

Lithiation–delithiation properties of new compound $\text{LiNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ with cubic structure

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Abstract

A new compound Li–Ni–Ti oxide-based material ($\text{LiNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$) with cubic structure was prepared by solid state reaction at 900 °C. Powder X-ray diffraction (XRD) was used to determine the phase purity and structure of the material. The Bragg peaks of $\text{LiNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ can be indexed based on a cubic unit with dimension $a=4.142$ Å, belonging to space group $Fd\bar{3}m$ (SG number 225). X-ray photoelectron spectroscopy (XPS) study showed that the chemical valences of Ni and Ti were +2 and +4, respectively. The electrochemical testing indicated that the Li^+ ions in $\text{LiNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ cannot be extracted until 4.8 V. However, two initial Li ions per $\text{LiNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ can be intercalated into $\text{LiNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ and one Li^+ ion can be extracted reversibly.

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1. Introduction

Lithium ion batteries have been well accepted as power sources ranging from portable electronic devices to zero-emission vehicles (ZEV) due to their longer cycle life and higher energy density than other rechargeable battery systems. Many compounds have been studied as cathode materials of the lithium ion batteries, such as LiCoO_2 , LiNiO_2 , LiMn_2O_4 , LiFePO_4 , LiMnO_2 and their derivatives. The layered compounds LiMO_2 ($M=\text{Co}, \text{Ni}, \text{Cr}, \text{V}$) are isostructural with $\alpha\text{-NaFeO}_2$, crystallizing in the rhombohedral space group $R\bar{3}m$ [1–4]. Recently, Ohzuku and Makimura [5] and Dahn and co-workers [6] reported a series of materials based on Ni–Mn oxides with the hexagonal structure, the same as that of LiNiO_2 . In order to improve the electrochemical performance and thermal stability, Gao et al. [7] substituted Ti and Mg for part of Ni to prepare $\text{LiNi}_{0.75}\text{Ti}_{0.125}\text{Mg}_{0.125}\text{O}_2$ with hexagonal structure. Kim and Amine [8] prepared layer-structured $\text{LiNi}_{1-x}\text{Ti}_x\text{O}_2$ ($0.025 \leq x \leq 0.2$) containing Ti^{4+} ions. They believed that this helps to preserve the hexagonal structural integrity of the

materials by preventing the migration of impurity Ni^{2+} into the lithium sites. All these materials exhibited layered structures belonging to the hexagonal system. In this article, we will report a new interesting compound with cubic structure, the same as that of LiTiO_2 , in which half of the Ti is replaced with Ni.

2. Experimental

Nanoscaled TiO_2 , $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{LiOH} \cdot \text{H}_2\text{O}$ were used as the starting materials. First, nano- TiO_2 was added to a 2 M $\text{Ni}(\text{NO}_3)_2$ solution and the molar ratio of Ti and Ni was 1:1. Then the 2 M NaOH solution was slowly dripped into the above solution and stirred. This led to the deposition of $\text{Ni}(\text{OH})_2$ on Nano- TiO_2 . The precipitate was filtered out and washed twice with additional distilled water to remove the residual Na^+ ions (in the form of NaOH and NaNO_3). The precipitate was dried in air at 120 °C overnight. The dried precipitate was mixed with stoichiometric amount of $\text{LiOH} \cdot \text{H}_2\text{O}$ and ball-milled. The mixture was then heated in air at 900 °C for 15 h.

Powder X-ray diffraction (XRD) was performed on Rigaku D/MAX-RC X-ray diffractometer with $\text{Cu K}\alpha$

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monochromatic radiation in order to identify the crystalline phase of the samples. XRD data were collected in the 2θ range from 35° to 135° with a step size of 0.02° and 1 s/step. X-ray photoelectron spectroscopic (XPS) study was carried out on Kratos XSAM 800 XPS spectrometer with Mg K α radiation. The binding energy was calibrated with respect to the contaminant C 1s in the vacuum chamber of the XPS instrument (285.0 eV). The contents of Ti, Ni and Li in the powder sample were determined by inductively coupled plasma (ICP).

