Facile molten salt synthesis of Li$_2$NiTiO$_4$ cathode material for Li-ion batteries

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Abstract

Well-crystallized Li$_2$NiTiO$_4$ nanoparticles are rapidly synthesized by a molten salt method using a mixture of NaCl and KCl salts. X-ray diffraction pattern and scanning electron microscopic image show that Li$_2$NiTiO$_4$ has a cubic rock salt structure with an average particle size of ca. 50 nm. Conductive carbon-coated Li$_2$NiTiO$_4$ is obtained by a facile ball milling method. As a novel 4 V positive cathode material for Li-ion batteries, the Li$_2$NiTiO$_4$/C delivers high discharge capacities of 115 mAh g$^{-1}$ at room temperature and 138 mAh g$^{-1}$ and 50°C, along with a superior cyclability.

Keywords: Lithium nickel titanate; Molten salt method; Cyclability; Li-ion battery

Background

The growing demand for high-energy Li-ion batteries in the development of portable electronic devices and electric vehicles has stimulated great research interest in advanced cathode materials with high voltage and specific capacity. Li$_2$MSiO$_4$ (M = Fe and Mn) has recently attracted particular attention owing to their high theoretical capacities (>330 mAh g$^{-1}$) and good thermal stability through strong Si-O bond [1-3]. However, the practical discharge capacity is mainly achieved below 3.5 V, resulting in a lower cell energy density. Substituting Si atom for Ti atom leads to another attractive cathode material of Li$_2$MTiO$_4$ (M = Fe, Mn, Co, Ni) with high theoretical capacity (approximately 290 mAh g$^{-1}$) [4]. The titanate family has a cubic cation disordered rock salt structure, in which the strong Ti-O bond could stabilize the M$^{3+}$/M$^{2+}$ and M$^{4+}$/M$^{3+}$ transition [5,6].

Recently, Küzma et al. [7] synthesized the carbon-coated Li$_2$FeTiO$_4$ and Li$_2$MnTiO$_4$ by a citrate-precursor method, which showed the reversible capacity of 123 and 132 mAh g$^{-1}$ at 60°C, respectively. In addition, the reported Li$_2$CoTiO$_4$/C presented a high discharge capacity of 144 mAh g$^{-1}$ at rate of 10 mA g$^{-1}$ [8]. In comparison with Fe, Mn and Co analogues, Li$_2$NiTiO$_4$ provides much higher discharge voltage plateau near 4.0 V. The electrochemical characterization of Li$_2$NiTiO$_4$ was initially published in 2004 [9]. In a LiBOB/EC-DMC electrolyte, Li$_2$NiTiO$_4$ could deliver a charge capacity of 182 mAh g$^{-1}$; however, more than 50% of this capacity was lost after 1 cycle [10]. Kawano et al. [11] reported that Li$_2$NiTiO$_4$ demonstrated a discharge capacity of 153 mAh g$^{-1}$ at the extremely low rate of 0.32 mA g$^{-1}$ but showed an inferior cycling stability. Li$_2$NiTiO$_4$ suffers from poor electrode kinetics caused by its intrinsically low ionic and electronic conductivity, leading to a poor electrochemical activity.

In this work, well-dispersed Li$_2$NiTiO$_4$ nanoparticles are successfully prepared by a molten salt process with a short reaction time. To enhance the surface electronic conductivity and reinforce the structural stability, Li$_2$NiTiO$_4$ nanoparticles are carbon-coated by ball milling with carbon black. The whole processes are facile and high-yielding, which are promising for industrial application.

Methods

An equal molar ratio of NaCl and KCl with a melting point of 658°C was used as a molten salt flux. Li$_4$CO$_3$, Ni (CH$_3$COO)$_2$·4H$_2$O, TiO$_2$ (5 to 10 nm) and NaCl-KCl (Aladdin, Shanghai, China) in a molar ratio of 1:1:1:4 were well mixed with a mortar and pestle. The mixture was decomposed at 350°C for 2 h, followed by treatment at 670°C for 1.5 h under air. The product was washed with deionized water to remove any remaining salt and dried under vacuum. The as-prepared Li$_2$NiTiO$_4$ powder was

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ball-milled with 20 wt.% acetylene black to obtain the Li$_2$NiTiO$_4$/C composite.

