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Porous sphere-like $LiNi_{0.5}Mn_{1.5}O_4$-CeO_2 composite with high cycling stability as cathode material for lithium-ion battery

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ABSTRACT

A new type of microsized porous spherical $LiNi_{0.5}Mn_{1.5}O_4$-CeO_2 cathode material composed of aggregated nanosized particles with $P4_332$ space groups was prepared by an ethanol-assisted hydrothermal method. The nanosized particle shortens the Li^+-ion diffusion path in the bulk $LiNi_{0.5}Mn_{1.5}O_4$ and then improves the fast charge–discharge performance of this material. Moreover, a thin CeO_2 layer with nanometer thickness on the surface of the $LiNi_{0.5}Mn_{1.5}O_4$ particles is helpful for suppressing the interfacial side reactions. Because of these advantages, the $LiNi_{0.5}Mn_{1.5}O_4$-CeO_2 materials exhibit excellent electrochemical properties. Compared with the pristine $LiNi_{0.5}Mn_{1.5}O_4$, $LiNi_{0.5}Mn_{1.5}O_4$-CeO_2 (3 wt%) exhibits outstanding discharge capacity, cycling stability and rate capability. $LiNi_{0.5}Mn_{1.5}O_4$-CeO_2 (3 wt%) delivers discharge capacities of 129.7, 121.2, 118.1, 109.8, and 86.3 mAh g^{-1} at 0.2, 0.5, 1, 2, and 5 C discharge rates, but the pristine one only delivers discharge capacities of 119.9, 103.7, 91.8, 84.7 and 34.4 mAh g^{-1} at the corresponding discharge rates. The introduction of CeO_2 is a valid approach to enhance the electrochemical property of the $LiNi_{0.5}Mn_{1.5}O_4$ material by forming an excellent electrical contact between CeO_2 layer and $LiNi_{0.5}Mn_{1.5}O_4$ surface, leading to an enhanced lithium-ion diffusion coefficient, reduced electrochemical polarization, and improved conductivity.

1. Introduction

Lithium-ion batteries (LIBs) have been regarded as one of the most promising power sources and energy storage devices due to their long cycle life, high energy densities, and environmental friendliness [1–3]. Nevertheless, a noticeable improvement on energy density is imminently required to meet society's needs for electric vehicles (EVs) and hybrid-electric vehicles (HEVs) [4]. As we know, the high energy density in a battery can be obtained by enhancing the specific capacity, by reducing the operating voltage of the negative electrode, or by improving the working potential of the positive electrode. Comparing to other cathodes, spinel $LiNi_{0.5}Mn_{1.5}O_4$ has received significant interest due to its stable and high discharge potential plateau at about 4.7 V (versus Li^0/Li^+) and high cycling stability with excellent cyclability, and then can be used as promising cathode of LIBs with high energy density [5–7]. $LiNi_{0.5}Mn_{1.5}O_4$ electrode delivers a higher energy density (650 Wh kg^{-1}) than that of $LiCoO_2$ (518 Wh kg^{-1}), $LiMn_2O_4$ (400 Wh kg^{-1}), $LiFePO_4$ (495 Wh kg^{-1}) and $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ (576 Wh kg^{-1}) due to its high work potential. $LiNi_{0.5}Mn_{1.5}O_4$ has two different crystallographic structures: the disordered space groups of Fd-3m and the ordered space groups of $P4_332$. Kunduraci et al. [7] reported that $LiNi_{0.5}Mn_{1.5}O_4$ with Fd-3m space groups has higher conductivity than the one with $P4_332$ space groups. However, previous reports also indicate that $LiNi_{0.5}Mn_{1.5}O_4$ with Fd-3m space groups losses oxygen and disproportionates to a spinel and $Li_yNi_{1-y}O$ when it is heated above 650 °C [8]. Hence, Mn^{3+} exists in the disordered $LiNi_{0.5}Mn_{1.5}O_4$ positive electrodes, and then it suffers severe Mn dissolution problem [9,10]. Only Mn^{4+} ions present in the ordered $LiNi_{0.5}Mn_{1.5}O_4$ with a space groups of $P4_332$. Obviously, $LiNi_{0.5}Mn_{1.5}O_4$ with a space groups of $P4_332$ has higher discharge

