

An electrochemical ac impedance study of $\text{Li}_x\text{Ni}_{0.75}\text{Co}_{0.25}\text{O}_2$ intercalation electrode

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Abstract

An EIS study on $\text{Li}_x\text{Ni}_{0.75}\text{Co}_{0.25}\text{O}_2$ intercalation cathode has been performed. The spectra have been interpreted on the basis of an equivalent circuit based on a combination of a Voigt-type analog (Li ion migration through surface film and charge transfer) in series with a Warburg type element, an element that takes into account the electronic resistance of the material and a capacitor (Li accumulation). © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

In a recent paper [1], it has been demonstrated that the EIS spectra of $\text{Li}_x\text{Ni}_{0.75}\text{Co}_{0.25}\text{O}_2$ during the early stage of lithium deintercalation reflect the change in conductivity of the compound. In the $0.9 > x > 1$ range the material shows semiconductive properties and the electronic conductivity dominates the transport. For $x \leq 0.9$ the properties change into those of a metal-like material in which the ionic conductivity becomes the limiting factor. The change in conductivity is related, in this as well as in all the compounds of the family $\text{Li}_x\text{Ni}_y\text{Co}_{1-y}\text{O}_2$ [2–9], to the decrease of the M–M distance (a parameter of the hexagonal cell) caused by lithium intercalation. In this paper the complete evolution of the EIS spectra as a function of the intercalation degree is reported.

2. Experimental

The $\text{LiNi}_{0.75}\text{Co}_{0.25}\text{O}_2$ samples were prepared following the sol–gel technique [10]. The working electrodes were assembled by spraying a dispersion of $\text{LiNi}_{0.75}\text{Co}_{0.25}\text{O}_2$ –poly(vinyl chloride) (PVC, high molecular weight, Fluka)–acetylene black carbon (90:5:5 w/o) in tetrahydrofuran

(HPLC grade, Carlo Erba) on a 10 μm thick, high-purity aluminum foil. The electrodes were dried at 80°C under vacuum for at least 24 h before being inserted into an electrochemical cell. This was formed by a spring-loaded PTFE holder equipped with stainless-steel (SS304) current collectors. Two high purity (Foote) lithium disks were used as reference and counter electrodes. The separator was a Whatman glass microfiber disk soaked with a 1 M LiClO_4 EC–DMC (1:1) solution. The cell was assembled and tested inside an argon filled dry-box with moisture and oxygen content below 2 ppm.

All the electrochemical measurements were performed using a CH Instruments 650 Electrochemical Station (Austin, TX, USA). The impedance spectra were taken on electrodes cycled at least twice between 3 and 4.3 V in the frequency range 0.001 Hz–100 kHz. Details on the measuring mode may be found in [1].

3. Results and discussion

Fig. 1 shows a series of Nyquist plots relative to $\text{Li}_x\text{Ni}_{0.75}\text{Co}_{0.25}\text{O}_2$ at different x values ranging from $x = 0.986$ to 0.338. The x values have been deduced from integration of the cyclic voltammograms [1] and from the charge passed during the equilibration of the electrode at the different potentials. As can be seen at high x values (see insert) the spectra are dominated by a low frequency semicircle that shows an increasing tendency to close on the real axis as the

