

Synthesis and electrochemical properties characterization of SnO₂-coated LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ cathode material for lithium ion batteries

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Key words: Li-ion battery; cathode materials; LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂; heterogeneous nucleation; SnO₂-coated; electrochemical performance

Abstract

LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ cathode materials have been coated with SnO₂ (3% wt) by heterogeneous nucleation process to improve its electrochemical performances and the physical and electrochemical properties were studied. The scanning electron microscope (SEM) images show that there is a uniform coating on the modified materials and the X-ray diffraction (XRD) patterns show that the structure of LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ is not affected by the SnO₂ coating. The electrochemical tests indicate that the SnO₂-coated LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ improves the cyclic performance and rate capability comparing the bare LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂. The electrochemical impedance spectroscopy (EIS) studies suggest that the presence of a thin SnO₂ layer could suppress the reaction between the cathode and electrolyte, and remarkably decreases the charge transfer resistance, which is attributed to the improvement in electrochemical performances.

Introduction

As a new generation of Li-ion cell cathode material, LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ is regarded as an alternative material to LiCoO₂ for its physical stability, low cost and slight toxicity [1, 2]. Furthermore, LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ has large capacity and wonderful circle performance, which regards it as promising cathode material in electric vehicle field [3, 4]. But the electrochemical properties of LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ material decreases dramatically at high charge-discharge current. Possible reasons for this phenomenon may be the electrolyte dissolution of SEI film [5-7]. In order to suppress the interface reaction between cathode material and electrolyte, physically isolate through oxide coating on the cathode material surface is an effective way [8-10]. The research of De-cheng LI et al showed that the capacity and cyclic performance of LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ at 0.5C in voltage range of 3~4.6V was increased after physical coating with 3% ZrO₂, TiO₂ or Al₂O₃ [8]. Hyun-Soo also found that electrochemical performance of LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ at high current was improved with LiAlO₂ coating [9]. After SnO₂ coating, the phase change of LiCoO₂ was restrained at high

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voltage and its capacity was remarkably enhanced [11]. But it had never been reported $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ coated with SnO_2 . In inorganic ceramics field, heterogeneous nucleation process was applied extensively for material surface coating [12, 13]. In present study, $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ coated with SnO_2 was prepared with heterogeneous nucleation method. The structure, morphology and electrochemical performances of synthesized sample were investigated by XRD, SEM, and charge-discharge tests, respectively. The electrochemical performance improvement mechanism of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ with SnO_2 coating was also discussed.

Experiment

Using $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}(\text{AR})$, $\text{CoSO}_4 \cdot 6\text{H}_2\text{O}(\text{AR})$, $\text{NaOH}(\text{AR})$ and $\text{NH}_3 \cdot \text{H}_2\text{O}(\text{AR})$ as starting material, Ni-Co-Mn hydroxide precursor was prepared with co-precipitation method, the obtained precursor was then mixed with lithium salt as and sintered at high temperature to synthesized $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode material. 1.8mol/L of mixed solution of metal (Ni, Co, Mn) sulfate with stoichiometric ratio was added into reaction vessel by peristaltic pump, 4mol/L NaOH solution used as precipitator and ammonia (as complexing agent) were added into the reactor separately. The co-precipitation reaction was control certain PH value and carried out at 30~85°C with stirring speed of 600~850r/min. After filtration and washing, obtained precursor was dried in vacuum drying cabinet. The mixtures of $\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}(\text{OH})_2$ precursor and $\text{LiOH} \cdot \text{H}_2\text{O}$ (AR) with stoichiometric ratio were ball milled by planet ball mill.

After drying and screen separation, the mixtures were thermal decomposed at 600°C and then sintered at 900°C in air atmosphere for a certain time to prepare $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ in tube furnace. After milling and screen separation, certain amount of the $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (Sample A) powder was added into SnCl_4 solution and vigorously stirred for 5h. Then, ammonia solution was added into suspension to adjust PH value, at which $\text{Sn}(\text{OH})_4$ sufficiently growth on the heterogeneous crystal nucleus. After filtration and drying, the obtained $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ coated with $\text{Sn}(\text{OH})_4$ was calcined at 500°C for 3h in muffle furnace to obtain SnO_2 -coated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ powder (Sample B).

The obtained $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ sample was characterized by D/max-2400 X-ray diffraction meter under the following conditions: Cu Ka radiation ($\lambda=1.5406\text{\AA}$), diffracted graphite mono-chromator, 50kV voltage, 10mA current, scan rate 4°/min in range of 10-90° with 0.01°step size. The sample morphology was observed by scanning electron microscopy (SEM: JSM-5600LV, JEOF, Japan).

