

THE EFFECTS OF LiNiPO_4 COATING ON SURFACE OF SULFUR DOPED $\text{Li}[\text{Co}_{0.1}\text{Ni}_{0.15}\text{Li}_{0.2}\text{Mn}_{0.55}]\text{O}_2$

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1 Introduction

Lithium cobalt oxide (LiCoO_2) is a cathode material with good electrochemical performances for using in lithium secondary batteries. However, the relatively high cost and high toxicity of cobalt have led to the study of other possible cathode materials. Recently, some groups have investigated the solid solution series between Li_2MnO_3 and LiMO_2 ($\text{M}=\text{Cr}$, Ni , Co) or $\text{Li}[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ as an alternative cathode material for LiCoO_2 . In previous research, the electrochemical properties of Li_2MnO_3 based compounds prepared by a simple combustion method. Compared to mixed hydroxide or sol-gel methods adopted by other researchers, the combustion method is very simple and cuts down the manufacturing cost of cathode powders. Among the various compositions used in the previous work, $\text{Li}[\text{Co}_{0.1}\text{Ni}_{0.15}\text{Li}_{0.2}\text{Mn}_{0.55}]\text{O}_2$ was introduced as one of the most promising LiCoO_2 based compounds for giving a high discharge capacity and a stable cycle life.

One approach to improvement of the properties of cathode materials is the surface modification of cathodes by surface coating with other stable materials. The important factor for determining coating effect is the exact composition of the coating material[1].

Another approach to improvement of the properties of cathode materials is to replace oxygen with other elements, such as anion (fluorine or sulfur). Anion substitution for oxygen was effective to reduced impedance and lattice changes during cycling and cycling life[2].

In this study, we used simple combustion method for the synthesis of nano-sized $\text{Li}[\text{Co}_{0.1}\text{Ni}_{0.15}\text{Li}_{0.2}\text{Mn}_{0.55}]\text{O}_2$. The advantage of this method is it can manufacture a large scale and synthesized particles are submicron size and easy to control. And sulfur anion has same oxidation state

with oxygen. So we can expect to the amount of anion what need for anion substitution for suppress presence of Ni^{2+} is decrease. And moreover sulfur anion substitution by simple combustion method is available for reduce the process cost. And we synthesized $\text{Li}[\text{Co}_{0.1}\text{Ni}_{0.15}\text{Li}_{0.2}\text{Mn}_{0.55}]\text{O}_2$ surface coated of LiNiPO_4 by sol-gel method. In principle, $\text{Li}_{3-x}\text{Ni}_x\text{PO}_4$ (a series of Li_3PO_4 -based material containing Ni) could act as stable lithium-ion-conducting solid electrolyte.

Therefore, we can expect that combination of sulfur anion substitution and LiNiPO_4 surface coating can bring about improvement of cycle life and rate capability of $\text{Li}[\text{Co}_{0.1}\text{Ni}_{0.15}\text{Li}_{0.2}\text{Mn}_{0.55}]\text{O}_2$ as cathode material.

We measured the effects of the sulfur anion substitution and LiNiPO_4 surface coating by XRD, FE-SEM, FE-TEM. We fabricate coin cell for evaluating the electrochemical properties and performance of these materials as cathode materials.

2 Experimental

2-1 Synthesis of $\text{Li}[\text{Co}_{0.1}\text{Ni}_{0.15}\text{Li}_{0.2}\text{Mn}_{0.55}]\text{O}_2$ and sulfur doped $\text{Li}[\text{Co}_{0.1}\text{Ni}_{0.15}\text{Li}_{0.2}\text{Mn}_{0.55}]\text{O}_2$

Nano-sized layered structure cathode material $\text{Li}[\text{Co}_{0.1}\text{Ni}_{0.15}\text{Li}_{0.2}\text{Mn}_{0.55}]\text{O}_2$ and sulfur doped $\text{Li}[\text{Co}_{0.1}\text{Ni}_{0.15}\text{Li}_{0.2}\text{Mn}_{0.55}]\text{O}_2$ were prepared by simple combustion method. At first, stoichiometric amounts of lithium acetate, manganese acetate and cobalt, nickel nitrates, which act as the oxidant, and acetic acid was act as fuel. Then, samples were annealed at 500 °C for 3h and at 850 °C for 5 h, in air.

2-2 Surface coating with LiNiPO_4 at of $\text{Li}[\text{Co}_{0.1}\text{Ni}_{0.15}\text{Li}_{0.2}\text{Mn}_{0.55}]\text{O}_2$ and sulfur doped $\text{Li}[\text{Co}_{0.1}\text{Ni}_{0.15}\text{Li}_{0.2}\text{Mn}_{0.55}]\text{O}_2$

To prepare the coating solution, lithium acetate, nickel nitrate, and diammonium hydrogen phosphate

were dissolved in ethanol with continuous stirring. Then, $\text{Li}[\text{Co}_{0.1}\text{Ni}_{0.15}\text{Li}_{0.2}\text{Mn}_{0.55}]\text{O}_2$ powder was added to the coating solution and mixed for 10 h at 50 °C. And when change to slurry, the slurry was dried in an oven at 120 °C for 12 h and annealed at 450 °C for 5h, in air.

