Characterization of $LiNi_{0.85}Co_{0.10}M_{0.05}O_2$ (M = Al, Fe) as a cathode material for lithium secondary batteries

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Abstract

The structural and electrochemical characteristics and the thermal behavior of four-cation oxides, $LiNi_{0.85}Co_{0.10}M_{0.05}O_2$ (M = Al, Fe) were examined by X-ray and neutron diffraction measurements, charge/discharge cycling and thermal analysis. $LiNi_{0.85}Co_{0.10}Al_{0.05}O_2$ showed enhanced electrochemical properties, i.e. a small polarization and a large reversible capacity during the charge/discharge cycling compared with $LiNiO_2$ and it is due to the structural stabilization of the nickelate in the wide range of x by Co and Al substitution. The substitution of Co, Al and Fe also had a beneficial effect on the thermal stability of $LiNiO_2$. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Four-cation oxides; Structural and electrochemical characteristics; Thermal behavior

1. Introduction

Due to the increased production and use of portable devices, lithium secondary batteries with extended lives and higher power output are in demand. Since the performance of the lithium secondary batteries is limited by the properties of the cathode, a significant amount of research has been focused on the synthesis, processing and/or electrochemical identification of cathode materials for use in these batteries [1]. Among those cathode materials $LiNiO_2$ has been considered as the most attractive one to substitute for commercially used $LiCoO_2$ because of its high specific capacity. $LiNiO_2$, however, has a few disadvantages as a cathode material for lithium secondary batteries. Its major disadvantages are (i) difficulty in synthesis of an electrochemically active form because of its tendency for non-stoichiometry [2], (ii) capacity fading with cycling resulted from the structural instability [3] and (iii) lower thermal stability due to the instability of nickel ions in the high oxidation state of +3 or +4 [4,5].

The most common method for improving the $LiNiO_2$ as a cathode material for lithium secondary batteries is the small substitution with other elements such as Co, Mn, Fe, Al, Ti, Mg for nickel [6–10]. Recently it has been reported that the multiple substitution with each element brings some peculiar advantages on reversibility, capacity fading or thermal stability for safety and a unique combination of two or more cations substituting for nickel in $LiNiO_2$ has some promising features [11,12].

As part of a larger study to develop nickel-based lithium transition metal oxides with a high reversible capacity and a high thermal stability for a cathode material in lithium secondary batteries, the structural, electrochemical characteristics and thermal behavior of the four-cation oxide, $LiNi_{0.85}Co_{0.10}M_{0.05}O_2$ (M = Al, Fe) was studied.

2. Experimental

$LiNi_{0.85}Co_{0.10}M_{0.05}O_2$ (M = Al, Fe) was synthesized by reacting stoichiometric amounts of $LiNO_3$ (Aldrich) and $Ni_{0.85}Co_{0.10}M_{0.05}(OH)_2$ composite hydroxide as described previously [13]. The mixture of $Ni_{0.85}Co_{0.10}M_{0.05}(OH)_2$ and $LiNO_3$ were pressed into pellet and precalcined at 600°C for 12 h in a stream of oxygen and then reacted at 800°C for 24 h in a oxygen flow. The reaction products were ground and stored in a desiccator. The exact compositions of the $LiNi_{0.85}Co_{0.10}M_{0.05}O_2$ (M = Al, Fe) were obtained from the values of the average oxidation state of $Ni_{0.85}Co_{0.10}M_{0.05}$ and Ni/Co/M ratio measured with iodometric titration and ICP-AES, respectively, and are shown in Table 1. The crystal

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Table 1
Compositions and structural parameters of as-prepared $LiNiO_2$ and $LiNi_{0.85}Co_{0.10}M_{0.05}O_2$ (M = Al, Fe)

