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Improved electrochemical performances of high voltage $LiCoO_2$ with tungsten doping*

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The effects of tungsten W doping and coating on the electrochemical performance of $LiCoO_2$ cathode are comparatively studied in this work. The amount of modification component is as low as 0.1 wt% and 0.3 wt% respectively. After 100 cycles between 3.0 V–4.6 V, 0.1 wt% W doping provides an optimized capacity retention of 72.3%. However, W coating deteriorates battery performance with capacity retention of 47.8%, even lower than bare $LiCoO_2$ of 55.7%. These different electrochemical performances can be attributed to the surface aggregation of W between doping and coating methods. W substitution is proved to be a promising method to develop high voltage cathodes. Practical performance relies on detailed synthesis method.

Keywords: cathode, lithium-ion batteries, lithium cobalt oxide, doping, coating

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1. Introduction

The rapid development of computers, communications, and consumer electronics requires more advanced lithium-ion batteries and battery materials. $LiCoO_2$ is the first commercialized cathode material and has been put into the 3 C field for a long time. At present, $LiCoO_2$ still owns the highest volumetric energy density benefiting from its high density. In the past few decades, $LiCoO_2$ has gone through a long process of development. In the 1990 s, the practical reversible capacity of $LiCoO_2$ used in the first commercialized lithium-ion battery was 140 mAh·g^{-1} ($\sim$ 4.2 V versus Li/Li$^+$), and now the value reaches as high as 170 mAh·g^{-1} ($\sim$ 4.4 V versus Li/Li$^+$). There is still room for further increase of the useable capacity at higher charging cut off voltage (theoretical capacity of $LiCoO_2$ is 274 mAh·g^{-1} for one mol of Li), however, the structural degradation during the phase transition process and interfacial instability between electrode and electrolyte are the main challenges to the successful application of high voltage $LiCoO_2$.[1,2]

The phase transition of $LiCoO_2$ at 4.6 V (extraction of more than 0.5 Li$^+$) causes severe changes in cell parameters. The phase transition from the hexagonal Li_xCoO_2 to the monoclinic CoO_2 can introduce more than 3.5% change along the c axis (compared with 2% change from $LiCoO_2$ to $Li_{0.5}CoO_2$).[3] This process is accompanied with a series of negative effects, including the dissolution of Co into the electrolyte, more active anions, and accumulation of mechanical strains.[4,5] As a result, the capacity will decay, oxygen will be released, and crack will be generated during battery cycle. Meanwhile, the formation of the unstable cathode electrolyte interphase (CEI) at high voltage can also affect the performance of $LiCoO_2$ at high cut-off voltage.[6–8] Numerous works have been devoted to solving the problems mentioned above. Detailed technical strategies include doping elements into $LiCoO_2$ crystal structure, coating the $LiCoO_2$ particles or electrode with different compounds, and adding additives into electrolyte.[9–11]

Doping or partial substituting of bare $LiCoO_2$ with different metal elements, such as Ti, Cr, Mn, Fe, and Zn, is known to be an effective way to enhance electronic conductivity and maintain structural stability.[12–16] One example of the bulk doping method is the high capacity $LiNi_xMn_yCo_{1-x-y}O_2$ solid solution cathode, which can be viewed as a co-doping of manganese and nickel in traditional layered $LiCoO_2$.[17] On the other hand, surface oxide coating on $LiCoO_2$ was introduced by Cho *et al.* in 2000, which can well improve surface stability and capacity retention.[18] After that, different compounds, such as oxide, phosphates, and fluorides, have also been used to improve the high voltage performances of $LiCoO_2$.[19–21] After doping or coating treatment, $LiCoO_2$ has more than 800 cycles at 4.4 V (with graphite as the anode) at 25 °C, which has been successfully applied in 2014.

Although different strategies have been used to enhance the electrochemical performance of $LiCoO_2$, the cut-off voltage of $LiCoO_2$ has not exceeded 4.45 V so far. Efforts are still being made to explore the limit voltage of $LiCoO_2$, such as charging the cathode materials to 4.6 V with a capacity of 220 mAh·g^{-1} (extraction about 0.8 Li$^+$). Considering

