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Short communication

The investigation of Ti-modified $LiCoO_2$ materials for lithium ion battery

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HIGHLIGHTS

- Almost no Ti can enter into the $LiCoO_2$ lattice in $LiCo_{0.998}Ti_{0.002}O_2$ phase.
- $LiCo_{0.998}Ti_{0.002}O_2$ phase shows excellent cycling stability between 3.0 and 4.3 V.
- The high rate performance of the Ti-modified $LiCoO_2$ materials has been discussed.

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ABSTRACT

EDAX measurement reveals that the atomic ratio of Ti/(Ti + Co) is much higher than the mole feed ratios in the preparation for the $LiCo_{0.99}Ti_{0.01}O_2$ material. XPS observation further tells that in $LiCo_{0.998}Ti_{0.002}O_2$ phase with quite low Ti amount, almost no Ti can enter into the $LiCoO_2$ lattice, it is more inclined to enrich in the particle surface. Electrochemical examinations show that the cycling stability of $LiCo_{0.998}Ti_{0.002}O_2$ is as good as that of $LiCoO_2/LiCo_{0.99}Ti_{0.01}O_2$ composite between 3.0 and 4.3 V, and the latter has a better rate performance. It is considered that the difference of the high rate performance between the Ti-modified $LiCoO_2$ materials is more likely to originate from the different particle characteristics, when their Ti amounts are low enough.

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1. Introduction

In our early study [1], we have tried to design a micron-sized $LiCoO_2/LiCo_{0.99}Ti_{0.01}O_2$ composite with the core–shell structure by solid-phase synthesis. As compared with $LiCoO_2$, the obtained phase shows a great improvement in electrochemical performance and a better thermal stability. Meanwhile, its packing density is higher than that of the former. Thus, the composite is believed to be a promising cathode material for practical use.

As well as known, partial doping of cobalt with metal ions leads to extended cyclability and increase in capacity of lithium ion cells by enhancing structural stability [2]. According to our previous conjecture, the excellent electrochemical properties of the composite would be ascribed to the protection and enhancement of the shell $LiCo_{0.99}Ti_{0.01}O_2$ material [3,4], although the shell is not enough perfect in the view of coating. However, it is not completely consistent with the test results. For instance, $LiCoO_2/LiCo_{0.99}Ti_{0.01}O_2$ composite shows much better rate capability than the doping phase of $LiCo_{0.99}Ti_{0.01}O_2$, especially at 4 C (1 C = 140 mA g^{-1}). So it is necessary to survey the improving mechanism of $LiCoO_2/LiCo_{0.99}Ti_{0.01}O_2$ composite more detailed.

Recently, it is found [5] that the element Sb is not likely to be introduced to the crystal lattice of $LiCoO_2$ only by the traditional route for synthesis the doping material. Interestingly, the ion radius of Sb^{5+} is very close to that of Ti^{4+} [6,7]. Moreover, the Ti-doped phase usually has lower average particle size than pristine $LiCoO_2$, which is also similar with the Sb-modified $LiCoO_2$ material. A question, therefore, is asked: is the added Ti also inclined to enrich in the particle surface in the case? It may be an important clue to help us to discuss the rate performance difference between $LiCo_{0.99}Ti_{0.01}O_2$ and $LiCoO_2/LiCo_{0.99}Ti_{0.01}O_2$ composite, and further understand the role of Ti modifying on $LiCoO_2$ particle as positive electrode material for lithium-ion batteries.

2. Experimental

According to the report [1], $LiCoO_2$, $LiCo_{0.99}Ti_{0.01}O_2$ and $LiCoO_2/LiCo_{0.99}Ti_{0.01}O_2$ composite were prepared respectively. Besides,

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Table 1
The Ti/(Ti + Co) atomic ratio of the resulting materials measured by EDAX.

Samples	$LiCo_{0.99}Ti_{0.01}O_2$	$LiCoO_2/LiCo_{0.99}Ti_{0.01}O_2$	$LiCoO_2$
Ti/(Co + Ti) (%)	1.918	0.868	0.007

$LiCo_{0.998}Ti_{0.002}O_2$ was also obtained through the same procedure with $LiCo_{0.99}Ti_{0.01}O_2$.

