Short communication

Sb$_2$O$_3$-modified Li$_{1.1}$CoO$_2$ phase as cathode material for lithium ion battery

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Sb$_2$O$_3$-modified Li$_{1.1}$CoO$_2$ material is successfully obtained by solid state reaction. The modified phase maintains the merit of high packing density of bare Li$_{1.1}$CoO$_2$; on the other hand, it is proved that the addition of Sb$_2$O$_3$ during the preparation effectively removes the excess Li and associated structure defect in the material. XRD, EDAX and ICP-AES measurements all reveal that the coating layer is a solid solution of LiCo$_{1-x}$Sb$_x$O$_2$. Cycling and thermal test indicates that, comparing to the bare Li$_{1.05}$CoO$_2$, Sb$_2$O$_3$-modified Li$_{1.1}$CoO$_2$ material shows improved cycleabilty as well as higher thermal stability.

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1. Introduction

Since the introduction of LiCoO$_2$ in the first commercialized lithium ion battery, LiCoO$_2$ keeps to be the chief choice as the cathode material due to its stable performance and facile preparation. Aiming to improve the performance of LiCoO$_2$ material, modified LiCoO$_2$ phase has attracted extensive interests. In general, the main approaches include partial substitution and surface coating.

To improve the structural stability and reduce the influence of local stress, the substitutions of Al [1,2], Mg [3], and Ga [4] for Co to give LiCo$_{1-x}$M$_x$O$_2$ were investigated in detail. However, when substituting with nontransition metal ions, any improvement in structural stability was achieved at the expense of the deliverable capacity, while transition metal ion substituent reduced the working voltage of the cell. Recently, Zou et al. reported that the doping phase of LiCo$_{0.95}$M$_{0.05}$O2 (M = Mn and Zr) showed high capacities as well as good cyclic performance in the voltage range 3.5–4.5 V [5,6].

The other alternate approach is to change the surface properties by coating cathode materials with metal oxides. Kweon et al. [7] firstly reported that the cycling performance of LiCoO$_2$ at high voltage (>4.2 V) has been fairly enhanced by Al$_2$O$_3$ coating. After that, various surface modifications of LiCoO$_2$ by coating MgO [8], ZrO$_2$ [9,10], SnO$_2$ [11], TiO$_2$ [12], and Co$_3$O$_4$ [13] have been widely

studied and have shown obvious improvement effects. At present, it is widely accepted that coating will not suppress the lattice expansion and phase transition of LiCoO$_2$ during the charge/discharge process, but it can change its surface property. For example, the authors [14] proposed that the Al$_2$O$_3$ coating layer can cover the active centers which serve as catalyst sites for electrolyte decomposition. Anyway, surface modification is verified to be a good way to enhance the cycleability of LiCoO$_2$, though the relative mechanism is still not yet understood. As also, the existence of the coating layer usually reduces the capacity of the resulting sample because of the introduction of the inactive component.

In view of achieving higher volume specific energy density of the cell, the cathode material with a higher packing density is continuously a potential interest to battery industry. So, although the packing density of LiCoO$_2$ is almost the biggest among all the possible cathode materials, high-density LiCoO$_2$ is still being pursued. Previous research has proved that preparing Li-overstoichioimtric Li$_{1+x}$CoO$_2$ is a direct and effective way to control the particle characteristic, such as: surface area and particle size [15,16]. It has shown that excessive Li$_2$CO$_3$ or its decomposition product of Li$_2$O can act as a flux during the LiCoO$_2$ preparation and helps to obtain the controlled-sized particles suitable for practical application. However, the residual Li$_2$O is highly reactive with moisture and carbon dioxide in air [17], thus the Li$_2$CO$_3$ surface layer will form, and its existence induces property deterioration of LiCoO$_2$.

