Sodium Storage and Diffusion in Amorphous Titania Nanotubes

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Ordered, nanostructured transition metal oxides are currently in the spotlight of battery research [1]. To exploit, however, the full potential of self-assembled titania nanotube layers in Na-ion battery technology we need to close the gap in knowledge about the underlying storage mechanisms as well as ion dynamics. For this purpose, amorphous TiO_2 nanotubes (70–130 nm in diameter, 4.5–17 µm in length, Fig. 1a) were fabricated by anodization, *i.e.*, electrochemical oxidation. The electrochemical behaviour with respect to sodium insertion was studied by cyclic voltammetry and galvanostatic cycling with potential limitation. It turned out that the nanotubes are very resilient to cycling, some being able to withstand more than 300 charge-discharge cycles without significant loss of capacity. Compared to classical insertion reactions, the mechanism of reversible electrochemical storage of Na^+ in the nanotubes seems to differ significantly. There is strong evidence that a large amount of the Na^+ ions is stored on the surface or in the surface-influenced regions while only a smaller fraction is inserted in the walls of the tubes [2]. The interfacial Na^+ storage is governed by a faradaic adsorption phenomena, which is essentially different from the (pseudo-)capacitive model hitherto used in the literature. The finding that, in the case of sodium, interfacial storage is more important than ion insertion into the crystal lattice is supported by the very low Na^+ diffusion coefficients determined at various electrode potentials (in the order of 10^{-20}–10^{-21} cm²·s⁻¹, Fig. 1b). This dominant interfacial storage mechanism may explain the high specific capacity and the very good cycling performance recently reported for some nanostructured titania phases [3] as well as for other nanosized titanate materials.
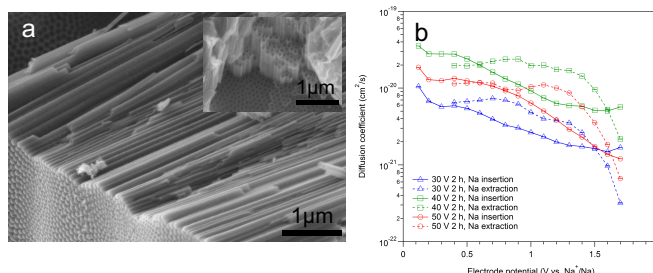

Figure 1: a) SEM micrographs of highly ordered TiO_2 nanotube arrays fabricated by anodization at 40 V for 2 h.
b) Chemical diffusion coefficient of Na^+ into amorphous TiO_2 at room temperature (23±1 °C) after subtracting the interfacial storage contributions for different sample types.

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