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the vital importance of the surface treatment on the battery performance at high voltage, different techniques have been carried out. Up to now, solid phase mixing, wet chemistry, and various film coating methods have been utilized to modify surface.[22–24] However, with the increase of the cut-off voltage, nearly all coating materials cannot deliver satisfactory performances. Therefore, more effective surface treatment methods are desired. Typically, cathodes materials contain 3d transition metal (TM) elements, such as Mn, Ni, and Co, and strong catalytic effect could trigger chemical or electrochemical side reactions of electrolyte on the surface. As a result, a buffer layer that consists of non-3d TM oxides may be a promising choice. Moreover, when battery is charged to higher voltage, oxygen release always occurs, accompanying with 3d TM migration. The structural instability will further accelerate the oxygen loss from crystal lattice.[25,26] It is presumed that 5d TM doping is likely to stabilize crystal structure and induce superior performance due to the larger radius and stronger chemical bonds.[27] As a result, 5d TM doping and surface coating is a potential method to develop high voltage cathodes of next generation, but there is still a lack of comprehensive investigations.

In this work, 5d TM doping tungsten (W) has been chosen as the modification element to improve the performance of $LiCoO_2$ at high cut off voltage (4.6 V versus Li/Li^+).

2. Experiment

2.1. Synthesis

A two-step solid-state sintering process was performed to synthesize the tungsten modified $LiCoO_2$ samples. For W-doped $LiCoO_2$, the Co_3O_4, Li_2CO_3, and WO_3 nano-powders were mixed together in air and sintered at 1000 °C for 15 hours. The obtained powder was grounded with a gate mortar and then annealed at 1000 °C for 15 hours to get the final product. For W-coated $LiCoO_2$, the Co_3O_4 and Li_2CO_3 were mixed in air and sintered at 1000 °C for 15 hours. The obtained powder was mixed with the WO_3 nano-powder and then annealed at 1000 °C for 15 hours to get the final product.

2.2. Electrochemical measurement

The working electrode was prepared by pasting the mixture of 80.0 wt% active material, 10.0 wt% carbon black, and 10.0 wt% polytetrafluoroethylene (PVDF) dissolved with N-methyl pyrrolidone (NMP) solvent onto thin Al foil (12 μm). The electrodes were punched into disks and then dried at 110 °C in vacuum for 6 hours. All the electrochemical tests were conducted using CR 2032 coin cell, assembled in an argon-filled glove box. 1-M $LiPF_6$ in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 in volume) was used as electrolyte. Li foil (500 μm) was used as the counter electrode and Al_2O_3 coated polyethylene (15 μm) was used as the separator. The charge and discharge tests were carried out using a Land CT2001 A battery test system (Land, Wuhan, China) in the voltage range of 3.0 V–4.6 V at room temperature. The electrochemical impedance spectroscopy measurements were performed at 25 °C by using an impedance analyzer (IM6ex) with a perturbation of 5 mV in the frequency range 10 mHz–1 MHz.

2.3. Characterization

The phase purity of $LiCoO_2$ was characterized using an x-ray diffractometer (D8 Advance, Bruker) equipped with a Cu Kα radiation source and a LynxEye_XE detector. The XRD patterns were collected in the scan range (2θ) of 10°–90° with an increment of 0.02°. The morphology of the $LiCoO_2$ samples was characterized by a field emission scanning electron microscope (FE-SEM, S4800, Hitachi). The mass spectroscopy was recorded by second ion mass spectroscope (SIMS) with the Hiden SIMS workstation. The XPS spectra and elemental XPS mapping were recorded by an ESCALAB 250 Xi, Thermo Fisher with monochromatic 150-W Al Kα radiation. The data was analyzed with software Avantage and the binding energies were calibrated by the C 1s line at 284.4 eV from adventitious carbon. The samples used for XPS and SIMS measurements are pellets which were pressed with powder under pressure of 5 MPa.

3. Results and discussion

As shown in the experimental section, the samples added WO_3 with $LiCoO_2$ precursors are described as doped materials. Similarly, the samples added WO_3 with first sintered $LiCoO_2$ are defined as coated materials. The SEM images of the bare and W modified $LiCoO_2$ are shown in Figs. 1(a)–1(e). The particle size of the W-doped $LiCoO_2$ is slightly smaller than that of the bare $LiCoO_2$. Figures 1(b) and 1(c) show the SEM images of W-doped $LiCoO_2$ particles with clean and smooth surface, implying that W has been successfully doped into the $LiCoO_2$ lattice. Figures 1(d) and 1(e) show the surface morphology of W-coated $LiCoO_2$ samples. Nano-sized dot-like species, which are identified as the WO_3 coating material, can be clearly seen and are uniformly distributed on the surface of $LiCoO_2$ particles. Note that we refer to WO_3 coated $LiCoO_2$ as W-coated $LiCoO_2$ for simplicity. With the increase in the amount of the coating material, the surface of $LiCoO_2$ demonstrates more complete coverage. It should be noted that the XRD patterns shown in Fig. 2 demonstrate that all five samples are the pure $LiCoO_2$ phase (S.G. R-3 m). Due to the small amount of the dopant, tungsten modification does not cause structural variation or introduce obvious impurity phase apparently. These results indicate that doping and coating samples exhibit a consistent crystal structure but present different surface structures. The difference in the electrochemical performance of doping and coating materials can be directly related to the surface structure due to different synthesis processes.

