

Surface modification of spherical $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ with Al_2O_3 using heterogeneous nucleation process

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Received 15 July 2007; accepted 10 September 2007

Abstract: To improve the cycle stability at high voltage and high charge/discharge rate, spherical $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ was coated with Al_2O_3 by using heterogeneous nucleation process, and the physical and electrochemical properties were studied. The SEM images show that there is a uniform coating on the modified spherical $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$. The electrochemical tests indicate that the properties of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ coated with 0.5% aluminum oxide are the best. The initial capacities are 150 and 173 mA·h/g at the rate of 1C in the voltage range of 2.7–4.3 V and 2.7–4.6 V, respectively, and the discharge capacities maintain about 99% and 85% after 30 cycles, respectively. While those of the bare $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ are only 90% and 75%, respectively. The CV tests of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ show that Al_2O_3 -coating can restrain the oxide-reduction peak currents fading during the charge/discharge course.

Key words: Li-ion battery; $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$; heterogeneous nucleation; Al_2O_3 -coated

1 Introduction

For its high discharge capacity, thermal stability and low cost, $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ has attracted much attention. While, due to its low tap-density, bad cycling performance at high working voltage and high charge/discharge rate, it can not completely substitute LiCoO_2 to become new generation commercial Li-ion battery cathode material[1–3]. LEE et al[4] and YING et al[5] have improved the tap density by sphericizing the materials and the tap density is nearly similar to that of LiCoO_2 . The bad cycling performance mainly relates to structural instability of material; otherwise, investigators have found that it also concerns with the material salvation in the electrolyte[6–8]. LI et al[7] revealed that interface film that has been formed during the course of active material interaction with electrolyte can be easily destroyed at high working voltage and high rate, and this leads to large capacity loss. By coating the cathode materials to physically isolate and reduce the contacting area in electrolyte, the speed of the interactions between cathode materials and electrolytes is controlled[8–9]. Compared with lattice doping, coating has less negative influence on the electrochemical characteristics of

electrode materials in virtue of its proper coating mass and coating only on the surface of the material, and it restrains the interactions obviously. Then, more efforts have been put on cathode materials coating with inert metal oxides, such as B_2O_3 , MgO , ZnO and Al_2O_3 [10–12]. However, the coating layer has no electrochemical activation, and thick and compact coating layer would deteriorate the rate capability of electrode materials. Some papers have reported the coating with LiAlO_2 and LiMn_2O_4 that react with electrolyte slightly and have certain electrochemical activation[7,13]. The technology of surface coating by heterogeneous nucleation in the field of inorganic ceramics is very mature and it has been applied to surface modification of other Li-ion battery materials, such as graphite and LiMn_2O_4 [14–17].

In this work, the alkalescency of $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ and acidity of the $\text{Al}(\text{NO}_3)_3$ in aqueous solution were used to coat $\text{Al}(\text{OH})_3$ on the surface of $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ by heterogeneous nucleation. Spherical $\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{CO}_3$ precursor was obtained by carbonate coprecipitation, and spherical $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ was synthesized by high-temperature solid reaction. The electrochemical characteristics of final Al_2O_3 coated $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ were meliorated.

2 Experimental

Spherical $\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{CO}_3$ precursor was prepared by coprecipitation. A mixed metal salt solution of NiSO_4 , MnSO_4 and CoSO_4 (cationic molar ratio of $\text{Ni}:\text{Mn}:\text{Co}=1:1:1$) with a concentration of 2.0 mol/L was pumped into a specially designed continuously stirred reactor, where the stirring speed was maintained at 1 000 r/min. At the same time, 2.0 mol/L Na_2CO_3 solution and $\text{NH}_3\cdot\text{H}_2\text{O}$ solution as a chelating agent were also separately pumped into the reactor. The pH of solution was carefully controlled by Na_2CO_3 solution. The obtained spherical $\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{CO}_3$ powders were filtered, washed by deionization water, dried at 120 °C, and fired at 500 °C in air. The fired powders were mixed thoroughly in Li_2CO_3 with a molar ratio of $\text{Li}:(\text{Ni}+\text{Mn}+\text{Co})=1.10:1$. Then, the mixed powder was calcined at 900 °C for 12 h to obtain spherical $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ powder.

