

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

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Titania (TiO_2) has been intensely investigated as a potential anode material for lithium-ion batteries (LIBs). It was concluded that because of its good electrochemical stability, high operating voltage, low cost and environmental compatibility TiO_2 has a promising future in LIB technology [1].

This paper will address the possibility to apply TiO_2 nanotube arrays fabricated by electrochemical anodization as anode material in Li ion containing electrolytes. The main focus is the impact of important factors such as electrolyte type and TiO_2 structure (crystalline or amorphous) on the electrochemical performance of self-organized TiO_2 nanotubes for Li ion exchange in ionic liquid media [2].

The TiO_2 nanotube layers were synthesized by means of Ti foil anodic oxidation performed in ethylene glycol containing fluoride ions [3]. A typical surface structure of TiO_2 nanotubular layer, well aligned nanotubes with inner diameter of 70-100 nm and wall thickness of about 10 - 15 nm was obtained (Fig. 1). Both amorphous and anatase nanotubes were mechanically stable and well adherent to the substrate.

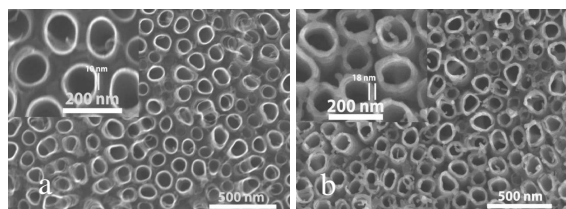


Fig. 1. Surface morphology of TiO_2 nanotube layers, as synthesized, - (a) and annealed at 450 °C - (b).

Although SEM suggests no significant morphological changes due to the phase transformation process certain differences between the two surface morphologies before and after thermal treatment can be seen. An increase of the nanotube wall thickness from 10 - 15 nm to about 18 - 20 nm was observed. Another feature of the morphology change is the appearance of structural imperfections at the upper end of the nanotubes. The discussed morphological changes can be ascribed to accumulation of carbon-containing side products during the anodization process and further related formation of local microdefects during the annealing [4].

The nanostructured Ti/ TiO_2 layers were tested as a current collector - anode material system for Li-ion intercalation in 1M LiPF_6 ethylene carbonate/dimethyl carbonate (EC:DMC) and in 1-butyl-1-methylpyrrolidinium bis (trifluoromethyl) sulfonylimide ([BMP][TFSI]) containing 1M $\text{Li}[TFSI]$. The potential window of [BMP][TFSI] measured on pristine Ti is only weakly influenced by addition of $\text{Li}[TFSI]$. The type of electrolyte does not affect the voltammetric behavior of the amorphous TiO_2 nanotube layers. The latter phenomenon is related to the larger amount of disordered

structural units and higher number of defects characteristic for the amorphous material compared to the crystalline phase, providing larger space for Li ion insertion and better accommodation of Li ions in the amorphous TiO_2 structure. In contrast, anatase displays a definite inhibition of the Li intercalation in 1M $\text{Li}[TFSI]$ [BMP][TFSI], expressed by an increasing peak-to-peak separation between the Li insertion and de-insertion processes and shifting of the galvanostatic plateaus toward higher overpotentials (Fig. 2). These phenomena are discussed in terms of viscosity difference between the electrolytes and inhibited electrochemical kinetics.

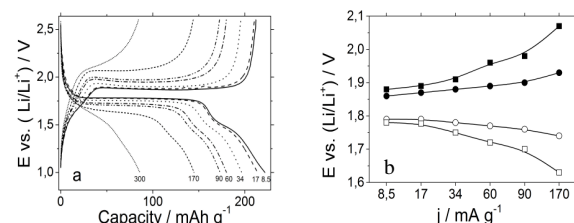


Fig.2 Galvanostatic cycling of anatase structures at different constant currents performed in 1 M $\text{Li}[TFSI]$ [BMP][TFSI]. The numbers denote the specific cycling current in mA g^{-1} (a). Potential of the galvanostatic plateau at 60 mAh g^{-1} vs. cycling current density for anatase nanotube structures studied in 1 M $\text{Li}[TFSI]$ [BMP][TFSI] (■-anodic, □-cathodic) and 1 M LiPF_6 EC:DMC (●-anodic, ○-cathodic) electrolytes - (b)

TiO_2 nanotube structures displayed a stable galvanostatic cycling, exceeding theoretical capacity and high current efficiencies. On the other hand, the rather open geometry of TiO_2 nanotubes in the present work can be the reason for the moderately high discharge capacities of about 180 - 200 mAh g^{-1} obtained from the galvanostatic cycling of the samples.

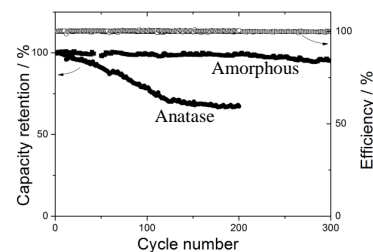


Fig.3 Discharge capacity of multiple galvanostatic cycling (closed symbols) and corresponding Coulomb efficiencies (open symbols) of amorphous and crystalline nanotube TiO_2 layers in 1M LiTFSI , [BMP][TFSI].

The long term cycling shows close to 100 % capacity retention for amorphous TiO_2 nanotube layer, while anatase structure displays a definite loss of capacity reaching a value of 70 % retention for 200 cycles (Fig. 3). The capacity fade of the crystalline structures is attributed to the appearance of microstructural defects formed during the annealing of the amorphous TiO_2 [4].

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