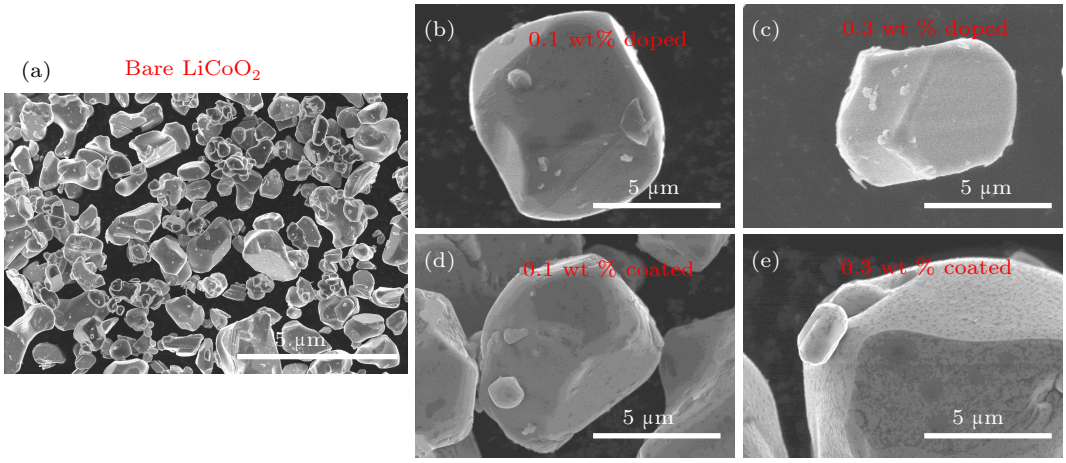


Fig. 1. (color online) SEM images of bare and W modified $LiCoO_2$ materials. (a) Bare $LiCoO_2$; (b) 0.1 wt% doped $LiCoO_2$; (c) 0.3 wt% doped $LiCoO_2$; (d) 0.1 wt% coated $LiCoO_2$; (e) 0.3 wt% coated $LiCoO_2$.

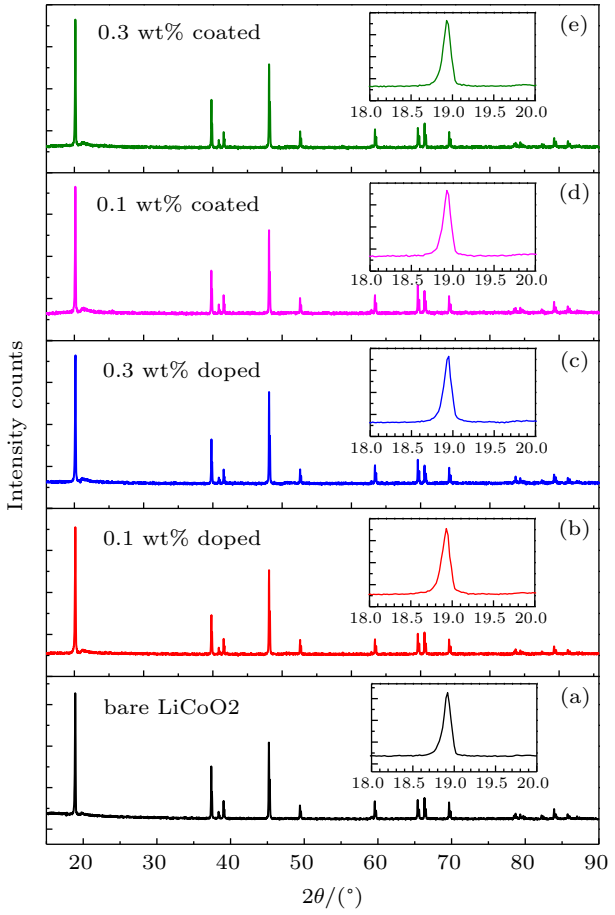


Fig. 2. (color online) XRD patterns of different $LiCoO_2$ materials, (a) bare material, (b) 0.1 wt% doped material, (c) 0.3 wt% doped material, (d) 0.1 wt% coated material, and (e) 0.3 wt% coated material. The insets show the magnified view of (003) peak of different $LiCoO_2$.