The morphology of the samples was observed on a Quanta 200 scanning electron microscope (SEM). The particle size and particle size distribution were determined further by laser scattering measurements (Mastersizer 2000, U.K.). X-ray photoelectron spectroscopy (XPS) data were obtained using an ESCALab250 electron spectrometer from Thermo Scientific Corporation with monochromatic 150 W Al Kα radiation. The base pressure was about 6.5×10^{-10} mbar. The binding energies were referenced to the C1s line at 284.8 eV from alkyl or adventitious carbon.

Galvanostatic cycling was performed on 2016 coin cells. The cathode electrode was made by mixing 80 wt. % active material, 10 wt. % PTFE binder and 10 wt. % acetylene black, then pressing them on an aluminium mesh. Thus prepared electrode was dried at 150 °C for 12 h before the cell assembling. Metallic lithium was used as the anode. The electrolyte was 1 M $LiPF_6$ in a 1:1 volume ratio mixture of ethylene carbonate (EC)/dimethyl carbonate (DMC), and the separator was Celgard 2300 membrane. The cells was assembled in the argon filled glove box (MECABOX80-1″s″, Switzerland). The electrochemical impedance spectroscopy (EIS) tests were performed using electrochemical workstation (Autolab PGSTAT30, Eco Chemie) with a voltage of 5 mV amplitude over a frequency range from 10^5 Hz to 10^{-2} Hz.

3. Results and discussion

As known, EDAX is effective to detect the surface concentration of the component. The measurements were conducted for $LiCo_{0.99}Ti_{0.01}O_2$ and $LiCoO_2/LiCo_{0.99}Ti_{0.01}O_2$ materials. Because the detecting signals of Ti element are all weak, $LiCoO_2$ was used as a reference for background correction. It is found from the Table 1 that the atomic ratio of Ti/(Ti + Co) of the samples decrease in the order of $LiCo_{0.99}Ti_{0.01}O_2 > LiCoO_2/LiCo_{0.99}Ti_{0.01}O_2 >> LiCoO_2$. Moreover, the value of $LiCo_{0.99}Ti_{0.01}O_2$ is much higher than the mole feed ratios in the preparation. The above observations seem to imply that the added Ti tends to stay on the particle surface in the form of TiO_2 or some unidentified "impurity".

To further prove the above idea, the $LiCo_{0.998}Ti_{0.002}O_2$ material, prepared under the same calcining condition, was investigated in terms of physical and electrochemical characterizations. Its nominal composition is equal to $LiCoO_2/LiCo_{0.99}Ti_{0.01}O_2$ composite. As shown in Fig. 1, $LiCo_{0.998}Ti_{0.002}O_2$ and $LiCoO_2/LiCo_{0.99}Ti_{0.01}O_2$ shows similar particle morphology. According to the results of particle size distribution analysis in Table 2, however, the latter, as well as $LiCo_{0.99}Ti_{0.01}O_2$, is smaller in the average particle size and presents a narrower particle size distribution range. Thus, the $LiCo_{0.998}Ti_{0.002}O_2$ electrode would be suggested to deliver a lowest capacity at higher rates than the others. The novel preparation method of the composite presents a huge advantage to optimizing the particle characteristics of Ti-modified $LiCoO_2$ material.

Table 2
The results of particle size distribution analysis on $LiCoO_2$, $LiCo_{0.99}Ti_{0.01}O_2$ and $LiCoO_2/LiCo_{0.99}Ti_{0.01}O_2$ powders.

Samples	D_{10} (μm)	D_{50} (μm)	D_{90} (μm)
$LiCo_{0.998}Ti_{0.002}O_2$	7.325	17.054	36.650
$LiCo_{0.99}Ti_{0.01}O_2$	5.005	10.596	21.075
$LiCoO_2/LiCo_{0.99}Ti_{0.01}O_2$	7.359	12.958	21.834

Fig. 2 displays the Ti2p and Co2p spectrum of $LiCo_{0.998}Ti_{0.002}O_2$. Ar ion etching was used to examine the concentration depth profiles of the $LiCo_{0.998}Ti_{0.002}O_2$ powder. The intensity for Ti becomes lower gradually upon Ar^+ etching. After 4000s' etching, it is hardly visible. On the other hand, the intensity for Co becomes obviously higher with the increasing sputtering time. The data in Table 3 further implies that the Ti/Co ratio of the resulting sample should decrease gradually with Ar^+ etching. As expected, the value is only 0.75% after etching 4000 s, while the one is 8.49% before etching. The notable difference clearly indicates that a Ti concentration gradient may exist in $LiCo_{0.998}Ti_{0.002}O_2$ sample and the added Ti is more likely to be enriched in the surface layer, although the element is usually used as a good choice for doping cathode materials in the past. According to these observations, it is reasonable to believe that adding a quite small amount of TiO_2 during the preparation cannot lead to the formation of $LiCo_{0.998}Ti_{0.002}O_2$ solid solution and Ti ions can also not replace Co in vacant 3a sites in the crystal structure of $LiCoO_2$ for improving the structural stability.

