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Room-temperature synthesis of crystallized $LiCoO_2$ thin films by electrochemical technique

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ABSTRACT

$LiCoO_2$ thin films have been directly synthesized on cobalt substrate in LiOH solution at room temperature by electrochemical method. The obtained $LiCoO_2$ thin films were characterized by X-ray diffraction (XRD), scanning electronic microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). The influence of electrochemical reaction time, current density and concentration of LiOH solution on the crystal structure and morphology of the obtained $LiCoO_2$ thin films was discussed emphatically. Our results show that the as-synthesized $LiCoO_2$ films all are pure hexagonal structure. The crystallinity, densification and uniformity of the films increase with increasing electrochemical reaction time, current density as well as concentration of LiOH solution and then decrease. The preferable electrochemical reaction conditions were optimized as: electrochemical reaction time is 50 h, current density is 1 mA cm^{-2} and concentration of LiOH solution is 3 mol dm^{-3}.

1. Introduction

Recently, solid-state lithium-ion rechargeable microbatteries have attracted much interest, because they have improved many problems of second microbatteries while retaining most of their favorable features [1–3]. As known, lithium transition metal double oxides with layered or spinel structures are efficient as cathode materials for lithium rechargeable batteries [4–7]. Among them, $LiCoO_2$ compound is regarded as the most promising candidate because of its good charge–discharge ability and excellent electrochemical properties [1,4,8]. As the miniaturization of electronic devices progresses, the need to develop suitable micro-battery systems as power sources for the microelectronic devices increases, so the fabrication of the lithiated intercalation cathode films has been intensively investigated lately [9–11]. The original pioneering works on the preparation of $LiCoO_2$ films have been performed mainly by using sol–gel [12], RF magnetron sputtering [13,14], chemical vapor deposition [15], polymeric precursor method [16], pulsed laser deposition [17–19], template synthesis [20] and spray pyrolysis [21] etc. Unfortunately, these synthetic methods require/involve sophisticated equipment; which require enormous energy consumption, expensive precursors as well as post-synthesis heat treatments. Generally speaking, all these techniques would result in environmental and economic problems to a certain extent. Therefore, an alternative synthetic route to produce the desired lithiated cathode films on a chip in economical, less energy and material consuming, and environmentally friendly ways is highly desirable. Electrochemical deposition technique seems to be able to fulfill the above needs [22–25]. Recently, our group have devoted to the preparation of tungstate and molybdate films with scheelite structure via constant current density electrochemical deposition technique and galvanic cell method at room temperature [26–28]. The previous researchers have carried out the preparation of $LiCoO_2$ and $LiNiO_2$ films with layer structure by electrochemical deposition technique at higher temperature (near 100 °C) or by hydrothermal–electrochemical method [29–32]. From those research results we can understand that the higher reaction temperature can quicken the oxidation–dissolution of Co substrate, it also increases the dissolution of $LiCoO_2$ grains accordingly. In addition, the stability of CoO_2^- ion decreases with increasing reaction temperature. In other words, the higher reaction temperature will result in the inferior crystallinity and densification of the as-prepared $LiCoO_2$ film. On the basis of above knowledge, we think the better electrochemical processing may be searched for the preparation of $LiCoO_2$ films by lowering the reaction temperature (such as room temperature) and changing the other electrochemical processing parameters (such as current density and reaction time etc.) accordingly. The previous researchers such as Tao's group [29–31] and Yoshimura's group [33] have done research work on the preparation of $LiCoO_2$ films using electrochemical technique. While these investigations mainly focused on the preparation of $LiCoO_2$ films, and there is little discussion on the influence of electrochemical processing parameters on

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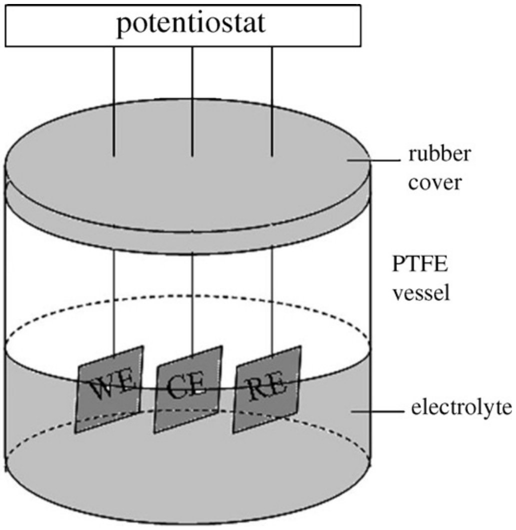

Fig. 1. Schematic illustration of experimental equipment for the preparation of $LiCoO_2$ thin film by electrochemical technique at room temperature.

the microstructure of the as-synthesized films. From our recent research work on the preparation of tungstate and molybdate films with scheelite structure via electrochemical deposition technique and galvanic cell method at room temperature, we have found that the room temperature electrochemical deposition technique is a very simple and easily controlled route for the synthesis of double oxide ceramic films. Based on this finding, we have carried out work on the synthesis of $LiCoO_2$ films by room temperature electrochemical deposition technique. Compared to previous reports on similar work, the present work is devoted to the preparation of $LiCoO_2$ films via electrochemical technique at room temperature, which has great advantages in experimental equipment and energy consumption, in other words, it is a very convenient and mild deposition route for $LiCoO_2$ films. Moreover, the influences of electrochemical reaction time, current density and concentration of LiOH solution on the morphology and crystal structure have been discussed emphatically, and the morphology and microstructures of the obtained $LiCoO_2$ films have been improved.

