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Sr doped Co substituted Li nickelate cathode materials for Li cells with improved cycling and thermal stability

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Abstract

Samples of cathode material were synthesized from a highly dispersed precursor containing 0.002 at.% Sr. The synthesis was performed from a mixture of the precursor with some overstoichiometric excess of LiOH at 720 °C in oxygen atmosphere. Part of the samples were coated with a thin film of Li-borate glass. The cathode active material (CAM) was mixed with 15 wt.% of Teflonized acethylene black and pressed on thin Al discs. The cathodes were cycled between 4.20 V and 3.20 V at 1 mA cm^{-2} first at 25 °C and then at 50 °C, whereafter the cycling continued up to 50–60 cycles. A pulse interruption method was applied to measure the DC area-specific resistivity of the cathodes R_c as a function of the state of discharge x. The evolution of the parameters of the R_c/x plots during cycling lent valuable information on the processes responsible for the degradation of the intercalation compound. The stability of the CAM during overdischarge was evaluated after 10 cycles at 25 °C and 24 cycles at 50 °C at 1 mA cm^{-2}. The cathode was shorted externally for 2 min to 0.00 V. In spite of the large current during the overdischarge the discharge capacity loss in the next cycle was only 3%.

1. Introduction

The Co containing Li nickelates, $LiNi_{1-x}Co_xO_2$ are presently recognized as the most efficient cathode active materials (CAM) for the cathodes in rechargeable Li cells as demonstrated by the results of the 5 leading Japanese producers [1].

The Research Group of the Samsung Display Device Co. Ltd. developed several new methods for the preparation of $LiNi_{0.8}Co_{0.2}O_2$ samples with very good cycling stability at high discharge rates at room temperature [2, 3]. Nevertheless in a later paper Kweon et al. [4] reported the use of commercially available CAM developed by the H Company, Japan which claimed that their material, containing a small amount of Sr, could meet the requirements for the thermal stability necessary for certain industrial applications. Indeed, the DSC measurements and the cycling tests confirmed the improved the thermal and cycling properties of the modified CAM.

It was recently established that some Li-borate glasses deposited on certain ceramic surfaces are good Li conductors and in very thin films can conduct electrons by tunneling [5–7].

The present paper is an attempt to explore the above recent trends for the optimization of the Co substituted Li nickelates as cathode materials for Li batteries.

2. Experimental

2.1. *Preparation of the precursor*

The mixed oxide precursor $Sr_{0.002}Ni_{0.8}Co_{0.2}O$, was prepared by a method recently developed in this laboratory avoiding the time-consuming sol–gel techniques often requiring sophisticated equipment. A mixed acetate solution was produced by dissolution of NiO, Co acetate and $Sr(OH)_2$ in dilute acetic acid. The clear solution was evaporated on a water bath and dried at 100–140 °C to eliminate completely the free acetic acid. The dry acetate was thermally decomposed to a mixed oxide at 300–400 °C in air. After grinding to a fine powder it was analysed for Ni and Co by complexometry and subjected to XRD diffraction.

2.2. *Synthesis and coating of the cathode active material (CAM)*

The precursor was mixed with some overstoichiometroic excess of LiOH in a mortar and annealed in an alumina crucible at 720 °C for 17–20 h in oxygen atmosphere. The obtained pellet was ball milled and the black powder was coated by a thin film of $Li_2O \cdot 2B_2O_3$ glass as described by Ying et al. [7]. The CAM was mixed with a methanolic solution of LiOH and H_3BO_3 in the appropriate ratio. The mixture was stirred at 60–70 °C to evaporate the methanol. The dry residue was annealed at 500 °C in air for 10 h, and the Li-borate glass was obtained. The content of the coating was only 1 wt.% with respect to the CAM. Based on the density of the Li-borate glass of ca. 2 g cm^{-3} and the specific surface area of the CAM (BET) of ca. 0.8 m^2 g^{-1} it was estimated that the thickness of the coating could vary between 50–70 Å.