The active material (85 wt%), carbon black (10 wt%) and binder (5 wt%, polyvinylidene fluoride (PVdF) dissolved in *N*-methyl-2-pyrrolidone, NMP) were mixed to form a slurry. The slurry was cast on a copper foil. Electrodes of 1 cm² were cut from the electrode sheet and dried in a vacuum oven at 120 °C for 24 h. One mole LiPF₆ dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1, v/v) was used as the electrolyte. Coin cells were assembled with Li foil as the anode and Celgard 2300 polypropylene and polyethylene as the separator in an Ar-filled glove box (MBraun). Charge–discharge performance of the material was characterized galvanostatically on Land 2000T (Wuhan, China) battery tester between 0.0 and 2.5 V versus Li/Li⁺.

3. Results and discussion

The TG/DSC traces of the reaction processes for preparing LiNi_{0.5}Ti_{0.5}O₂ are shown in Fig. 1. The reaction process is clearly divided into two temperature regions. The decomposition of Ni(OH)₂ occurs between 250 and 275 °C with a weight loss of about 7%. The compound LiNi_{0.5}Ti_{0.5}O₂ comes into being at 725 °C with an endothermic reaction and a weight loss of about 18%. After that, no further reaction takes place and the weight of the sample keeps unchanged although the temperature is further increased to 800 °C.

The chemical analysis results by inductively coupled plasma (ICP) were shown in Table 1. The actual Ni content in the compound is slightly lower than the calculated value;

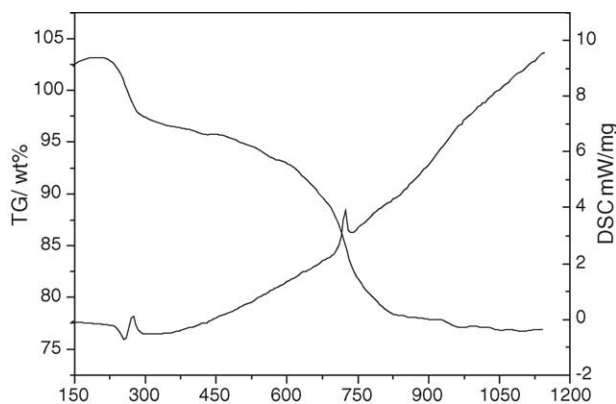


Fig. 1. TG/DSC traces of the LiNi_{0.5}Ti_{0.5}O₂ preparation process.

Table 1
Comparison of the experimental (measured) and the theoretical (calculated) contents of the metallic elements in the new compound (wt%)

	Li	Ni	Ti
Measured	7.60	29.5	25.5
Calculated	7.52	31.82	25.96

the lithium content is slightly higher than the calculated value, and the Ti content basically consists with the calculated result. This indicates that a target composition of stoichiometric LiNi_{0.5}Ti_{0.5}O₂ is obtained. Fig. 2 shows the XRD pattern of thus prepared LiNi_{0.5}Ti_{0.5}O₂. There exist no diffraction peaks before $2\theta = 35^\circ$ and all the diffraction lines can be indexed assuming that LiNi_{0.5}Ti_{0.5}O₂ is cubic in structure, indicating that the obtained sample is a single phase of LiNi_{0.5}Ti_{0.5}O₂. Its structure is the same as that of LiTiO₂, belonging to space group *Fd3m* (SG number 225) and half of the Ti in LiTiO₂ is replaced with Ni. The lattice constant of LiNi_{0.5}Ti_{0.5}O₂ is determined to be $a = 4.142 \text{ \AA}$, slightly larger than that of the LiTiO₂ ($a = 4.14 \text{ \AA}$) [9] in cubic setting by a least square method using nine diffraction lines. The Li, Ni and Ti atoms are located at the 4*b* (0.5, 0.5, 0.5) site, while the O atoms are located at the 4*a* (0, 0, 0) sites. Although LiTiO₂ is not stable in air, LiNi_{0.5}Ti_{0.5}O₂ is very stable in air.

XPS was used to determine the oxidation states of the elements Ni and Ti in LiNi_{0.5}Ti_{0.5}O₂ (Fig. 3). Ref. [10] points out that the binding energies of Ti in TiO₂ and TiO are 458.7 and 455.1 eV, respectively. As seen in Fig. 3a, the binding energy of Ti 2p in LiNi_{0.5}Ti_{0.5}O₂ is 457.4 eV, very close to that of Ti in TiO₂. Therefore, the oxidation state of Ti is believed to be +4 in LiNi_{0.5}Ti_{0.5}O₂, the same as that of Mn in LiNi_{0.5}Mn_{0.5}O₂. Ref. [10] also shows that the binding energies of Ni in Ni₂O₃ and NiO are 857.3 and 854.3 eV, respectively. As seen in Fig. 3b, the binding energy of Ni 2p in LiNi_{0.5}Ti_{0.5}O₂ is 854.6 eV, very close to that of Ni in NiO.

