

Preparation of Nanosized Lithium-Titania Compounds from Vapour Phase

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Abstract. The synthesis of nanosized lithium titanates is studied by evaporation of coarse grained commercially available titania and lithium carbonate particles in a radio-frequency plasma flow with subsequent controlling formation and growth conditions of product particles. Accordingly the XRD analysis the phase composition of the obtained powders is determined by feeding rate of precursors, cooling rate of products, particle size of TiO_2 , and strongly by ratio of lithium and titania. The Li_2TiO_3 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles with small amounts of extra phases were obtained at ratio of $\text{Li/Ti}=2$ and $\text{Li/Ti}=0.8$ respectively and feeding rate of precursors in the range of 0.6-0.9 kg/h. Specific surface area of powders is in the range of 20-40 m^2/g depending on concentration of vapours in gas flow and cooling rate of the products. Additional calcination at 800-900 °C of nanosized particles 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 - Li_2TiO_3 , $\text{Li}_2\text{Ti}_5\text{O}_{12}$ - with very promising application.

Li_2TiO_3 has been considered as an excellent blanket material for fusion reactors [1]. The $\text{Li}_2\text{Ti}_5\text{O}_{12}$ 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.

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

2. Experimental

The plasma technique is based on the evaporation of coarse-grained commercially available precursors in an inductively coupled air plasma using technological apparatus described in [7]. The precursors Li_2CO_3 (99.9) and TiO_2 (99.9) with particle size in the range of 20-80 μm and 10-40 μm respectively were mechanically mixed at several ratio components 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 injection velocity. The formation of particles from vapours and their growth was controlled by introducing cold air into reaction chamber.

Chemical and phase composition of the prepared powders was determined by conventional chemical and X-ray analysis. The specific surface area was defined by the argon absorption-desorption method. The crystallite size of the lithium titanates was determined by the X-ray line broadening method using Scherrer's equation. The particle size and shape were studied by scanning electro microscopy (SEM).

3. Results and discussion

Evaporation of the raw powders in inductively coupled plasma flow results in the obtaining nanosized powders, which characteristics depend on ratio of lithium and titanium (Table 1). From data follows that influence of ratio Li/Ti on specific surface area of the prepared powders are very weak. However crystallite size of the main crystalline phase increases with increase of lithium content in the samples. Obviously formation of several phases at low ratio Li/Ti limits growth of crystallites. Accordingly SEM studies size of the prepared particles is in the range of 60-120 nm.

Table 1. Characteristics of the samples (feeding rate of powder 0.9 kg/h)

Samples No	Ratio Li/Ti	Specific surface area (m ² /g)	Crystallite size (nm)	Phase composition
1	0.67	21	57	Li ₄ Ti ₅ O ₁₂ ; Li ₂ Ti ₃ O ₇ TiO ₂ , an., rut. (tr.)
2	0.8	24	62	Li ₄ Ti ₅ O ₁₂ ; Li ₂ Ti ₃ O ₇ (tr.) TiO ₂ , an., rut. (tr.)
3	1.0	22	68	Li ₄ Ti ₅ O ₁₂ ; Li ₂ TiO ₃
4	2.0	24	74	Li ₂ TiO ₃ ; LiTiO ₂
5	2.1	26	74	Li ₂ TiO ₃ ; LiTiO ₂

The particles have mainly spherical form although separate particles form short chains (Fig. 1). 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 of particles formed in inner and outer sections of gas.