	$LiNiO_2$[a]	$LiNi_{0.85}Co_{0.10}Al_{0.05}O_2$[b]	$LiNi_{0.85}Co_{0.10}Fe_{0.05}O_2$
Oxidation state of Me[c]	2.907	2.927	2.907
Ni/Co/M ratio[d]	–	0.860/0.095/0.045	0.853/0.096/0.051
Composition	$Li_{0.951}Ni_{1.049}O_2$	$Li_{0.962}Ni_{0.893}Co_{0.099}Al_{0.046}O_2$	$Li_{0.951}Ni_{0.895}Co_{0.101}Fe_{0.053}O_2$
Lattice parameter (Å)	$a = b = 2.8813$, $c = 14.201$	$a = b = 2.8721$, $c = 14.186$	$a = b = 2.8760$, $c = 14.203$
Cationic distribution	$[Li_{0.951}Ni_{0.049}]_{3a}$	$[Li_{0.962}Ni_{0.038}]_{3a}$	$[Li_{0.951}Ni_{0.049}]_{3a}$
	$[Ni]_{3b}O_2$	$[Ni_{0.855}Co_{0.099}Al_{0.046}]_{3b}O_2$	$[Ni_{0.846}Co_{0.101}Fe_{0.053}]_{3b}O_2$

[a] The results for $LiNiO_2$ was quoted from the [13].

[b] Nominal compositions of the samples are calculated from the relative content of Ni, Co, M nitrate and $Li(NO)_3$.

[c] Obtained by iodometric titration method.

[d] Obtained by ICP-AES.

structures of $LiNi_{0.85}Co_{0.10}M_{0.05}O_2$ were characterized by neutron powder diffraction measurements.

Composite electrodes were prepared by mixing of 88 wt.% of $LiNi_{0.85}Co_{0.10}M_{0.05}O_2$, 6 wt.% of acetylene black, and 6 wt.% of PVDF-HFP co-polymer (Kynar FLEX 2801, Elf-Atochem) dissolved in NMP. The mixed slurry was coated onto Al foil and dried for >24 h. A three-electrode cell system was employed for the electrochemical measurements. Lithium foil was used as a reference elec-

trode and a counter electrode and 1 M $LiClO_4$ in PC was used as an electrolyte. All electrochemical measurements were conducted at room temperature in a glove box filled with purified argon.

In order to obtain a charged sample for structural and thermal analysis, the cell was charged to a desired composition at a constant current of a 20 h rate. After a relaxation of several days, the electrode was taken from the cell. It was then washed with tetrahydrofuran and dried thoroughly in a
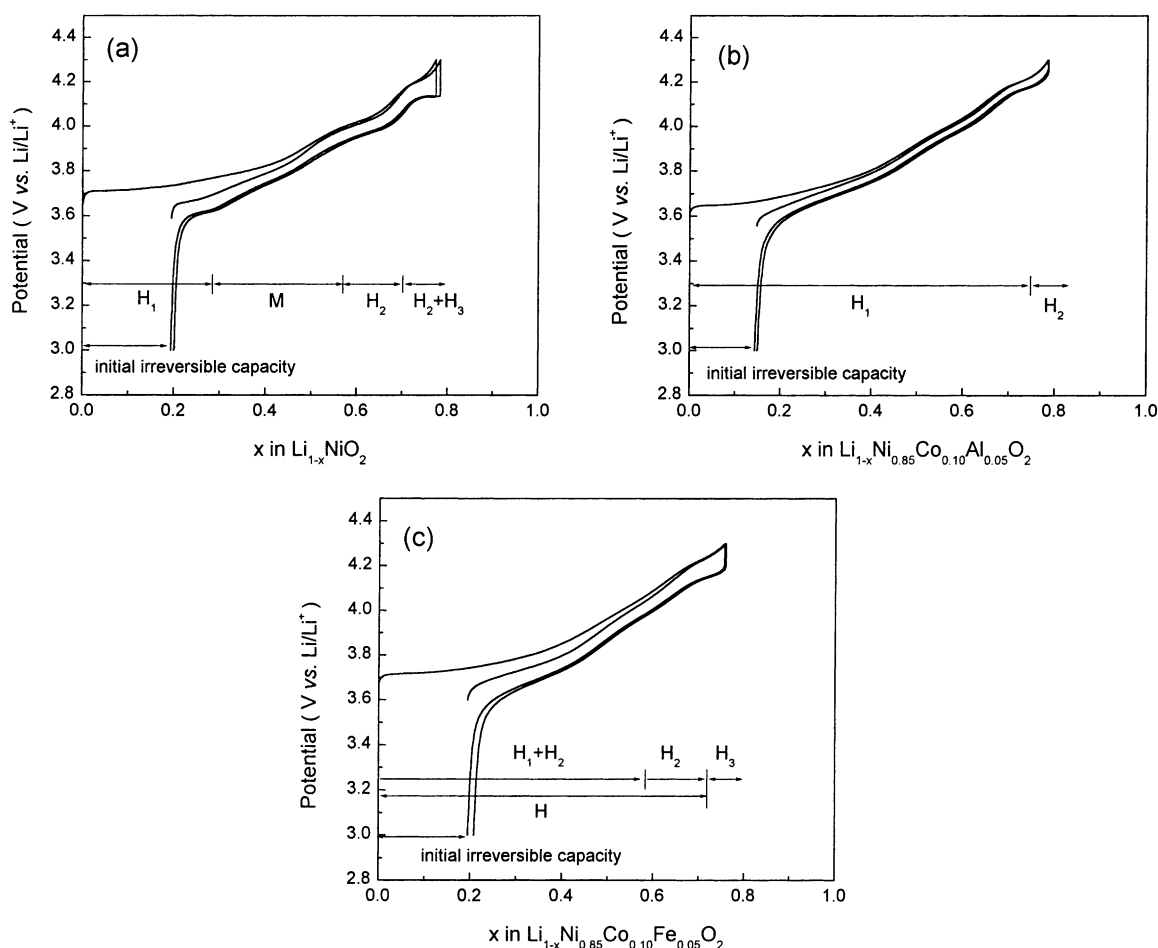

