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EXHIBIT A



Short communication

The investigation of Ti-modified LiCoO₂ materials for lithium ion battery

Jinpeng Yu^{a, b}, Zenghui Han^a, Xiaohong Hu^a, Hui Zhan^a  , Yunhong Zhou^a, Xingjiang Liu^b^a College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, China^b National Key Laboratory of Power Source, Tianjin Institute of Power Sources, Tianjin 300384, China

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Highlights

- Almost no Ti can enter into the LiCoO₂ lattice in LiCo_{0.998}Ti_{0.002}O₂ phase.
- LiCo_{0.998}Ti_{0.002}O₂ phase shows excellent cycling stability between 3.0 and 4.3V.
- The high rate performance of the Ti-modified LiCoO₂ materials has been discussed.

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}O₂ material. XPS observation further tells that in LiCo_{0.998}Ti_{0.002}O₂ phase with quite low Ti amount, almost no Ti can enter into the LiCoO₂ 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}O₂ is as good as that of LiCoO₂/LiCo_{0.99}Ti_{0.01}O₂ composite between 3.0 and 4.3V, and the latter has a better rate performance. It is considered that the difference of the high rate performance between the Ti-modified LiCoO₂ materials is more likely to originate from the different particle characteristics, when their Ti amounts are low enough.



Previous

Next



Keywords

Core-shell structure; Doping; Lithium batteries; Rate performance

1. Introduction

In our early study [1], we have tried to design a micron-sized LiCoO₂/LiCo_{0.99}Ti_{0.01}O₂ composite with the core-shell structure by solid-phase synthesis. As compared with LiCoO₂, 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}O₂ 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, LiCoO₂/LiCo_{0.99}Ti_{0.01}O₂ composite shows much better rate capability than the doping phase of LiCo_{0.99}Ti_{0.01}O₂, especially at 4 C (1 C=140 mA g⁻¹). So it is necessary to survey the improving mechanism of LiCoO₂/LiCo_{0.99}Ti_{0.01}O₂ composite more detailed.

Recently, it is found [5] that the element Sb is not likely to be introduced to the crystal lattice of LiCoO₂ only by the traditional route for synthesis the doping material. Interestingly, the ion radius of Sb⁵⁺ is very close to that of Ti⁴⁺ [6], [7]. Moreover, the Ti-doped phase usually has lower average particle size than pristine LiCoO₂, which is also similar with the Sb-modified LiCoO₂ 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}O₂ and LiCoO₂/LiCo_{0.99}Ti_{0.01}O₂ composite, and further understand the role of Ti modifying on LiCoO₂ particle as positive electrode material for lithium-ion batteries.

2. Experimental

According to the report [1], LiCoO₂, LiCo_{0.99}Ti_{0.01}O₂ and LiCoO₂/LiCo_{0.99}Ti_{0.01}O₂ composite were prepared respectively. Besides, LiCo_{0.998}Ti_{0.002}O₂ was also obtained through the same procedure with LiCo_{0.99}Ti_{0.01}O₂.

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 150W Al K α radiation. The base pressure was about 6.5 $\times 10^{-10}$ 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 80wt. % active material, 10wt. % PTFE binder and 10wt. % acetylene black, then pressing them on an aluminium mesh. Thus prepared electrode was dried at 150°C for 12h before the cell assembling. Metallic lithium was used as the anode. The electrolyte was 1 M LiPF₆ 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 10⁵ Hz to 10⁻² Hz.

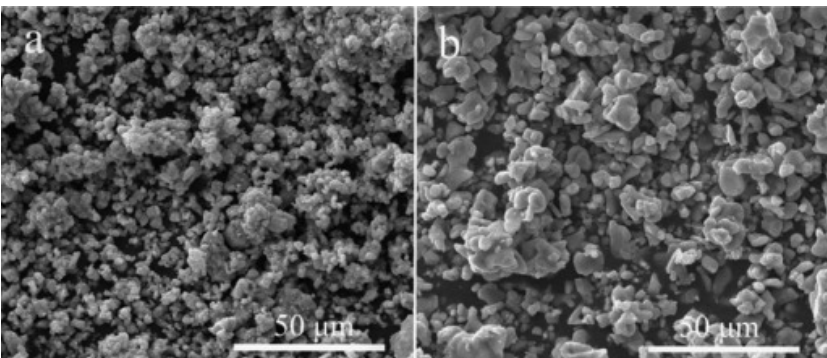
3. Results and discussion

As known, EDAX is effective to detect the surface concentration of the component. The measurements were conducted for LiCo_{0.99}Ti_{0.01}O₂ and LiCoO₂/LiCo_{0.99}Ti_{0.01}O₂ materials. Because the detecting signals of Ti element are all weak, LiCoO₂ 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}O₂>LiCoO₂/LiCo_{0.99}Ti_{0.01}O₂>>LiCoO₂. Moreover, the value of LiCo_{0.99}Ti_{0.01}O₂ 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 TiO₂ or some unidentified “impurity”.

