A potential 3D cathode material for Li-ion microbatteries based on TiO$_x$S$_y$ nanotubes

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To date, thin-film microbatteries represent a promising track to supply energy to many microelectronic devices\cite{1}. One interesting alternative to ensure miniaturization as well as high volumetric energy and power densities consists in using nano-architected systems\cite{2}. Compared to planar configurations, the larger specific surface area offered by 3D nano-architected electrodes is responsible for their superior performances\cite{3,4} as it has been reported for self-organized TiO$_2$ nanotubes\cite{5,6}. In this context, different positive electrode materials are being studied for designing high-performance 3D microbatteries\cite{7}. 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\cite{8,9}. For over two decades, a derivative of TiS$_x$, given by TiO$_x$S$_y$, has been studied by sputtering techniques as a cathode material for microbatteries\cite{10}. It has been shown that the non-deliberate incorporation of oxygen has a rather beneficial effect on the performance of the TiO$_x$S$_y$ compared to TiS$_2$\cite{10,11}. In this work, post heat treatment of self-organized TiO$_2$ nanotubes in a sulphur atmosphere is studied for the production of TiO$_x$S$_y$ nanotubes. The sulfidation of TiO$_2$ nanotubes stands as an alternative to achieve nanostructured TiO$_x$S$_y$ (Fig. 1).

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$_x$, Ti$_{1-x}$S$_y$) 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$_x$S$_y$ thin films (~185 µAh cm$^{-2}$·µm$^{-1}$ at 3 µA cm$^{-2}$). These first results open interesting perspectives for TiO$_x$S$_y$ nanotubes as a high-performance cathode material for 3D Li-ion microbatteries\cite{12}.

![Fig. 1 SEM image of TiO$_x$S$_y$ nanotubes obtained by the sulfidation treatment of anodized TiO$_2$ nanotubes (top view).](image1)

![Fig. 2 Galvanostatic cycle life performance of the TiO$_x$S$_y$ nanotubes at 70 µA cm$^{-2}$ in the 1.6 ≤ 3V ≤ 3.3 voltage range, using a two-electrode Swagelok cell [Li-metal/|LiP|, (EC:DEC)/TiO$_x$S$_y$].](image2)

References