

Fabrication of copolymer-embedded titania nanotubes as a negative electrode for 3D Li-ion microbatteries

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Nowadays, microbatteries are in demand as a power source to drive small devices such as smartcards, medical implants, sensors, etc. Due to their nanostructure, titania nanotubes (TiO₂nt) as a negative electrode for Li-ion batteries offer good rate capability, capacity and cycling performance¹⁻³. In order to fabricate 3D Li-ion microbatteries, conventional liquid electrolytes for Li-ion batteries (e.g. LiPF₆) need to be replaced by solid electrolytes such as polymer electrolytes.

We have reported the conformal electrodeposition of a copolymer electrolyte; poly(methyl methacrylate)-polyethylene oxide (PMMA-(PEO)₅) incorporated with Li salt into TiO₂nt⁴⁻⁶. The in-depth chemical characterization of the electrodeposited polymer by different techniques has shown that i) the thickness of the copolymer layers can be controlled by varying electrodeposition parameters ii) LiTFSI salt is incorporated in the thin film iii) the polymer is mainly consisting of dimers. However, the drawback of the copolymer is that it dissolves in aqueous media. It is important to improve the stability of the copolymer, which can withstand various kinds of solvents. The better stability of the copolymer will facilitate the subsequent filling of the polymer-coated nanotubes with cathode materials and improve the mechanical properties. By shortening the length of the PEO chain (hydrophilic) in the copolymer PMMA-PEO, better mechanical strength and stability in aqueous media should be achieved.

In this work, self-organized TiO₂nt was fabricated by anodization of Ti foil in glycerol containing 1.3%wt NH₄F and 2%wt water. Electrodeposition of PMMA-(PEO)_n (with n<8) electrolytes were performed in an electrolyte containing 0.035M lithium bis(trifluoromethane-sulfone)imide (LiTFSI) and 2 g MMA-(PEO)_n, using cyclic voltammetry technique.

The smooth and homogeneous TiO₂nt with the length of 1.5 μm and diameter of 100 nm is obtained after the anodization (Fig. 1a). As an example, the conformal electrodeposition of PMMA-(PEO)₅ copolymer is shown in Fig 1b after 100 cycles of cyclic voltammetry. The copolymer layers of PMMA-(PEO)₅ are clearly observed along the nanotubes and the inter-tube spaces are filled with the copolymer. The top ends of the nanotubes remain open.

These results show that electrodeposition technique is a viable approach to achieve the conformal deposition of the polymer electrolyte leaving free spaces for subsequent insertion of the cathode material. The influence of the length of the PEO chain upon the electrochemical properties will be presented.

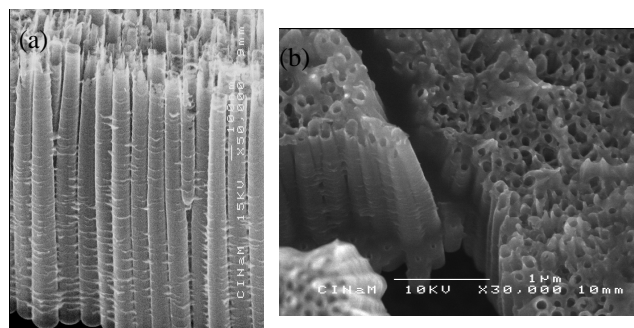


Fig. 1. SEM images of (a) as-formed TiO₂nt and (b) PMMA-(PEO)₅ copolymer-embedded TiO₂nt.

Fig. 2 shows the areal capacity vs cycle number of PMMA-(PEO)₅ copolymer-embedded TiO₂nt. The electrochemical tests were performed in a half-cell against Li foil using the Swagelok cell. LiPF₆ (EC:DEC) was used as an electrolyte. A Whatman glass microfiber was used as a separator. The cells were cycled at 1C in the potential window ranging between 0.5 to 2.6 V vs Li/Li⁺. It delivers stable capacity ~ 55 μAh/cm²-μm during 50 cycles. Furthermore, the capacity fading is low.

During this work, the electrochemical performance of all-solid-state microbatteries consisted of polymer-coated titania nanotubes will be discussed.

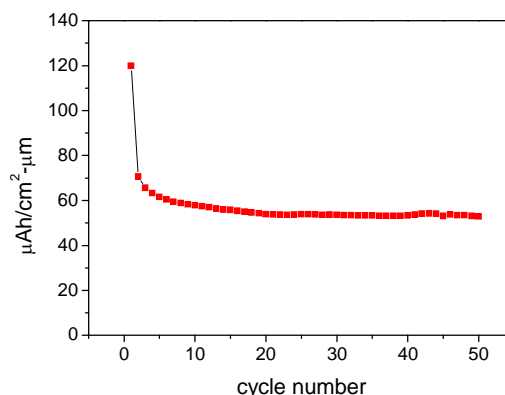


Fig. 2. Specific capacity versus cycle number of PMMA-(PEO)₅ copolymer-embedded TiO₂nt.

References

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