2. Experimental

Cobalt substrate with 99.5 wt% purity and dimensions of 10 mm × 18 mm × 0.3 mm was used as working electrode (WE). After being mechanical polished, the cobalt flake was degreased in acetone for 10 min, subsequently etched in dilute hydrochloric acid and composite acid for 20 h, and then washed in distilled water with ultrasonic cleaner. The platinum slice and the saturated calomel electrode were used as counter electrode (CE) and reference electrode (RE), respectively. LiOH solution was used as electrolytic solution, which was purged with N_2 gas for 20 min to remove dissolved CO_2, and then immediately poured into a polytetrafluoroethylene (PTFE) beaker. Finally, the whole setup was totally sealed, the schematic illustration of experimental equipment is shown in Fig. 1. $LiCoO_2$ films were directly deposited on cobalt substrates in LiOH solution with a fixed concentration between 1 and 4 mol dm^{-3} and a fixed current density between 0.3 and 1.5 mA cm^{-2} through 5–70 h electrochemical reaction at room temperature. In order to discuss the influence of each processing parameter on the microstructures of $LiCoO_2$ films, we have kept the other processing parameters unchanged (located in the obtained optimal point, i.e., select current density as 1 mA cm^{-2}, concentration of LiOH solution as 3 mol dm^{-3} and electrochemical treatment time as 50 h).

The as-prepared $LiCoO_2$ films were washed in warm water and absolute alcohol in turn, and dried naturally in air. The resultant phase of the obtained films was analyzed using X-ray diffraction (XRD), the surface morphology and microstructure were observed using a scanning electronic microscopy (SEM), the compositions and chemical valence were confirmed using X-ray photoelectron spectroscopy (XPS).

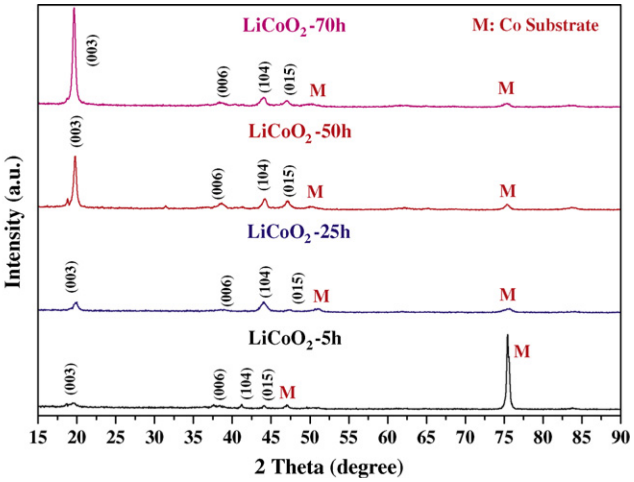

Fig. 2. XRD patterns of $LiCoO_2$ thin films prepared by electrochemical technique at room temperature under different reaction time (current density is 1 mA cm^{-2} and concentration of LiOH solution is 3 mol dm^{-3}).

3. Results and discussion

Fig. 2gives the XRD patterns of $LiCoO_2$ thin films prepared by electrochemical technique at room temperature under different reaction time (current density is 1 mA cm^{-2} and concentration of LiOH solution is 3 mol dm^{-3}). It can be seen that the *d*-space, relative intensity as well as diffraction angle of the observed peaks are in agreement with JCPDS files (No. 44-0145 and 82-0340), especially for several strong peaks, which can be attributed to (0 0 3), (0 0 6), (1 0 4) and (0 1 5) crystal plane, respectively. The XRD results confirm that the as-synthesized films all are single-phase $LiCoO_2$ with hexagonal layered structure. According to the JCPDS cards and other articles on $LiCoO_2$, $LiCoO_2$ with layered rock salt structure shows more XRD peaks from 15° to 90°, and the (1 0 4) peak is the largest of all peaks. However, our samples exhibited fewer peaks within the degree range, and the (1 0 4) peak observed for these samples is very weak in comparison with the other peaks. This may be originated from the orientation of the Co substrate. Similar results have been reported in Tao's paper [29] and Han's paper [34]. In her paper, Tao pointed out "About films on cobalt, it indicate that the more of the (0 0 3) reflection for the films, the more of grains are aligned with its (0 0 3) plane parallel to cobalt substrate, i.e., the more grains have those *c* axes aligned normal to the plane of films." It is also noted that the intensity of the diffraction peaks for $LiCoO_2$ films increases with increasing reaction time, while that one for Co substrate decreases, suggesting that the crystallinity of the $LiCoO_2$ films become better after long electrochemical reaction.

Fig. 3 shows the SEM micrographs of $LiCoO_2$ thin films prepared by electrochemical technique at room temperature under different reaction time (current density is 1 mA cm^{-2} and concentration of LiOH solution is 3 mol dm^{-3}). One can see that the crystallinity and densification of the obtained $LiCoO_2$ films increase with the increasing reaction time. It also can be seen that the grain size of $LiCoO_2$ gradually increases with the increasing reaction time. Especially when the reaction time is up to 50 h, the as-prepared $LiCoO_2$ thin film is highly crystallized, having dense and uniform surface, and the grains are shaped of octahedron with the average grain size of ~2 μm. While with the further increase of reaction time (Fig. 3d), although the larger $LiCoO_2$ grains can be obtained, there are also some small $LiCoO_2$ grains produced. In other words, the uniformity of the obtained $LiCoO_2$ films decreases in this case.

