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The effect of thermal stability for high-Ni-content layer-structured cathode materials, $LiNi_{0.8}Mn_{0.1-x}Co_{0.1}Mo_xO_2$ ($x = 0, 0.02, 0.04$)

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HIGHLIGHTS

- Thermal stability of $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ was improved by Mo substitution.
- Mo substitution suppressed the crystal structure change from spinel to rock-salt and reduced oxygen release by heating.
- Li-rich Mo-substituted cathode, $Li_{1.10}Ni_{0.8}Mn_{0.06}Co_{0.1}Mo_{0.04}O_2$, satisfied both high capacity and high thermal stability.

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ABSTRACT

Improving thermal stability is one of the most serious issues concerning Ni-based cathode materials for Li ion batteries. To increase the capacity for maintaining good thermal stability, we substitute Mo for Mn. We apply differential scanning calorimetry (DSC), thermal desorption spectrometry-mass spectrometry (TDS-MS), and X-ray diffraction (XRD) to elucidate the effect of Mo substitution. The application of DSC indicates that Mo substitution effectively reduces the exothermic reaction between the cathode and electrolyte. The applications of TDS-MS and XRD indicate that Mo substitution suppresses crystal structure change and reduces the oxygen release that accompanies heating below 350 °C. However, the discharge capacities of Mo-substituted samples are lower than that of sample without Mo substitution. We optimize the Li/transition metal ratio and obtain $Li_{1.10}Ni_{0.8}Mn_{0.06}Co_{0.1}Mo_{0.04}O_{2+\delta}$, which satisfy both high capacity and high thermal stability requirements.

1. Introduction

Lithium ion batteries for plug-in hybrid electric vehicles (PHEV) and electric vehicles (EV) are required to be safer and exhibit a higher energy density than conventional batteries. Therefore, high-Ni-content layer-structured cathode materials are expected to be promising as cathode active materials.

It has been reported that increased Ni content increases charge–discharge capacity [1–4]. However, materials with high Ni content are negatively affected by their poor thermal stability, especially at a high charge state [5–8]. It was reported that in $Li_{1-a}NiO_2$ [9–13] and in $Li_{1-a}NiMO_2$ (M: metal) [14–26] the crystal structure of $Li_{1-a}MO_2$ changed from layer to spinel to rock-salt and released oxygen as the temperature increased. In order to improve structural stability, a number of elements, i.e., Co [27–29], Mn [28,30], Ti [28,29,31], Mg [29,32,33], TiMg [34], Al [35–38], Fe [38], Zn [39], Si [40], Ga [41,42], and Mo [43–45], were substituted. In our previous paper [26], we attributed the reason for the instability of Ni-based cathode materials to the instability of the high valence state of Ni. Therefore, the substituted element was selected from the viewpoint of stability in the high valance state. In this research, we focused on substituting Mo for Mn. There are two reasons Mo is thought to be an effective substitute material. First, since its high valence state is more stable than its low valance state, it may be stable at a high charge state. Second, if Mo^{6+} is substituted for Mn^{4+}, the rate of Ni^{2+} to Ni^{3+} increases. Therefore, the Ni valence of Mo-substituted cathode materials is lower than that of non-substituted cathode materials, and this may improve thermal stability. Therefore, we studied the effect of Mo substitution on the thermal stability of Ni-based cathode materials.

We evaluated the exothermic reaction between the cathodes and electrolyte by differential scanning calorimetry (DSC), oxygen release from the cathodes by thermal desorption spectrometry-mass spectrometry (TDS-MS), and crystal structure change by X-ray diffraction (XRD).

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2. Experimental

The cathode materials $LiNi_{0.8}Mn_{0.1-x}Co_{0.1}Mo_xO_2$ ($x = 0$, 0.02, 0.04) were synthesized by solid state reaction. The stoichiometric amounts of LiOH, NiO, MnO_2, Co_3O_4, and MoO_3 with 3% excess Li were thoroughly mixed and pressed into pellets. The pellets were precalcined in oxygen atmosphere at 600 °C for 10 h. The precalcined materials were then ground and pressed into pellets, which were calcined in oxygen atmosphere at 850 °C for 10 h.