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

To further prove the above idea, the LiCo_{0.998}Ti_{0.002}O₂ material, prepared under the same calcining condition, was investigated in terms of physical and electrochemical characterizations. Its nominal composition is equal to LiCoO₂/LiCo_{0.99}Ti_{0.01}O₂ composite. As shown in [Fig. 1](#), LiCo_{0.998}Ti_{0.002}O₂ and LiCoO₂/LiCo_{0.99}Ti_{0.01}O₂ 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}O₂, is smaller in the average particle size and presents a narrower particle size distribution range. Thus, the LiCo_{0.998}Ti_{0.002}O₂ 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 LiCoO₂ material.



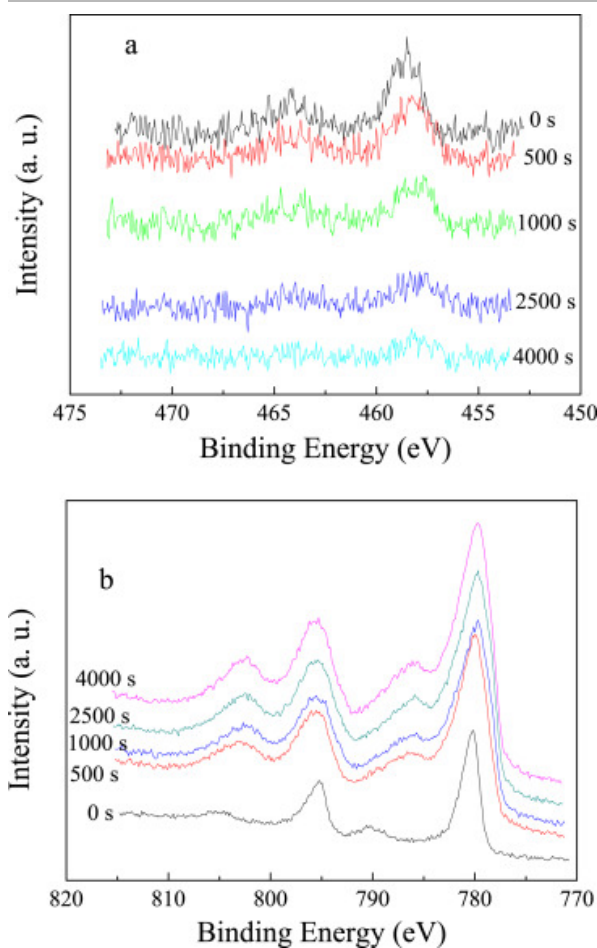
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Fig. 1. SEM images of (a) LiCo_{0.998}Ti_{0.002}O₂ and (b) LiCoO₂/LiCo_{0.99}Ti_{0.01}O₂.

Table 2. The results of particle size distribution analysis on LiCoO₂, LiCo_{0.99}Ti_{0.01}O₂ and LiCoO₂/LiCo_{0.99}Ti_{0.01}O₂ 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}O₂. Ar ion etching was used to examine the concentration depth profiles of the LiCo_{0.998}Ti_{0.002}O₂ 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 4000s, while the one is 8.49% before etching. The notable difference clearly indicates that a concentration gradient may exist in LiCo_{0.998}Ti_{0.002}O₂ 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 TiO₂ during the preparation cannot lead to the formation of LiCo_{0.998}Ti_{0.002}O₂ solid solution and Ti ions can also not replace Co in vacant 3a sites in the crystal structure of LiCoO₂ for improving the structural stability.



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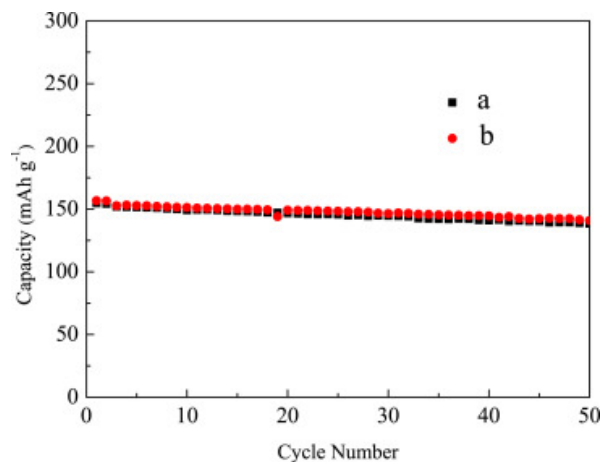
Fig.2. (a) Ti2p and (b) Co2p XPS spectra of LiCo_{0.998}Ti_{0.002}O₂ powders with different sputtering times: 0, 500, 1000, 2500, 4000s.

