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Short communication

Li-rich layered composite $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$ synthesized by a novel approach as cathode material for lithium ion battery

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HIGHLIGHTS

- ► Li-rich layered composite $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$ is synthesized by a novel approach.
- ► Carbon felt is used to control the particles growth and simplify the preparation.
- ► The composite exhibits high reversible capacity and excellent cycling stability.
- ► First-principles calculation is performed to identify the crystalline structure.

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ABSTRACT

Li-rich layered composite $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$ is prepared by a novel approach in which carbon felt acts as a carrier for synthesis reaction. The as-prepared material is characterized by SEM, ICP and XRD, its electrochemical performance is also examined with galvanostatic charge/discharge and CV measurements. It is showed that the facile process controls effectively the particle growth (in size around 100–200 nm) of the composite and its chemical composition. The as-prepared material shows a high initial discharge capacity about 288 mAh g^{-1} when charged to 4.8 V, and a retained value of 246.8 mAh g^{-1} in the 40th cycle. The crystalline structure of the composite is simulated further by Material Studio. It is revealed that the composite has a compatible layer structure merged by Li_2MnO_3 and $LiNi_{0.5}Mn_{0.5}O_2$, which makes substantial contribution to the cycleability of the electrode. In addition, the lithiation/delithiaion properties including charge transfer resistance and lithium ion diffusion coefficient are studied with electrochemical impedance spectra.

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1. Introduction

As electric vehicles develop rapidly, high energy density, long cycle life and excellent thermal stability become the requirements for the next generation of lithium ion battery. Cathode material plays an important role in the electrochemical performance of lithium ion battery and contributes approximately 40% to the price of a cell [1]. Recently, more and more interests have been focused on the series of Li-rich cathode materials because of their high capacity [2–8].

However, several problems still obstruct the commercial application of the promising $xLi_2MnO_3\cdot(1-x)LiNi_{0.5}Mn_{0.5}O_2$ cathode materials. Firstly, the charge mechanism at high voltage plateau above 4.5 V is not well clarified. Meanwhile, large irreversible capacity loss in the first cycle seriously restricts its development as well [9,10]. Especially, the performance of this kind of materials is closely related to its structure which is influenced heavily by synthesis conditions. Therefore, much attention is paid to the fabrication and optimization of the material with co-precipitation method, sol–gel method, etc [11–15]. As we know, the optimized electrochemical performance reported is that the initial discharge capacity at 0.1 C generally locates in the range of 250–280 mAh g^{-1}, the retained discharge capacity is about 200–240 mA h g^{-1} after 40 cycles [12,16–18]. This study proposes a novel approach to controllably prepare Li-rich layered composite with the aim of realizing a facile synthesis of high capacity cathode materials for lithium ion battery.

The novel synthesis process was investigated to fabricate the Li-rich layered composite $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$, i.e., $xLi_2MnO_3\cdot(1-x)LiNi_{0.5}Mn_{0.5}O_2$ ($x = 0.6$), in which carbon felt acted as the carrier of solution using its porous structure to control the growth of composite particles in combination with selected calcination

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treatment. Characterizations were conducted to examine the morphology, chemical composition and crystalline structure of the composite material. Material Studio software was adopted to simulate the composite structure so as to discuss its effect on electrode property in-depth. The electrochemical performance of the cathode was studied as well.

2. Experimental

2.1. A novel synthesis for composite $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$

A certain amount of $LiNO_3$ (Shanghai Aladdin, GR), $Mn(NO_3)_2$ (Shanghai Aladdin, 50 wt.%, AR) and $Ni(NO_3)_2\cdot 6H_2O$ (Shanghai Aladdin, 99%, GR) were dissolved in distilled water according to the element ratio of $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$ to form nitrate solution. Citric acid (Shanghai Aladdin, 99.5%, AR) was added to the solution under continuous stirring for 12 h. The molar ratio of $(Li + Mn + Ni):C_6H_8O_7\cdot H_2O$ is 1:1. Then, the mixed solution was adsorbed by carbon felt (Jiangsu TongKang) with S_{BET} of 1281 $m^2\ g^{-1}$ and dried at 80 °C in an oven until the formation of a fluffy precursor. The precursor was decomposed at 350 °C for 10 h in air and calcinated subsequently at 900 °C for 4 h in air. Finally, the products were obtained after being slowly cooled to room temperature at a cooling rate of 5 °C min^{-1}.

2.2. Material characterization

The morphology of the synthesized material was observed by field emission scanning electron microscope (FE-SEM, S-4800, Hitachi) with an accelerating voltage of 15 kV. The thermal decomposition behavior of the precursor was examined by thermogravimetry (TG) and differential thermal analysis (DTA) using SEIKO TG/DTA6300 at a ramping rate of 10 °C min^{-1} in air. The chemical composition of the sample was analyzed by inductively coupled plasma (ICP, SPECTRO ARCOS EOP, SPECTRO Analytical Instruments GmbH) measurement. The powder X-ray diffraction (XRD, UltimaIV-185, Rigaku) measurement using Cu-Kα radiation was employed to characterize the crystalline structure of the material. XRD data were acquired with a step size of 0.02° from 10 to 70°, the acquisition step time of 0.0025 min. The source tension and current are 40 kV and 40 mA, respectively. The simulation of the crystalline structure was performed on the Material Studio platform.

