Organic acid assisted solid-state synthesis of $Li_{1.2}Ni_{0.16}Co_{0.08}Mn_{0.56}O_2$ nanoparticles as lithium ion battery cathodes

Chenhao Zhao [a], Qiang Shen [b],[*]

[a] College of Chemistry & Materials Science, LongYan University, Fujian LongYan 364012, China
[b] Key Laboratory for Colloid and Interface Chemistry of Education Ministry, School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, China

A B S T R A C T

Lithium-rich layered oxide $Li_{1.2}Ni_{0.16}Co_{0.08}Mn_{0.56}O_2$ can be referred as a crystalline mixture of Li_2MnO_3 and $LiNi_{0.4}Co_{0.2}Mn_{0.4}O_2$ at equal molar ratio. In the paper, the solid state reaction of $M(AC)_2 \cdot 4H_2O$ (M = Mn, Co and Ni) and $LiOH \cdot H_2O$ has been performed to obtain nanocrystalline $Li_{1.2}Ni_{0.16}Co_{0.08}Mn_{0.56}O_2$ using a small molecular organic acid (i.e., oxalic acid (OA), citric acid (CA) or tartaric acid (TA)) as additive. The introduction of organic acids can help to improve the layered structure and inhibit the particle growth of $Li_{1.2}Ni_{0.16}Co_{0.08}Mn_{0.56}O_2$, and the different organic acids exert distinct influences on the structural and electrochemical properties of $Li_{1.2}Ni_{0.16}Co_{0.08}Mn_{0.56}O_2$. In detail, the nanoparticles obtained in the presence of OA have the smallest average size of 50–150 nm, which correspondingly exhibit the highest initial discharge capacity of 267.52 mAh g^{-1} at 0.1C and the best high-rate capability (e.g., 152.22 mAh g^{-1}, 5C) when applied as a lithium ion battery cathode. Furthermore, the active substance obtained from TA shows the best cycling stability and a discharge capacity of 202.42 mAh g^{-1} can be retained after 50 cycles at 0.5C.

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1. Introduction

The ever-growing need for high-performance lithium ion batteries (LIBs) has prompted an intensive research and development of novel electrode materials [1,2]. At present, a type of lithium-rich layered oxides, generally defined as a chemical formula of $xLi_2MnO_3 \cdot (1-x)LiM'O_2$ (M' = Ni, Co, Mn, Fe, Cr, $Ni_{1/2}Mn_{1/2}$, $Ni_{1/3}Co_{1/3}Mn_{1/3}$, etc.), has attracted specialists more and more attentions due to their high discharge capacity (>230 mAh g^{-1}) comparing with commercial $LiCoO_2$, $LiMn_2O_4$, $LiFePO_4$ and $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (100–2002 mAh g^{-1}) [3–6]. This is because that, when $xLi_2MnO_3 \cdot (1-x)LiM'O_2$ electrodes are charged to 4.5 V or higher, the Li_2MnO_3 component can be activated and simultaneously transformed into another active component MnO_2, resulting in high discharge capacity of lithium-rich layered oxides [3–6]. Also, the Li_2MnO_3 and resultant MnO_2 can be treated as a structural stabilizer to improve cycling stability of another component $LiM'O_2$ within a wide voltage widow (e.g. 2.0–4.8 V) [7].

Among all lithium-rich layered oxides, $0.5Li_2MnO_3 \cdot 0.5LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ or the equal $Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.54}O_2$ stands out due to its high discharge capacity, moderate cycling performance and good rate capability [8–11]. Recently, further studies show that a slight increase of Ni content and the corresponding decrease of Co content can effectively improve the electrochemical performances of $Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.54}O_2$ and reduce the cost [12–16]. Thus, the other $Li_{1.2}Ni_{0.16}Co_{0.08}Mn_{0.56}O_2$ (i.e., $0.5Li_2MnO_3 \cdot 0.5LiNi_{0.4}Co_{0.2}Mn_{0.4}O_2$) may be one of more promising lithium-rich layered oxides than the $Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.54}O_2$.

