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EFFECTS OF ELECTRODEPOSITED LITHIUM PHOSPHATE ON THE ELECTROCHEMICAL PROPERTIES OF SELF ORGANIZED TITANIA NANOTUBES

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Solid electrolyte interfaces are crucial for the development of lithium-ion batteries. An alternative approach is to coat the electrodes with a convenient ionic conductor that warrants lithium ion diffusion from the electrolyte. Thin film electrodes prepared directly onto current collectors are particularly suitable to this approach. The compound Li_3PO_4 is known to be a potential candidate for thin film lithium electrolyte due to its light weight, wide potential range of stability vs. lithium and also because of its thermal and mechanical stability.¹

The aim of this work is to prepare nanoarchitected electrodes containing a thin layer of Li_3PO_4 . The covering effect of Li_3PO_4 can be observed for 1 min of electrodeposition at 37.5 mA cm^{-2} as the nanotubes are filled (Fig. 1). Firstly, self organized TiO_2 nanotubes are used to improve their electronic and ionic conductivity. The annealing condition allowed preparing $\beta\text{-Li}_3\text{PO}_4$ (R.T. – $300 \text{ }^\circ\text{C}$) and $\gamma\text{-Li}_3\text{PO}_4$ ($\geq 500 \text{ }^\circ\text{C}$).² The discharge and charge plateau of Li_3PO_4 -free ntTiO_2 samples were at approximately 1.75 and 1.9 V, respectively. For $\beta\text{-Li}_3\text{PO}_4/\text{ntTiO}_2$ and $\gamma\text{-Li}_3\text{PO}_4/\text{ntTiO}_2$ samples deposited 1 min at 3.75 mA cm^{-2} a discharge/charge plateaus are observed at 1.78 and 1.86 V, which is $\sim 0.1 \text{ V}$ lower in energy as compared with uncoated samples. The best capacity value of $500 \mu\text{A h cm}^{-2}$ was achieved for $\text{TiO}_2/\gamma\text{-Li}_3\text{PO}_4$.

The optimum parameters for electrodeposition to achieve $\gamma\text{-Li}_3\text{PO}_4$ coating on the entire ntTiO_2 array are 1 min and $3.75 \mu\text{A cm}^{-2}$. The performance of the $\text{ntTiO}_2/\gamma\text{-Li}_3\text{PO}_4$ (LiPF_6 in EC:DEC)/ LiFePO_4 rocking-chair microbattery delivered a maximum capacity of 110 mA h g^{-1} at 5C rate when imposing a cathode-limited active mass ratio to the electrodes.² The obtained low-voltage microbattery ($<2.0 \text{ V}$) could fit to applications demanding small-scale electrical power.

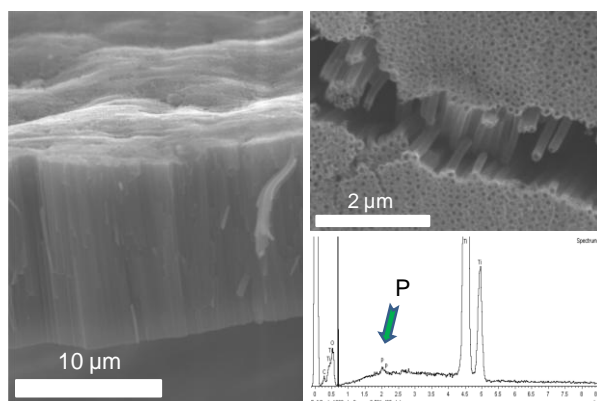


Figure 1. SEM image of nt-TiO_2 with electrodeposited Li_3PO_4 .

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¹ Bates, J. B.; Dudney, N. J.; Gruzalski, G. R.; Zuhr, R. A.; Choudhury, A.; Luck, D. F.; Robertson, J. D. *J. Power Sources* **1993**, *43*, 103.

² López, M.C.; Ortiz, G.F.; González, J.R.; Alcántara, R.; Tirado, J.L. *ACS Appl. Mater. Interfaces* **2014**, *6*, 5669.