Short communication

Synthesis of $LiCo_{1-x}Ni_xO_2$ from a low temperature solution combustion route and characterization

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Abstract

Nickel substituted lithium–cobalt oxides, $LiCo_{1-x}Ni_xO_2$ ($0 < x < 0.4$), have been synthesized in a very short time by a solution combustion method at 350 °C using diformyl hydrazine as a fuel. Pure phases with hexagonal lattice structure have been obtained. These compounds facilitate reversible insertion/extraction of Li^+ ions with good discharge capacity between 3.0 and 4.4 V versus Li/Li^+. Results of the studies by powder X-ray diffraction, scanning electron microscopy, cyclic voltammetry, galvanostatic charge–discharge cycling and ac impedance measurements are presented.
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1. Introduction

After the first commercial lithium-ion battery was produced about a decade ago, extensive research activities have been devoted to several aspects of different cell components. Among the positive electrode materials, $LiCoO_2$ has been studied widely, as this was the first compound shown to undergo the electrochemical insertion/extraction of Li^+ ions reversibly [1], and as this compound was used in the first commercial Li-ion battery. At present, a majority of the Li-ion battery technologies employ $LiCoO_2$ as the positive electrode material.

It is generally believed that $LiCoO_2$ is expensive as it consists of the costly element, cobalt. There has been interest, therefore, to substitute Co in $LiCoO_2$ either partially or completely by a less expensive element such as Ni, Mn, etc. Thus, the synthesis and electrochemical evaluation of $LiCo_{1-x}Ni_xO_2$ have been undertaken and reported [2]. In addition to decreasing the quantity of Co required, the partial substitution by Ni is expected to enhance the structural stability of the compound over a large number of charge–discharge cycles. Thus, the cycle-life of the $LiCo_{1-x}Ni_xO_2$

positive electrode materials is expected to be greater than that of $LiCoO_2$.

The $LiCo_{1-x}Ni_xO_2$ compounds have been synthesized by several methods [3–9]. They include the conventional solid state reaction at about 1000 °C [3–5], soft chemical route from oxalate precursors at about 750 °C [6], co-precipitation of the metal oxides followed by heating at 700 °C [7], solution combustion synthesis using urea as a fuel at 700 °C [8] and polyvinyl alcohol precursor method at 750 °C [9]. In all these methods, the compounds are formed at high temperatures and the time required for the synthesis ranges from hours to days.

In the present study, $LiCo_{1-x}Ni_xO_2$ ($0 < x < 0.4$) oxides are synthesized by a solution combustion method at 350 °C. The procedure takes only a few minutes to produce the compound. The electrochemical properties of these compounds as positive electrode materials are evaluated.

2. Experimental

Analar-grade Li_2CO_3, $Co(NO_3)_2 \cdot 6H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ were purchased from S.D. Fine Chemicals Ltd., and $LiBF_4$, ethylene carbonate, dimethyl carbonate, *n*-methylpyrolidinone (NMP), polyvinylidene fluoride (PVDF) and lithium ribbon

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(0.7 mm thick) were obtained from Aldrich. Diformyl hydrazine (DFH) was prepared by dropwise addition of formaldehyde to a stoichiometric quantity of hydrazine hydrochloride at $0\,^\circ C$ [10]. A solution mixture of Li_2CO_3, $Co(NO_3)_2 \cdot 6H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ was prepared by dissolving the required quantities of these compounds in a minimum quantity of water. Li_2CO_3 was taken 25% in excess of stoichiometric proportion, to avoid any loss of Li as Li_2O. The DFH fuel was added at a weight ratio of 20% to the solution and mixed thoroughly. This solution mixture was transferred to a petri-dish and introduced into a furnace pre-heated to $350\,^\circ C$. The fuel got ignited and a solid residue was formed within a few minutes. The product was cooled to room temperature, washed with methanol, dried in air and annealed at $850\,^\circ C$ for 6 h. Several compositions of $LiCo_{1-x}Ni_xO_2$ ($0 < x < 0.4$) were synthesized.

