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A facile synthesis and electrochemical performance of $Na_{0.6}Li_{0.6}[Mn_{0.72}Ni_{0.18}Co_{0.10}]O_2$ as cathode materials for Li and Na ion batteries

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ABSTRACT

The $Na_{0.6}Li_{0.6}[Mn_{0.72}Ni_{0.18}Co_{0.10}]O_2$ with well crystallized and high specific capacity is prepared by doping of Na and Li for Li and Na ion battery. The $Na_{0.6}Li_{0.6}[Mn_{0.72}Ni_{0.18}Co_{0.10}]O_2$ composite is easily synthesized by molten-salt method. The effects of annealing temperature, time, Na contents, and electrochemical performance are investigated. In XRD analysis, the substitution of Na-ion resulted in the P2–$Na_{2/3}MO_2$ structure ($Na_{0.70}MO_{2.05}$), which co-exists in the $Na_{0.6}Li_{0.6}[Mn_{0.72}Ni_{0.18}Co_{0.10}]O_2$ composites. The discharge capacities of cathode materials exhibited 284 mAh g^{-1} for Li and 237 mAh g^{-1} for Na ion battery with higher initial coulombic efficiency.

1. Introduction

Energy storage device such as Li and Na ion battery is widely used in many power applications because of their potential high energy density and environmental friendliness [1–5]. However, there are still problems in order to meet growing demands for clean energy source. The cathode materials for Li and Na ion battery are crucial component because the electrical performance and cost of batteries are depending on the cathode materials. Especially, lithium cobalt oxide which is currently used in commercial lithium ion batteries (LIBs) suffers from safety issue and being expensive and toxic [6–8]. Thus, many efforts have been devoted to develop alternative cathode materials for LIBs. Among the alternative cathode materials for Li-ion battery, the lithium-rich Mn-based oxide materials ($xLi_2MnO_3\cdot(1-x)LiMO_2$ show the reversible specific capacity (~300 mAh g^{-1}), which is about twice the capacity of present cathode materials such as $LiCoO_2$, $LiFePO_4$, and $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$. However, the Li-rich Mn-based materials have disadvantages such as low initial coulombic efficiency, poor rate capability and low capacity retention. In order to resolve these obstacles, we have improved the low coulombic efficiency and cycle stability by an acid treatment and alumina coating on the electrode [9]. In spite of this effort, our method require several preparation steps and still show low capacity than other Li-rich Mn-based materials. In the case of Na-ion batteries (NIBs), the layered transition metal oxide ($NaMO_2$, M = Co, Cr, Mn) have been developed as cathode materials, but the discharge capacity is still low (~120 mAh g^{-1}) compared to Li-ion battery. In addition, these materials show multiple voltage steps during Na insertion/extraction reaction, resulting in cycling instability with capacity decay [10].

Doping into the lattice by certain elements is also another way to improve their electrochemical properties. Recently, Na-doped layered cathode materials for LIBs have been reported [11–14]. Na ion into the layered cathode materials could enhance the electrochemical performance in the capacity, coulombic efficiency, rate capability and cycle stability. It is attributed to introduction of Na ion, which could enlarge the Li slab space resulting in fast Li ion diffusion. Jian. et al., has synthesized the Li-rich layered oxide as cathode materials for NIBs with high reversible capacity [15]. However, the introduction of Li or Na for LIBs or NIBs still shows low reversible capacity or the preparation of cathode materials

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requires a number of steps.

In this work, we have easily synthesized $Na_{0.6}Li_{0.6}[Mn_{0.72}Ni_{0.18}Co_{0.10}]O_2$ by a molten-salt method as cathode materials for Li and Na ion battery. The strategy of Na and Li ion substitution of layered oxide would be helpful to improve their electrochemical performance due to larger internal space and structure stability for reversible Li and Na intercalation reaction.

2. Experimental

The $Na_{0.6}Li_{0.6}$ $[Mn_{0.72}Ni_{0.18}Co_{0.10}]O_2$ (denoted as NLNCM) was synthesized by molten salt method reported in Ref. 16. For the preparation of NLNCM, sodium carbonate, lithium carbonate, nickel acetate, cobalt acetate, and manganese acetate were mixed in a mortar. The cationic molar ratio Mn, Ni, and Co was 72:18:10. The potassium chloride (KCl) was also used as a molten salt flux. 5% excess lithium was added in order to compensate the possible evaporated lithium loss during the sintering. The mixture was placed in an alumina crucible followed by sintering at 500 °C for 8 h and 800 °C for 6 h under air atmosphere, respectively. After cooling down to room temperature, the resulting powders was washed with water and sintered at 300 °C to get final product.