The formation mechanism of $LiCoO_2$ thin film under a constant current electrochemical condition is based on the

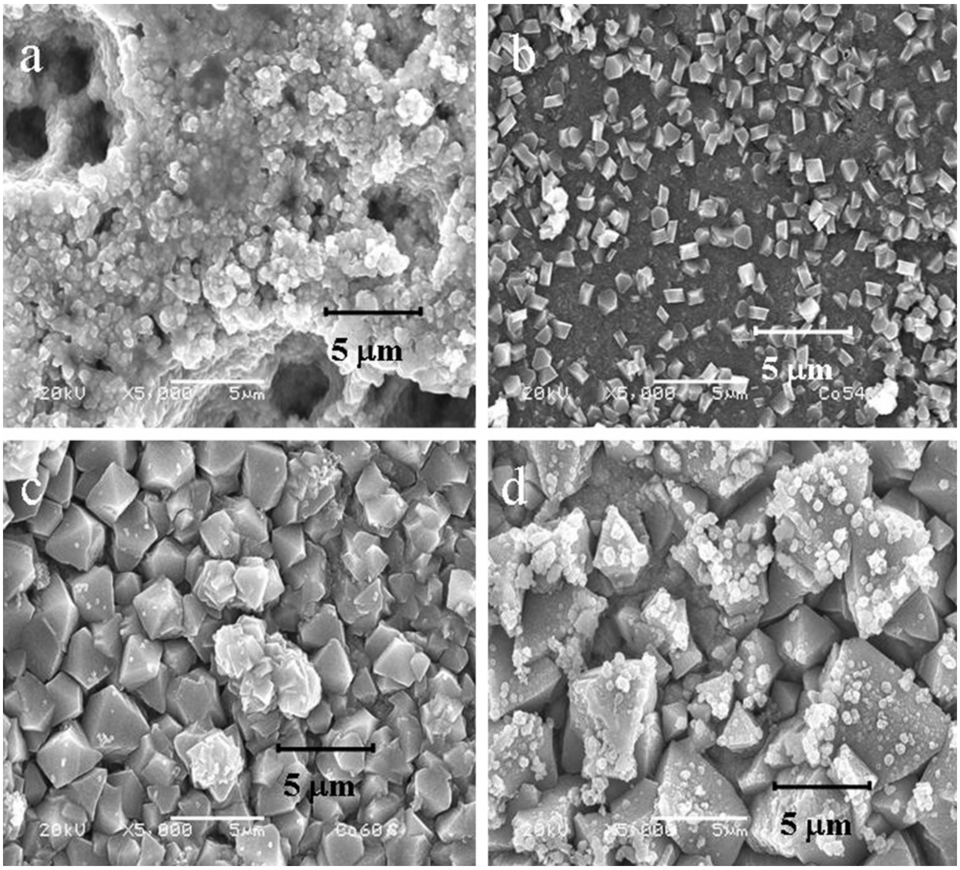

Fig. 3. SEM micrographs of $LiCoO_2$ thin films prepared by electrochemical technique at room temperature under different reaction time (current density is 1 mA cm^{-2} and concentration of LiOH solution is 3 mol dm^{-3}). (a) 5 h; (b) 25 h; (c) 50 h; (d) 70 h.

dissolution–precipitation process [35]; it can be described as follows:

$$Co + 4OH^- \rightarrow CoO_2{}^- + 2H_2O + 3e^- \qquad (1)$$

$$CoO_2{}^- + Li^+ \rightarrow LiCoO_2 \qquad (2)$$

Reaction (1) is an oxidation–dissolution process, it is a faradic process accompanied by charge transfer between the solution and electrode. The applied current density, the reaction temperature as well as the pH value of solution have important influence on the reaction. Whereas reaction (2) is a solution precipitation process, which is mainly controlled by the reaction temperature, reaction time and the concentration of the LiOH solution.

Under the feasible applied current density and reaction temperature, reaction (1) can easily generate. According to The Rule of Solubility Product, as long as Q (the ionic product of Li^+ ions and $CoO_2{}^-$ ions) exceeds $K_{spLiCoO_2}$ (the solubility product of $LiCoO_2$), the solution is oversaturated, and then $LiCoO_2$ grains can be formed. It can be described in the following expression (3):

$$Q = c_{Li^+} \cdot c_{CoO_2{}^-} > K_{spLiCoO_2} \qquad (3)$$

where c_{Li^+} and $c_{CoO_2^-}$ represent the concentration of Li^+ ions and $CoO_2{}^-$ ions in the solution, respectively.

Obviously, the higher c_{Li^+} and $c_{CoO_2^-}$ are propitious to the formation of $LiCoO_2$ grains.

If the reaction time is short, the produced $CoO_2{}^-$ ions in the solution will be deficient, and the crystallized $LiCoO_2$ nucleus will be few, so the formed $LiCoO_2$ grains cannot sufficiently grow. As a result, the grains are small and films are not dense. On the other hand, the longer electrochemical reaction can effectively promote the formation of $LiCoO_2$ nucleus and the orientation growth of $LiCoO_2$ grains, result in the significant improvement in the crystallinity, densification and uniformity of the synthesized films. So when the reaction time is up to 50 h, the highly crystallized, dense and uniform $LiCoO_2$ film can be obtained.