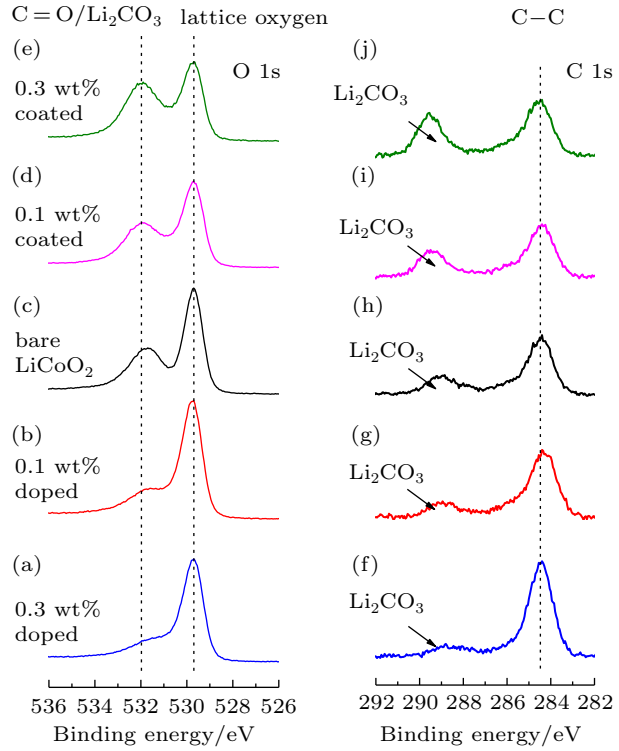


Fig. 3. (color online) The O 1s (left column) and C 1s (right column) XPS spectra of different $LiCoO_2$, (a) and (f) 0.3 wt% doped $LiCoO_2$, (b) and (g) 0.1 wt% doped $LiCoO_2$, (c) and (h) bare $LiCoO_2$, (d) and (i) 0.1 wt% coated $LiCoO_2$, (e) and (j) 0.3 wt% coated $LiCoO_2$.

X-ray photoelectron spectroscopy (XPS) measurements are performed to investigate the surface chemical states of the bare and W modified $LiCoO_2$. Figure 3 shows the spectra of C 1s and O 1s in different materials. For easy interpretation, the assignments of each XPS peak are summarized in Table 1. The signal from lattice oxygen and Li_2CO_3 residuals dominate the landscape of O 1s spectra of the bare $LiCoO_2$. Li_2CO_3 signal can also be found in C 1s spectrum, indicating the existence of Li_2CO_3 on bare $LiCoO_2$. Li_2CO_3 can often be found on layered oxide cathode materials due to the chemical reaction with moisture and CO_2 in the air during storage. After W doping, the peak at $\sim$ 532 eV in O 1s spectra demonstrating the presence of Li_2CO_3 or O–C=O type groups becomes weak. At the same time, peak at $\sim$ 289.5 eV in C 1s spectra is also weak, confirming less Li_2CO_3 accumulated on the surface. However, W coating seems unable to suppress the accumulation of Li_2CO_3 on the surface of $LiCoO_2$, as significant signal belonging to Li_2CO_3 can be observed in O 1s spectra

of surface coated $LiCoO_2$. Dahn *et al.* have suggested that the surface species caused by air or moisture exposure could cause the poor performance of $LiCoO_2$ at high voltage.[28] The XPS results are consistent with the different electrochemical performances between bare and doping/coating $LiCoO_2$, as discussed below. With more Li_2CO_3 on the surface, poorer electrochemical performances can be detected in W-coated $LiCoO_2$.

Table 1. Summary of XPS peak assignments.

Binding energy/eV	Peak	Assignments
~ 529.7	O 1s	lattice oxygen in $LiCoO_2$
~ 532.0		carbonate or O–C=O
~ 284.4	C 1s	C–C
~ 289.5		Li_2CO_3

XPS mapping experiments are also performed to uncover the detailed element distributions of W, Co, and O on the surface of $LiCoO_2$ particles. As shown in Fig. 4, the XPS mapping can be achieved by software Avantage, which presents element spatial distributions from W, Co, and O separately in each map. The strongest peak is selected as the identification standard for the three elements. For bare $LiCoO_2$, the XPS mapping demonstrates symmetric distribution of Co (green dots) and O (red dots). The relative spatial distribution of W (blue dots), Co (green dots), and O (red dots) can be viewed as the indicator of uncovered $LiCoO_2$. The XPS mapping results of W-doped and W-coated materials are shown in Fig. 4. It is obvious that with the increase of the modification element, the surface areas of the exposed pure $LiCoO_2$ become smaller. Moreover, combing with the XPS spectra of W 4f in Fig. 5, the coated materials present higher W concentration compared to the doped ones despite the consistent nominal W stoichiometry. The valence of W in both doped and coated materials is W^{6+}, confirmed by the peak position of W 4f. The XPS mapping results verifies the distinguishable W distribution in samples from different synthesis methods.