In order to compare the effects of molten salt and sodium, the $Li_{1.2}$ $[Mn_{0.72}Ni_{0.18}Co_{0.10}]O_2$ composite (denoted as CP-method) was synthesized via a co-precipitation method. The manganese sulfate, nickel sulfate, cobalt sulfate, sodium carbonate (Na_2CO_3) and ammonium hydroxide were used as the starting materials for $Mn_{0.72}Ni_{0.18}Co_{0.10}CO_3$ precursor. The desired amounts of transition

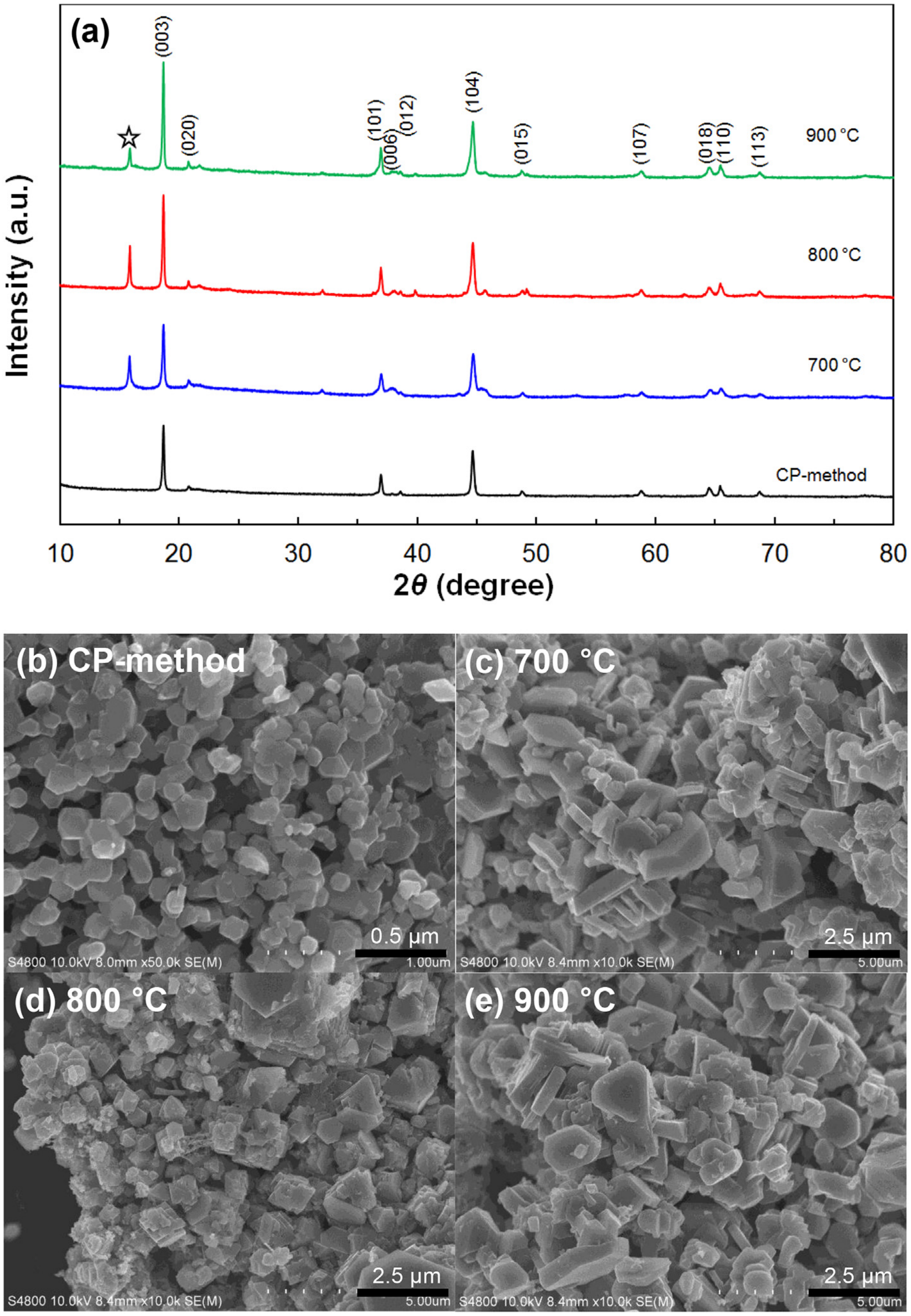

Fig. 1. XRD patterns (a) and SEM images of $Na_{0.6}Li_{0.6}[Mn_{0.72}Ni_{0.18}Co_{0.10}]O_2$ composites with different annealing temperature: (b) CP-method (c) 700 °C, (d) 800 °C, and (e) 900 °C.