Table3. The Ti/Co atomic ratio of LiCo_{0.998}Ti_{0.002}O₂ 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

Therefore, the previous interpretation is not accurate that the excellent electrochemical properties of the LiCoO₂/LiCo_{0.99}Ti_{0.01}O₂ composite could be achieved from the LiCo_{0.99}Ti_{0.01}O₂ outer layer composition. The reason may be directly related to the distributed state with Ti element in LiCoO₂ particles for the improvement, even if its amount is very small.

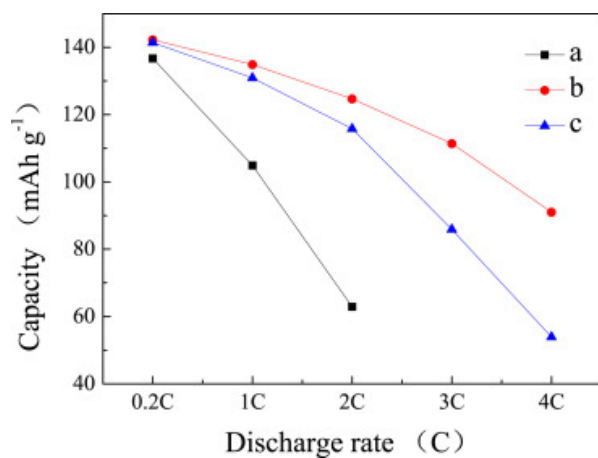
Fig.3 compares the cycling stability of LiCo_{0.998}Ti_{0.002}O₂ and LiCoO₂/LiCo_{0.99}Ti_{0.01}O₂ between 3.0 and 4.3V at room temperature. In order to verify the expectation, the cycling tests were carried out following a given procedure. The cells were cycled at 30mA g⁻¹ in the first two cycles, and then cycling was continued at 100mA g⁻¹. The first discharge capacity of LiCo_{0.998}Ti_{0.002}O₂ is about 154.7mA h g⁻¹, corresponding to the coulomb efficiency of 95.0%. After 50 cycles, the capacity decreases to 138.4mA h g⁻¹. It is very interesting that the capacity retention with cycling of LiCo_{0.998}Ti_{0.002}O₂ 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 LiCoO₂ [1]. The result suggests that the cycleability improvement of either LiCo_{0.998}Ti_{0.002}O₂ or LiCoO₂/LiCo_{0.99}Ti_{0.01}O₂ 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}O₂ as LiCoO₂/LiCo_{0.99}Ti_{0.01}O₂ 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 3.0–4.2V. For LiCo_{0.998}Ti_{0.002}O₂, the discharging capacity at 1 C (1 C=140mA g⁻¹) is about 130.9mA h g⁻¹, which is close to the value (134.3mA h g⁻¹) of the composite. However, the capacity has been decreasing quickly with increasing the current rate, and only maintains a lever of 53.9mA h g⁻¹ at 4 C. In order to figure out the different rate performance of LiCo_{0.998}Ti_{0.002}O₂ 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 LiCoO₂. The difference between LiCo_{0.998}Ti_{0.002}O₂ and the composite phase starts to get notable when the current increases to 3 C rate, where LiCo_{0.998}Ti_{0.002}O₂ 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}O₂ than the composite phase should be the reason for their different rate performance. In our previous SEM observation, LiCo_{0.998}Ti_{0.002}O₂ 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.



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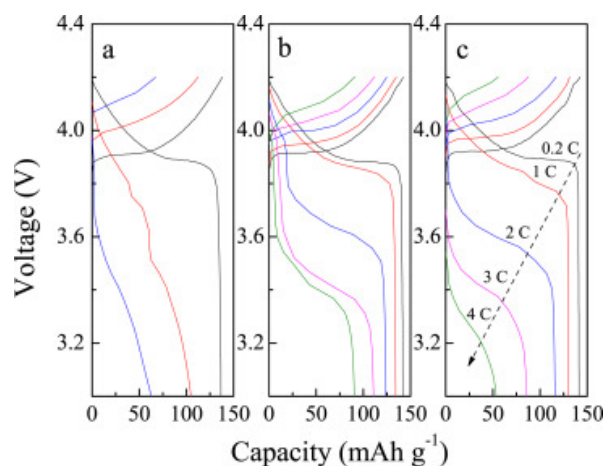
Fig.3. Comparison of the cycling stability of (a) LiCo_{0.998}Ti_{0.002}O₂ and (b) LiCoO₂/LiCo_{0.99}Ti_{0.01}O₂ between 3.0 and 4.3V at room temperature.



