The possibility of voltage prediction from the Coulomb potential created by the atoms of a cathode active material for Li ion cells

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Abstract

We studied the contribution of internal energy change to cathode voltage assuming that the cathode material was completely ionic and only the Coulomb potential was effective. From the internal energy change caused by one Li^+ and one electron insertion, we derived a cathode voltage equation related to the Coulomb potential, which we calculated using a personal computer. We calculated the cathode voltage of an ideal structure Li_xMO_2 ($R\bar{3}m$) (Li–O: 2A, Ni–O: 2A), which is a model compound of Li_xNiO_2. From this calculation, we found that Li_xMO_2 has a two-phase co-existence for $0 < x < 0.25$, and one phase for $0.25 < x < 1$. © 2000 Elsevier Science S.A. All rights reserved.

1. Introduction

Lithium ion cells [1] are widely used for portable equipment because of their high energy density. These cells employ lithium intercalation materials as their anode and cathode active materials.

Recently, there have been several studies predicting the cell voltage of cathode active materials in lithium ion cells based on the first principles quantum chemistry [2–4]. Deiss et al. [2] predicted the cell voltage of LiC_6/NiO_2. They calculated the average voltage between the fully charged and the discharged states, neglecting the effect of the entropy term.

In this paper, we study the Coulomb potential created by the atoms of a cathode active material for Li ion cells and consider the possibility of predicting the voltage from the Coulomb potential. The cell voltage is described thermodynamically. We considered the contribution of the internal energy change to the cell voltage (E vs. Li/Li^+) assuming that the cathode material was completely ionic and only the Coulomb potential was effective in terms of

changing the internal energy. The process of evaluating the internal energy change involves the insertion of one Li^+ ion and one electron, which are charged particles, into the host matrix. Therefore, the Coulomb potential may have a significant effect on the internal energy change.

2. Coulomb potential

We assume that a cathode active material is an ionic crystal and that the charge is at the center of each atom. We ignored any forces between atoms other than the Coulomb force.

Let r_{ij} (A) be the distance from a certain atom k to the surrounding atoms of species i in an ionic crystal, and Z_i be the charge number of species i. Then the Coulomb potential at atom k is expressed by:

$$\Phi_k = \frac{e^2}{4\pi\varepsilon_0} \sum_{i,j} \frac{Z_i}{r_{i,j}} = 14.399 \sum_{i,j} \frac{Z_i}{r_{i,j}} \tag{1}$$

where Φ_k (eV) is the Coulomb potential at atom k, e is the elementary charge, ε_0 is the permittivity of free space.

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3. The voltage measured from Li/Li$^+$

The basic equations for calculating the voltage are derived from thermodynamics.

$$E = -\frac{\Delta G_r}{nF} \tag{2}$$

$$\Delta G_r = \left(\frac{\partial G}{\partial \xi}\right)_{P,T} \tag{3}$$

$$G = U + PV - TS \tag{4}$$

where E is cell voltage (V), ΔG_r is the reaction Gibbs function (J/mol), ξ is the reaction coordinate (mol), n is electrons per molecule oxidized or reduced, F is the Faraday constant (C/equiv.), G is the Gibbs free energy (J), P is the pressure (Pa), T is the temperature (K), U is the internal energy (J), V is the volume (m^3), and S is the entropy (J/K).

If we consider Li insertion into host matrix $\langle\text{HOST}\rangle$, ΔG_r is obtained from the difference of G for the following reaction divided by $d\xi$.

$$\partial\xi\,\text{Li} + \text{Li}_x\langle\text{HOST}\rangle \rightarrow \text{Li}_{x+\partial\xi}\langle\text{HOST}\rangle. \tag{5}$$
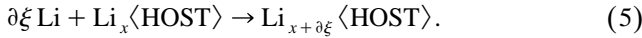
From Eqs. (2)–(4), we have:

$$E = -\frac{1}{nF}\left[\left(\frac{\partial U}{\partial \xi}\right)_{P,T} + P\left(\frac{\partial V}{\partial \xi}\right)_{P,T} - T\left(\frac{\partial S}{\partial \xi}\right)_{P,T}\right]. \tag{6}$$