Therefore, the previous interpretation is not accurate that the excellent electrochemical properties of the $LiCoO_2/LiCo_{0.99}Ti_{0.01}O_2$ composite could be achieved from the $LiCo_{0.99}Ti_{0.01}O_2$ outer layer composition. The reason may be directly related to the distributed state with Ti element in $LiCoO_2$ particles for the improvement, even if its amount is very small.

Fig. 3 compares the cycling stability of $LiCo_{0.998}Ti_{0.002}O_2$ and $LiCoO_2/LiCo_{0.99}Ti_{0.01}O_2$ between 3.0 and 4.3 V at room temperature. In order to verify the expectation, the cycling tests were carried out following a given procedure. The cells were cycled at 30 mA g^{-1} in the first two cycles, and then cycling was continued at 100 mA g^{-1}.

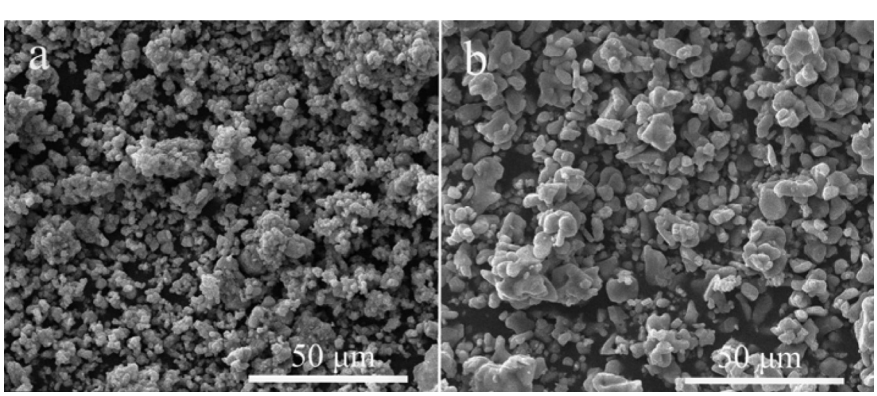

Fig. 1. SEM images of (a) $LiCo_{0.998}Ti_{0.002}O_2$ and (b) $LiCoO_2/LiCo_{0.99}Ti_{0.01}O_2$.