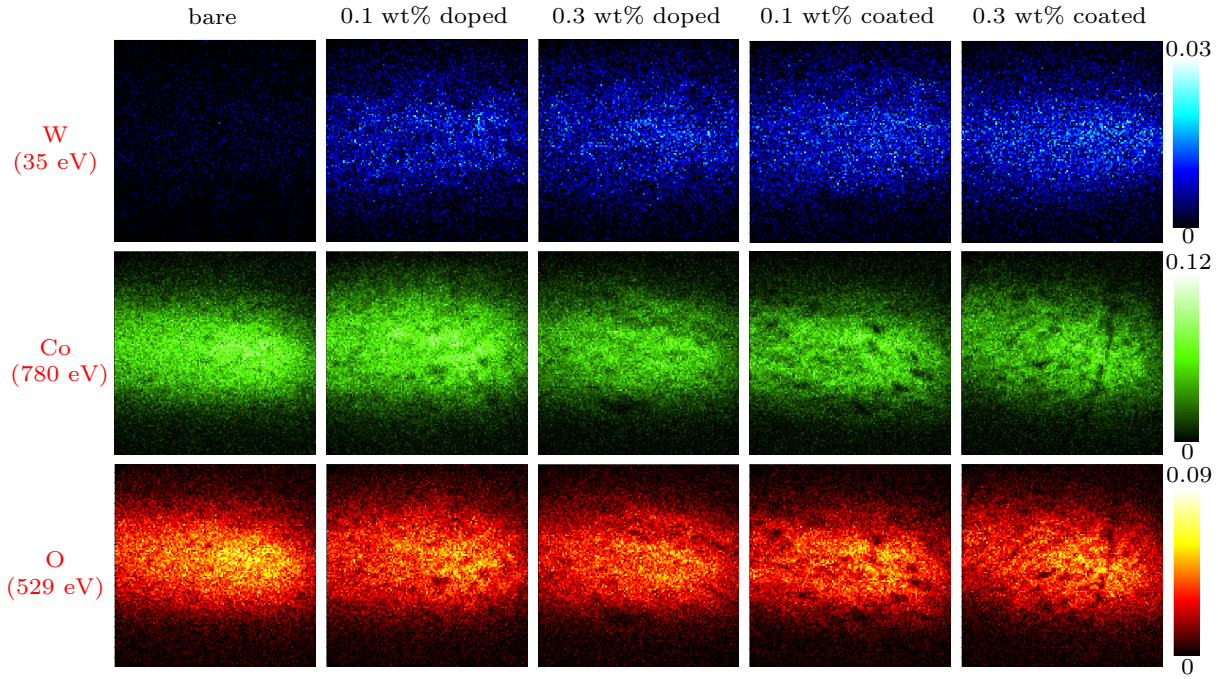


Fig. 4. (color online) XPS mapping on the surface areas of different materials. The binding energy at 35 eV (W, blue dots), 780 eV (Co, green dots), and 529 eV (O, red dots) are chosen as the characteristic peaks for each element.

In order to further verify the spatial elemental distribution, depth profiles of W are characterized. A raster mode of SIMS provided by the Hiden SIMS is used, and a bigger ion beam current (100 nA) is applied to reflect the depth profile more accurately. Figure 6(a) shows the depth profile of tungsten on different $LiCoO_2$ derivatives, which indicates the W concentration distribution from surface to inner core of $LiCoO_2$ particles. It is obvious that the tungsten is enriched on the W coated $LiCoO_2$. The W-doped $LiCoO_2$ also shows a decay of the W signal, indicating a relatively higher surface concentration of W than bulk as well. The schematic diagram of the mechanism of two different surface treatment methods is shown in Fig. 6(b).

