ISSN1027-5495. Functional Materials, 32, No.4 (2025), p. 562-566
doi:http://dx.doi.org/10.15407/fm32.04.562

Electrochemical properties of composite materials "lithium titanate–TiO_2" synthesized by one-step rapid synthesis method

A.S.Smolyar[1], A.O.Burkhan[1], O.M.Bloshchanevich[1], A.I.Stegniy[1], A.V.Stepanenko[1], M.P.Brodnikovskyy[1], V.E.Sheludko[1], V.G.Khomenko[2], O.V.Kovtun[3]

[1] I.N. Frantsevich Institute for Problems of Materials Science, National Academy of Sciences of Ukraine, 3 Omeliana Pritsaka (Krzhizhanovsky) Str., 03142 Kyiv, Ukraine
[2]Kyiv National University of Technologies and Design, Department of Chemical Technology and Resource Saving, 2 Mala Shyianovska Str., 01011 Kyiv, Ukraine
[3]M.P. Semenenko Institute of Geochemistry, Mineralogy and Ore Formation, National Academy of Sciences of Ukraine, 34 Akademika Palladina Ave., 03142 Kyiv, Ukraine

Received January 23, 2025

Lithium titanates are known as promising materials for anodes of lithium-ion batteries. Intensive research is being conducted on the synthesis of various lithium titanate composites to improve the electrophysical characteristics of batteries. Micropowders of the composites (lithium titanate – TiO_2) were obtained by heat treatment of the batch (Li_2CO_3 + Ti) in the temperature range of 900-1000 °C for 4 minutes using the one-step rapid synthesis method developed by the authors. The phase composition and structure of the composites were studied using a DRON-3M diffractometer and a JSM-6700F SEM. Based on the composites synthesized at a temperature of 975 °C, prototypes of experimental cells with a lithium electrode were manufactured. Cycling in the range of 0-3 V relative to the lithium electrode at a current density of 15 mA/g showed a reversible capacity of 101 mA·h/g. The obtained test results confirm the possibility of using composites for lithium-titanium batteries.

Keywords: lithium titanate, TiO_2, composite, electrochemical properties

Електрохімічні властивості композиційних матеріалів "титанат літію–TiO_2", синтезованих методом одностадійного швидкісного синтезу. *А.С.Смоляр, А.О.Бурхан, О.М.Блощаневич, А.І.Стегній, А.В.Степаненко, М.П.Бродніковський, В.Є.Шелудько, В.Г.Хоменко, О.В.Ковтун.*

Титанати літію відомі як перспективні матеріали для анодів літій-іонних акумуляторів. Проводяться інтенсивні дослідження синтезу різних композитів титанату літію для покращення електрофізичних характеристик акумуляторів. Мікропорошки композитів (титанат літію – TiO_2) отримані термообробкою шихти (Li_2CO_3 + Ti) в інтервалі температур 900-1000 °С за 4 хвилини методом одностадійного швидкісного синтезу, розробленого авторами. Фазовий склад та структуру композитів вивчено за допомогою дифрактометру DRON-3M та скануючого електронного мікроскопу JSM-6700F. На основі синтезованих при температурі 975 °С композитів було виготовлено прототипи дослідних елементів з літієвим електродом. Циклювання в діапазоні 0-3 В відносно літієвого електрода при густині струму 15 мА/г показало зворотну ємність 101 мА год/г. Отримані результати випробувань підтверджують можливість застосування композитів для літій-титанових акумуляторів.

1. Introduction

The intensive development of technology drives scientific and applied research on the synthesis of various composites based on lithium titanates. For instance, lithium pentatitanate $Li_4Ti_5O_{12}$ (LTO) is a promising non-deformable anode material for lithium-ion batteries, offering high stability during cycling without significant capacity loss [1, 2]. Lithium metatitanate Li_2TiO_3 is considered one of the main materials for future fusion reactors due to its high tritium release rate at relatively low temperatures (from 200 to 400 °C) and chemical stability [3].

At the same time, intensive research is being conducted on the synthesis of various composites based on lithium titanates, which offer advantages in electrophysical properties compared to pure titanates [4, 5]. One such system is "lithium titanate-TiO_2". The choice of titanium dioxide as a material for improving the electrophysical characteristics, for instance, of LTO, is explained by its high potential for Li+ insertion reactions (1.5–1.8 V) and minimal volume change (3–4%) during the charge/discharge process [5, 6].

The synthesis of lithium titanates and their composites is most commonly achieved through methods such as solid-state synthesis, the sol-gel process, solution combustion, and hydrothermal techniques [7–10]. However, these methods are often complex, time-consuming (lasting several hours), and require expensive equipment and reagents.

