Fabrication and electrochemical properties of 1D mesoporous TiO_2 nanorods doped-$LiNi_{0.7}Mn_{0.2}Co_{0.1}O_2$ as the anode material for lithium ion battery

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One dimensional (1D) mesoporous TiO_2 nanorods have been prepared via the foaming-assisted electrospinning and high temperature calcinations method. Meanwhile, the ternary precursor of $LiNi_{0.7}Mn_{0.2}Co_{0.1}O_2$ has been obtained by the hydroxide co-precipitation method. The anode materials (sample 2) have been prepared by calcinations of $LiNi_{0.7}Mn_{0.2}Co_{0.1}O_2$ precursor with 1D mesoporous TiO_2 nanorods (0.5 wt %) at 820°C for 40 h. The structure and properties of sample 2 have been investigated and characterised by Scanning electron microscopy, X-ray diffraction and battery charge–discharge cycle methods, respectively. The first reversible capacity of the electrode for lithium ion batteries based on sample 2 was 159.4 $mAhg^{-1}$, and 149.4 $mAhg^{-1}$ was remained after 20 cycles. The electrochemical properties of sample 2 have been improved due to the introduction of mesoporous TiO_2 nanorods in the pristine of $LiNi_{0.7}Mn_{0.2}Co_{0.1}O_2$.

1. Introduction: During the past decades, extensive research on lithium ion batteries (LIBs) has been widely stimulated due to their advantages of high energy density, long lifespan, no memory effect and environmental benignity [1–3]. Among the diverse materials that have been researched as potential anode materials for LIBs, $LiNi_xCo_yMn_{1-x-y}O_2$ have been regarded as potential electrodes for the development of next generation LIBs due to their favourable performance [4–6]. Lu and Lin [7] have prepared the layer-structured $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathode material for LIBs. The obtained powder showed an initial discharge capacity of 187.2 $mAhg^{-1}$ at room temperature. Zhang *et al*. [8] have reported the synthesis of the spherical $Ni_{1/3}Co_{1/3}Mn_{1/3}(OH)_2$ agglomerates by the co-precipitation method in the presence of ammonia. Kim *et al*. [9] have demonstrated the improvement of the cycling performance of $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ cathode active materials by a dual-conductive polymer coating. However, bulk $LiNi_xCo_yMn_{1-x-y}O_2$ as anode materials still shows relatively low charge voltage and discharge capacity.

To improve the capacity of $LiNi_xCo_yMn_{1-x-y}O_2$, fabrication of the anode materials blending with one dimensional (1D) nanostructures was an effective way to enhance the electrochemical performance for LIBs [10, 11]. Armstrong *et al*. have reported the rechargeable LIBs, which was constructed with a TiO_2 nanowire, a gel electrolyte and $LiFePO_4$. The rechargeable LIBs showed excellent cycling stability [12]. Yoon *et al*. have prepared the N-doped mesoporous carbon decorated TiO_2 nanofibres [13]. After 100 cycles, at the current density of 33 $mAhg^{-1}$, the discharge capacity of the as-prepared samples exhibited a high capacity of 264 $mAhg^{-1}$. Recently, the thoroughly 1D mesoporous nanorods with high purity and surface areas have been fabricated by Yang's group [14]. We are interested that whether the anode materials based on $LiNi_xCo_yMn_{1-x-y}O_2$ doping with 1D mesoporous TiO_2 nanorods could further improve the electrochemical performance for LIBs.

In this Letter, we have successfully prepared the anode material (sample 2) by calcinations of $LiNi_{0.7}Mn_{0.2}Co_{0.1}O_2$ precursor with the mesoporous TiO_2 nanorods (0.5 wt %) at 820°C for 40 h. The electrochemical properties of sample 2 have been investigated in detail for their applications on LIBs. Compared with $LiNi_{0.7}Mn_{0.2}Co_{0.1}O_2$, the anode based on sample 2 for LIBs exhibited relatively higher capacity and better cycle ability.