To help us get out of the dilemma, Sb$_2$O$_3$-modified Li$_{1.1}$CoO$_2$ phase is proposed firstly in this paper. It is expected that Sb$_2$O$_3$ can react with the residual Li$_2$CO$_3$ and the solid solution of

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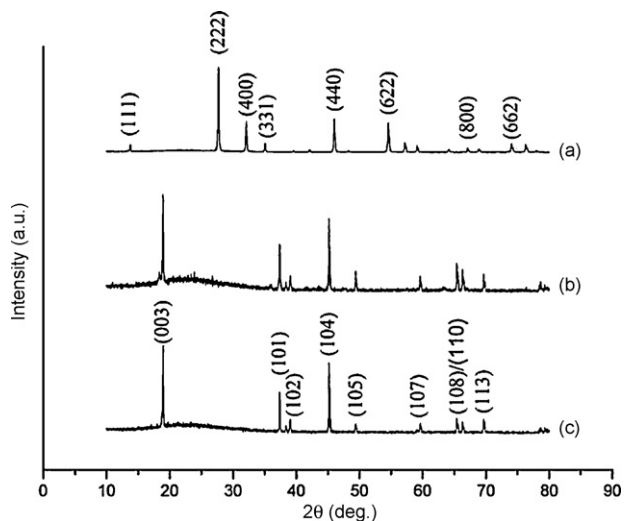*E-mail address:* zhanhui3620@126.com (H. Zhan).

Fig. 1. XRD patterns of (a) Sb_2O_3, (b) Sb_2O_3-modified $Li_{1.1}CoO_2$ and (c) $Li_{1.1}CoO_2$.

$LiCo_{1-x}Sb_xO_2$ is formed as the protection surface layer. It is also hoped that the Sb_2O_3 modification will help to obtain the high-density $LiCoO_2$ material with improved surface property, electrochemical property and thermal safety. The structure, surface charereristic, cycleabilty and thermal stability of Sb_2O_3-modified $Li_{1.1}CoO_2$ cathode are discussed in detail.

2. Experimental

The Li_xCoO_2 powders were prepared by high-temperature calcination from the mixture of Li_2CO_3 and Co_3O_4 in air (x denotes the nominal Li/Co ratio in the starting mixture, x = 1.0, 1.05 and 1.1). The finely ground mixtures were first heated at 850 °C for 5 h and then annealed at 920 °C for another 5 h without intermediate grinding.

Sb_2O_3-modified $Li_{1.1}CoO_2$ was also synthesized by solid state reaction. The above-prepared $Li_{1.1}CoO_2$ was mixed with Sb_2O_3 in the molar ratio of Co/Sb being 1/0.03, and then the mixture was also heated at 600 °C for 5 h and annealed at 920 °C for another 5 h consequently to obtain the final product.

The pH value of the materials was determined as follows. 1 g sample was added to 10 mL distilled water and the mixture was stirred mechanically for 1 h, after a complete settling, the pH value of the solution was measured.

XRD analysis was conducted with XRD-6000 diffractometer (Shimadzu, Japan), Cu Kα radiation and a scan rate of 4 °C min^{-1}. Rietveld refinement was conducted to obtain the cell parameters of the product. The morphology of the samples was observed on a Quanta 200 scanning electron microscope (SEM). The atomic ratio of the samples was obtained by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on a ThermoElemental IRIS Intrepid II XSP instrument.

Galvanostatic cycling was performed on 2016 coin cells. The cathode electrode was made by mixing 80 wt.% active material, 10 wt.% PTFE binder and 10 wt.% acetylene black, then pressing them on a aluminum mesh. Thus prepared electrode was dried at 150 °C for 12 h before the cell assembling. Typical loading of the active material was about 8.98 mg cm^{-2}. Metallic lithium was used as the anode. The electrolyte was 1M LiPF$_6$ in a 1:1 volume ratio mixture of ethylene carbonate (EC)/dimethyl carbonate (DMC), and the separator was Celgard 2300 membrane. The cells were assembled in the argon filled glove box (MECABOX80-1"s", Switzerland). Cycling tests were carried out following a given procedure. The cell was first charged and discharged at 30 mA g^{-1} for three times

between 3.0 and 4.2 V, then another three cycling was performed at 30 mA g^{-1} between 3.0 and 4.3 V, and finally the cell was tested at 100 mA g^{-1} between 3.0 and 4.3 V in the following cycles, in which a 1 h potentiostatic charging at 4.3 V was adopted.

The cyclic voltammetry (CV) experiment was carried out on a CHI660 Electrochemical Workstation at a scan rate of 0.05 mV s^{-1} in the potential range of 3.0–4.3 V. In CV measurement, three-electrode cell was used, in which the working electrode had a same composition as being described above, lithium foil worked as both the counter electrode and the reference one. All electrochemical measurements were carried out at room temperature.