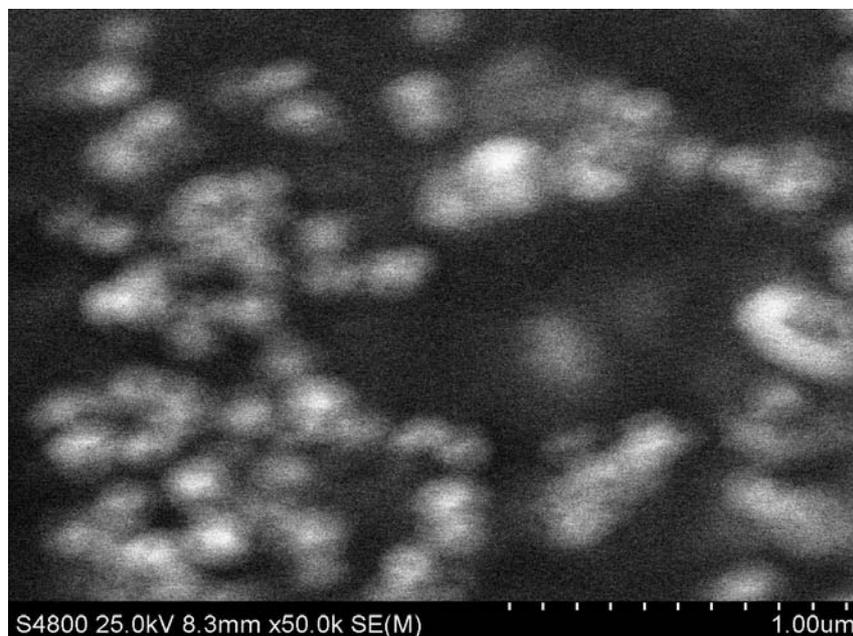


Fig. 1. SEM micrograph of lithium titanate (sample no 4)

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 growth time of products that is determined by a plasma velocity, formation and melting temperature of compounds as well as by a cooling rate of growing particles. The increase of the concentration of particles in the

plasma flow by changing feeding rate of precursors decreases the specific surface area according to parabolic law (Fig. 2) because a high concentration of vapours stimulates growth of the product particles. On the other side increasing feeding rate of raw powder decreases temperature of the plasma flow leading to incomplete evaporation of the precursors, especially TiO_2 having higher boiling temperature. As result the content of admixture of TiO_2 phase strongly depends on the feeding rate of the raw powder.

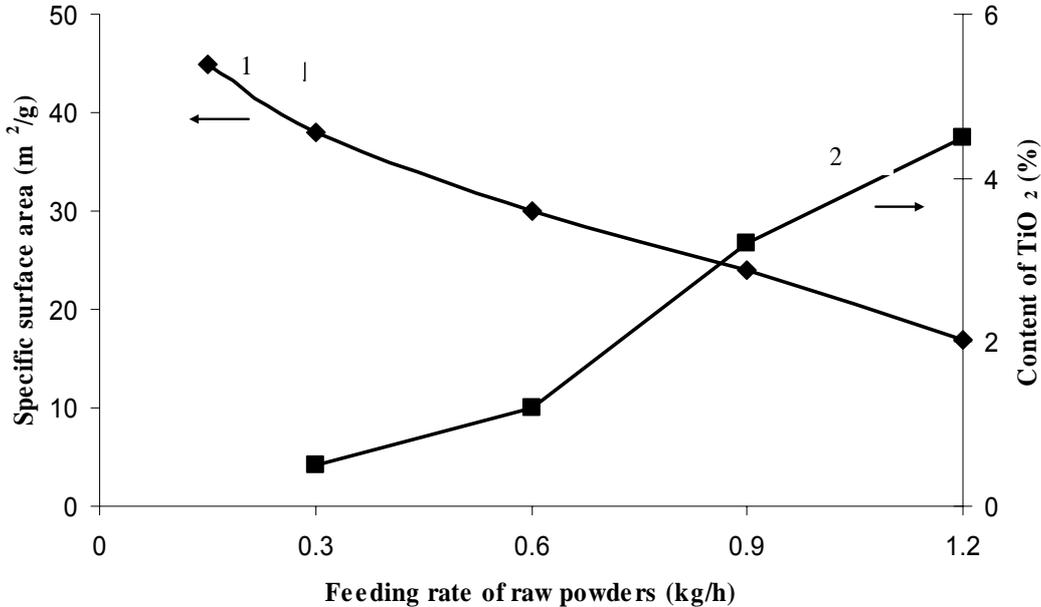


Fig. 2. Dependence of specific surface area (1) and content of TiO_2 (2) in as-prepared powder at ratio $\text{Li/Ti}=2$ on feeding rate of raw powder.