In order to study the electrochemical properties of $LiCo_{1-x}Ni_xO_2$, electrodes were prepared on Al foil substrates. A foil of area $1.2\,cm^2$ with a tag for electrical connection was polished with successive grades of emery, washed with doubly distilled water and etched for about 2 min in dilute HCl, washed again, rinsed with doubly distilled water and air dried. $LiCo_{1-x}Ni_xO_2$ (80 wt.%), acetylene black (15 wt.%) and PVDF (5 wt.%) were mixed using NMP to form a homogeneous paste, spread on the pre-treated Al foil and dried at $80\,^\circ C$ under vacuum. The spreading and drying steps were repeated thrice and finally dried at $80\,^\circ C$ under vacuum for about 12 h. An electrode thus made contained about 10 mg of $LiCo_{1-x}Ni_xO_2$. The electrochemical cells were assembled in glass containers with three-electrode configuration, using Li for both the counter- and reference-electrodes. A micro-porous polypropylene (Celgard 2400) film was used as the separator. The electrolyte was 1 M $LiBF_4$ in 1:1 ethylene carbonate and dimethyl carbonate mixture. The solvents were triply distilled under argon atmosphere and repeatedly treated with molecular sieves (4 Å) before preparing the electrolyte.

The X-ray diffraction patterns of the samples were recorded on a Jeol (JDX-8P) diffractometer and their microstructure was observed by means of Jeol (JSM-5600 LV) scanning electron microscope. The cyclic voltammograms were recorded using a potentiostat/galvanostat model Versastat. Impedance spectra were recorded using an excitation signal of 5 mV by EG&G PARC electrochemical impedance analyzer Model 6390. Impedance data were subjected to the non-linear least squares (NLLS) fitting procedure due to Boukamp [11]. Constant current charge–discharge cycling of the electrodes was performed using a galvanostatic circuit consisting of a dc regulated power supply, a high resistance, and an ammeter in series with the cells. A digital multimeter of high input impedance was employed for measuring the electrode potentials. To make measurements in the temperature range from -10 to $40\,^\circ C$, a Julabo refrigerator cum heater Model F 25, with ethylene glycol and water mixture as the thermal medium, was employed. At each desired temperature, the cell was equilibrated for 3 h

before measurements. The ambient temperature experiments were carried out at $20 \pm 1\,^\circ C$ in an air-conditioned room.

3. Results and discussion

Metal oxides are synthesized by a solution combustion method at a temperature as low as $350\,^\circ C$ and in a few minutes of reaction time [12,13]. The method involves the addition of a mild fuel to an aqueous solution of a metal salt, and heating of the mixture at about $350\,^\circ C$. At this low temperature, the fuel burns, and the solution temperature increases to a high value. As a result, the corresponding metal oxide is formed. During this process, which lasts only a few minutes (typically, 5 min), there is an evolution of large quantities of vapors (CO_2, NO_2 and H_2O), and the
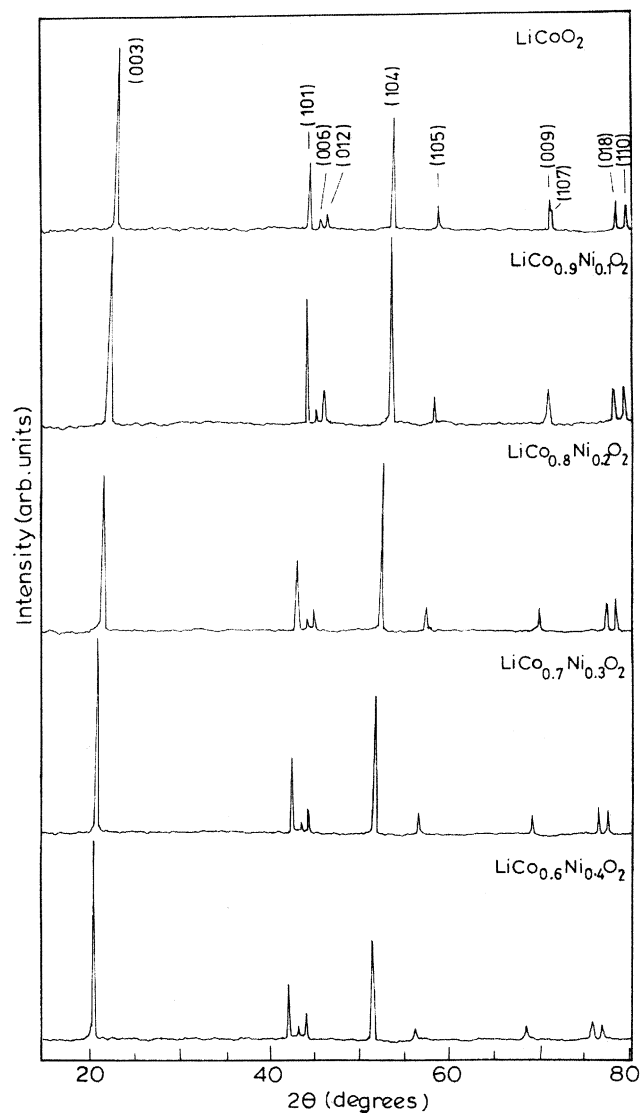

