Effects on electrochemical performances for host material caused by structure change of modifying material

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High ionic conductive lithium niobium oxides were selected as the modifying material to investigate the effects on the electrochemical performances for host material LiNi_{1/3}Co_{1/3}Mn_{1/3}O_{2} caused by the structure change of the modifying material at various calcination temperatures and modifying amounts. X-ray diffraction (XRD) studies revealed that the structure of the modifying material was single LiNbO_{3} phase after being calcined at 500 °C and changed to LiNbO_{3}–Li_{2}NbO_{4} mixture phases at 600 and 700 °C, and further changed to single Li_{3}NbO_{4} phase at 800 °C. Electrochemical tests displayed that both LiNbO_{3} and Li_{3}NbO_{4} phases of modifying material could contribute to the improvement of the cycle performances for the host material, but the improvement degree of Li_{3}NbO_{4} phase was more evident. The cycle performances and high rate performances of the modified host material (calcined at 700 °C) electrodes were improved with the right modifying amount.

1 Introduction

Recent research results have confirmed the importance of structural surface features to the electrochemical performances of cathode materials for lithium ion batteries. Modification as an important method is applied to achieve improved electrochemical performances. Surface modification by coating phosphates, metal oxides or other substances has demonstrated significant improvements in capacity retention of cathode materials, such as AlPO_{4}-coated LiV_{2}O_{5}, Al_{2}O_{3}-coated LiV_{2}O_{5}, MgO-coated LiCoO_{2}, MgO-coated Li_{2}MnO_{2}, NiO_{2}, V_{2}O_{5}-coated Li_{2}MnO_{2}, Sm_{2}O_{3}-coated Li_{2}MnO_{2} and so on. It is usually believed that the structure and composition of the above-mentioned modifying materials almost do not vary with tiny changes of preparation conditions. However, sometimes, the structure and composition of the obtained modifying materials could change and deviate from the initial design when the preparation conditions alter. Up to now, researcher have paid little attention to the structure change of modifying materials and its electrochemical performance effects on host materials.

In our previous work, an inactive material, LiNbO_{3}, was used to modify LiCoO_{2} for an all-solid-state Li-ion battery for the first time due to its high ionic conductivity of 10^{-3} S cm^{-1} at the amorphous state. The results showed that the interfacial resistance of the cathode was greatly reduced and high-rate capabilities were obviously enhanced. Herein, lithium niobium oxides are selected as the modifying material to modify the host material LiNi_{1/3}Co_{1/3}Mn_{1/3}O_{2}, the effects on the electrochemical performances for the host material caused by the structure change of the modifying material at various calcination temperatures and modifying amounts are investigated in detail.

2 Experimental

Spherical precursor Ni_{1/3}Co_{1/3}Mn_{1/3}(OH)_{2} was synthesized via a co-precipitation method. Stoichiometric amounts of NiSO_{4}, 6H_{2}O, MnSO_{4}, H_{2}O and CoSO_{4}, 7H_{2}O were dissolved in deionized water as the starting materials. The aqueous solution of NiSO_{4}, 6H_{2}O, MnSO_{4}, H_{2}O, and CoSO_{4}, 7H_{2}O (cationic ratio of Ni : Co : Mn = 1 : 1 : 1) with a concentration of 2.5 mol L^{-1} was pumped into a continuously stirring tank reactor (CSTR, capacity of 170 L) under N_{2} atmosphere. At the same time, a blend solution of 10.0 mol L^{-1} NaOH solution (aq, the pH controller) and 2 mol L^{-1} of NH_{4}OH solution (aq, the chelating agent) was fed into the reactor. The solution pH, temperature and stirring speed of the mixture in the reactor were set to 11.2, 50 °C and 600 rpm, respectively. Then the obtained precipitate of Ni_{1/3}Co_{1/3}Mn_{1/3}(OH)_{2} was filtered, washed,
Lithium niobium oxides-modified LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2 was prepared via a chemical deposition method. The synthesized LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2 was dispersed in a stirring ethanol solution, and then niobium ethoxide was dripped into the suspension. Niobium ethoxide was hydrolyzed immediately to the precipitate of hydrous niobium oxide that coated on the surface of LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2. Then, a stoichiometric amount of Li_2CO_3 (molar ratio of Li: Nb = 1: 1) was put into the suspension. After evaporating ethanol at 100 °C for 10 h, the mixtures were calcinated at 500, 600, 700 and 800 °C for 10 h, respectively, to form lithium niobium oxides-modified LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2.

X-ray powder diffraction (XRD, Rigaku D/Max-2500 Japan) and Scanning Electron microscopy (SEM, JMS-6700F, JEOL, Japan) were employed to characterize the structure and morphology of the prepared materials.