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

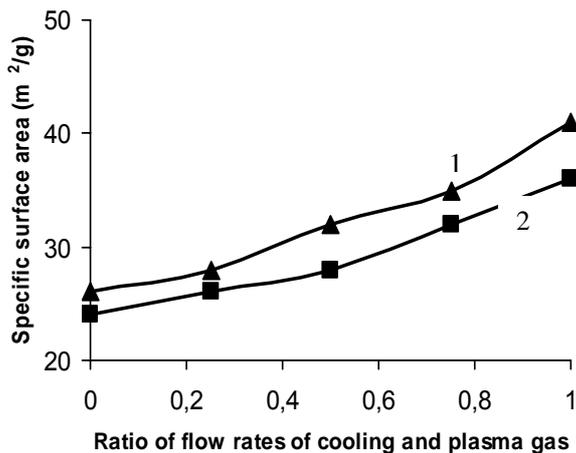


Fig. 3. Dependence of the specific surface area of lithium titanates prepared at ratio $\text{Li/Ti} = 0.8$ (1) and 2 (2) and feeding rate of precursors 0.9 kg/h on ratio of flow rates of cooling and plasma gas.

Phase composition of prepared nanosized particles strongly depends on the ratio Li/Ti (Table 1). The powder prepared at $\text{Li/Ti} = 2$ (sample no. 4) besides main Li_2TiO_3 phase contains extra phase of LiTiO_2 . The XRD pattern of sample prepared at $\text{Li/Ti} = 0.8$ (sample no. 2) besides main phase $\text{Li}_4\text{Ti}_5\text{O}_{12}$ shows weak maxima of both TiO_2 phases and $\text{Li}_2\text{Ti}_3\text{O}_7$ phase. Intensity of TiO_2 extra phase's maxima increases with content of titania in the system and it 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 the other components. It can promote formation of titania particles from vapour phase before condensation of other components.

This assumption is confirmed by studies of dependence of the phase composition and content of TiO_2 in the prepared lithium titanate on particle size of raw TiO_2 and ratio of flow rates of cooling and plasma gases (Table 2).

Additional calcinations of the as-prepared at $\text{Li/Ti} = 0.8$ and $\text{Li/Ti} = 2$ nanosized powders at 800-900 °C improves their phase composition because high activity of particles promotes their chemical interaction. According XRD analysis the calcinated samples contain only Li_2TiO_3 or $\text{Li}_4\text{Ti}_5\text{O}_{12}$ phases. However the calcination reduces simultaneously the specific surface area to 12-16 m^2/g .

Table 2. Dependence of product phase composition and TiO_2 content on particle size of raw TiO_2 and ratio of flow rates of cooling and plasma gases (G_c/G_{pl}). Ratio of $\text{Li/Ti} = 0.8$, feeding rate of raw powders 0.9 kg/h.

Synthesis parameters		Characteristics of products	
particle size of TiO_2 , μm	G_c/G_{pl}	phase composition	Content of TiO_2
10-40	-	$\text{Li}_4\text{Ti}_5\text{O}_{12}$, $\text{Li}_2\text{Ti}_3\text{O}_7$ (tr.) TiO_2 an., rut. (tr.)	3.2
10-40	0.4	$\text{Li}_4\text{Ti}_5\text{O}_{12}$, $\text{Li}_2\text{Ti}_3\text{O}_7$ (tr.) TiO_2 an., rut. (tr.)	3.0
10-40	0.8	$\text{Li}_4\text{Ti}_5\text{O}_{12}$, $\text{Li}_2\text{Ti}_3\text{O}_7$ (tr.) TiO_2 an., rut. (tr.)	2.6
20-40	0.4	$\text{Li}_4\text{Ti}_5\text{O}_{12}$, $\text{Li}_2\text{Ti}_3\text{O}_7$ (tr.) TiO_2 an., rut. (tr.)	2.1
20-40	0.8	$\text{Li}_4\text{Ti}_5\text{O}_{12}$ TiO_2 an., rut. (tr.)	1.8
10-20	0.4	$\text{Li}_4\text{Ti}_5\text{O}_{12}$ TiO_2 an., rut. (tr.)	1.6
10-20	0.8	$\text{Li}_4\text{Ti}_5\text{O}_{12}$	<1.0

Therefore the combining of the plasma technique with additional calcination allows produce technical amounts of nanosized Li_2TiO_3 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders. The size of the prepared spherical particles exceeds particle size of the powders prepared by sol-gel method but the production rate is higher.

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 ratio of lithium and titanium and feeding rate of raw powders, particle size of used titania and cooling rate of the products.
3. The phase composition of the lithium titanates could be improved by additional calcinations of as-prepared powders at 800-900 °C.

5. References

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