Nanosized lithium titanates produced by plasma technique

J. Grabis, A. Orlovs, Dz. Rasmane
Miera 34, Salaspils, LV-2169, Latvia
grabis@nki.lv

Abstract. The synthesis of nanosized lithium titanates is studied by evaporation of coarse grained commercially available titanium and lithium carbonate particles in radio-frequency plasma flow with subsequent controlling formation and growth conditions of product particles. In accordance with the XRD analysis the phase composition of the obtained powders is determined by feeding rate of precursors and strongly by ratio of lithium and titanium. The Li2TiO3 and Li4Ti5O12 particles containing small amounts of extra phases were obtained at ratio of Li/Ti=2 and Li/Ti=0.8 respectively, feeding rate of precursors being in the range of 0.6-0.9 kg/h. Specific surface area of powders is in the range of 20-40 m2/g depending on concentration of vapours in gas flow and cooling rate of the products. Additional calcination of nanosize particles at 800-900 °C improves phase composition of lithium titanates.

1. Introduction
Several compounds are known in the lithium-titania system. They differ by ratio of components and crystal structure. Among them there are at least two types of lithium titanates - Li2TiO3, Li2Ti5O12 - with very promising application.

Li2TiO3 has been considered as an excellent blanket material for fusion reactors [1]. Li2Ti5O12 is promising electrode material for lithium ion batteries [2]. Recent studies have shown that characteristics of nanostructural lithium titanates are remarkably higher with respect to conventional materials [3, 4]. At present nanocrystalline lithium titanates have been prepared by using wet chemical synthesis such as sol-gel process [4], hydrothermal [5] or combustion synthesis [6]. The wet chemical methods ensure preparation of pure nanocrystalline lithium titanates with the smallest particle size (10-20 nm) but they include many stages and production rate is low.

Considering the promising application of nanocrystalline lithium titanates the aim of the present work was to develop the simple stage vapour phase process for preparation of technical amounts of lithium titanates using plasma technique.

2. Experimental
The plasma technique is based on the evaporation of coarse-grained commercially available precursors in inductively coupled air plasma using technological apparatus described in [7]. The precursors Li2CO3 (99.9) and TiO2 (99.9) with particle size in the range of 20-80 μm and 10-40 μm respectively were mechanically mixed and introduced into plasma flame with average temperature 5500 K by carrier gas. Evaporation of raw powders was achieved by varying the power of the plate of RF oscillator, the flow rate of the plasma forming gas, the feed rate of precursors and their sampling velocity. The formation of particles from vapours and their growth was controlled by introducing cold air into the reaction chamber.
Chemical and phase composition of the prepared powders was determined by conventional chemical and X-ray analysis methods (Bruken 28). The specific surface area was defined by the argon absorption-desorption method. The lithium titanates crystallite size was determined by the X-ray line broadening method using Scherrer’s equation. The particle size and shape were studied by the scanning electron microscopy (S-4800, Hitachi Ltd.).

3. Results and discussion
Evaporation of the raw powders in inductively coupled plasma flow results in the obtaining nanosized powders, which characteristics depend on the ratio of lithium and titanium (Table 1).

| Samples No | Ratio Li/Ti | Specific surface area (m²/g) | Crystallite size (nm) | Phase composition |
|------------|-------------|-------------------------------|-----------------------|-------------------|
| 1          | 0.67        | 21                            | 57                    | Li₄Ti₅O₁₂; Li₂Ti₃O₇; TiO₂, an., rut. (tr.) |
| 2          | 0.8         | 24                            | 62                    | Li₄Ti₅O₁₂; Li₂Ti₃O₇ (tr.) TiO₂, an., rut. (tr.) |
| 3          | 1.0         | 22                            | 68                    | Li₄Ti₅O₁₂; Li₂TiO₃ |
| 4          | 2.0         | 24                            | 74                    | Li₂TiO₃; LiTiO₂ |
| 5          | 2.1         | 26                            | 74                    | Li₂TiO₃; LiTiO₂ |

The obtained results indicate that the influence of Li/Ti ratio on the specific surface area of the prepared powders is very weak. However the crystallite size of the main crystalline phase increases with increase of lithium content in the samples. Obviously formation of several phases at low Li/Ti ratio limits growth of crystallites. Accordingly SEM studies size of the prepared particles is in the range of 60-120 nm. The particles are mainly spherical shape although separate particles form short chains (Fig. 1).

![SEM micrograph of lithium titanate (sample No 4)](image)

**Figure 1.** SEM micrograph of lithium titanate (sample No 4)

The wide particle size distribution is characteristics for powders prepared by plasma technique. It can be explained by influence of temperature and velocity gradients existing in plasma flow. The large temperature and velocity gradients of plasma flow provide different growth conditions for particles formed in inner and outer sections of gas.

At determined Li/Ti ratio the specific surface area and average particle size of powders depend on the concentration of vapours in the gas flow and the growth time of crystals that is determined by plasma.
velocity, formation and melting temperature of compounds as well as by the cooling rate of growing particles. The increase of the concentration of particles in the plasma flow by changing the feeding rate of precursors causes the decrease of the specific surface area according to parabolic law (Fig. 2) because the high concentration of vapours stimulates growth of the product particles. On the other side increasing feeding rate of raw powder causes the decrease of temperature of the plasma flow leading to incomplete evaporation of the precursors having higher boiling temperature, especially TiO\textsubscript{2}. As result, the content of admixture of TiO\textsubscript{2} phase strongly depends on the feeding rate of the raw powder.