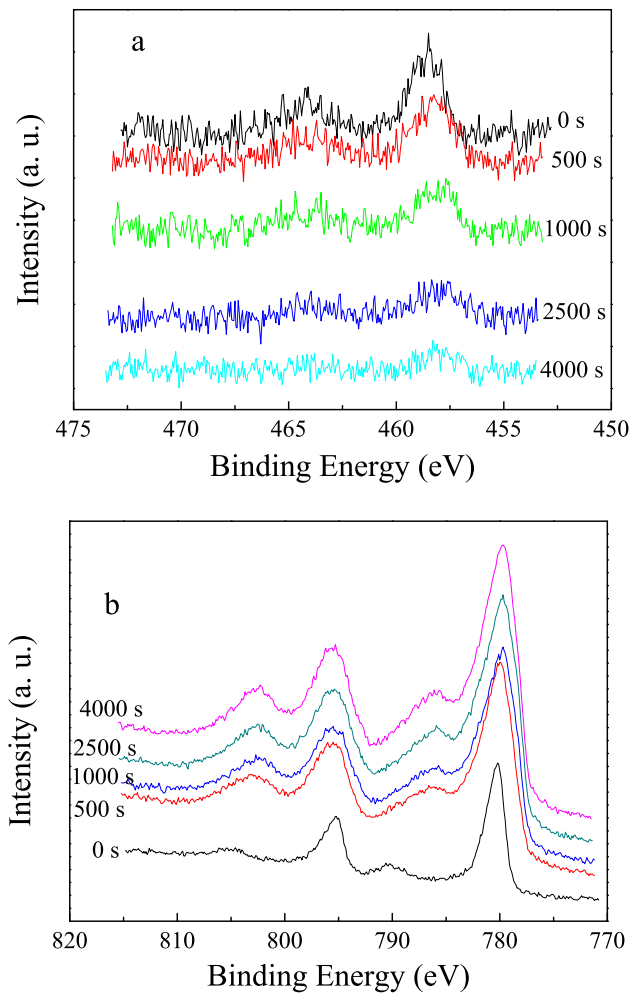

Fig. 2. (a) Ti2p and (b) Co2p XPS spectra of $LiCo_{0.998}Ti_{0.002}O_2$ powders with different sputtering times: 0, 500, 1000, 2500, 4000 s.

The first discharge capacity of $LiCo_{0.998}Ti_{0.002}O_2$ is about 154.7 mAh g^{-1}, corresponding to the coulomb efficiency of 95.0%. After 50 cycles, the capacity decreases to 138.4 mAh g^{-1}. It is very interesting that the capacity retention with cycling of $LiCo_{0.998}Ti_{0.002}O_2$ is as good as that of the composite in Fig. 3, and the two modified samples both show a much better cycling stability than the bare $LiCoO_2$ [1]. The result suggests that the cycleability improvement of either $LiCo_{0.998}Ti_{0.002}O_2$ or $LiCoO_2/LiCo_{0.99}Ti_{0.01}O_2$ composite could be explained by the same "interface protection" mechanism, which will be later witnessed by the impedance result. In addition, the same cycling stability of $LiCo_{0.998}Ti_{0.002}O_2$ as $LiCoO_2/LiCo_{0.99}Ti_{0.01}O_2$ further implied that the surface-enriched Ti in both phases achieve the similar effect in the cycling behaviour, though the two phases were obtained through different procedure. On the other hand, Fig. 4 indicates the capacity vs. current rate of the resulting samples in the voltage range of 3.0–4.2 V. For $LiCo_{0.998}Ti_{0.002}O_2$, the discharging capacity at 1 C (1 C = 140 mA g^{-1}) is about 130.9 mAh g^{-1}, which is close to the value (134.3 mAh g^{-1}) of the composite. However, the capacity has been

Table 3
The Ti/Co atomic ratio of $LiCo_{0.998}Ti_{0.002}O_2$ powders with different sputtering times.

Sputtering time (s)	0	500	1000	2500	4000
Ti/Co (%)	8.49	3.02	2.17	1.25	0.75

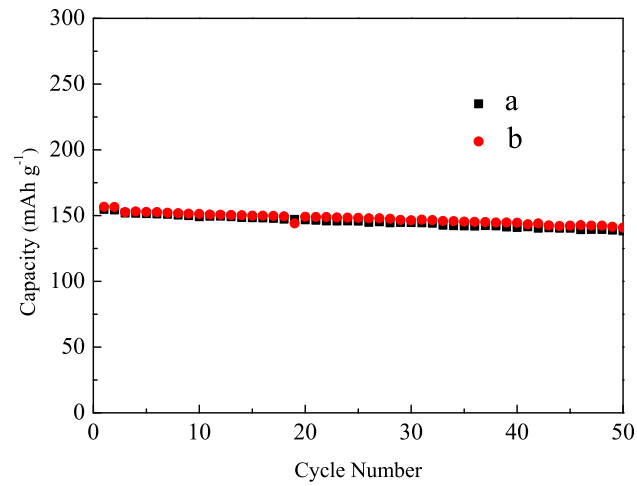

Fig. 3. Comparison of the cycling stability of (a) $LiCo_{0.998}Ti_{0.002}O_2$ and (b) $LiCoO_2/LiCo_{0.99}Ti_{0.01}O_2$ between 3.0 and 4.3 V at room temperature.