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Fig.4. Comparison of the rate performance of (a) LiCoO₂, (b) LiCoO₂/LiCo_{0.99}Ti_{0.01}O₂ and (c) LiCo_{0.998}Ti_{0.002}O₂ materials. (Potential range: 3.0–4.2V).

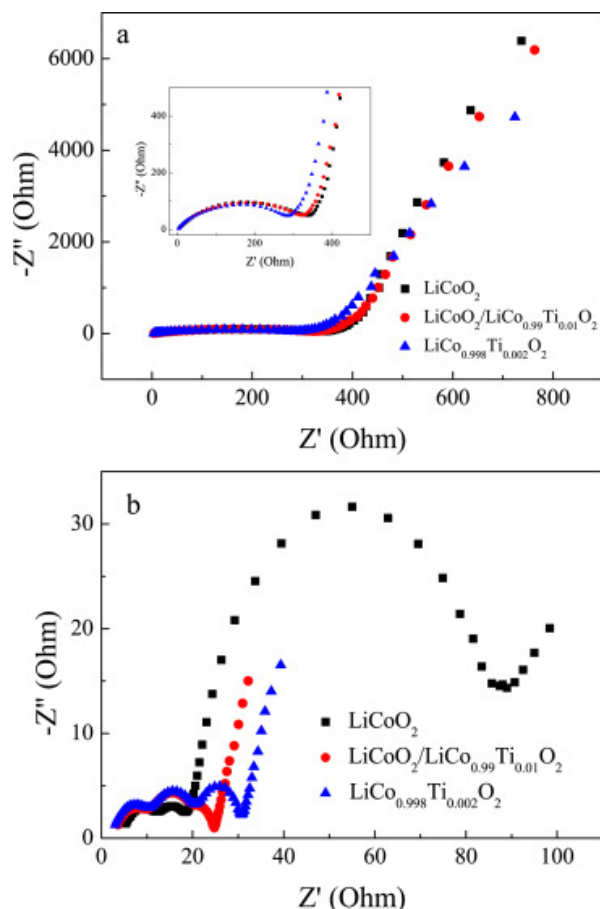


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Fig.5. The typical charge-discharge profiles of (a) LiCoO₂, (b) LiCoO₂/LiCo_{0.99}Ti_{0.01}O₂ and (c) LiCo_{0.998}Ti_{0.002}O₂ materials at different C-rates. (Potential range: 3.0–4.2V).

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 LiCoO₂, LiCoO₂/LiCo_{0.99}Ti_{0.01}O₂ and LiCo_{0.998}Ti_{0.002}O₂ 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}O₂ 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. LiCoO₂ has the largest semicircle in low frequency range as being expected for, suggesting the biggest R_{ct} of LiCoO₂. Meanwhile, the composite shows a smaller semicircle in low frequency range than LiCo_{0.998}Ti_{0.002}O₂, 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.



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Fig.6. AC impedance spectrums of (a) fresh and (b) cycled electrodes for pristine and Ti-modified LiCoO₂ materials.

Above experiment results further confirm that although introducing a quite small amount of TiO₂ during preparation, the performance of the LiCoO₂ 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 LiCoO₂ materials with the low Ti content. For instance, LiCoO₂/LiCo_{0.99}Ti_{0.01}O₂ composite shows more uniform particle size distribution than the LiCo_{0.99}Ti_{0.01}O₂ phase in Table2, 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 LiCoO₂ material) can effectively improve the electrochemical performance of the LiCoO₂ 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 LiCoO₂ 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_xO₂ solid solubility to higher x values. Therefore, further experimental verification of this proposed guideline is underway.

Acknowledgements

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...Doping with various metals is also widely used to suppress the phase transition and improve structure reversibility of LiCoO₂ at high voltage [33]. The element with larger ionic radius than Co³⁺, such as Mg²⁺ [34,35], Ti⁴⁺ [36,37] and Zr⁴⁺ [38] ions, as a dopant, could increase the inter-slab space, thus resulting in a “pillaring effect” to produce a larger inter-slab distance for the (de)intercalation of Li ion and to suppress the distortion of the structure. The multi-elements doping was further used to improve the electrochemical properties of LiCoO₂....

