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Solvothermal Synthesis Of Electrochemically Active Nanocrystalline Li-Ti-O Spinel

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ABSTRACT

Nanocrystalline Li-Ti-O spinel samples were prepared by solvothermal reaction of TiO_2 with lithium hydroxide in water and ethanol. The hydrothermal reaction proceeds at temperature higher than 130 °C. The reaction proceeds via dissolution-precipitation mechanism and its course is not sensitive to titanium dioxide polymorph used in the reaction. Product of the reaction in water has cubic rock salt type structure. It converts, however, to spinel if annealed to temperatures exceeding 250 °C. The re-crystallization is accompanied with water removal from the structure. Solvothermal reaction in ethanol leads directly to a product with spinel structure without need for annealing. Both products are active for Li insertion; theelectrochemical activity. The specific capacity ranges between 100 and 160 mAh/g depending on the annealing temperature.

INTRODUCTION

Nano-crystalline materials play an important role in design of new electrochemical energy related applications namely in development of new rechargeable batteries or photo-electrochemical cells. The use of nano-crystalline materials allows one to improve both the size and quality[1],[2] of the electrode-electrolyte interface as well as to shorten significantly the characteristic diffusion lengths. Nanocrystalline Ti(IV) based oxides, particularly TiO_2 anatase and $Li_4Ti_5O_{12}$ spinel make prospective materials for 2V lithium ion batteries.

Solvothermal synthsis in Ti oxides chemistry is usually used to prepare large crystals of perovskites [3],[4]. The potential of the hydrothermal synthesis in preparation of nanocrystals was, on the other hand, also demonstrated on controlled growth of anatase nanocrystals in tetramethylammonium containing solutions at 190-270 °C [5]. Li-Ti-O ternary phases are usually prepared by solid-state reaction at elevated temperatures. Hydrothermal synthesis of electrochemically active nanocrystalline Li-Ti-O ternary phases like e.g. $Li_4Ti_5O_{12}$ spinel has not been reported.

EXPERIMENTAL

Nanocrystalline titanium dioxide (Bayer) was used as starting materials in syntheses. Parallel experiments were performed on anatase (PKP 5538) and mixture of anatase and rutile (1:3, P25 Bayer). All other chemicals in all experiments, i.e. LiOH and NaOH were obtained from Fluka. The water used in experiments was of Millipore MilliQ quality, used ethanol was of p.a. grade.

Reactions were carried out in poly(tetrafluoroethylene) (PTFE) - lined stainless steel autoclaves. The molar ratio of TiO_2 and LiOH in reaction mixture ranged between 2:1 and 1:5; the pH of the reaction mixture was adjusted to 14 by addition of concentrated NaOH solution. Syntheses were performed at temperatures between 130-200°C for 2 - 24 hours. Products of the reactions were filtered and carefully washed with water.

X-ray power diffraction of the prepared materials was measured using Siemens X500 powder X-ray diffractometer and CuKα radiation. Crystal morphology and size distribution was examined by field-emission SEM S-4500 (Hitachi). Additional estimate of crystal size distribution was done by Fourier transform analysis of peak shapes in X-ray diffractograms using Winfit program [6].Thermal analysis of hydrothermal powders was performed on NETZSCH STA 409 TG/DTA apparatus complemented with mass spectrometer QMS 403/4 (Balzers) allowing for qualitative analysis of gases evolved during heating.

The electrochemical activity of prepared phases was examined by cyclic voltammetry in three-electrode arrangement with Li counter and reference electrodes on PAR263A potentiostat in 1M solution of $Li(CF_3SO_2)_2N$ in 1:1 (w/w) mixture of ethylene carbonate (EC) and dimethoxyethane (DME). Li-Ti-O electrodes were prepared by mixing of powder samples with teflonized carbon black (ca 15% of carbon black).

DISCUSSION

X-ray powder diffraction patterns of the starting titania and materials prepared in water and ethanol at 200 °C are shown in Fig. 1. The solvothermal synthesis at this temperature leads to complete removal of starting material. The products of both reactions contain small amounts of lithium carbonate, which was not removed by washing. The diffraction pattern of the product prepared in water shows three resolved diffraction peaks at approximately 4.81 Å, 2.81 Å and 1.54 Å. The broad peak at about 18 ° could be attributed to an amorphous phase. Such a phase, however, was not found in SEM. The diffraction peaks of the material prepared in water show good agreement with those of cubic rock salt $LiTiO_2$ ($a \approx 4.14$ Å, *Fm3m*). Annealing of the material prepared in water leads to its re-crystallization to spinel structure (*Fd3m*). This process is accompanied by removal of the structural water, which starts at temperatures above 250 °C.

