

Preparation and electrochemical properties of Co_3O_4 -coated layered manganese oxide by a novel coating method

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Abstract Potassium type birnessite (K-bir) was synthesized by O_2 oxidizing Mn^{2+} in aqueous solution of KOH. Co_3O_4 -coated K-bir (Co-K-bir) was prepared by employing a novel coating method, in which the remaining OH^- ions on the particle surface of the as-precipitated K-bir reacted with Co^{2+} ions in aqueous solution, forming CoOOH coverage; the coating layer of CoOOH was subsequently annealed at 300°C to transform into Co_3O_4 . All the K-bir and Co-K-birs were investigated by scanning electron microscopy, transmission electron microscopy, inductive coupled plasma-atomic emission spectroscopy, Brunauer–Emmett–Teller specific area, and laser particle size analyzing techniques. Their electrochemical properties were also studied by discharging–charging at constant current. The results show that the covering layers of Co_3O_4 are incompact, and their average thickness are about $0.65\text{--}0.78\ \mu\text{m}$. Compared to the as-prepared and the annealed K-bir, the Co_3O_4 -coated samples have higher initial discharge capacities and show distinctly improved cycleability performance.

Keywords Layered manganese oxide · Birnessite · Coating · Cobalt oxide · Electrochemical performance

Introduction

Manganese oxides, as candidates for rechargeable lithium battery, have attracted a lot of interest because of their economy and environmental friendly properties [1, 2]. Birnessite, as one of polymorphs of manganese oxide, has a good layered structure with some cations, such as K^+ , Na^+ , and other cations as well, occluded in the interlayer. Lithium ion insertion and extraction into this layered structure was not an exception and was consequently investigated intensively [3–6]. However, the practical application of birnessite is still a challenge because its cyclic performance, as so far, behaves poorly due to structural instability and Mn dissolution, etc. Bach et al. [7] used Bi^{2+} ions as pillaring species to limit structural swelling in birnessite and succeeded in improving its cycleability. Such heavy, inactive pillared ions reduced the capacity of material; hence, Zhang et al. [8] employed vanadium as redox active immobile pillar ions to obtain a higher capacity. However, their vanadium pillared birnessite $(\text{VO}_y)_{0.15}\text{MnO}_2 \cdot n\text{H}_2\text{O}$, from hydrothermal treatment of vanadyl permanganate, declined faster than Bach's bismuth pillared birnessite and retained 74% of its highest capacity after ten cycles. In addition, Ba^{2+} , Sr^{2+} , and ZrO^{2+} were also introduced to the interlayer of birnessite to modify its reversible capacity [9]. Besides acting as pillar species, some other cations used as impurities were also doped as framework ions to improve cycleability of birnessite; e.g., Tsuda et al. [10] synthesized Co-doped birnessite by replacing MnCl_2 partially with CoCl_2 when they were oxidized by O_2 gas in aqueous NaOH solution. They believed that the doped cobalt was inactive as Co^{3+} state but could fix Na^+ in the interlayer and stabilize the layered structure.

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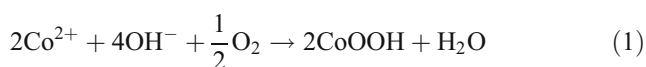
In another approach, coating method usually was used to separate the bulk material from electrolyte and expected to suppress Mn dissolution which was seldom reported, for example; Cho et al. [11] prepared Al₂O₃ and CoO-coated orthorhombic lithium manganate (*o*-LiMnO₂) by sol–gel method, and they reported that the coated protective layer could reduce Mn dissolution and improved the cycling behavior. However, coated birnessite has not been reported up until now to the best of our knowledge, which might be due to difficulty in obtaining a uniform coverage of birnessite.

In this work, we employed a novel method to obtain Co₃O₄ coated birnessite, where the as-precipitated birnessite was washed only one time and then the remained OH[−] ions on the particle surface was employed to obtain the coating layer. Such Co₃O₄-coated materials are expected to reduce Mn dissolution and suppress extraction of interlayer K⁺ then improve the cycleability compared to the pristine birnessite as cathode electrodes for lithium ion battery.