The as-prepared Li$_2$NiTiO$_4$ was studied by X-ray diffraction (XRD, Rigaku D/Max-2200, Rigaku Corporation, Tokyo, Japan) analysis using Cu Kα radiation (40 kV, 30 mA). The morphologies of the Li$_2$NiTiO$_4$ and Li$_2$NiTiO$_4$/C samples were observed by scanning electron microscope (SEM, JEOL JSM-7401 F, Ltd., Akishima, Tokyo, Japan) with an accelerating voltage of 5.0 kV and transmission electron microscope (TEM, JEOL JEM-2100, Ltd., Akishima, Tokyo, Japan) operating at 200 kV. The chemical valence states of transition metals was analyzed by X-ray photoelectron spectroscopy (XPS) acquired with a Kratos Axis Ultra spectrometer (Axis Ultra DLD, Kratos, Japan) using a monochromatic Al Kα source (1,486.6 eV). The amount of carbon was determined from PE 2400II elemental analyzer (Perkin Elmer, USA). The metal content (lithium, nickel, and titanium) of the as-prepared Li$_2$NiTiO$_4$ was analyzed using an inductively coupled plasma optical emission spectroscopy (ICP-OES) measurements (iCAP6300, Thermo, USA).

Electrochemical tests were performed with CR2016-type coin cells using Li foil as anode. The cathode consisted of 85 wt.% Li$_2$NiTiO$_4$/C, 5 wt.% Super P carbon black, and 10 wt.% polyvinylidene difluoride binder. An aluminum disk with $\Theta = 1.2$ cm was used as current collector in the cathode side, and the pure Li$_2$NiTiO$_4$ loading is 1.5 mg cm$^{-2}$. The electrolyte was 1 M LiPF$_6$ in the mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1, v/v). Galvanostatic charge-discharge measurements were carried out on a LAND CT2001A battery tester (Wuhan, China) in a potential range of 2.4 to 4.9 V at room temperature and 2.4 to 4.8 V at 50°C. The cyclic voltammogram (CV) was measured between 2.4 and 5.1 V using a CHI660D electrochemical workstation (Shanghai, China) with a scan rate of 0.1 mV s$^{-1}$. The specific capacity was calculated based on the mass of pure Li$_2$NiTiO$_4$ active material.

**Results and discussion**

Figure 1 shows the indexed XRD pattern of the as-prepared Li$_2$NiTiO$_4$ powders. Li$_2$NiTiO$_4$ can be assigned to the rock salt phase with $Fm\overline{3}m$ space group. The refined cell parameters of $a = 4.1436(5)$ Å and $V = 71.14$ Å$^3$ are in agreement with previously reported values for Li$_2$NiTiO$_4$ [10,11]. The diffraction peaks are quite sharp, indicating the good crystallinity of the material. The molten salt enables molecular level mixing of reacting species and thus leads to a rapid formation of well-crystallized Li$_2$NiTiO$_4$ at a moderate temperature. Furthermore, no any residual impunity phases are observed. ICP analysis indicates 2.10:1:0.99 for the atomic ratio of Li/Ni/Ti in the obtained cubic phase, which proves the efficacy of the molten salt method to yield the pure-phase product in a short reaction time.