Thermal characterization of $Li_{1.05}CoO_2$ and the modified powders was done on a PerkinElmer differential scanning calorimeter. The measurements were conducted in a nitrogen atmosphere from ambient temperature to 400 °C at a heating rate of 10 °C min^{-1} for checking the thermal stability of the material in electrolyte solution. And unless specified, all electrodes were charged to 4.7 V at 14 mA g^{-1} and kept at the constant potential of 4.7 V for 8 h before being subjected to DSC measurement.

3. Results and discussion

Fig. 1 shows the XRD patterns of Sb_2O_3, $Li_{1.1}CoO_2$ and Sb_2O_3-modified $Li_{1.1}CoO_2$. From the exhibited XRD peaks, there is no proof for the existence of Li_2CO_3 impurity in Sb_2O_3-modified and pristine $Li_{1.1}CoO_2$, and all diffraction peaks can be indexed by the α-NaFeO$_2$ type structure. According to the result of Imanishi et al., the $Li_{1+x}CoO_2$ product still appeared as a single phase in the XRD pattern even when the nominal Li/Co value was up to 1.3 [17]. It was usually ascribed to the amorphous nature of residual Li_2CO_3 or the formation of overstoichiometric $Li_{1+x}CoO_2$ phase. It is also noticed that there is no substantial difference between the XRD patterns of Sb_2O_3-modified and pristine $Li_{1.1}CoO_2$. This result may be explained by the formation of amorphous Sb_2O_3 or solid solution of $LiCo_{1-x}Sb_xO_2$. Besides, the low concentration of added Sb_2O_3 may limit the detection of relative impurity by XRD technique.

A slight contraction of the lattice constants a and c to a = 2.8169 Å and c = 14.0535 Å is observed in the modified $Li_{1.1}CoO_2$, from a = 2.8173 Å and c = 14.0545 Å for bare $Li_{1.1}CoO_2$. Similar c contraction was reported by Kim and co-workers [18] and Fey [12], and it is proposed to be originated from the formation of $LiCo_{1-x}M_xO_2$ surface layer. Accordingly, the observed contraction in c for the Sb_2O_3-modified $Li_{1.1}CoO_2$ seems to imply the formation of $LiCo_{1-x}Sb_xO_2$ coating layer, which may possibly result from the reaction between Sb_2O_3 and $Li_{1.1}CoO_2$ substrate. Considering the high-temperature stability of Sb^{5+} and the small difference between the ion radius of Sb^{5+} and Co^{3+}, Sb^{5+} replacing Sb^{3+} has the great possibility to enter the [CoO_6] slab and occupy the 3b sites. To give more proof for the formation of $LiCo_{1-x}Sb_xO_2$ coating layer, ICP-AES and EDAX measurements were conducted. As known, ICP-AES can be used to determine the bulk phase composition, while EDAX is more effective to detect the surface concentration of the component. It is found that the Sb/Co ratio detected by EDAX is 0.05/1, while ICP-AES measurement shows a Sb/Co ratio of 0.02/1. The notable difference obviously indicates that the added Sb is more likely to be enriched in the layer near the particle surface.