Fig. 1. The first two charge and discharge curves of (a) $Li_{1-x}NiO_2$, (b) $Li_{1-x}Ni_{0.85}Co_{0.10}Al_{0.05}O_2$ and (c) $Li_{1-x}Ni_{0.85}Co_{0.10}Fe_{0.05}O_2$ in 1 M $LiClO_4$ in PC during a constant-current cycling at a 20 h rate.

vacuum. The structural change of the electrode on the lithium deintercalation was examined by X-ray diffraction measurement and the thermal behavior of the charged compounds was measured with TG and DSC in an air atmosphere at a heating rate of 5°C/min.

3. Results and discussion

3.1. Powder characterization

The neutron diffraction patterns of as-prepared $LiNi_{0.85}Co_{0.10}M_{0.05}O_2$ (M = Al, Fe) could be indexed assuming a trigonal structure with space group of $R\bar{3}m$. The Rietveld refinement results of the diffraction patterns are listed in Table 1. During the refinement, the composition of the oxides obtained by iodometric titration method and ICP-AES were held constant. More details related to the neutron diffraction measurements and the Rietveld refinements were described previously [13].

3.2. Electrochemical characterization of $LiNi_{0.85}Co_{0.10}M_{0.05}O_2$ (M = Al, Fe)

Fig. 1 shows the first two cycles during a constant-current charge and discharge cycling at a 20 h rate for $Li_{1-x}NiO_2$

and $Li_{1-x}Ni_{0.85}Co_{0.10}M_{0.05}O_2$ (M = Al, Fe) in 1 M LiClO$_4$-PC solution in the potential range 3.0 to 4.3 V versus Li/Li$^+$. The removed lithium content, x, was calculated from the mass of the oxide and the charge transferred during cycling. The Co and Al substituted nickelates showed enhanced electrochemical properties, i.e. a small polarization and a large capacity compared with LiNiO$_2$. Fe substitution, however, had a detrimental effect on the electrochemical properties of LiNiO$_2$. The $Li_{1-x}Ni_{0.85}Co_{0.10}Al_{0.05}O_2$ also showed a reduction in initial irreversible capacity during the first cycling which resulted from the presence of extra-nickel ions in Li layer [14], because the amount of the extra-nickel ions in these materials were less than in LiNiO$_2$ as listed in Table 1.

