The effect of Al(OH)$_3$ coating on the Li[Li$_{0.2}$Ni$_{0.2}$Mn$_{0.6}$]O$_2$ cathode material for lithium secondary battery

Y.-J. Kang [a], J.-H. Kim [a], S.-W. Lee [b], Y.-K. Sun [a,*]

[a] *Department of Chemical Engineering, Hanyang University, Seungdong-Gu, Seoul 133-791, Republic of Korea*
[b] *Daejoo Electronic Material Company, Siheung-Si, Kyunggi-do, Republic of Korea*

Abstract

Layered Li[Li$_{0.2}$Ni$_{0.2}$Mn$_{0.6}$]O$_2$ powder was modified by coating its surface with amorphous Al(OH)$_3$. Energy dispersive spectroscopy (EDS) showed that nano-sized Al(OH)$_3$ powders were homogeneously dispersed in the parent Li[Li$_{0.2}$Ni$_{0.2}$Mn$_{0.6}$]O$_2$ powders. Al(OH)$_3$ coated Li[Li$_{0.2}$Ni$_{0.2}$Mn$_{0.6}$]O$_2$ exhibited an greater retention capacity at higher rates compared to uncoated Li[Li$_{0.2}$Ni$_{0.2}$Mn$_{0.6}$]O$_2$. The low area specific impedance (ASI) value of the Al(OH)$_3$ is the major factor for its higher rate performance. The 1.4 wt.% Al(OH)$_3$ coated sample had an impedance of 41 Ω cm^2 while uncoated Li[Li$_{0.2}$Ni$_{0.2}$Mn$_{0.6}$]O$_2$ had a 57 Ω cm^2 at 30–80% state of charge. Electrochemical impedance spectroscopy (EIS) also showed that the Al(OH)$_3$ coated sample had a lower charge transfer resistance (R_{ct}) than the uncoated sample. Differential scanning calorimetry (DSC) analysis showed that Al(OH)$_3$ coating improved the thermal stability. Al(OH)$_3$ coating increased the onset temperature of thermal decomposition and reduced the amount of heat for the exothermic peak.
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1. Introduction

In recent years, the concept of making solid solutions of two layered materials, LiMO$_2$ (M = Co, Cr, Ni$_{1/2}$Mn$_{1/2}$) and Li(Li$_{1/3}$M$_{2/3}$)O$_2$ (M = Mn, Ti), has been adopted to stabilize the structure and to improve the electrochemical properties of the layered cathode materials used for rechargeable lithium batteries [1–11]. For example, Dahn et al. attempted to stabilize the layered structure by using a solid solution, such as Li[Ni$_x$Li$_{(1−2x)/3}$Mn$_{(2−x)/3}$]O$_2$ for Ni^{2+} ions and Li[M$_x$Li$_{(1−2x)/3}$Mn$_{(2−x)/3}$]O$_2$ for Co^{3+} and Cr^{3+} ions, between Li[Li$_{1/3}$Mn$_{2/3}$]O$_2$ (or Li$_2$MnO$_3$) and LiMO$_2$ [3–7]. These results show that the electrochemically inactive Li[Li$_{1/3}$Mn$_{2/3}$]O$_2$ can participate in the charge/discharge process when the [Li$_{1/3}$Mn$_{2/3}$] is partially replaced by M^{n+} ions. Interestingly, a Li/Li[Ni$_x$Li$_{(1−2x)/3}$Mn$_{(2−x)/3}$]O$_2$ cell with

x = 1/3 delivered a reversible capacity of about 230 mAh g^{-1} between 2.0 and 4.6 V, even though it was cycled at a very slow specific current of 5 mA g^{-1}. This means that this compound can be used as a cathode material for high capacity lithium secondary batteries. However, this material has to overcome low rate capability and improve thermal stability for a commercial use.

One approach to improve the electrochemical performance is to substitute a small amount of dopant ion at the transition metal sites. Kim et al. have reported increased electrical conductivity by doping Co in Li[Li$_{(1−2x)/3}$Ni$_x$Mn$_{(2−x)/3}$]O$_2$ [12].

Another approach for improving the electrochemical performance is surface modification of the cathode materials with electrochemically inactive metal ions [13–19]. Recently, Cho et al. reported that a Al$_2$O$_3$-coated LiCoO$_2$ cathode exhibited excellent capacity retention without a decrease in the original capacity. They also reported the formation of a solid solution Li$_z$Mn$_{2x}$Co$_x$O$_4$ thin-film phase in Co$_3$O$_4$ coated LiMn$_2$O$_4$ [17,18]. Sun et al. reported the electro-

* Corresponding author. SE member. Tel.: +82 2 2220 0524;
fax: +82 2 2282 7329.
E-mail address: yksun@hanyang.ac.kr (Y.-K. Sun).

chemical performance of ZnO-coated $LiNi_{0.5}Mn_{1.5}O_4$ [19]. They found that the electrochemical performance of the ZnO-coated $LiNi_{0.5}Mn_{1.5}O_4$ electrode improves with increasing amounts of ZnO at elevated temperature

In this paper, we investigated the effect of the $Al(OH)_3$ coating on the electrochemical properties and the thermal stability of $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$.

2. Experimental

The $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$ compound was synthesized by reacting stoichiometric quanities of a co-precipitated double hydroxide of manganese and nickel(cationic ratio of Ni:Mn = 1:3) with lithium hydroxide.