Fig. 1. Powder X-ray diffraction patterns of $LiCo_{1-x}Ni_xO_2$ oxides using Co Kα radiation.

resulting metal oxide is in the form of a fine powder form with a large surface area. $LiCoO_2$ has been synthesized by this method and the electrochemical activity has been studied [14]. In the present study, Co in $LiCoO_2$ is partly substituted by Ni, and the compounds of general formula $LiCo_{1-x}Ni_xO_2$ with the value of x in the ranges of 0–0.4 are prepared. In the solution used for combustion, stoichiometric quantities of Co and Ni were taken. The oxide samples were analyzed for Li by flame photometry, and it was found that the Li content corresponds to the composition $LiCo_{1-x}Ni_xO_2$.

In Fig. 1, the XRD patterns of $LiCo_{1-x}Ni_xO_2$ are shown. The compounds of different compositions (x) are formed in pure phases, and the XRD reflections are indexed to the hexagonal lattice of the α-$NaFeO_2$. In this structure, the transition metal atoms, namely Co and Ni are surrounded by 6O atoms forming $Co_{1-x}Ni_xO_2^-$ slabs by edge sharing of the octahedral. The Li^+ ions are located in between the $Co_{1-x}Ni_xO_2^-$ layers. The $LiCo_{1-x}Ni_xO_2$ samples have rhombohedral structure belonging to the R3m space group and the unit cell parameter are defined in terms of the hexagonal settings.

The lattice parameters a and c and the ratio c/a were determined by least squares refinement of the XRD data. The results are as shown in Fig. 2. The parameter a, which is related to the metal–metal distance, increases monotonously

with increasing Ni content (x). This is due to the difference in sizes between the Co^{3+} and Ni^{3+} ions. The c-value as well as the slab thickness increase with x.

It has been reported that, if the c/a ratio lies between 4.96 and 4.99, the cation mixing between M^{3+} (M = Co or Ni) and Li^+ in octahedral sites does not occur [15]. For all the compositions of the $LiCo_{1-x}Ni_xO_2$ samples, the c/a ratio lies between 4.97 and 4.99 as shown in Fig. 2(B) suggesting the absence of cation mixing. The XRD patterns of the samples prepared with $x > 0.4$ indicated the presence of two separate oxide phases, thus limiting the formation of single phase only for $x = 0.4$. The particle size calculated from the XRD data using the Debye–Sherrer formula provided the particle size in the range 0.5–0.95 μm for all the samples. A typical SEM image (Fig. 3) shows an average particle size of 1.5 μm for $LiCo_{0.8}Ni_{0.2}O_2$.

Cyclic voltammograms of the $LiCo_{1-x}Ni_xO_2$ electrodes in 1 M $LiBF_4$ electrolyte between 3.0 and 4.4 V are characterized by a cathodic and an anodic peaks. A typical voltammogram is as shown in Fig. 4. The shape of the voltammograms is nearly the same as that reported in the literature for similar compounds [16] wherein the inequality between the cathodic and anodic peaks has been attributed to the slow scan rate (50 μV s^{-1}) of the measurement. Nevertheless, the cyclic voltammetric data suggest that the compounds prepared from the low temperature route are electrochemically active.