2.3. *XRD characterization*

The XRD measurements of the samples were carried out on a Philips APD 15 diffractometer provided with a computer and appropriate software at a 0.02° 2θ step size with 2 s counting time and a wavelength $\lambda = 1.54178$ Å. The profiles were fitted to Pseudo-Voigt functions. For a better precision the two criterial pairs of peaks (100)(006) + (102) and (108)(110) were recorded in a narrow range of angles. The data of the first pair were used to estimate the integrated intensity ratio R_d derived by Dahn et al. [8] for $LiNiO_2$. The data of the second pair served for the estimation of the criterial lattice parameters: $\bar{a}, \bar{c}, \bar{c}/\bar{a}$, V_h as well as the splitting between the maxima of the (108) and (110) peaks, $\Delta 2\theta$.

2.4. *Cathodes, cells and cycling conditions*

The cathodes were prepared from a mixture of the CAM with 15 wt.% Teflonized acetylene black. The physical characteristics of the cathodes such as thickness, apparent density and porosity were made close to those adopted by the 5 leading Japanese companies producing Li-ion batteries [1]. The cathode mixture was pressed on an Al disc 15 mm in diameter. The stainless steel laboratory cell housed the cathode and the metal Li anode was separated by a glass fibre sheet. A Li/Li^+ reference electrode served to measure the cathode potential.

The cathodes were vacuum impregnated with the electrolyte solution of 1 M $LiClO_4$ in PC + EC (1:1). The cells were assembled in a dry box with less than 20 ppm of water.

The cathodes were charged at constant current of 80 mA g^{-1} (1.3–1.6 mA cm^{-2}) up to the limiting voltage of 4.20 V. The latter was maintained constant while the current fell exponentially to 0.1–0.2 mA cm^{-2}, whereupon the cell was automatically switched to discharge at a constant c.d. down to 2.80 V, where the new cycle was started. The cycling was carried out continuously at 25 °C or 50 °C in an air thermostat. The cycling conditions were similar to those adopted by the five leading Japanese producers of Li-ion batteries [1]. The cycling instrument was designed and constructed in the electronic workshop of this Institute.

2.5. *Method for in-situ measurements of the DC area-specific cathode resistivity of the catodes*

In our previous paper [9] the method developed in this laboratory was described in detail. In the present paper only the more essential features are presented for a better comprehension of its practical application and theoretical basis. The most important equations are given and discussed in terms of the concepts of Ueda and Ohzuku [10]. Six to eight short pulses (1–2 s) were applied by interruption of the current during the discharge of the cathode, which takes 4–5 h. Thus the interruption time is less than 0.11%, indicating that the method is non-destructive, and can be repeated periodically during a long-term cycling test, without affecting the shape of the polarization curves and, respectively the kinetics of the discharge process.

The area-specific DC resistivity of the cathodes is expressed by Eq. 1

$$R_c = \frac{\Delta E_x}{i_d} \ \mathrm{Ohm\,cm^2} \tag{1}$$

where ΔE_x is the vertical ohmic part of the voltage transient in mV obtained upon the discharge current interruption at the state of discharge $x = \tau_x/\tau_1$ with τ_x the time of the pulse application and τ_1 the time for full discharge. The discharge c.d. i_d is in mA cm^{-2}. It was found that in a wide range of x the values of R_c remain practically constant at $R_c = R_0$. At a certain value of $x = x_s$ R_c begins to rise steeply and linearly. For convenience the plots can be presented as $\Delta R_c(R_c - R_o)/x$. Figure 1 presents four typical $\Delta R_c/x$ plots obtained during cycling of a $LiSr_{0.002}Ni_{0.8}Co_{0.2}O_2$ coated cathode at 25 °C and 50 °C and at 1.0 mA cm^{-2} between 4.20 V and 2.80 V.

Up to the 44th cycle the extrapolation of the linear rising part of the plots down to $R_c = R_0$ yields the value of $x_s = 0.75$, while the extrapolation to $x = 1$ gives the maximum value of R_1.

