Synthesis and properties of nickel-doped \( \text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C} \) nano-composite: an anode for lithium ion batteries

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Abstract
Composite of nickel-doped \( \text{Li}_4\text{Ti}_5\text{O}_{12} \) and carbon (designated as \( \text{Ni-Li}_4\text{Ti}_5\text{O}_{12}/\text{C} \)) is synthesized by solid-state reaction with sucrose added as the conductive carbon source. For comparison, nickel-doped \( \text{Li}_4\text{Ti}_5\text{O}_{12} \) (designated as \( \text{Ni-Li}_4\text{Ti}_5\text{O}_{12} \)) is obtained under similar conditions. Both materials are characterized by x-ray diffraction, scanning electron microscopy, energy-dispersive x-ray spectroscopy, charge–discharge cycling and cyclic voltammetry. Analysis of SEM images shows that \( \text{Ni-Li}_4\text{Ti}_5\text{O}_{12}/\text{C} \) consists of smaller particles than \( \text{Ni-Li}_4\text{Ti}_5\text{O}_{12} \). Charge/discharge cycling as well as cyclic voltammetry studies prove that \( \text{Ni-Li}_4\text{Ti}_5\text{O}_{12}/\text{C} \) electrodes perform much better than those made from \( \text{Ni-Li}_4\text{Ti}_5\text{O}_{12} \). The specific capacities of the \( \text{Ni-Li}_4\text{Ti}_5\text{O}_{12}/\text{C} \) composite are close to the theoretical capacity of \( \text{Li}_4\text{Ti}_5\text{O}_{12} \) even at high current rates—the discharge capacity of \( \text{Ni-Li}_4\text{Ti}_5\text{O}_{12}/\text{C} \) at 2C is equal to 164 mA h g\(^{-1}\).

Keywords: Li-ion batteries, nano-composite, lithium intercalation, charge/discharge cycle

Classification numbers: 2.03, 4.00, 5.11

1. Introduction

Lithium-ion batteries are considered to be promising energy storage devices and are widely applied in e.g. portable electronic instruments or electric vehicles [1–3] because of their high energy and power density as well as long cycle-life [4–6]. The properties of electrode materials are crucial for the performance of the battery. Therefore, study of these materials is very important. Regarding anodes, only materials based on carbon (especially graphite) or \( \text{Li}_4\text{Ti}_5\text{O}_{12} \) (LTO) are commercialized. Carbonic materials possess excellent electrochemical properties. However, they exhibit volume change during charge/discharge cycles which cause problems with safe usage of the battery. LTO is an attractive alternative to anodes based on carbon [7, 8]. LTO has a high working potential (~1.55 V versus Li/Li\(^+\)) [9, 10]. LTO is considered to be a zero-strain material, because during lithium intercalation and deintercalation the lattice parameter does not change almost at all [11]. Although the high working potential limits significantly the energy density, the operating potential occurs within the thermodynamic stability window of electrolytic solutions, so that it is not necessary to form a solid electrolyte interphase (SEI) layer for proper functioning of the electrode. Anodes based on \( \text{Li}_4\text{Ti}_5\text{O}_{12} \) exhibit long cycle-life, are resistant to overcharge and can be used in a wide temperature range [10]. Theoretical capacity of non-doped LTO is equal to 175 mA h g\(^{-1}\), because of insertion of 3 moles of lithium ion into LTO structure. \( \text{Li}_4\text{Ti}_5\text{O}_{12} \) has a stable \([\text{Li}_3\text{Ti}_5\text{O}_{12}]^{32-} \) framework, where all tetrahedral (8a) sites and 1/6 of the 16d sites are taken by Ti atoms, while the rest 5/6 of the 16d sites are occupied by Ti atoms. Oxygen atoms reside at 32e sites and the octahedral (16c) sites are empty [12, 13]. After intercalation of lithium ions \( \text{Li}_4\text{Ti}_5\text{O}_{12} \) transforms to rock salt structure of \( \text{Li}_7\text{Ti}_5\text{O}_{12} \), which framework is presented by \([\text{Li}_6\text{Ti}_5\text{O}_{12}]^{32-} \) [12]. Unfortunately, LTO has one significant disadvantage—it has low electronic conductivity (10\(^{-13}\) S cm\(^{-1}\)) [14]. There are many ways to improve the electronic and ionic conductivity of \( \text{Li}_4\text{Ti}_5\text{O}_{12} \). It can be done by obtaining...
nano-materials [7, 14–16] doping with metal cations [17–19] or composing LTO with carbon.

