

Yttrium-doped $\text{Li}(\text{Ni}, \text{Co})\text{O}_2$: an improved cathode for Li-ion batteries

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Abstract

Yttrium-doped mixed oxides, $\text{Li}(\text{Ni}_{0.7-y}\text{Y}_y\text{Co}_{0.3})\text{O}_2$, $y = 0.00\text{--}0.05$ have been synthesized and characterized. Their cathodic behavior has been examined in cells with lithium metal as anode. The limit for Y solubility is ≤ 0.05 . The beneficial effect of Y is evident by way of increased capacity — retention during charge–discharge cycling, up to 100 cycles at $0.2C$ rate and up to 50 cycles at $1C$ rate. Cyclic voltammograms indicate that the phase transitions which usually occur in LiNiO_2 during cycling, are suppressed by Co- and Y-doping but not completely eliminated. A reduced hysteresis in the anodic and cathodic peak voltages observed for $y = 0.05$ is an indication of excellent reversibility of the electrode. Thermal stability of the charged cathode is not, however, improved by Y-doping. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Recently mixed oxides of the formula $\text{Li}(\text{Ni}_{1-x}\text{Co}_x)\text{O}_2$, $x = 0.1\text{--}0.3$ have been examined as possible substitute for LiCoO_2 as the cathode material in lithium-ion batteries [1–6]. Cobalt-doping has a large beneficial effect in suppressing the crystallographic phase transitions in LiNiO_2 and thereby reducing the capacity-fading. It has been shown that mainly the Ni-ions participate in the charge–discharge process in $\text{Li}(\text{Ni}_{1-x}\text{Co}_x)\text{O}_2$ for the voltage window of 2.5–4.3 V. Optimization of the parameters like particle size and morphology can yield higher initial capacities and lower capacity-loss during the first charge–discharge [5,6]. However, capacity-fading ranging from 30–50% occurs after 50–100 cycles in cells with the above mixed oxide cathodes. In addition to cobalt, other transition and non-transition elements have been tried as dopants into LiNiO_2 . Small amounts (2–5 at.%) of Ga [7], Nb [8], and multiple substitution of elements of the type (Ga, Mg) [9], (Ti, Mg) [10], (Co, Mg) [11], (Co, Mn) [12], with dopant concentrations ranging from 0.05 to 0.3 were found to improve the cathodic behavior of LiNiO_2 . Studies by Gao et al. [10] and

Brousselet et al. [11] have shown that multiple substitution of ions can also significantly improve the thermal stability of LiNiO_2 in the charged state. We employed yttrium (Y^{3+}) as an additional dopant and studied the cathodic behavior of phases, $\text{Li}(\text{Ni}_{1-x-y}\text{Co}_x\text{Y}_y)\text{O}_2$ with various x and y values. Presently, results on phases with $x = 0.3$ and $y = 0.0, 0.02, 0.05$ are reported here. The thermal stability of the cathodes in the charged-state was also examined.

2. Experimental

The compounds were synthesized by the high temperature reaction in an oxygen atmosphere. High-purity raw materials were used to prepare 10–15 g batches. They were characterized by X-ray diffraction (XRD), SEM and surface area analysis. Electrochemical tests were done on coin cells, fabricated in a glove-box, with the mixed oxide as cathode, Li metal foil as anode and 1 M LiPF_6 in EC + DEC (1:1 v/v) as electrolyte and Macpile (France) or Bitrode (USA) battery-tester. Cathode was fabricated with about 15 mg of oxide, super P carbon as conducting additive and PVDF as binder and NMP as the solvent. Charge–discharge tests were done up to 50 or 100 cycles at various current ratings in the range 3.0–4.2 V (4.3). DSC scans were done using TA Instrument, USA, model 2010 in the range 100–350°C at 3°C/min.

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3. Results and discussion

Compounds with $x = 0.3$ and $y = 0.00, 0.02, 0.05$ have been prepared by the solid state method. Thoroughly mixed raw materials LiNO_3 , NiO , Co_3O_4 and Y_2O_3 were heated at 300°C for 5 h, and then at 750°C for 13–20 h followed by slow cooling at the rate of $60^\circ\text{C}/\text{h}$ in flowing O_2 gas (at the rate of 0.2–0.6 l/min). Select compounds were also synthesized by the solution method using LiOH , Ni- and Co-acetates and Y-nitrate. These were dispersed in water and subsequently evaporated to dryness using a rotary evaporator. The obtained powder was decomposed first at 500°C for 5 h (instead of at 300°C), followed by the above heating and cooling procedures. Black colored, free-flowing powders with surface area (BET) ranging from 0.5 to $1.4 \text{ m}^2/\text{g}$ and particle size less than $10 \mu\text{m}$ were obtained. XRD showed that single phase compounds are formed with the $\alpha\text{-NaFeO}_2$ structure. The compound with $y = 0.05$ showed a small impurity line, due to LiYO_2 indicating that the solid solubility of Y is 5 at.%. The lattice parameters for $y = 0.00$ ($a = 2.868 \text{ \AA}$; $c = 14.10 \text{ \AA}$) are in agreement with those reported in the literature [5,13]. The hexagonal, c lattice parameter increases slightly with Y-doping, whereas the a value is unchanged. The ratio of the intensities $(0\ 0\ 3)/(1\ 0\ 4)$ lines in the XRD patterns are 1.9–2.2 and 1.3–1.7 for the phases prepared by solid state and solution methods, respectively, which indicates the 2D nature of the crystal lattice.

