In situ dynamic Ohmic resistivity measurement of $LiNi_{1-y}Co_yO_2$ cathodes as a function of the state of discharge

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Abstract

A method for the in situ dynamic measurement of the Ohmic resistivity, R_c, of $LiNi_{1-y}Co_yO_2$ cathodes as a function of the state of discharge, x, is developed. It follows the evolution of R_c with only a negligible interference of the discharge process by applying 6–10 short current interruptions and by recording the voltage transients between the cathode and a Li/Li^+ reference electrode. It was established with several tens of different $LiNi_{1-y}Co_yO_2$ cathodes that the area-specific Ohmic resistivity remains constant in a wide range of x, from 0 up to ca. 0.75, above which a steep linear rise of R_c is observed. This behaviour is in agreement with the expression of the redox potential of the Li insertion electrodes as a function of x proposed by Armand [1] and developed later by Ohzuku et al. [2]. In addition to the logarithmic Volmer–Tafel term this expression contains a linear one kx, which accounts for the close range in layer Li–Li interaction. The parameters of the R_c/x plots can yield valuable information for the effect of the cathode design as well of the cathode active material on the cyclig performance of the cathodes.
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Keywords: Li-ion cells; Ohmic resistivity; Voltage drop; Co doped nickelates; Cathode materials

1. Introduction

The DC impedance of commercial Li-ion cells has been measured by several authors under conditions which do not allow to determine the separate contributions in the overall voltage drop, obtained either by short pulse application or by longer current interruption.

Nagasubramanian et al. [3] determined the voltage drop of commercial Li-ion batteries with $LiCoO_2$ cathodes at three OCV, corresponding to three states of discharge by applying short 1 s current pulses from 50 to 1000 mA. However, the ample data is not presented in area-specific resistivity units and there are no values of the state of discharge in order to construct R_c/x plots. Besides this, their voltage drop values include components due to the resistances of the anode. Hong et al. [4] report the resistivities of commercial Li-ion cells in $\Omega\,cm^2$ as a function of x, estimated from the voltage drops recorded after rather long current interruptions of 15 s. In this case, the measured resistivity comprises components due to the charge transfer and diffusion processes and, therefore, cannot be used to assess the Ohmic behavior of the $LiCoO_2$ cathodes in the Li-ion cells.

In contrast with the above measurement we determined the Ohmic voltage rise during discharge of the cathodes in cells with Li reference electrodes. The voltage rise was obtained by a short current interruption of 2–3 s at several states of discharge and the voltage transients were recorded.

2. Experimental

2.1. Cathode material, cathodes and cells

The synthesis of $LiNi_{1-y}Co_yO_2$ samples with y from 0.20 to 0.30 is described in [5]. The six samples annealed at 720 and 760 °C exhibited quite similar XRD criterial parameters: $\bar{a} = 2.861 \pm 0.001$ Å^3, $\bar{c} = 14.152 \pm 0.004$ Å^3, $\bar{c}/\bar{a} = 4.947 \pm 0.001$, and $V_h = 100.2 \pm 0.2$ Å. These values are characteristic for cathode materials with a high stoichiometry and a low cation disorder, which suppose a good cycling performance. Indeed, the results of the cycling tests confirmed these expectation [5].

The ball milled and sieved synthesis products, mixed with 10% (w) acetylene black and 5% (w) Teflon were pressed on Al thin foil discs, 15 mm in diameter. The cathodes had a loading of 18 ± 3 mg/cm^2, apparent density of 2.5 ± 0.1 g/cm^3 and a porosity of $41 \pm 2\%$. The cathodes were assembled in stainless steel laboratory cells with a Li metal anode and a

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Li/Li$^+$ reference electrode. Two sheets of glass fiber paper served as separators and the electrolyte was 1M LiClO$_4$ in EC + PC (1:1) with less than 20 ppm of water. All assembly operations were conducted in a dry box with less than 20 ppm of water.

2.2. Measurement of the Ohmic resistivity of the cathodes

The thermodynamic voltage profile during the constant current discharge of a single phase layered intercalation cathode material is described according to Armand [1] by a Volmer–Tafel type relationship between the potential E_x and the state of discharge, x, by Eq. (1).

$$E_x = E_o - \left(\frac{nRT}{F}\right)\ln\left(\frac{x}{1-x}\right) + kx \qquad (1)$$

Here, x is the ratio of the occupied to the available sites in the insertion electrode at a given energy of the system and E_o is the standard potential at $x = 1/2$ for the redox couple. The term kx accounts for the short-range in-layer attractive or repulsive forces between the Li-ions.

Under load the discharge curve is shifted to lower voltages and the cathode utilization is reduced. As pointed out by Atlung et al. [6] two limitations can be responsible for the end of the discharge. One is the depletion in the concentration of the Li-ions in the electrolyte solution at the interface is C_{el}. The discharge is terminated when C_{el} becomes zero. The discharge time in this case depends on the limiting current density, i_1, which is a complex function of the equilibrium concentration and the diffusivity of the Li-ions in the solution as well as of the thickness and porosity of the cathode.

