The Synthesis of $\text{Na}_{0.6}\text{Li}_{0.6}[\text{Mn}_{0.72}\text{Ni}_{0.18}\text{Co}_{0.10}]\text{O}_2$ and its Electrochemical Performance as Cathode Materials for Li ion Batteries

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ABSTRACT

The layered $\text{Na}_{0.6}\text{Li}_{0.6}[\text{Mn}_{0.72}\text{Ni}_{0.18}\text{Co}_{0.10}]\text{O}_2$ composite with well crystalized and high specific capacity is prepared by molten-salt method and using the substitution of Na for Li-ion battery. The effects of annealing temperature, time, Na contents, and electrochemical performance are investigated. In XRD analysis, the substitution of Na-ion resulted in the $\text{P2-Na}_{2/3}\text{MO}_2$ structure ($\text{Na}_{0.70}\text{MO}_{2.05}$), which co-exists in the $\text{Na}_{0.6}\text{Li}_{0.6}[\text{Mn}_{0.72}\text{Ni}_{0.18}\text{Co}_{0.10}]\text{O}_2$ composites. The discharge capacities of cathode materials exhibited 284 mAhg^{-1} with higher initial coulombic efficiency.

Keywords : $\text{Na}_{0.6}\text{Li}_{0.6}[\text{Mn}_{0.72}\text{Ni}_{0.18}\text{Co}_{0.10}]\text{O}_2$ composites, Sodium substitution, Cathode materials, Electrochemical performance, Li-ion battery

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1. Introduction

Li-ion battery (LIB) 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 LIB 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 ($x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$) show the reversible specific capacity ($\sim 300 \text{ mAhg}^{-1}$), which is about twice the capacity of present cathode

materials such as LiCoO_2 , LiFePO_4 , and $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$. 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 [9,10]. In spite of this effort, our method require several preparation steps and still show low capacity than other Li-rich Mn-based materials. It is reported that the Li_2MnO_3 -based electrode exhibited high capacity resulting from Li^+ and oxygen extraction from Li_2MnO_3 component above $\sim 4.5 \text{ V}$. However, these materials have large irreversible capacity at initial cycle due to Li_2O loss and electrolyte oxidation. Moreover, the synthesis route of electrode is prepared by sol-gel and co-precipitation method, which is complicated and costly. In order to solve these problems, well-crystallized structure of electrode should be developed, which could enhance electrochemical property leading to higher capacity and shorten the diffusion length for Li-ion and electron.

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In this work, we have synthesized $\text{Na}_{0.6}\text{Li}_{0.6}[\text{Mn}_{0.72}\text{Ni}_{0.18}\text{Co}_{0.10}]\text{O}_2$ by a molten-salt method as cathode materials for LIB. This strategy is a facile and versatile method, which is based on the use of salt such as NaCl, LiCl, CaLC_2 , and KCl. In molten media, the reactions proceed much faster than solid-state reactions. The Na substitution of layered oxide would be also helpful to improve their electrochemical performance due to larger internal space and structure stability for reversible Li intercalation reaction.

2. Experimental Section

The $\text{Na}_{0.6}\text{Li}_{0.6}[\text{Mn}_{0.72}\text{Ni}_{0.18}\text{Co}_{0.10}]\text{O}_2$ (denoted as NLNCM) was synthesized by molten salt method reported in Ref. 11. 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 8h and 800°C for 6h 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 $\text{Li}_{1.2}[\text{Mn}_{0.72}\text{Ni}_{0.18}\text{Co}_{0.10}]\text{O}_2$ 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 $\text{Mn}_{0.72}\text{Ni}_{0.18}\text{Co}_{0.10}\text{CO}_3$ precursor. The desired amounts of transition metal sulfate, sodium carbonate and ammonia solution (0.45M) was dissolved in 1 L of deionized water. These solutions are vigorously reacted in a Couette-Taylor reactor. The co-precipitated slurry was then washed with deionized water and filtered, followed by drying at 100°C in an oven overnight. The transition metal precursors were ground with lithium hydroxide (5% excess) and then sintered at 500°C for 8 h and 900°C for 6 h to get active materials.