decreasing quickly with increasing the current rate, and only maintains a lever of 53.9 mAh g^{-1} at 4 C. In order to figure out the different rate performance of $LiCo_{0.998}Ti_{0.002}O_2$ and the composite phase, we compare their voltage profiles at different rates in Fig. 5. It can be seen that in a low-rate mode, all the samples show similar charge/discharge curves. With increasing the charge-discharge current, the gaps between charge and discharge plateau keep widening for all the samples but most obviously in $LiCoO_2$. The difference between $LiCo_{0.998}Ti_{0.002}O_2$ and the composite phase starts to get notable when the current increases to 3 C rate, where $LiCo_{0.998}Ti_{0.002}O_2$ presents a greatly sloped plateau while the composite phase still shows a rather flat plateau, and then the different is more obvious at 4 C rate. The results indicate that the more increased polarization in $LiCo_{0.998}Ti_{0.002}O_2$ than the composite phase should be the reason for their different rate performance. In our previous SEM observation, $LiCo_{0.998}Ti_{0.002}O_2$ showed a slightly smaller particle size but less uniform size distribution than the composite, it may incur more interaction between the cathode and electrolyte and increasing surface impedance. In the low-rate charge/discharge, the effect of the surface impedance is not very obvious, but when the current rate increases to 3 C or higher, the bigger surface impedance will impose more notable "barrier" on Li^+ transfer.

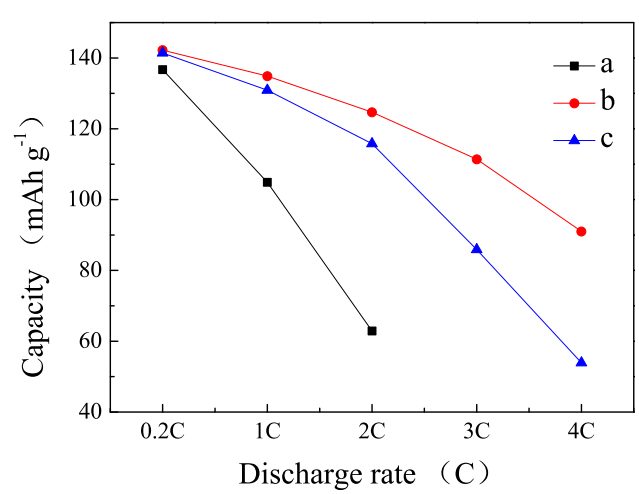

Fig. 4. Comparison of the rate performance of (a) $LiCoO_2$, (b) $LiCoO_2/LiCo_{0.99}Ti_{0.01}O_2$ and (c) $LiCo_{0.998}Ti_{0.002}O_2$ materials. (Potential range: 3.0–4.2 V).

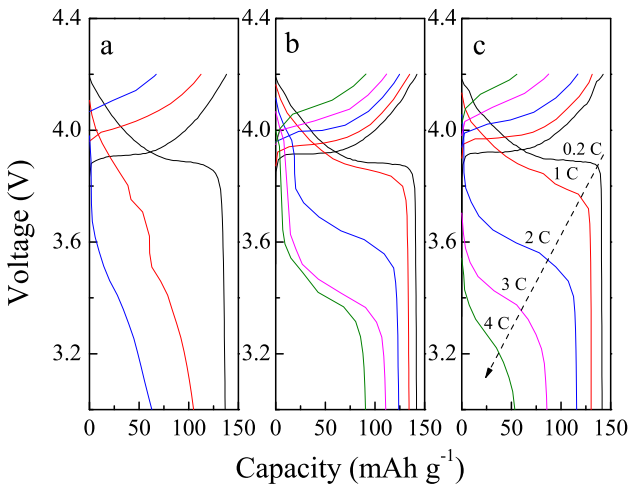

Fig. 5. The typical charge-discharge profiles of (a) $LiCoO_2$, (b) $LiCoO_2/LiCo_{0.99}Ti_{0.01}O_2$ and (c) $LiCo_{0.998}Ti_{0.002}O_2$ materials at different C-rates. (Potential range: 3.0–4.2 V).