The $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ was dissolved to aqueous solution with certain concentration. The pH value was about 2.0. According to the coating mass, 0.5%, 1%, 3% and 5% of the mass of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, the $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ powders were slowly added into vigorously stirred $\text{Al}(\text{NO}_3)_3$ solution. With different adding masses, the pH value of obtained suspending liquid was from 4.5 to 5. The solution was stirred for 12 h. Then, $\text{Al}(\text{OH})_3$ was nucleated on the surface of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ particles. The pH value was adjusted to 9.0 by $\text{NH}_3\cdot\text{H}_2\text{O}$ solution in order to make the $\text{Al}(\text{OH})_3$ sufficiently grown on the heterophase crystal nucleus to assure the cladding layer more compact. The spherical $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ coated with $\text{Al}(\text{OH})_3$ was filtered, washed, dried and heat-treated at 500 °C for 10 h to obtain spherical $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ powders coated with Al_2O_3 .

The particle morphology of the powders was observed using a scanning electron microscope (SEM, JSM6301F). The electrochemical characteristics were studied by coin cells and CV tests. The electrode formulation consisted of 80% $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ powders, 10% carbon black and 10% (mass fraction) binder(PVDF). The prepared electrode pellets were dried at 100 °C under vacuum for 12 h. The test coin cells (CR2025) were assembled in a dry glove box filled with argon. The separator was a Celguard 2400 microporous polypropylene membrane. The electrolyte was 1 mol/L LiPF_6 in EC+DEC (1:1, volume ratio). A lithium metal anode was used in this study. The charge—discharge cycling was galvanostatically performed at a current of 160 mA/g (about 1 C) with voltage range of 2.70–4.30 V and 2.70–4.60 V at room temperature. The cyclic voltammogram(CV) tests were performed in the voltage

range of 2.8–4.6 V (vs Li/Li^+) and the scan speed was 0.2 mV/s.

3 Results and discussion

During the process of heterogeneous nucleation, the alkalescency $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ is used to neutralize faintly acid $\text{Al}(\text{NO}_3)_3$ solution to control the pH value. The spherical material is composed of many microcrystals. Comparatively, it is easy to preferentially nucleate and grow on the crystal edges, such as grain boundary and corners, while it is not easy to form on the surface of crystal. When the reaction system is on the condition of heterogeneous nucleation macroscopically and microcosmically, the partial high pH value on the surface of spherical particles will lead to growth of $\text{Al}(\text{OH})_3$. Otherwise, $\text{Al}(\text{OH})_3$ particles are much inclined to nucleate and grow at the grain boundary.

Fig.1 shows the SEM images of the bare spherical $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ (without Al_2O_3 coating treatment) and Al_2O_3 -coated spherical $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$. Comparing Fig.1(c) with Fig.1(d), we can see that, the surface of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ coated with Al_2O_3 looks obscure. Fig.2 reveals that such obscure surface actually has been formed during Al_2O_3 coating. The contour of crystallites is not distinct, and the surface is obviously covered with mesh-type matters. This shows that the surface is entirely coated by Al_2O_3 in submicron order of magnitude.

Fig.3(a) shows the initial discharge curves of the materials in the voltage range of 2.7–4.3 V and at the rate of 1C. The $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ without any treatment shows the most high initial discharge capacity, 158 mA·h/g. The material coated with 5% Al_2O_3 shows most low capacity, only 141 mA·h/g. The initial discharge capacity of $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ only treated in water is 146 mA·h/g. With the coating content of 0.5%, 1.0% and 3.0%, the materials show minor difference of the capacity, 149, 150 and 151 mA·h/g, respectively. In the voltage of 2.7–4.6 V (Fig.3(b)), the material with coating content of 0.5% shows the highest capacity, 173 mA·h/g. The capacity of $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ without any treatment shows a bit lower capacity, 170 mA·h/g. The capacity of material coated with 5.0% Al_2O_3 is the lowest (156 mA·h/g). It can be deduced that the appropriate Al_2O_3 coating treatment can improve the discharge capacity at high working voltage. While too much coating content will exert bad influence on the discharge capacity. It mainly concerns with the inert electrochemical activity of Al_2O_3 .