2. Experimental: 1D mesoporous TiO_2 nanorods have been prepared according to the reported literatures [14]. The ternary precursor of $LiNi_{0.7}Mn_{0.2}Co_{0.1}(OH)_2$ has been synthesised by the hydroxide co-precipitation method [15]. $LiNi_{0.7}Mn_{0.2}Co_{0.1}(OH)_2$ and $LiCO_3$ was grinded in a ball mill for 3 h. The above mixtures were calcined at 820°C for 40 h for the preparation of $LiNi_{0.7}Mn_{0.2}Co_{0.1}O_2$. Sample 2 was obtained by the following procedure. 0.5% weight of 1D mesoporous TiO_2 nanorods was added to the mixtures of $LiNi_{0.7}Mn_{0.2}Co_{0.1}(OH)_2$ and $LiCO_3$, and the mixtures were milled for another 3 h. Sample 2 was obtained by calcinations of the above mixtures at 820°C for 40 h. The structures of the mesoporous TiO_2 nanorods, $LiNi_{0.7}Mn_{0.2}Co_{0.1}O_2$ and sample 2 have been investigated and characterised by X-ray diffraction (XRD, D8ADVANCE, BrukerAXS Inc., Germany), field emission scanning electron microscope (FE-SEM) (Leo-1525, Carl Zeiss., Germany) and transmission electron microscopy (TEM) (JEM-2011, Japan). Electrochemical measurements were carried out by using two electrode cells with lithium metal as the counter electrode. The working electrode was prepared by mixing the active materials, poly (vinylidene fluoride) binder, acetylene black and conducting carbon black at a mass ratio of 80:10:5:5. N-methylpyrrolidone was used as a solvent to form homogeneous slurry. Microporous polypropylene membrane of Celgard 2400 was used as a separator. The electrolyte was made by 1 M $LiPF_6$ in a mixture of ethylene carbonate/diethyl carbonate/ethylene methyl carbonate (volume ratio of 1:1:1). The cells were assembled in an Ar-filled grove box. The electrochemical performances of the samples were measured on the battery test system (Xianwei TC 53) between 2.8 and 4.5 V at room temperature. The discharge–charge cycle tests were run at different current densities of 0.5 and 1 C (120 mA/g was assumed to be 1 C rate) between 2.8 and 4.5 V at room temperature.

3. Results and discussion

3.1. Structures and properties of 1D mesoporous TiO_2 nanorods, $LiNi_{0.7}Mn_{0.2}Co_{0.1}O_2$ and sample 2: 1D mesoporous TiO_2 nanorods have been fabricated by calcinations of precursor fibres, which were obtained by electrospinning the solution of polyvinylpyrrolidone, tetrabutyl titanate and foaming agent diisopropyl azodiformate

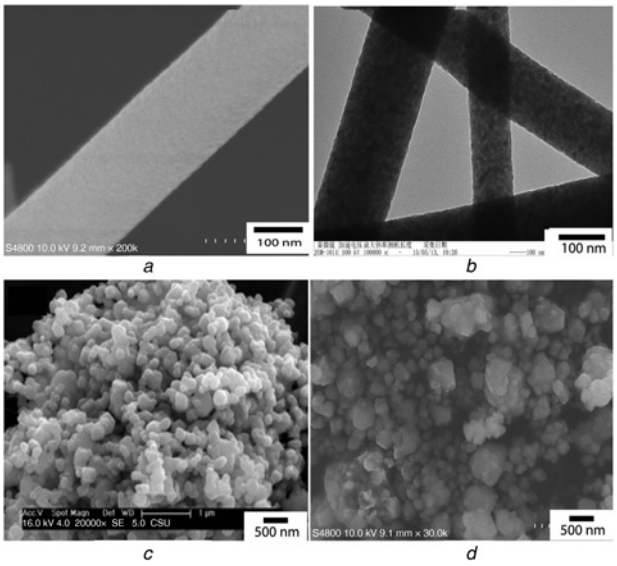

Fig. 1 *SEM images of mesoporous TiO_2 nanorod, $LiNi_{0.7}Mn_{0.2}Co_{0.1}O_2$, Sample 2, and TEM image of 1D mesoporous TiO_2 nanorod*
a Mesoporous TiO_2 nanorod
b TEM image of mesoporous TiO_2nanorod
c $LiNi_{0.7}Mn_{0.2}Co_{0.1}O_2$
d $LiNi_{0.7}Mn_{0.2}Co_{0.1}O_2$/M-$TiO_2$-N composite

according to the reported literatures [14]. We have previously investigated the electrochemical properties of $LiNi_{0.7}Mn_{0.2}Co_{0.1}O_2$, which was calcined of $LiNi_{0.7}Mn_{0.2}Co_{0.1}(OH)_2$ and $LiCO_3$ at different temperatures (820, 860 and 920°C) for about 40 h. The research results indicated that the highest first specific discharge efficiency of 67.9% was obtained for $LiNi_{0.7}Mn_{0.2}Co_{0.1}O_2$, which was prepared at calcinations temperature of 820°C for 40 h. Therefore, the temperature for the fabrication of sample 2 was selected at 820°C for 40 h. The structures of 1D mesoporous TiO_2 nanorods, $LiNi_{0.7}Mn_{0.2}Co_{0.1}O_2$ and sample 2 have been investigated by SEM, TEM, and XRD, respectively. As shown in Fig. 1*a*, the diameter of the mesoporous electrospun TiO_2 nanorod was in the range of 300 nm. Fig. 1*b* provided a representative TEM image of a single TiO_2 nanorod, confirming that densely distribution pores existed through the whole fibres body. $LiNi_{0.7}Mn_{0.2}Co_{0.1}O_2$ was composed of small layered particles (about 250 nm), as shown in Fig. 1*c*. Compared with SEM imagine of the pristine $LiNi_{0.7}Mn_{0.2}Co_{0.1}O_2$, as shown in Fig. 1*d*, sample 2 was composed of small layered particles (about 250 nm) and relatively large pores (about 300–500 m).