Materials and methods

Synthesis of birnessite Potassium type birnessite (K-bir) was synthesized as reported in our previous work [12]. In brief, 8.95 g Mn(NO₃)₂ aqueous solution (50 wt.%) was added dropwise to 30 mL solution of 11.2 g KOH at 0 °C. The solution was stirred with a continuous O₂ flow (100 mL min^{−1}) for 8 h, settled overnight, filtered and washed several times, and then dried at 120 °C for 24 h.

To obtain Co₃O₄-coated materials, the as-synthesized K-bir was filtered and washed for one time, refiltered, and then poured into Co(NO₃)₂ aqueous solutions. The OH[−] ions remained on the surface of K-bir particles and, therefore, reacted with Co²⁺ ions and formed CoOOH according to Eq. 1:



The obtained CoOOH coated K-bir was dried at 80 °C, ground, and subsequently annealed at 300 °C for 24 h to form Co₃O₄ coated K-bir (Co-K-bir); here, the annealing temperature was determined based on thermal analysis. The Co contents in three coated samples were designed by Co/Mn molar ratio of 0.05, 0.10, and 0.20 for samples 5% Co-K-bir, 10% Co-K-bir, and 20% Co-K-bir, respectively.

Physical properties and characterization Thermogravimetric–differential thermal analysis (TG–DTA) experiments were carried out by STA 409 PC analyzer (Netzsch, Germany) at heating rate of 10 °C min^{−1} under Ar flow (50 mL min^{−1}). A mass spectrometer (MS) was connected to DTA analyzer, when necessary, to analyze the evolved gas.

X-ray diffraction (XRD) and temperature-programmed XRD (TP-XRD) measurements were performed on a PANalytical X'Pert diffractometer with Cu K α radiation (Philips). A non-ambient sample stage (Anton Paar XRK 900) was employed to perform TP-XRD experiments, where samples were heated at a rate of 10 °C min^{−1}, maintained for 5 min at assigned temperatures before XRD measurement. After all the heating processes, the samples cooled down to 100 °C at a rate of 20 °C min^{−1} and subsequently to 40 °C at a rate of 4 °C min^{−1}.

Scanning electron microscopy (SEM) studies were performed on LEO1530. Transmission electron microscopy (TEM) studies were performed on H600 (Hitachi, Japan).

Laser particle size analyzer (LPSA, LS-POP III, China) was employed to measure mean particle size of K-bir and its Co₃O₄ coated samples. The specific surface area was determined by Brunauer–Emmett–Teller (BET) nitrogen gas adsorption using a NOVA 4000e surface area and pore size analyzer (Quantachrome, USA).

The manganese and potassium contents were determined by inductive coupled plasma–atomic emission spectroscopy (ICP–AES), carried out on IRIS Intrepid II XSP (Thermo Electron).

Electrochemical properties The preparation of electrodes were straightforward, first the active material was mixed with 10 wt.% acetylene black and 5 wt.% binder polyvinylidene fluoride and then ground by ball milling. The mixture was pressed to aluminum foil (current collector) and, thereafter, dried at 110 °C, under vacuum for 2 h to obtain the cathode. Coin cells were fabricated with the prepared cathode, lithium anode, Celgard 2400 polypropylene separator, and 1 M LiClO₄ in a mixture of propylene carbonate and 1,2-dimethoxyethane (PC:DME; 1:1, v/v) electrolyte as described in our previous work [13]. All the electrochemical capacity tests for these cells were carried out at 30 °C.