As pointed out in [9] this behaviour agrees with the theoretically derived expression of Ueda and Ohzuku [10], for the cathode potential as a function of x.

$$E_x = E_o - \frac{\mathrm{RT}}{\mathrm{F}} \ln \frac{x}{(1-x)} \pm k(x - x_s) \quad \mathrm{V} \tag{2}$$

Here E_o is the standard potential at $x = 0.5$. The logarithmic term reflects the usual Nernst equation with

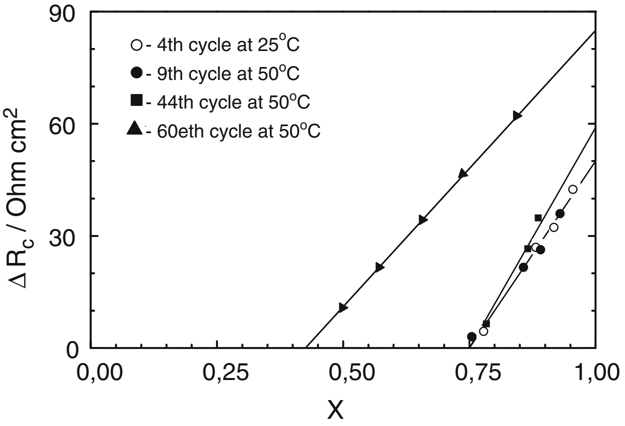

Fig. 1 Typical $\Delta R_c/x$ plots recorded at several cycles of a $LiSr_{0.002}Ni_{0.8}Co_{0.2}O_2$ coated cathode at 25 °C and 50 °C and 1.0 mA cm^{-2} between 4.20 V and 2.80 V.

$x/(1-x)$ the ratio of the occupied to available Li^+ sites in the intercalation compound. The linear term k accounts for the short-range in-layer repulsive forces between the Li^+ ions.

Ueda and Ohzuku [10], established that when x attains a critical value x_s, there appear definite superstructures and short-range in-layer repulsive or attractive forces between the Li^+ ions arise. The negative sign of k in Eq. (2) was obtained experimentally in all our measurements, confirming the repulsive forces between Li^+ ions.

From Eq. 1 and the value of R_1 at $x = 1$ the value of k can be calculated by (3)

$$k = \frac{i_d \cdot R_1}{(1 - x_s)} \text{ V}. \tag{3}$$

In order to increase the precision of the ΔR_c measurements part of the voltage transients was compensated by the cycling instrument. The correctness of our ΔR_c measurements was corroborated by the fact that their values remained constant when the discharge c.d. was increased from 0.5 mA cm^{-2} to 1.5 mA cm^{-2}.

3. Results and discussion

3.1. *XRD characterization*

It was found unexpectedly that the presence of Sr^{2+} has a beneficial effect on XRD criterial lattice parameters of the CAM. Two samples were synthesized with the same precursor $Ni_{0.8}Co_{0.2}O$ and the same excess of LiOH, 1 at.%. In the synthesis mixture for sample A there was no Sr^{2+}, while for sample B 0.002 at.% of Sr^{2+} was added. The conditions during the solid state reaction were the same: 720 °C for 17 h in oxygen atmosphere. The data presented in Table 1 clearly show that all the XRD parameters with the exception of the FWHM of the (108) peak and the integrated intensity ratio R_d of Dahn [8] are significantly improved in the presence of Sr^{2+}.

The similarity of the FWHM values suggests that the grain size of the CAM is not affected by the presence of Sr^{2+}. The XRD parameters of both samples are typical for the crystal lattice of the R $\bar{3}$m space group.

The beneficial effect of Sr on the XRD parameters suggests that the Sr doped CAM could yield better cycling performance. As shown further by the data of Fig. 2 this assumtion was justified. Hence in all our cycling experiments we used the Sr doped compounds.

It seems strange that the Sr^{2+} ions with a radius of 1.27 Å can be inserted into the crystal lattice of the Co substituted Li nickelate wherein the radii of all cations (Li^+, Ni^{3+}, Co^{3+}), as well as of the octahedral sites formed by the O^{2-} anions, are much smaller. Sr^{2+} is an alkali-earth metal and could occupy sites in the Li^+ slabs but, on account of its negligible content, this did not reduce the number of Li^+ cations noticeably.

The values of the R_d ratio of the present samples vary between 0.37 and 0.39. This is lower than 0.41 corresponding to $x = 1.00$ for Li_xNiO_2 [8] and also lower than that of a stoichiometric $LiCoO_2$ sample of 0.43. These low R_d ratios are reliable evidence for a high stoichiometry and low cation mixing of the present cathode material.

