Sputtering TiO₂ on LiCoO₂ composite electrodes as a simple and effective coating to enhance high-voltage cathode performance

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Abstract:

Surface coating is a key strategy in lithium-ion battery technologies to achieve a high and stable battery performance. Increasing the operation voltage is a direct way to increase the energy density of the battery. In this work, TiO_2 is directly sputtered on as-fabricated LiCoO_2 composite electrodes, enabling a controllable oxide coating on the topmost of the electrode. With an optimum coating, the discharge capacity is able to reach 160 mAh g^{-1} (86.5 % retention) after 100 cycles within 3.0–4.5 V at 1 C, which is increased by 40 % compared to that of the bare electrode. The high-voltage rate capability of LiCoO_2 is also remarkably enhanced after TiO_2 -coating as reflected by the much larger capacity at 10 C (109 vs. 74 mAh g^{-1}). The artificially introduced oxide coating is believed to make the LiCoO_2 electrode more resistant to interfacial side reactions at high voltage and thus minimizes the irreversible loss of the active material upon long cycling. The TiO_2 coating layer is also possible to partially react with the decomposition product of electrolyte (e.g. HF) and form a more stable and conductive interphase containing TiF_x , which is responsible for the improvement of the rate capability.

Keywords: LiCoO_2 ; surface coating; magnetron sputtering; TiO_2 ; high voltage; high temperature

1. Introduction:

To meet the increasing demand of power units for future electronic devices, high-voltage Li-ion batteries (LIBs) are under intensive research with the aim to push up the energy density limit [1]. For long, LiCoO₂ has been the dominating cathode material for commercial LIBs due to its high capacity, stable cycling and easy production. Compared with other known materials, LiCoO₂ also has the largest true density (5.2 g cm⁻³), which is a highly weighted factor in particular for small-format power units. Although LiCoO₂ has been studied for tens of years, the efforts to further improving its performance has never stopped and the exploration of its high-voltage limit becomes increasing active in recent years [2-7].

Theoretically, it is still possible to further increase the capacity of LiCoO₂ by elevating its charging potential above the normal limit of 4.25 V vs. Li/Li⁺ in order to push up its energy density. However, it experiences disastrous degradation of the cycling and rate performances when charged e.g. to 4.5 V. Several reasons including reduced structural stability, dissolution of metal ions and fast growth of solid electrolyte interphase (SEI) are ascribed to this degradation [8, 9]. In order to address this issue, surface coating has been extensively studied using a number of different materials. Carbon coatings, which are commonly used in LIB electrode materials [10-12], have been studied to tune electronic/ionic properties of LiCoO₂ [13-15]. Besides, the usage of metal oxides such as ZnO [16], MgO [17] and Al₂O₃ [18] as coating materials are found even more promising due to the synergetic effects of physical protection (partial electrolyte isolation) and chemical interactions (e.g. scavenging HF) [19, 20]. In addition to the species of coating material, the coating approach and thickness are other important factors need to be considered for obtaining the best effect. In previous reports,

wet-chemical methods were enormously reported for coating electrode materials [21-23]. However, precise and reproducible control of the coating thickness seems to be inconvenient in these cases, and an additional high-temperature annealing is usually needed to complete the coating. Beside these approaches, some other methods that enable precise control of the coating thickness have been developed. Atomic layer deposition (ALD) is one example which is successful to bring remarkable improvement for many electrode materials [24-29]. Besides, magnetron sputtering (MS) is another newly developed coating method gaining increasing attention [30-40]. As we know, MS has been widely used in diverse fields for fabrication of thin film materials [41, 42]. It is less costly and more time-efficient than ALD. The major feature of MS-coating is that the sputtered material is coated mainly on the outer surface of the composite electrode, while for other coatings a conformable coating structure is normally derived, with all the powders of the active materials being equally coated at all sites. In this consideration, MS-coating is supposed to modify only the surface of the composite electrode while the interior electrode remains basically unchanged, imposing little effect on the electronic conduction of the bulk electrode. Furthermore, for MS coating, no additional annealing is required to accomplish the transformation from the precursor to the desired coating material, which however is necessary for wet-chemical coatings. Recently, ZnO and alumina-doped ZnO (AZO) MS-coatings on LiCoO₂ composite electrodes were studied and have shown great improvements of the high-voltage electrochemical performance [37, 38].