Fig. 4 shows the XRD patterns of $LiCoO_2$ thin films prepared by electrochemical technique at room temperature under differ-

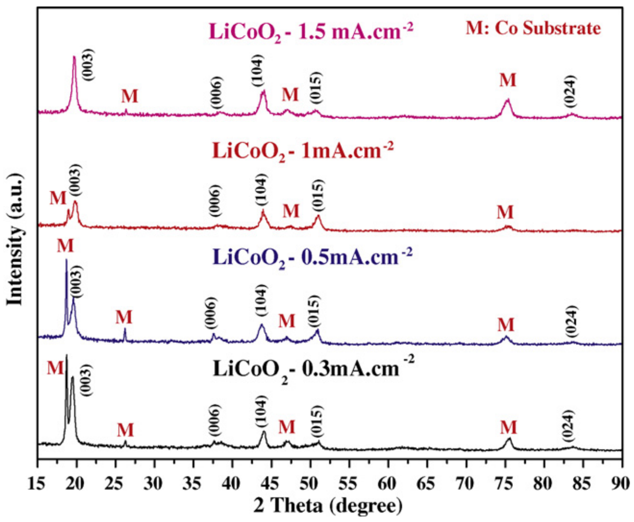

Fig. 4. XRD patterns of $LiCoO_2$ thin films prepared by electrochemical technique at room temperature under different current density (concentration of LiOH solution is 3 mol dm^{-3} and electrochemical reaction time is 50 h).

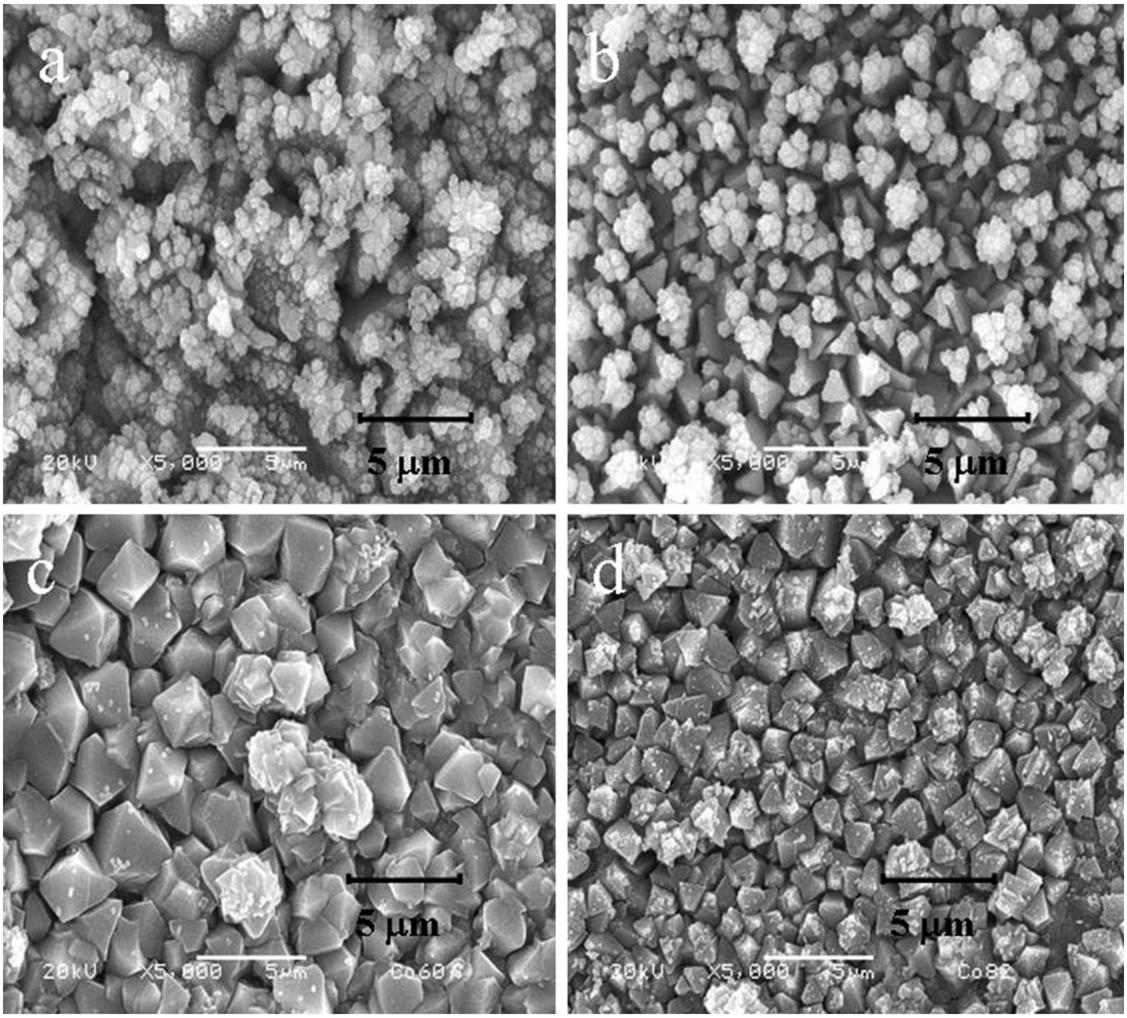

Fig. 5. SEM micrographs of $LiCoO_2$ thin films prepared by electrochemical technique at room temperature under different current density (concentration of LiOH solution is 3 mol dm^{-3} and electrochemical reaction time is 50 h). (a) 0.3 mA cm^{-2}; (b) 0.5 mA cm^{-2}; (c) 1 mA cm^{-2}; (d) 1.5 mA cm^{-2}.