The authors developed a one-step rapid synthesis method for composites based on lithium titanate. This approach was previously applied to the synthesis of calcium titanate $CaTiO_3$ (perovskite) [11]. Experiments were conducted to achieve rapid synthesis of composites at temperatures ranging from 700 to 1000 °C within 2–10 minutes. Lithium carbonate (Li_2CO_3) was used as the lithium source in the batch preparation.

The aim of this work is to synthesize the "lithium titanate-TiO_2" composite using a one-step rapid synthesis method, investigate its electrochemical properties, and evaluate its potential application as an anode material for lithium-titanate batteries.

2. Experimental

The starting materials for the synthesis included chemically pure lithium carbonate Li_2CO_3 (LLC "UKRKHIMEXPO", Kyiv, Ukraine) and titanium powder PTOM (TU 14-22-57-92). The thermal treatment of the mixture (Li_2CO_3/Ti = 1:1) was performed in a tubular furnace using a thermal shock process (T = 700–1000 °C, holding time 2–10 minutes) according to the method described in [11, 12]. During the synthesis of the composites, the following reactions may occur:

$$Ti + O_2 \rightarrow TiO_2$$

$$Li_2CO_3 \rightarrow Li_2O + CO_2$$

$$xLi_2O + yTiO_2 \rightarrow Li_xTi_yO_z$$

The composite materials were analyzed using X-ray diffraction on a DRON-3M diffractometer with Cu-Kα radiation. Diffraction patterns were recorded using point scanning with a step size of 0.05° and an exposure time of 5 seconds, in 2θ intervals of 15°–45° and 15°–85°. For qualitative phase analysis, the Analyze software package with the PDF-2 database was used. The structure of the composites was examined using a JSM-6700F scanning electron microscope equipped with a JED-2300 energy-dispersive microanalysis system ("JEOL," Japan). Imaging conditions included an accelerating voltage of 20 kV, a probe current of 5×10^{-10} A, and a probe diameter of 1 μm. The electrode composition "lithium titanate-TiO_2" with graphitized carbon black (90:10) was prepared according to the method [13]. A suspension of the active material based on polyvinylidene fluoride (PVDF) in N-methylpyrrolidone was applied to a copper current collector, dried at 100 °C (30 min), rolled, punched into discs with a diameter of 16 mm, and further dried in a vacuum at 120 °C (6 h). The cells were assembled in an argon-filled glovebox (MBRAUN Inc., USA) with O_2 and H_2O concentrations ≤ 5 ppm, using CR2016 lithium cell cases, a Celgard2400 separator with a thickness of 20 μm, an electrolyte (1M $LiPF_6$ in a solvent mixture of ethylene carbonate, dimethyl carbonate, and diethylene carbonate in a 1:1:1 ratio), and a lithium counter electrode. The charge-discharge characteristics of the cells were studied using an MSTAT potentiostat (Arbin Instruments, USA) in galvanostatic mode according to [13, 14].

3. Results and discussion

In the temperature range of 700–800 °C, a small amount of titanate is formed. Its formation becomes more intensive in the tempera-

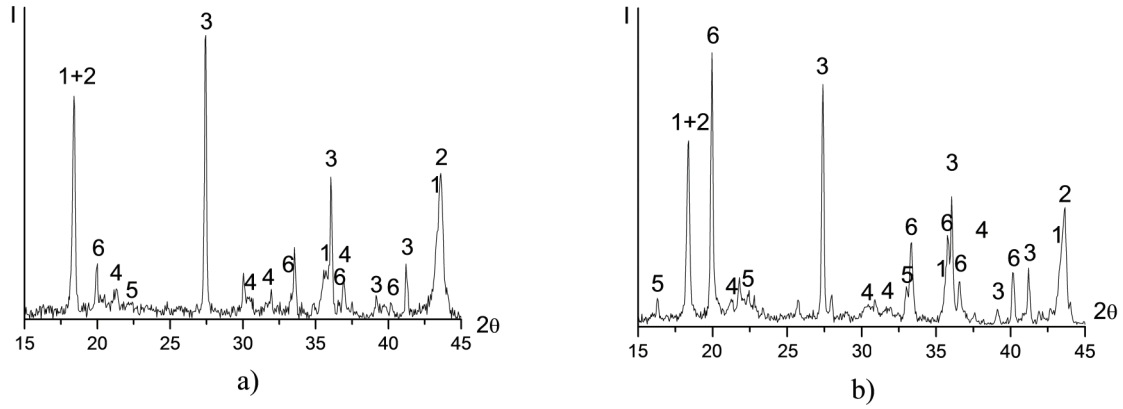

Fig. 1 – Diffraction patterns of the obtained "lithium titanate-TiO_2" composite after thermal treatment of the batch at the following temperatures: a – 900 °C, b – 1000 °C. 1 – $Li_4Ti_5O_{12}$, 2 – ß-Li_2TiO_3, 3 – TiO_2 (rutile), 4 – Li_2CO_3, 5 – Li_4TiO_4, 6 – $Li_2Ti_3O_7$