Results and discussion

The XRD pattern of the as-prepared K-bir is shown in Fig. 1a, confirming its monoclinic symmetry and a *d*-spacing of ~7.2 Å (JCPDS no. 42–1317). Rehydration of dehydrated birnessites (below 250 °C) in air has been reported in the previous studies [14–18]. Considering the effect of synthetic conditions on the thermal behavior of birnessites, we employed here TG/DTA-MS and TP-XRD techniques to analyze structural variation of the as-prepared K-bir, which is very important for the subsequent annealing process of coated materials. Figure 2 shows the TG/DTA-MS behavior of such a K-bir. Below ~320 °C, the mass loss resulted mainly from release of physically adsorbed water

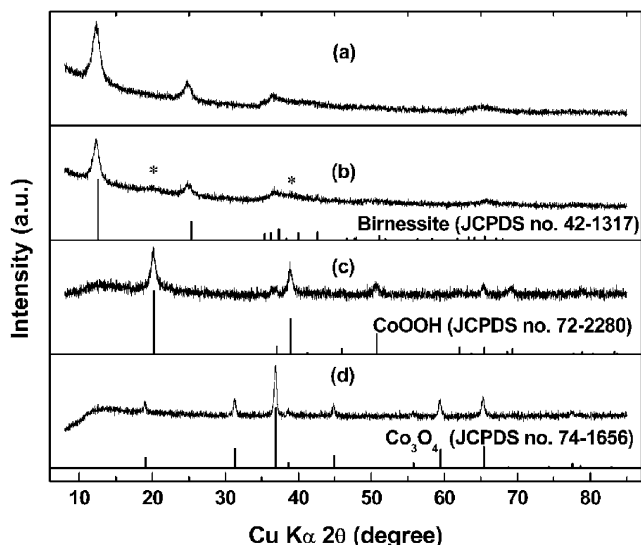


Fig. 1 XRD patterns of (a) K-bir, (b) CoOOH coated K-bir, (c) CoOOH, and (d) Co₃O₄

and interlayer water, corresponding to the shoulder peaks at ~120 °C and the peaks at ~170 °C in the DTG and MS curves. When up to ~320 °C, O₂ gas evaluation was observed as indicated by its mass spectra curve (Fig. 2b), accompanying with phase transformation of K-bir to cryptomelane as indicated by XRD patterns (not shown). Further increase of the temperature to ~600 °C would decompose the formed cryptomelane to Mn₃O₄. TP-XRD experiment showed that the *d*-spacing of the as-prepared K-bir decreased from ~7.2 to 6.6 Å upon heating to 300 °C, and regained its original value immediately when cooling to 40 °C (Fig. 3). Such a variation of *d*-spacing with the temperature (below 320 °C) is repeatable, suggesting removal of interlayer water of the as-prepared K-bir do not destroy its layered structure.

The XRD pattern of the obtained CoOOH coated K-bir, compared to that of K-bir, shows two new weak peaks at

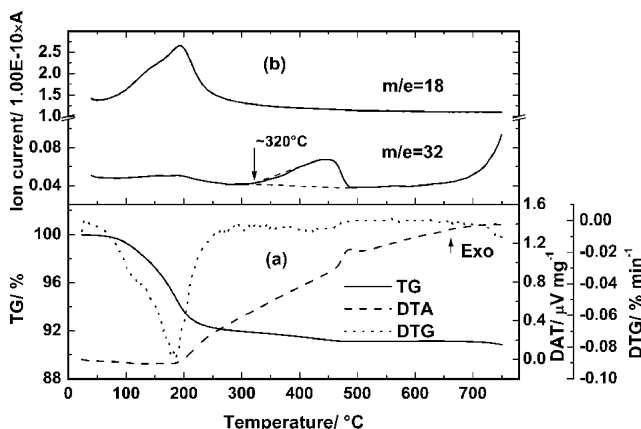


Fig. 2 (a) TG/DTA behavior of K-bir with a heating rate of 10 °C min⁻¹ and (b) its simultaneous MS spectra during the process

