

High Energy and Power Density  $\text{TiO}_2/\text{Li}_4\text{Ti}_5\text{O}_{12}$  Nanotube Electrodes for 3D Li-ion Microbatteries

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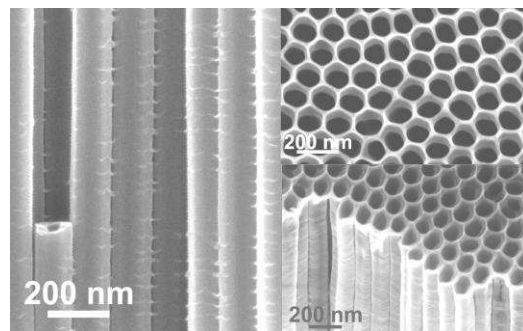
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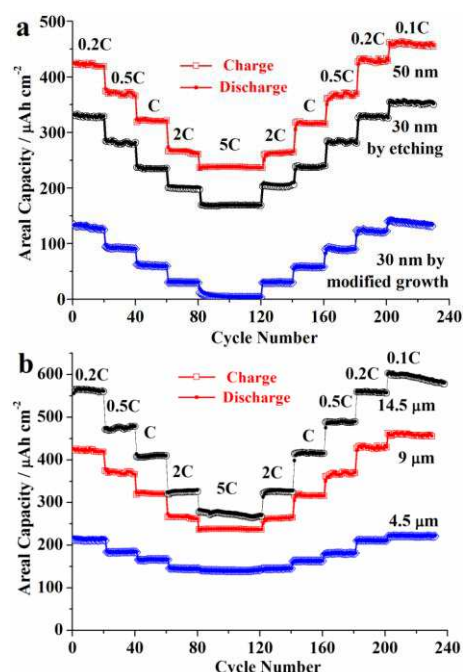
Over the past decades, thin-film Li-ion microbatteries with thicknesses up to 100  $\mu\text{m}$  have become the dominant power sources for a wide variety of miniature electronic devices and implantable medical devices. Nevertheless, due to the increasing power requirements of the latter devices and emerging technologies (e.g., wireless transmission), the next generation of Li-ion microbatteries is expected to provide even higher energy and power densities on a small footprint area (e.g.,  $<1\text{ cm}^2$ ). To date, the most promising way to maximize the energy and power densities of a microbattery is to build 3D microbatteries, in which the battery components – current collectors, electrodes, and electrolyte – are incorporated into a 3D micro- or nanoarchitecture.<sup>[1]</sup> Due to the limited packing size as well as high safety issues, the electrodes for microbatteries generally lack binders and conductive additives, which complicates the electrode fabrication. So far, the studies have been mainly dedicated to the development of free-standing 3D micro- and nanostructured electrodes rather than full 3D-microbatteries, since the attainment of 3D electrodes with both high areal capacities and high rate capabilities, in addition to long term cycling stability, still is not straightforward.

In the present work, we demonstrate that by using highly ordered anatase  $\text{TiO}_2$  nanotube electrodes (as shown in Figure 1), an areal capacity of  $0.24\text{ mAh cm}^{-2}$  at a charge/discharge current density of  $2.5\text{ mA cm}^{-2}$  (corresponding to a rate of 5C), and  $0.46\text{ mAh cm}^{-2}$  at  $0.05\text{ mA cm}^{-2}$ , can be achieved. The present nanotube electrodes, which have been cycled for 500 cycles with only a 6% loss of capacity, exhibited higher energy and power densities, as well as an excellent cycling stability, compared to earlier reported 3D Li-ion microbattery electrodes. The influence of the parameters such as, the ordering, geometry and crystallinity of the nanotubes, on the microbattery performance was investigated, as shown in Figure 2. It is also demonstrated that the rate capability of the nanotube electrode depends mainly on the rate of the structural rearrangements associated with the lithiation/delithiation reaction and that the areal capacity at various charge/discharge rate can be increased by increasing the tube wall thickness or the length of the nanotubes, up to  $0.6\text{ mAh cm}^{-2}$  for 100 cycles.

With further modification of the obtained  $\text{TiO}_2$  nanotube electrodes, free-standing  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  nanotube electrodes can also be achieved. The present  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  nanotube electrodes have shown excellent rate capability and cycling stability. Even after cycling at a 20C rate, using a current density of  $6.2\text{ mA cm}^{-2}$ , an areal capacity of  $0.12\text{ mAh cm}^{-2}$ , i.e., 42% of that found for the C rate, was obtained. Moreover, after cycling for more than 500 cycles at 1C rate, an areal capacity of  $0.28\text{ mAh cm}^{-2}$ , corresponding to 96.6% of the initial capacity, was found.



**Figure 1.** Cross-sectional SEM micrograph depicting a high ordered  $\text{TiO}_2$  nanotube layer formed by two-step anodization of a Ti foil. The insets show a cross-sectional view at tube top (upper) as well as the top view (lower).



**Figure 2.** (a) Rate capabilities of anatase nanotube electrodes with tube wall thicknesses of 50 nm, 30 nm by etching, and 30 nm by modified growth. (b) Rate capabilities of anatase nanotube electrodes with lengths of 14.5, 9 and 4.5  $\mu\text{m}$

## References

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- [2] W. Wei, G. Oltean, C. Tai, K. Edström, F. Björefors, L. Nyholm, *J. Mater. Chem. A* **2013**, in press.