The $LiCo_{1-x}Ni_xO_2$ electrodes were subjected to charge–discharge cycling at $C/10$ rate between 3.0 and 4.4 V. Typical charge–discharge curves for the compound $LiCo_{0.8}$-$Ni_{0.2}O_2$ are as shown in Fig. 5(A). The values of capacity during the charging and discharging processes, respectively, are 107.7 and 107 mAh g^{-1}. Thus, the efficiency of cycling is close to unity. The cycle-life data of all compositions are as shown in Fig. 5(B). Discharge capacity of about 110 mAh g^{-1} is obtained for the compositions of $x = 0.1$ and 0.2. As the concentration of the Ni increases, the discharge capacity decreases, and it is about 55 mAh g^{-1} for $LiCo_{0.6}Ni_{0.4}O_2$.

A $LiCo_{0.8}Ni_{0.2}O_2$ electrode was subjected to charge–discharge cycles at different rates at 20 °C, and the variation of capacity and coulombic efficiency with cycling rate is as shown in the Fig. 6(A). The discharge capacity decreases from 135 mAh g^{-1} at C/20 rate to 60 mAh g^{-1} at C/2 rate. Similarly, the coulombic efficiency also decreases from 99% at C/20 rate to 69% at C/2 rate. Further more, the electrode was subjected to charge–discharge cycles at several temperatures in the range 0–40 °C. The variation of discharge capacity and coulombic efficiency with temperature is as shown in Fig. 6(B). The discharge capacity is low with a value of 25 mAh g^{-1} at 0 °C, and it increases to 144 mAh g^{-1} at 40 °C. The coulombic efficiency increases from 64% at 0 °C to 98% at 40 °C.

Electrochemical impedance spectra of the electrodes were recorded at different state-of-charge (SOC) values. A typical data are as shown in Fig. 7 in the Nyquist form. The
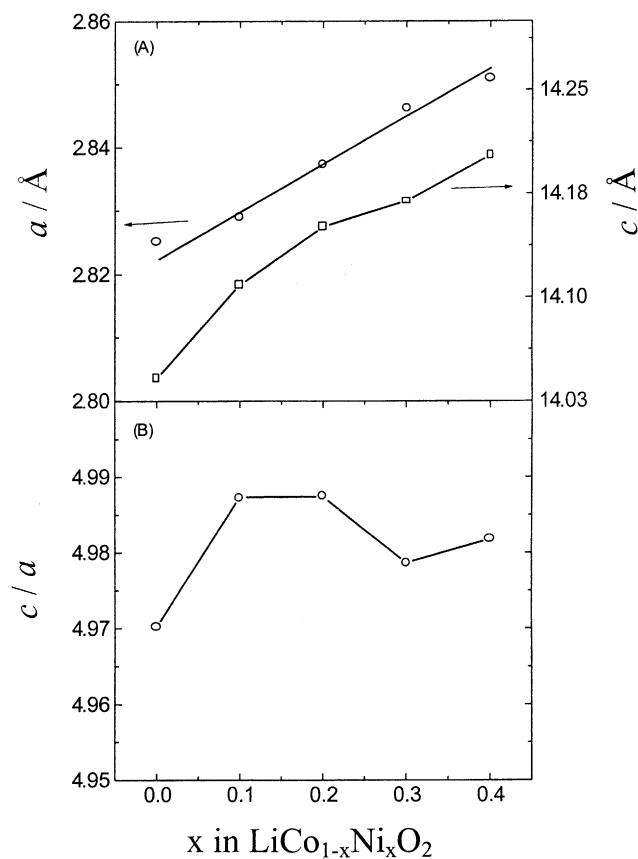