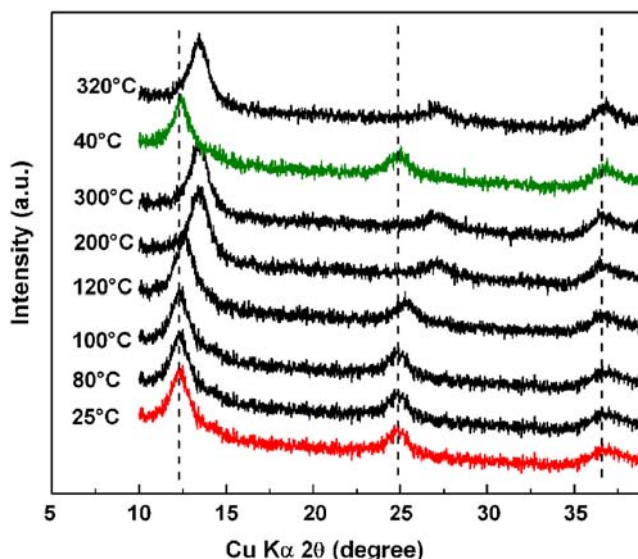


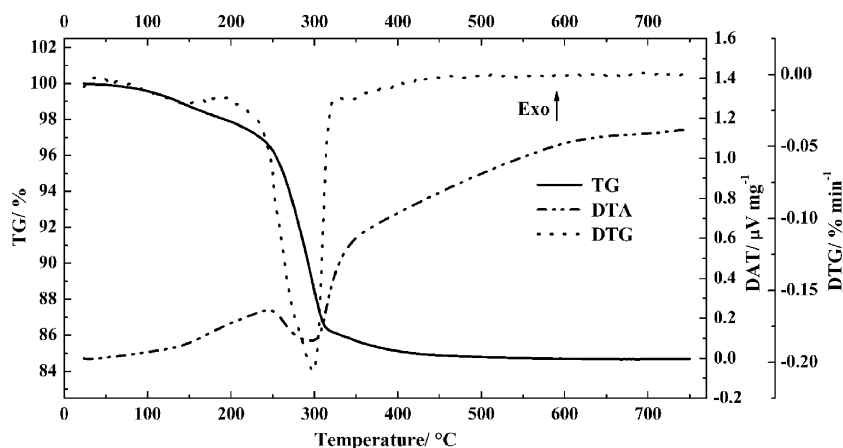
Fig. 3 XRD patterns of K-bir recorded in situ at various temperatures

around 20° and 39° (marked by asterisks, Fig. 1b), which could index to CoOOH. The formed CoOOH might decompose and release H₂O and ion-exchange with Li⁺ and form dissociative H⁺ ions in nonaqueous lithium ion electrolyte. In both cases, this will lead to some destruction of the good properties of the electrodes and electrolyte; hence, we should anneal the covered layer of CoOOH to form cobalt oxide. In order to obtain good cobalt oxide coverage and, meanwhile, maintain K-bir in its layered structure form, we should determine the optimum annealing temperature, which was carried out by the help of TGA-DTA technique.

A CoOOH was synthesized by wet chemical method, where aqueous solution of Co(NO₃)₂ was added to aqueous solution of KOH dropwisely until the formation of blue precipitate of Co(OH)₂ which is easily oxidized to gray CoOOH by air. The obtained CoOOH was subsequently analyzed by TG/DTA to determine its condition of decomposition. As shown in Fig. 4, CoOOH had a single sharp peak at ~300 °C in its DTG and its corresponding peak in DTA plots, which is the temperature that CoOOH decomposed to Co₃O₄ (Fig. 1d). Meanwhile, K-bir begins to lose some lattice oxygen at ~320 °C and release O₂ gas accompanied with structure change as discussed above. Therefore, we chose 300 °C as the annealing temperature to obtain Co-K-birs.

The result of elemental analysis shows that the experimental Co₃O₄ contents are very close to the designed values (Table 1). The XRD patterns of coated K-bir with various Co₃O₄ contents were shown in Fig. 3, suggesting that the annealed samples still have the peak at around 12° with no detection of any other peaks. The intensity of the peaks at around 12° decreased with the increase of Co₃O₄

Fig. 4 TG/DTA plots of CoOOH



content. Although the thickness increased with Co_3O_4 content (vide infra), the signal intensity of the XRD was weak since the absorption of radiation from Cu $\text{K}\alpha$ is expected to be high by cobalt oxide which affects the intensity of these signals. The intensity of the diffraction peak at $\sim 37^\circ$ is overlapping result of Co_3O_4 and K-bir; however, this peak, as the strongest peak of Co_3O_4 , increased its relative intensity with Co_3O_4 content while the peak at $\sim 12^\circ$, as the strongest peak of K-bir, decreased. The variation of the relative intensity of such two diffraction peaks, despite weakness, is in good agreement with that of coated Co_3O_4 content and indicates the successful coating.