In this study Li$_2$Ti$_5$O$_{12}$ was doped with 3 wt.% Ni$^{2+}$ ions to enhance electronic conductivity and reduce the electrode polarization. One of the samples was additionally composed with sucrose as a carbon source. The samples were characterized by x-ray diffraction (XRD), scanning electron microscopy (SEM) and energy-dispersive x-ray spectroscopy (EDS). What is more, the electrochemical properties were tested by charge–discharge cycling and cyclic voltammetry.

2. Experimental

Ni–Li$_4$Ti$_5$O$_{12}$ was obtained by a solid state method using Li$_2$CO$_3$ (Aldrich, 99.8%), TiO$_2$-anatase (Acros, 99 %) and Ni(NO$_3$)$_2$·6H$_2$O (Aldrich, 99.8%). The starting materials were mixed at the Li:Ti:Ni molar ratio of 4:5:0.24. The mixed reactants were ball-milled for 20 min with a propanol. After drying, powders were calcined at 800 °C for 4 h in the air. The Ni–Li$_4$Ti$_5$O$_{12}$/C composite was obtained by using a similar solid-state method mentioned above. In this case, however, the sample was prepared from a mixture of Li$_2$CO$_3$, TiO$_2$-anatase, Ni(NO$_3$)$_2$·6H$_2$O and saccharose (Aldrich, 99.8%). Dried powder was calcinated in the flowing argon.

Powder x-ray diffraction was performed using panalytical empyrean diffractometer using Cu-$K_\alpha$ radiation in an angular range of 10–110° ($2\theta$) with a 0.02° ($2\theta$) step ($\lambda = 1.5406$ Å). Rietveld analysis of XRD data were done using GSAS/EXPGUI set of software [20, 21]. Morphology and structure of samples were analysed by NanoSEM 200 FEI scanning electron microscope equipped with low vacuum detector (LVD). The particle size was obtained using SEM analysis.

The electrochemical measurements were done using CR2032 coin-type cells. The working electrodes were prepared by making a black slurry containing 80 wt.% of active material, 10 wt.% of carbon black and 10 wt.% of polyvinylidene fluoride (PVDF) dissolved in N-methyl-2-pyrrolidone. The slurry was spread on an aluminium foil and dried at 70 °C for 1 h in a vacuum drying oven. After that disks with 8 mm diameter were punched out of the foil and roll-pressed. Metal lithium foil served as a counter electrode. 1 M LiPF$_6$ solution in the 1:1 mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) was used as an electrolyte. Batteries were prepared in the glove-box (UNILAB, M. Braun) under argon atmosphere with controlled oxygen and water vapor pressure (<0.1 ppm). The electrochemical properties of the samples were measured by galvanostatic charge/discharge cycles at different rates over a voltage range of 1.3–2.2 V. The C rate was calculated based on the weight of the electrode and theoretical capacity of LTO. Cyclic voltammetry measurements were carried out at different scanning rates in the range of 0.01–5 mV s$^{-1}$ and in 1.3–2.0 V voltage range. Cells were tested at a computer-controlled galvanostat (KEST 32k multichannel) and on the electrochemical test instrument (ATLAS). All the electrochemical tests were carried out at room temperature.