The cathode for lithium-ion cell was prepared by pressing the mixtures of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, conductive reagent (acetylene black) and binder (PVDF) with mass ratio of 85:10:5. After vacuum drying at 100°C for 12h, the electrode disk was

punched and weighed. Li foil was used as negative electrode, and Celgard 2300 as separator. The conductive solution consisted of $1\text{mol}\cdot\text{L}^{-1}$ LiPF_6 , EC and DMC (volume ratio 1:1). The lithium-ion cells were assembled in an argon-filled dry box. Using a LAND CT2001A computer-controlled battery testing system, the charge-discharge capacity and cycling performance of the cells were galvanostatically conducted at constant current density of $0.1\sim 1\text{C}$ (about $170\text{mAh}\cdot\text{g}^{-1}$) with voltage window of $2.75\sim 4.5\text{V}$ (vs. Li/Li^+) at room temperature. Electrochemical impedance spectroscopy (EIS) of the cells was measured at frequencies ranging from 0.01 Hz to 1MHz with amplitude voltage of 0.01V .

Results and discussion

Structure and morphology

X-ray diffraction (XRD) pattern of sample A and B was presented in Fig.1, respectively. Sample A and B are well crystallized with $\alpha\text{-NaFeO}_2$ layered structure. No extraneous peaks are found in the XRD pattern, which indicates crystal phase is homogeneous and pure. As shown in Fig.1, the peak pairs of (006)/ (102) and (108)/ (110) are split clearly, which reveals a well-ordered layered structure [14]. The pattern of Sample B is identical to that of Sample A, and therefore it can be concluded that $3\%\text{SnO}_2$ coating has less influence on the crystal structure of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$. The absence of any other signals in the spectrum indicating the SnO_2 is probably not crystal but amorphous in nature.

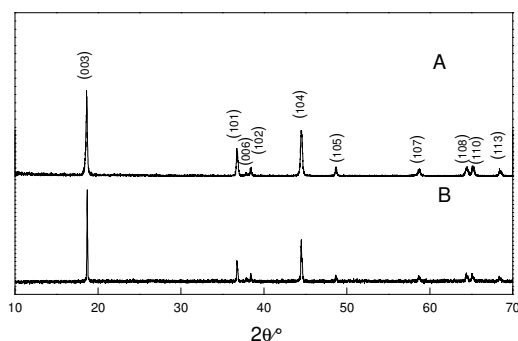


Fig.1. X-ray diffraction pattern of Sample A (uncoated) and B ($3\%\text{SnO}_2$ -coated)

Fig.2 shows the SEM images of Sample A and B. It is demonstrated that Sample A and B are uniform spherical particles with grain diameter about $10\mu\text{m}$. As shown in Fig.2 (b) and (d), the spherical particle of Sample A and B is agglomerated by many smaller size primary particles, which makes the $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ sample has higher density and better wettability. However, there is different between coated and

uncoated sample. Compared with Sample B, the particle surface of Sample A is smooth and clean. On the surface of coated sample B, it is covered with a thin film and looks obscure.

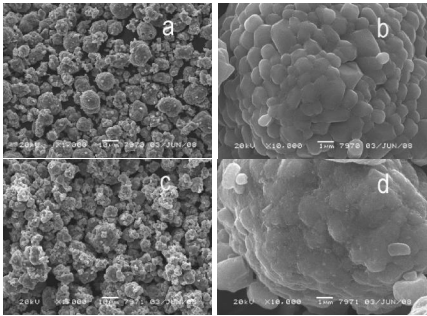


Fig.2. SEM images of the $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ powders: (a), (b)-Sample for uncoated (A): (c),(d)-Sample for coated (B)

The surface composition of Sample B was analyzed by scanning electronic microscope energy spectrum, and the results were illustrated in Fig.3. The characteristic peak of Sn is found in EDS pattern, Sn and O components appear on the surface of coated particle. It can be concluded that SnO_2 is coated on the surface of the $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ particles.

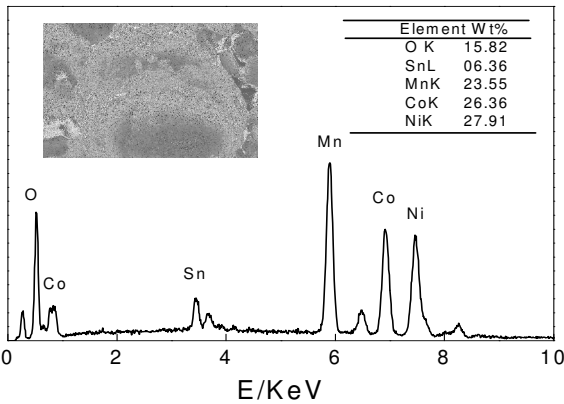


Fig.3. EDS pattern of SnO_2 -coated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ sample

Electrochemical properties

The first charge-discharge curves of sample A and B at different current in voltage range of 2.75~4.5V were presented in Fig.4. At 0.1C, Sample A and B has high

capacity as 218.5/180.6mAh/g and 211.5/177.5mAh/g, respectively. The capacity of Sample B is lower than that of Sample A due to electrochemical negativity of SnO_2 during charge-discharge period. As shown in Fig.4, the capacity of Sample A and B obviously decreases and the voltage remarkably enhances with the increasing of charge-discharge current, which indicates the occurrence of serious polarization at higher current. At 1C, the capacity of sample A and B decreases to 168.3/138.6mAh/g and 173.6/145.1mAh/g, respectively. Because of SnO_2 coating, Sample B exhibits better chargeable performance at higher current. It is also indicated in Fig.4 that there is large irreversible capacity in the first charge-discharge cycle. The reason for this phenomenon may be as follows: during charge period, Li-ions were extracted from the crystal cell, but part of them could not reset during discharge period because of cation mixing in cathode material and SEI film formed on the electrode surface [15].