**Figure 2.** Dependence of specific surface area (1) and content of TiO\textsubscript{2} (2) in as-prepared powder at ratio Li/Ti=2 on feeding rate of raw powder.

Reduction of growth time of particles by introducing cold gas into the vapour region increases the specific surface area of the product independently on lithium/titanium ratio (Fig. 3).

**Figure 3.** Dependence of the specific surface area of lithium titanates prepared at ratio Li/Ti = 0.8 (1) and 2 (2) and feeding rate of precursors 0.9 kg/h on ratio of flow rates of cooling and plasma gas.
Phase composition of the prepared nanosized particles strongly depends on the Li/Ti ratio (Table 1). The powders prepared at Li/Ti = 2 (sample No. 4) besides main Li$_2$TiO$_3$ phase contain extra phase of LiTiO$_2$. The XRD patterns of samples prepared at Li/Ti = 0.8 (sample No. 2) besides main phase Li$_4$Ti$_5$O$_{12}$ show weak maxima of the both TiO$_2$ and Li$_2$Ti$_3$O$_7$ phases (Fig. 4).

![XRD patterns of as-prepared lithium titanate (sample No. 2): • Li$_4$Ti$_5$O$_{12}$; • TiO$_2$ (rut.); ▲ TiO$_2$ (an.), = Li$_2$Ti$_3$O$_7$.](image)

**Figure 4.** XRD patterns of as-prepared lithium titanate (sample No.2): • Li$_4$Ti$_5$O$_{12}$; • TiO$_2$ (rut.); ▲ TiO$_2$ (an.), = Li$_2$Ti$_3$O$_7$.

Intensity of TiO$_2$ extra phase’s maxima increases along with increase of the content of titania in the system. This can be explained by incomplete evaporation of the used raw coarse-grained titania as well as by higher boiling temperature of TiO$_2$ with respect to other components. The above conditions can promote formation of titania particles from vapour phase before condensation of other components.

Obviously, optimization of the TiO$_2$ particle size and cooling rate of vapours will promote formation of single desirable phase.

Additional calcinations of the as-prepared at Li/Ti = 0.8 and Li/Ti = 2 nanosized powders at 800-900 °C improves their phase composition because high the activity of particles enables their chemical interaction. According XRD analysis data the calcinated samples contain Li$_2$TiO$_3$ or Li$_4$Ti$_5$O$_{12}$ phases (Fig. 5). Moreover the calcination reduces simultaneously the specific surface area to 12-16 m$^2$/g.

Therefore the combining of the plasma technique with additional calcination allows obtain technical amounts of nanosized Li$_2$TiO$_3$ and Li$_4$Ti$_5$O$_{12}$ powders. The size of the prepared spherical particles exceeds the particle size of the powders prepared by the sol-gel method but the productivity is higher. It seems that the further studies focused on mixing of the raw powders, optimization of the size and control of formation conditions of the products will improve process efficiency.
Figure 5. XRD patterns of lithium titanate (prepared at ratio Li/Ti = 0.8) after calcination at 900 °C ( ■ Li$_4$Ti$_5$O$_{12}$, ▲ TiO$_2$ (rut.).

4. Conclusions
1. Developed plasma technique is useful for producing technical amounts of nanosized lithium titanates with regular spherical shape and size in the range of 60-120 nm depending on the feeding rate of the precursors and cooling rate of the products.
2. The phase composition of the produced powders is determined by lithium/titanium ratio and feeding rate of raw powders.
3. The phase composition of titanium titanates could be improved by additional calcinations of as-prepared powders at 800-900 °C.

References
[1] Tsuchiya K, Kawamura H, Casadio S and Alvani C 2005 Effect of gelation and sintering conditions on granulation of Li$_2$TiO$_3$ pebbles from Li-Ti complex solution Fussion Eng. and Design 75-79 877-880
[2] Jung Choon-Hwan 2005 Sintering characterization of Li$_2$TiO$_3$ ceramic breeder powders prepared by solution combustion synthesis process J. Nucl. Mater. 341 148-152
[3] Singhal A, Skandeen G, Amatucci G, Badway F, Ye Nn Manthiram A, Ye H and Xu J J 2004 Nanostructured electrodes for next generation rechargeable electrochemical device J. Power Sources 129 1 38-44
[4] Venkateswarlu M, Chen C H, Do J S, Lin C W, Chou T C and Hevang B J 2005 Electrochemical properties of nano-sized Li$_4$Ti$_5$O$_{12}$ powders synthesized by a sol-gel process and characterized X-ray absorption spectroscopy J. Power Sources 146 204-208
[5] Kalbač M, Zukalova M and Kavan L 2003 Phase-pure nanocrystalline Li$_4$Ti$_5$O$_{12}$ for a lithium-ion battery J. Solid State Electrochem. 8 2-6

[6] Choong-Hwan Jeng 2005 Sintering characterization of Li$_2$TiO$_3$ ceramic breeder powders prepared by the solution combustion synthesis process J. Nucl. Mater. 341, 148-152

[7] Grabis J 2000 Nanosized nitride-based composite powders produced by ICP technique Interfaced Controlled Materials eds M Ruehle and H Gleiter Willey-YCH 9 267-272