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Influence of cerium doping on structure and electrochemical properties of $LiNi_{0.5}Mn_{1.5}O_4$ cathode materials

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Abstract: Pristine $LiNi_{0.5}Mn_{1.5}O_4$ and cerium doped $LiCe_xNi_{0.5-x}Mn_{1.5}O_4$ (x=0.005, 0.01, 0.02) cathode materials were synthesized by solid-state method. The effect of Ce doping content on structure and electrochemical properties of $LiNi_{0.5}Mn_{1.5}O_4$ cathode material was systematically investigated. The samples were characterized by X-ray diffraction (XRD), Fourier transformation infrared spectrometer (FT-IR), scanning electron microscopy (SEM), electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) and constant-current charge/discharge tests. The results showed that Ce doping did not change the cubic spinel structure with $Fd3m$ space group, but effectively restrained the formation of $Li_xNi_{1-x}O$ impurity phase. Appropriate Ce doping (x=0.005) could decrease the extent of confusion between lithium ions and transition metal ions, increase the lattice parameter and Ni/Mn disordering degree (Mn^{3+} content). The synergic effects of the above factors led to the optimal electrochemical performance of $LiCe_{0.005}Ni_{0.495}Mn_{1.5}O_4$ sample. The discharge capacity at 10C rate could reach 115.4 mAh/g, 94.82% of that at 0.2C rate, and the capacity retention rate after 100 cycles at 1C rate could reach 94.51%. However, heavier Ce doping had an adverse effect on the electrochemical properties, which might be due to the lower disordering degree and existence of more CeO_2 secondary phase.

Keywords: lithium ion battery; cathode material; $LiNi_{0.5}Mn_{1.5}O_4$; cerium doping; rare earths

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High-voltage $LiNi_{0.5}Mn_{1.5}O_4$ spinel is one of the most attractive cathode materials for lithium ion batteries owing to its high operating voltage around 4.7 V (vs. Li/Li^+), excellent reversible capacity (~130 mAh/g) and superior specific energy (~650 Wh/kg)[1]. However, the high temperature calcination often results in oxygen loss, accompanied with the co-existence of $Li_xNi_{1-x}O$ impurity phase and the formation of Mn^{3+} [2]. $LiNi_{0.5}Mn_{1.5}O_4$ spinel with the presence of Mn^{3+} has higher electronic and ionic conductivity to exhibit better rate performance[3]. However, Mn^{3+} ions are unstable and tend to undergo a disproportionation reaction $2Mn^{3+}=Mn^{2+}+Mn^{4+}$, and the generated Mn^{2+} will dissolve into the electrolyte[3,4], thus leading to the deterioration of electrochemical property. It has been reported that the quantity of disorder phase in the material, that is, the Ni/Mn disordering degree can be directly reflected by the Mn^{3+} content for they are closely related with each other and change concurrently[5]. Therefore, controlling appropriate Mn^{3+} content is critical for $LiNi_{0.5}Mn_{1.5}O_4$ cathode material to achieve superior electrochemical performance.

Up to now, cation doping is one of the most effective ways to control $Li_xNi_{1-x}O$ impurity phase and Mn^{3+} content. Most researchers have put focus on ordinary transition metal ions doping, such as Mg[6], Fe[7], Co[8], Zn[9], Cu[10], Cr[3,11], Ti[12], V[13,14]. Recently, some researchers have successively used rare-earth elements La, Nd, Er, Y, Sm and Ce as dopants in $LiMn_2O_4$ spinel[15–19]. However, the rare-earth element doping into $LiNi_{0.5}Mn_{1.5}O_4$ spinel has less been reported. Mo et al.[20] investigated the influence of Sm substitution for Mn on the cycling and rate performance of $LiNi_{0.5}Mn_{1.5}O_4$ and found that Sm doping led to an enhancement in cation disordering degree, resulting in the improved electrochemical performance of $LiNi_{0.5}Mn_{1.5}O_4$. Zhang et al.[21] substituted Y simultaneously for Ni and Mn and found that $LiNi_{0.49}Mn_{1.49}Y_{0.02}O_4$ exhibited better cycling and rate performance. But the substitution of Ni alone by rare-earth element has not yet been reported. Therefore, in this paper, the pristine $LiNi_{0.5}Mn_{1.5}O_4$ and Ce-doped samples $LiCe_xNi_{0.5-x}Mn_{1.5}O_4$ (x=0.005, 0.01, 0.02) with different Ce contents were prepared by solid-state method, and the influence of Ce

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doping content on the structural and electrochemical performances of $LiNi_{0.5}Mn_{1.5}O_4$ materials was systematically investigated.

1 Experimental

1.1 Material synthesis

$LiCe_xNi_{0.5-x}Mn_{1.5}O_4$ (x=0, 0.005, 0.01, 0.02) spinels were prepared by solid-state method. The mixture of stoichiometric amounts of Li_2CO_3, NiO, Mn_3O_4 and CeO_2 was ball-milled for 1 h, then calcined at 850 ºC for 8 h with a heating rate of 5 ºC/min in the air and cooled naturally to obtain the product. The as-prepared samples with Ce doping contents of 0, 0.005, 0.01, 0.02 were named as Ce-0, Ce-0.005, Ce-0.01 and Ce-0.02, respectively.