Fig.4 shows the cycling performance of materials at the rate of 1C. The coated materials exhibit good cycle stability no matter that the upper cut-off potential is 4.3 or 4.6 V. In comparison, the uncoated $\text{LiNi}_{1/3}\text{Mn}_{1/3}$ -

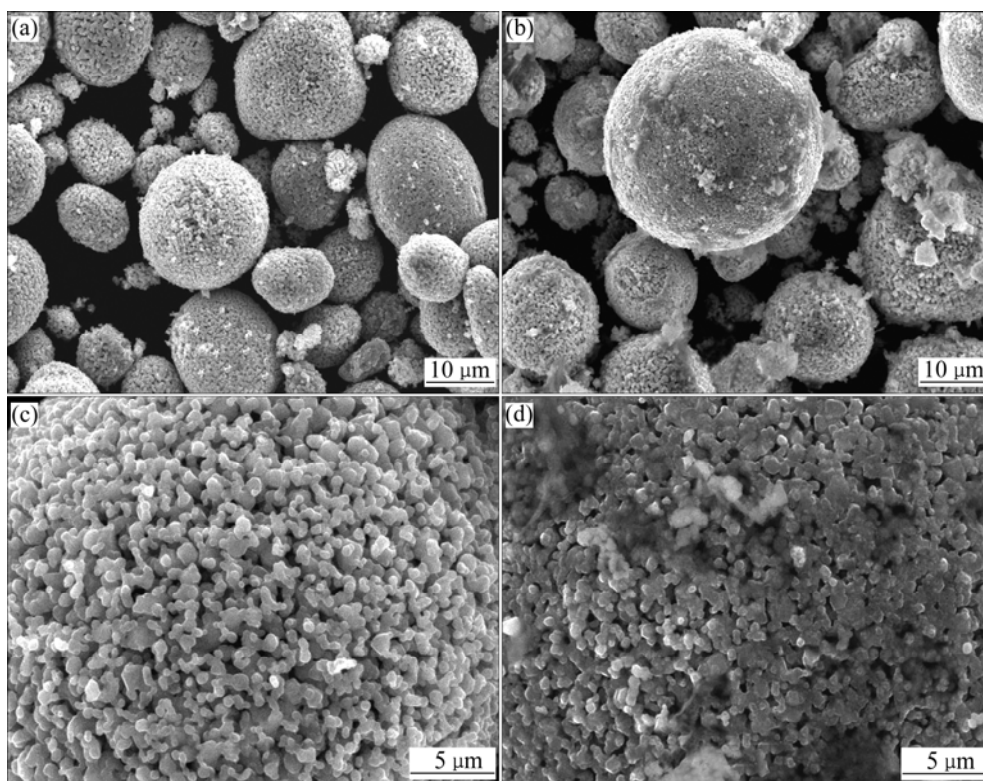


Fig.1 SEM images of bare $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ and Al_2O_3 -coated $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$: (a) and (b) Bare $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$; (b) and (d) Al_2O_3 -coated $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$

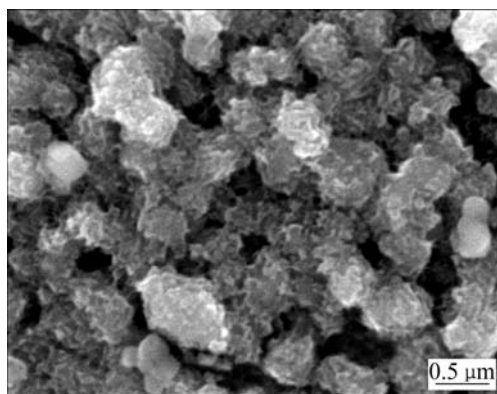


Fig.2 SEM image of $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ with Al_2O_3 dosage of 3%

$\text{Co}_{1/3}\text{O}_2$ shows a poor cycle stability during cycling. Fig.4(a) reveals that in 2.7–4.3 voltage range, after 30 cycles, the capacity of $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ with coating keeps up to 95%, while that of $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ without any treatment is only 90% and that of $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ only treated in water is 92%. The $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ with 0.5% coating content shows the best cycling performance and the capacity maintains as high as 99%. In the voltage range of 2.7–4.6 V, at 1C discharge rate, the cycle performances of coated materials are all better than those of material without coating. After 30 cycles, the capacity of $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ with 0.5% Al_2O_3 maintains 85%,

while that of $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ without Al_2O_3 coating is only 75%. However, excessive amount of coating will have a harmful effect on discharge capacity. So, we can draw a conclusion from Fig.3 and Fig.4 that when the coating content is 0.5%, the performance of material is comparatively the best.