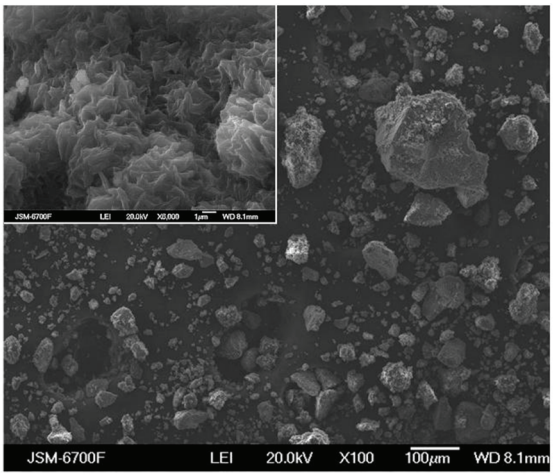

Fig. 2 – Microstructure of the "lithium titanate-TiO_2" composite obtained after thermal treatment of the batch at 900 °C (inset – magnified fragment)

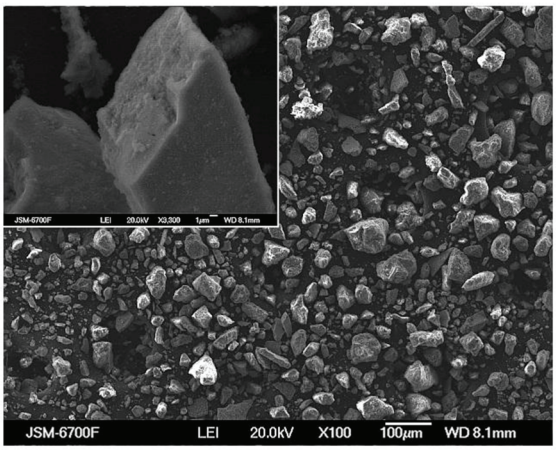

Fig. 3 – Microstructure of the "lithium titanate-TiO_2" composite obtained after thermal treatment of the batch at 1000 °C (inset – magnified fragment showing a single crystal fracture)

ture range of 900–1000 °C (τ = 4 min). Figure 1 shows the X-ray diffraction patterns of composite material powders obtained by the one-step rapid synthesis method. As can be seen from the diffraction patterns, the composite consists of several crystalline phases of lithium titanates ($Li_4Ti_5O_{12}$, ß-Li_2TiO_3, $Li_2Ti_3O_7$, and Li_4TiO_4) and titanium oxide TiO_2 (rutile), with the ratio of these phases varying depending on the synthesis temperature within the 800–1000 °C range.

The microstructure of the samples synthesized at T = 900 and 1000 °C is presented in Fig. 2 and Fig. 3. The as-synthesized powder, without additional grinding, consists of particles of various shapes with sizes ranging from ~1 μm and smaller, along with agglomerates up to 280 μm in size.

The diffraction pattern (Fig. 4) shows that the composite consists of several crystalline phases of lithium titanates with a minimal amount of titanium dioxide (rutile). It can be concluded that the most favorable conditions for composite formation correspond to a temperature of 975 °C and a holding time of 3 minutes. Under these conditions, the composite contains the lowest TiO_2 (rutile) content, with lithium titanates forming the majority phase.

The phase ratio of lithium titanates to TiO_2 can be controlled by adjusting the synthesis time and temperature within the range of 800–1000 °C. The formation of rutile depends on the holding time after loading into the furnace. At τ = 2-3 min, the minimum amount of rutile is formed, at 4-10 min this amount is much more.

After grinding the composite in an agate mortar, particle-size analysis revealed that 90% of the powder particles range in size from 100 nm to 22.2 μm.