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...In contrast, for LiCoO₂(D) in 3.0–4.3 V the specific discharge capacity at 5.0C is no less than 130 mAh g⁻¹, and in 3.0–4.5 V it is 135 mAh g⁻¹. The enhanced rate capability properties have earlier been attributed to the Ti doping [14,15], and this is most likely the case for LiCoO₂(D) as well. Based on the EELS results reported in Chapter 3.1, it seems that the Ti doping decreases the Co valence, increasing the amount of electrons in the orbital and making it more metallic....

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Short communication

The investigation of Ti-modified LiCoO_2 materials for lithium ion batteryJinpeng Yu ^{a,b}, Zenghui Han ^a, Xiaohong Hu ^a, Hui Zhan ^{a,*}, Yunhong Zhou ^a, Xingjiang Liu ^b^a College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, China^b National Key Laboratory of Power Source, Tianjin Institute of Power Sources, Tianjin 300384, China

H I G H L I G H T S

- Almost no Ti can enter into the LiCoO_2 lattice in $\text{LiCo}_{0.998}\text{Ti}_{0.002}\text{O}_2$ phase.
- $\text{LiCo}_{0.998}\text{Ti}_{0.002}\text{O}_2$ 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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A B S T R A C T

EDAX measurement reveals that the atomic ratio of $\text{Ti}/(\text{Ti} + \text{Co})$ is much higher than the mole feed ratios in the preparation for the $\text{LiCo}_{0.99}\text{Ti}_{0.01}\text{O}_2$ material. XPS observation further tells that in $\text{LiCo}_{0.998}\text{Ti}_{0.002}\text{O}_2$ 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 $\text{LiCo}_{0.998}\text{Ti}_{0.002}\text{O}_2$ is as good as that of $\text{LiCoO}_2/\text{LiCo}_{0.99}\text{Ti}_{0.01}\text{O}_2$ 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 $\text{LiCoO}_2/\text{LiCo}_{0.99}\text{Ti}_{0.01}\text{O}_2$ 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 $\text{LiCo}_{0.99}\text{Ti}_{0.01}\text{O}_2$ 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, $\text{LiCoO}_2/\text{LiCo}_{0.99}\text{Ti}_{0.01}\text{O}_2$

composite shows much better rate capability than the doping phase of $\text{LiCo}_{0.99}\text{Ti}_{0.01}\text{O}_2$, especially at 4 C ($1\text{ C} = 140\text{ mA g}^{-1}$). So it is necessary to survey the improving mechanism of $\text{LiCoO}_2/\text{LiCo}_{0.99}\text{Ti}_{0.01}\text{O}_2$ 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 $\text{LiCo}_{0.99}\text{Ti}_{0.01}\text{O}_2$ and $\text{LiCoO}_2/\text{LiCo}_{0.99}\text{Ti}_{0.01}\text{O}_2$ 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 , $\text{LiCo}_{0.99}\text{Ti}_{0.01}\text{O}_2$ and $\text{LiCoO}_2/\text{LiCo}_{0.99}\text{Ti}_{0.01}\text{O}_2$ composite were prepared respectively. Besides,

* Corresponding author. Tel.: +86 27 68756931; fax: +86 27 68754067.
E-mail address: zhanhui3620@126.com (H. Zhan).

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}O₂ was also obtained through the same procedure with LiCo_{0.99}Ti_{0.01}O₂.

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 K α 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 LiPF₆ 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 10⁵ 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}O₂ and LiCoO₂/LiCo_{0.99}Ti_{0.01}O₂ materials. Because the detecting signals of Ti element are all weak, LiCoO₂ 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}O₂ > LiCoO₂/LiCo_{0.99}Ti_{0.01}O₂ >> LiCoO₂. Moreover, the value of LiCo_{0.99}Ti_{0.01}O₂ 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 TiO₂ or some unidentified "impurity".

To further prove the above idea, the LiCo_{0.998}Ti_{0.002}O₂ material, prepared under the same calcining condition, was investigated in terms of physical and electrochemical characterizations. Its

Table 2The results of particle size distribution analysis on LiCoO₂, LiCo_{0.99}Ti_{0.01}O₂ and LiCoO₂/LiCo_{0.99}Ti_{0.01}O₂ 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

nominal composition is equal to LiCoO₂/LiCo_{0.99}Ti_{0.01}O₂ composite. As shown in Fig. 1, LiCo_{0.998}Ti_{0.002}O₂ and LiCoO₂/LiCo_{0.99}Ti_{0.01}O₂ 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}O₂, is smaller in the average particle size and presents a narrower particle size distribution range. Thus, the LiCo_{0.998}Ti_{0.002}O₂ 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 LiCoO₂ material.