1.2 Characterization and electrochemical measurements

The structural properties of the synthesized materials were studied by an X-ray diffractometer (D8-FOCUS, Bruker, Germany) using a Cu Kα X-ray radiation (λ= 0.15406 nm) over 2θ range of 10º–80º. The particle morphology and size of the materials were examined by scanning electron microscopy (Nova Nano SEM450, FEI, USA). The ordered structure of $LiNi_{0.5}Mn_{1.5}O_4$ material was identified by a Fourier transformation infrared spectrometer (V80, Bruker, Germany) using KBr pellet method over the range of 400–700 cm^{-1}.

The electrochemical performance of the as-obtained $LiCe_xNi_{0.5-x}Mn_{1.5}O_4$ (x=0, 0.005, 0.01, 0.02) samples was characterized by a coin-type cell (size 2032) with a lithium metal anode. 80% active materials, 15% ethylene black and 5% polytetrafluoroethylene (PTFE) were mixed to form the working electrode. The CR2032 test coin cells were assembled in an argon-filled glove box using lithium foil as the counter electrode. The diaphragm is polypropylene microporous membrane. The electrolyte is 1 mol/L $LiPF_6$ in a mixture of ethylene carbonate (EC), dimethyl carbonate (DMC) and ethylmethyl carbonate (EMC) (1:1:1, *v/v/v*). The charge-discharge performance tests were carried out on the battery test system CT2001A (Land, Wuhan, China) between 3.5 and 4.95 V (vs. Li/Li^+). Cyclic voltammetry and electrochemical impedance spectroscopy (EIS) were carried out on CHI660D electrochemical workstation. The CV curves were measured from 3.4 to 5.0 V (vs. Li/Li^+) at a scan rate of 0.1 mV/s. EIS measurement was conducted with an ac amplitude of 5 mV in a frequency range from 10 mHz to 100 kHz at fully discharged state after 3 cycle test.

2 Results and discussion

The X-ray diffraction patterns of the as-obtained $LiCe_xNi_{0.5-x}Mn_{1.5}O_4$ (x=0, 0.005, 0.01, 0.02) samples are shown in Fig. 1. As shown in Fig. 1, all samples display the typical profile of cubic spinel structure (JCPDS card No. 80-2162) with a space group of *Fd*3*m*. From the magnification between 35º–45º in Fig. 1 we can see that, besides the main spinel phase, there also exists rock-salt impurity phase $Li_xNi_{1-x}O$ at positions of 2θ=37.6 and 43.7º (marked with asterisk), because of oxygen loss at high temperature calcination[22–24], whose diffraction peak becomes weaker with the increase of Ce doping content, indicating that Ce doping can effectively suppress the formation of impurity phase. The peak intensity of CeO_2 secondary phase at 2θ=28.5º, 33.1º, 47.5º, 56.3° is becoming gradually stronger with Ce doping content increasing from 0.005 to 0.02. It can be inferred that part of Ce^{4+} ions cannot be incorporated into the spinel crystal lattice with high doping. In order to prove the successful incorporation of part of Ce ions into the spinel lattice, the $LiCe_{0.003}Ni_{0.497}Mn_{1.5}O_4$ material was prepared and its XRD pattern is shown in Fig. 2. For comparison, the XRD patterns of $LiCe_xNi_{0.5-x}Mn_{1.5}O_4$ (x=0, 0.005) samples are also provided. It can be seen that the CeO_2

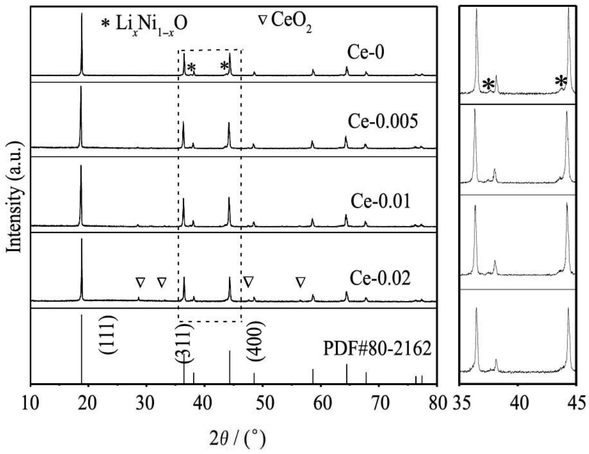

Fig. 1 XRD patterns and magnification between 35º–45º of $LiCe_xNi_{0.5-x}Mn_{1.5}O_4$ (x=0, 0.005, 0.01, 0.02) cathode materials

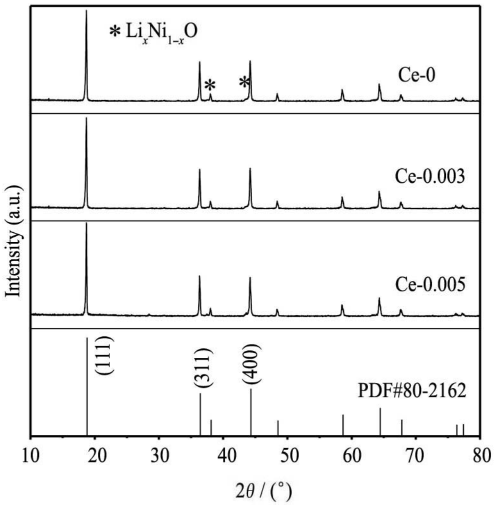

Fig. 2 XRD patterns of $LiCe_xNi_{0.5-x}Mn_{1.5}O_4$ (x=0, 0.003, 0.005) cathode materials