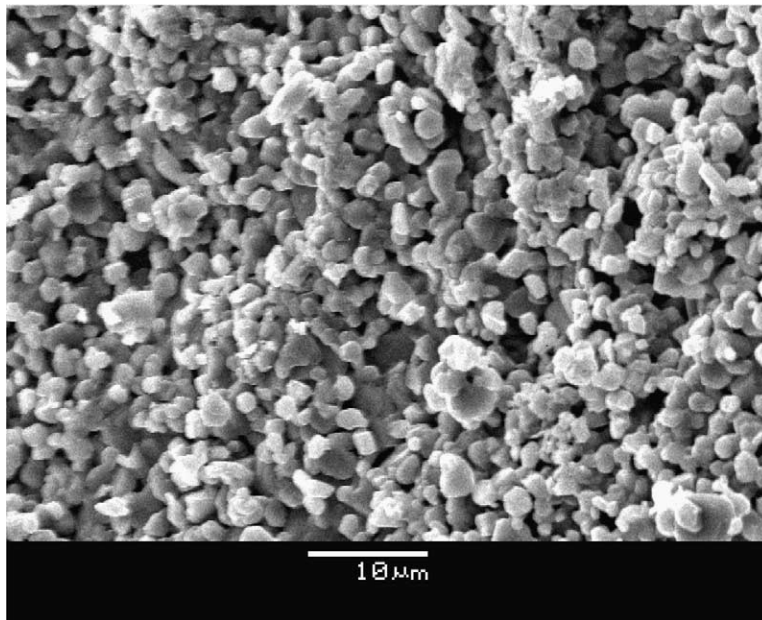Fig. 2. Variation of (A) lattice parameters, a and c and (B) c/a ratio with x in $LiCo_{1-x}Ni_xO_2$.

Fig. 3. Scanning electron micrograph of $LiCo_{0.8}Ni_{0.2}O_2$.

spectrum contains a small semicircle at the high frequency range and an incomplete large semicircle in the low frequency range. The data were analyzed using an equivalent circuit as shown in Fig. 7. The parameters in the circuit are explained as follows: R_o is the ohmic resistance of the cell, which includes the resistance of the electrolyte, separator, current collectors, electrical leads etc. R_1 is the resistance of the surface film on the electrode and R_2 is the charge-transfer resistance. Q_1 and Q_2 are the constant phase elements (CPE), which are used in the place of capacitances [11]. The
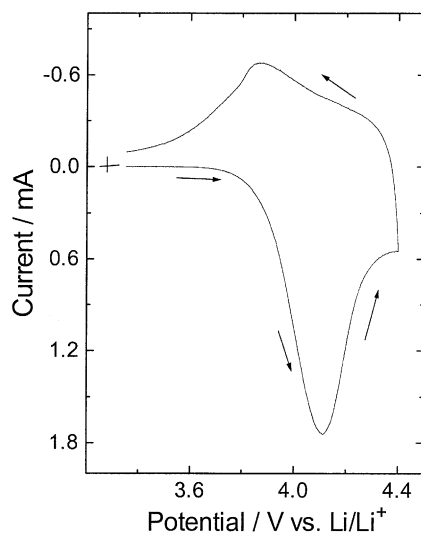

Fig. 4. Cyclic voltammogram of $LiCo_{0.8}Ni_{0.2}O_2$ in 1 M $LiBF_4$ electrolyte of ethylene carbonate and dimethyl carbonate. Scan rate = 50 $\mu V\,s^{-1}$; electrode area = 1.2 cm^2; and mass of the active material = 10 mg.
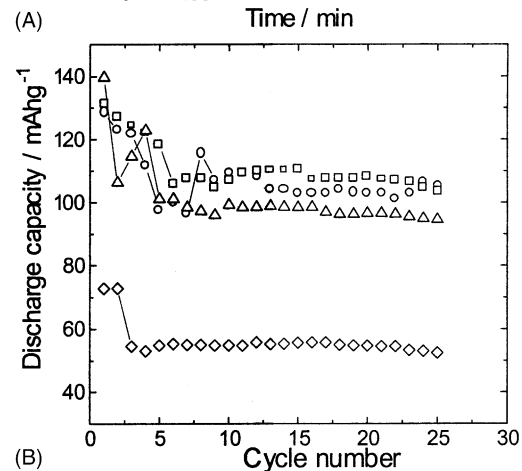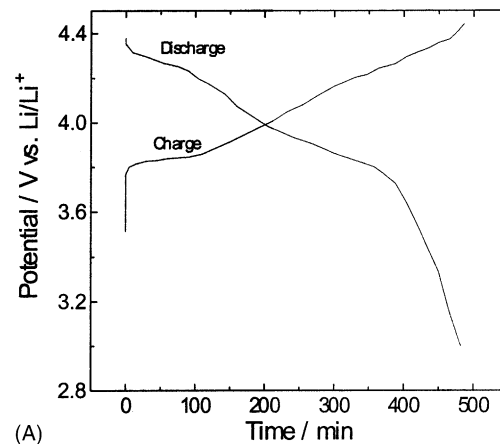