In traditional approaches obtaining coating layer, such as by sol-gel method or by adding Co^{2+} into mother liquor after formation of birnessite, it is prone to form individual particles separated from or attached to the bulk material. By contrast, in our method, the coverage formed by reaction between OH^- species remaining on the particle surface with Co^{2+} , helped to obtain a uniform coverage, which was investigated here by the LPSA and TEM techniques.

The result of LPSA shows that the mean particle size of the annealed K-bir is $6.46 \mu\text{m}$, while those of 5% Co-K-bir, 10% Co-K-bir, and 20% Co-K-bir are 7.76 , 7.97 , and $8.02 \mu\text{m}$ (Table 1); their thickness of Co_3O_4 coverage are consequently estimated as about 0.65 , 0.76 , and $0.78 \mu\text{m}$, respectively. The mean particle size increased significantly

when 5% Co was coated, however, changed gently with the further increase of coated Co_3O_4 content. When K-bir was poured into $\text{Co}(\text{NO}_3)_2$ aqueous solution, the OH^- ions, remained on the surface of K-bir particle, reacted fast with Co^{2+} ions and formed incompact layer of CoOOH. The inner OH^- ions then diffused to the surface to continue reacting and increased thickness of CoOOH coverage. Hence, a thicker coverage would result in a slower reaction rate, which consequently benefited forming a more compact outside coverage than inside one. This interpretation is also supported by the comparison of specific areas of K-bir and Co-K-birs. All the Co_3O_4 -coated samples had higher specific areas than K-bir; however, the specific areas of 10% Co-K-bir was significantly higher than that of K-bir whereas slightly lower than 20% Co-K-bir (Fig. 5).

It is just because of the incompact coverage of Co-K-bir that we are able to observe it by TEM as shown in Fig. 6, where the TEM image of particle fringe is much brighter than that of its bulk. If the coated cobalt oxide is physically similar to bulk of K-bir, we could not observe such distinguish interface between them by the TEM. The estimated average thickness of Co_3O_4 coverage is about $1.1 \mu\text{m}$, which is higher than the value calculated from mean particle size analysis ($\sim 0.76 \mu\text{m}$) for 10% Co-K-bir. Comparing the TEM and LPSA results, respectively, the average thickness of Co_3O_4 coverage from LPSA seems

Table 1 Analysis of some physical properties of the as-prepared, the annealed, and the coated K-birs

Sample	Element content, wt.%			Atomic ratio		Mean particle size, μm	BET specific surface area, $\text{m}^2 \text{g}^{-1}$
	Mn	Co	K	Co/Mn	K/Mn		
K-bir	49.4	—	9.8	—	0.279	6.88	99.9
Annealed K-bir	50.8	—	9.94	—	0.275	6.46	96.3
5% Co-K-bir	53.8	2.7	5.52	0.047	0.144	7.76	128.6
10% Co-K-bir	50.0	5.5	4.82	0.103	0.135	7.97	139.5
20% Co-K-bir	50.2	10.8	2.34	0.200	0.066	8.02	142.5

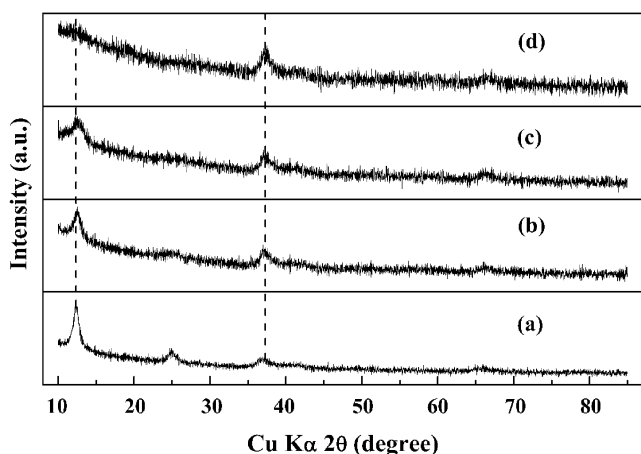


Fig. 5 XRD patterns of samples (a) K-bir, (b) 5% Co-K-bir, (c) 10% Co-K-bir, and (d) 20% Co-K-bir

more acceptable for the experimental limitations observing locally from TEM; meanwhile, the thickness of coverage from TEM observation close to that from LPSA result supports the validity of the latter technique.

