Synthesis and Electrochemical Properties of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2/C$ composite

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Abstract: $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2/C$ composite material was prepared by a rheological phase reaction method and successive annealing procedure. In the synthesis procedure, citric acid was selected as carbon source. The electrochemical tests showed that the $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2/C$ could greatly improve the discharge capacity, rate capability and cycling stability due to the improved electric conductivity. The $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2/C$ shows good electrochemical performance (the discharge capacity of 175 mAh g^{-1} at 50 mA/g, after 50 cycles). These results indicate that the samples could be a promising cathode material for lithium ion batteries.

Introduction

Lithium-ion batteries (LIBs) are extensively used in portable electronics, and they are being intensively pursued as power sources for vehicles, digital cameras and mobile phones. The currently available cathodes have a limited capacity, and cannot meet the high energy requirements of certain practical applications, however, and there is therefore a strong impetus towards developing new cathode materials. In recent years, layer-structured $LiNi_xCo_yMn_zO_2$ (LNCM) has demonstrated a high theoretical capacity, good thermal stability, high safety, low cost, and low toxicity, so this family of compounds is regarded as one of the most promising types of alternative cathode materials.

In this work, we have prepared $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ and $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2/C$ composites using the rheological phase reaction method and successive calcination procedure. When the prepared materials were evaluated as cathode for lithium ion batteries, they shows good electrochemical performance, in terms of rate capability, and cycling stability.

Experimental

Synthesis and characterization of the samples

The raw material are $LiOH{\cdot}H_2O$, $Ni(Ac)_2{\cdot}6H_2O$, $Co(Ac)_2{\cdot}6H_2O$, $Mn(Ac)_2{\cdot}6H_2O$ and citric acid (C.A). The molar ratio of reactants was [n(Li): (n(Ni):n(Co):n(Mn):C.A=1.05:1/3: 1/3: 1/3:2.05], the suitable distilled water was added in it and then milled for 4 h in a planetary mill. The rotating speed was 300rpm and the weight ratio of ball-to-power was 20:1. After 4 hours, rheological phase mixture was reacted to form precursor in an oven at 120℃ for 24 h. Then, a mixture of precursor was ground into fine powder in a mortar of agate. The powder of precursor was heated at 600℃for 6 h in air. After being cooled to room temperature, the mid-product of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ was obtained. Then the mid-product of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ was ground to a fine powder and calcined at 850□in air for 12h to obtain different expected samples. For convenience, samples was labeled as $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$.

Different amounts of PVA were dissolved in hot distilled water at 90 °C and then $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powders were added to obtain suspensions with weight ratios of PVA to $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ of 5:100, 10:100, 15:100 and 20:100, respectively. The water in the suspensions was evaporated with continuous stirring until black viscous gel-like substances were obtained. Then the gel-like substances were calcined at 600 °C for 30 min in air to obtain carbon-coated $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$. The final products were marked as $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2/C$.

Powder X-ray diffraction patterns of the samples were obtained with a Rigaku XRD diffractometer. The morphologies of the samples were observed by using a scanning electron microscope (SEM; LEO 1530VP, Germany).

The electrochemical characterization was performed using CR2032 coin-type test cells. The cell consisted of a cathode with the composition of 70 wt.% active materials, 20 wt.% carbon black, and 10 wt.% PVDF, a lithium metal anode separated by a Celguard 2400 microporous film. The electrolyte was l $molL^{-1}$ $LiPF_6$/ (EC) and (DEC) (1:1). Charge-discharge tests were carried out at different current densities in the range of 2.5 V to 4.5 V.

Results and discussion

The crystallographic structures of the $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ and $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2/C$ samples are first confirmed by XRD analysis as shown in Figure 1. The diffraction peaks in Fig. 1 could be readily indexed to the hexagonal α-$NaFeO_2$ layered structure. The defined XRD patterns display the hexagonal doubles (006)/(012) and (108)/(110) with a clear splitting, which indicates that the samples have good hexagonal ordering and good layered characteristics. The quite narrow reflection peaks indicate that these samples have a high crystallinity.

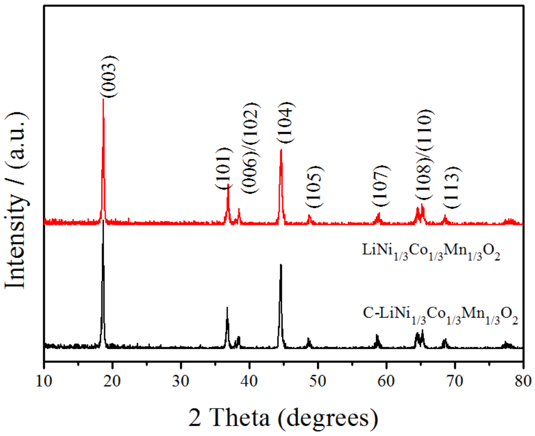

Fig. 1. XRD patterns of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ and $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2/C$.

The surface morphological features of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ and $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2/C$ were investigated by SEM. As shown in Fig.2, they are all composed of non-uniform particles with different sizes. From Fig. 2a, it can be observed that the particles of the bare $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ sample were agglomerated with the particles sized with ca. 0.5–10 μm, which were much larger than those of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2/C$.