Galvanostatic charge–discharge curves have been recorded for the voltage window 3.0–4.2 V (or 4.3) versus Li metal, at current ratings of 0.2 or 0.1C for the cathodes up to 100 cycles. The current ratings were calculated from the actual currents and the weights of the active cathode material. The first-charge capacity varied from 196 to 207 mAh/g for the composition with $y = 0.00$, and from 178 to 180 mAh/g for $y = 0.02$ and 0.05 depending on the method of preparation (Table 1). The irreversible capacity loss, after the first discharge, ranged from 23 to 29 mAh/g and 40 to 66 mAh/g for compounds prepared by solid state and solution methods, respectively. We noted a slight increase in the discharge capacity during 2–5 cycles, possibly due to the activation of the cathode. The charge–discharge capacities in the range 5–100 cycles remained the same ($\pm 1\%$) for all

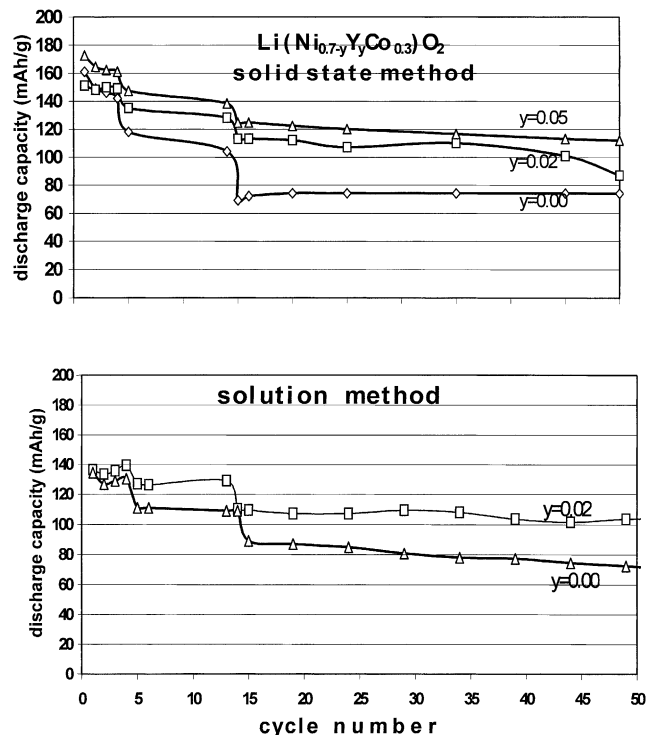


Fig. 1. Plots of discharge capacity vs. the number of charge–discharge cycles for the cathodes, $\text{Li}(\text{Ni}_{0.7-y}\text{Y}_y\text{Co}_{0.3})\text{O}_2$, $y = 0.00, 0.02$ and 0.05, prepared by the solid state and solution methods. Voltage window is 2.75–4.3 V (vs. Li-metal). Tests were done at 0.1C rate for the 1st cycle, 0.2C rate for 2–4th cycle, 0.5C rate for 5–14th cycle and finally at 1C rate for 15–50th cycle. The charge–discharge capacities are within 1% from the 2nd cycle onwards.

the compounds indicating excellent reversibility of the cathodes. After 100 cycles, the capacity-retention ranged from 65 to 67% for $y = 0.00$ and 71–84% for the Y-doped phases (Table 1).

In order to explore the high-rate capability of the cathodes, which is of relevance in the practical Li-ion cells, tests were done on another batch of coin cells in the voltage range 2.75–4.3 V, using the following procedure, viz. charge–discharge cycling at 0.1C rate for the 1st cycle, 0.2C rate for 2–4th cycle, 0.5C rate for 5–14th cycle and finally at 1C rate for 15–50th cycle. Results are shown in Fig. 1. The

Table 1

Cathodic charge–discharge and irreversible capacities of the compounds, $\text{Li}(\text{Ni}_{0.7-y}\text{Y}_y\text{Co}_{0.3})\text{O}_2^a$

	Solid state method (3.0–4.2 V, 0.2C rate)			Solution method (3.0–4.3 V, 0.1C rate)	
	$y = 0.00$	$y = 0.02$	$y = 0.05$	$y = 0.00$	$y = 0.02$
First charge capacity	196 (192)	180 (186)	178 (178)	207 (192)	179 (186)
First discharge capacity	167	151	155	141	139
Irreversible capacity	29	29	23	66	40
Reversible capacity after 50 cycles	128	143	125	98	134
Reversible capacity after 100 cycles	111	124	110	92	117
Discharge capacity retention after 100 cycles	67%	82%	71%	65%	84%
Reversible capacity after 50 cycles (1C rate)	74	87	112	67	103

^a Values in brackets are theoretical values assuming that only Ni-ions participate in the charge–discharge process; values are in mAh/g.