Comparison of SEM images between K-bir and 10% Co-K-bir was shown in Fig. 7. From their low magnified image, they seem similar; however, closer look shows their obvious difference on their particle surface. There is some thorn-like structure appeared on the surface of K-bir, which, however, is not shown on Co_3O_4 coated samples. Taking 10% Co-K-bir as an example (Fig. 7b inset), its surface seems smoother. A less rich surface structure with a higher BET specific surface area for Co-K-bir, compared to K-bir, also implied that the covered Co_3O_4 of Co-K-birs were incompact, which is consistent with the results from LPSA and BET experiments.

Cycleability performance was employed to evaluate the effect of coating Co_3O_4 on electrochemical performance of K-bir. As shown in Fig. 8, K-bir and its annealed sample

behaved poorly and their capacities after 20 cycles, declined to 57% and 55% of their highest one, respectively. In contrast, the retained capacities of Co-K-birs were improved significantly upon cycling. Seventy-five percent capacity of 20% Co-K-bir retained, compared with 57% of K-bir and 55% of its annealed form, suggesting that this novel covering method is contributed to effectively improving the cycleability performance of K-bir. The improving cycleability performance may result as Mn dissolution and interlayer K^+ extraction were suppressed by coated layer of Co_3O_4 . A normalized specific capacity is used instead of capacity in Fig. 8 to compare the cyclic performances of K-bir and Co-K-bir more directly and clearly.

When discharged at 200 mA g^{-1} , K-bir and its annealed sample delivered capacities of 125 and 137 mAh g^{-1} , respectively. They are common in that their initial charge capacities were much higher than their corresponding discharge capacities, which is also consistent with the previous reports [3, 19]. The reason for this phenomenon is not clear yet; however, it might result from many factors, as reported previously, such as extract of potassium ions in the interlayer [14] and oxidation of structural water [19]. In contrast, Co-K-birs have no such character of much higher initial charge capacity compared to its initial discharge capacity.

In addition, the discharge capacities of Co-K-birs are higher than those of K-bir and its annealed form, which is due to that conductivity of cobalt oxide is better than that of manganese oxide [20]. However, the discharge plateau of Co_3O_4 is much lower than that of K-bir [21] which consequently reduced the plateau of Co-K-birs; therefore, the plateau of 20% Co-K-bir decreased most obviously. Combining the above effect factors, it is acceptable that 5% Co-K-bir and 10% Co-K-bir behaved similarly but had higher capacities compared to K-bir and 20% Co-K-bir.