In cells with a well conductive electrolyte discharged at low to moderate rates, e.g. $C/10$ to $C/2$, using cathodes with a loading of ca. 20 mg/cm^2 and a porosity of 35–43%, the value of C_{el} will remain large enough to the end of the discharge. In this case the discharge is cut off when the interfacial Li$^+$ concentration in the solid phase, C_s, has reached its saturation value for the given limiting voltage, C_{max}, and according to the logarithmic term in Eq. (1) the voltage will decrease very steeply.

It is evident that the Ohmic resistivity of the cathode can be measured correctly as a function of x only if the conditions of the above limitations are fulfilled.

The method adopted in our investigation is based on the measurement of the initial voltage rise between the cathode and the Li/Li$^+$ reference electrode obtained upon a short pulse interruption of the discharge current and recording the voltage transient. A typical transient during the discharge of a Li/LiNi$_{0.8}$Co$_{0.2}$O$_2$ cell at 0.65 mA/cm^2 and at $x = 0.35$ is presented in Fig. 1. It is seen that the overall cathode potential is strongly compensated for a more accurate assessment of the small vertical voltage rise, usually in the range of 5–50 mV. The Ohmic voltage rise is followed by a slower voltage increase related to the decay of the charge transfer and diffusion processes. The transients were
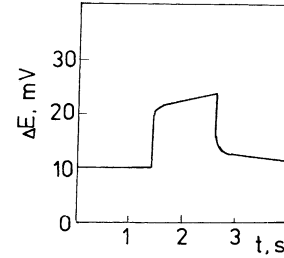

Fig. 1. Typical voltage transient during discharge of a LiNi$_{0.75}$Co$_y$O$_{25}$O$_2$ cathode obtained by short current interruption of 0.65 mA/cm^2 at $x = 0.25$.

recorded by a fast rise recorder (ca. 60 mV/s). It was found experimentally that the area-specific resistivity R_c determined by Eq. (2).

$$R_c = \frac{\Delta E}{i_d} \quad \Omega\,cm^2 \qquad (2)$$

is independent of the interrupted discharge c.d. i_d in the range from 0.3 to 1.3 mA/cm^2 in the first 2–10 cycles. This is a clear evidence for the Ohmic character of R_c. The state of discharge was determined by the ratio τ/T, with τ the discharge time at the moment of the pulse application and T the total discharge time.

3. Results and discussion

Due to the position of the Li/Li$^+$ reference electrode in our cells the measured Ohmic resistivity estimated by Eq. (2) comprised those of the cathode and of the electrolyte soaked separator ($R_c + \underline{R}_{el}$). It was established, however, that the resistivity R_{el} between a bare Al current collector covered only by the electrolyte soaked separator is less then 0.2 Ω cm^2 and can be therefore neglected in comparison even with the lowest resistivities of cathodes amounting to 11–15 Ω cm^2.

Fig. 2 illustrates the evolution of R_c with the increase of the state of discharge x, measured during the second cycle of a cathode with $y = 0.25$ discharged at 0.64 mA/cm^2. It is seen that R_c remains constant in a wide range of x and will be further denoted as R_o, which in the given example is 11 Ω cm^2. Above a certain value of $x = x_s$, R_c increases
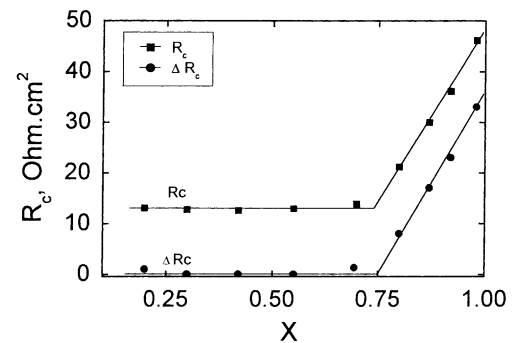

Fig. 2. R_c/x plot of a LiNi$_{0.75}$Co$_{0.25}$O$_2$ cathode recorded at the second discharge at 0.64 mA/cm^2 between 4.00 and 3.00 V.

Table 1
Data of R_o, x_s, R_1 and k obtained from R_c/x plots of LiNi$_{0.75}$Co$_{0.15}$O$_2$ cathodes with increasing loading

No.	Loading (mg/cm^2)	Cycle no.	i_d (mA/cm^2)	R_o (Ω cm^2)	x_s	R_1 (Ω cm^2)	kV (Eq. (5))
1	18	3	0.65	15	0.75	56	0.15
2	26	4	0.66	15	0.75	66	0.17
3	39	2	0.62	15	0.75	52	0.13

steeply and almost linearly with x. The extrapolation of this linearly rising portion of the R_c/x plot to R_o yields the value of $x_s = 0.75$, while by extrapolation to $x = 1$ the value of $R_1 = 40$ Ω cm^2 is obtained. It was considered more convinient to plot the difference $\Delta R_c = (R_c - R_o)$ as shown in Fig. 2.

