Structural, electrochemical and thermal properties of LiNi_{0.8-y}Ti_yCo_{0.2}O_2 as cathode materials for lithium ion battery

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Abstract

Multiple substitution compounds with the formula LiNi_{1−x}Ti_{x}Co_{y}O_{2} (0 ≤ y ≤ 0.1) were synthesized by sol–gel method using citric acid as a chelating agent. The effects of titanium substitution on the structural, electrochemical and thermal properties of the cathode materials are investigated. A solid solution phase (R3m) is observed in the range of 0 ≤ y ≤ 0.1 for the titanium-doped materials. Rietveld refinement of X-ray diffraction (XRD) patterns indicates that titanium substitution changes the materials’ structure with different cationic distribution. An increase of the NiO amount in the Sr Li site is found with the addition of titanium amount. An improved cycling performance is observed for titanium-doped cathode materials, which is interpreted to a significant suppression of phase transitions and lattice changes during cycling. The thermal stability of titanium-doped materials is also improved, which can be attributed to its lower oxidation ability and enhanced structural stability at delithiated state.

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Keywords: LiNi_{0.8-y}Ti_yCo_{0.2}O_2; Titanium substitution; Cycling performance; Thermal stability; Lithium ion batteries

1. Introduction

Layered structure transition metal oxides, such as LiCoO_2, LiNiO_2 and LiMnO_2, have been investigated extensively as the cathode materials for lithium ion batteries [1–10]. The goal of most research is to develop and optimize different cathode materials for replacing the high cost and toxic LiCoO_2 cathode material, which is still the main cathode material for the most of commercial lithium ion batteries. Among these oxides, LiNiO_2 with lower cost and higher energy density has aroused significant interests in recent years. However, it has been assumed that the individual compound LiNiO_2 is not competent for the candidate material because of its shortcomings [3–9]. Doped LiNiO_2 compounds, such as LiNi_{1−x}Co_{x}O_2, are then considered new candidate materials to replace LiCoO_2. Many studies [11–19] on the LiNi_{1−x}Co_{x}O_2 compounds have provided promising results that the Co substitution for Ni stabilizes the two-dimensional layered structure and decreases the initial capacity loss with the improvement of cycle performance. Nevertheless, these studies have also demonstrated that LiNi_{1−x}Co_{x}O_2 materials are yet not able to improve the thermal stability at charged state satisfactorily, which is a key issue of safety consideration for lithium ion batteries. It has been suggested and confirmed that the addition with another doping metal element (Al, Mn, Mg, Fe, Y, Sr, etc.) may further improve cycle performance and thermal stability of the LiNi_{1−x}Co_{x}O_2 materials [20–26]. Tetravalent titanium (Ti^{4+}) was also applied to substitute Ni for improving the properties of LiNiO_2. The LiNi_{1−x}Ti_{x}O_2 [27,28] and LiNi_{1−x}Ti_{x/2}Mg_{x/2}O_2 [29] materials have been reported with good electrochemical properties and thermal stability. More recently, LiNi_{0.5}Co_{0.5}Ti_{y}O_2 [30], LiNi_{0.8}Co_{0.2−2y}Ti_{y}Mg_{y}O_2 [31] and LiNi_{y}Co_{2−2y}Ti_{y}O_2 [32] were also reported with improved cycling performance and enhanced thermal stability. Hence, it seems that tetravalent titanium has a good effect on the properties of layered structure LiNiO_2-based materials.

In this work, tetravalent titanium was introduced into LiNi_{0.8−y}Ti_{y}Co_{0.2}O_2 compound as a substitute for Ni through a sol–gel routine, which allows a better mixing of the reactants...
at atomic level and produces highly homogeneous materials. The effects of titanium substitution on the structural, electrochemical and thermal properties of LiNi$_{0.8-y}$Ti$_{y}$Co$_{0.2}$O$_{2}$ compounds were studied in detail.