Fig. 6 TEM images of samples (a) K-bir and (b) 10% Co-K-bir

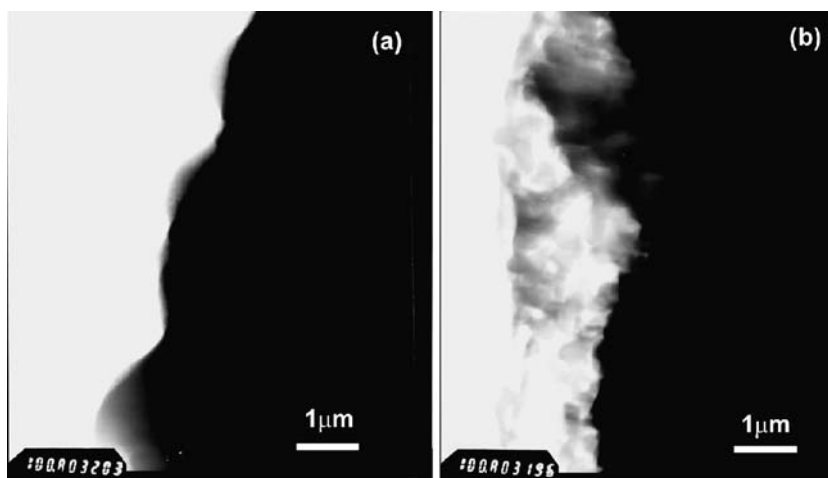
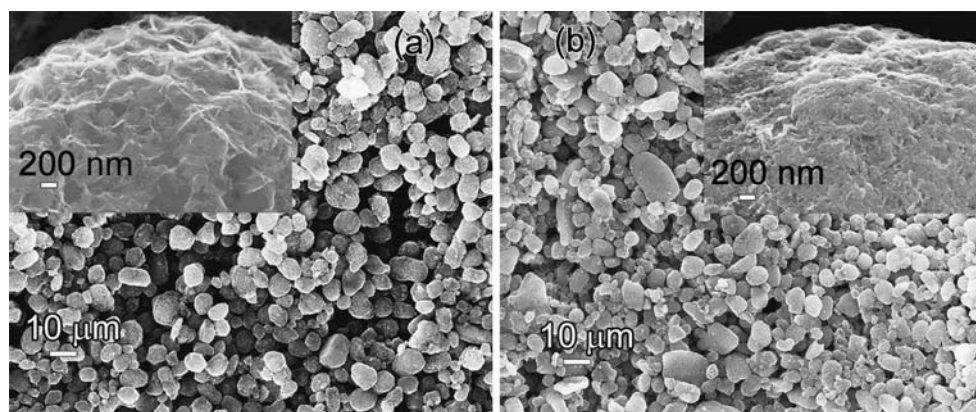


Fig. 7 SEM images of (a) K-bir and (b) 10% Co-K-bir



Comparison of initial two discharge–charge processes among the as-prepared, the annealed, and the coated samples indicated that all the coated samples delivered higher initial capacities than the as-prepared sample and its annealed form (Fig. 9). After initially charging, the as-prepared and the annealed samples increased their discharge capacities significantly while those coated samples showed almost equal to their initial value. This is attributed to high potassium content (~10%) in K-bir and its annealed form, and some of K^+ would be extracted at high charging potential while oxidation value of Mn increase near to +4; consequently, their second discharge processes delivered higher capacities. In contrast, although the Co_3O_4 -coated samples also contained potassium, e.g., 5.52 wt.% for 5% Co-K-bir, the covered Co_3O_4 might prevent K^+ from leaching into electrolyte. Therefore, we can observe that the first charge capacities of Co_3O_4 -coated samples were close to their discharge capacities.

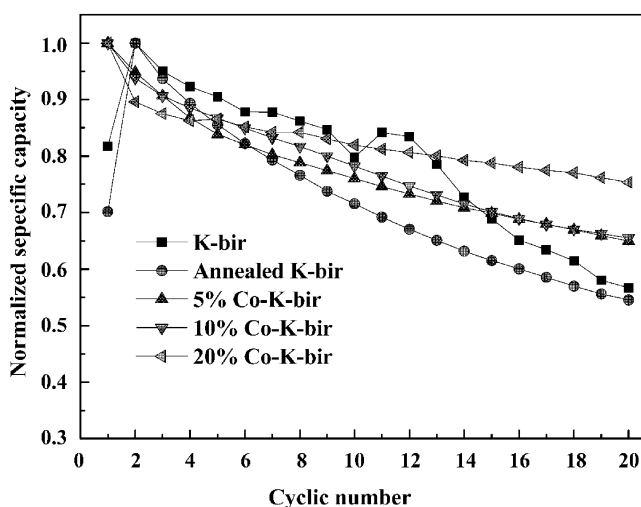


Fig. 8 Cycleability performances of K-bir and Co-K-birs

Conclusion

Co_3O_4 -coated K-bir was prepared by applying a novel coating method, in which the as-precipitated K-bir was washed once only and the remained OH^- ions on the particle surface reacted with Co^{2+} ions in aqueous solution, forming $CoOOH$ coated coverage; the obtained $CoOOH$ coated sample was subsequently annealed at $300^\circ C$ deliberately to transform into Co_3O_4 coated K-birs. The merit of this coating method is to help to obtain a uniform coverage.