2-3 Measurements of physical properties

The powder X-ray diffraction (XRD, Rikacu, ultra-X) measurement using CuK_α radiation was employed at room temperature to identify the crystalline phase of the synthesized materials. The particle size and morphology of the prepared materials were observed by scanning electron microscope (FE-SEM, JEOL, JSM-820) with an accelerating voltage of 15 kV. And more detailed morphologies were also observed with a transmission electron microscopy (FE-TEM, JEM 2100F, 200kV).

2-4 Measurements of electrochemical properties

The electrochemical properties of synthesized cathode material were performed using 2032 coin cell. For positive electrode fabrication, the prepared powders were mixed with 7.5 % (mass fraction) carbon black and 7.5 % (mass fraction) polyvinylidene fluoride in *N*-methyl pyrrolidinone until slurry was obtained. And then, the blended slurries were pasted onto an aluminum foil current collector, and the electrode was dried at 100 °C for 12 h in oven. The test cell consisted of the positive electrode and lithium foil negative electrode separated by a porous polypropylene film, with 1.15 mol/L LiPF_6 in EC:EMC:DMC (3:2:5 in volume ratio) as the electrolyte. The assembly of the cells was carried out in a dry Ar-filled glove box.

The cells were charged and discharged over a voltage range from 2.0 V to 4.6 V versus Li/Li^+ at room temperature. Cycling performances and rate capability were carried out at different C-rates.

3 Results and discussion

Fig.1. shows the discharge capacity of a test cell using the $\text{Li}[\text{Co}_{0.1}\text{Ni}_{0.15}\text{Li}_{0.2}\text{Mn}_{0.55}]\text{O}_2$ of different current densities after the first charge and discharge (4.8~2.0 V) in the range of 4.6~2.0 V. The capacity slowly decreased as the C-rate increased.

Fig.2. shows the capacity vs. the cycle number of a test cell using the $\text{Li}[\text{Co}_{0.1}\text{Ni}_{0.15}\text{Li}_{0.2}\text{Mn}_{0.55}]\text{O}_2$. The

first charge (cutoff range <4.8 V) and discharge capacity (cutoff range >2.0 V) of the $\text{Li}[\text{Co}_{0.1}\text{Ni}_{0.15}\text{Li}_{0.2}\text{Mn}_{0.55}]\text{O}_2$ are each 247 mAh/g, 242 mAh/g and After the second cycle, the capacity of discharge slowly decreased as the increase of cycle number.

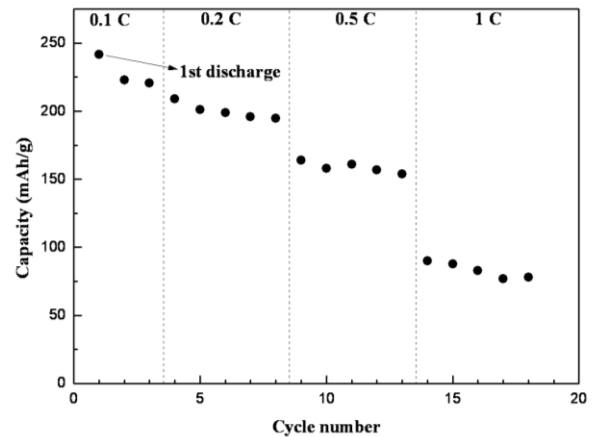


Fig.1. Discharge capacity of $\text{Li}[\text{Co}_{0.1}\text{Ni}_{0.15}\text{Li}_{0.2}\text{Mn}_{0.55}]\text{O}_2$ at various C-rate.

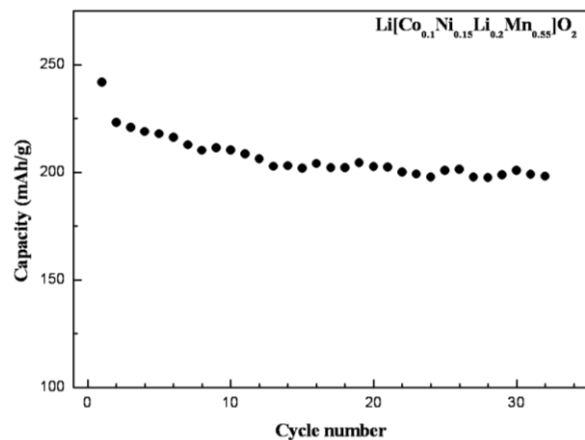


Fig.2. Cycle performance of $\text{Li}[\text{Co}_{0.1}\text{Ni}_{0.15}\text{Li}_{0.2}\text{Mn}_{0.55}]\text{O}_2$ at 0.1 C.

References

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