To further investigate the reason of improved electrochemical property in the composite, AC impedance measurements were done and the results are shown in Fig. 6. Fig. 6a presents the Nyquist plots of the fresh $LiCoO_2$, $LiCoO_2/LiCo_{0.99}Ti_{0.01}O_2$ and $LiCo_{0.998}Ti_{0.002}O_2$ electrodes. Typically, the semicircle in the high frequency range (seeing the inset graph) represents the charge transfer resistance (R_{ct}) and a sloping line at low frequency is Warburg resistance. We can see that the three electrodes show very similar impedance signal before the cycling. The fact that $LiCo_{0.998}Ti_{0.002}O_2$ has a relatively smaller semicircle than the composite corresponds well with its slightly smaller particle size. After cycling, the impedance was collected again and the results are displayed in Fig. 6b. The Nyquist plot clearly consists of three semicircles and one inclined line for all the cycled electrodes. According to the previous reports [8,9], the high-frequency, the middle-frequency, and the low-frequency semicircles can be attributed to Li^+ migration through the SEI film (R_f), the electronic properties of the material (R_e) and charge transfer resistance (R_{ct}), respectively. R_f and R_e value do not differ much in the three cycled electrodes as being reflected by the similar diameter of the semicircles in the high-frequency and the middle-frequency range. $LiCoO_2$ has the largest semicircle in low frequency range as being expected for, suggesting the biggest R_{ct} of $LiCoO_2$. Meanwhile, the composite shows a smaller semicircle in low frequency range than $LiCo_{0.998}Ti_{0.002}O_2$, suggesting a smaller R_{ct} of the composite phase. The order of the R_{ct} value agrees well with the comparison in the rate capability.

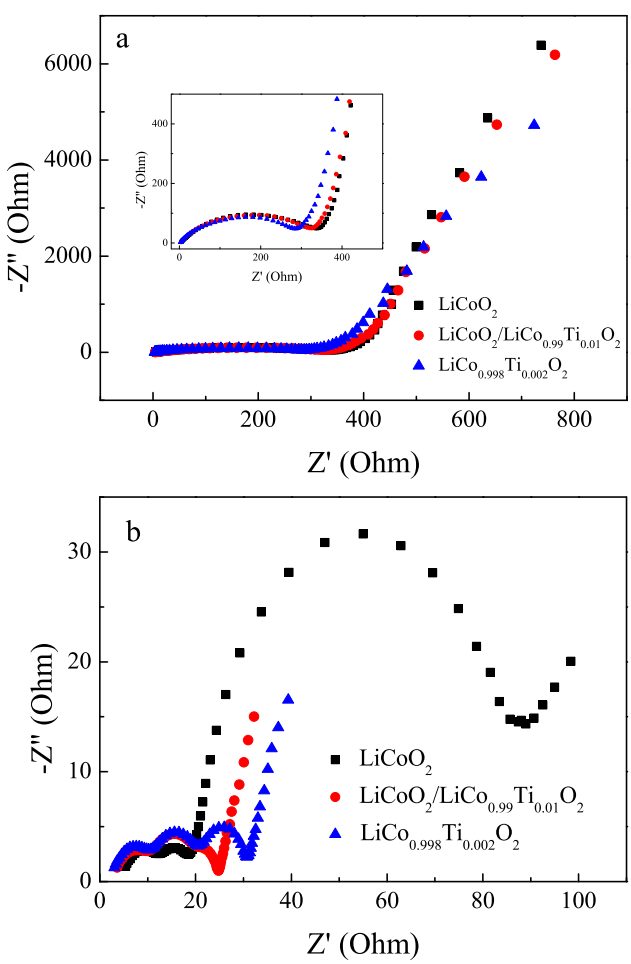

Fig. 6. AC impedance spectrums of (a) fresh and (b) cycled electrodes for pristine and Ti-modified $LiCoO_2$ materials.

Above experiment results further confirm that although introducing a quite small amount of TiO_2 during preparation, the performance of the $LiCoO_2$ material is improved effectively. Moreover, it can be reasonably believed that the different particle characteristics result in the obvious difference of the high rate performance among the Ti-modified $LiCoO_2$ materials with the low Ti content. For instance, $LiCoO_2/LiCo_{0.99}Ti_{0.01}O_2$ composite shows more uniform particle size distribution than the $LiCo_{0.99}Ti_{0.01}O_2$ phase in Table 2, which helps to present a better rate performance.

4. Conclusion

It is found that even a very small amount of Ti addition (the molar ratio of Ti:Co is about 0.002 in the average formula of the Ti-modified $LiCoO_2$ material) can effectively improve the electrochemical performance of the $LiCoO_2$ material, while almost no Ti can enter into the lattice by a traditional route for synthesis the doping material. It can also be believed that the difference of the high rate performance among the Ti-modified $LiCoO_2$ materials is more likely to originate from the different particle characteristics, when their Ti amounts are low enough. Finally, it should be point out that we cannot affirm that the impossibility of Ti replacing Co and chemical precursor techniques may help in enhancing the $LiCo_{1-x}Ti_xO_2$ solid solubility to higher x values. Therefore, further experimental verification of this proposed guideline is underway.

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