Fig. 2 shows the X-ray diffraction patterns of $Li_{1-x}Ni_{0.85}Co_{0.10}M_{0.05}O_2$ (M = Al, Fe) measured after charging the electrode to a desired compositions and Fig. 3 shows the variation of the lattice parameters with x. For $Li_{1-x}Ni_{0.85}Co_{0.10}Al_{0.05}O_2$, a single hexagonal phase was preserved in the whole composition range, however, a significant shrinkage of c-axis was observed at the highly oxidized phase of $x = 0.8$ indicated as a shift of (0 0 3) peak to a higher angle in X-ray diffraction pattern as shown in Fig. 2(a). It has been reported that the hexagonal phase with a reduced c-axis is observed in a highly oxidized phase of $x > 0.7$ in $Li_{1-x}NiO_2$ and the capacity fading during the cycling of LiNiO$_2$ is caused by structural instability resulted from the presence of
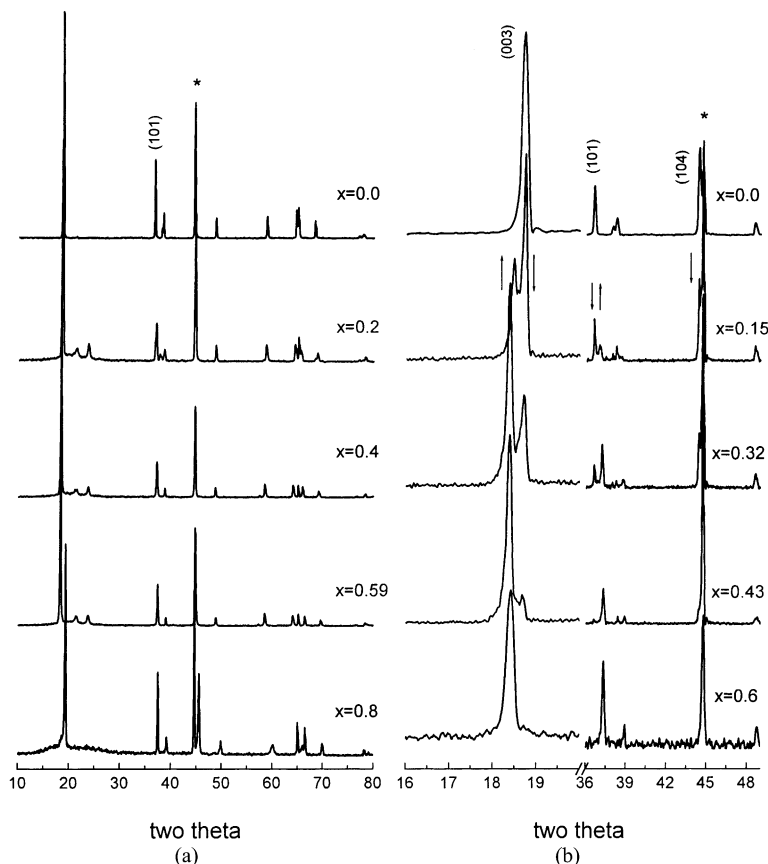