ent current density (concentration of LiOH solution is 3 mol dm^{-3} and electrochemical reaction time is 50 h). One can see that the *d*-space, relative intensity as well as diffraction angle of the strong diffraction peaks such as (0 0 3), (0 0 6), (1 0 4), (0 1 5) and (0 2 4) are consistent with the standard JCPDS files (No. 44-1045 and 82-0340), suggesting that the obtained films all are pure $LiCoO_2$ with a hexagonal structure. Compared with the other samples, it is noted that the strong diffraction peaks of Co substrate in the $LiCoO_2$ film (obtained under the current of 1 mA cm^{-2}) weakened, implying that the crystallinity and densification of the $LiCoO_2$ film enhanced in this case.

Fig. 5 gives the SEM micrographs of $LiCoO_2$ thin films prepared by electrochemical technique at room temperature under different current density (concentration of LiOH solution is 3 mol dm^{-3} and electrochemical reaction time is 50 h). It can be seen that the observed grain size, densification and uniformity of the obtained $LiCoO_2$ films increase with increasing current density and then decrease, giving the best results at the current density of 1 mA cm^{-2} (Fig. 5c).

The current density plays an important role in the formation of $LiCoO_2$ thin films. Larger current density can promote the reaction (1) (i.e., the formation of ${CoO_2}^-$ ions), while it does not always help to the growth, because that the reaction (2) is a reversible process, in which there is a competition between the formation and dissolution of $LiCoO_2$ grains. Under lower applied current density (such as 0.3 and 0.5 mA cm^{-2}), the generation speed of ${CoO_2}^-$ ions (i.e., the oxidation–dissolution of Co substrate) will be very slow, the degree of supersaturation of solution is relatively low, the formed ${CoO_2}^-$ ions cannot effectively combine with Li^+ ions to produce stable $LiCoO_2$ grains, and result in the inferior crystallinity and densification of the obtained film. On the other hand, when the current density is too large (1.5 mA cm^{-2}), the formation of ${CoO_2}^-$ ions will be very quick, the degree of supersaturation is too high, result in the appearance of more and small $LiCoO_2$ nucleus. As a result, the formed $LiCoO_2$ nucleus also cannot enough grow into large grains, and the morphology and uniformity of the $LiCoO_2$ film would be affected remarkably. Considering the nuclear formation and grain growth of $LiCoO_2$, the preferable current density was recommended as 1 mA cm^{-2}.

Fig. 6 shows the XRD patterns of $LiCoO_2$ thin films prepared by electrochemical technique at room temperature under different LiOH concentrations (current density is 1 mA cm^{-2} and electrochemical reaction time is 50 h). All the films possess a single-phase hexagonal structure and no second phase is observed. Comparing the relative intensity of the observed diffraction peaks, it is noted that the sample obtained in 3 mol dm^{-3} LiOH solution exhibits stronger diffraction peaks of $LiCoO_2$ (such as (0 0 3), (1 0 4) and (1 0 5)) and relative weaker diffraction peaks of Co substrate, and this implies that the $LiCoO_2$ film sample having the better crystallinity and densification.

The SEM micrographs of $LiCoO_2$ thin films prepared by electrochemical technique under different concentrations of LiOH solution

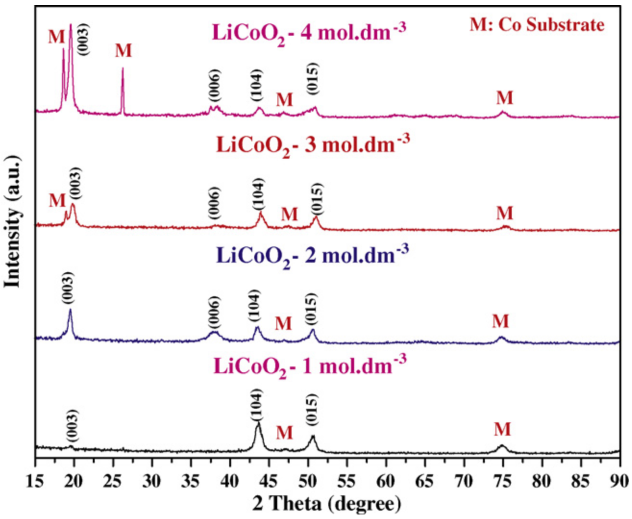

Fig. 6. XRD patterns of $LiCoO_2$ thin films prepared by electrochemical technique at room temperature under different LiOH concentration (current density is 1 mA cm^{-2} and electrochemical reaction time is 50 h).

are shown in Fig. 7 (current density is 1 mA cm^{-2} and electrochemical reaction time is 50 h). It is noted that the concentration of LiOH solution has an important influence on the crystallinity and morphology of the $LiCoO_2$ thin films. When the concentration of LiOH solution is 1 mol dm^{-3}, there are only very small and disordered $LiCoO_2$ grains observed in the $LiCoO_2$ film (Fig. 7a). This should be attributed to the lower degree of supersaturation of the solution (because c_{Li^+} is relative low), the crystallized $LiCoO_2$ nucleus are unstable and can easily redissolve. Therefore, the growth of formed $LiCoO_2$ grains is inhibited, and results in a poor crystallinity and densification in the obtained $LiCoO_2$ films. Whereas with the increase of the concentration of LiOH solution, c_{Li^+} increases accordingly, the degree of supersaturation of the solution also increases. As a result, there are more $LiCoO_2$ nucleus can be formed, and they can effectively grow into the stable and large grains (Fig. 7b and c). It is also noted that if the concentration of LiOH solution is too high (Fig. 7d), although larger $LiCoO_2$ grains can be obtained, there are also some small $LiCoO_2$ grains produced, and the uniformity of the films decreased. This may be partly attributed to the higher degree of supersaturation of the solution. As a result, the morphology and uniformity of $LiCoO_2$ film would be affected significantly. And this is similar to the influence of the reaction time and applied current density on the $LiCoO_2$ films.