Fig. 2 compares the SEM images of $Li_{1.05}CoO_2$, $Li_{1.1}CoO_2$ and Sb_2O_3-modified $Li_{1.1}CoO_2$. It is clearly seen that the particles of $Li_{1.05}CoO_2$ sample have a smooth surface; while for $Li_{1.1}CoO_2$ sample, a few fine crumb adheres to the particle surface, which probably implies the existence of residual Li_2CO_3. Fig. 2e and f present the SEM micrographs of Sb_2O_3-modified $Li_{1.1}CoO_2$, the addition of Sb_2O_3 during the calcination directly leads to the formation of a coating layer on the $Li_{1.1}CoO_2$ substrate and the
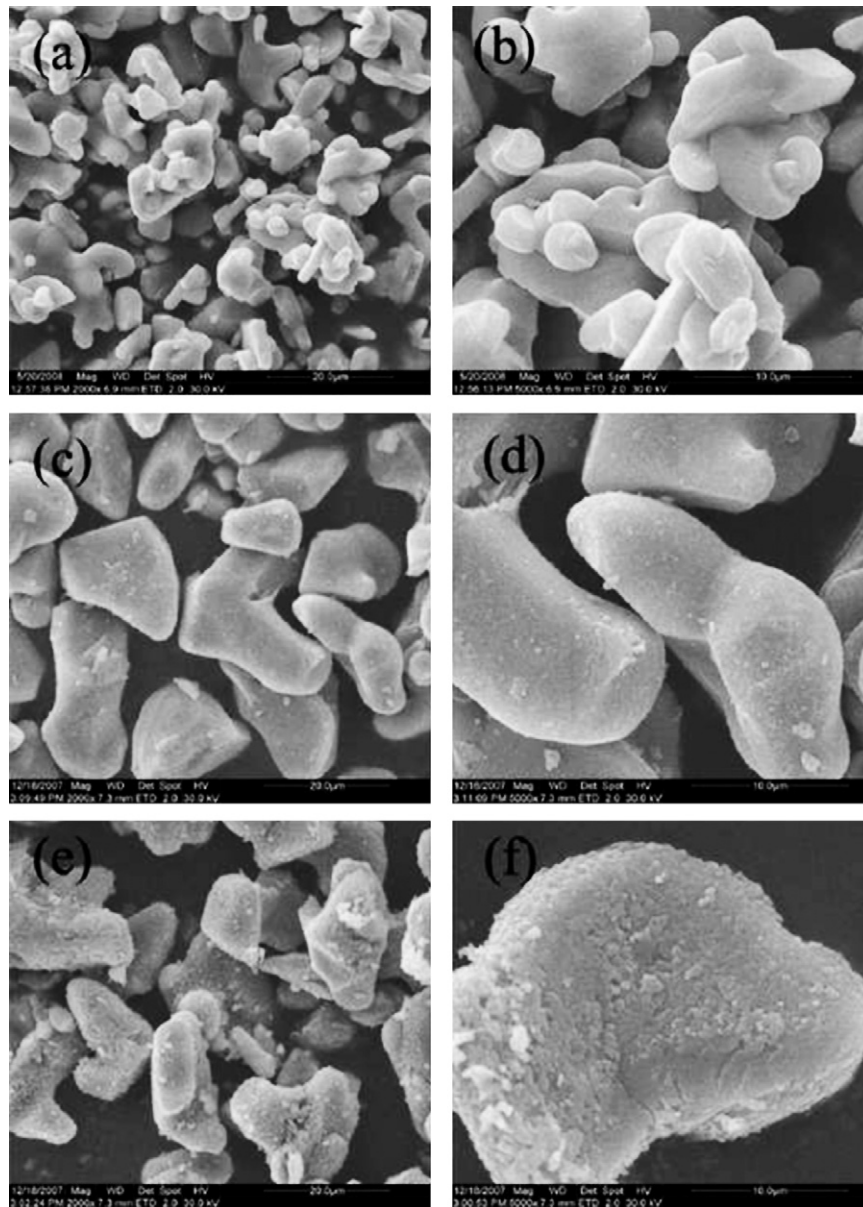
Fig. 2. SEM images of (a) low- and (b) high-magnification of $Li_{1.05}CoO_2$; (c) low- and (d) high-magnification of $Li_{1.1}CoO_2$; (e) low- and (f) high-magnification of Sb_2O_3-modified $Li_{1.1}CoO_2$.

product with rough surface. In addition, it is found from Fig. 2 that the average particle size of the products decreases in the order of $Li_{1.1}CoO_2 > Sb_2O_3$-modified $Li_{1.1}CoO_2 > Li_{1.05}CoO_2$. As being reported in previous study, overstoichiometric $Li_{1+x}CoO_2$ phase has a higher packing density than the stoichiometric one, the comparison of the SEM images seems to indicate that modification of Sb_2O_3 helps to maintain the larger particle size of the $Li_{1.1}CoO_2$ phase, which usually means a relatively higher packing density.