3. Results and discussion

3.1. Structure

Powders were examined by room-temperature x-ray diffraction in order to detect phase composition in the sintered material (figure 1). The study shows that Ni–Li$_4$Ti$_5$O$_{12}$ and Ni–Li$_4$Ti$_5$O$_{12}$/C exhibit similar phase composition. Peaks located at $2\theta = 18.4^\circ$, 43.3°, 35.6° and 62.8° can be observed.
in the XRD patterns of both samples. This corresponds with the characteristic diffraction peaks of the cubic \( \text{Li}_4\text{Ti}_5\text{O}_{12} \) spinel-type phase with the Fd-3m space group and phase indices (1 1 1), (2 2 0), (3 1 1), (2 2 2), (4 0 0), (3 3 1), (4 2 2), (3 3 3), (5 1 1), (4 4 0), (5 3 1) and (4 4 4)—according to ICDD 04-007-9267. All the observed peaks in the x-ray diffraction pattern of Ni–\( \text{Li}_4\text{Ti}_5\text{O}_{12} \) sample (shown in figure 1(a)) correspond to the main spinel phase. The XRD pattern of Ni–\( \text{Li}_4\text{Ti}_5\text{O}_{12} \)/C sample show several peaks at \( 2\theta = 18.5^\circ, 20.5^\circ, 43.6^\circ \) and \( 43.9^\circ \) which correspond with the diffraction peaks of the monoclinic-type \( \text{Li}_2\text{TiO}_3 \) with the C2/c space group, listed in the ICDD 04-009-2812. Peaks detected at \( 2\theta = 44.5^\circ, 51.9^\circ \) and \( 76.4^\circ \) are correlated with the diffraction peaks of the cubic-type Ni with the Fm-3m space group, listed in the ICDD 04-007-9326. The analysis of the XRD patterns was carried out by using Rietveld method. Basing on that phase composition of the samples was calculated. The Ni–\( \text{Li}_4\text{Ti}_5\text{O}_{12} \)/C sample consists of three phases: 89 wt.% of LTO, 9 wt.% \( \text{Li}_2\text{TiO}_3 \) and 2 wt.% of Ni. Reducing atmosphere of argon caused the reduction of Ni(NO\(_3\))\(_2\) \( \cdot \) 6H\(_2\)O to Ni. Carbon present in the sample might have influenced the calcination so that some \( \text{Li}_2\text{TiO}_3 \) was obtained instead of \( \text{Li}_4\text{Ti}_5\text{O}_{12} \). Based on the literature [22] LTO was named ‘zero strain’ material. It means that phase transition from spinel to the structure of rock salt and intercalation of lithium ions causes only a slight shrinkage of the lattice parameter from 8.3595 Å to 8.3538 Å, with only a 0.2% change in a cell volume. Table 1 contains lattice parameters \( a \) of the samples. The cell parameters of the prepared powders are equal to 8.3608(1) and 8.3628(1) Å. It can be observed that addition of carbon caused a slight increase of the lattice parameter from 8.3608(1) Å for Ni–\( \text{Li}_4\text{Ti}_5\text{O}_{12} \) to 8.3628(1) Å for Ni–\( \text{Li}_4\text{Ti}_5\text{O}_{12} \)/C.

Figure 2 shows SEM images and EDS patterns of the as-synthesized Ni–\( \text{Li}_4\text{Ti}_5\text{O}_{12} \) and Ni–\( \text{Li}_4\text{Ti}_5\text{O}_{12} \)/C. SEM image
in the figure 2(a) clearly indicates that the average particle
size of the Ni–Li4Ti5O12 sample is in the range of 125.14–
585.89 nm. The crystallites have irregular shape with fuzzy
edges and the grains are sintered. Ni–Li4Ti5O12/C has much
lower particle size which is in the range of 70.90–215.48 nm.
Application of carbon from saccharose influenced calcination
so that smaller particles were obtained. EDS spectra (figures
2(c) and (d)) further confirms the presence of Ti, O, C and Ni
elements.

The sol-gel method is very well known, practically dis-
placed method of solid phase synthesis. Mu et al [23] pre-
pared main anode material with the use tetrabutyl titanate
and anhydrous ethanol. Their composite particles obtained by
sol-gel are sized 100–200 nm. However, smaller particles size
(figure 2(b)) may be obtained by a solid state which is simpler
and less harmful to the environment.

3.2. Electrochemical and transport properties

Figure 3 presents discharge capacities of the Li|Li+|Ni–
Li4Ti5O12 and Li|Li+|Ni–Li4Ti5O12/C cells at different current
rates and in a voltage range between 1.3 V and 2.2 V.

The discharge capacity of Ni–Li4Ti5O12 composite is quite
high at lower current rates 0, it reaches 157 mA h g⁻¹ at 0.2
C and 148 mA h g⁻¹ at 0.5 C. However it decreases suddenly
for higher current rates exhibiting only 53 mA h g⁻¹ at 5 C
and 22 mA h g⁻¹ at 10 C. Ni–Li4Ti5O12/C gives much better electro-
chemical performance. Its discharge capacity at 0.2 C is equal
to 170 mA h g⁻¹, it is about 97% of theoretical capacity. Ni–
Li4Ti5O12/C exhibits high discharge capacity even at high cur-
rent rates—e.g. its capacity at 2 C is equal to 164 mA h g⁻¹, only
6 mA h g⁻¹ less than the capacity at 0.2 C and at 10 C is equal
to 140 mA h g⁻¹ (about 80% of theoretical capacity). At the end
Ni–Li4Ti5O12/C was cycled again at 0.2 C and specific capacity

Figure 4. Reversibility of Li|Li+|Ni–Li4Ti5O12 (a) and Li|Li+|Ni–Li4Ti5O12/C (b) cells as a function of cycle number for different discharge rates.