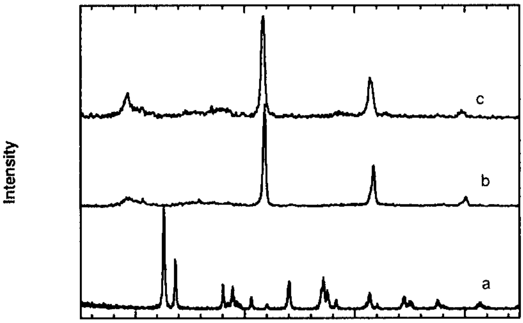

Figure 1 X-ray diffraction patterns of: a) the starting TiO_2 (mixture of rutile and anatase 1:3), b) product of the reaction in water, c) product of the reaction in ethanol. In both cases the reaction proceeded at 200 ° for 24 hours.

The diffraction pattern of the material prepared in ethanol, on the other hand, shows good agreement with that of $Li_4Ti_5O_{12}$ spinel (a=8.357 Å). Small amounts of a material identical with product of the reaction in water can be traced in diffraction pattern. We attribute the presence of this impurity phase to the fact that the used ethanol contained ca 5 % of water (v/v). Low intensity of the signal and rather broad diffraction peaks indicate small crystal size of the prepared materials.

Analysis of the XRD patterns indicates average coherent domain size in the range 10-25 nm. SEM measurements, however, revealed the actual particle size to be about twice bigger. Slightly bigger particles were found in the case of water prepared materials. The reaction time has no pronounced effect on the particle growth. Also the annealing of the materials to temperatures below 500 °C does not lead to pronounced particle size increase.

ELECTROCHEMICAL BEHAVIOR

Insertion behavior of the Li-Ti-O oxides prepared by solvothermal reaction is shown in Fig. 2. For both hydrothermal as well as solvothermal materials the lithium insertion and extraction proceeds in single step. The standard potential characterizing the thermodynamics of the

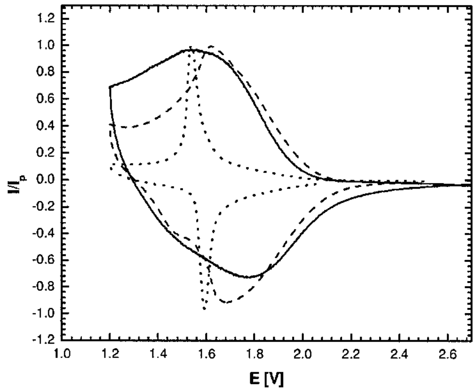

Figure 2 Cyclic voltammograms of Li insertion into solvothermally prepared Li-Ti-O spinel annealed at 0, 200 and 300 °C. The material was prepared by reaction at 200 °C in water.

Table 1 Standard potential of the Li insertion into Li-T-O oxides prepared in water and ethanol

Annealing temperature	**E^0[V]**	
	H_2O	**Ethanol**
0	1.616	1.664
200	1.740	1.649
300	1.577	1.561

insertion process obtained are summarized in Table 1. The annealing causes a shift of the standard potential towards more negative potentials what indicates an increase in activation barriers for the insertion process. The specific capacity of the materials is between 100-160 mAh/g and improves with increasing temperature of the post-synthesis treatment. The upper specific capacity values are comparable with those reported for microcrystalline Li-Ti-O spinels. The kinetics of the insertion process into solvothermally prepared nanocrystaline spinels is, however, superior to that of materials prepared at high temperature (see Figure 3).

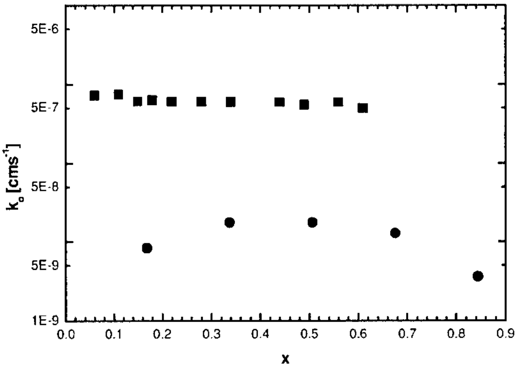

Figure 3 Heterogeneous rate constant of the lithium insertion into high temperature prepared (circles) and solvothermally prepared $Li_4Ti_5O_{12}$ spinel

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