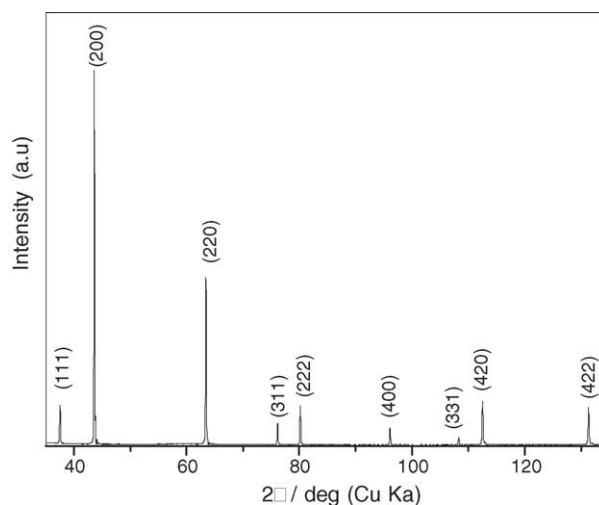


Fig. 2. Powder XRD pattern of sample LiNi_{0.5}Ti_{0.5}O₂ (*Fd3m*).

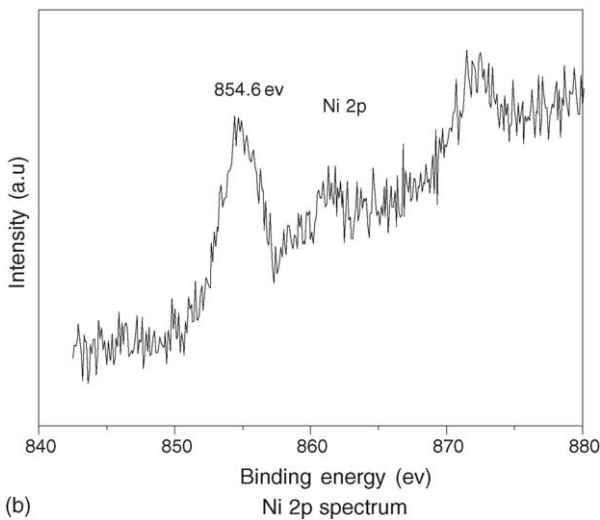
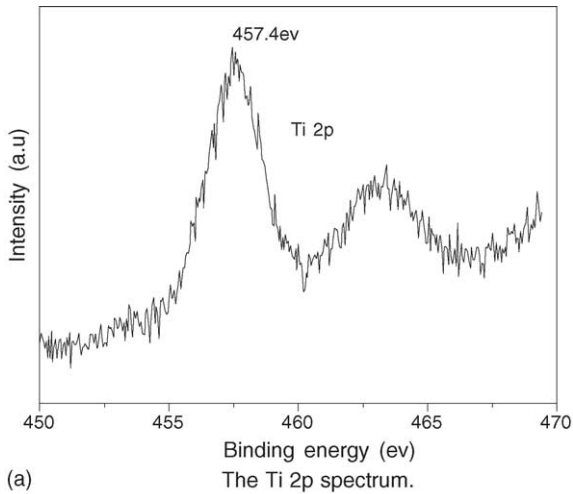


Fig. 3. Ti 2p and Ni 2p spectra of the sample $\text{LiNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$: (a) Ti 2p spectra and (b) Ni 2p spectra.

So we believe that the oxidation state of Ni in $\text{LiNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ is +2, the same as that of Ni in $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$.

Fig. 4 shows the IR spectra of the $\text{LiNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ sample. There exists a broad and strong peak at 462 cm^{-1} is attributed to the M–O (M=Li, Ni and Ti) vibration. No other peaks appear at higher frequencies.

The paramagnetic behavior at low temperature is responsible for the localization of electrons around the oxygen vacancies. The temperature dependence of magnetic susceptibility for $\text{LiNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ (Fig. 5) indicates that $\text{LiNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ maintains its Pauli-paramagnetic behavior above 50 K. Below 50 K, its magnetic susceptibilities increase with rising temperature.

