Materials Chemistry and Physics 135 (2012) 533–540

Contents lists available at SciVerse ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Sulfur anion doping and surface modification with $LiNiPO_4$ of a $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ cathode

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HIGHLIGHTS

- ► $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ and $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_{1.98}S_{0.02}$ were prepared by simple combustion method.
- ► Surface coating was carried out by the sol–gel method.
- ► The rate capability and cycling performance of $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ have been enhanced.

ARTICLE INFO

Article history:
Received 4 July 2011
Received in revised form
2 May 2012
Accepted 6 May 2012

Keywords:
Lithium secondary battery
Cathode
Layered structure
Anion doping
Surface coating

ABSTRACT

$LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ and $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_{1.98}S_{0.02}$ were prepared using a simple combustion method. Surface coating was carried out by the sol–gel method using $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$, $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_{1.98}S_{0.02}$, and $LiNiPO_4$. Physical properties of the synthesized materials were measured by XRD, SEM, and TEM. Electrochemical performance was assessed by measuring parameters such as charge and discharge capacity, cycling performance, rate capability, EIS testing, and the XANES. Sulfur-doped cathode material conferred improved cycling performance compared with $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ and had a low capacity decrease after 50 cycles. $LiNiPO_4$ provided an enhancement of rate capability for discharging at 0.1–5 C. In addition, the 3 wt% $LiNiPO_4$-coated $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_{1.98}S_{0.02}$ cathode material had improved cycling performance, rate capability, and EIS testing results compared with the other samples. The rate capability and cycling performance of $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ cathode material for lithium ion batteries have been enhanced by the stabilization of the surface of cathode with a $LiNiPO_4$ coating and sulfur doping.

1. Introduction

Lithium cobalt oxide ($LiCoO_2$) is a cathode material with good electrochemical performance for use in lithium secondary batteries. However, the relatively high cost and high toxicity of cobalt have led to the evaluation of other possible cathode materials. Recently, several groups have investigated the solid solution series $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ as an alternative cathode material for $LiCoO_2$. Recently, several treatment methods have been developed to enhance the electrochemical properties of cathode materials.

One approach to the improvement of cathode material properties is the surface modification of cathodes by surface coating with stabilizing materials [1–3]. An important factor that determines the effect of coating is the exact composition of the coating material. The coating material is likely to easily diffuse into the cathode surface and react with elements of the bare material such as Li, Co, Mn, and Ni because of the high surface free energy of nanoparticles, which is attributable to their size. Several studies have reported that the physical and chemical properties of cathodes can be improved by coating them with oxides [4] and phosphates [5]. Phosphate is often used as a coating material because the strong P═O bond of phosphate often leads to good chemical resistance of the cathode to acidic electrolytes. In addition, the strong covalency of PO_4 polyanions with metal ions may improve the thermal stability of the coated cathode [6]. These metal phosphates are effective for preventing unwanted reactions between cathodes and electrolytes resulting in improved battery cycle life at high C-rate and thermal stability.

Another approach to the improvement of cathode material properties is to replace oxygen with other anionic elements such as fluorine or sulfur [7,8]. Anion substitution for oxygen in the lithium nickelate system was effective in reducing impedance and lattice changes during cycling and improving cycle life. In the lithium

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doi:10.1016/j.matchemphys.2012.05.021

nickelate system, the oxidation states of Ni and Co in the electrode convert from Ni^{2+} to Ni^{4+} during the initial stages and from Co^{3+} to Co^{4+} in later stages. The similarity in size between Ni^{2+} and Li^{+} ($r = 0.72$ Å) results in disruption of the ordering and monoclinic distortion as indicated by the no longer apparent splitting of the (101) and (104) diffraction lines [9]. However, when oxygen is substituted with sulfur, it suppresses the formation of Ni^{2+} and prevents disruption of the ordering of the Li layer. The resulting lithium nickelate does not show restrained monocyclic distortion, and the cycle life is improved compared with unsubstituted material.

In this study, we used a simple combustion method for the synthesis of nano-sized $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ and $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_{1.98}S_{0.02}$ layered materials. The advantages of this method are that it could allow manufacturing on a large scale and the synthesis of submicron sized particles is easy to control [10,11]. In addition, sulfur anion substitution by the simple combustion method reduces the processing cost. We carried out surface coating with $LiNiPO_4$ on $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ and $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_{1.98}S_{0.02}$ by a sol–gel method. In principle, $Li_{3-x}Ni_{x/2}PO_4$, a series of Li_3PO_4-based materials containing Ni, could act as stable lithium ion-conducting solid electrolytes resulting in rate capability improvements over uncoated material [12].

Therefore, we may expect to reduce process cost by using the combustion method. The combination of sulfur anion doping and $LiNiPO_4$ surface coating should also improve both cycle life and rate capability of the $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ cathode material. We studied the structural change and improved electrochemical properties of sulfur anion substitution and $LiNiPO_4$ surface coating of $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$. In particular, to determine the effect of sulfur doping, X-ray absorption near-edge structure (XANES) measurement was performed as a function of state-of-charge during the first cycle. The oxidation state of the Ni ion was also analyzed.