The morphology of the as-prepared Li$_2$NiTiO$_4$ is shown in Figure 2a. The Li$_2$NiTiO$_4$ powder consists of spherical particles with an average size of ca. 50 nm. Because Ni$^{2+}$ ion may be reduced to metallic Ni by carbon at high temperature, it is difficult to employ polymer pyrolysis method to get carbon coated phase-pure Li$_2$NiTiO$_4$. In order to improve the poor electronic conductivity, the bare Li$_2$NiTiO$_4$ nanoparticles are carbon-coated by simple ball milling with conductive carbon. The carbon content in the Li$_2$NiTiO$_4$/C composite is 19.8 wt.%. The TEM image of Figure 2b demonstrates that the Li$_2$NiTiO$_4$ nanoparticles are in close contact with the dispersed carbon particles. Thus, the active material particles are interconnected by a carbon network, which is favorable for fast electron transfer and lithium extraction/insertion kinetics.

The valence variations of Ni element in the Li$_2$NiTiO$_4$ electrode during cycling are analyzed by the XPS spectra and fitted in Figure 3. The characteristic binding energy located at 854.6 eV with a satellite peak at 860.5 eV in the Ni 2p$_3/2$ XPS spectrum for uncharged Li$_2$NiTiO$_4$ electrode could be assigned to Ni$^{2+}$ species. The above observations are in agreement with the reported values in LiNi$_{0.5}$Mn$_{0.5}$O$_2$, LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ and LiNi$_{0.5}$Mn$_{1.5}$O$_4$ [12-14]. The Ni 2p$_3/2$ binding energy gives positive shift when the electrode is charged to 4.9 V, and the two peaks at 855.5 and 856.9 eV are corresponding to the binding energy of Ni$^{3+}$ and Ni$^{4+}$ [15], respectively. When discharged to 2.4 V, the Ni 2p$_3/2$ binding energy moves back to almost the original position. The best fit for the Ni 2p$_3/2$ spectrum consists of a major peak at 854.6 eV and a less prominent one at 855.5 eV. The above results indicate that Ni$^{2+}$ is oxidized to Ni$^{3+}$ and Ni$^{4+}$ during charging, and most
of the high valence Ni\(^{3+}/4^+\) is reduced to Ni\(^{2+}\) in the discharge process.

Figure 4 exhibits the CV curves of the Li\(_2\)NiTiO\(_4\)/C nanocomposite. For the first CV curve, a sharp oxidation peak at 4.15 V corresponds to the oxidation of Ni\(^{2+}\) to Ni\(^{3+}/4^+\). Another oxidation peak appears around 4.79 V and almost disappears in the second and third cycles, which might be attributed to the electrolyte decomposition and the irreversible structure transitions [8,9]. The wide reduction peak at 3.85 V is assigned to the conversion from Ni\(^{3+}/4^+\) to Ni\(^{2+}\). The second and third CV curves are similar, indicating a good electrochemical reversibility of the Li\(_2\)NiTiO\(_4\)/C electrode.

Figure 5a shows the galvanostatic charge-discharge curves of the Li\(_2\)NiTiO\(_4\)/C nanocomposite at 0.05 C rate (14.5 mA g\(^{-1}\)) under room temperature. The charge/discharge capacities in the first, second, and third cycles are 180/115 mAh g\(^{-1}\), 128/111 mAh g\(^{-1}\), and 117/109 mAh g\(^{-1}\), respectively, with corresponding coulombic efficiencies of 64%, 87%, and 94%. The Li\(_2\)NiTiO\(_4\)/C exhibits superior electrochemical reversibility after the first cycle, which is in accordance with the CV result. The dQ/dV vs. potential plot for the first charge-discharge curve is presented in the inset in Figure 5a. Two oxidation peaks located at 4.2 and 4.5 V in the charge process may be ascribed to the two-step oxidation reactions of Ni\(^{2+}/3^+\) and Ni\(^{3+}/4^+\) [10]. However, only one broad peak is observed at approximately 3.9 V belonging to Ni\(^{4+}/2^+\) in the discharge process, which may be resulted from strong hysteresis during the reduction of Ni\(^{4+}\) to Ni\(^{2+}\) via Ni\(^{3+}\) [16].

