

Hydrothermal Synthesis of Nanocrystalline Insertion Hosts in Li-Ti-O system and Their Electrochemical Characterization

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Insertion electrochemistry of tetravalent titanium compounds has been intensively investigated in connection with possible applications in lithium/lithium ion batteries. Besides of various forms of TiO_2 ^{1, 2} there was considerable interest in ternary Li-Ti-O phases³⁻⁵. The Li-Ti-O ternary phases are usually prepared by solid state reaction from the oxide (hydroxide) mixtures of corresponding stoichiometry. A low temperature ($t < 200^\circ\text{C}$) solvo-thermal synthesis of nanocrystalline spinels or spinel precursors was also reported recently¹. The electrochemical behavior of the low temperature prepared phases has not yet been fully characterized. This paper focuses on comparison of hydrothermally and solid-state reaction prepared Li-Ti-O oxides with respect to their ability to act as lithium insertion hosts. Also the role of post-synthesis extraction and heat treatment on the electrochemical performance of these materials is addressed.

Hydrothermal synthesis does not lead to direct synthesis of spinel structures. Prepared oxides have Li:Ti ratio about 1:2 and their structure is cubic of the rock-salt type. Upon annealing they convert to spinels (see Fig.1). This transition is accompanied with removal of structural water and is reflected in on both TG/DTA behavior and in the cyclic voltammetry (see Fig.2). The insertion potential shifts toward more negative potentials with increasing annealing temperature. The increase of annealing temperature also improves coulombic efficiency and stability against self-discharge reactions. On the other hand, the lithium insertion/extraction kinetics slows down with increasing annealing temperature. Hydrothermally synthesized Li-Ti-O spinels show more favorable charge transfer kinetics as well as lithium transport comparing with spinels prepared by solid-state reaction.

Extraction of the hydrothermally synthesized Li-Ti-O oxide in water and diluted acids leads to a decrease of the Li content in the material. This is accompanied with a shift of the diffraction peak positions towards higher 2θ values. The insertion potential shifts toward negative values. The peak of the Li extraction at the same time shows a pronounced splitting.

Thermodynamics of Li insertion into hydrothermally prepared phases can be described by Frumkin insertion isotherm. The low temperature prepared spinels seem to be less susceptible to lithium insertion triggered phase transition than the high temperature synthesized materials

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References

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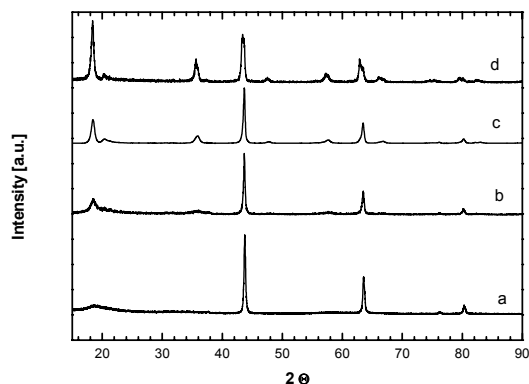


Figure 1 The XRD pattern of solvothermally prepared Li-Ti-O oxides before annealing (a), and after annealing at 300°C (b), 400°C (c) and 500 °C (d) C.

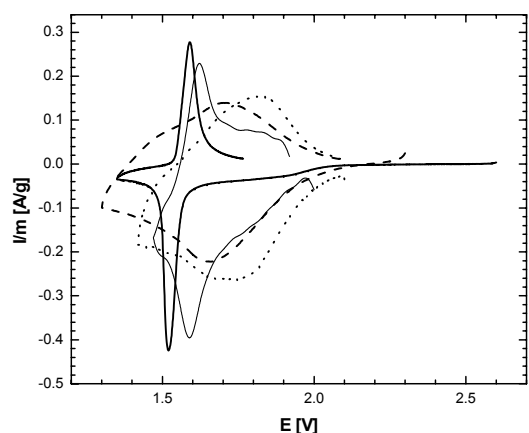


Figure 2 Cyclic voltammograms of hydrothermally prepared spinel electrodes annealed at various temperatures: 500°C (thick solid line), 300°C (thin solid line), 200°C (dashed line) without annealing (dotted line). Voltammograms were measured in 1 M $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}/\text{EC}/\text{DME}$; scan rate 0.2 mV/s. The electrodes contained 85 % (m/m) of active phase.

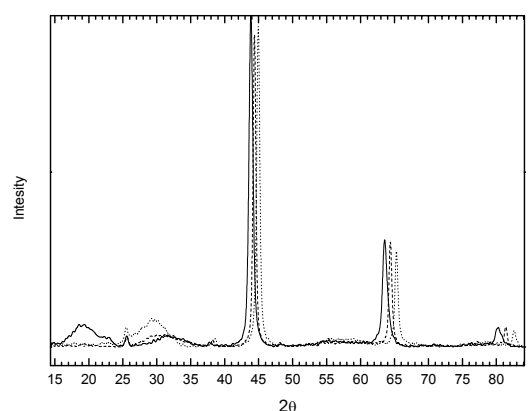


Figure 3 XRD patterns of the hydrothermally prepared material (solid line) and of the material extracted in acetic acid (dashed line) and nitric acid (dotted line) solutions.