Considering the nuclear formation and grain growth of $LiCoO_2$, the preferable electrochemical reaction conditions were optimized as: electrochemical treatment time is 50 h, current density is 1 mA cm^{-2} and concentration of LiOH solution is 3 mol dm^{-3}.

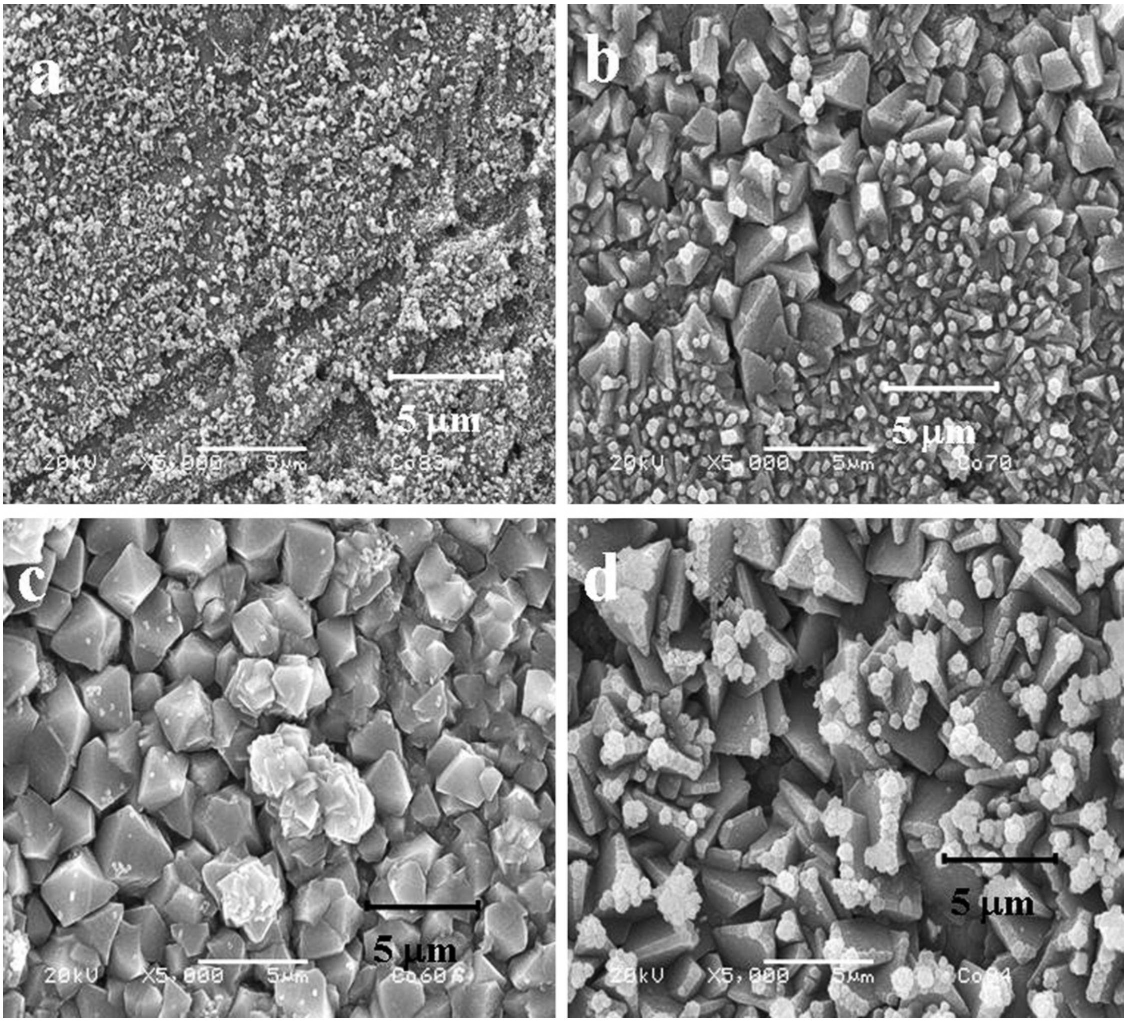

Fig. 7. SEM micrographs of $LiCoO_2$ thin films prepared by electrochemical technique at room temperature under different LiOH concentration (current density is 1 mA cm^{-2} and electrochemical reaction time is 50 h). (a) 1 mol dm^{-3}; (b) 2 mol dm^{-3}; (c) 3 mol dm^{-3}; (d) 4 mol dm^{-3}.