In the present study, we aim to further explore the MS-coating for extending the high-voltage performance of LiCoO₂. Titanium dioxide (TiO₂), which is another highly interested wide band-gap semiconductor, is selected for this study due to its easy availability

and numerous applications [43]. TiO_2 itself has also been studied as an anode material for LIBs, with the redox potential of ~ 1.8 V vs. Li/Li^+ [44]. In fact, the use of TiO_2 in LiCoO_2 coating has been attempted by a few researchers with wet-chemical and ALD approaches. Using titanium tetrabutoxide as the sol-gel precursor, Fey et al. [45] realized improved cycling stability of LiCoO_2 within 2.75–4.4 V. The effect of TiO_2 coating was explained by the Ti doping during high-temperature annealing, forming a $\text{Li}_x\text{Ti}_y\text{Co}_{1-y}\text{O}_{2+0.5y}$ surface layer which could suppress the hexagonal/monoclinic/hexagonal phase transitions of LiCoO_2 . However, the rate performance of the TiO_2 -coated electrode was unknown and the analysis of the coating layer was lacking. Chen et al. [46] reported TiO_2 ALD coating on LiCoO_2 composite electrodes using titanium isopropoxide as the Ti precursor, but the obtained improvement of the high-voltage cycling performance (3.0–4.5 V) was very limited, and the rate capability of the electrodes was unreported either. To our knowledge, the use of direct MS for TiO_2 coating has not yet been reported to modify the LiCoO_2 cathode.

In this work, TiO_2 is one-step coated on as-fabricated LiCoO_2 composite electrodes via facial MS technique. The high-voltage (3.0–4.5 V, maximum to 4.7 V) electrochemical performances of the LiCoO_2 electrodes, including the room-temperature (RT) and high-temperature (50 °C) cycling stability and rate capability are systematically reported, which all showed remarkable improvements after optimized TiO_2 coating. With a combination of electrochemical and material characterization techniques, the mechanisms of the protective TiO_2 coating layer during high-voltage cycling are discussed.

2. Experimental

2.1. LiCoO₂ composite electrodes and TiO₂ coating

LiCoO₂ composite electrodes were prepared by spreading well-mixed LiCoO₂ powders (HUNAN CHANGYUAN LICO CO., LTD., China.), acetylene black (AB) and polyvinylidene fluoride (PVDF) on a piece of Al foil. The weight ratio of LiCoO₂, AB and PVDF is 8:1:1. The coating layer was directly deposited on the as-fabricated composite electrodes by radio-frequency (RF) magnetron sputtering using a commercial TiO₂ target. The MS-coating were performed with the electrode temperature of 110 °C, while the sputtering power and Ar pressure were 80 W and 0.5 Pa, respectively. During sputtering, the electrode was rotated to guarantee a uniform coating on the surface. The uncoated and TiO₂-coated electrodes are labeled as LCO-bare and LCO/TO_x, respectively, where x represents the sputtering time in min. The deposition rate of TiO₂ is evaluated to be 2 nm min⁻¹ by measuring the thickness of a TiO₂ film additionally deposited on a quartz substrate.

2.2. Material characterizations and electrochemical tests

X-ray diffraction (XRD) were performed on a Panalytical X'Pert Pert Pro MPD using Cu K_α radition ($\lambda = 1.5406 \text{ \AA}$) to study the phase structure of the material. The morphology of the electrodes was observed by using a field emission scanning electron microscopy (FESEM, Hitachi S3400N). X-ray photoelectron spectroscopy (XPS, Kratos XSAM800) was used to analyze the surface of the electrodes using Al-K_α (1486.6 eV) radiation as the primary excitation source operated at 150 W. The binding energies were calibrated using the C 1s level (284.6 eV) as an internal reference.

LiCoO₂/Li half-cells were assembled in a glove-box filled with Ar. The electrodes and

separators (polypropylene, Celgard 2400) were dried in vacuum overnight at 110 °C and 50 °C, respectively, **prior to the cell assembly**. 1 M LiPF₆ dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1 : 1, v/v) was used as the liquid electrolyte. The galvanostatic charge/discharge tests were performed between 3.0 V and 4.5 V *vs.* Li/Li⁺ at various C rates (1 C = 140 mA g⁻¹) using a CT2001A cell test instrument (LAND Electronic Co.). Electrochemical impedance spectroscopy (EIS) measurements were performed on half-cells charged to 4.5 V using an electrochemical workstation (CHI660B) in the frequency range from 10⁵ to 10⁻² Hz.

