

Effect of syntheses and post synthetic treatments on mixed titanium niobium oxides for use as negative electrode in high power Li-ion batteries

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The use of Li metal in Li-ion batteries led to safety issues related to the formation of dendrites at the anode side resulting in short-circuiting and auto-ignition of the cell. To prevent self-ignition, Li metal was replaced by $\text{Li}_4\text{Ti}_5\text{O}_{12}$. The higher red/ox potential of the $\text{Ti}^{\text{IV}}/\text{Ti}^{\text{III}}$ couple (1.5V) compared to Li^+/Li (0V) prevents the formation of dendrites. While the theoretical capacity of this material is high (292 mAh/g for the exchange of 5 electrons), its actual capacity is rather limited (175 mAh/g corresponding to a 3 electron exchange process). To increase the experimental capacity, we looked into adding another electro-active element such as niobium. Niobium is involved in two red/ox couples ($\text{Nb}^{\text{V}}/\text{Nb}^{\text{IV}}$ and $\text{Nb}^{\text{IV}}/\text{Nb}^{\text{III}}$) at an average potential of 1.5 V vs. Li^+/Li . We will report the electrochemical performances of TiNb_2O_7 and $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ depending on different synthesis methods and post-synthetic treatments.

We first prepared TiNb_2O_7 and $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ via solid state reaction. TiO_2 and Nb_2O_5 were mixed in appropriate stoichiometric ratios and mechanically ground for 5 hours. After firing at 1150°C for 24 hours, TiNb_2O_7 and $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ were obtained in the monoclinic phase, with space groups $\text{I}2/\text{m}$ and $\text{A}2/\text{m}$ respectively, without any impurities. The size of the primary particles is in the μm range for both materials (Figure 1). A second ball milling reduced the particle size but did not improve the electrochemical performances of the material. We also tried coating the particles with carbon (up to 1.5%) to increase the electronic conductivity and facilitate the electrochemistry process. Although the coating stabilized the performances of the material over time, the initial capacity values were much smaller than with the non-coated material. In the same way mixing TiNb_2O_7 with a fluor containing material did not affect the electrochemical performances positively.

We also prepared TiNb_2O_7 and $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ by hydrothermal synthesis. TiOSO_4 and NbCl_5 were mixed in appropriate molar ratios and transferred into a pressure vessel. After a short hydrothermal treatment, the powder were washed, dried and then fired for a couple of hours, leading to porous networks of nanoparticles (Figure 2a). The porosity of the network allows close contact between the electrolyte and the active material leading to higher electrochemical performances compared to our solid state synthesis (Figure 3). An additional step during the synthesis process led to a more dense yet still porous network (Figure 2b), not only increasing the electrochemical performances of TiNb_2O_7 and $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ (compared to our solid state synthesis) but also stabilizing the performances over time (Figure 3).

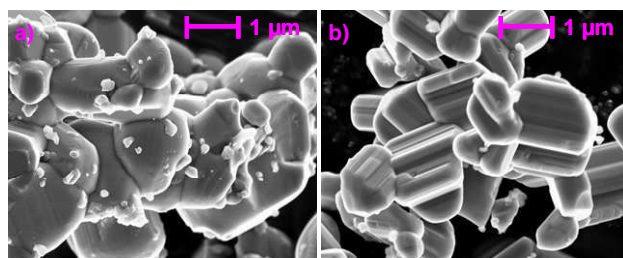


Figure 1. Scanning electron microscopy of a) TiNb_2O_7 and b) $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ both prepared by solid state synthesis.

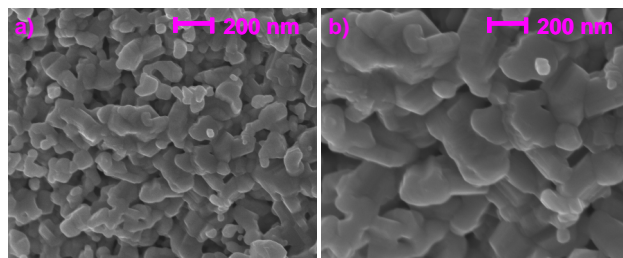


Figure 2. Scanning electron microscopy of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ after a) hydrothermal treatment and firing at 950°C and b) hydrothermal treatment, additional step and firing at 950°C .

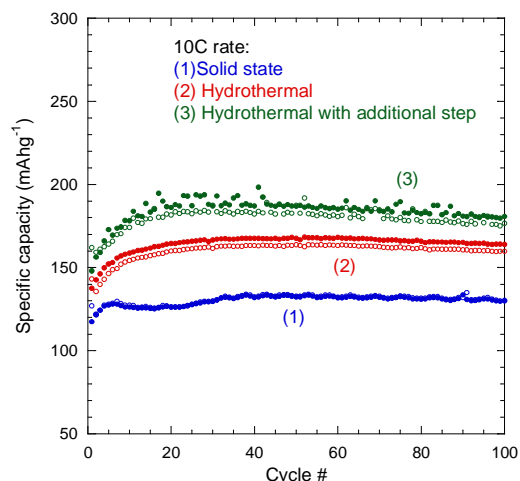


Figure 3. Effect of the synthesis route on the capacity at a 10C cycling rate for TiNb_2O_7 .