Electrochemical impedance spectroscopy (EIS) is carried out to investigate the internal resistance, as shown in Fig. 7. Overall, the impedance spectra of all cells with different $LiCoO_2$ materials show gradual increase upon electrochemical cycling. For each individual curve, three regions can be clearly identified, including a high frequency semicircle (R_{SEI}), a mediate frequency semicircle (R_{CT}), and a slope line at low frequency (W). The initial resistance of the doped $LiCoO_2$ is smaller than that of the bare $LiCoO_2$, while the re-

sistance of the coated $LiCoO_2$ shows the highest resistance value (Fig. 7(a)). Upon electrochemical cycling, the increase of the impedance becomes more significant for the cell with W coated $LiCoO_2$ (Fig. 7(b)). The highest impedance of the coated material demonstrates that a large amount of W accumulation on surface hinders the Li diffusion across the interface. While doping can effectively lower the impedance and favor the Li^+ migration, the effect of foreign atoms introduction strongly relies on the detailed synthesis method. With W doping into crystal lattice, especially accumulating at particle surface, $LiCoO_2$ surface area may well form lithium tungsten oxide compounds. As has been reported, lithium tungsten oxides, such as Li_2WO_4 and $Li_2\ W_2O_7$, exhibited good lithium ion conductivity.[29] And Hayashi *et al.* further proved that lithium tungsten oxides deposited on positive active materials could decrease the interfacial resistance of $LiCoO_2$.[30] As a result, the formation of lithium tungsten oxide compounds on particle surface could enhance the transportation of lithium ion on the surface area. As for the coated materials, the WO_3 is enriched on the surface of $LiCoO_2$. The lithium intercalation potential of WO_3 is lower than 3.0 V (1.589 V versus Li/Li^+), so the surface enriched WO_3 cannot participate into the Li transmission process and further hinders the transport of lithium ion.[31,32]

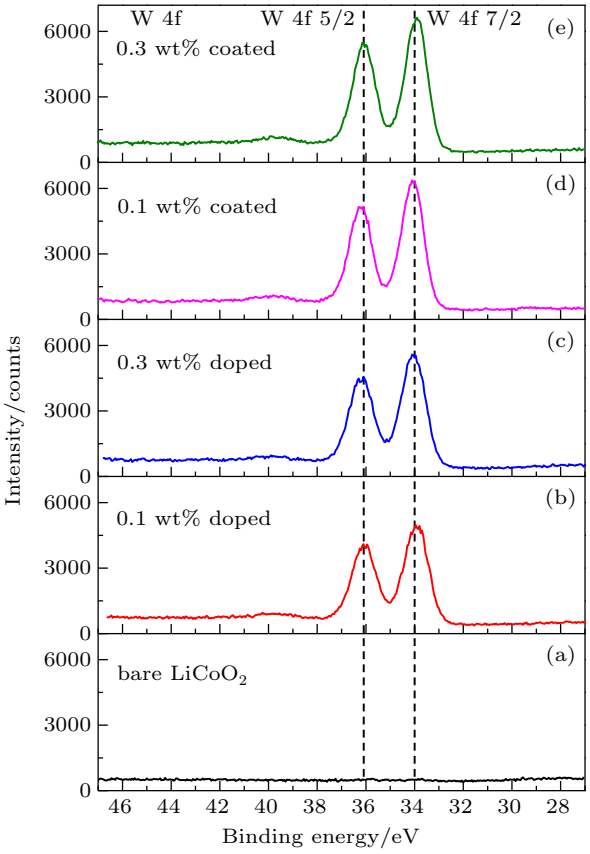


Fig. 5. (color online) The W 4f spectra of different $LiCoO_2$ powders, (a) bare material, (b) 0.1 wt% doped material, (c) 0.3 wt% doped material, (d) 0.1 wt% coated material, and (e) 0.3 wt% coated material.