3.2. *Cycling performance*

The beneficial effect of the coating with a thin film of Li-borate glass of a Sr^{2+} doped cathode cycled at 1.0 mA cm^{-2} between 4.20 V and 2.80 V at 25 °C and 50 °C is presented in Fig. 2. By raising the temperature from 25 °C to 50 °C the discharge capacity, q_d, of a non-coated cathode is increased to 14 mAh g^{-1} or by 8.6%, while for the coated cathode the increase is 16 mAh g^{-1} or 9.0%. The final q_d value of the non-coated cathode after 41 cycles at 50 °C is 157 mAh g^{-1}, while that of the coated one after 46 cycles at 50 °C is 177 mAh g^{-1}, i.e., the increase is 20 mAh g^{-1} or 12.7%. These results reveal the positive effect of the coating on the cycling and thermal stability of the Sr doped cathodes.

From the data in Fig. 3 it was possible to estimate the accumulated discharge capacity Q_{ac} obtained during cycling at 50 °C by $Q_{ac} = n \cdot \bar{q}_d$, where n is the number

Table 1.

Sample	Sr^{2+}	Δ 2θ	$\bar{a}$ (Å)	$\bar{c}$ (Å)	$\bar{c}/\bar{a}$	V_h (Å)	FWHM of (108)	R_d
A	0.000	0.456	2.869	14.159	4.946	100.5	0.23	0.37
B	0.002	0.524	2.856	14.139	4.951	99.8	0.24	0.37
Δ (B – A)	–	+0.068	−0.007	−0.020	+0.005	−0.7	+0.01	0

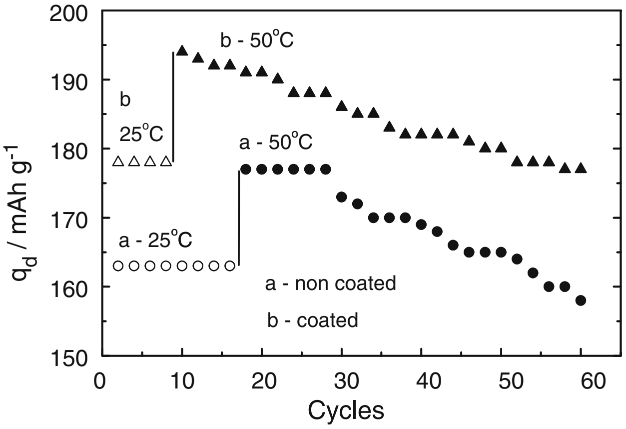

Fig. 2 Cycling of (a) non-coated and (b) coated $LiSr_{0.002}Ni_{0.8}Co_{0.2}O_2$ cathodes cycled at 1.0 mA cm^{-2} between 4.20 V and 2.80 V at 25 °C and 50 °C.

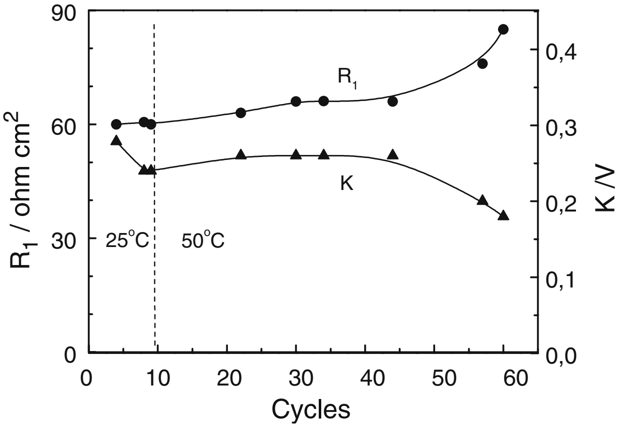

Fig. 4 Evolution of the R_l and k parameters of the R_o/x plots obtained during cycling of a coated cathode between 4.20 V and 2.80 V at 1.0 mA cm^{-2} described in Fig. 2.