Beside the chemical compositions, controlling of preparation conditions and/or modifying the synthesis methods also should be critical for the electrochemical performances of lithium-rich layered oxides [17]. Conventional preparation methods, such as the sol-gel [18], solid-state reaction [19], co-precipitation [20,21], combustion [22] and molten salt [23], have been successfully used to synthesize lithium-rich layered oxides. And, these literature results demonstrate that the electrochemical performances of serial $xLi_2MnO_3 \cdot (1-x)LiM'O_2$ are determined by their structure, morphology and particle size. Arouse by the fact that the organic acids can help to prepare layered cathode materials in spray-drying [24] and sol-gel [17] method. Herein, upon the initial solid-state reaction of $M(AC)_2 \cdot 4H_2O$ (M = Mn, Co and Ni) and $LiOH \cdot H_2O$ and

the subsequent electrochemical characterization of resulting $Li_{1.2}Ni_{0.16}Co_{0.08}Mn_{0.56}O_2$ nanoparticles, the comparative influence of a small molecular organic acid (i.e., oxalic acid (OA), citric acid (CA) or tartaric acid (TA)) has been focused in this paper, which will be discussed in detail in context.

2. Experimental

2.1. Synthesis of $Li_{1.2}Ni_{0.16}Co_{0.08}Mn_{0.56}O_2$

All the chemical reagents are of A.R. grade and were used without further purification. Lithium-rich layered oxide $Li_{1.2}Ni_{0.16}$-$Co_{0.08}Mn_{0.56}O_2$ was prepared by organic acid-assisted solid-state reaction, described as the follows. Firstly, 1.3725 g Mn $(AC)_2\cdot4H_2O$, 0.1993 g Co$(AC)_2\cdot4H_2O$, 0.3982 g Ni$(AC)_2\cdot4H_2O$ and 0.5186 g LiOH$\cdot H_2O$ (3% excess) were mixed well with a certain amount (50% excess) of organic acid (oxalic acid ~ 1.89 g, citric acid ~ 2.10 g or tartaric acid ~ 2.25 g) in an agate mortar, using a small amount of ethanol as dispersant. Secondly, the resulting mixture was pre-treated at 450 °C for 4 h, assuring the complete evaporation of ethanol, water and acetic acid. Thirdly, the resulting powders were ground uniformly, crystallization-treated at 800 °C for 10 h under air atmosphere, and then cooled naturally to room temperature. Finally, the obtained lithium-rich nickel–cobalt–manganese layered oxides were simply referred to as OA-, CA- and TA-LNCMO according to the added organic acids, respectively. For a comparative purpose, the control sample of nanocrystalline $Li_{1.2}Ni_{0.16}$-$Co_{0.08}Mn_{0.56}O_2$ was also prepared in the absence of organic acids, denoted as Blank-LNCMO.

2.2. Crystal characterization

X-ray diffraction (XRD) patterns were collected on a Rigaku D/max-2400 powder X-ray diffractormeter (XRD, 0.04° step/s). Transmission electron microscope (TEM) (JEM-100CX11, 100 kV) measurements were conducted to characterize the morphologies and sizes of $Li_{1.2}Ni_{0.16}Co_{0.08}Mn_{0.56}O_2$ samples.

2.3. Electrochemical characterization

All the electrochemical experiments were performed using $Li_{1.2}Ni_{0.16}Co_{0.08}Mn_{0.56}O_2$/Li coin cells (CR 2032) at room temperature. The working electrodes were prepared as following: after the mixing of $Li_{1.2}Ni_{0.16}Co_{0.08}Mn_{0.56}O_2$, acetylene black and poly (vinyl difluoride) (PVDF) at a weight ratio of 80: 10: 10, the resulting mixtures were slurried with N-methyl-2-pyrrolidone, pasted onto aluminum foils, cut into discs, and then dried at 80 °C for 5 h. Glass fibers (Whatman) were used as separators, and the electrolyte was the commercial LBC 305-01 $LiPF_6$ solution (Shenzhen Xinzhoubang). The cells were assembled in an argon-filled glove box. Galvanostatic cycling tests were conducted on a Land CT2001A battery system at various current rates ($1C = 200$ mA g^{-1}) within 2.0–4.7 V.