Table 1 displays the data obtained from pH value and packing density measurement. As known, although the addition of excess

lithium salt during the $LiCoO_2$ preparation benefits the formation of the products with higher density, the existence of residue Li_2CO_3 certainly induces the increased pH value of the product, which is unfavorable for electrode manufacture and achieving the desired cycleability. So, the packing density as well as the pH value is both critical when practical applications are required. The data presented in Table 1 agrees well with the SEM observation, the packing density of the products increases by the order of $Li_{1.1}CoO_2 > Sb_2O_3$-modified $Li_{1.1}CoO_2 > Li_{1.05}CoO_2$. Also noticed from Table 1 is that, as being expected, the unfavorable increase in pH value originating from Li-overstoichiometry in $LiCoO_2$ can be effectively suppressed when Sb_2O_3 is added. The results tell that Sb_2O_3 modification helps to maintain a high packing density and a relatively lower pH value of the resulting material. To make clear the origin of the decrease in the pH value, an additional experiment was conducted. The mixture of Li_2CO_3 and Sb_2O_3 was heated at 600 °C for 5 h and annealed at 920 °C for another 5 h consequently as same as that in the preparation of Sb_2O_3-modified $Li_{1.1}CoO_2$. Fig. 3 displays its XRD pattern.
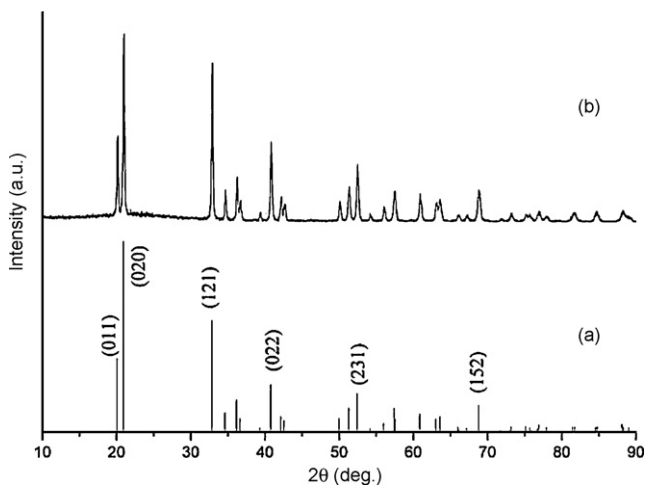
Table 1
The pH value and the packing density of the resulting samples

	pH	density (g cm^{-3})
$Li_{1.05}CoO_2$	11.80	2.31
$Li_{1.1}CoO_2$	12.16	2.85
Sb_2O_3-modified $Li_{1.1}CoO_2$	11.42	2.70

Fig. 3. XRD patterns of (a) LiSbO$_3$ (JCPDS card no. 84-2003); (b) LiSbO$_3$ prepared by calcination from the mixture of Li$_2$CO$_3$ and Sb$_2$O$_3$.

It is revealed that thus treatment gives the product of LiSbO$_3$ with orthorhombic structure and Pncn space group (JCPDS card no. 84-2003). Therefore, it is inferred that the added Sb$_2$O$_3$ consumes the unwanted Li$_2$CO$_3$ residue on the particle surface and then forms another coating layer composed of LiCo$_{1-x}$Sb$_x$O$_2$.

In the above discussion, the influence of Sb$_2$O$_3$ modification on the particle morphology has been analyzed in detail, and its beneficial effect has been proved. It is expected that the existence of LiCo$_{1-x}$Sb$_x$O$_2$ coating layer can also improve the cyclic performance of Li$_{1.1}$CoO$_2$ material. It has been widely proved that residual Li$_2$CO$_3$ existing in Li-overstoichiometric LiCoO$_2$ phase increases the electrode impedance and leads to the degradation of cyclic performance in this case [19,20].