Fig. 5. (A) Charge–discharge curves of $LiCo_{0.8}Ni_{0.2}O_2$, and (B) cycle life data of $LiCo_{0.9}Ni_{0.1}O_2$ (□), $LiCo_{0.8}Ni_{0.2}O_2$ (○), $LiCo_{0.7}Ni_{0.3}O_2$ (△), and $LiCo_{0.6}Ni_{0.4}O_2$ (◇) at C/10 rate.
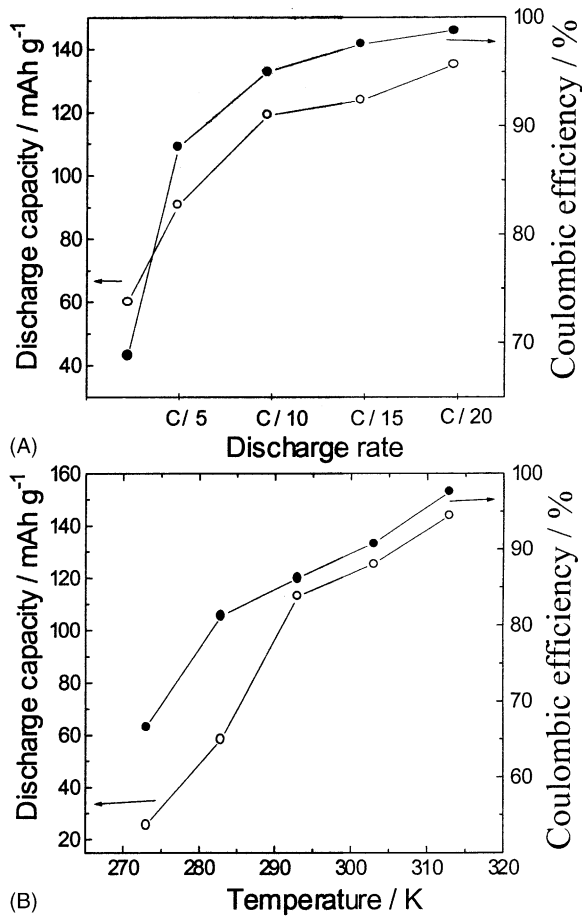
(A)

(B)

Fig. 6. Discharge capacity and coulombic efficiency of $LiCo_{0.8}Ni_{0.2}O_2$ (A) at various cycling rates at 20 °C and (B) at various temperatures.

Fig. 7. Nyquist impedance spectrum of $LiCo_{0.8}Ni_{0.2}O_2$ electrode at SOC = 1. Electrode area = 1.2 cm²; and mass of the active material = 12 mg. Equivalent circuit is shown as the inset.

Fig. 8. Variation of charge-transfer resistance (R_2) with x in $LiCo_{1-x}Ni_xO_2$.