Fig. 2. X-ray diffraction patterns of (a) $Li_{1-x}Ni_{0.85}Co_{0.10}Al_{0.05}O_2$ and (b) $Li_{1-x}Ni_{0.85}Co_{0.10}Fe_{0.05}O_2$ (asterisk denotes the Al foil).
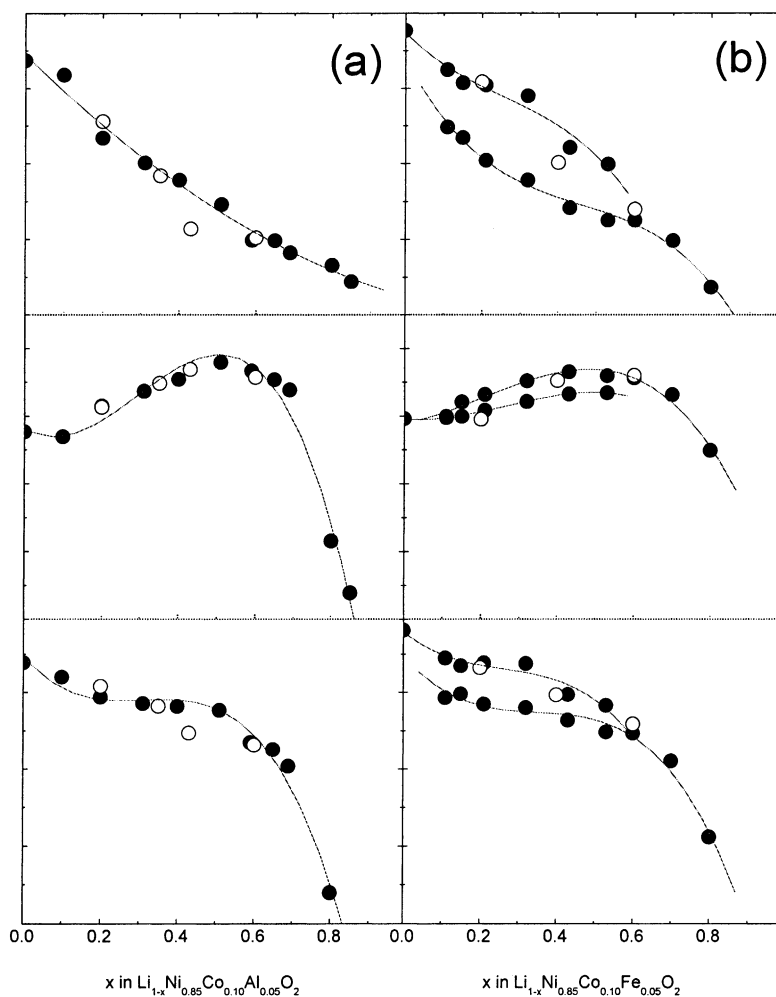
Fig. 3. Lattice parameters of (a) $Li_{1-x}Ni_{0.85}Co_{0.10}Al_{0.05}O_2$ and (b) $Li_{1-x}Ni_{0.85}Co_{0.10}Fe_{0.05}O_2$ during the first charge (filled circle) and discharge (open circle) cycling.

this phase [3]. For $Li_{1-x}Ni_{0.85}Co_{0.10}Al_{0.05}O_2$, the significant shrinkage of c-axis was observed in a more highly oxidized phase of $x > 0.8$ and therefore more Li-ion can be removed from the Co and Al substituted nickelate without structural destruction than from the $LiNiO_2$. The reduced initial irreversible capacity during the first cycle and the enhanced structural stability in highly oxidized phase make the Co and Al substituted nickelates to have a large reversible capacity during the charge/discharge cycling without any significant capacity fading as shown in Fig. 4.

Contrary to the Co and Al substituted nickelates, $Li_{1-x}Ni_{0.85}Co_{0.10}Fe_{0.05}O_2$ underwent a phase transition at the beginning of the first charge. As x increased, as-prepared $LiNi_{0.85}Co_{0.10}Fe_{0.05}O_2$ gradually turned into the second hexagonal phase which had a smaller a lattice constant and larger c lattice as shown in Figs. 2(b) and 3(b). The phase transition to the second hexagonal phase was completed at $x = 0.6$ and further lithium deintercalation and reintercalation progressed in a single phase. The poor electrochemical characteristics of $Li_{1-x}Ni_{0.85}Co_{0.10}Fe_{0.05}O_2$
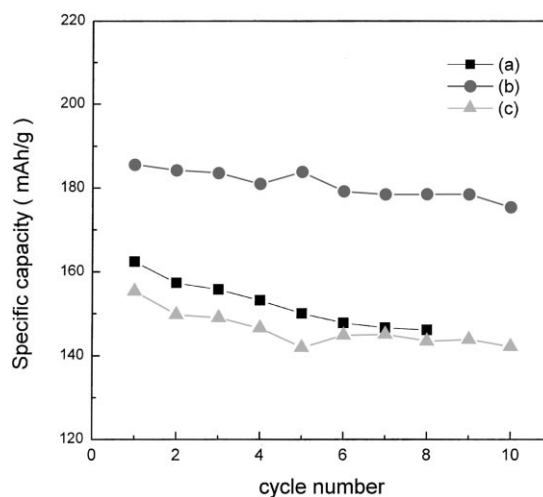

Fig. 4. Discharge capacities of (a) $LiNiO_2$, (b) $LiNi_{0.85}Co_{0.10}Al_{0.05}O_2$ and (c) $LiNi_{0.85}Co_{0.10}Fe_{0.05}O_2$ as a function of cycle life in a constant-current cycling at a 20 h rate between 4.3 and 3.0 V vs. Li/Li^+.