Figure 5. Comparison of 3rd discharge curves for: Li|Li+|Ni–Li4Ti5O12 (a) and Li|Li+|Ni–Li4Ti5O12/C (b) cells at different rates.
had the same value as it had before (170 mA h g\(^{-1}\)). It can be clearly seen that the addition of carbon from saccharose to Ni–Li_4Ti_5O_12/C greatly enhances its electrochemical performance.

For comparison Mu et al [23] studied ultrafast charge/discharge nano-sized Li_4Ti_5O_12/C anode material without Ni. The sample were prepared by sol-gel method with the use of tetrabutyl titanate (TBT), anhydrous ethanol, lithium hydroxide monohydrate and sucrose. The authors concluded that their composite anode displays a distinguished electrochemical charge/discharge performance, especially, quite high rate capability along with a stable cyclability. It delivered the initial discharge specific capacities of 156.7 and 142.1 mA h g\(^{-1}\) at 40 C and 60 C, respectively, and remained the values of 114.2 and 98.1 mA h g\(^{-1}\) after 200 cycles.

Figure 4 presents reversibility of Li|Li\(^+\)|Ni–Li_4Ti_5O_12 (a) and Li|Li\(^+\)|Ni–Li_4Ti_5O_12/C (b) cells as a function of cycle number for different discharge rates. As can be seen in figure 4 the cells assembled with anode based on these materials show about 100% of reversibility.

Discharge curves of Li|Li\(^+\)|Ni–Li_4Ti_5O_12 and Li|Li\(^+\)|Ni–Li_4Ti_5O_12/C cells at different rates are presented in the figure 5. It can be seen that both samples exhibit almost
constant voltage at intermediate states-of-charge and their working voltage is in the range of 1.48–1.53 V.

For Ni–Li$_4$Ti$_5$O$_{12}$/C a sharp drop of voltage can be seen near the end of the discharge cycle while for Ni–Li$_4$Ti$_5$O$_{12}$ the voltage decreases more slightly. It is probably because Ni–Li$_4$Ti$_5$O$_{12}$ consists of bigger grains in comparison to Ni–Li$_4$Ti$_5$O$_{12}$/C. Figure 6 presents charge/discharge curves for: Li|Li$^+$/Ni–Li$_4$Ti$_5$O$_{12}$ (a) and Li|Li$^+$/Ni–Li$_4$Ti$_5$O$_{12}$/C (b) cells of 3rd cycle at 0.2 C. Polarization at 0.2 C scan rate in both cases is very small and it is equal to ca. 0.02 V. Cyclic voltammograms of Ni–Li$_4$Ti$_5$O$_{12}$ and Ni–Li$_4$Ti$_5$O$_{12}$/C are showed in the figure 7. Figure 8 shows cyclic voltammograms of Ni–Li$_4$Ti$_5$O$_{12}$ (a) and Ni–Li$_4$Ti$_5$O$_{12}$/C (b) at different sweep rates.

In order to check the stability and reversibility of process, the cell was tested three times at the 0.2 mV s$^{-1}$ scan rate. It can be seen that the anodic peaks occur at 1.77 and 1.62 V for the Ni–Li$_4$Ti$_5$O$_{12}$ and Ni–Li$_4$Ti$_5$O$_{12}$/C sample, respectively, while the corresponding cathodic peaks are 1.40 and 1.49 V. The cathodic/anodic peaks can correspond to both intercalation/deintercalation of lithium ions at the empty 16c octahedral sites and the Ti$^{3+}$/Ti$^{4+}$ redox couple. It can be clearly seen that Ni–Li$_4$Ti$_5$O$_{12}$/C has higher lithiation and lower delithiation potential than Ni–Li$_4$Ti$_5$O$_{12}$ at every scan rate. It proves that Ni–Li$_4$Ti$_5$O$_{12}$/C has better reversibility of the Li-ion insertion/extraction process.