parameters obtained by NLLS fit of the impedance spectra of $LiCo_{0.8}Ni_{0.2}O_2$ at different SOC values are given in Table 1. It is found that the ohmic resistance (R_o) is independent of the SOC. R_1 and R_2 decrease with increase of SOC. The electrochemical impedance data of commercial Li-ion cells have been analyzed and the dependence of impedance parameters on SOC has been examined [17]. Similar to the studies on Li-ion cells, the R_1 and R_2 of the $LiCo_{0.8}$-$Ni_{0.2}O_2$ electrodes also decrease with increase of SOC (Table 1). The variation of R_2 with x in $LiCo_{1-x}Ni_xO_2$ is as shown in Fig. 8 for SOC = 1. Similar trend is observed for the other SOC values also. The value of R_2 is minimal at $x = 0.2$, and it increases very substantially at higher values
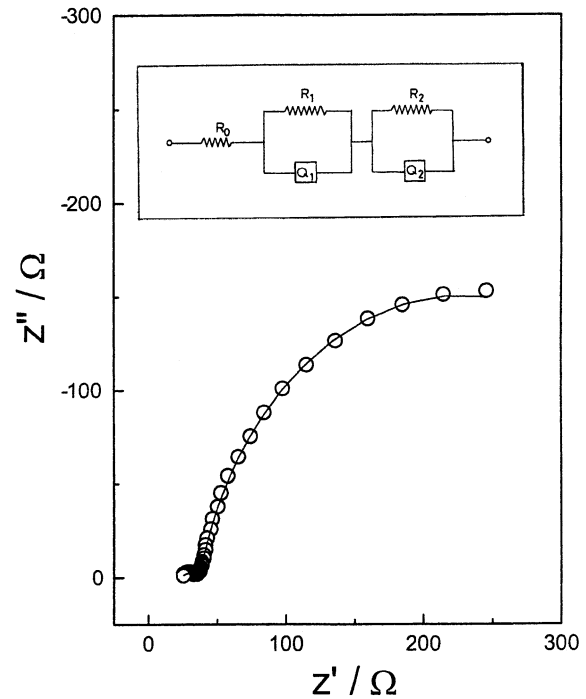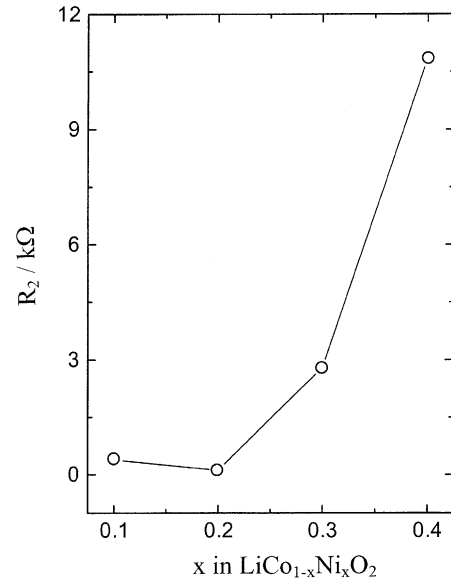
Table 1
Impedance parameters obtained from NLLS fit at different SOC values of $LiCo_{0.8}Ni_{0.2}O_2$

SOC	Parameters						
	R_o (Ω)	R_1 (Ω)	Q_1	n_1	R_2 (Ω)	Q_2	n_2
0	11.40	50.7	1.97×10^{-4}	0.59	3.82×10^3	9.85×10^{-3}	0.72
0.25	11.38	19.69	2.12×10^{-4}	0.51	3.36×10^3	1.50×10^{-2}	0.87
0.5	11.71	15.40	2.26×10^{-4}	0.64	4.48×10^2	1.51×10^{-2}	0.88
0.75	11.52	15.20	2.41×10^{-4}	0.64	1.90×10^2	1.79×10^{-2}	0.88
1	10.95	7.19	3.12×10^{-4}	0.63	1.11×10^2	1.99×10^{-2}	0.89

of x. A high value of R_2 is in agreement with the discharge capacity, which is the lowest for $x = 0.4$ (Fig. 5).

4. Conclusions

Nickel substituted lithium cobalt oxides, $LiCo_{1-x}Ni_xO_2$ ($0 < x < 0.4$), are synthesized by solution combustion method at 350 °C using diformyl hydrazine as a fuel. Pure $LiCo_{1-x}Ni_xO_2$ phases with hexagonal lattice structure corresponding to α-NaFeO$_2$ are obtained. The cyclic votammograms are characterized by well-defined peaks suggesting the electrochemical activity of the compounds as positive electrode materials. Discharge capacity of about 110 mAh g^{-1} is obtained for the compositions $x = 0.1$ and 0.2. However, the capacity decreases with increasing of Ni and it is about 55 mAh g^{-1} for $x = 0.4$. The charge-transfer resistance decreases with an increase of SOC. Further more, it is found to be minimum for $LiCo_{0.8}Ni_{0.2}O_2$.

Acknowledgements

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