Fig. 4 presents the first charge and discharge profiles of the resulting sample. It can be seen that the first charge/discharge capacity of Li$_{1.05}$CoO$_2$, Li$_{1.1}$CoO$_2$ and Sb$_2$O$_3$-modified Li$_{1.1}$CoO$_2$ is about 142.1/134.6, 143.6/133.7, 134.3/125.8 mAh g^{-1} respectively, corresponding to the efficiency of 94.4, 93.1 and 93.7% for each sample. As regards to the average coulombic efficiency, the modified sample is about 98.6%, which is slightly superior to that of Li$_{1.05}$CoO$_2$ (about 98.0%) and far surpasses that of Li$_{1.1}$CoO$_2$ (about 93.6%).
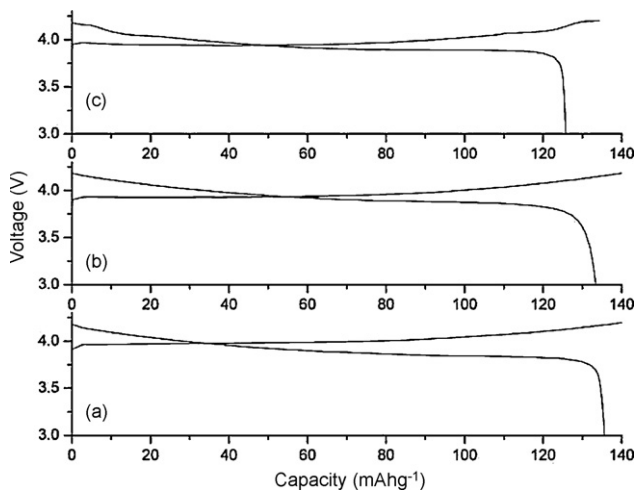

Fig. 4. The initial charge and discharge curves of (a) Li$_{1.05}$CoO$_2$, (b) Li$_{1.1}$CoO$_2$ and (c) Sb$_2$O$_3$-modified Li$_{1.1}$CoO$_2$.
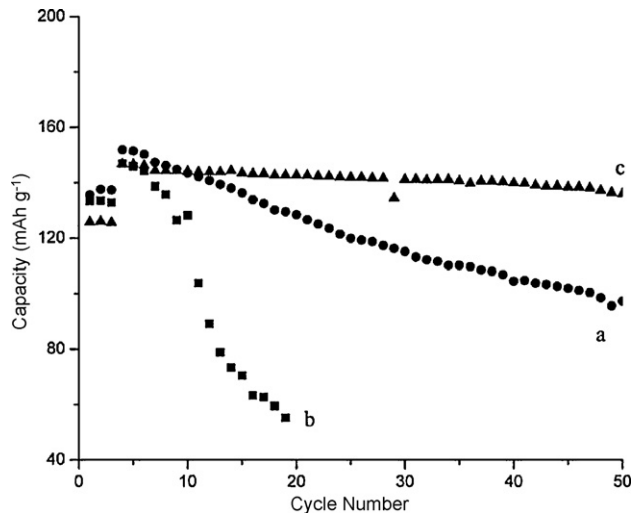
Fig. 5. Cycling performance of (a) Li$_{1.05}$CoO$_2$, (b) Li$_{1.1}$CoO$_2$ and (c) Sb$_2$O$_3$-modified Li$_{1.1}$CoO$_2$.

Fig. 5 exhibits the cycling property of Li$_x$CoO$_2$ and Sb$_2$O$_3$-modified Li$_{1.1}$CoO$_2$. The result shows that the modified phase exhibits the best cyclic performance among the three samples while the Li-overstoichiometric Li$_{1.1}$CoO$_2$ exhibits the poorest cycleablity. It is considered that the addition of Sb$_2$O$_3$ not only consumes the detrimental residue of Li$_2$CO$_3$, but also repairs the structural defect resulting from Li-overstoichiometry. As regards to the decreased capacity of the modified phase, it can be explained by the electrochemically inactive dopant in the coating layer. Obviously, the high efficiency and excellent cycleability of the modified LiCoO$_2$ phase determine it to be a promising candidate as the cathode material for Li-ion batteries.

To examine the electrochemical behavior of the resulting material, cyclic voltammograms of bare Li$_{1.1}$CoO$_2$ and Sb$_2$O$_3$-modified Li$_{1.1}$CoO$_2$ electrodes were recorded and the results are presented in Fig. 6. It is clearly seen from Fig. 6a that only a pair of redox peaks is observed for Li$_{1.1}$CoO$_2$ electrode, which locates at 3.81/4.10 V, and no more peaks other than these can be observed. This result does not accord well with the typical cyclic voltammogram of LiCoO$_2$, which always exhibits three pairs of redox peaks corresponding to three phase transformation during the Li$^+$ insertion/de-insertion [13,21] (shown in Fig. 6c). A further comparison of the CV curves of
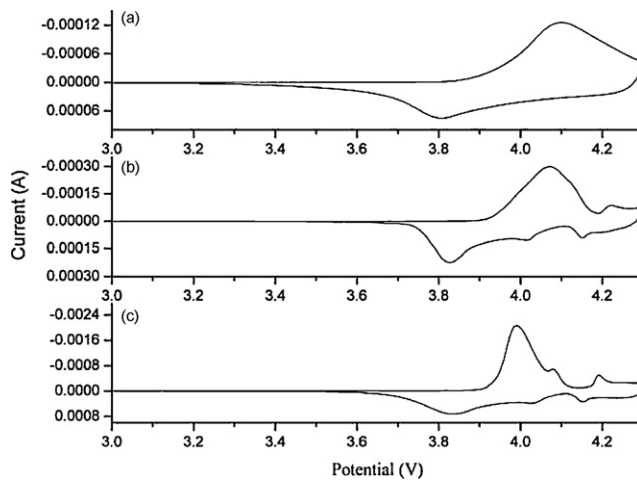