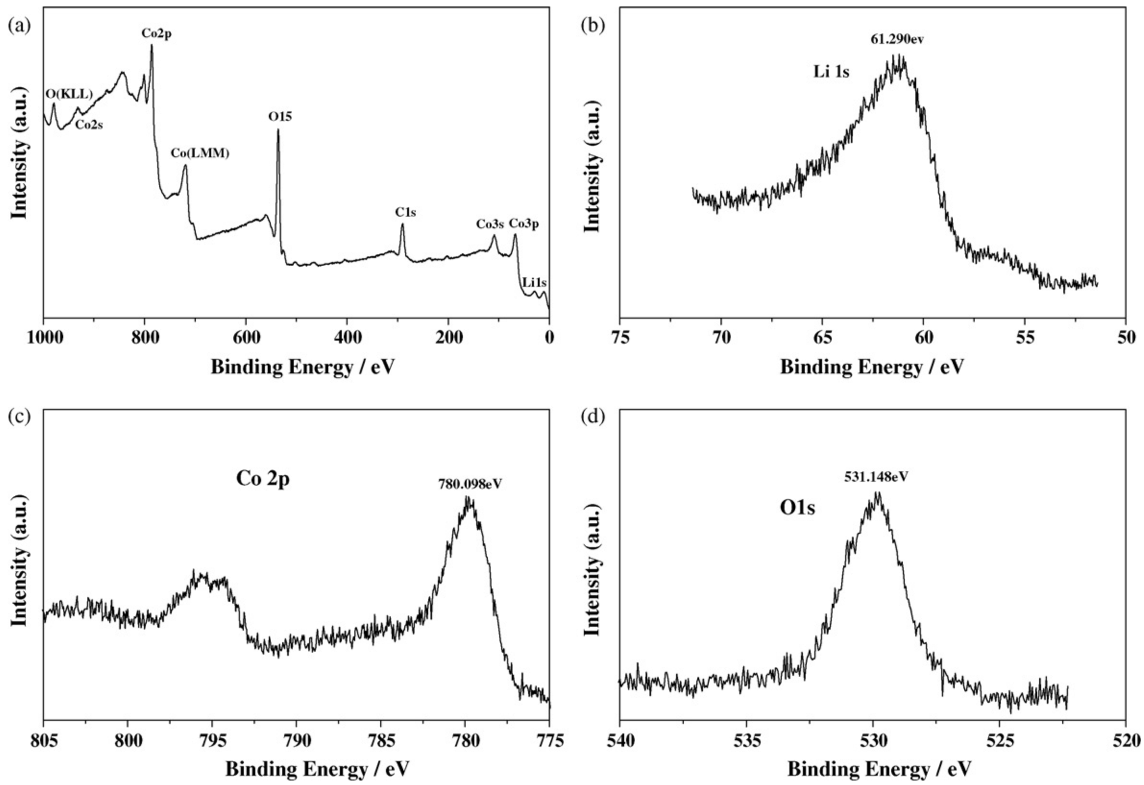

Fig. 8. X-ray photoelectron spectra of the $LiCoO_2$ thin film prepared by an electrochemical technique at room temperature under optimal processing conditions (current density is 1 mA cm^{-2}, concentration of LiOH solution is 3 mol dm^{-3} and electrochemical treatment time is 50 h). (a) XPS survey spectra of $LiCoO_2$ thin film; (b) Li1 s XPS spectrum of $LiCoO_2$ thin film; (c) Co_{2p} XPS spectrum of $LiCoO_2$ thin film; (d) O_{1s} XPS spectrum of $LiCoO_2$ thin film.

In order to further verify the above results, XPS measurement was carried out.

As an example, Fig. 8 gives the XPS spectra of the as-prepared $LiCoO_2$ film under optimal processing conditions, all of the binding energies at various peaks in Fig. 8 are calibrated using the binding energy of C_{1s} (285.0 eV). The wide-scan XPS spectrum of the as-synthesized $LiCoO_2$ thin film in the binding energy range of 1000–0 eV is given in Fig. 8a. It can be seen that the as-prepared $LiCoO_2$ thin film contains Li, Co, O and C elements, and no impurity element is detected in the spectrum up to 1000 eV except for the calibrated carbon.

Fig. 8b–d gives the narrow-scan XPS spectra for Li, Co and O elements of the resultant $LiCoO_2$ thin film, respectively. As shown, Li_{1s} band of the $LiCoO_2$ thin film presents at 61.290 eV, $Co_{2p(3/2)}$ band and O_{1s} band locate at 780.098 eV and 531.148 eV, respectively. The results are almost consistent with those reported in the literature [33], which reveal that Li, Co and O elements all exist in the surface of the film with exhibiting the valence of +1, +3 and −2, respectively. Therefore, the above data strongly support that the actually synthesized film is exactly $LiCoO_2$.

Fig. 9 shows the surface and cross-section SEM micrographs of the as-prepared $LiCoO_2$ film under the optimal electrochemical conditions. As shown in Fig. 9a, the obtained $LiCoO_2$ film is dense and homogeneous, having the average grain size ~3 μm. The cross-section SEM micrograph clearly demonstrates that the thickness of the film is about 5 μm. Fig. 10 gives the XRD patterns of the obtained