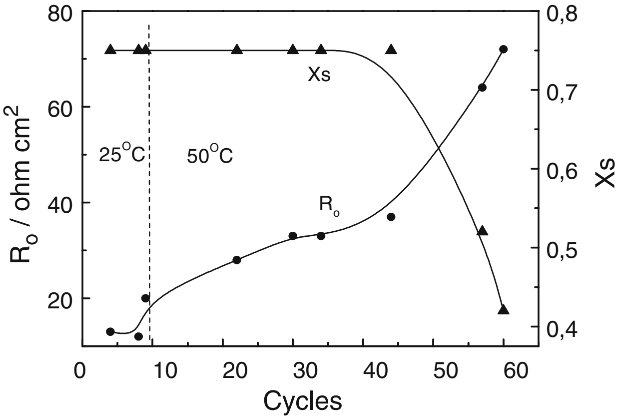

Fig. 3 Evolution of the R_o and x_s parameters of the R_c/x plots obtained during cycling of the coated cathode between 4.20 V and 2.80 V and at 1.0 mA cm^{-2} at 25 °C and 50 °C described in Fig. 2.

of the of the cycles and $\bar{q}_d$ the average discharge capacity at $n = 1/2$. For the non-coated cathode Q_{ac} is 7.23 Ah g^{-1}, while for the coated one it amounts to 9.25 Ah g^{-1} or an increase of 27.9% due to the coating of the Sr doped cathode.

Two factors could be responsible for the increase in q_d with increase in temperature from 25 °C to 50 °C: the increase in the conductivity either of the electrolyte solution σ_e or that of the cathode material σ_c. Literature data for the 1 M solution of $LiClO_4$ in PC + EC (1:1) used in our cells are ca. 8 mS cm at 25 °C and ca. 16 mS cm at 50 °C. Using the average resistivity of our discharged cathodes of R_l = 60 Ohm cm^2 and their average thickness of 75 μm their specific conductivity is estimated to 1.25 mS cm. On the other hand it is seen in Fig. 4 that the value of R_l does not change with temperature from 25 °C to 50 °C. Hence the value of σ_e is larger than σ_c by one order of magnitude. It can be concluded that the increase in q_d at 50 °C is associated basically with the 2-fold increase in σ_e, whereby the rate of supply of Li$^+$ ions to the crystalline surface in the pores of the cathode is considerably enhanced. It was further established that the mid-discharge voltage at 50 °C decreases in the first 45 cycles from 3.68 V to 3.63 V reaching 3.55 at the 60th cycle. This decrease was practically the same for the coated and non-coated cathode materials, which indicates that the thin Li borate glass film is a good electronic conductor.

3.3. *Overdischarge*

In their pioneering paper on $LiNiO_2$ Dahn et al. [8] showed that during overdischarge at 25 °C to 1.70 V the crystal structure is transformed from R $\bar{3}$m to 1T with a phase composition of Li_2NiO_2. When cycled at 40 h rate the overdischarged cathode exhibited high polarization and a drastic reduction in discharge capacity. In order to evaluate the effect of overdischarge on the cycling behaviour of one of our coated $LiSr_{0.002}Ni_{0.8}Co_{0.2}O_2$ cathodes it was cycled at 25 °C at 1.0 mA cm^{-2} between 4.20 V and 2.80 V for 24 cycles. The cell temperature was then raised to 50 °C whereby q_d increased from 169 mAh g^{-1} to 189 mAh g^{-1}. After 10 more cycles at the same capacity the cell was shorted externally to 0.0 V for 2 min. In the subsequent charging at 80 mA g^{-1} the cell recovered its normal initial charging voltage of 3.60 V within 20 min. It was estimated that during the 2 min short-circuit the cathode has consumed 26.4 mAh g^{-1} corresponding to an average current of ca. 0.79 A g^{-1}. In spite of this large current and the increase in the Li$^+$ content in the cathode from 0.69 at.% to 0.79 at.%, causing a considerable expansion of the unit cell volume, the discharge capacity in the next cycle was reduced by only 3%. In the following 32 cycles at 50 °C the capacity fade was only slightly increased. Comparison of the overdischarge effect on $LiNiO_2$ at 25 °C reported in [8], where the final voltage was 1.70 V and the current only 4 mA cm^{-2}, with the present results, demonstrates the strong stabilizing effect of Co^{3+} on the crystal lattice structure of $LiNiO_2$ whereby it can sustain much heavier overdischarge conditions at 50 °C and achieve good cycling stability.