The cycle performance curves of Sample A and B in voltage range of 2.75~4.5V at different current were shown in Fig.5. At 0.1C, the discharge capacity of Sample A decreases from 180.6mAh/g to 143.2mAh/g with conservation ratio of 79.3% after 30 cycles, and that of Sample B reduces from 177.5mAh/g to 163.1mAh/g with conservation ratio of 91.9%. At 1C, the discharge capacity of Sample A decreases from 138.6mAh/g to 93.9mAh/g with conservation ratio of 67.7% after 30 cycles, and that of Sample B debases from 145.1mAh/g to 136.2mAh/g with conservation ratio of 93.87%. It is clearly demonstrated that SnO_2 coating has favorable influences on the cycle performance of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ material.

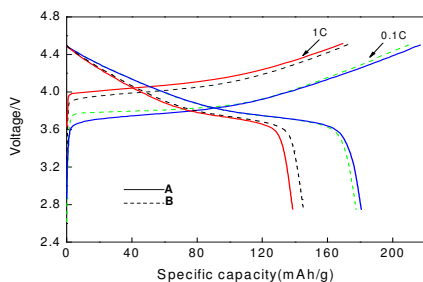


Fig.4. Initial charge-discharge curves of Sample A and B in voltage of 2.75 ~4.5V at different current

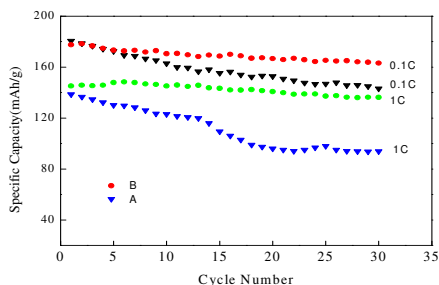


Fig.5. Cycle performance of Sample A and B at different current

In order to study electrochemical performance improvement mechanism of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ with SnO_2 coating, AC impedance tests of Sample A and B in 3rd and 14th cycle at 1C were carried out at 4.5V, and results were presented in Fig.6. All spectrums have two semicircles and one straight line. The depressed semicircle in high-frequency range is related to the Li-ion migration resistance through SEI film formed on cathode surface. The second semicircle in middle-frequency range represents the charge transfer resistance. The 45° inclined line in low-frequency range is Li-ion diffusion resistance [16]. As shown in Fig.6, the semicircles radius of Sample A and B are very close at the beginning of charge-discharge cycle. After some cycles, the semicircles in high-frequency range are still similar but variable in middle frequency range. The semicircle radius of Sample A increases noticeably in middle-frequency range, indicating its charge transfer resistance increases fast after some cycles. It had been found that the increase of charge transfer resistance after long cycling should be the main reason for the capacity fading of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$. The part reason ascribed to the change in the particle surface of the $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ composite electrode [8]. After SnO_2 coating, its presence can isolate the cathode, which can effectively suppress the reaction between the cathode and electrolyte and also restrain the decomposition of the electrolyte solution on the charged particle surface, which the enlargement of charge transfer resistance is restrained in cycles, and the reversibility of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ material is strengthen consequently.

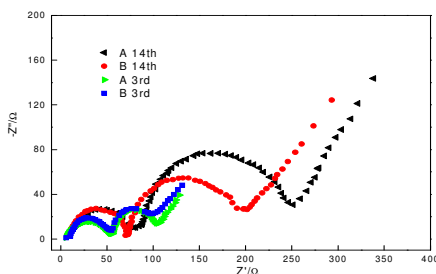


Fig. 6.Complex impedance Nyquist plots of Sample A and B

Conclusion

SnO₂ coated LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ cathode material is synthesized by heterogeneous nucleation. 3%SnO₂ coating has less influence on the crystal structure of LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂. After coated, the cyclic performance of the material is greatly increased and is more noticeable at high charge-discharge rate. The discharge capacity of coated sample decrease from 145mAh/g to 136.2mAh/g after 30 cycles at 1C with a conservation rate of 93.87%, while that of bare sample decreases from 138.6mAh/g to 93.9mAh/g with only 67.7% conservation rate. The improvement in cyclic performance of SnO₂-coated LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ is related to isolate cathode material and restrains the increasing of charge transfer resistance in electrochemical reaction.

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