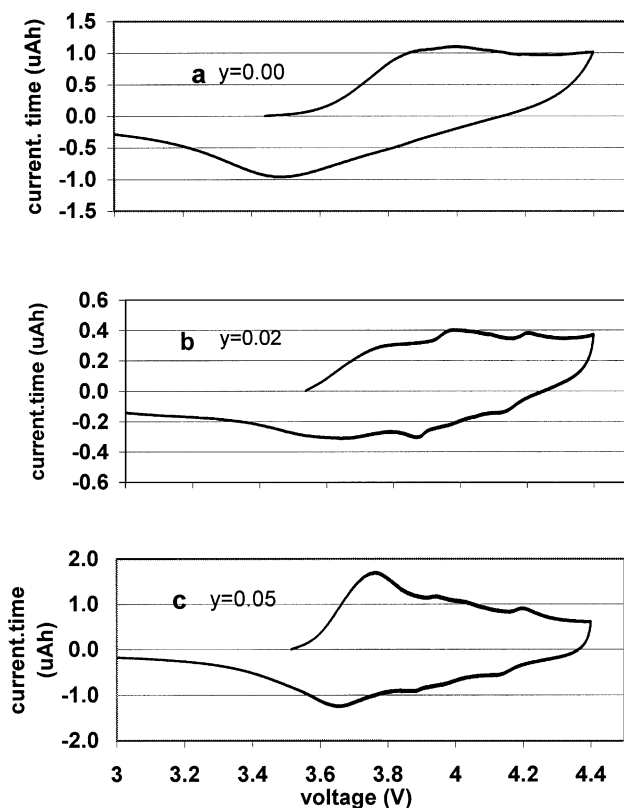


Fig. 2. Cyclic voltammograms (3rd cycle) for the cathodes, $\text{Li}(\text{Ni}_{0.7-y}\text{Y}_y\text{Co}_{0.3})\text{O}_2$, $y = 0.00, 0.02$ and 0.05 prepared by the solid state reaction. Li-metal was used as the reference/counter electrode in coin type test cells. The voltage scan rate is 0.058 mV/s and voltage range is $3.0\text{--}4.4 \text{ V}$.

effect of Y-doping is clearly seen in giving consistently large cathodic capacities even at the $1C$ rate, and the $y = 0.05$ compound shows the best behavior. Again, the charge–discharge capacities in the range 3–50 cycles were found to remain within $\pm 1\%$, at these high current ratings.

Cyclic voltammograms on the phases with various values of y indicate that the phase transitions originally exhibited by the undoped LiNiO_2 are greatly suppressed for $y = 0.0$ and 0.02 , but not completely eliminated even with $y = 0.05$. One significant effect of Y-doping was clearly observed: the anodic and cathodic peaks occur at 3.75 and 3.65 V , respectively for $y = 0.05$, and thus the hysteresis is only 0.1 V . This indicates excellent reversibility of charge–discharge and improved Li-ion mobility in the lattice. For $y = 0.00$ and 0.02 , the hysteresis values are $>0.15 \text{ V}$ (Fig. 2).

Thermal stability of the charged cathodes was studied by DSC, after charging the cells at 4.3 V at $0.1C$ rate,

equilibrating for 20 h , dismantling and recovering the powder. Exothermic peaks corresponding to the decomposition of the cathodes were found at $T_d = 222, 220$ and 211°C , respectively for $y = 0.00, 0.02$ and 0.05 . For the compounds prepared by the solution method, the T_d values are 216 and 225°C for $y = 0.00$ and 0.02 . Our values for $y = 0.0$ agree well with those reported by Cho et al. [6]. There are minor differences in T_d depending on the synthesis method, but no systematic variation was found with various y values and we conclude that Y-doping does not significantly affect the thermal stability of the cathodes in the charged state.

4. Conclusions

The cathodic behavior of the LiNiO_2 can be greatly improved by simultaneous doping of cobalt and yttrium, and our results on $\text{Li}(\text{Ni}_{0.7-y}\text{Y}_y\text{Co}_{0.3})\text{O}_2$ show that the composition with $y = 0.05$ exhibits the best high current rate ($1C$) capability up to 50 cycles. Thermal stability of the cathodes in the charged state however, is not improved by Y-doping.

Acknowledgements

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