3.4. *Evolution of the parameters of the R_c/x plots*

The evolution of the parameters of the R_c/x plots R_o, x_s, R_1, and k during the cycling of the cathodes yields useful information on the processes involved in the capacity decay. Figures 3 and 4 present the evolution of these parameters obtained in the cycling test of the coated $LiSr_{0.002}Ni_{0.8}Co_{0.2}O_2$ cathode described in Fig. 2. The increase in q_d by 9% upon increasing the temperature of the cathode from 25 °C to 50 °C was discussed in paragraph 2 of this Section. Unexpectedly, however, the values of the above parameters were not affected by this considerable temperature increase. They remained fairly constant from the 9th to the 44th cycle during which the discharge capacity decreased slightly. This finding indicates that the cycling and thermal stabilities of the cathode are determined by the rigid crystal structure of the intercalation compound protected by the Li-borate film. The increase in R_o in this cycle range is more pronounced and does not correspond to the small capacity fade. The evolutions of x_s, R_1, and k observed after the 44th cycle are more strongly expressed at the 60th cycle, where x_s falls to 0.42, R_1 is increased to 85 Ohm cm^2 and k is reduced to 0.18 V. Accordingly q_d is also considerably lowered to 177 mAh g^{-1}. These changes are associated with the degradation of the crystal lattice of the cathode material. One of the possible reasons is the oxidation of its O^{2-} anions to molecular oxygen [11]. In this some part of the octahedral sites in the lattice, where Li^+ ions can be reversibly intercalated, are permanently lost. On the other hand, it may be supposed that the decrease in x_s from 0.75 to 0.42 is associated with the formation of new superstructures in the Li slabs which retard the diffusion of Li^+ ions. Further, the decrease in the number of available sites for Li^+ in the slabs will increase the distance between the Li^+ cations, so that the repulsion forces between them will be reduced, as inferred by the lower values of the energy coefficient k.

Finally the molecular oxygen evolved might be partially consumed for the oxidation of organics in the cell (solvents, binders), forming solid products, which could be deposited on the cathode surface as passivating layers leading to an increase in R_o and R_1. The increased polarization of the cathode reduces the effective voltage range during cycling and the discharge capacity of the cathode is decreased.

4. Discussion

The intercalation compound $LiSr_{0.002}Ni_{0.8}Co_{0.2}O_2$ was used as a cathode active material (CAM) in Li rechargeable cells. It was synthesized from LiOH and a highly dispersed precursor obtained by a new method, avoiding the usual sol–gel complex procedures and unconventional equipment. The XRD patterns of the CAM samples revealed their rhombohedral crystal structure of the $R\bar{3}m$ space group with a high stoichiometry and a low cation disorder. It was established for the first time that the XRD criterial parameters of the Sr^{2+} doped compound significantly exceed those of the Sr-free samples. It was also reasonable to expect that the improvement in crystal structure of the samples should bring about better cycling and thermal stability. The results obtained in the cycling tests justified these expectations. The cathode material was coated by a very thin film of Li-borate glass ($Li_2O \cdot 2B_2O_3$) with a good ionic permeability and electronic conductivity which facilitate charge transfer during cycling.

It is shown that the cycling performance of the coated cathodes at 25 °C and particularly at 50 °C is superior to that of the non-coated ones.

The method for the dynamic in-situ measurement of the DC area-specific resistivity of the cathodes R_c as a function of the state of discharge x [8] was applied, which yields 4 specific parameters. Their evolution during a long-term cycling lends valuable information on the possible degradation processes of the CAM. The shape of the R_c/x plots is in conformity with the concepts of Ueda and Ohzuku [10] for the formation of superstructures leading to the increase in short-range in-layer repulsion forces between the Li^+ ions upon reaching a critical occupation level x_s in the CAM.

The rigid crystal structure of the coated CAM was illustrated by an overdischarge test. A cathode cycled 10 times at 25 °C and 24 times at 50 °C and 1 mA cm^{-2} was shorted for 2 min to 0.00 V. When it was recharged to 3.60 V the cathode consumed 26.4 mA g^{-1}, corresponding to an average c.d. of 0.79 A g^{-1} during the 2 min short-circuit test. In spite of this high c.d. and the increased Li^+ contents in the cathode the discharge capacity in the next cycle was reduced by only 3%.

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