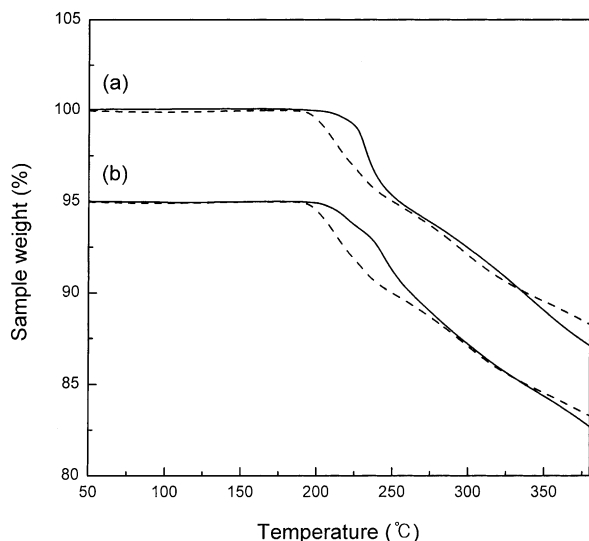Fig. 5. TGA results for (a) $Li_{0.2}Ni_{0.85}Co_{0.10}Al_{0.05}O_2$ and (b) $Li_{0.2}Ni_{0.85}Co_{0.10}Fe_{0.05}O_2$ in an air atmosphere at a heating rate of 5°C/min. The dashed line shows a TG trace of $Li_{0.2}NiO_2$ and the data have been offset vertically by 5% sequentially to clarify.

shown in Figs. 1(c) and 4 might be caused by the structural instability due to the lattice mismatch between the two hexagonal phases in the composition range of $0 < x < 0.6$.

3.3. Thermal behavior of $Li_{0.2}Ni_{0.85}Co_{0.10}M_{0.05}O_2$ (M = Al, Fe)

Fig. 5 shows the TGA results for the washed composite electrodes containing a highly oxidized $Li_{0.2}Ni_{0.85}Co_{0.10}M_{0.05}O_2$ (M = Al, Fe), an acetylene black and a PVDF-HFP co-polymer at a heating rate of 5°C/min in an air atmosphere. For $Li_{0.2}NiO_2$, the weight of the samples began to decrease gradually with the temperature at around 190°C. The weight losses measured with the TGA were almost entirely due to the loss of oxygen resulted from the thermal decomposition of lithium nickelate [4]. $Li_{0.2}Ni_{0.85}Co_{0.10}M_{0.05}O_2$ (M = Al, Fe) showed an elevated decomposition temperature compared with $Li_{0.2}NiO_2$ as shown in Fig. 5 and it indicated that the substitution of Co, Al and Fe had a beneficial effect on the thermal stability of $LiNiO_2$. In order to investigate the effect of the substitutes on the safety of the lithium batteries employing lithium nickelates as a cathode, further studies of the thermal behavior of these materials with the electrolyte should be pursued.

4. Conclusions

The structural and electrochemical characteristics and the thermal behavior of four-cation oxides, $LiNi_{0.85}Co_{0.10}M_{0.05}O_2$

(M = Al, Fe) were examined by X-ray and neutron diffraction measurements, charge/discharge cycling and thermal analysis.

$LiNi_{0.85}Co_{0.10}Al_{0.05}O_2$ could preserve a stable single phase up to a highly oxidized region and showed enhanced electrochemical properties, i.e. a small polarization, a small initial irreversible capacity during the first charge/discharge cycling and a large reversible capacity compared with $Li_{1-x}NiO_2$. The reduced initial irreversible capacity during the first cycle and the improved structural stability in highly oxidized phase made the Co and Al substituted nickelates to have a good cycle life with a large reversible capacity. The thermal decomposition of $Li_{0.2}Ni_{0.85}Co_{0.10}M_{0.05}O_2$ (M = Al, Fe) occurred at more elevated temperature compared with $Li_{0.2}NiO_2$ and it indicated that the substitution of Co, Al and Fe had a beneficial effect on the thermal stability of $LiNiO_2$.

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