For the fabrication of cathode electrodes, the pristine or lithium niobium oxides-modified host materials were mixed with acetylene black and PVDF (83: 10: 7 in weight) in NMP. The obtained slurry was coated onto Al foil, and then dried under vacuum. Prior to use, the electrodes were roll-pressed and divided into small patches. The electrodes were electrochemically characterized using a 2032 type of coin cell with lithium foil as the anode, 1 M LiPF_6 in ethylene carbonate/diethyl carbonate (1: 1 in volume) as the electrolyte and Celgard 2400 microporous film as the separator. The charge–discharge tests were performed between 3.0 and 4.5 V (versus Li⁺/Li) at 0.1 C (1 C = 150 mA g⁻¹) mA g⁻¹ for initial three cycles and 1 C mA g⁻¹ for the subsequent cycles at 25 °C. Electrochemical impedance spectra (EIS) were measured using a Zahner IM6ex electrochemical workstation in the frequency range of 100 kHz to 1 mHz.

3 Results and discussion

In order to research the structure change of the modifying material on the surface of host material LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2 after being calcined at different calcination temperatures, 8.0 wt% modified host materials were prepared at various calcination temperatures. Fig. 1 shows the XRD patterns of the pristine and 8.0 wt% modified host materials at 500, 600, 700 and 800 °C, respectively. All the diffraction peaks of the pristine host material are indexed to a NaFeO_2 structure (space group R-3m) and the splitting of the (006)/(102) and (108)/(110) peaks indicates a well-layered structure. When the calcination temperature is 500 °C, the obvious diffraction peaks (marked by a, b, c and d) are indexed to pure LiNbO_3 phase. Interestingly, when the calcination temperature increases to 600 and 700 °C, Li_2NbO_5 phase (characteristic peaks marked by e, f and g) is generated and LiNbO_3–Li_2NbO_5 mixture phases co-exist. When the calcination temperature reaches 800 °C, LiNbO_3 phase completely disappears and only pure LiNbO_3 phase is detected. Because Li_2CO_3 put into the suspension during the modifying process is stoichiometric (molar ratio of Li:Nb = 1: 1), the structure change of the modifying material indicates that hydrous niobium oxide can react with Li_2CO_3 and transforms to LiNbO_3 after calcination at 500 °C, and the generated LiNbO_3 can further react with the host material and transforms to Li_3NbO_4 after calcination over 600 °C. In addition, it seems that the diffraction peak positions and (003)/(104) value of the host material do not change with the structure change of the modifying material, indicating that the reaction between LiNbO_3 and the host material only occurs on the surface of the host material, and the layered structure of the host material is not obviously destroyed during the calcination progress.

The morphology of pristine and 4.0 wt% modified host materials at various calcination temperatures is shown in Fig. 2. As shown in Fig. 2(a) and (b), the surface morphology of the pristine host material secondary particle is close-grained and well-edged, meanwhile, the crystal faces and edges on the surface are very clean. By contrast, the surface morphology of the modified host materials becomes rough and blurry. A lot of grains are observed on the surface of the host material at 500 °C in Fig. 2(c), and the number of grains decreases with increasing calcination temperature and some big particles appear at 600 and 700 °C in Fig. 2(d) and (e). When the calcination temperature is elevated to 800 °C, some blurry crystals instead of grains appear on the surface of the host material in Fig. 2(f). The differences of surface morphology verify the change of the modifying material, which is consistent with the XRD results.

Initial charge–discharge and cycle performances of pristine and 8.0 wt% modified host materials electrodes at various calcination temperatures are shown in Fig. 3 and 4. As shown in Fig. 3, the 8.0 wt% modified host material electrodes display the similar initial discharge capacities of 174.8, 171.9, 170.9 and 170.9 mA h g⁻¹ at 500, 600, 700 and 800 °C, respectively. The discharge capacities decrease gradually as the calcination temperature increases, and all the discharge capacities are less than that of the pristine one (189.5 mA h g⁻¹), which is due to the electrochemical inactivity of the modifying material.
However, after the 120th cycle, the modified host material electrodes retain the discharge capacities of 125.3, 131.2, 135.7 and 134.4 mA h g\(^{-1}\) with respect to that of the pristine one (126.0 mA h g\(^{-1}\)) as Fig. 4 depicts. The cycle performances of the modified host material electrodes are enhanced gradually at 500 to 700 °C, indicating that both LiNbO\(_3\) and Li\(_3\)NbO\(_4\) phases in the modifying material can contribute to the improvement of the cycle performances, but the improvement degree of Li\(_3\)NbO\(_4\) phase is more evident. The more Li\(_3\)NbO\(_4\) phase is formed, the better the cycle performance. We know that the formation of Li\(_3\)NbO\(_4\) phase is accompanied by host material’s decomposition, the higher calcination temperature the more Li\(_3\)NbO\(_4\) phase is formed but the more host material is decomposed, so the cycle performances of the modified host material electrodes decrease from 700 to 800 °C.