2. Experimental

LiNi$_{0.8-y}$Ti$_{y}$Co$_{0.2}$O$_{2}$ ($y = 0, 0.025, 0.050, 0.075, 0.1$) compounds were synthesized by sol–gel method using citric acid as a chelating agent as previously reported [33]. Stoichiometric amounts of A.R. purity Ni(NO$_3$)$_2$·6H$_2$O, Co(NO$_3$)$_2$·6H$_2$O, (C$_4$H$_9$O)$_4$Ti and LiOH·H$_2$O with excess 10% lithium were dissolved in citric acid solution (the acid-to-metal ions ratio is 1:1), which previously dissolved in distilled water, to form a transparent dark-green solution. The mixture was stirred at 80°C for 12 h to form a dark-green gel. The gel was heated at 120°C for 24 h to form a dry-gel, which was put into Muff oven for precalcination at 500°C for 6 h. Then, the dark-brownish decomposed powders were sintered in a horizontal quartz tube oven at 750°C for 36 h with a fixed oxygen flux (500 sccm/min). The reaction products were ground and filtrated lastly.

The samples were characterized by powder X-ray diffraction (XRD), using a Rigaku Rotaflex Dmax-C diffractometer with graphite monochromator and Cu Kα radiation operated at 40 kV and 30 mA. Data were collected in the range 10–90° using a step size of 0.02° and a counting time of 2 s per step. Rietveld refinement structural analysis was operated using general structure analysis system (GSAS) [34]. XRD experiments were also carried out to determine the structural changes of delithiated cathode materials. In order to determine the oxidation state of elements in LiNi$_{0.8-y}$Ti$_{y}$Co$_{0.2}$O$_{2}$, the powder samples were pressed into slices, and X-ray photoelectron spectroscopy (XPS) analysis was performed using a Quantum 2000 ESCA spectrometer (Physical Electronics, USA) with monochromatic Al Kα 1486.6-eV radiation operated at 23.2 W in a vacuum of <10$^{-8}$ Torr. The binding energy was calibrated with reference to the C 1s level of hydrocarbon (284.6 eV).

The electrochemical properties of the synthesized samples were assessed using CR2025 coin cells. The cathodes were prepared by mixing 85% of the active material with 10% carbon black and 5% PVDF. The mixture was made into a slurry using NMP as solvent by ball-milling method. The electrodes were formed by coating the slurry onto Al foils and pressing at 16 MPa after drying 1 h at 120°C. The cells were assembled with the cathode as prepared, lithium metal as anode, and Celgard 2300 film as separator. The electrolytes were 1 M LiPF$_6$ dissolved in EC + DMC (1:1 volume ratio). Cell assembling was carried out in an argon-filled glove box (Braun Lab Master 100, Germany), where water and oxygen concentration was kept less than 4 ppm. Charge and discharge experiments were performed at various conditions (current rate and voltage range) using a home-made LAND CT2001A battery tester.

Thermal stability of the cathode materials at charged state was examined by differential scanning calorimetry (NET-ZSCH DSC 204, Germany). The cathode materials were electrochemically delithiated by galvanostatically charging coin cells to 4.3 V with a 0.1 C rate current, followed by potentiostatically charging at constant voltage 4.3 V for 40 h. Then the cells were disassembled in an argon-filled glove box. The cathode powders with residual electrolyte were removed from the Al substrates used doctor blade, and 5–10 mg samples were sealed in Al crucibles at once. The DSC experiments were carried out at 20°C/min rate in the range 100–500°C.

3. Results and discussion

3.1. Crystal structure and cationic distribution

Fig. 1 shows the XRD patterns of the LiNi$_{0.8-y}$Ti$_{y}$Co$_{0.2}$O$_{2}$ powder samples. All of the patterns can be indexed to a single phase of α-NiFeO$_2$ type with space group $R-3m$. With the increase of titanium, FWHM of the peaks broadens and the peak intensity decreases, which indicates the crystalization is weakened for the titanium-doped materials. It is found that the $I(003)/I(104)$ peak intensity ratio shows a decreasing tendency with increase of titanium amount from 1.64 for $y = 0$ to 1.30 for $y = 0.1$. The degree of either $I(003)/I(104)$ or $I(006)/I(102)$ peak splitting changes from clear to indistinct with increase of $y$ value. Since the two characters of XRD patterns, i.e. $I(003)/I(104)$ ratio and $I(006)/I(102)$ peak splitting, were considered the evidence for the degree of ordering layered structure as well as the amount of transition metal in the inter-slab space [5,7], it implies that the titanium substitution for nickel in LiNi$_{0.8-y}$Ti$_{y}$Co$_{0.2}$O$_{2}$ compounds has affected the cationic distribution and the crystal structure. In order to
determine the cationic distribution and thereby the crystal structure more accurately, XPS was used to determine the oxidation state of elements in LiNi$_{0.8-y}$Ti$_y$Co$_{0.2}$O$_2$ firstly, and Rietveld refinement analysis of these XRD patterns followed to be performed.