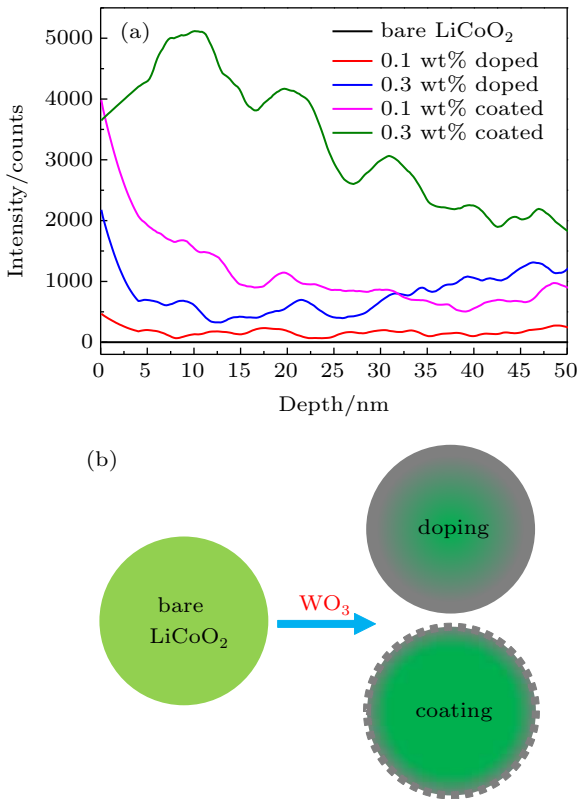


Fig. 6. (color online) (a) The depth profile of tungsten abundance at the interface of different $LiCoO_2$ materials. (b) The schematic diagram of the mechanism of two different surface treatment methods.

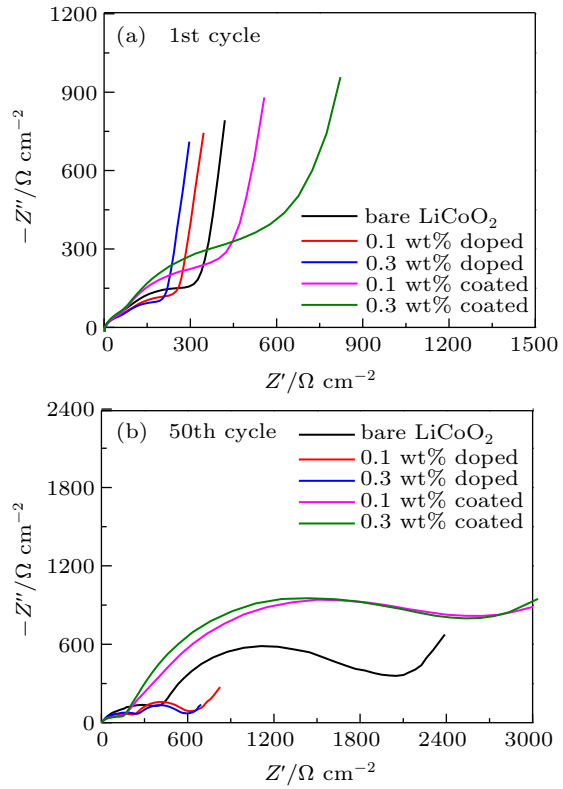


Fig. 7. (color online) The electrochemical impedance spectra of $LiCoO_2$/Li battery measured after (a) 1st cycle and (b) 50th cycle. The spectra were collected at 25 °C between 1 MHz and 1 mHz.

Figure 8(a) shows the cycle performance of bare and W modified $LiCoO_2$ (1 wt% and 3 wt%) with different contents of W. It is very interesting that the capacity of $LiCoO_2$

has increased gently after minute quantities of W modified. This phenomenon is consistent with the results of Ti-doped $LiCoO_2$. The ionic radius of W^{6+} (0.6 Å) is similar to that of Ti^{4+} (0.605 Å), so they may express similar effects on the performance of $LiCoO_2$.[13] The values of the typical capacity are shown in Table 2. The W doped $LiCoO_2$ materials show much improved cycle performances than bare $LiCoO_2$. 70.1% of initial capacity can be retained for 0.3 wt% W-doped $LiCoO_2$ after 100 cycles in the charge–discharge voltage range of 3.0 V–4.6 V, while only 55.7% for the bare one (compare with the 2nd cycle). In contrast, W coating does not benefit battery performances, as both the initial capacity and cycle stability decrease for coated $LiCoO_2$. The detailed mechanism of different electrochemical behaviors can be attributed to the modification of the surface properties of $LiCoO_2$ active particles. Figure 8(b) shows the charge–discharge curves of 0.1% W-doped sample at 1st and 200th cycles. The polarization of the battery increases dramatically after cycling, which is corresponding to the result of EIS.

Table 2. Typical discharge capacity values of different $LiCoO_2$ (in unit $mAh{\cdot}g^{-1}$).