Fig. 6. Cyclic voltammograms of (a) Li$_{1.1}$CoO$_2$, (b) Sb$_2$O$_3$-modified Li$_{1.1}$CoO$_2$ and (c) Li$_{1.0}$CoO$_2$ (sweep range: 3.0–4.3 V, sweep rate: 0.05 mV s^{-1}).

Table 2
The result of DSC measurement of $Li_{1.05}CoO_2$ and Sb_2O_3-modified $Li_{1.1}CoO_2$

	Peak 1		Peak 2	
	Onset temperature (°C)	Exothermic amount (J g^{-1})	Onset temperature (°C)	Exothermic enthalpy (J g^{-1})
$Li_{1.05}CoO_2$	215.93	121.8340	–	–
Sb_2O_3-modified $Li_{1.1}CoO_2$	235.72	41.5745	283.23	76.8139

$Li_{1.0}CoO_2$ and $Li_{1.1}CoO_2$ electrode shows that with the increasing Li content in $Li_{1+x}CoO_2$ phase, the oxidation peak becomes broader. Besides that, the oxidation peak shifts toward the positive direction, while the reduction peak toward the negative direction, and more serious peak separation thus engenders. This phenomenon indicates that more pronounced electrochemical polarization occurs on overstoichiometric $LiCoO_2$ phase, which is most likely due to the nonconductive nature of Li_2CO_3 residue and structural defects in the material. The CV profile of Sb_2O_3-modified $Li_{1.1}CoO_2$ is displayed in Fig. 6b, it resembles well to that exhibited by stoichiometric $LiCoO_2$ electrode, except the slightly shifted and relatively broadened oxidation peak. As seen in Fig. 6b, three pairs of redox peak located at 3.83/4.07, 4.02/4.12 and 4.15/4.22 V can be observed, though the oxidation peak at 4.12 V is partially overlapped and presents as a shoulder peak. In the early report of Levasseur et al. the authors believed that excess lithium and associated structural defects in the $Li_{1+x}CoO_2$ material could be removed in the form of Li_2O after an additional thermal treatment at 900 °C under atmospheric O_2 pressure for 10 days and then stoichiometric $LiCoO_2$ would be formed [22]. They also claimed that thus treatment resulted to a notable change in the charge/discharge curve, such as more abrupt voltage drop at the end of discharge. Summarizing the data obtained from CV and charge/discharge measurement, it is concluded that the addition of Sb_2O_3 effectively helps to eliminate the negative effect of excess lithium.

The thermal stability of $Li_{1.05}CoO_2$ and Sb_2O_3-modified $Li_{1.1}CoO_2$ is compared in Table 2. It can be clearly seen that after being modified by Sb_2O_3, the exothermic reaction of the over-charged $LiCoO_2$ electrode is delayed from 216 °C for the bare $Li_{1.05}CoO_2$ to 236 °C for Sb_2O_3-modified $Li_{1.1}CoO_2$. Although the total exothermic amount for the modified and unmodified phase is nearly the same, it is found that if the exothermic enthalpy corresponding to the reaction occurring in the lower temperature range is concerned, the higher decomposition temperature of the modified phase is complemented by its lower enthalpy of reaction (41.5745 J g^{-1}) compared to the bare $Li_{1.05}CoO_2$ (121.8340 J g^{-1}). The result obviously tells that the modification helps to reduce the reactivity of the cathode material towards the electrolyte and thus enhances its thermal safety.