Fig. 2 displays the Ti2p and Co2p spectrum of LiCo_{0.998}Ti_{0.002}O₂. Ar ion etching was used to examine the concentration depth profiles of the LiCo_{0.998}Ti_{0.002}O₂ powder. The intensity for Ti becomes lower gradually upon Ar⁺ 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}O₂ 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 TiO₂ during the preparation cannot lead to the formation of LiCo_{0.998}Ti_{0.002}O₂ solid solution and Ti ions can also not replace Co in vacant 3a sites in the crystal structure of LiCoO₂ for improving the structural stability.

Therefore, the previous interpretation is not accurate that the excellent electrochemical properties of the LiCoO₂/LiCo_{0.99}Ti_{0.01}O₂ composite could be achieved from the LiCo_{0.99}Ti_{0.01}O₂ outer layer composition. The reason may be directly related to the distributed state with Ti element in LiCoO₂ particles for the improvement, even if its amount is very small.

Fig. 3 compares the cycling stability of LiCo_{0.998}Ti_{0.002}O₂ and LiCoO₂/LiCo_{0.99}Ti_{0.01}O₂ 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.

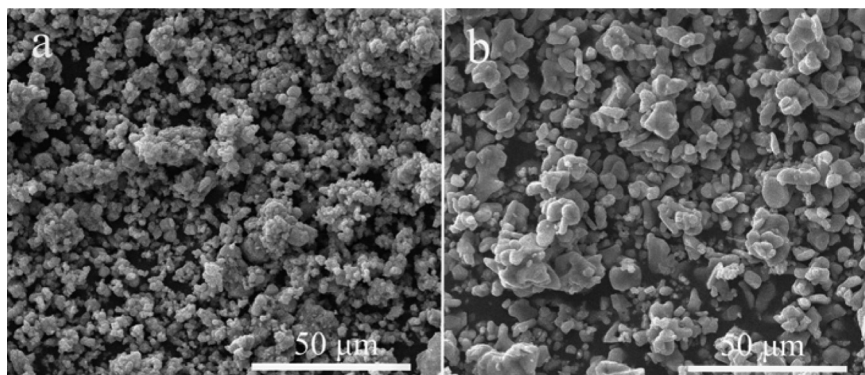


Fig. 1. SEM images of (a) LiCo_{0.998}Ti_{0.002}O₂ and (b) LiCoO₂/LiCo_{0.99}Ti_{0.01}O₂.

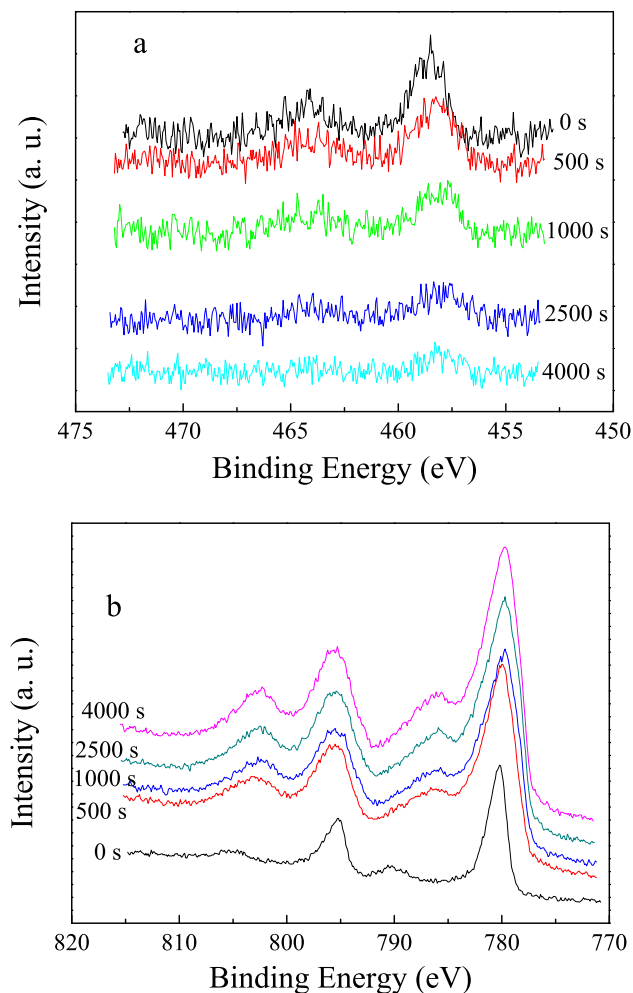


Fig. 2. (a) Ti2p and (b) Co2p XPS spectra of $\text{LiCo}_{0.998}\text{Ti}_{0.002}\text{O}_2$ powders with different sputtering times: 0, 500, 1000, 2500, 4000 s.