The electrochemical testing results indicate that Li^+ ions in $\text{LiNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ cannot be extracted even when the cell is charged to 4.8 V. Fig. 6 shows that two Li^+ ions can be intercalated into one unit of $\text{LiNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ but only one of them can be extracted reversibly. There exists a flat discharge plateau around 0.15 V in the initial discharge. However, no

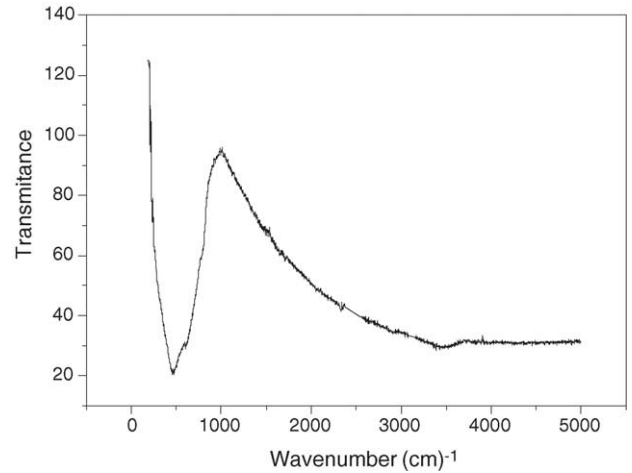


Fig. 4. IR spectrum of the $\text{LiNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ sample.

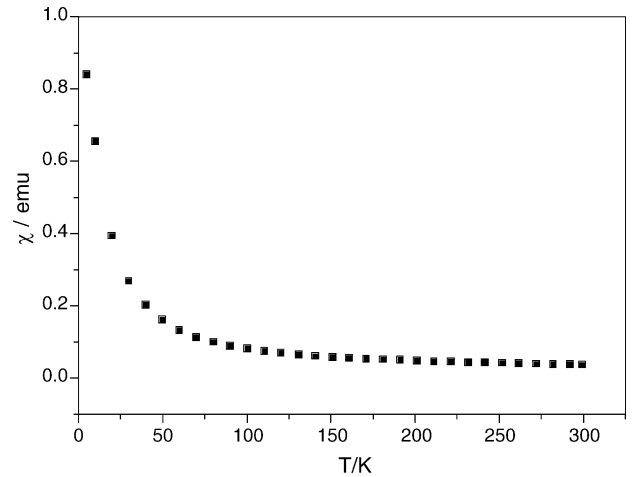


Fig. 5. Temperature dependence of magnetic susceptibilities of the $\text{LiNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ sample.

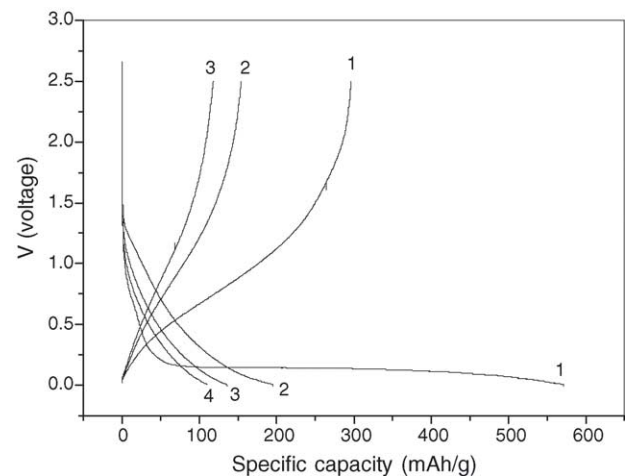


Fig. 6. The charge–discharge curves of $\text{LiNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ in the first few cycles.

corresponding flat plateau is observed in the charge process. The discharge capacity reaches 571 mA h g^{-1} and the charge capacity is 296 mA h g^{-1} , so the first charge–discharge efficiency is more than 50%.

In the subsequent cycles, the coulombic efficiency rises to ca. 95% but the discharge capacity keeps dropping. In addition, the long discharge plateau in the initial cycle disappears.

4. Conclusions

The structure of $\text{LiNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ prepared by solid-state reaction is found to be cubic, completely different from other layered lithium insertion materials such as LiCoO_2 , LiNiO_2 and $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$. The oxidation states of Ni and Ti in $\text{LiNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ are determined to be +2 and +4, respectively. Two Li^+ ions can be intercalated into one unit of $\text{LiNi}_{0.5}\text{Ti}_{0.5}\text{O}_2$ and one of Li^+ ions can be reversibly extracted in the first cycle. Studies of other properties of the new compound are now in progress in this laboratory.

Acknowledgement

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