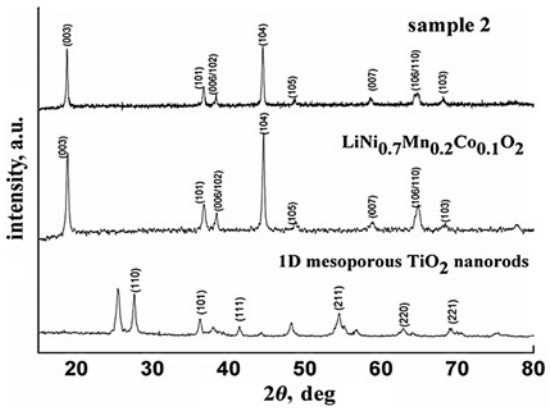

Fig. 2 *XRD patterns of the mesoporous TiO_2 nanorods, $LiNi_{0.7}Mn_{0.2}Co_{0.1}O_2$ and sample 2*

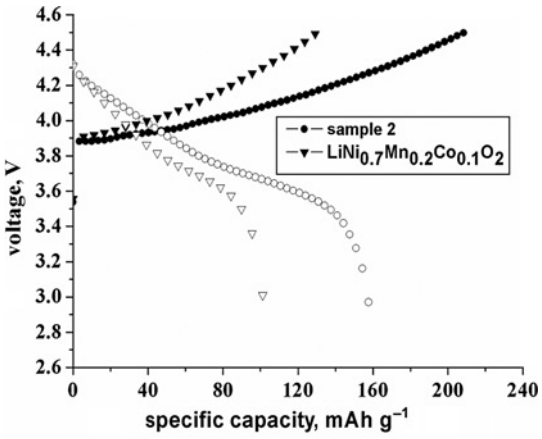

Fig. 3 *First charge–discharge profile of $LiNi_{0.7}Mn_{0.2}Co_{0.1}O_2$ and Sample 2 between 2.8 and 4.5 V at 0.5 C*

The XRD patterns of 1D mesoporous TiO_2 nanorods, $LiNi_{0.7}Mn_{0.2}Co_{0.1}O_2$ and sample 2 was shown in Fig. 2. As shown in Fig. 2, the peaks of the XRD patterns of the TiO_2 nanorods were rather sharp, which indicated that the obtained electrospun TiO_2 nanorods showed relatively high crystalline phase. All of the peaks of $LiNi_{0.7}Mn_{0.2}Co_{0.1}O_2$ and sample 2 can be indexed based on the hexagonal α-$NaFeO_2$ structure. In the XRD patterns of $LiNi_{0.7}Mn_{0.2}Co_{0.1}O_2$, the intensity ratio of the (003) and (104) lines was larger than 1.1, and splitting of the (006, 102) and (106, 110) lines was clearly observed. These results implied that less cation mixing was present in $LiNi_{0.7}Mn_{0.2}Co_{0.1}O_2$. The XRD pattern of sample 2 was similar to $LiNi_{0.7}Mn_{0.2}Co_{0.1}O_2$. However, the intensity ratios of the (003) and (104) lines for sample 2 were reduced to 1.0 due to the introduction of the mesoporous TiO_2 nanorod in the pristine $LiNi_{0.7}Mn_{0.2}Co_{0.1}O_2$.

3.2. Electrochemical properties of $LiNi_{0.7}Mn_{0.2}Co_{0.1}O_2$ and sample 2: The electrochemical properties of the $LiNi_{0.7}Mn_{0.2}Co_{0.1}O_2$ and sample 2 for LIBs have been investigated on the battery test system between 2.8 and 4.5 V at room temperature. The first charge–discharge profile of the anode based on sample 2, cycled between 2.8 and 4.5 V at 0.5 C rates was given in Fig. 3. The curves were quite smooth without any plateau. The first specific discharge–charge capacities of sample 2 were 208.8 and 159.8 $mAhg^{-1}$ at 0.5 C rates, while they were 164 and 111 $mAhg^{-1}$ for $LiNi_{0.7}Mn_{0.2}Co_{0.1}O_2$. The results indicated that the first specific discharge–charge capacities have been increased due to the introduction of 1D mesoporous TiO_2 nanorods in $LiNi_{0.7}Mn_{0.2}Co_{0.1}O_2$.