The first discharge capacity of $\text{LiCo}_{0.998}\text{Ti}_{0.002}\text{O}_2$ 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 $\text{LiCo}_{0.998}\text{Ti}_{0.002}\text{O}_2$ 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 $\text{LiCo}_{0.998}\text{Ti}_{0.002}\text{O}_2$ or $\text{LiCoO}_2/\text{LiCo}_{0.99}\text{Ti}_{0.01}\text{O}_2$ 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 $\text{LiCo}_{0.998}\text{Ti}_{0.002}\text{O}_2$ as $\text{LiCoO}_2/\text{LiCo}_{0.99}\text{Ti}_{0.01}\text{O}_2$ 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 $\text{LiCo}_{0.998}\text{Ti}_{0.002}\text{O}_2$, 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 $\text{LiCo}_{0.998}\text{Ti}_{0.002}\text{O}_2$ 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

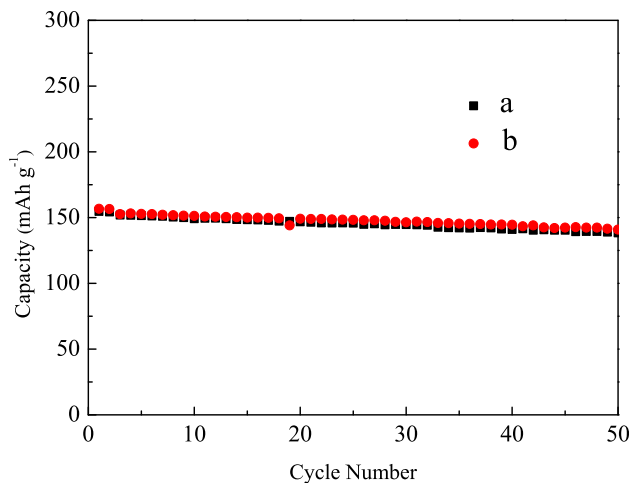


Fig. 3. Comparison of the cycling stability of (a) $\text{LiCo}_{0.998}\text{Ti}_{0.002}\text{O}_2$ and (b) $\text{LiCoO}_2/\text{LiCo}_{0.99}\text{Ti}_{0.01}\text{O}_2$ between 3.0 and 4.3 V at room temperature.

decreasing quickly with increasing the current rate, and only maintains a level of 53.9 mAh g^{-1} at 4 C. In order to figure out the different rate performance of $\text{LiCo}_{0.998}\text{Ti}_{0.002}\text{O}_2$ 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 $\text{LiCo}_{0.998}\text{Ti}_{0.002}\text{O}_2$ and the composite phase starts to get notable when the current increases to 3 C rate, where $\text{LiCo}_{0.998}\text{Ti}_{0.002}\text{O}_2$ 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 $\text{LiCo}_{0.998}\text{Ti}_{0.002}\text{O}_2$ than the composite phase should be the reason for their different rate performance. In our previous SEM observation, $\text{LiCo}_{0.998}\text{Ti}_{0.002}\text{O}_2$ 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.

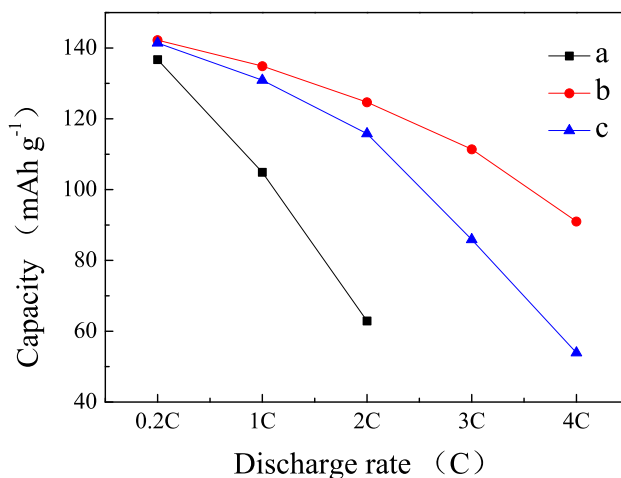


Fig. 4. Comparison of the rate performance of (a) LiCoO_2 , (b) $\text{LiCoO}_2/\text{LiCo}_{0.99}\text{Ti}_{0.01}\text{O}_2$ and (c) $\text{LiCo}_{0.998}\text{Ti}_{0.002}\text{O}_2$ materials. (Potential range: 3.0–4.2 V).