The C 1s, O 1s, Li 1s, Ni 2p, Co 2p and Ti 2p XPS spectra for LiNi$_{0.8-y}$Ti$_y$Co$_{0.2}$O$_2$ materials are shown in Fig. 2. Similar to the XPS results of previous investigations [35,36], a little of Li$_2$CO$_3$ on the surface of LiNi$_{0.8}$Co$_{0.2}$O$_2$ is also observed according to the calculation of relative intensity in this case. For LiNi$_{0.8}$Co$_{0.2}$O$_2$ powder, the C 1s spectrum showed peaks at 284.6 and 289.4 eV, which were attributed to hydrocarbon contaminants in the chamber and CO$_3^{2-}$ presented on the powder surface, respectively. The Li 1s peak centered at ~55 eV and the O 2p peak centered at ~531 eV were also attributed to Li$^+$ and O$^{2-}$ species of LiNi$_{0.8}$Co$_{0.2}$O$_2$ and Li$_2$CO$_3$, respectively. The peaks of the C 1s, O 1s and Li 1s spectra for the titanium-doped materials almost have not insensitive changes on the binding energy, compared to pristine LiNi$_{0.8}$Co$_{0.2}$O$_2$ material. However, the Ni 2p and Co 2p spectra have distinctive changes after titanium substitution. For LiNi$_{0.8}$Co$_{0.2}$O$_2$, the Ni 2p spectrum shows the main peak (2p$_{3/2}$) at 855.6 eV and the satellite peak at 861.0 eV, which agree with the energy characteristic of Ni valence state in Ni$_2$O$_3$ (855.8 and 861.4 eV) [37]. Although it is well known that there may be Ni$^{2+}$ at the interstitial Li site in layered structure LiNiO$_2$, the Ni 2p spectrum could not provide the distinct characteristic of divalent NiO (854.5 and 856.3 eV) [37]. It suggests that the surface Ni of LiNi$_{0.8}$Co$_{0.2}$O$_2$ is trivalent, though the presence of Ni$^{2+}$ cannot be excluded. But, after titanium substitution, the Ni 2p spectrum shows the characteristic of divalent NiO more and more distinctive with the increase of titanium amount. It indicates that there are both Ni$^{2+}$ and Ni$^{3+}$ in the titanium-doped materials. A same change occurs at the Co 2p spectrum. The Co 2p spectrum of LiNi$_{0.8}$Co$_{0.2}$O$_2$ shows the main peak (2p$_{3/2}$) at 780.0 eV and the satellite peak at 795.1 eV without the characteristic shake-up structure satellites of Co$^{2+}$ [38]. It indicates that the Co in LiNi$_{0.8}$Co$_{0.2}$O$_2$ is trivalent. For titanium-doped materials, the Co 2p spectra show discriminable satellites near the main peak with shake-up structure, and the main peak broadens considerably towards lower binding energy side. It shows that both Co$^{3+}$ and Co$^{2+}$ present in the titanium-doped materials. Additionally, the Ti 2p spectra of the titanium-doped materials show the main peaks (2p$_{3/2}$) at 457.8 eV, which is the characteristic of Ti$^{4+}$ [39]. The perceptible Ni$^{2+}$ and Co$^{2+}$ of titanium-doped materials could be attributed to the charge compensation for Ti$^{4+}$. It is worthy to note that XPS may...
reveal mainly information of compositions on the surface of materials. The exact oxidation state in bulk materials need be confirmed by X-ray absorption spectroscopy. But based on the changes of surface cationic valence with the increase of Ti amount in LiNi$_{1-x}$Ti$_x$Co$_2$O$_4$, we may propose that there are five transition metal ions—Ni$^{2+}$, Ni$^{3+}$, Co$^{3+}$, Co$^{4+}$ and Ti$^{4+}$—presented in the titanium-doped materials.