Fig.5 shows CVs of $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ and $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ coated with Al_2O_3 . As it can be seen that the materials have two oxidation/reduction peaks in the voltage range of 2.8–4.8 V. The oxidizing peak of $\text{Ni}^{2+/4+}$ appears in the voltage range of 3.9–4.1 V, and reductive peak appears in the voltage range of 3.5–3.7 V. The oxidation/reduction peaks of $\text{Co}^{3+/4+}$ are in the voltage range of 4.5–4.7 V. Fig.5(a) shows that at the scan rate of 0.2 mV/s, oxidation/reduction peaks show a bit excursion, while the peak current of oxidizing peaks shows little difference. The bare $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ shows the highest oxidant peak current and reductive peak current is comparatively small. Fig.5(b) shows that during the second cycle, the polarization is small, and the area of the oxidant peaks is almost consistent with that of the reductive peaks. This reveals that the material reversibility is perfect. From Figs.5(a) and (b), we can see that during the first and second cycles, the oxidation/reduction peak current of $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ with Al_2O_3 coating is increased, while bare $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ peak current decreases much. During the second cycle, the reductive peak currents of

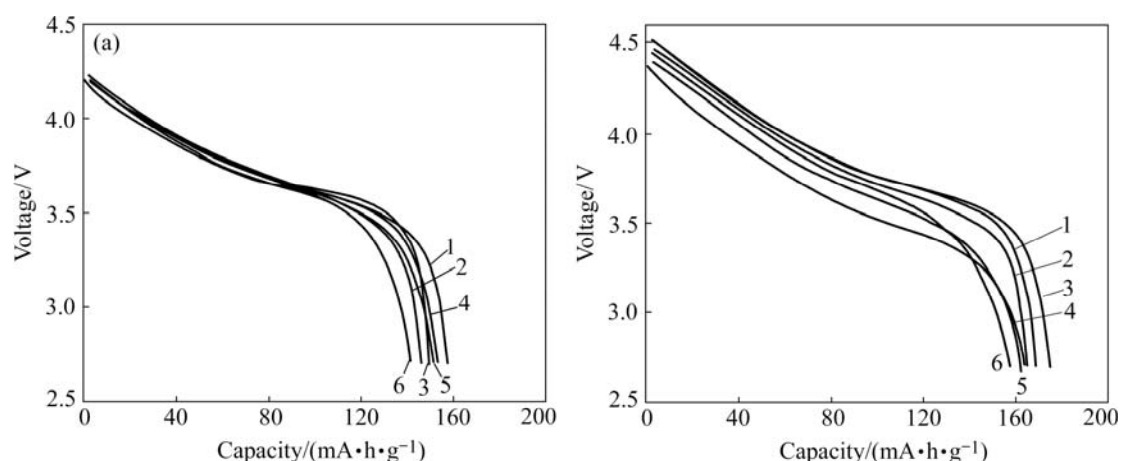


Fig.3 Discharge curves of bare $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ and Al_2O_3 -coated $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$: (a) 2.7–4.3 V; (b) 2.7–4.6 V; 1 $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$; 2 $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ treated in water; 3 Coated with 0.5% Al_2O_3 ; 4 Coated with 1.0% Al_2O_3 ; 5 Coated with 3.0% Al_2O_3 ; 6 Coated with 5.0% Al_2O_3