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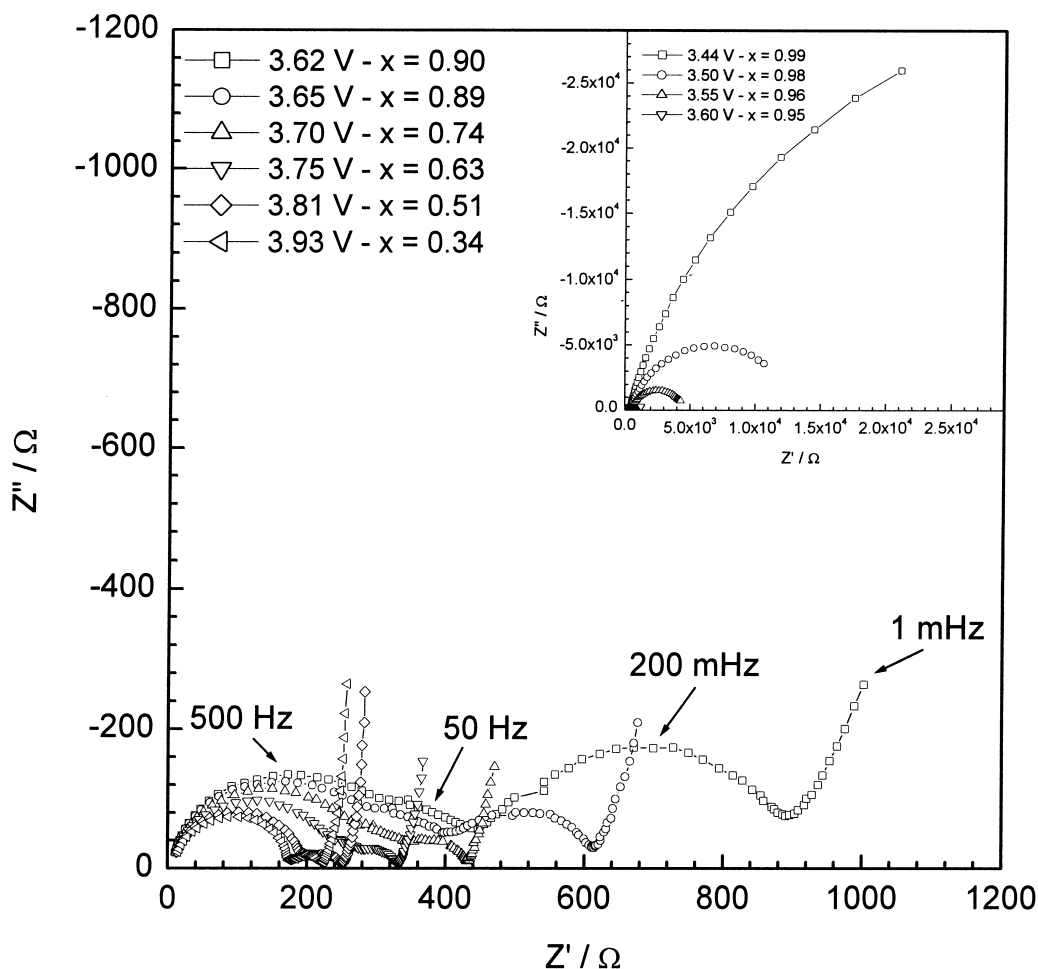


Fig. 1. Experimental Nyquist plots at different potential values.

voltage increases. This has been interpreted as due to the electronic conductivity of the material that decreases as the deintercalation proceeds. The impedance decreases drastically as the potential becomes more positive. At x values close to about 0.9 ($E = 3.62$ V versus Li) the dispersion shows evidences of the features typically associated with the physical phenomena that characterize a charge transfer at passivated materials, i.e.: (i) a high frequency (>1 kHz) dispersion characteristic of a passivating layer (not visible in the dispersions in the insert because of large scale but present); (ii) an intermediate frequency dispersion (between 10 Hz and 1 kHz) due to charge-transfer; (iii) a well-developed low-frequency (<1 Hz) semicircle associated with electron transfer; (iv) the spike at low frequency associated with the well-known thin-layer ionic diffusion. The same general trend is observed during the reverse process (lithium intercalation). The general trend of the Nyquist plots at the different potentials is quite similar to that of the parent compound $\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$ [11]. However, the dispersions and the interpretation appear to be somewhat different from those of Levi et al. [12] for the same compound. These authors do not take into account the electronic resistance and attribute the high impedance values at low potentials to a

capacitive behavior and/or to an extremely high value of the charge transfer resistance thus modeling the spectra on the basis of two (RC) semicircles: i.e. the high frequency one as due to the surface layer and the one at low frequency to the charge transfer.

Based on the evidences provided in [1], and on the fact that a third semicircle becomes increasingly evident in the frequency range 10 Hz to 1 kHz a different interpretation of the dispersions sequence may be offered. This is based on an equivalent circuit comprising the solution resistance, three RQ elements (where Q is the constant phase element defined in [13]) representing in order of decreasing frequency the passivating layer, the charge transfer and the electronic resistance in addition to a Warburg element in series with a capacity representing the active mass intercalation capacity. The circuit is substantially similar to the one proposed by Levi et al. [14] for the interpretation of the impedance spectra of LiCoO_2 . The dispersions over the entire x range have been fitted using the same circuit using the Boukamp program [13]. Fig. 2 shows the relevant parameters as obtained from the fit.