We measured the charge–discharge capacities of these cathode materials. Cathodes were formed on aluminum foil by blade-coating of a slurry consisting of the active material, carbon, polyvinylidene difluoride (PVDF) (85:10:5 wt.%), and *N*-methyl pyrrolidone (NMP) solvent, followed by drying, pressing, and cutting. The delithiated electrodes were prepared according to the following process. Test cells were assembled with a cathode electrode, a lithium metal as an anode electrode, a microporous polypropylene separator, and a 1 M $LiPF_6$ solution of a mixture of carbonate solvents in an argon glove box. The cells were charged and discharged at a C/20 rate between 3.0 and 4.3 V.

Samples for DSC measurement (DSC6100; Seiko Instruments Inc.) were prepared using the following method. Cathodes containing $Li_{1-y}Ni_{0.8}Mn_{0.1-x}Co_{0.1}Mo_xO_2$ ($x = 0$, 0.02, 0.04) were charged to a prescribed composition ($y = 0.8$) at a C/20 rate of constant current. After charging, the electrodes were removed from the cells, washed with dimethyl carbonate (DMC), and dried. The charged $Li_{0.2}Ni_{0.8}Mn_{0.1-x}Co_{0.1}Mo_xO_2$ ($x = 0$, 0.02, 0.04) electrodes were put into a SUS sample pan with 1 ml of electrolyte. They were set in the DSC equipment and heated to 350 °C in argon atmosphere at a rate of 5 °C min^{-1}.

Samples for TDS-MS (EMD-WA-1000; ESCO, Ltd.) were prepared using the same method as that for the DSC samples; the charged $Li_{0.2}Ni_{0.8}Mn_{0.1-x}Co_{0.1}Mo_xO_2$ ($x = 0$, 0.04) electrodes were set in the TDS-MS sample chamber and heated to 350 °C in a vacuum at a rate of 5 °C min^{-1}. The released oxygen was detected using a quadrupole mass spectrometer with a step of 0.02 s.

Samples for XRD (Rint-2200 UltimaIII; Rigaku) were prepared as follows. The charged $Li_{0.2}Ni_{0.8}Mn_{0.1-x}Co_{0.1}Mo_xO_2$ ($x = 0$, 0.04) electrodes were heated in argon atmosphere for 1 h at 150–350 °C to expose them to anomalous high temperatures that might occur during unsafe incidents and cooled to room temperature. Then XRD was applied to identify the crystal structures of the prepared samples before and after heating at high temperatures using a Rigaku diffractometer with a graphite monochromator and Cu Kα radiation at 40 kV and 40 mA. The diffraction angles were scanned from 10 to 70° using a step scan method with a step of 0.02° and a counting time of 1.5 s per step.

