A potential 3D cathode material for Li-ion microbatteries based on TiO_xS_y nanotubes

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To date, thin-film microbatteries represent a promising track to supply energy to many microelectronic devices [1]. One interesting alternative to ensure miniaturization as well as high volumetric energy and power densities consists in using nano-architectured systems[2]. Compared to planar configurations, the larger specific surface area offered by 3D nano-architectured electrodes is responsible for their superior performances[3, 4] as it has been reported for self-organized TiO_2 nanotubes[5, 9]. In this context, different positive electrode materials are being studied for designing high-performance 3D microbatteries[2]. Among them, TiS_x (x = 2 or 3), operating below 3V vs. Li^+/Li, is of a considerable interest. TiS_x compounds were among the first intercalation materials studied as cathodes for Li-ion batteries[10, 11]. For over two decades, a derivative of TiS_x given by TiO_xS_y, has been studied by sputtering techniques as a cathode material for microbatteries[12]. It has been shown that the non-deliberate incorporation of oxygen has a rather beneficial effect on the performance of the TiO_xS_y compared to TiS_x[12, 13].

In this work, post heat treatment of self-organized TiO_2 nanotubes in a sulphur atmosphere is studied for the production of TiO_xS_y nanotubes. The sulfidation of TiO_2 nanotubes stands as an alternative to achieve nanostructured TiO_xS_y (Fig. 1).

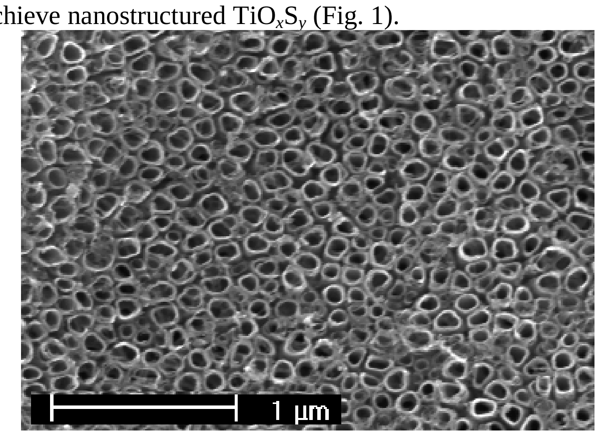

Fig. 1 SEM image of TiO_xS_y nanotubes obtained by the sulfidation treatment of anodized TiO_2 nanotubes (top view).

First, the influence of the thermal treatment conditions on the morphology of the nanotubes will be presented. Then, the structural and electrochemical characterization that evidenced the presence of new compounds (TiS_3, $Ti_{5.5}S_7$) able to react with Li-ions will be discussed. As an example, a typical galvanostatic cycle life performance is shown in Fig. 2. The very high capacity values delivered in the first 20 cycles make this material a potential cathode material for 3D Li-ion microbatteries. Actually, the first discharge capacity (> 300 µAh cm^{-2}-µm^{-1} at a current density of 70 µA cm^{-2}) is much higher than the values reported previously for TiO_xS_y thin films (~185 µAh cm^{-2}-µm^{-1} at 3 µA cm^{-2}). These first results open interesting perspectives for TiO_xS_y nanotubes as a high-performance cathode material for 3D Li-ion microbatteries[14].

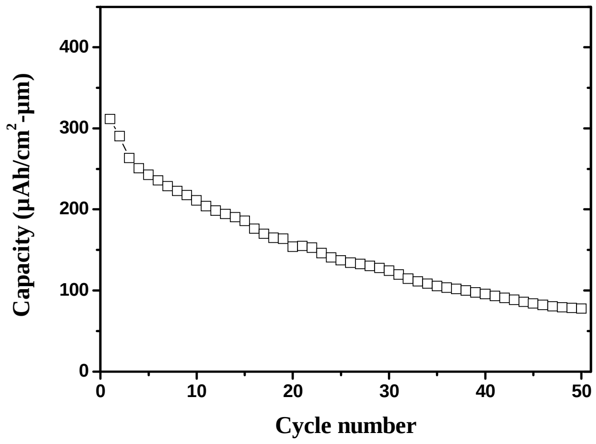

Fig. 2 Galvanostatic cycle life performance of the TiO_xS_y nanotubes at 70 µAcm^{-2} in the 1.6 ≤ U/V ≤ 3.3 voltage range, using a two-electrode Swagelok cell [Li-metal/$LiPF_6$ (EC:DEC)/TiO_xS_y].

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