Cycle numbers	Bare $LiCoO_2$	0.1% doped	0.3% doped	0.1% coated	0.3% coated
1st	220	223	220	224	220
2nd	192	202	211	205	205
50th	121	158	166	114	110
100th	107	146	148	98	101

It can be concluded from the above discussion that 5d TM elements, such as tungsten, could effectively improve the performance of $LiCoO_2$ at high voltage. However, how to use these elements to get the best results relies on the detailed synthesis method. A small amount of W can increase the discharge capacity of $LiCoO_2$ from 220 $mAh{\cdot}g^{-1}$ to 224 $mAh{\cdot}g^{-1}$, but a large amount of impurity element will certainly lead to a decline in specific capacity. Another notable question is the existent form of W in the materials. Whether tungsten ionic are present in crystal lattice or just enriched at the grain boundary still needs further research. First principles calculation can forecast the results from the view of thermodynamic stability. Maybe the ABF-STEM or synchrotron radiation imaging technology can help us to uncover the truth of these questions. Although in this work the performance of coating materials is not as good as the doping ones, surface coating is still an effective mean to enhance the electrochemical stability of cathode materials. On the other hand, the process conditions during synthesis have great influence on the properties of the material, so further explorations are still needed to confirm the conclusion in this work. At the same time, only W-doped materials are not good enough to improve the performance of high voltage $LiCoO_2$ to meet the requirement of practical applications. The Coulombic efficiency of W-modified materials is only 99.4%, far from the target of 99.9%. Various modification methods, such as ultrathin surface protect layer, homogeneous bulk doping, and concentration gradient design, are also needed to improve the performance. Further research may focus on the process optimization and new element exploration.

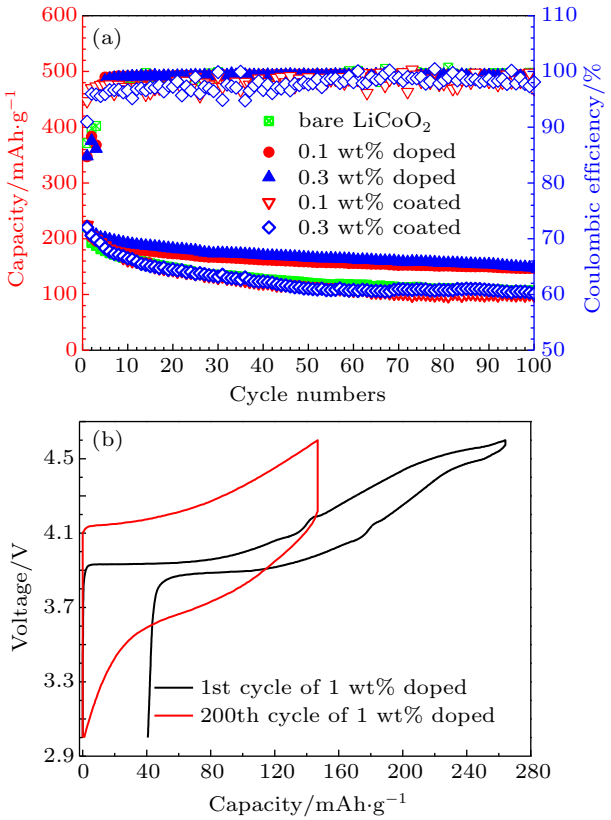


Fig. 8. (color online) (a) The cycling performance and coulombic efficiency of $LiCoO_2$/Li battery for the first 100 cycles. All batteries are activated by a cycle of low-rate (0.1 C, 1 C = 274 $mAh{\cdot}g^{-1}$) charge/discharge before the stability test at 1 C (1 C = 274 $mAh{\cdot}g^{-1}$) in the voltage range of 3.0 V–4.6 V (versus Li/Li^+). (b) The charge–discharge curves of 0.1% W-doped sample at 1st and 200th cycles.

4. Conclusion and perspectives

In summary, a small amount (0.1 wt% and 0.3 wt%) of tungsten-modified (doped and surface coated) $LiCoO_2$ is synthesized via a solid-state reaction method. The capacity retention of W-doped material is 72.3% after 100 cycles at 3.0 V–4.6 V, which is higher than that of the bare material (55.7%) and the coated one (47.8%). We find that W is enriched on the surface of $LiCoO_2$, especially in the coated materials. The W mainly concentrates on the surface of $LiCoO_2$ particles with a depth of 30 nm. It means that W is not easily to be doped into the materials uniformly. Trace W-modified materials can contribute to the specific capacity of $LiCoO_2$ (improved with 4 $mAh{\cdot}g^{-1}$ of the 0.1 wt% modified material). The surface impurity (such as Li_2CO_3) on the active particles is also proved

to be harmful to the electrochemical stability of $LiCoO_2$. This work highlights that the appropriate treated method is very important for the application of new modified element. The 5d TM elements may be promising candidates as the modified elements for the next generation high voltage cathode materials.

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