The morphology of the samples was investigated by a field emission scanning electron microscopy (FE-SEM, S-4800, Hitachi) working at 30 kV. The powder X-ray diffraction (XRD, X-pert PRO MPD, Philips) patterns of composites were conducted with

Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) operating at 40 kV and 30 mA between 10° and 90° at a scan rate of 0.01°, 2 θ /min.

The electrochemical performance of the NLNCM was evaluated by 2032 coin cells consisting of the anode (Li metal), electrolyte (1 M LiPF_6 dissolved in ethylene carbonate and dimethyl carbonate (1:1 in volume)), and separator (Celgard 2400). The cathode electrode was prepared with active material (84 wt%), carbon black (Super P, 8 wt%) as a conducting agent, and polyvinylidene difluoride (PVDF, 8 wt%) as a binder using *N*-methyl-2-pyrrolidone. Consequently, the paste was casted onto an Al foil. The Li ion cells were charged at 0.1 C and discharged at different current density between 2.0-4.6 V using battery cycler (TOCAT-3100, TOYO system). The typical electrode mass and thickness was about 4 mg cm^{-2} and 30 μm , respectively. All of the electrochemical measurement was carried out at room temperature and all capacity values were calculated based on the weight of active material.

3. Results and Discussion

The powder X-ray patterns of $\text{Na}_{0.6}\text{Li}_{0.6}[\text{Mn}_{0.72}\text{Ni}_{0.18}\text{Co}_{0.10}]\text{O}_2$ composites are shown in Fig. 1. All major peaks are well indexed to a hexagonal α - NaFeO_2 structure (*R*-3 m space group). In the XRD peaks, the peaks are clearly observed at 37.6°-38.7° and 63.9°-65.4°, respectively, indicating a typical layered structure formed in the crystal lattice [12,13]. The lower peaks which cannot be indexed to *R*-3 m symmetry between 20 and 25° are indexed to a monoclinic symmetry (*C*2/ m) which shows the Li_2MnO_3 -like fea-

Fig. 1. XRD patterns of $\text{Na}_{0.6}\text{Li}_{0.6}[\text{Mn}_{0.72}\text{Ni}_{0.18}\text{Co}_{0.10}]\text{O}_2$ composites with different annealing temperature.

Fig. 2. SEM images of $\text{Na}_{0.6}\text{Li}_{0.6}[\text{Mn}_{0.72}\text{Ni}_{0.18}\text{Co}_{0.10}]\text{O}_2$ composites with different annealing temperature. (a) CP-method, (b) 700°C, (c) 800°C, and (d) 900°C.

tures with LiMn_6 cation ordering in transition metal layers [14,15]. We found the new peaks (denoted by star) at about 15.8° in NLNCM composite, which can be assigned to the $\text{Na}_{0.70}\text{MO}_{2.05}$ crystal structure [16]. However, no impurity peaks are observed except for $\text{Na}_{0.70}\text{MO}_{2.05}$ peak, indicating that Na^+ ions did not influence the transition metal layer. Thus, the P2- $\text{Na}_{2/3}\text{MO}_2$ structure co-exists in the $\text{Na}_{0.6}\text{Li}_{0.6}[\text{Mn}_{0.72}\text{Ni}_{0.18}\text{Co}_{0.10}]\text{O}_2$ composites.

The morphology of as-synthesized NLNCM composite with different annealing temperature was observed by SEM and displayed in Fig 2. All the composites have secondary particles consist with small primary particles. The primary particles prepared by CP-method in Fig. 2a are relatively smaller than that of molten-salt method. However, no morphology differences of annealing time is observed in NLNCM composites. It can be noticeable that the electrochemical performance of NLNCM is different as a function of annealing temperature.