As may be seen, the values of the resistance of the RQ element present at the lowest frequencies and attributed to

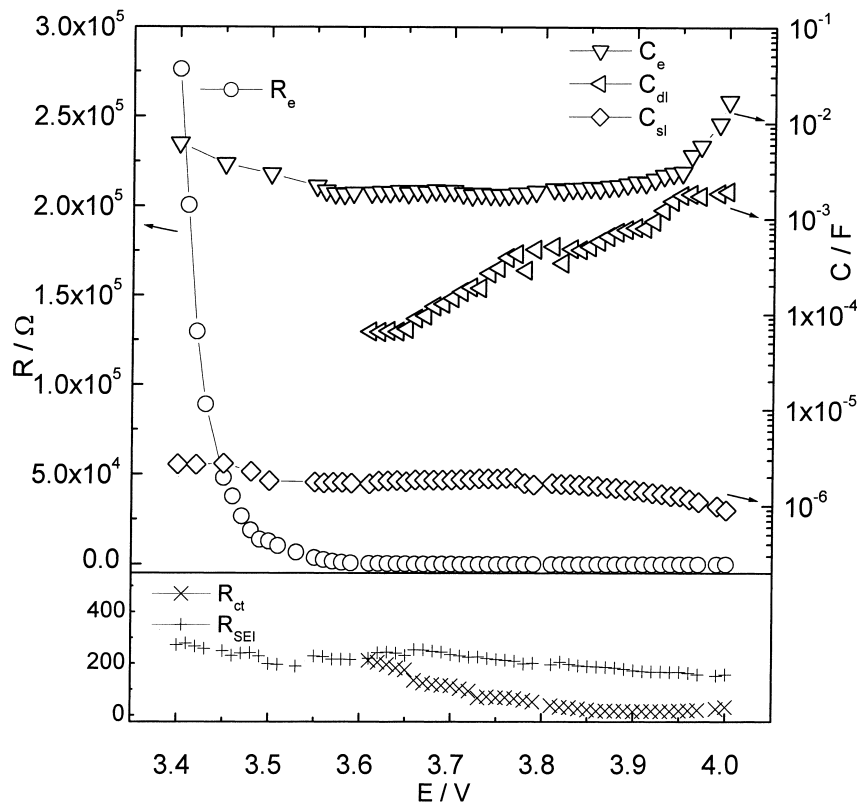


Fig. 2. Relevant parameters of the different elements of the equivalent circuit used in the simulation of the spectra vs. E (see text for details).

the electronic conductivity of the material drop drastically over the potential range 3.4–3.6 V versus Li (x range 1–0.9) in agreement with the experimental and theoretical data [1,4] that indicate the presence of a semiconductor to metal transition over this x range. The capacity associated to this latter frequency dispersion is very high following the same trend of the resistance up to about 3.9 V (also if the variation is less pronounced) and then starting to increase again. A possible physical explanation for the presence of this capacity is the formation of capacitors due to electron accumulation at the nano size crystallite domains of the material [15]. The values of the capacity associated to the electronic resistance are of the same order of magnitude of those quoted by Levi et al. [12] as double layer capacity in their model for $\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$.

The R_{ct} and associated double layer capacity are shown for potentials above 3.6 V. Below this potential the relative semicircle is still poorly defined and, due to the extremely high impedance due to the electronic resistance that dominates the dispersions, the values derived from the fit are affected by high uncertainties. As may be seen the R_{ct} values may be considered almost potential independent if one excludes the points below 3.65 V ($x \cong 0.89$) where the electronic resistance is still very high. This is consistent with the model proposed by Bruce et al. [16] in which the charge transfer in intercalation type electrodes, contrary to what happens in classical oxidation–reduction processes, is related to electrons that interact with the ions in the crystal

lattice and not with incoming ions. In this case no potential dependence of R_{ct} is expected. The double layer capacity associated to the charge transfer increases monotonically with increasing potential. The resistance and associated capacity of the surface layer are practically potential independent, demonstrating that the passivating layer is rather stable.