According to the oxidation state and ionic radius, a model of cationic distribution for LiNi$_{1-x}$Ti$_x$Co$_2$O$_4$ materials can be deduced. For ideal $R$-3m LiNiO$_2$ crystal, atomic coordinates were regulated as Li at the $3a$ site (0, 0, 0), Ni at the $3b$ site (0, 0, 0.5) and O at the $6c$ site (0, 0, 0.25) [40]. In practice, due to easy formation of non-stoichiometric Li$_{1-x}$Ni$_x$O$_2$ material, it was assumed that a little of Ni would go to the 3$a$ site. $

$\[
\begin{align*}
\text{Sample} & \quad \text{a (Å)} \quad \text{c (Å)} \quad \text{c/a} \quad 2\theta_0 \quad \rho_{\text{obs}} \quad \rho_{\text{calc}} \quad \text{Li-O (Å)} \quad \text{M-O (Å)} \quad \text{R}_{wp} \quad \text{R}_{F} \quad \chi^2
\end{align*}
\]

$^a$ $\rho_{\text{ob}}$ is the occupancy of transition metal ions at the 3$a$ Li site.

$^b$ $R_{wp} = \sum (F_{\text{obs}} - F_{\text{calc}})/\sum F_{\text{obs}}$.

$^c$ $R_{F} = \sum |F_{\text{obs}} - F_{\text{calc}}|/\sum F_{\text{obs}}$.

$^d$ $\chi^2 = (R_{wp}/R_{F})^2$.

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>c/a</th>
<th>2\theta_0</th>
<th>2\theta_0 (°)</th>
<th>ρ_{\text{obs}} (%)</th>
<th>ρ_{\text{calc}} (%)</th>
<th>Li-O (Å)</th>
<th>M-O (Å)</th>
<th>R_{wp} (%)</th>
<th>R_{F} (%)</th>
<th>χ^2</th>
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Fig. 3. The experimental, calculated and difference patterns of XRD for LiNi$_{0.75}$Ti$_0.25$Co$_2$O$_4$ material. The small ‘*’ signs indicate the observed pattern, and the solid line indicates the calculated pattern. The difference curve is shown at the bottom of the plot. The stick marks show the Bragg reflections.

The Rietveld refinement results are shown in Table 1. It is clear that the lattice parameters $a$ and $c$ increase with the increase of $y$ values. But the $c/a$ ratio decreases with the increasing $y$ values from 4.953 for $y = 0$ to 4.944 for $y = 0.1$, which indicates that a disordered phase with more lithium deficiency will be formed with the increase of the titanium amount. The data of the amount of transition metal (Ni and/or Co) at the 3$a$ Li site (named $\rho_{\text{a}}$ in this paper) supported this conclusion. With the increasing $y$ values, $\rho_{\text{a}}$ increases from 0.009 for $y = 0$ to 0.037 for $y = 0.1$. This
result is in accordance with the conclusion of Croguenec et al. [42] on the structure studies of LiNi$_1$$_y$Ti$_{y}$O$_2$, and other than the opinion of Kim et al. [27,28], who assumed that titanium substitution prevents the migration of Ni$^{3+}$ into the 3a Li site of LiNi$_1$$_y$Ti$_{y}$O$_2$ materials. The data of interatomic distances also demonstrated the supposition of cationic distribution. The intra-slab M–O distance increases with the titanium amount, which could attribute to the larger ionic radius of Ni$^{3+}$ and Ti$^{4+}$ than that of Ni$^{2+}$ and Co$^{3+}$. While the interslab Li–O distance decreases with the titanium amount due to the less ionic radius of Ni$^{3+}$ and Co$^{3+}$ than that of Li$^+$. Thus, titanium substitution affects the cationic distributions with Ni$^{2+}$ and/or Co$^{3+}$ at the 3a site and Ni$^{3+}$, Co$^{2+}$, Ti$^{4+}$ at the 3b site, and thereby causes the structural modification of LiNi$_{1}$$_x$Ti$_y$Co$_{1-x}$O$_2$ materials, which will result in corresponding changes in electrochemical and thermal properties.