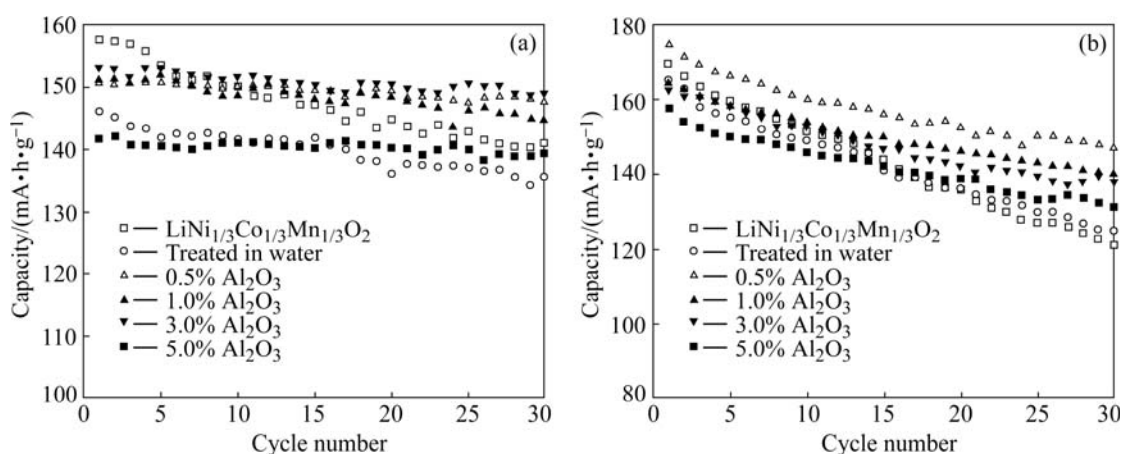


Fig.4 Cycling performances of bare $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ and Al_2O_3 -coated $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ at 1C rate: (a) 2.7–4.3 V; (b) 2.7–4.6 V

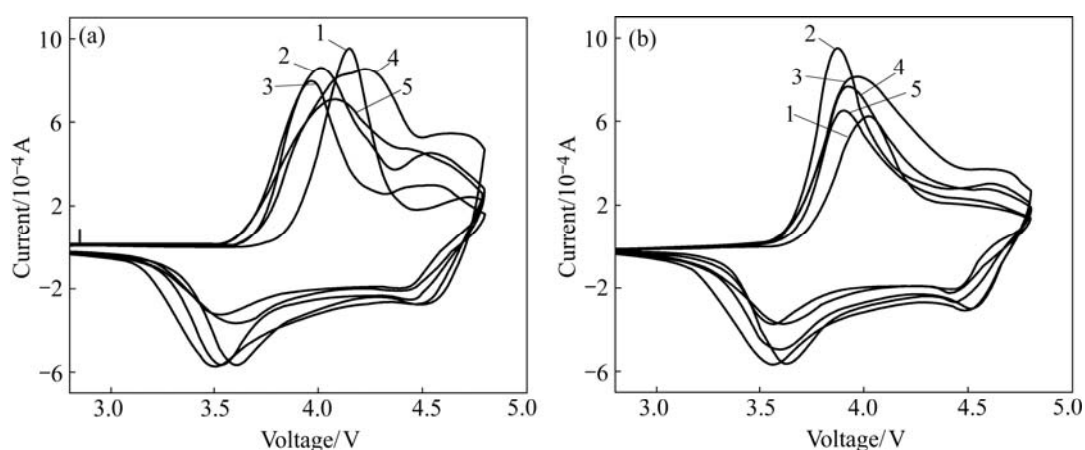


Fig.5 CVs of bare $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ and Al_2O_3 -coated $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ at scan rate of 0.2 mV/s: (a) First cycle; (b) Second cycle; 1 Bare $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$; 2 Coated with 0.5% Al_2O_3 ; 3 Coated with 1.0% Al_2O_3 ; 4 Coated with 3.0% Al_2O_3 ; 5 Coated with 3.1% Al_2O_3

$\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ coating with Al_2O_3 are larger than that of bare $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$. Otherwise, with the increase of Al_2O_3 coating content, the peak currents of

oxidation/reduction decrease, which shows that Al_2O_3 coating can improve the reversibility of materials, while too much coating will deteriorate the reversibility to

some degree.

4 Conclusions

1) Heterogeneous nucleation process is applied to Al_2O_3 coating on the surface of spherical $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ and a uniform coating layer can be obtained.

2) The cycling performance of spherical $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ is improved in the voltage range of 2.7–4.3 V and 2.7–4.6 V at 1C rate by coating. When the coating content is 0.5%, it shows the best result after 30 cycles. The capacities of the materials maintain about 99% and 85%, and the initial discharge capacity is as high as 173 mA·h/g, which is higher than that of $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ without coating. While, too much coating will deteriorate the performances.

3) The tests of CVs testify that proper Al_2O_3 coating will meliorate the electrochemical reversibility of spherical $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$. Hence, proper Al_2O_3 coating will helpful to structural stability of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ and improving the electrochemical characteristics at high working voltage and high charge/discharge rate.

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(Edited by YANG Bing)