–28]. By using this technique the obtained TiO₂ layer consists of self-organized nanotubes/nanopores with adjustable length, diameter and large active surface. The influence of structure geometry on the electrochemical Li ion insertion in nanoporous/nanotubular TiO₂ layers has been discussed in terms of pore diameter, nanotube wall thickness and length [8,29–34]. Generally, the TiO₂ nanotube capacity is dependent on the specific surface area, enhanced at high aspect ratio of the nanotubes (small diameter and increased length). At constant length, the increase of pore diameter in nanoscale dimensions until certain critical size induces an increase in TiO₂ structure capacity [8,29], whereas further increase of the diameter should result in a drop of the capacity values since the specific surface decreases. In view of that, it was found that the reduction of pore diameter from 70 to 30 nm facilitates the decrease of the diffusion length of Li ions and increases the specific surface area, resulting in capacity enhancement from 130 to 230 mAh g⁻¹ [32]. Furthermore,

* Corresponding author. Tel.: +49 3677692842.

E-mail address: svetlozar-dimitrov.ivanov@tu-ilmenau.de (S. Ivanov).

significant contribution of pseudocapacitance was recently discussed, elucidating that the enlargement of the internal surface area of the self-organized TiO₂ nanotubes stimulates the capacitive surface Li storage [31,33]. The strong pseudocapacitive contribution is concerned to be a possible reason for the overtheoretical capacity values reported for anatase TiO₂ nanopore structures. It was demonstrated that the wall thickness plays as well central role for the electrochemical performance of TiO₂ nanotube structure. It was established that the capacity retention improves significantly with the decrease of the wall thickness from 50 down to 10 nm [30]. When the nanotubes have thin walls, the diffusion length is short, facilitating Li mobility and enhancing conductivity of TiO₂. Beside other geometrical factors, the influence of the length of anodically obtained TiO₂ nanotubes on their cycling performance in Li ion containing electrolyte has been studied [31,34]. Remarkably, it became evident that the layer thickness change in the range of 0.6–3.8 μm has no substantial impact on the TiO₂ specific capacity in broad cycling rate interval [31]. Nevertheless, further increase of the length to the critical value of 35 μm limits TiO₂ nanotubes application for high power electrochemical energy storage due to the hindered Li ion kinetics, characteristic for very long nanotubes [34].

Another important aspect of Li ion battery technology is the development of advanced and reliable electrolyte solutions for high power and energy storage systems. It was shown that the typically used alkyl carbonate based electrolytes can bring operational and safety issues, since they are flammable and the onset of their electrochemical oxidation can be below 4 V vs. Li/Li⁺, depending on the substrate [35,36]. Additionally, the thermal instability of alkyl carbonate solvents was confirmed by considerable number of studies [35,37].

In the recent years ionic liquids (ILs) appeared to be a promising alternative to the conventional electrolytes for Li ion batteries [13,38–52]. Initially applied for deposition of different metals and polymers, which is not possible from aqueous electrolytes, ILs attracted high attention as solvents for Li ion batteries due to their very low vapor pressure, non-flammability and very high anodic potential limit of decomposition, which can improve the operational and thermal stability of the battery. On the other hand, their high viscosity, low conductivity and considerable cost limit the final application of ILs as commercial electrolytes [38]. Taking into account the cathodic instability of organic carbonate based electrolytes for Li ion batteries, ILs display many similarities. In the same way to the organic carbonate electrolytes, in number of cases ILs were mixed with additional components to complete stable cathodic passivation in the first electrochemical cycle [38–44]. The possibility to implement different types of ionic liquid for application in 5 V Li ion batteries was investigated [13,38,45,46]. The authors demonstrated the larger potential window of the ILs in comparison with EC/DMC based electrolytes and found that the active material performance regarding the mechanism, kinetics and efficiency of their passivation in ionic liquid electrolytes is related to the particular characteristics of both IL and electrode material [13,38]. It was shown that ILs can potentially improve the electrochemical and thermal performance of the battery due their non-flammable nature and bring a good electrochemical stability at high potentials.