Fig. 3 shows the first charge-discharge voltage profiles of NLNCM at 0.1 C in the potential range of 2.0-4.6 V. It is reported that the charge capacity below 4.4 V is mainly attributed to lithium extraction from LiMO_2 ($\text{M}=\text{Ni}, \text{Co}, \text{Mn}$), and further Li ions are extracted from Li_2MnO_3 component with release of oxygen [17-19]. The NLNCM composites prepared by molten-salt shows the higher discharge capacity

Fig. 3. The first charge-discharge profiles at 0.1 C of the $\text{Na}_{0.6}\text{Li}_{0.6}[\text{Mn}_{0.72}\text{Ni}_{0.18}\text{Co}_{0.10}]\text{O}_2$ composites with different annealing temperature.

than that of co-precipitation method except for synthesis at 700°C. The NLNCM composite synthesized at 800°C is the optimum temperature to maximize the discharge capacity (284 mAh g^{-1}) at 0.1 C, which is lower annealing temperature than that of co-precipitation method. The higher discharge capacity of NLNCM may be attributed to the effect of Na introduction into the Li slab layer, which leads to ordered layered structure. It could also decrease the $\text{Li}^+/\text{Ni}^{2+}$ mixing that lower the activation barrier of Li ion mobility in the layered structure. Moreover, the Na addition in layered structure could expand internal

Fig. 4. The XRD patterns of the $\text{Na}_{0.6}\text{Li}_{0.6}[\text{Mn}_{0.72}\text{Ni}_{0.18}\text{Co}_{0.10}]\text{O}_2$ composites with different annealing time.

Fig. 5. The first charge-discharge profiles of the $\text{Na}_{0.6}\text{Li}_{0.6}[\text{Mn}_{0.72}\text{Ni}_{0.18}\text{Co}_{0.10}]\text{O}_2$ composites with different annealing time.

space, improved kinetic charge transfer reaction, and diffusion of Li ion transport during charging/discharging [20,21]. It is noticeable that the coulombic efficiency of NLNCM synthesized at 800 and 900°C is 91%, which is enhanced as compared with CP-method. This is attributed to the facilitation of Li ion diffusion during discharge, resulting from expanded layered structure. Detailed study will be conducted in follow-up study.

In order to evaluate the effects of synthesis factor, the annealing time and Na contents were varied at constant annealing temperature of 800°C during the synthesis of NLNCM. Fig. 4 shows the XRD patterns of NLNCM as a function of annealing time. The intensity ratio of $\text{Na}_{0.70}\text{MO}_{2.05}$ (denoted by star) and (003) peak is the highest at 6 hours. The first charge-discharge profiles are also similar results. As shown in Fig. 5, the discharge capacities are 226 mA g^{-1} , 284 mA g^{-1} , and 254 mA g^{-1} for 3h, 6h, and 12h,

Fig. 6. The XRD patterns of the $\text{Na}_{0.3}\text{Li}_{0.6}[\text{Mn}_{0.72}\text{Ni}_{0.18}\text{Co}_{0.10}]\text{O}_2$, $\text{Na}_{0.6}\text{Li}_{0.6}[\text{Mn}_{0.72}\text{Ni}_{0.18}\text{Co}_{0.10}]\text{O}_2$, $\text{Na}_{0.9}\text{Li}_{0.6}[\text{Mn}_{0.72}\text{Ni}_{0.18}\text{Co}_{0.10}]\text{O}_2$ composites as a function of Na contents.

Fig. 7. The first charge-discharge profiles of the $\text{Na}_{0.3}\text{Li}_{0.6}[\text{Mn}_{0.72}\text{Ni}_{0.18}\text{Co}_{0.10}]\text{O}_2$, $\text{Na}_{0.6}\text{Li}_{0.6}[\text{Mn}_{0.72}\text{Ni}_{0.18}\text{Co}_{0.10}]\text{O}_2$, $\text{Na}_{0.9}\text{Li}_{0.6}[\text{Mn}_{0.72}\text{Ni}_{0.18}\text{Co}_{0.10}]\text{O}_2$ composites as a function of Na contents.