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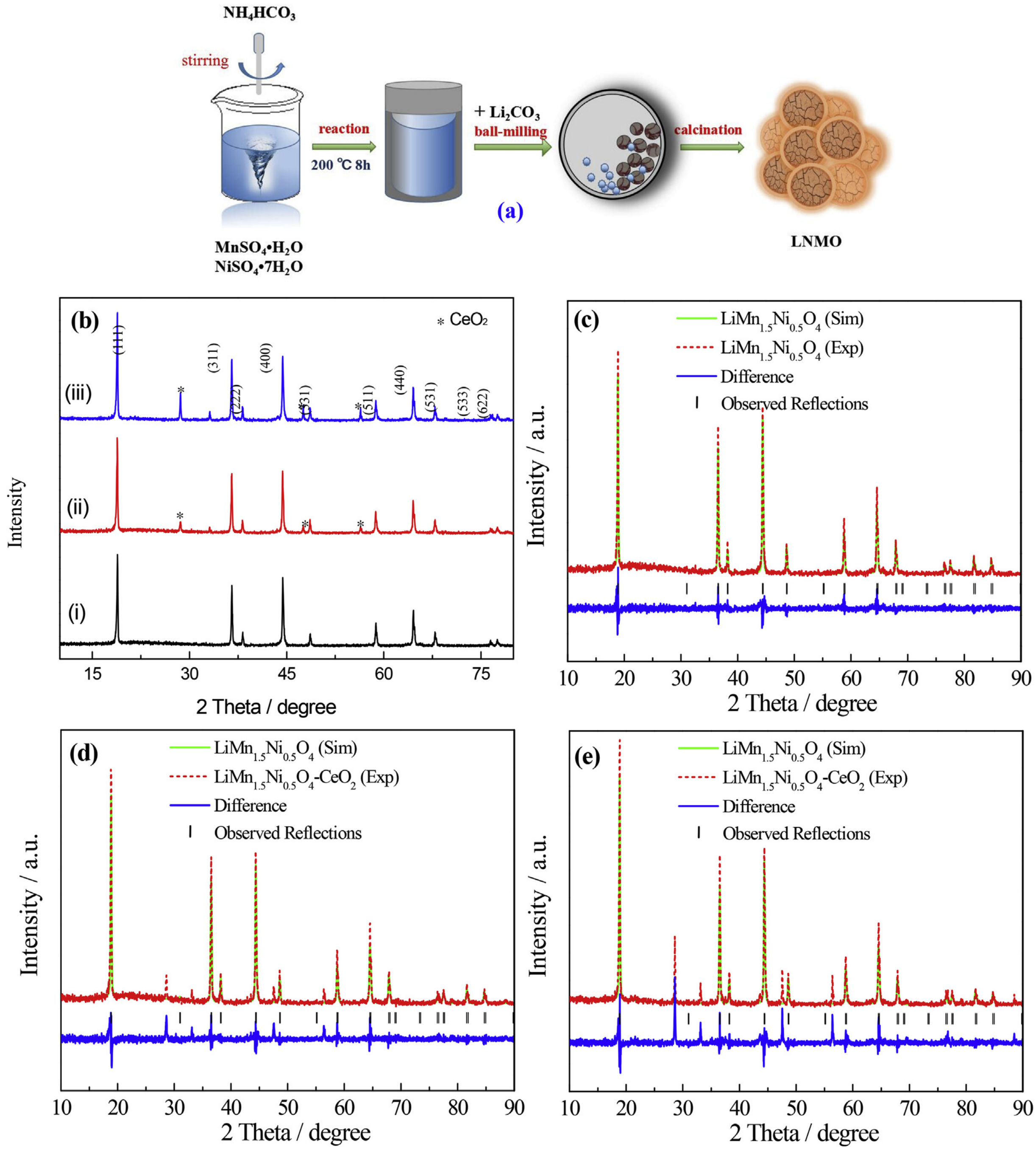

Fig. 1. (a)Schematic of the preparation process of $LiNi_{0.5}Mn_{1.5}O_4$, (b) XRD patterns of (i) pristine $LiMn_{1.5}Ni_{0.5}O_4$, (ii) $LiNi_{0.5}Mn_{1.5}O_4$-CeO_2 (3 wt%) composite and (iii) $LiNi_{0.5}Mn_{1.5}O_4$-CeO_2 (5 wt%) composite and the Rietveld refinement results of (c) pristine $LiMn_{1.5}Ni_{0.5}O_4$, (d) $LiNi_{0.5}Mn_{1.5}O_4$-CeO_2 (3 wt%) composite and (e) $LiNi_{0.5}Mn_{1.5}O_4$-CeO_2 (5 wt%) composite.

capacity at 4.7 V than the one with a space groups of Fd-3m, and then the ordered $LiNi_{0.5}Mn_{1.5}O_4$ has higher energy density than the disordered one [6]. In addition, $LiNi_{0.5}Mn_{1.5}O_4$ also suffers from the oxidative decomposition of electrolyte solutions and results in the degradation of electrodes and poor rate stability [11,12].

In order to overcome the problem mentioned above, several feasible ways were developed. These methods include ion doping in the metal or oxygen sites [13–24], and surface coating with metals [25], oxides (Li_2TiO_3 [26], $LiNbO_3$ [27], Fe_2O_3 [28], Al_2O_3 [29], RuO_2 [30], $CoAl_2O_4$ [31]), phosphates (Li_3PO_4 [32]), fluorides (AlF_3 [33] and GaF_3 [34]), carbon material [35,36], conducting polymers [37], exploring electrolyte additives and solvents [38], developing nanostructured $LiNi_{0.5}Mn_{1.5}O_4$ materials [6], preparing octahedral $LiNi_{0.5}Mn_{1.5}O_4$ crystal [39], and preparing composite electrodes [40]. Previous report indicated that ceria (CeO_2) could form an excellent electrical contact between CeO_2 oxides and cathode material, and then facilitated the electron transfer from CeO_2 to the supported cathode [41]. It has been reported that the CeO_2-coated $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ [42], Li-rich cathodes [43] and $Li_4Ti_5O_{12}$ anode [44] showed increased electrochemical performance because of the direct and fast transformation between Ce(III) and Ce(IV). As we know, the electrochemical performance of electrode materials is strongly influenced by the crystallinity, particle size, morphology and cation ordering degree, which are affected by the preparation