3. Results and discussion

Fig. 1 shows the XRD patterns and FESEM images of the LiCoO₂ composite electrodes coated with TiO₂ for different time. The **LiCoO₂ active material** can be well indexed to the α-NaFeO₂ structure (space group: R3m). It is found that the MS-coating brings no change to the material's phase structure. Some peaks of the Al current collector are detected due to limited thickness of the electrode. No diffraction peaks related with any TiO₂ phase can be observed within the resolution of the diffractometer, which is probably due to the small amount, or the amorphous nature of the sputtered coating layer. **By comparison of the surface morphologies, it is not easy to distinguish the oxide coating layer because of the co-existence of some nanoparticles from the additives. Further proof of the existence of TiO₂ coating layer will be provided later by XPS measurements.**

Fig. 1. (a) XRD patterns and (b-f) FESEM images of the bare and TiO_2 -coated LiCoO_2 .

While MS-coating of TiO_2 causes no vital change in the electrode's phase structure and morphology, it leads to a significant change of their electrochemical performances as shown in **Fig. 2**. From the initial charge/discharge curves (Fig. 2a) it is found that the charging potential plateaus of the electrodes are increased after TiO_2 coating, while the **discharging potential plateau** is decreased. More clearly, the potential **difference** between the anodic and cathodic peaks becomes larger as the sputtering time increases (Fig. 2b), indicating increased polarization of the electrode with the increase of TiO_2 thickness. This can be ascribed to the low electrical conductivity of TiO_2 as well as inadequate electrode-electrolyte wetting. Nevertheless, **we can observe** that all TiO_2 -coated electrodes exhibit higher initial coulombic efficiency than the bare electrode (93% vs. 85%). This is a strong indication of suppressed irreversible redox reactions such as electrolyte decomposition and SEI formation **on the modified electrode**. Due to an obvious improvement **in** the first cycle, the subsequent cycling stability of **LiCoO_2 electrodes with all coating thicknesses** are promoted. With increase of the sputtering time, as shown in Fig. 2c and 2d, the cycling performance is improved monotonically at first and then slightly attenuated, yielding the best performance when coated

for 5 min (approximates a thickness of 10 nm). After 100 cycles, LCO/TO5 shows the largest capacity retention of 86.5 % among all electrodes. The discharge capacity of this electrode has reached 160 mAh g^{-1} , which is increased by over 40% as compared to that of the bare one (115 mAh g^{-1}). **Fig. 3** compares the rate capability of the bare electrode and LCO/TO5. At the largest rate of 10 C, LCO/TO5 is able to deliver a reversible capacity of 109 mAh g^{-1} , which is enhanced by 47 % as compared to LCO-bare (74 mAh g^{-1}). After returning to 0.2 C, the capacity of LCO/TO5 can also be recovered to a higher level than the bare one ($179\text{--}184 \text{ mAh g}^{-1}$ vs. $171\text{--}177 \text{ mAh g}^{-1}$).

Fig. 2. Room-temperature electrochemical performances of the bare and TiO_2 -coated electrodes. (a) Initial charge/discharge curves, with the initial coulombic efficiency in the inset; (b) dQ/dV differential curves for the first cycle; (c) cycling performance at 1 C within

3.0 V and 4.5 V vs. Li/Li^+ ; (d) capacity retention of the 100th cycle.

Fig. 3. Room-temperature rate capability of LCO-bare and LCO/TO5 cycled within 3.0–4.5 V vs. Li/Li^+ .

The above cycling stability and rate capability improvements can indicate an important protective role of the TiO_2 coating layer, which can be evidenced by ex-situ XRD measurement. **Fig. 4** shows the XRD patterns of the electrodes before and after 50 cycles. It is observed that the cycled LCO/TO5 shows relatively **higher intensity in** the (003) peak than the cycled LCO-bare. In addition, the broadening of the (003) peak after cycling is much less significant in LCO/TO5 as seen from the calculated full width at half maximum (FWHM) values. The ex-situ XRD results suggest that the TiO_2 -coating is able to considerably relieve the unfavorable grain disintegration of LiCoO_2 during high-voltage cycling, **an important reason** for the high-voltage capacity degradation of bare LiCoO_2 .

Fig. 4. Comparison of the XRD patterns of the electrodes before and after 50 cycles.