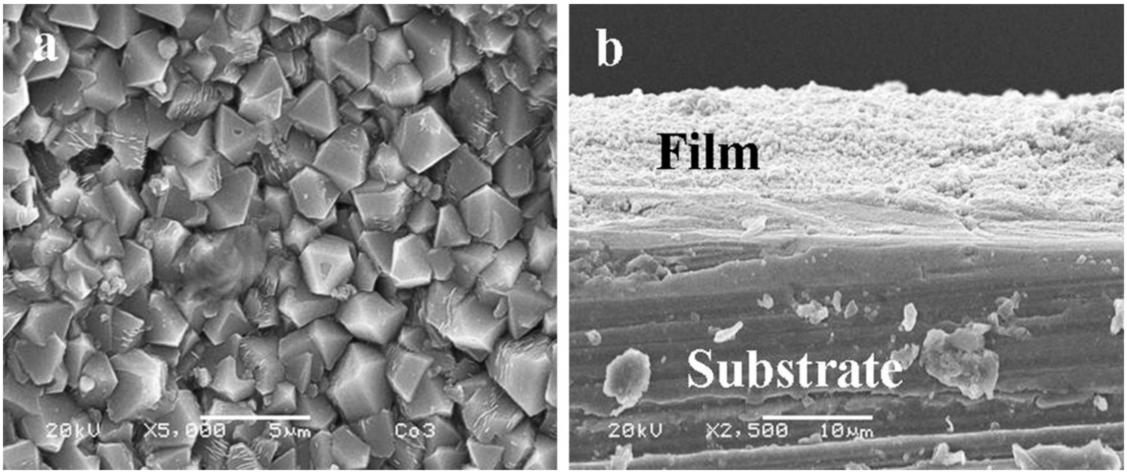

Fig. 9. The surface (a) and cross-section (b) SEM micrographs of the $LiCoO_2$ thin film prepared by an electrochemical technique at room temperature under the optimal processing conditions (current density is 1 mA cm^{-2}, concentration of LiOH solution is 3 mol dm^{-3} and electrochemical treatment time is 50 h).

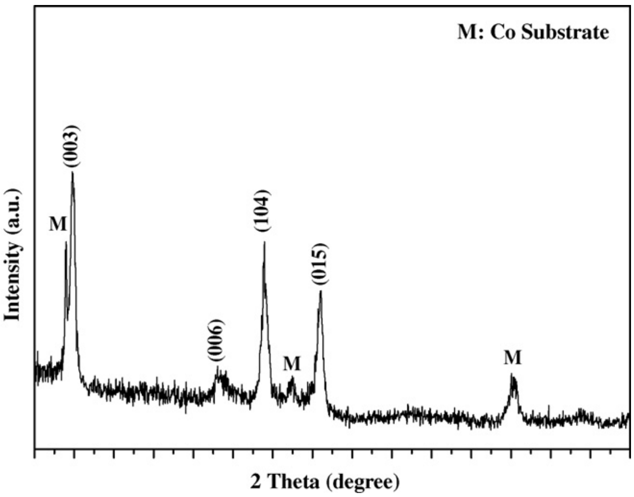

Fig. 10. XRD patterns of $LiCoO_2$ thin film prepared by an electrochemical technique at room temperature under the optimal processing conditions (current density is 1 mA cm^{-2}, concentration of LiOH solution is 3 mol dm^{-3} and electrochemical treatment time is 50 h).

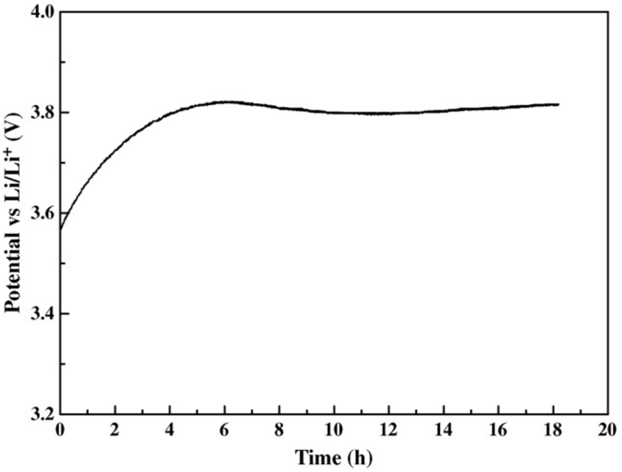

Fig. 11. The first charge curve at 10 μA cm^{-2} in a beaker cell with 1.0 mol dm^{-3} $LiPF_6$/EC/DEC for the $LiCoO_2$ thin film prepared by an electrochemical technique at room temperature under the optimal processing conditions (current density is 1 mA cm^{-2}, concentration of LiOH solution is 3 mol dm^{-3} and electrochemical treatment time is 50 h).

$LiCoO_2$ film under the optimal electrochemical conditions, it also reveals that the film possesses a pure hexagonal structure.

Fig. 11 shows the first charge curve of the deposited $LiCoO_2$ films under the optimal electrochemical processing conditions. The initial open circuit voltage of ~3.2 V and the potential plateau at ~3.9 V are the typical properties for the layered $LiCoO_2$ phase. And this is consistent with the result reported in the literature [33].

4. Conclusions

$LiCoO_2$ thin films have been directly synthesized on cobalt substrate in LiOH solution by electrochemical technique at room temperature. The as-synthesized films all exhibit a single-phase hexagonal structure and no second phase is observed. Our results show that the electrochemical reaction time, applied current density as well as concentration of LiOH solution have important influence on the crystal phase structure and microstructure of the obtained films. The observed crystallinity, densification and uniformity of the $LiCoO_2$ films increase with increasing electrochemical reaction time, current density as well as concentration of LiOH solution and then decrease. The preferable processing parameters are suggested as: electrochemical reaction time is 50 h, current density is 1 mA cm^{-2} and concentration of LiOH solution is 3 mol dm^{-3}.

Acknowledgements

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