3. Results and discussion

The lithium-rich layered oxides $Li_{1.2}Ni_{0.16}Co_{0.08}Mn_{0.56}O_2$ are prepared by organic acid assisted solid-state reaction. In this preparation process, the stoichiometric metal acetates $M(AC)_2\cdot4H_2O$ (M = Ni, Co and Mn) react with LiOH$\cdot H_2O$ in the absence and presence of additives (i.e., one of the organic acid R–COOH), intermediately resulting in metal-organic acid precursors (R–COO(MLi)). This helps to achieve the uniformly mixing of raw materials, perhaps at the molecular level [25,26]. And then, the subsequent low-temperature decomposition and high-temperature crystallization help to the formation of LNCMO

target compounds. Chemically, the synthesis procedure can be represented as the following:
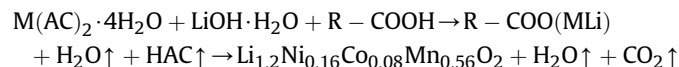
$$M(AC)_2\cdot4H_2O + LiOH\cdot H_2O + R-COOH \rightarrow R-COO(MLi)$$
$$+ H_2O\uparrow + HAC\uparrow \rightarrow Li_{1.2}Ni_{0.16}Co_{0.08}Mn_{0.56}O_2 + H_2O\uparrow + CO_2\uparrow$$

Fig. 1 is the digital photographs of precursor R–COO(MLi) and product $Li_{1.2}Ni_{0.16}Co_{0.08}Mn_{0.56}O_2$ powders. Interestingly, the obtained precursors display the color of white (OA), red (CA), pink (TA) or brown (blank), respectively. These differences on colors should be attributed to the formation of different R–COO(MLi). After annealing the precursors at high temperature (450 °C and subsequent 800 °C), all of products show the color of dark brown, as shown in Fig. 1, which is the general color of Li_2MnO_3-$LiNi_xCo_yMn_{1-x-y}O_2$-type lithium-rich layered oxides.

XRD patterns of $Li_{1.2}Ni_{0.16}Co_{0.08}Mn_{0.56}O_2$ prepared in the absence and presence of additives are shown in Fig. 2. All of the indexed diffraction peaks coincide well with the standard data of the hexagonal structure of layered $LiMO_2$, which is same as those of layered α-$NaFeO_2$ with space group R-$\overline{3}$ m [3–9]. Also, the asterisk-marked diffraction peaks in the 2θ range of 20° and 25° belong to the XRD characteristics for the occupation of Li ions in the transition metal layers of crystalline $LiMO_2$, indicating the coexistence of Li_2MnO_3 (also referred to as $Li(Li_{1/3}Mn_{2/3})O_2$) phase [3–9]. It also should be pointed out that the diffraction peaks of Li_2MnO_3 characterization isn't strong in Fig. 2, which may be attributed to moderate calcination temperature (i.e., 800 °C) [27,28]. Another observation is the degree of peak splitting of (006)/(102) and (018)/(110) reflections increase after the introduction of organic acids by comparing Fig. 2a–c with Fig. 2d, suggesting the organic acids can help to improve the layered structure of lithium-rich layered oxide [29].

Differences among morphologies and particle sizes of the four samples of $Li_{1.2}Ni_{0.16}Co_{0.08}Mn_{0.56}O_2$ are observed by TEM, as shown in Fig. 3. The order of particle size is OA-LNCMO<CA-LNCMO $\approx$ TA-LNCMO < Blank-LNCMO, indicating the introduction of organic acids can effectively inhibit the particle growth. The OA-LNCMO

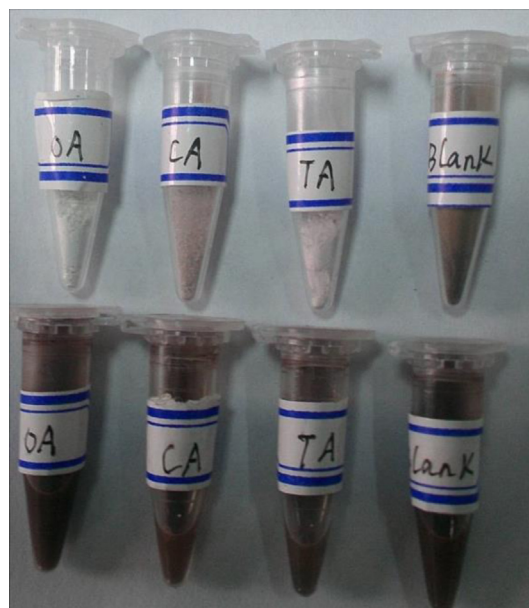Fig. 1. The colors of precursors metal-organic acid complex (R–COO(MLi)) and products $Li_{1.2}Ni_{0.16}Co_{0.08}Mn_{0.56}O_2$, it should be mentioned that the product $Li_{1.2}Ni_{0.16}$-$Co_{0.08}Mn_{0.56}O_2$ is dispersed in the ethanol solvent. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)