3.2. Electrochemical performance

The initial charge–discharge curves for LiNi$_{0.8}$Ti$_{0.2}$O$_2$ materials with a current rate of C/5 in a voltage range of 2.7–4.5 V, are shown in Fig. 4. And a part of charge–discharge data for LiNi$_{1}$$_y$Ti$_{y}$Co$_{0.5}$O$_2$ materials are provided in Table 2. It can be seen that a decrease of charge specific capacity with an increase of doped-titanium amount, from 249 mAh/g for $y = 0$ to 230 mAh/g for $y = 0.1$. And discharge-specific capacity decreases from 206 mAh/g for $y = 0$ to 188 mAh/g for $y = 0.1$, with a large capacity loss of about 16–18%. A slight raise of charge voltage plateau with the increasing titanium amount is also observed in Fig. 4. The decrease of specific capacity could be attributed to the increase of inactive titanium as well as the raise of voltage plateau, because less lithium will be de-intercalated with the increase of doped titanium at the same terminated-charge-voltage. A large capacity loss at the first charge–discharge cycle was also occurred in LiNiO$_2$ and LiNi$_{1}$$_y$Co$_{0.5}$O$_2$ cathodes. The extra nickel at the 3a Li site was considered as a primary cause for the initial capacity loss, because the irreversible oxidation of the extra Ni$^{3+}$ during the first charge induced a local collapse of the structure and hindered lithium re-intercalation [8]. However, the initial capacity losses of LiNi$_{0.8}$Ti$_{0.2}$O$_2$ cathodes in this work do not increase with the increase of the extra transition metal at the 3a Li site ($\Delta$$q_0$) as the results of structural analysis by Rietveld refinement. It should be attributed to the improved structure stability during cycling and lower oxidation ability at high delithiated state as revealed at the later section. The decrease of the capacity losses originated from lattice changes and interface reactions compensate the increase of the capacity losses caused by the extra transition metal at the 3a Li site, so that the initial capacity losses of LiNi$_{1}$$_x$Ti$_y$Co$_{0.5}$O$_2$ cathodes have not obvious changes compared to that of LiNi$_{0.8}$Co$_{0.2}$O$_2$ cathode.

The cycle life curves for LiNi$_{1}$$_x$Ti$_y$Co$_{0.5}$O$_2$ cathode materials were recorded at 0.2 C current rate for one to five cycles, 0.5 C current rate for 6–10 cycles and 1 C current rate for 11–100 cycles in the voltage range of 2.7–4.5 V, shown in Fig. 5. It is clear that titanium substitution improves the cycle stability of the cathode materials, though there has slightly fast capacity fading at the beginning 10 cycles. Discharge capacity of LiNi$_{0.8}$Co$_{0.2}$O$_2$ cathode decreases from 205 to 122 mAh/g after 100 cycles with capacity retention of 60%. It seems that our results of capacity and capacity retention of LiNi$_{0.8}$Co$_{0.2}$O$_2$ are slightly different from some previous reports in the literature, which may be attributed to the differences of sample synthesis and optimizations of electrode preparation. However, for LiNi$_{1}$$_y$Ti$_{y}$Co$_{0.5}$O$_2$ cathode, discharge capacity only fades from 188 to 148 mAh/g after 100 cycles with high capacity retention of 80%. The enhanced cycle stability could be interpreted by the suppression of phase transitions during intercalation and deintercalation.
Fig. 5. Plots of discharge-specific capacity vs. cycle number for LiNi$_{0.8-y}$Ti$_y$Co$_{0.2}$O$_2$ ($y = 0, 0.025, 0.050, 0.075, 0.100$) cathode materials. Cycling was carried out with a current rate of 0.2 C for one to five cycles, 0.5 C for 6–10 cycles and 1 C for 11–100 cycles.