respectively. The effect of Na contents are also investigated by XRD pattern and the initial charge-discharge profiles are depicted in Figs. 6 and 7. Based on the synthesis parameters, the NLNCM with annealing time of 6 hours and 0.6 M Na content exhibits the highest initial discharge capacity compared with other synthesis condition. It is indicating that Li and Na ions are well-crystallized in transition metal layer. It is also reported that a certain amount of secondary phase of $\text{Na}_{0.7}\text{MO}_{2.05}$ could promote the removal of Li_2O from the Li_2MnO_3 -like region and the intercalation of lithium during the subsequent discharge process [22]. Thus, we concluded that the optimized synthesis condition for NLNCM composite was sintered at 800°C and for 6 h with 0.6 M Na content for Li-ion battery.

Fig. 8. The rate capability of the (a) $\text{Li}_{1.2}[\text{Mn}_{0.72}\text{Ni}_{0.18}\text{Co}_{0.10}]\text{O}_2$ composites prepared by CP-method and (b) $\text{Na}_{0.6}\text{Li}_{0.6}[\text{Mn}_{0.72}\text{Ni}_{0.18}\text{Co}_{0.10}]\text{O}_2$ composites at different current rate.

Fig. 9. The cycle performance of the $\text{Na}_{0.6}\text{Li}_{0.6}[\text{Mn}_{0.72}\text{Ni}_{0.18}\text{Co}_{0.10}]\text{O}_2$ composites at 0.5 C with different annealing temperature.

The rate capability of NLNCM has shown in Fig. 8. The cells are charged at 0.1 C and discharge from 0.1 C to 10 C in the potential range of 2.0–4.6 V. The discharge capacities are decreased with increasing discharge rate for all samples. However, the rate capability of the NLNCM is improved compared to CP-method. For example, the discharge capacity of NLNCM at 10 C rate is 134 mAh g^{-1} , which is higher than CP-method (102 mAh g^{-1}). The higher discharge capacity at high C-rate is attributed to Na substitution, which resulted from fast Li ions through the transition metal layer and enhanced the structure stability.

To further investigate the effect of Na substitution on cycle performance, as-prepared NLNCM composites were cycled at 0.5 C for 50 cycles in the potential range of 2.0–4.6 V. As shown in Fig. 9, even though the NLNCM electrode shows higher discharge capacity, the NLNCM electrode exhibits relatively

low capacity retention ratio compared to CP-method (90%), which is consistent with previous report [11]. The possible reason is that the relatively low capacity retention could be attributed to the side reaction resulting from increase in the electrolyte-electrode interface area. The capacity retention ratio of NLNCM-700, 800, and 900 is 73, 75, 68%, respectively. Small amount of Na doping in $\text{Li}_{1.2}[\text{Co}_{0.13}\text{Ni}_{0.13}\text{Mn}_{0.54}]\text{O}_2$ improved cycling stability because the presence of Na ions could stabilize the lattice structure to alleviate the crystal lattice change during Li intercalation [23]. However, much Na amount in transition metal layer enhances the side reaction arising from the electrode and electrolyte interface area. Thus, further effort is need to improve its cycle performance.

4. Conclusion

We have synthesized $\text{Na}_{0.6}\text{Li}_{0.6}[\text{Mn}_{0.72}\text{Ni}_{0.18}\text{Co}_{0.10}]\text{O}_2$ composite by molten-salt method and evaluated as high capacity cathode materials for Li-ion battery. We observed that the substitution of Na-ion did not affect the layered structure and the $\text{P2-Na}_{2/3}\text{MO}_2$ structure ($\text{Na}_{0.70}\text{MO}_{2.05}$) co-exists in the $\text{Na}_{0.6}\text{Li}_{0.6}[\text{Mn}_{0.72}\text{Ni}_{0.18}\text{Co}_{0.10}]\text{O}_2$ composites. The NLNCM composite showed higher discharge capacity 284 mAhg^{-1} . The NLNCM synthesized at 800°C with 6 hours of annealing time and 0.6 M of Na content exhibits the highest electrochemical performance. However, the cycle stability of NLNCM for both cells should be improved.

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