4. Conclusion

Sb_2O_3-modified $Li_{1.1}CoO_2$ material is successfully obtained by solid state reaction. The merit of high packing density of the $Li_{1.1}CoO_2$ phase is well maintained by addition of Sb_2O_3 during the calcination; on the other hand, the unfavorable effect resulting from introducing overstoichiometric Li in $LiCoO_2$, such as: pH increase and structure defect, are greatly reduced. XRD and EDAX measurements both reveal the existence of the $LiCo_{1-x}Sb_xO_2$ coating layer, which is believed to be formed by the reaction among added Sb_2O_3, residue Li_2CO_3 on the surface and the $Li_{1+x}CoO_2$ substrate. Above all, Sb_2O_3-modified $Li_{1.1}CoO_2$ material shows a great improvement in cycleabilty, packing density and thermal safety comparing to the bare $Li_{1.05}CoO_2$.

References

[1] W.S. Yoon, K.K. Lee, K.B. Kim, J. Power Sources 97–98 (2001) 303–307.
[2] W.S. Yoon, K.K. Lee, K.B. Kim, J. Electrochem. Soc. 149 (2002) A146–A151.
[3] S. Levasseur, M. Ménétrier, C. Delmas, J. Power Sources 112 (2002) 419–427.
[4] S.M. Lala, L.A. Montoro, V. Lemos, M. Abbate, J.M. Rosolen, Electrochim. Acta 51 (2005) 7–13.
[5] M. Zou, M. Yoshio, S. Gopukumar, J. Yamaki, Chem. Mater. 15 (2003) 4699–4702.
[6] M. Zou, M. Yoshio, S. Gopukumar, J. Yamaki, Chem. Mater. 17 (2005) 1284–1286.
[7] H.J. Kweon, G.B. Kim, D.G. Park, K.R. Patent Appl. 1998/0012005.
[8] Z. Wang, C. Wu, L. Liu, F. Wu, L. Chen, X. Huang, J. Electrochem. Soc. 149 (2002) A466–A471.
[9] Z. Chen, J.R. Dahn, Electrochem. Solid State Lett. 5 (2002) A213–A216.
[10] J. Cho, Y.J. Kim, T.J. Kim, B. Park, Angew. Chem. Int. Ed. 40 (2001) 3367–3369.
[11] J. Cho. Chen, C.S. Kim, S.I. Yoo, Electrochem. Solid-State Lett. 3 (2000) 362–365.
[12] G.T.K. Fey, C.Z. Lu, T.P. Kumar, Y.C. Chang, Surf. Coat. Technol. 199 (2005) 22–31.
[13] G.T.K. Fey, Y.Y. Lin, T.P. Kumar, Surf. Coat. Technol. 191 (2005) 68–75.
[14] L. Liu, L. Chen, X. Huang, X.-Q. Yang, W.-S. Yoon, H.S. Lee, J. McBreen, J. Electrochem. Soc. 151 (2004) A1344–A1351.
[15] M. Ménétrier, S.H. Yang, A. Wattiaux, L. Fournès, C. Delmas, Chem. Mater. 17 (2005) 4653–4659.
[16] E. Antolini, L. Giorgi, M. Carewska, J. Mater. Sci. Lett. 18 (1999) 325–327.
[17] N. Imanishi, M. Fujii, A. Hirano, Y. Takeda, M. Inaba, Z. Ogumi, Solid State Ionics 140 (2001) 45–53.
[18] J. Cho, Y.J. Kim, B. Park, Chem. Mater. 12 (2000) 3788–3791.
[19] N. Pereira, C. Matthias, K. Bell, F. Badway, I. Plitz, J. Al-Sharab, F. Cosandey, P. Shah, N. Isaacs, G.G. Amatucci, J. Electrochem. Soc. 152 (2005) A114–A125.
[20] Z. Chen, J.R. Dahn, Electrochim. Acta 49 (2004) 1079–1090.
[21] H.F. Wang, Y.I. Jang, B.Y. Huang, D.R. Sadoway, Y.M. Chiang, J. Electrochem. Soc. 146 (1999) 473–480.
[22] S. Levasseur, M. Ménétrier, S.-H. Yang, L. Gautier, A. Audemer, G. Demazeau, A. Largeteau, C. Delmas, Chem. Mater. 15 (2003) 348–354.