The process as the differential capacity curves show. Fig. 6 illustrated the derivative $d\tau/dV$ versus $V$ curves of the second cycle for LiNi$_{0.8-y}$Ti$_y$Co$_{0.2}$O$_2$ cathode materials. As shown, LiNi$_{0.8}$Co$_{0.2}$O$_2$ material exhibits a sharp peak and several

Fig. 6. Differential capacity $(-d\tau/dV)$ against voltage curves derived from the second charge-discharge cycle (0.14 C, 2.7–4.5 V) of LiNi$_{0.8-y}$Ti$_y$Co$_{0.2}$O$_2$ ($y = 0, 0.025, 0.050, 0.075, 0.100$) cathode materials.

small peaks in the high voltage range, which has suppressed many sharp peaks compared to LiNiO$_2$ as reported by Li et al. [6]. With titanium doping in LiNi$_{0.8-y}$Ti$_y$Co$_{0.2}$O$_2$ cathode materials, the sharp peak changes to a broad peak and the small peaks diminish gradually. As Li et al. reported [6], the sharp peaks are first-order phase transitions (two-phase coexistence), and the broad ones are one-phase continuous phase transitions. Thus, the first-order phase transitions have largely suppressed in the LiNi$_{0.8-y}$Ti$_y$Co$_{0.2}$O$_2$ cathode materials, and even LiNi$_{0.7}$Ti$_{0.1}$Co$_{0.2}$O$_2$ material has no longer first-order phase with only a continuous phase transition for the entire region. Therefore, titanium substitution enhances cycle stability of LiNi$_{0.8-y}$Ti$_y$Co$_{0.2}$O$_2$ cathode materials by a significant suppression of phase transitions.

In order to further confirm the effects of titanium substitution on the structural changes of LiNi$_{0.8-y}$Ti$_y$Co$_{0.2}$O$_2$ cathode materials during cycling, ex situ XRD characterization of the Li$_{1-x}$Ni$_x$Co$_{0.2}$O$_2$ and Li$_{1-x}$Ni$_x$Ti$_{0.1}$Co$_{0.2}$O$_2$ deintercalated materials was undertaken. The coin cells, made of LiNi$_{0.8}$Co$_{0.2}$O$_2$ or LiNi$_{0.7}$Ti$_{0.1}$Co$_{0.2}$O$_2$ cathode material, were charged to different Li contents with a slow current rate (C/100). The charge times were calculated by the capacities corresponding to Li contents. After charging, the cathodes were carefully removed from the coin cells in an argon-filled glove box, and then rinsed with diethylene carbonate (DEC) to remove the residual electrolyte followed by drying at room temperature in vacuum for 6 h. The dry cathodes were characterized by XRD at a scan rate 4° min$^{-1}$ in the range of 10–90°. The XRD patterns of deintercalated cathodes for Li$_{1-x}$Ni$_x$Co$_{0.2}$O$_2$ and Li$_{1-x}$Ni$_x$Ti$_{0.1}$Co$_{0.2}$O$_2$ are shown in Figs. 7 and 8, respectively. The peaks of aluminum foil, which used as the current collector, were identified with dash lines in the figures. In Fig. 7, a new phase (Fd3m space group) is observed at $x = 0.5$ for Li$_{1-x}$Ni$_x$Co$_{0.2}$O$_2$, which implies that hexagonal layered Li$_{0.8}$Ni$_{0.2}$Co$_{0.2}$O$_2$ transfers partially to cubic spinel structure at this time. By contrary, no new diffraction lines were found in the ex situ XRD patterns of
Fig. 8. XRD patterns for the Li$_{1-x}$Ni$_0.7$Ti$_0.1$Co$_0.2$O$_2$ delithiated materials.