2. Experimental

2.1. Synthesis of $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ and $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_{1.98}S_{0.02}$

The cathode materials, $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ and $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_{1.98}S_{0.02}$, with nanocrystalline layered structures were prepared by a simple combustion method. Stoichiometric amounts of lithium acetate (Aldrich), manganese acetate (Aldrich), cobalt nitrate, and nickel nitrate (Aldrich) were dissolved in distilled water with continuous stirring for 5 h at 100 °C, and acetic acid (Daejung Chemicals & Metals, Shiheung-City, Korea) was added as fuel. The amount of acetic acid used was chosen for an oxidant/fuel ratio = 1:1. When the resulting viscous gel was fired at about 400 °C, a powder, which looked like ash, was produced by vigorous decomposition of the organic material. For the substitution of oxygen with sulfur, sulfur powder (Aldrich) was added to the material when the combustion reaction was complete. In order to improve crystallinity and to increase the crystallite size of the as-prepared samples, samples were then annealed at 500 °C for a 3 h preheating and then at 850 °C for 5 h in air.

2.2. Surface coating with $LiNiPO_4$ on $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ and $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_{1.98}S_{0.02}$

To prepare the coating solution, stoichiometric amounts of lithium acetate (Aldrich), nickel nitrate (Aldrich), and diammonium hydrogen phosphate (Aldrich) were dissolved in ethanol with continuous stirring for 5 h at 30 °C with citric acid (DAEJUNG) used as a chelating agent. $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ or $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_{1.98}S_{0.02}$ powder was added to the coating solution (pH = 5.0–5.4) and mixing was continued for 10 h at 50 °C. When this solution changed to slurry, the slurry was dried in an oven at 120 °C for 12 h and annealed at 450 °C for 5 h in air.

2.3. Measurements of physical properties

Powder X-ray diffraction (XRD, Rikacu, ultra-X) measurements using CuK_α radiation ($\lambda = 1.5418$ Å) were employed in the 2θ value range of 10–80° in increments of 0.02° at room temperature in order to identify the crystalline phase of the $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$, $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_{1.98}S_{0.02}$, and $LiNiPO_4$ surface-coated $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ and $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_{1.98}S_{0.02}$ powders. The composition results were calculated using inductively coupled plasma (ICP, Thermo Electron, IRIS DUO) analysis. The particle size and morphology of these samples were observed by scanning electron microscopy (FE-SEM, JEOL, JSM-820) with an accelerating voltage of 15 kV. More detailed morphologies were also observed by transmission electron microscopy (FE-TEM, JEM 2100F, 200 kV). To define the distribution of sulfur anions and transition metal, a mapping image was produced for each element.

2.4. Measurements of electrochemical properties

The electrochemical properties of the synthesized $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$, $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_{1.98}S_{0.02}$, and $LiNiPO_4$ surface-coated $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ and $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_{1.98}S_{0.02}$ cathode materials were measured using a pouch type cell (2.0 × 2.0 cm). Cathodes for evaluating electrochemical performance were prepared by mixing 85 wt% active materials with 7.5 wt% carbon black and 7.5 wt% polyvinylidene fluoride in *N*-methylpyrrolidinone to create the electrode slurry. The blended slurries were then pasted onto aluminum foil as a charge collector and the electrodes were dried at 100 °C for 12 h in an oven. The test cell consisted of the positive electrode and a lithium foil negative electrode separated by a porous polypropylene film with 1.15 M $LiPF_6$ in EC:EMC:DMC (3:2:5 volume ratio) as the electrolyte. Assembly of the cells was carried out in Ar-filled glove box.

A galvanostatic charge–discharge test was carried out using a Maccor charge–discharge system. The cells were charged and discharged over a voltage range from 2.8 to 4.3 V versus Li/Li^{+} at room temperature. Cycling performance was carried out at 0.2 C-rate, and rate capability was carried out at 0.1, 0.2, 0.5, 1, 2, 3, and 5 C-rate. EIS experiments were carried out using an IVIUMSTAT. The A.C. perturbation signal was ±3 mV, and the frequency range was from 50,000 to 1 Hz. Impedance spectra were analyzed using Z-View software. Nickel K-edge X-ray absorption spectra were recorded on the BL7C1(EC) beam line of Pohang Light Source (PLS) with a ring current of 140 or 170 mA at 2.5 GeV. A Si(311) double crystal monochromator was used and detuned to 75% intensity to eliminate high-order harmonics. The data were collected in transmission mode using nitrogen gas-filled ionization detection chambers.

3. Results and discussion

Fig. 1 shows X-ray diffraction patterns of the synthesized $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$, $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_{1.98}S_{0.02}$, and $LiNiPO_4$ surface-coated $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ and $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_{1.98}S_{0.02}$ powders. There were no impurity peaks, and the peaks that were present indicated the formation of an α-$NaFeO_2$ type layered hexagonal structure belonging to the $R\bar{3}m$ space group. When excess lithium was added to metal oxides that contained Mn^{4+} ions, there was the possibility that Li_2MnO_3 regions or nanodomains within the composite structure of intergrown rock salt phases would be created. No new peaks appeared for the $LiNiPO_4$-coated and sulfur-doped material, potentially due to less material coating