The covered layers of Co_3O_4 are incompact as suggested by LPSA, BET, and TEM experiments, and their average thicknesses are about $0.65\text{--}0.78\ \mu m$.

The first discharge capacities of Co-K-birs were higher than that of K-bir and its annealed form, i.e., coating Co_3O_4 in the novel method improved the first discharge capacity. More important, the cycleability performance of K-bir improved after coating of Co_3O_4 .

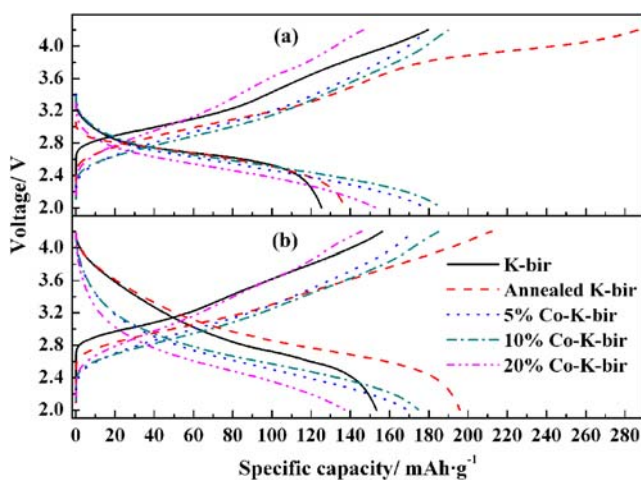


Fig. 9 Discharge/charge profiles of K-bir and Co-K-birs during the first (a) and second cycle (b) at 200 mA g^{-1}

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References

1. Liu H, Wu YP, Rahm E, Holze R, Wu HQ (2004) *J Solid State Electrochem* 8:450
2. Whittingham MS, Zavalij PY (2000) *Solid State Ionics* 131:109
3. Bach S, Pereira-Ramos JP, Baffier N (1996) *J Electrochem Soc* 143:3429
4. Kim SH, Kim SJ, Oh SM (1999) *Chem Mater* 11:557
5. Lu YL, Wei M, Wang ZQ, Evans DG, Duan X (2004) *Electrochim Acta* 49:2361
6. Renuka R, Ramamurthy S (2000) *J Power Sources* 87:144
7. Bach S, Pereira-Ramos JP, Cachet C, Bode M, Yu LT (1995) *Electrochim Acta* 40:785
8. Zhang F, Ngala K, Whittingham MS (2000) *Electrochem Commun* 2:445
9. Lu Y, Yang L, Wei M, Xie Y, Liu T (2007) *J Solid State Electrochem* 11:1157
10. Tsuda M, Arai H, Sakurai Y (2002) *J Power Sources* 110:52
11. Cho JP, Kim TJ, Park B (2002) *J Electrochem Soc* 149:A288
12. Yang Y, Shu D, Yu H, Xia X, Lin ZG (1997) *J Power Sources* 65:227
13. Huang XK, Yue HJ, Attia A, Yang Y (2007) *J Electrochem Soc* 154:A26
14. Le Cras F, Rohs S, Anne M, Strobel P (1995) *J Power Sources* 54:319
15. Thackeray MM (1997) *Prog Solid State Chem* 25:1
16. Leroux F, Guyomard D, Piffard Y (1995) *Solid State Ionics* 80:299
17. Chen R, Chirayil T, Zavalij P, Whittingham MS (1996) *Solid State Ionics* 86–88:1
18. Johnson EA, Post JE (2006) *Am Mineral* 91:609
19. Leroux F, Guyomard D, Piffard Y (1995) *Solid State Ionics* 80:307
20. Sharma PK, Moore GJ, Zhang F, Zavalij P, Whittingham MS (1999) *Electrochem Solid State Lett* 2:494
21. Kang Y-M, Song M-S, Kim J-H, Kim H-S, Park M-S, Lee J-Y, Liu HK, Dou SX (2005) *Electrochim Acta* 50:3667