For further study, EIS tests were performed on the cycled electrodes and the Nyquist plots are shown in **Fig. 5**. The Nyquist plots are composed of a linear part at low frequencies (Warburg resistance), and two semicircles at high frequencies which correspond respectively to the surface layer resistance (R_f) and the interfacial charge transfer resistance (R_{ct}). Using a Voigt-type equivalent circuit for the data fitting, the R_f and R_{ct} values of the LCO/TO5 after 100 cycles are determined to be 34 Ω and 145 Ω , respectively, which are smaller than those of the bare electrode (42 Ω and 449 Ω) after the same number of cycles. In particular, the reduction of the charge transfer resistance is more significant for LCO/TO5, suggesting much easier Li^+ and electron transfer at the interface of the coated electrode. Also, the greater slope of the Warburg impedance ($k = 0.89$ for LCO/TO5 vs. $k = 0.64$ for LCO-bare) reveals enhanced Li^+ transport in the **bulk electrode** [47, 48]. In order to quantitatively determine the apparent Li^+ diffusion coefficient (D_{Li^+}) of the electrode, CV measurements were carried out with varying sweeping rates, and the results are displayed in **Fig. 6**. It is observed that the current densities (I_p) of the anodic peaks show good linear relationship with the square root of

the sweeping rate ($v^{1/2}$). By using the Randles-Sevcik equation [38, 49], the derived Li^+ diffusion coefficient of the TiO_2 -coated electrode ($3.67 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$) is slightly greater than that of the bare one ($2.48 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$), which basically agrees with the EIS results.

Fig. 5. EIS Nyquist plots of the bare and TiO_2 -coated electrodes after the 100th charge (4.5 V), with a zoom-in part of the figure and the equivalent circuit model in the inset.

Fig. 6. CV profiles of (a) LCO-bare and (b) LCO/TO5 with varying sweeping rates; (c) I_p - $v^{1/2}$ plots and the calculated D_{Li^+} .

In order to see the behavior of the electrodes in more rigorous environments, such as over-heated or over-charged, the electrodes were tested at elevated temperature (50 °C) or voltage (charged to 4.7 V). The obtained electrochemical performances are summarized in

Fig. 7. Due to the high-voltage/temperature intensified electrolyte decomposition, interface side reactions and the reduced structural stability of LiCoO_2 , the cycling performances of both LCO-bare and LCO/TO5 become much worse than tested at RT and 4.5 V. Even though, the effect of the TiO_2 coating can be observed after certain number of cycles. As reflected by the faster capacity decay at 4.7 V than that at 4.5 V in the first ten cycles, which are similar for LCO-bare and LCO/TO5, we can see that the TiO_2 coating shows little effect to withstand the intrinsic structural collapse of LiCoO_2 at extremely high voltage. However, one notices that when cycled at 4.5 V, the capacity can be much earlier improved (since the second cycle) by TiO_2 . For the cycling at 50 °C, the initial capacity of the coated electrode is slightly improved, and a more obvious improvement of the cycling stability begins after 60 cycles. For the case of elevating the voltage (4.7 V, RT), this improvement appears relatively earlier (after 25 cycles). In addition, the high-temperature rate capability of the electrode is also greatly enhanced after TiO_2 -coating (Fig. 7b). Although the capacity degradation are still too fast to enable ultra-high-voltage or high-temperature application of LiCoO_2 , the effect of TiO_2 sputter-coating in improving the cycling stability and rate capability of LiCoO_2 electrodes are clearly demonstrated by such extreme tests.

Fig. 7. (a) Comparison of the electrodes' cycling performances at different temperatures (RT and 50 °C) or charged to higher potentials (4.5 V and 4.7 V); (b) high-temperature (50 °C) rate capability of the bare and TiO₂-coated electrodes cycled within 3.0–4.5 V vs. Li/Li⁺.