Comprehensive studies on cyclability of anode materials in ILs were performed mainly for graphite [38,39,41–43,51,52], Si [38,44,49], Li₄Ti₅O₁₂ (LTO) [38,40,48,53] and metallic Li [38,47]. Particularly to TiO₂ polymorphs, there is limited number of investigations on their cyclability in ILs [47], furthermore electrochemical properties of self-organized TiO₂ nanostructures obtained by anodization have not been yet approached in ionic liquid media.

In the current study, we explore the possibility to apply TiO₂ nanotube arrays fabricated by means of electrochemical

anodization as anode material functioning in Li ion containing ionic liquid electrolyte. The main focus of the present work is the impact of important factors such as electrolyte type and TiO₂ structure (crystalline or amorphous) on the electrochemical performance of self-organized TiO₂ for Li ion exchange.

2. Experimental

2.1. Chemicals and reagents

Ti foil with thickness 0.25 mm with purity 99.95% (Alfa Aesar) was used for the process of anodization. Ethylene glycol, NH₄F, EC, DMC, LiPF₆, LiTFSI were obtained from Alfa Aesar. [BMP][TFSI] was purchased from IoLiTech. All reagents needed for electrochemical experiments were dried under inert argon atmosphere until a value of 15 ppm H₂O was reached. The water content in the electrolyte solutions was monitored by Carl–Fisher titration by using 831 KF Coulometer (Metrohm).

2.2. Electrochemical measurements, SEM and XRD

Cyclic voltammetry was performed using a potentiostat/galvanostat Biologic VMP3. A home-made PTFE electrochemical cell equipped with Li metal counter and reference electrodes was used for electrochemical tests. The area of Ti electrodes was 0.2 cm². The galvanostatic cycling of the samples was performed in coin type cells (CR2016). The cell assembly and part of electrochemical measurements were performed in a glove-box (M-BROWN) maintaining H₂O and O₂ levels below 0.1 ppm. The surface morphology of the samples was investigated using an ultrahigh resolution scanning electron microscope (FE-SEM, Hitachi S-4800). The XRD diffractograms of the samples were recorded using Siemens D5000 X-Ray diffractometer, using Cu Kα X-ray radiation with wavelength λ = 1.5406 Å/0.15406 nm.

2.3. Synthesis of TiO₂ nanotube layers

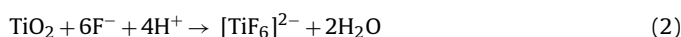
Prior to the synthesis the Ti substrates were washed with distilled water, afterwards in acetone and treated under ultrasonication in the same solvents. The electrochemical synthesis of TiO₂ ordered nano-tubes was carried out in a two electrode electrochemical cell equipped with Pt counter electrode at 40 V in 0.5% NH₄F ethylene glycol electrolyte. The anodization was performed at room temperature for 5 h without stirring of the electrolyte.

After the completion of the anodization the nanoporous layers were washed with water, dried at 60 °C for 5 h in air, dried at 120 °C under vacuum for another 5 h and transferred into a glove-box. Part of TiO₂ samples was transformed into anatase form by annealing at 450 °C for 5 h in air.

3. Results and discussion

3.1. Formation of TiO₂ nanotube layers

TiO₂ nanotube layers were synthesized by anodic oxidation of Ti foil in ethylene glycol based electrolyte containing fluoride ions [17,18]. The nanotube growth is described in the literature as a competition between anodic oxide formation (Eq. (1)) and its simultaneous dissolution (Eq. (2)). The process is accompanied by anion transfer from the electrolyte to the metal/oxide interface [9].



Download English Version:

<https://daneshyari.com/en/article/6617808>

Download Persian Version:

<https://daneshyari.com/article/6617808>

[Daneshyari.com](https://daneshyari.com)