The linear rise of the R_c/x plot evidently is associated with the term kx in Eq. (2), accounting for the short-range in-layer repulsion forces between the Li-ions. As shown by Ueda et al. [7], however, such an interaction becomes possible only after the formation of definite superlattice structures, whereby the energy for the insertion of more Li-ions is increasing linearly with the Li occupancy. These structures can appear at certain occupancy fractions of $x_s = 0.25$ or $x_s = 0.75$, of which the latter is in an agreement with our results. When $x < x_s$ the potential profile follows the Nernst equation and it is only when $x \geq x_s$ that the negative dE/dx slope could increase. It means that the energy term kx in Eq. (1) should be modified to

$$-k(x - x_s) \tag{3}$$

where the negative sign corresponds to repulsive interaction.

The deviation from the Nernst behaviour is presented in resistivity units by

$$R_c = \frac{-k(x - x_s)}{i_d}, \quad \Omega \, \text{cm}^2 \tag{4}$$

where i_d is the interrupted discharge curent in A/cm^2.

The interaction energy coefficient k can be estimated from the data of the R_c/x plots by Eq. (5) derived from Eq. (4) using the value of R_1 extrapolated to $x = 1$.

$$k = \frac{R_1 i_d}{(1 - x_s)} \, \text{V} \tag{5}$$

From a series of R_c/x plots of LiNi$_{1-y}$Co$_y$O$_2$ cathodes recorded in the first 2–10 cycles it was found that the values of the parameters R_o, x_s, R_1 and k are only slightly dependent on the number of cycles, of the loading of the cathode in the range from 16 to 36 mg/cm^2 and respectively of the thickness from 75 to 160 μm as shown in Table 1. These results imply that the above parameters are surface rather than volume properties of the intercalation material. This is in agreement with the definition of the state of discharge x in Eq. (1) given by Ohzuku et al. [2] as ratio of the number of the occupied Li sites at the interface of the solid phase to the number of the available sites at the given potential. As mentioned above both x_s and R_1 change slightly in the first 2–10 cycles, which explains the constancy of k. Following a longer cycling test R_1 increases considerably due to the degradation of the cathode structure as well as of the crystal

structure of the CAM. This leads to the increase of k, showing that Eq. (1) is no more valid.

The average experimental value of $k = -0.16 \pm 0.02$ V was calculated from the data of 12 R_c/x plots with different cathodes recorded in the first 2–6 cycles. This value is in disagreement with $k = 0$ obtained by Ohzuku et al. [2] from their OCV versus x discharge plots of a LiNi$_{0.5}$Co$_{0.5}$O$_2$ cathode for $x \geq 0.75$. It can be supposed that the main reason for this discrepancy is due to the different experimental conditions used in this paper and in [7]. Our measurements are performed under dynamic conditions and at cathodic polarization, while in [7] the experiment is made under steady state conditions at open circuit voltage.

It is worth noting that the average experimental voltage corresponding to $x_s = 0.75$, estimated from the data of 15 R_c/x plots of different cathodes is 3.56 ± 0.02 V. This is only by 0.02 V more negative than the value obtained by Ueda et al. [7] from their OCV versus x plots at $x = 0.75$ with a LiNi$_{0.5}$Co$_{0.5}$O$_2$ cathode. The difference is evidently due to the cathodic overvoltage imposed in our measurements at a load 0.5–0.7 mA/cm^2.

In addition to their theoretical aspect the above parameters derived from R_c/x plots may have a valuable practical meaning inasmuch as their lower values could provide a better power capability. Thus, they can be helpful in the optimization of the CAM and of the cathode design. The evolution of these parameters is considerably faster in some cases than the decay of discharge capacity of the cathode and could serve as an early signal for the debasement processes in the cathode, the electrolyte or in the cell as a whole.

4. Conclusion

A method is developed for the in situ dynamic measurement of the area-specific resistivity of LiNi$_{1-y}$Co$_y$O$_2$ cathodes R_c as a function of the state of discharge x in cells with Li/Li$^+$ reference electrodes. The voltage rise transients, obtained by short pulse interruptions of the discharge current are free of polarization components due to charge transfer and diffusion processes. The steep rise of R_c at $x \geq 0.75$ is in accord with the expression relating the cathode redox potential E_x with the state of discharge x proposed by Armand [1] and developed by Ohzuku [2], which, in addition to the Nernst logarithmic term contains a linear term kx, accounting for the short-range in-layer Li$^+$–Li$^+$ interaction forces. The values of the parameters derived from the R_c/x plots obtained in the first several cycles are reliable early

indications for eventual degradation of the cathode and can serve as a basis for its optimization.

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