Fig. 3 shows the intercalation capacity C_{int} [14] as derived from the slow scan rate cyclic voltammetry ($C_{int} = I(E)/v$) and from the EIS measurements $C_{int} = -1/(\omega Z''_{\omega \rightarrow 0})$. As expected the relevant curves have the same shape and peak at about the same potentials. The relative magnitudes are different, as explained by Levi et al. [12] because of the different time scale of the two experiments: i.e. EIS (because of the lower time window, 1000 s in the present case) is more sensitive to incomplete active mass utilization than SSCV. Fig. 3 also shows the potential dependence of the characteristic solid-state diffusion time constant $\tau = l^2/D$ where D is the chemical diffusion coefficient and l the characteristic diffusion length [14] as computed from the Warburg slope ($\tau = 2(Q_t A_w dx/dE)^2$). As may be seen, as expected [14], τ versus E has the same shape of the intercalation capacity. By assuming an average l value of 1.5×10^{-5} cm, as deduced from SEM micrographs of the electrode, the chemical lithium diffusion coefficient computed at the peak potential assumes the minimum value of $10^{-11.6}$ $\text{cm}^2 \text{s}^{-1}$, of the same order of magnitude of that quoted by Levi et al. [14] in Li_xCoO_2 or Li_xNiO_2 [17].

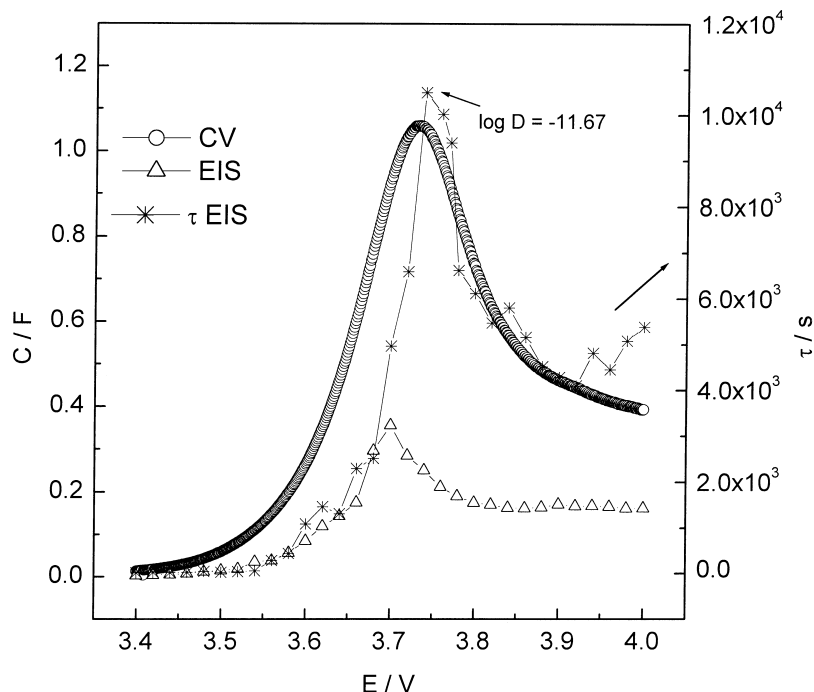


Fig. 3. Plots of the intercalation capacity as obtained from SSCV at $10 \mu\text{V s}^{-1}$ (○); EIS (Δ) vs. E . Plot of the solid-state diffusion time constant τ (*) as obtained from EIS measurements vs. E .

4. Conclusions

The results obtained in this EIS study demonstrate that the Nyquist plots relative to a $\text{Li}_x\text{Ni}_{0.75}\text{Co}_{0.25}\text{O}_2$ electrode can be conveniently simulated by an equivalent circuit that include three RQ element corresponding, in order of decreasing frequency to a passivating layer, charge transfer and electronic resistance, in addition to a Warburg element and the intercalation capacity. It has been demonstrated that while the electronic resistance drops drastically over the $x = 1-0.9$, consistently with the presence of a semiconductor to metal transition of the material, both charge transfer resistance (R_{ct}) and the surface layer resistance (R_s) are potential independent. The lithium chemical diffusion coefficient with a potential dependence corresponding to that of the current in slow scan rate cyclic voltammetry or intercalation capacity has a minimum value of about $10^{-11.6} \text{ cm}^2 \text{ s}^{-1}$ at a potential value close to the peak potential of the corresponding cyclic voltammogram.

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