2.3. Electrochemical performance

Electrochemical tests were conducted on CR2025-type coin cell. The procedure to fabricate the cathode was as follows: 80 wt.% $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$, 10 wt.% Super P and 10 wt.% polyvinylidene fluoride (PVDF) in N-methyl pyrrolidinone (NMP) solvent were mixed and ground to form a homogeneous slurry. The slurry was then spread onto an aluminium foil current collector and dried at 80 °C in oven. With lithium sheet as the counter electrode, Celgard2300 film as the separator, the cells were assembled with an electrolyte of 1 M $LiPF_6$ in a mixture of ethylene carbonate (EC)/dimethyl carbonate (DEC) (1:1 volume ratio of EC:DEC) in an argon-filled glove box where both moisture and oxygen contents were less than 1 ppm. Charge/discharge performance was tested by LAND CT2001A battery testing system at a current density of 20 mA g^{-1} (0.1 C rate) and a voltage range of 2.0 V–4.8 V. Cyclic voltammetry (CV) curves were recorded from 2 V to 5 V at a scan rate of 0.1 mV s^{-1}. Electrochemical impedance spectroscopy (EIS) measurement was performed in a frequency range of 100 kHz–10 mHz with a signal amplitude of 5 mV. The impedance spectra of the cathodes at different state of charge (SOC) were measured. The applied voltages were 3 V (open-circuit), 4 V (during charging) and 4.8 V (after charging) respectively. All of the CV and EIS measurements were carried out on CHI600C electrochemical workstation. The voltages mentioned in the paper were referred to Li^+/Li redox couple.

3. Results and discussion

It is inferred that the meshed micro-porous carbon felt adsorbs a large number of solution as carrier by comparing the images of Fig. 1(a) and (b). It will also provide reaction sites before being burned up to obtain the final composite. Besides the precursor treatment, the calcination is also crucial to the formation of the composite. Fig. 2 gives TG/DTA curves of the precursor in the temperature range from 40 °C to 900 °C. The small weight-loss is mainly associated with the loss of adsorbed water and crystal water from $Ni(NO_3)_2\cdot 6H_2O$ and $C_6H_8O_7\cdot H_2O$, accompanying an exothermic peak of the precursor at 180 °C. The obvious weight-loss corresponding to large exothermic peak appears between 300 °C and 350 °C due to the formation of preliminary particles, which helps determining the pre-treatment temperature. The related reactions may be assigned to the decomposition of the complexing agent and the crystallization of solid solution phases. With the calcination treatment at 900 °C, fine crystal particles smaller than 200 nm in size are obtained, as seen in Fig. 1(c). The crystallite size calculated from XRD data is in the range of 80–100 nm which is smaller than the particle size observed from SEM image. It is also shown that the as-prepared $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$ particles have uniform crystal morphology, which can promote sufficient contact of the oxide material to the electrolyte allowing then a large surface area to proceed electrochemical reaction. The composition of the as-prepared composite is listed in Table 1. The element contents in the practical formula are almost the same as that in the nominal formula $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$. It is clear that the particle growth with no aggregation is controlled effectively by the novel approach as well as the chemical composition.

XRD pattern of $LiNi_{0.5}Mn_{0.5}O_2$ is calculated based on the physical parameters of space group $R\overline{3}m$ and cell parameters $a = 2.897$ Å and $c = 14.31$ Å [19] using Reflex module of Material Studio, as shown in Fig. 3. The measured XRD characteristic peaks of the as-prepared $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$ i.e., $xLi_2MnO_3\cdot(1-x)LiNi_{0.5}Mn_{0.5}O_2$ $(x = 0.6)$ are similar to the simulated XRD pattern of $LiNi_{0.5}Mn_{0.5}O_2$. It indicates that the composite has the α-$NaFeO_2$ layer structure. But there still appear some peaks around 22–25° in the measured XRD pattern, as many reports pointed out [9,11], they are relevant to the $LiMn_6$ cation ordering that occurs in the transition metal layers of Li_2MnO_3, and can be indexed to the Li_2MnO_3 (JCPDS Card No. 27-1252) with monoclinic unit cell and space group C2/m. On the other hand, the lattice parameters of the composite are calculated as $a = 2.8522$ Å and $c = 14.2236$ Å from the measured XRD pattern by a least squares method with an assumption of $R\overline{3}m$ structure. The high c/a ratio of 4.9869 (greater than 4.899) implies an explicit layer structure. Furthermore, the divergence of lattice parameter indicates the phase transition which can be attributed to the formation of solid solution phase consisting of Li_2MnO_3 and $LiNi_{0.5}Mn_{0.5}O_2$. The sharp splits in (006)/(102) and (108)/(110) peaks further identify the layer structure of the as-prepared material and the good structural compatibility between Li_2MnO_3 and $LiNi_{0.5}Mn_{0.5}O_2$ [20]. In addition, it is indicated that the material has a low level of Li^+ and Ni^{2+} disordering because the I_{003}/I_{104} ratio of 1.4881 is greater than 1.2. It is also confirmed that a well-ordered structure is obtained in the composite according to the low $(I_{006} + I_{102})/I_{101}$ ratio of 0.3465. Thus, the composite structure may benefit the reversible insertion/extraction of lithium ion through the two-dimension channel built by MO_6 [21,22], leading to the enhancement of cycling performance.

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