The rate performances of the discharge capacities based on $LiNi_{0.7}Mn_{0.2}Co_{0.1}O_2$ and sample 2 anode at 0.5, 1 and 5 C were

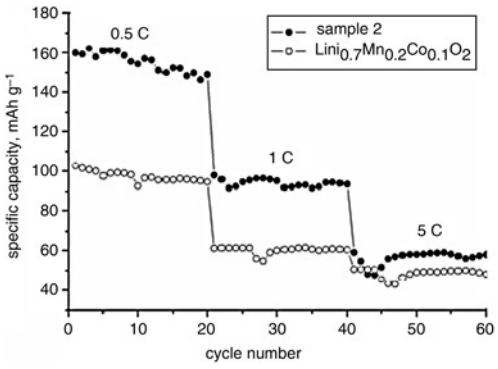

Fig. 4 *Rate performances of the discharge capacities based on $LiNi_{0.7}Mn_{0.2}Co_{0.1}O_2$ and sample 2 anode at 0.5 C, 1 C and 5 C*

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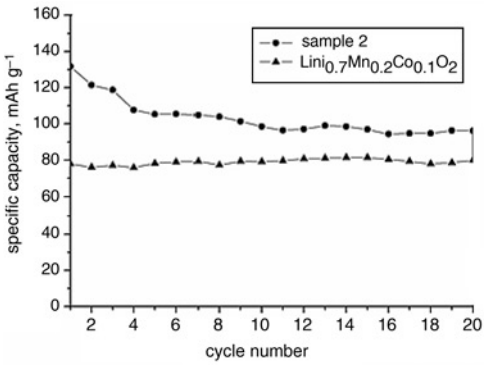

Fig. 5 *Cycling stability of the discharge capacities of $LiNi_{0.7}Mn_{0.2}Co_{0.1}O_2$ and sample 2 electrode between 2.8 and 4.5 V at 0.5 C–1 C–2 C–5 C–0.5 C in turn*

shown in Fig. 4. At 0.5 C, the specific discharge capacitates and capacity retention of sample 2 after 20th cycle were 149.4 $mAhg^{-1}$ and 94.3%, respectively, which was higher than that of pristine $LiNi_{0.7}Mn_{0.2}Co_{0.1}O_2$. At 1 C, the specific discharge capacitates sample 2 after 40th cycle were 93.6 $mAhg^{-1}$, higher than that of pristine $LiNi_{0.7}Mn_{0.2}Co_{0.1}O_2$ (60.5 $mAhg^{-1}$). At 5 C, the specific discharge capacitates of $LiNi_{0.7}Mn_{0.2}Co_{0.1}O_2$ and sample 2 after 60th cycle were 58.2 and 48.4 $mAhg^{-1}$, respectively (Fig. 4). It can be concluded that the rate performances of the discharge capacities based on sample 2 have been improved by the introduction of 1D mesoporous TiO_2 nanorods in LiNi0.7Mn0.2Co0.1O2. Fig. 5 showed the specific discharger capacities of the $LiNi_{0.7}Mn_{0.2}Co_{0.1}O_2$ and sample 2 electrode between 2.8 and 4.5 V at 0.5 C–1 C–2 C–5 C–0.5 C in turn. As shown in Fig. 5, the specific discharge capacity of LIBs based on $LiNi_{0.7}Mn_{0.2}Co_{0.1}O_2$/M-$TiO_2$-N composite electrode was 96 $mAhg^{-1}$ at 20th cycle, which was 73.2% of its initial value.

4. Conclusions: In summary, 1D mesoporous TiO_2 nanorods and $LiNi_{0.7}Mn_{0.2}Co_{0.1}O_2$ have been prepared and characterised. The anode materials (sample 2) have been prepared by calcinations of $LiNi_{0.7}Mn_{0.2}Co_{0.1}O_2$ precursor with 1D mesoporous TiO_2 nanorods (0.5 wt %) at 820°C for 40 h. The initial specific discharge and charge capacities of sample 2 for LIB were 208.8 and 159.8 $mAhg^{-1}$ at 0.5 C rates, respectively, which was higher than that of the pristine $LiNi_{0.7}Mn_{0.2}Co_{0.1}O_2$. The electrochemical properties of the anode materials have been improved due to the introduction of 1D mesoporous TiO_2 nanorods.

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