delithiated Li$_{1-x}$Ni$_0.7$Ti$_0.1$Co$_0.2$O$_2$ (Fig. 8), and all patterns still maintain hexagonal structure ($R-3m$ space group). It shows that there is only a continuous single-phase transition at the deintercalation process for LiNi$_0.8$Co$_0.2$O$_2$. For observation more clearly, a series of enlarged (003) diffraction peaks, which reflected the characteristic inter-slab distance, were shown in Fig. 9. For Li$_{1-x}$Ni$_0.8$Co$_0.2$O$_2$, the (003) peak slightly shifts toward lower diffraction angles when the deintercalated lithium content increases until $x$ value excesses 0.5, after which it slightly shifts back to higher diffraction angles. The angle shift of (003) peak is corresponding to the reciprocating changes of inter-slab distance, which is also occurred in LiNiO$_2$ and other derivates as reported in previous studies [6,23]. However, this shift is different in the XRD patterns for Li$_{1-x}$Ni$_0.7$Ti$_0.1$Co$_0.2$O$_2$.

in which the (003) peak slightly shifts toward lower diffraction angle from $x = 0$ up to $x = 0.8$, and back to higher diffraction angle only at $x = 0.9$. It implies that titanium substitution suppresses the lattice changes at the deintercalation process. Therefore, titanium substitution for nickel in LiNi$_0.8$Co$_0.2$O$_2$ improves the structure stability and thereby decreases the irreversible capacity losses of LiNi$_{0.8-x}$Ti$_x$Co$_0.2$O$_2$ cathodes during cycling.

3.3. Thermal stability

Differential scanning calorimetry (DSC) experiments were carried out to investigate the effect of titanium substitution on thermal stability of LiNi$_{0.8-x}$Ti$_x$Co$_0.2$O$_2$...
cathode materials at high charge voltage 4.3 V. Fig. 10 shows the results of thermal analyses by DSC. As shown, the Li(Ni4.8Co0.2)O2 material has a sharp exothermic peak occurred at 233 °C, with 786 J/g exothermic heat. With the increasing titanium amount, the Li(Ni8−y, Ti)Co2O4 materials show less and less exothermic heat as well as the postponed exothermic temperature. For the Li(Ni8−y, Ti)Co2O4 material, only a broad-peak centered at ~315 °C with 139 J/g exothermic heat was observed. This indicates that titanium substitution has improved the thermal stability of Li(Ni8−y, Ti)Co2O4 cathode materials at charged state.

It is well known that the delithiated LiNiO2 cathode material with the high oxidation state Ni4+ will evolve oxygen at elevated temperature and induce exothermic decomposition reactions between cathode and electrolyte [9]. As mentioned above, the titanium-doped cathodes show higher charge voltage plateau and lower charge capacity at a same terminated-charge-voltage than that of LiNi0.8Co0.2O2 cathode. It indicates that there is less high oxidation state Ni4+, and therefore lower oxidation ability for the delithiated titanium-doped cathodes. Moreover, these titanium ions at the slab space and nickel/cobalt ions at the inter slab space, as “rivets” in the structural lattice, are also able to stabilize the structure at the high voltage and prevent the evolution of oxygen from the delithiated titanium-doped cathodes. Hence, the improved thermal stability of Li(Ni8−y, Ti)Co2O4 cathode materials originates from the lower oxidation ability and the enhanced structural stability at delithiated state.

4. Conclusions

The titanium substitution compounds with the formula of Li(Ni8−y, Ti)Co2O4 show a solid solution at the range of 0 ≤ y ≤ 0.1. Compared to LiNi0.8Co0.2O2, the cationic distributions of these titanium-doped materials are re-arranged with more +2 valence transition metal ions (Ni2+ and/or Co2+) at both the 3a and 3b site. For titanium-doped cathode materials, the increasing initial capacity losses caused by the extra NiCo at the 3a Li site can be compensated by the decreasing capacity losses originated from lattice changes and interface reactions. The charge and discharge capacity of titanium-doped materials decreased gradually due to the inactive titanium component and the raise of voltage plateau, but cycle performance was improved remarkably, which was interpreted to a significant suppression of phase transitions. An improved thermal stability is also observed for titanium-doped cathodes, which is attributed to their lower oxidation ability and enhanced structural stability at delithiated state. Therefore, it can be concluded that the titanium substitution for nickel had a beneficial effect on the cycle performance and thermal stability of LiNi0.8Co0.2O2 material.

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