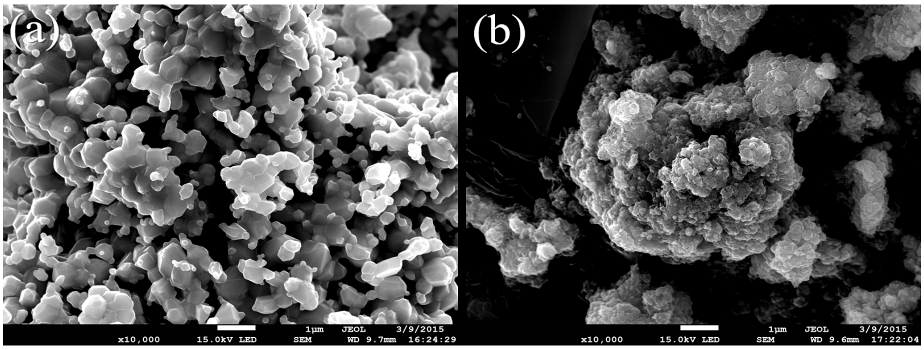

Fig. 2. SEM images of the samples: (a, b) $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ and (c, d) $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$/C.

The electrochemical performances of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ and $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$/C were measured via coin cell testing. Fig.3 (a, b) showed the typical discharge/charge cycles of the as-prepared $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ and $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$/C electrodes cycled between 2.5 and 4.5 V with a current density of 50 mA g^{-1}at room temperature, respectively. In the curves, with an anodic peak centered at 3.85 V and the corresponding cathodic peak at 3.56 V, are clearly observed in all samples. $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ electrode delivers an initial discharge capacity of 182 mA h g^{-1} (Fig.3c). The discharge capacity reduces to 159 mA h g^{-1} after 50 cycles, the capacity retention was 87.8%. For $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$/C, the initial discharge capacity was 190 mA h g^{-1} (Fig.3c). After 50 cycles, the discharge capacity dropped to 176 mA h g^{-1}, the capacity retention was 92.6%. It is obvious that $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$/C show improved cycling performance with higher specific capacities at the same cycle with the same current density as compared with the bare $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$. Obviously, carbon coating provides the improved conductivity and connectivity between the active particles present in the electrode, which give rise to improve the capacity of the material.

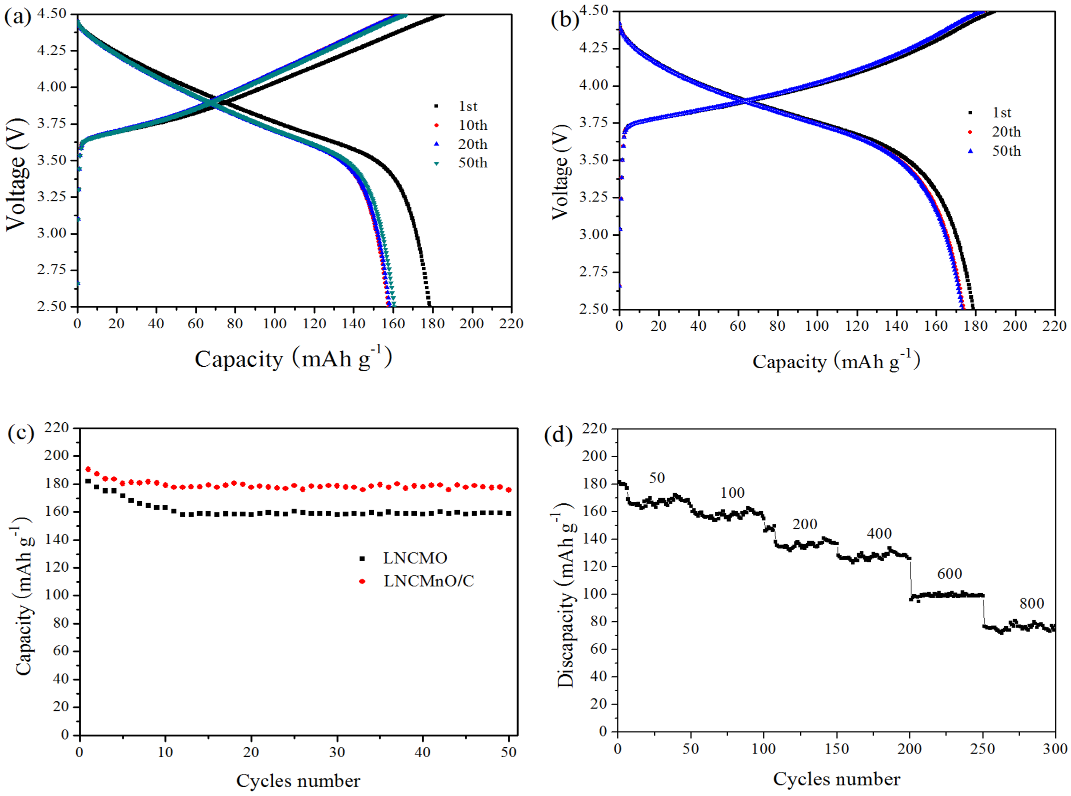

Fig. 3. Typical discharge/charge cycles of (a) $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$,(b) $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$/C, and

Cycling performance (c) of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ and $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2/C$ and rate performance (d) of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2/C$.

Fig.3d shows the rate capability of the $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2/C$ electrode at various current densities. Apparently, the $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2/C$ electrode displays good capacity retention at different current densities. When the current rates were 50, 100, 200, 400, 600, and 800 mA g^{-1}, the specific capacities were 181, 160, 146, 128, 96, and 77 mA h g^{-1}, respectively. That is, the $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2/C$ electrode shows both better reversibility, and better rate capability.

Conclusion

$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ and $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2/C$ were successfully prepared by a rheological phase reaction method. $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2/C$ displays the best electrochemical performance. It shows a large the initial discharge capacity was 190 mA h g^{-1}, after 50 cycles, the discharge capacity dropped to 176 mA h g^{-1}, the capacity retention was 92.6%, and good cycling stability at various current densities. The research results provides one possible direction for future cathode of lithium ion batteries. These results indicate that $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2/C$ could be a promising cathode material for lithium ion batteries.

Acknowledgements

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