$(NiMn_3)(OH)_x$ was prepared as follows. An aqueous solution of $NiSO_4$ and $MnSO_4$ (cationic ratio of Ni:Mn = 1:3) with a concentration of 2.0 mol/L was pumped into a continuous stirred tank reactor (CSTR) under nitrogen atmosphere. At the same time, 2.0 mol/L NaOH solution and 1.2 mol/L NH_4OH solution as a chelating agent were also separately fed into the reactor. The $(NiMn_3)(OH)_x$ particles were filtered, washed and dried. The obtained $(NiMn_3)(OH)_x$ was dried at 110 °C and the $LiOH·H_2O$ powders were mixed thoroughly. The mixture was heated at 500 °C for 5 h, calcined at 900 °C for 3 h and then quenched to room temperature.

$Al(OH)_3$ was coated on the $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$ powders surface by first dissolving the $Al(C_3H_7O)_3$ in ethyl alcohol. The synthesized $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$ powders were then added to the coating solution, and mixed thoroughly at 80 °C for 2 h. The amount of Al in the coating solution corresponded to 1.4, 2.8, 5.6 wt.% of the $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$ powders. Then the mixture was added to a suitable excessive amount of water. The coating procedure proceeded according to the following hydrolysis reaction:

$$Al(C_3H_7O)_3 + 3H_2O \rightarrow Al(OH)_3 + 3C_3H_7OH \quad (1)$$
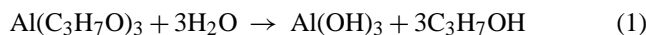
The resulting powders were dried at 110 °C for 1 day.

Powder X-ray diffraction (XRD, Rint-2000, Rigaku, Japan) analysis using Cu Kα radiation was employed to identify the crystalline phase of the synthesized material. Rietveld refinement was then performed on the XRD data to obtain lattice constants. Scanning electron microscopy (SEM, JSM-6340F, JEOL, Japan) and energy dispersive spectroscopy (EDS) were used to observe the powder morphology and distribution of $Al(OH)_3$.

Galvanostatic charge/discharge cycling was performed in a 2032-type coin cell. For the fabrication of the positive electrode, 20 mg cathode active materials was mixed with 5 mg of conductive binder (3.33 mg of teflonized acetylene black and 1.67 mg of graphite). The mixture was pressed onto 200 mm^2 stainless steel mesh used as the current collector and dried at 130 °C for 5 h in a vacuum oven. Lithium foil was used as the negative electrode. The electrolyte solution was 1 M $LiPF_6$ in a mixture of ethylene carbonate (EC) and diethyl carbonate

(DEC) in a 1:1 volume ratio (Merck, Germany). The cell was assembled in an argon-filled glove box.

AC impedance measurements were performed using a Zahner Elektrik IM6 impedance analyzer over the frequency range from 1 MHz to 1 mHz with an amplitude of 10 mV_{rms}. Each sample was allowed to equilibrate for 10 h before measurement. The obtained impedance spectra were simulated by CNLS fitting.

The thermal stability of the coated sample was studied using Differential Scanning Calorimetry (DSC, NETZSCH-TA4, Germany). The coin cells were charged to 4.4 and 4.6 V, respectively, and then they were opened in an agron filled glove box and cathode electrodes were recovered from the cells. The recovered cathode materials, including the electrolyte (ca. 20 wt.% of the recovered cathode), were sealed in high-pressure stainless steel DSC pans. The DSC scan was carried at a rate of 2 °C min^{-1} from 50 to 350 °C.

3. Results and discussion

3.1. Physical properties of $Al(OH)_3$ coated $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$

Fig. 1 shows the XRD patterns and Miller indices of the uncoated and $Al(OH)_3$ coated $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$ powders (1.4, 2.8, 5.6 wt.%). In Fig. 1(a), most of the reflections of the uncoated $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$ could be indexed with a $R\bar{3}m$ space group like an O_3 – $LiCoO_2$. Some reflections, however, could not be indexed with the $R\bar{3}m$ space group between 20° and 25°. A recent study reported that the inability to index these reflections was due to the superlattice ordering of Li and Mn atoms in the transition metal layers [4]. Calculated lattice constants of $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$ were $a = 2.859$ Å and $c = 14.246$ Å. In Fig. 1(b)–(d), the $Al(OH)_3$
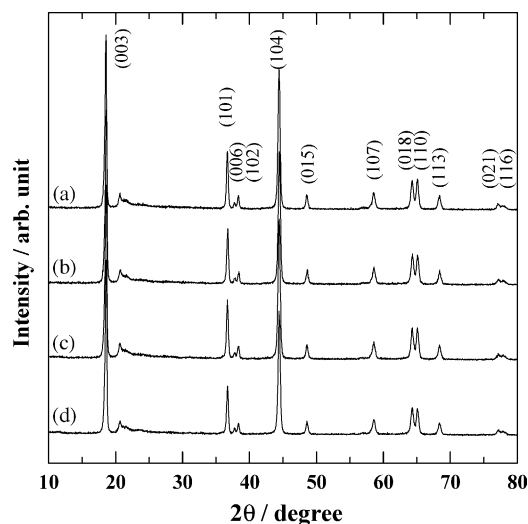
Fig. 1. X-ray diffraction patterns of uncoated and $Al(OH)_3$ coated $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$ powders: (a) uncoated $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$, (b) 1.4 wt.%, (c) 2.8 wt.%, (d) 5.6 wt.% $Al(OH)_3$ coated $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$.