Figure 5b shows the charge-discharge curves of the Li\(_2\)NiTiO\(_4\)/C nanocomposite at 50°C. It delivers a high initial charge capacity of 203 mAh g\(^{-1}\) at 0.05 C rate, corresponding to 1.4 lithium extraction per formula unit. Also, the discharge capacity of 138 mAh g\(^{-1}\) is much higher than that tested at room temperature, demonstrating its enhanced electrode kinetics at high temperature. Figure 5c compares the cycling performances of the Li\(_2\)NiTiO\(_4\)/C nanocomposite at room temperature and 50°C. Li\(_2\)NiTiO\(_4\)/C exhibits a stable cycle life after several cycles, and its capacity retentions after 50 cycles are 86% at room temperature and 83% at 50°C. At the end of 80 cycles,
Li$_2$NiTiO$_4$/C retains 82% of its initial capacity with typical coulombic efficiency of 95% at room temperature, displaying a high electrochemical reversibility and structural stability during cycling. Figure 5d presents the rate capability of the Li$_2$NiTiO$_4$/C nanocomposite at room temperature. The charge rate remains constant at 0.1 C to insure identical initial conditions for each discharge. The Li$_2$NiTiO$_4$/C retains about 63% of its capacity from 0.05 to 1 C rate. The nanoparticles may reduce Li$^+$ diffusion length and improve the ionic conductivity. Moreover, the highly conductive carbon coated on the surface of Li$_2$NiTiO$_4$ nanoparticles facilitates the rapid electrical conduction and electrode reactions, thus gives rise to capacity delivery and high rate performance.

In order to investigate the phase change of Li$_2$NiTiO$_4$ during the charge-discharge process, the ex situ XRD of the Li$_2$NiTiO$_4$/C electrode is employed as shown in Figure 6. XRD peaks corresponding to the Li$_2$NiTiO$_4$ phase are observed from the pristine cathode sheet. The positions of diffraction peaks are hardly changed during cycling, which indicates that the extraction/insertion of lithium cannot change the framework of Li$_2$NiTiO$_4$. However, the $I_{220}/I_{200}$ ratio is 0.43 before charging, 0.50 after charging to 4.9 V, 0.48 after discharging to 2.4 V, and 0.47 after 2 cycles. The $I_{220}/I_{200}$ ratios at different charge-discharge states are very close after the first charge, indicating an incompletely reversible structural rearrangement upon initial lithium extraction. Trócoli et al. [10] suggest that lithium ions move from 4a octahedral sites to 8c tetrahedral sites, resulting in an irreversible loss of crystallinity in the material during the first charge process. The above results together with the CV data suggest that the crystal structure can be mainly retained upon the process of lithium extraction/insertion.
Conclusions
Nanostructured Li$_2$NiTiO$_4$/C composite has been successfully prepared by a rapid molten salt method followed by ball milling. Cyclic voltammetry together with the ex situ XRD analysis indicate that Li$_2$NiTiO$_4$ exhibits reversible extraction/insertion of lithium and retains the cubic structure during cycling. This Li$_2$NiTiO$_4$/C nanocomposite exhibits relatively high discharge capacities, superior capacity retentions, and rate performances at room temperature and 50°C. The improved electrochemical performances can be ascribed to the nanoscale particle size, homogeneous carbon coating, and phase retention upon cycling.

Competing interests
The authors declare that they have no competing interests.

Authors’ contributions
YMW carried out the experiment and prepared the manuscript. YJW gave the advice and guided the experiment. FW conceived the study and revised the manuscript. All authors read and approved the final manuscript.