For further elucidation of the mechanism of TiO₂-coating, the composite electrodes after the first ten cycles were subjected to XPS studies and the results are displayed in **Fig. 8**. As seen from the full spectra (Fig 8a), evident signals of Ti and O are identified in the cycled LCO/TO5, while the signal of Co is very weak, indicating the cycled LCO/TO5 has a different surface layer with the bare electrode. In the detailed spectra of Ti 2p (Fig. 8b) and O 1s (Fig. 8c), one can determine the existence of TiO₂ in the form of Ti⁴⁺ on the electrode surface from the Gaussian-distributed Ti 2p_{3/2} and O 1s peaks centered at 458.7 eV and 530.4 eV, respectively [50]. A broad shoulder on the high binding energy side of the O 1s spectra is

found, which can be attributed to O–H bonds from hydroxyl groups or water molecules adsorbed on the electrode surface [50, 51]. After cycling of the bare electrode, the F 1s peak centered at ~ 688 eV (associated with PVDF and other C-F bonds) becomes stronger and shows a slight shift toward higher binding energies. Meanwhile, from Fig. 8d we can see that the C 1s peak centered at 284.6 eV (associated with carbon additive) is decreased while those at 291 eV (CF₂ in PVDF) evolve into some carbonates (290.5 eV), with an increase of another C-F-related peak at (285.8 eV). These changes indicate that the surface constitutes of the bare electrode become more complicated after cycling, forming some carbonates (possibly Li₂CO₃) and other complex organic products by consumption of some PVDF, carbon and active material, which can also be inferred by the reduction of the Co 2p peaks. From this information, it is to understand that a highly impeding SEI layer has been resulted on the surface of the unmodified electrode by continuous formation of these complex carbonates, especially at high voltage, which consequently results in deteriorated electrochemical performance. In contrast, after TiO₂ sputter-coating, the electrode's C 1s spectrum experiences only limited change, with much less formation of C-F and carbonate-related phases. Another important information from the XPS results is that the LCO/TO5 surface seems to be covered by a certain amount of fluoride layer as inferred by the F 1s spectra (Fig. 8e). With a less intense peak at ~ 687 eV which comes from the complex SEI, an additional peak is observed at 685.8 eV in the F 1s spectrum of LCO/TO5. This peak can be associated with either residuals of the F-containing electrolyte, or some newly formed metal fluorides such as LiF and TiF_x. The latter inference is considered to be more likely as the bare electrode witnesses this peak neither before nor after cycling. The presence of the fluoride layer has even covered

the signal of Co as shown in Fig. 8f. In our previous study using ZnO as the coating material, the presence of certain metal fluoride layer was also similarly observed after the electrode experienced several cycles (in the form of ZnF_x or AlO_xF_y) [37]. Because TiO_2 and ZnO are both Lewis bases which can react with HF, we believe that a part of TiO_2 materials on the electrode surface is transformed into fluorides after high-voltage electrochemical cycling in the acidic electrolyte. This metal fluoride layer is believed to have a higher chemical stability and ionic conductivity than the active material as well as the unfriendly SEI, which can to a great extent prevent further surface passivation and capacity degradation of the electrode during prolonged cycling. Dynamically, once the fluoride layer is formed which consumes most of the HF, the TiO_2 layer can be very stable on the electrode surface, which provide effective protections against further electrolyte decomposition and surface dissolution. In one word, the sputtered oxide layer and the reacted fluoride layer may have a synergetic effect in improving the the capacity retention and rate capability of LiCoO_2 at high voltage.

Fig. 8. XPS spectra of LCO-bare and LCO/TO5 after 10 cycles at 1C. (a) full spectra; (b) Ti

2p spectra; (c) O 1s spectra; (d) C 1s spectra; (e) F 1s spectra; (f) Co 2p spectra.

4. Conclusions

TiO₂ is studied as a coating material directly sputtered on LiCoO₂ composite electrodes to improve the high-voltage electrochemical performance of the electrode. The room-temperature cycling stability of the electrode is remarkably improved by ~ 10 nm TiO₂ coating. The discharge capacity of the TiO₂-coated electrode reaches 160 mAh g⁻¹ after 100 cycles within 3.0–4.5 V at 1 C, which is increased by 40 % compared to that of the bare electrode. In addition, the capacity of the TiO₂-coated electrode at 10 C (109 mAh g⁻¹) is 47 % larger than that of the uncoated one (74 mAh g⁻¹). Even at elevated temperature (50 °C) or voltage (charged to 4.7 V), the effect of TiO₂-coating can still be observed. It is believed that the oxide coating is able to mitigate the high-voltage induced electrolyte decomposition and interfacial side reactions due to its electron-blocking but ion-diffusive effect. The possible reaction between TiO₂ and the HF may also generate a new metal fluoride layer, which can be more resistant to further electrolyte attack and enable easier transfer of Li⁺ through the interfaces. Magnetron sputtering coating using TiO₂ is believed as a promising approach to enhance the high-voltage performance of LiCoO₂, which may be also applicable to other cathode materials.

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