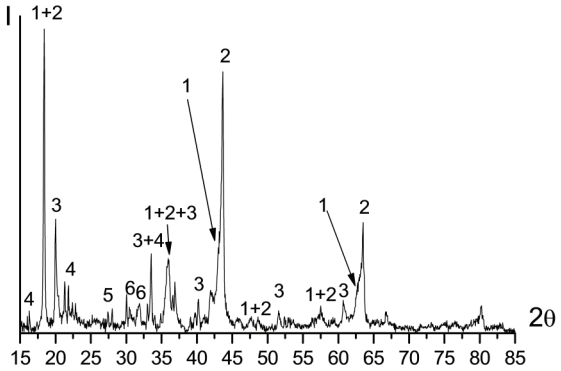

Fig. 4 – Diffraction pattern of the "lithium titanate-TiO_2" composite obtained after thermal treatment of the batch at 975 °C. 1 – $Li_4Ti_5O_{12}$, 2 – ß-Li_2TiO_3, 3 – $Li_2Ti_3O_7$, 4 – Li_4TiO_4, 5 – TiO_2(rutile), 6 – Li_2CO_3

Prototypes of experimental cells with a lithium electrode were fabricated using the "lithium titanate-TiO_2" composites synthesized at 975 °C (Fig. 4). A thorough analysis of the electrical characteristics of these experimental samples was performed (Fig. 5 and Fig. 6).

Fig. 5 illustrates the charge-discharge characteristics during the first cycle of the experimental sample produced using the synthesized composite (Fig. 4) as the anode material. Cycling was performed within a potential range of 0 to 3.0 V relative to the lithium electrode at a current density of 15 mA/g. According to the experimental results, the reversible capacity of the sample was 101 mA·h/g. This is close to the 106 mA·h/g achieved for similar materials prepared via solid-state sintering without the use of nano-additives [15]. However, this capacity is lower compared to commercial LTO samples, which demonstrate capacities in the range of 150–170 mA·h/g [16]. The Coulombic efficiency during the first cycle was approximately 61%, indicating losses during the initial charging process, likely due to side reactions such as the formation of a solid electrolyte interphase (SEI). Subsequently, the Coulombic efficiency approaches nearly 100%, indicating high stability of the charge-discharge characteristics of the synthesized material.

It should be noted that high capacity is achieved by cycling in the potential range of 0 to 3.0 V (Fig. 6). In contrast, cycling in the LTO electroactive range (1.2–2.2 V) results in a low capacity of approximately 20 mA·h/g. This suggests that the composite contains an electrochemically inactive lithium titanate phase. The main reasons for the reduced capacity of the obtained lithium titanate may be the unevenness of particle sizes and the formation of agglomerates, which reduce the active surface area of the material. Rapid synthesis can lead to the formation of crystalline defects, such as oxygen vacancies, that limit the ability of the material to reversibly intercalate lithium. Additionally, the limited electronic conductivity of TiO_2 and weak interparticle bonding within the composite increase resistance and slow down charge transfer processes.

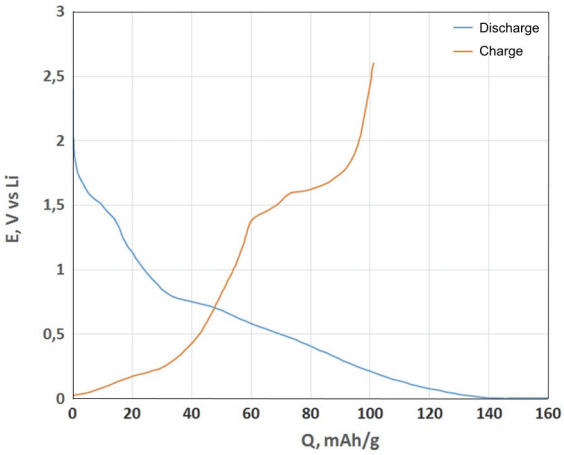

Fig. 5 – Charge-discharge characteristic of the "lithium titanate-TiO_2" composite during the first cycle

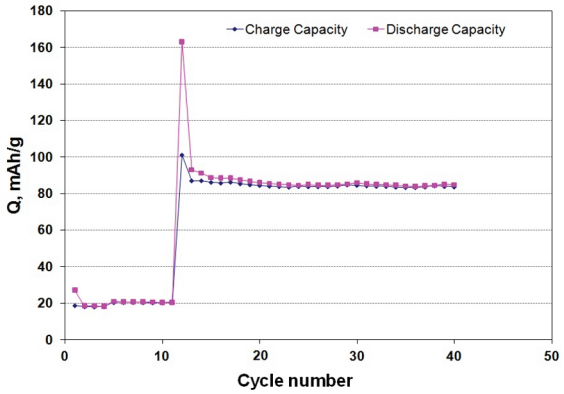

Fig. 6 – Changes in capacity and Coulombic efficiency during charge-discharge cycling of the "lithium titanate–TiO_2" composite in the cycling range of 1.2–2.0 V (up to the 12th cycle) and in the potential range of 0–3.0 V (from the 12th to the 40th cycle)

The test results confirm the possibility of using the material for lithium titanate batteries. Despite its low capacity, the composite has advantages over graphite, in particular, it is non-flammable. To enhance the electrochemical performance of "lithium titanate-TiO_2" composites, it is necessary to refine synthesis methods, control particle morphology, and optimize the phase composition.