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References
1. Świętoławski M, Molenda M, Furtorzi K, Dziembaj R: Nanocomposite C/Li$_3$MnSiO$_4$ cathode material for lithium ion batteries. J Power Sources 2013, 244:510–514.
2. Li Y, Cheng X, Zhang Y: Achieving high capacity by vanadium substitution into Li$_x$FeSiO$_4$. J Electrochem Soc 2012, 159:A469–A474.
3. Aono S, Tsurudo T, Urita K, Moriguchi I: Direct synthesis of novel homogeneous nanocomposites of Li$_3$MnSiO$_4$ and carbon as a potential Li-ion battery cathode material. Chem Commun 2013, 49:2939–2941.
4. klar L, Gopalakrishnan A: Li$_2$MnTiO$_4$ (M = Mn, Fe, Co, Ni): new cathode-disordered rocksalt oxides exhibiting oxidative deintercalation of lithium. Synthesis of an ordered Li$_2$NiTiO$_4$. J Solid State Chem 2003, 172:171–177.
5. Kuezma M, Dominko R, Hanzel D, Kodre A, Arčon I, Meden A, Gabersček M: Detailed in situ investigation of the electrochemical processes in Li$_x$FeTiO$_4$ cathodes. J Electrochem Soc 2009, 156:A809–A816.
6. Dominko R, Vidal-Abraca Garrido C, Bele M, Kuezma M, Arčon I, Gabersček M: Electrochemical characteristics of Li$_2$V$_{1-x}$Ti$_x$O$_4$ rock salt phase in Li-ion batteries. J Power Sources 2011, 196:6856–6862.
7. Kuzma M, Dominko R, Meden A, Makovec D, Bele M, Jarnnik M, Gabersček M: Electrochemical activity of Li$_x$FeTiO$_4$ and Li$_x$MnTiO$_4$ as potential active materials for Li-ion batteries: a comparison with Li$_x$NiTiO$_4$. J Power Sources 2009, 189:81–88.
8. Yang M, Zhao X, Bian Y, Ma L, Ding Y, Shen X: Cation disordered rock salt phase Li$_x$CoTiO$_4$ as a potential cathode material for Li-ion batteries. J Mater Chem 2012, 22:6200–6205.
9. Prabaharan SRS, Michael MS, Ikuta H, Uchimoto Y, Wakkara M: Li$_2$NiTiO$_4$–a new positive electrode for lithium batteries: soft-chemistry synthesis and electrochemical characterization. Solid State Ion 2004, 172:39–45.
10. Tróccoli R, Cruz-Yusta M, Morales I, Santos-Peña J: On the limited electroactivity of Li$_x$NiTiO$_4$ nanoparticles in lithium batteries. Electrochem Acta 2013, 100:93–100.
11. Kawano Y, Kitajou A, Okada S: Synthesis and cathode properties of a cubic rocksalt-type Si-doped Li$_2$NiTiO$_4$ for lithium-ion batteries. J Power Sources 2013, 242:768–774.
12. Shaju KM, Subba Rao GV, Chowdari BV R: X-ray photoelectron spectroscopy and electrochemical behaviour of a 4 V cathode, Li(Ni$_{1/3}$Mn$_{1/3}$)O$_2$. Electrochem Acta 2003, 49:1505–1514.
13. Shaju KM, Subba Rao GV, Chowdari BV R: Performance of layered Li(Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$)O$_2$ as cathode for Li-ion batteries. Electrochem Acta 2002, 48:145–151.
14. Mo M, Hui KS, Hong X, Guo J, Ye C, Li A, Hu N, Huang Z, Jiang J, Liang J, Chen H: Improved cycling and rate performance of Sm-doped LiNi$_{1/3}$Mn$_{1/3}$O$_4$ cathode materials for 5 V lithium ion batteries. Appl Surf Sci 2014, 290:412–418.
15. Marco JF, Gancedo JR, Gracia M, Gautier JL, Rios EL, Palmer HM, Greaves C, Berry FJ: Cation distribution and magnetic structure of the ferromagnetic spinel NiCo$_2$O$_4$. J Mater Chem 2001, 11:3027–3033.
16. Shi SJ, Tu JP, Tang Y, Zhang YQ, Liu XY, Wang XL, Gu CD: Enhanced electrochemical performance of LiF-modified LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ cathode materials for Li-ion batteries. J Power Sources 2013, 225:338–346.

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