3. Results and discussion

3.1. Crystal structure of $LiNi_{0.8}Mn_{0.1-x}Co_{0.1}Mo_xO_2$ ($x = 0$, 0.02, 0.04)

Fig. 1 shows the XRD patterns of $LiNi_{0.8}Mn_{0.1-x}Co_{0.1}Mo_xO_2$ ($x = 0$, 0.02, 0.04). All the peaks were assigned to a hexagonal α-$NaFeO_2$ structure of the *R*3m space group. Therefore, Mo^{6+} is substituted for Mn^{4+}, and is thought to occupy the octahedral site. Table 1 shows the lattice parameters and intensity ratio of *I*(003)/*I*(104). The lattice parameter *a* increased as Mo content increased. On the other hand, the lattice parameter *c* changed little regardless of the amount of Mo substitution. The lattice parameter *a* is related to the change in transition metal ionic size. The ionic sizes of Mo^{6+}(0.59 Å) is closer to that of Ni^{2+}(0.69 Å), Ni^{3+}(0.56 Å), Co^{3+}(0.545 Å), and Mn^{4+}(0.53 Å) than to that of Li^{+}(0.76 Å) [46]. Therefore, Mo^{6+}(0.59 Å) is thought to occupy the transition metal site. As Mo^{6+} is increasingly substituted for Mn^{4+}, the rate of Ni^{2+} to Ni^{3+} increases. Since the ionic sizes of Ni^{2+}(0.69 Å) and Mo^{6+}(0.59 Å) are larger than those of Ni^{3+}(0.56 Å) and Mn^{4+}(0.53 Å) [46], the lattice parameter *a* increases with increasing Mo substitution. Since the lattice parameter *c* is related not only to the transition metal ionic size but also to lattice strain and cation mixing, it may not increase monotonically as the Mo content increases. The decreased intensity ratio of *I*(003)/*I*(104) indicates that Ni in the Li site increases [47,48]. Mo substitution increases the ratio of Ni^{2+} to Ni^{3+}. Since the ionic size of Ni^{2+}(0.69 Å) is similar to that of Li^{+}(0.76 Å), the degree of cation mixing may be increased.

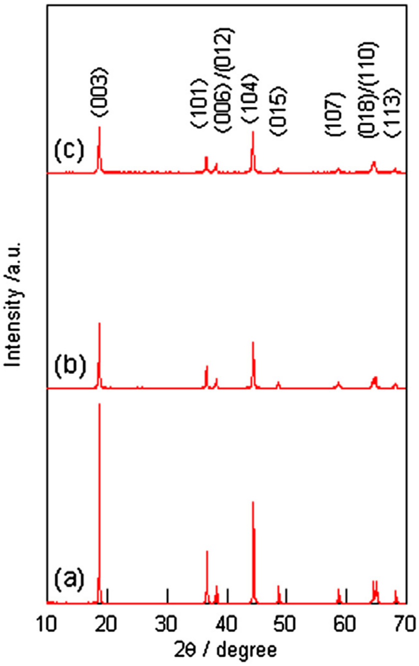

Fig. 1. XRD patterns of $LiNi_{0.8}Mn_{0.1-x}Co_{0.1}Mo_xO_2$ ($x = 0$, 0.02, 0.04) (a) $x = 0$, (b) $x = 0.02$, (c) $x = 0.04$.

3.2. Charge–discharge capacities of $LiNi_{0.8}Mn_{0.1-x}Co_{0.1}Mo_xO_2$ ($x = 0$, 0.02, 0.04)

Fig. 2 shows the initial charge–discharge capacities of $LiNi_{0.8}Mn_{0.1-x}Co_{0.1}Mo_xO_2$ ($x = 0$, 0.02, 0.04) at a C/20 rate between 3.0 and 4.3 V. The discharge capacities of Mo-substituted samples were lower than that of sample without Mo substitution. This leads us to believe that Ni in the Li site disturbs Li diffusion in Mo-substituted samples.

3.3. Exothermic reaction between cathodes and electrolyte by heating

We applied DSC to elucidate the exothermic reaction between the cathodes and electrolyte. Fig. 3 shows the DSC spectra of $Li_{0.2}Ni_{0.8}Mn_{0.1-x}Co_{0.1}Mo_xO_2$ ($x = 0$, 0.02, 0.04). Heat flow decreased

Table 1
Lattice parameters and intensity ratio of *I*(003)/*I*(104) in $LiNi_{0.8}Mn_{0.1-x}Co_{0.1}Mo_xO_2$ ($x = 0$, 0.02, 0.04).

x	*a*/Å	*c*/Å	*I*(003)/*I*(104)
0	2.871	14.20	1.95
0.02	2.876	14.22	1.38
0.04	2.882	14.22	1.08