Fig. 5 shows the coulombic efficiencies of pristine and 8.0 wt% modified host material electrodes at various calcination temperatures. Compared with the pristine host material electrode, modified ones have stable coulombic efficiencies and small fluctuations. The changes of coulombic efficiency are consistent with the changes of cycle performance (Fig. 4). Combining Fig. 4 and 5, the modified host material electrode at 700 °C displays the best cycle performance, so a further study for this modified host material calcined at 700 °C with various modifying amounts is executed.

The XRD patterns of pristine and modified host materials (calcined at 700 °C) with various modifying amounts are shown in Fig. 6(a), and the enlarged view of rectangle region 2 is shown...
Fig. 6 (a) XRD patterns of pristine and modified host materials (calcined at 700 °C) with various modifying amounts, and (b) the enlarged view of rectangle region 2.

Fig. 7 SEM images of (a) pristine and (b) 1.0, (c) 2.0, (d) 4.0 and (e) 8.0 wt% modified host materials (calcined at 700 °C).

Fig. 8 Initial charge–discharge curves of pristine and modified host material (calcined at 700 °C) electrodes with various modifying amounts.

in Fig. 6(b). As marked in rectangle region 1 and Fig. 6(b), both LiNbO₃ and Li₃NbO₄ peaks are detected for 1.0 and 2.0 wt% modified host materials, although the diffraction peaks intensities are very weak. As the modifying amount increases to 4.0 and 8.0 wt%, the diffraction peaks of both LiNbO₃ and Li₃NbO₄ become obvious in Fig. 6(b), indicating that the more modifying amount at 700 °C, the more LiNbO₃ and Li₃NbO₄ phases are formed, meanwhile, more host material should be decomposed. The SEM images of pristine and modified host materials (calcined at 700 °C) with various modifying amounts are shown in Fig. 7. It is obvious there are some gaps between the primary particles of pristine host material. After modifying, a lot of tiny particles appear and scatter on the surface of host material. As the modifying amount increases, more modifying material particles are observed and the surface becomes rougher and blurrier. In addition, some tiny modifying material particles emerge in the gaps after being modified. As shown in Fig. 7(d), most gaps are filled with modifying material when the modifying amount increases to 8.0 wt%.

Fig. 8 depicts the initial charge–discharge curves of the pristine and modified host material (calcined at 700 °C) electrodes with various modifying amounts. The pristine host material electrode presents a discharge capacity of 189.5 mA h g⁻¹. By contrast, the modified ones display slightly less discharge capacities, and the initial discharge capacities decrease from 187.1 to 170.9 mA h g⁻¹ as the modifying amount increases from 1.0 to 8.0 wt%. It is speculated that there are two reasons for the initial discharge capacity fading for the modified ones as the modifying amount increases, one is the increasing...
modifying material without electrochemical inactivity, the other is the increasing decomposition of the host material caused by the reaction between LiNbO₃ and the host material.

The cycle performances of pristine and modified host material (calcined at 700 °C) electrodes with various modifying amounts are shown in Fig. 9. The 1.0 and 2.0 wt% modified ones display slightly lower discharge capacities than that of the pristine one during the initial three cycles at 0.1 C, but after the 4th cycle, the modified ones release higher discharge capacities than the pristine one and the cycle performances are enhanced greatly in subsequent cycles at 1 C. For example, the modified ones display the discharge capacities of 147.7 (1.0 wt%) and 148.8 mA h g⁻¹ (2.0 wt%) at the 120th cycle, respectively, much higher than that of the pristine one (126 mA h g⁻¹). As the modifying amount increases to 4.0 and 8.0 wt%, the discharge capacities of the modified ones after the 120th cycle are 144.6 and 135.7 mA h g⁻¹, higher than that of the pristine one, but lower than that of the 1.0 and 2.0 wt% modified ones, which is similar to Fig. 8. These results indicate that the cycle performances of the modified host material electrodes with various modifying amounts are improved significantly compared with that of the pristine one, but the discharge capacities of the modified host materials after several cycles are not always improved as the modifying amount increases, which is also caused by the above-mentioned two reasons, increasing the modifying material without electrochemical inactivity and increasing the decomposition of the host material.