Mu et al [23] studied cyclic voltammograms of the as-prepared LTO/C and LTO electrodes. All plots demonstrated a pair of oxidation/reduction peaks similarly and symmetrically in shape. The course of the curves confirmed lithium ion insertion and extraction accompanying with electrochemical reaction. The increase of the scanning rate from 0.1 to 5 mV s$^{-1}$ leads to the oxidation and reduction peaks of every curve move away from each other in opposite direction, along with broader peaks and large peak current. The same effect was observed for the studied in this work composite with nickel. These results suggest that a change in polarization may adversely affect the reversibility and the cyclical performance of the electrode.

4. Conclusion

Two powders—Ni–Li$_4$Ti$_5$O$_{12}$ and Ni–Li$_4$Ti$_5$O$_{12}$/C—were obtained by solid-state method. The crystal structures of the materials were investigated using XRD and SEM. Our findings suggest that Ni–Li$_4$Ti$_5$O$_{12}$ consists of micrometric grains with irregular shape, while the crystallites of Ni–Li$_4$Ti$_5$O$_{12}$/C are partially nano-sized, with regular shape and wide Li-diffusion pathways. Decreasing sizes of grains improved electrochemical performance of the material. Nano-sized Ni–Li$_4$Ti$_5$O$_{12}$/C composite exhibits the best electrochemical properties and reversibility during Li intercalation/deintercalation process.

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References

[1] He Z, Wang W, Wu F, Guo H, Li X and Xiong X 2012 J. Alloys Compd. 540 39
[2] Gedziorowski B, Kondracki Ł, Świerczek K and Molenda J 2014 Solid State Ion. 262 124
[3] Li J, Jin Y, Zhang X and Yang H 2007 Solid State Ion. 178 1590
[4] Goriparti S, Miele E, De Angelis F, Di Fabrizio E, Proietti Zaccaria R and Capiglia C 2014 J. Power Sources 257 421
[5] Yuan T, Wang K, Cai R, Ran R and Shao Z 2009 J. Alloys Compd. 477 665
[6] Lin C, Lai M O, Lu L, Zhou H and Xin Y 2013 J. Power Sources 244 272
[7] Wu D and Cheng Y 2013 Ionics 19 395
[8] Liu J, Li X, Yang J, Geng D, Li Y, Wang D, Li R, Sun X, Cai M and Verbrugge M W 2012 Electrochem. Acta 63 100
[9] Liu J, Li X, Cai M, Li R and Sun X 2013 Electrochem. Acta 93 195
[10] Pohjalanen E, Räsänen S, Jokinen M, Yliniemi K, Worsley D A, Kuusivaa J, Juurikkivi J, Ekqvist R, Kallio T and Karppinen M 2013 J. Power Sources 226 134
[11] Zheng X D, Dong C C, Huang B and Lu M 2012 Ionics 19 385
[12] Zhao H 2015 Lithium titanate-based anode materials Rechargeable Batteries (Green Energy and Technology) ed Z. Zhang and S Zhang (Berlin: Springer) pp 157–87
[13] Bhatti H S, Anjum D H, Ullah S, Ahmed B, Habib A, Karim A and Hasanain S K 2016 J. Phys. Chem. C 120 9553
[14] Lai C, Wu Z, Zhu Y, Wu Q, Li L and Wang C 2013 J. Power Sources 226 71
[15] Zhang Y, Wu L, Zhao J and Yu W 2015 Mater. Chem. Phys. 166 182
[16] Li M, Liang J, Wang X and Yu K 2016 J. Alloys Compd. 681 471
[17] Zhang Q and Li X 2013 Int. J. Electrochem. Sci. 8 6449
[18] Jeong E D, Han H J, Jung O S, Ha M G, Doh C H, Hwang M J, Yang H S and Hong K S S 2012 Mater. Res. Bull. 47 2847
[19] Lin C, Ding B, Xin Y, Cheng F, Lai M O, Lu L and Zhou H 2014 J. Power Sources 248 1034
[20] Larson C and Von Dreese R B 2004 General System Analysis System (GSAS) Los Alamos National Laboratory Report No LAUR 86–748
[21] Toby B H 2006 Powder Diffr. 21 67
[22] Ohzuku T, Ueda A and Yamamoto N 1995 J. Electrochem. Soc. 142 1431
[23] Mu D, Chen Y, Wu B, Huang R, Jiang Y, Li L and Wu F 2016 J. Alloys Compd. 671 157