4. Conclusions

1. A one-step rapid synthesis method was used to produce the "lithium titanate–TiO_2" composite. The best results were achieved at a temperature of 975°C and a holding time of 3 minutes.

2. Electrochemical studies have confirmed the potential of the synthesized "lithium titanate–TiO_2" composite for use in electrodes of lithium-titanate batteries. The material exhibits stable capacity at 101 mAh/g and acceptable Coulombic efficiency. However, further research should focus on optimizing the synthesis process and material structure to enhance its electrochemical performance.

3. The obtained results of experiments on rapid synthesis in the temperature range of 900–1000 °C open up opportunities for developing energy-efficient laboratory and industrial technologies for the production of "lithium titanate–TiO_2" composite powders. These technologies could be applied in various industries. For instance, a 5 kW installation can produce 2.5–3 kg/h, or up to 60–70 kg/day, of composite micropowder using a conveyor production scheme.

References

1. G.Zubi, R.Dufo-López, M.Carvalho et al., *Renew. Sust. Energ. Rev.*, **89**, 292 (2018). https://doi.org/10.1016/j.rser.2018.03.002.
2. Wen Qi, J.G.Shapter, Qian Wu et al., *J. Mater. Chem. A.*, **5**, 19521 (2017). https://doi.org/10.1039/C7TA05283A.
3. I.L.Tazhibaeva, E.A.Kenzhin, T.V.Kulsartov et al., *VANT. Ser. Termoyadernyj sintez*, **2**, 3 (2008).
4. Y.Wang, A.Zhou, X.Dai et al., *J. Power Sources*, **266**, 114 (2014). doi: 10.1016/j.jpowsour.2014.05.002.
5. Yu Zhang, Yun Zhang, Ling Huang et al, *Electrochim. Acta*, **195**, 124 (2016). https://doi.org/10.1016/j.electacta.2016.02.092.
6. Zhenguo Yang, Daiwon Choi, S.Kerisit et al., *J. Power Sources*, **192**, 588 (2009). https://doi.org/10.1016/j.jpowsour.2009.02.038.
7. T.Ohtake and K.Iijima, *J. Mater. Sci. Chem. Eng.*, **3**, 68 (2015). https://doi.org/10.4236/msce.2015.39009.
8. K.Kanamura, T.Chiba, K.Dokko, *J. Eur. Ceram. Soc.*, **26,** 577 (2006). https://doi.org/10.1016/j.jeurceramsoc.2005.06.014.
9. Tao Yuan, Rui Cai, Ke Wang et al., *Ceram. Int.*, **35**, 1757 (2009). https://doi.org/10.1016/j.ceramint.2008.10.010.
10. Ting-Feng Yi, Zi-Kui Fang, Ying Xie et al., *ACS Appl. Mater. Interfaces.*, **6**, 20205 (2014). https://doi.org/10.1021/am5057568.
11. O.M.Ponomarenko,L.M.Stepanyuk,A.S.Smolyar et al., *Mineralogical J.*, **45**, 3 (2023). https://doi.org/10.15407/mineraljournal.45.04.003.
12. A.O.Burkhan,O.M.Bloshchanevich,A.S.Smolyar et al., in: Book Abstr. Int. Conf. "Materiali dlya roboti v ekstremalnih umovah — 11", Kyiv, Ukraine (2021), p. 168.
13 I.V.Lisovskyi, S.O.Solopan, A.G.Belous et al., J. Appl. Electrochem., **52**, 1701 (2022). https://doi.org/10.1007/s10800-022-01773-1.
14. V.Barsukov, V.Khomenko, and O. Chernysh, Mater. Today, **50**, 415 (2022). https://doi.org/10.1016/j.matpr.2021.12.263.
15. Yanan Li, Qianlin Chen, Qiangqiang Meng et al., *ACS Appl. Mater. Interfaces.*, **11**, 25804 (2019). https://doi.org/10.1021/acsami.9b04041.
16. S.Goripart, E.Miele, F.De Angelis et al., *J. Power Sources*, **257**, 421 (2014). https://doi.org/10.1016/j.jpowsour.2013.11.103.