The rate performances of pristine and modified host material (calcined at 700 °C) electrodes with various modifying amounts at 0.1–5.0 C are shown in Fig. 10. At a low rate (0.1 to 1.0 C), the discharge capacities of the host material electrodes after modification are not obviously improved, but at a high rate (2.0 and 5.0 C), the modified ones display higher discharge capacities than that of the pristine one. Especially at 5.0 C, the discharge capacities of the 1.0, 2.0 and 4.0 wt% modified ones are 142.6, 137.8 and 134.3 mA h g⁻¹, while that of the pristine one is only 122.2 mA h g⁻¹. It is obvious that the right amount of modifying material can increase the discharge capacities of the host material electrodes at a high discharge rate.

To understand the beneficial effect of modifying materials on the rate performance of host material electrodes, Electrochemical Impedance spectroscopy (EIS) was measured after the first charge–discharge cycle. The corresponding Nyquist plots and equivalent circuit model are shown in Fig. 11. The plots of the pristine and 2.0 wt% modified host material electrodes in the first cycle consist of two semicircles in the high-frequency region and a sloped straight line and an arc-like profile in the low-frequency region. The semicircles in the high-frequency region are related to the surface film resistance and charge-transfer process, and the straight line and arc-like profile in the low-frequency region are attributed to a semi-infinite Warburg
diffusion process in the bulk and a finite Nernst diffusion process in a thin layer, respectively. The simulated electrochemical parameters are shown Table 1 by using the equivalent circuit in Fig. 11(b), in which $R_{\text{ef}}$ and $R_{\text{ct}}$ separately mean the surface film resistance and charge transfer resistance, $W_e$ and $W_0$ point to the finite Nernst diffusion impedance in the thin layer and semi-infinite Warburg diffusion impedance in the bulk, respectively. Actually, the finite Nernst diffusion impedance in the thin layer is almost identical for the two electrodes after the first cycle. As expected, the surface film resistance and charge transfer resistance of the 2.0% modified electrode is much smaller compared with the pristine one. In addition, the semi-infinite Warburg diffusion impedance in the bulk is also smaller for the modified one. Combining the SEM images (in Fig. 7) and EIS results (in Fig. 11 and Table 1), we know more about the reason for the enhancement of the high rate performances for the modified electrodes, and it is believed that modifying material particles with high ionic conductivity emerge in the gaps of the host materials primary particles, and can increase the inner ionic conductivity of spherical host materials. Meanwhile, modifying material particles scattered on the surface can increase the ionic conductivity between electrode and electrolyte. Moreover, the modifying material particles scattered on the surface of the host material can protect host material particles from the side reaction with the electrolyte. This also leads to the improvement in cycle performance of the modified ones by reducing the contact area of the charged active material with the electrolyte. Similar results were also observed in many other modified cathode materials, such as $\text{Al}_2\text{O}_3$- and $\text{ZrO}_2$-coated $\text{LiCoO}_2$, $\text{LiAlO}_2$-coated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, $\text{Mn}_{1/3}\text{O}_2$, and $\text{ALPO}_4$-coated $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$.

### 4 Conclusions

Host material $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ is successfully modified with modifying material lithium niobium oxides. The modifying material displays different phase structures at various calcination temperatures, indicating that hydrous niobium oxide can react with $\text{Li}_2\text{CO}_3$ and transforms to $\text{LiNbO}_3$ at 500 °C, and the generated $\text{LiNbO}_3$ can further react with $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ and transforms to $\text{Li}_2\text{NbO}_4$ at over 600 °C. The effects on the electrochemical performances for the host material caused by the structure change of the modifying material are investigated in detail. Both $\text{LiNbO}_3$ and $\text{Li}_2\text{NbO}_4$ phases can contribute to the improvement of the cycle performances, but the improvement degree of $\text{Li}_2\text{NbO}_4$ phase is more evident, the more $\text{Li}_2\text{NbO}_4$ phase is formed, the better the cycle performance, so the cycle performances of the modified one are improved gradually from 500 to 700 °C. Meanwhile, the formation of $\text{Li}_2\text{NbO}_4$ phase is accompanied by the host materials' decomposition, the high temperature of Li$_3$NbO$_4$ phase is formed but the more host material is decomposed, so the cycle performances are reduced from 700 to 800 °C. The cycle performances of the modified host material electrodes with various modifying amounts are improved significantly compared with that of the pristine one, but because of the increasing modifying material without electrochemical inactivity and increasing decomposition of the host material, the discharge capacities after several cycles are not always improved as the modifying amount increases. In addition, the discharge capacities of the host material electrodes with the right amount of modifying material are improved at a high discharge rate. The reason for the enhancement of high rate performances for the modified electrodes is also analyzed.

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### Notes and references