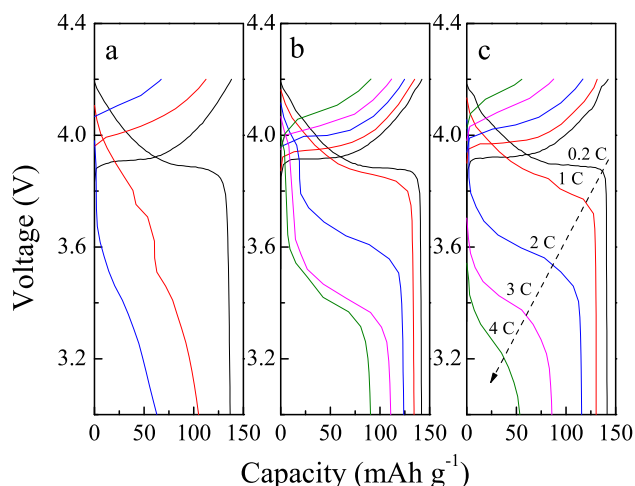


Fig. 5. The typical charge-discharge profiles of (a) LiCoO_2 , (b) $\text{LiCoO}_2/\text{LiCo}_{0.99}\text{Ti}_{0.01}\text{O}_2$ and (c) $\text{LiCo}_{0.998}\text{Ti}_{0.002}\text{O}_2$ materials at different C-rates. (Potential range: 3.0–4.2 V).

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 , $\text{LiCoO}_2/\text{LiCo}_{0.99}\text{Ti}_{0.01}\text{O}_2$ and $\text{LiCo}_{0.998}\text{Ti}_{0.002}\text{O}_2$ electrodes. Typically, the semicircle in the high frequency range (seeing the inset graph) represents the charge transfer resistance

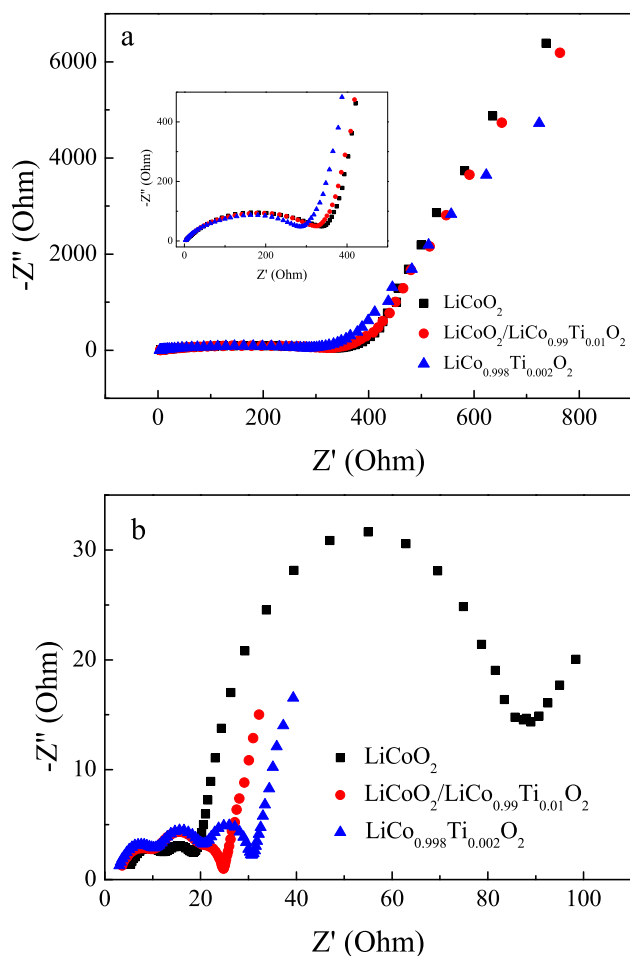


Fig. 6. AC impedance spectrums of (a) fresh and (b) cycled electrodes for pristine and Ti-modified LiCoO_2 materials.

(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 $\text{LiCo}_{0.998}\text{Ti}_{0.002}\text{O}_2$ 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 $\text{LiCo}_{0.998}\text{Ti}_{0.002}\text{O}_2$, 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.

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, $\text{LiCoO}_2/\text{LiCo}_{0.99}\text{Ti}_{0.01}\text{O}_2$ composite shows more uniform particle size distribution than the $\text{LiCo}_{0.99}\text{Ti}_{0.01}\text{O}_2$ 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 $\text{LiCo}_{1-x}\text{Ti}_x\text{O}_2$ solid solubility to higher x values. Therefore, further experimental verification of this proposed guideline is underway.

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