We will ignore the second term in Eq. (6) because the value is very small. The third term (E_{ent}) is the entropy term, which is caused by the number of different states of the lithium arrangement in the host matrix. Let N be the total number of Li sites in the host matrix, 'a' is the number of Li atoms inserted in the host matrix, and N_A is Avogadro's number. The number of ways that 'a' indistinguishable Li$^+$ atoms can be placed in N numbered sites, no more than one to a site, is $N!/[a!(N-a)!]$. If we assume an equal probability of Li occupation, $\Omega_p = N!/[a!(N-a)!]$, we obtain:

$$E_{ent} \equiv \frac{kT}{nF}\left(\frac{\partial \ln \Omega_p}{\partial \xi}\right)_{P,T}$$

$$= \frac{kTN_A}{nF}\left\{\ln\left[\frac{N!}{(N-a-1)!(a+1)!}\right]\right.$$

$$\left. -\ln\left[\frac{N!}{(N-a)!a!}\right]\right\}$$

$$= \frac{RT}{nF}\ln\left[\frac{N-a}{a+1}\right] \simeq \frac{RT}{nF}\ln\left[\frac{1-y}{y}\right] \tag{7}$$

where $y = a/N$. This is a well-known result obtained from thermodynamics [5]. In this paper, we study the entropy term contribution within the framework of Eq. (7). A more accurate approximation of the insertion system is discussed by Kudo and Hibino [6]. However, for simplicity, we do not adopt their approximation here.

The first term in Eq. (6) is the internal energy term (E_{int}). Let U_a be the internal energy change caused by the insertion of one Li. Then we have:

$$E_{int} \equiv \frac{1}{nF}\left(\frac{\partial U}{\partial \xi}\right)_{P,T} = \frac{U_a}{ne}. \tag{8}$$

U_a corresponds to the energy change that occurs during the process in which Li metal is separated into one Li$^+$ and one electron followed by the insertion of one Li$^+$ atom and one electron into a host matrix.

Let I_{Li} be the ionization potential (eV) of Li metal, and Φ_{Li} be the Coulomb potential at a vacant Li$^+$ insertion site such as the site in NiO$_2$. If we ignore any contribution besides the Coulomb potential, the increase in internal energy caused by the insertion of Li$^+$ is Φ_{Li}. Next, we insert an electron. We assume that the electron is inserted into the nearest metal atom of the inserted Li$^+$ site. The increase in internal energy caused by the insertion of an electron is assumed to be $-\Phi_M + I_M$, where Φ_M is the Coulomb potential of the electron insertion site and I_M is the LUMO energy of an isolated metal atom in vacuum. When Φ_M is calculated for a cathode before the Li$^+$ insertion, we have to add the contribution of the inserted Li$^+$. Thus, we have to add $-14.399/R_{Li-M}$ to Φ_M, where R_{Li-M} is the distance between the inserted Li$^+$ and the electron. Finally, we obtain the following equation for U_a:

$$U_a = \Phi_{Li} - \Phi_M + I_M - I_{Li} - \frac{14.399}{R_{Li-M}} \tag{9-1}$$

where Φ_{Li} and Φ_M are calculated from the cathode structure before the Li$^+$ and electron insertion.

If we use the structure after the Li$^+$ and electron insertion such as LiNiO$_2$ for the Φ_{Li} and Φ_M calculation, the following equation (Eq. 9-2) has to be used.

$$U_a = \Phi_{Li} - \Phi_M + I_M - I_{Li} + \frac{14.399}{R_{Li-M}} \tag{9-2}$$

Finally, the cathode voltage is:

$$E = E_{int} + E_{ent}$$

$$= -\frac{1}{ne}\left(\Phi_{Li} - \Phi_M + I_M - I_{Li} \pm \frac{e}{4\pi\varepsilon_0 R_{Li-M}}\right)$$

$$-\frac{RT}{nF}\ln\frac{y}{1-y} \tag{10}$$

where the sign after I_{Li} is $+$ if there is already Li at the center of k, and $-$ if there is no Li at the center of k. In the case of Li ion cells, $n = 1$.

4. Calculation of cathode voltage

First, we ignore the entropy term (E_{ent}) in Eq. (10). We will add the term after calculating E_{int}.

$LiCoO_2$ or $LiNiO_2$ is used as a cathode active material for Li ion cells. Such $LiMO_2$ materials have a rhombohedral $R\bar{3}m$ α-$NaFeO_2$ layered structure. The structure is an ordered rocksalt structure with edge sharing MO_6 octahedra, which form MO_2 sandwich sheets. The sheets are linked by LiO_6 octahedra. Arai et al. [7] obtained the nearest lengths of Ni–O, Li–O, Ni–Ni, and Li–Li which are 1.957, 2.126, 2.875, and 2.875 A, respectively, for $LiNiO_2$. In this paper, we assume an ideal $LiNiO_2$ which has the same nearest length of 2.000 A for Ni–O and Li–O. In this ideal material, oxygen atoms form regular tetrahedrons linked at their edges to form oxygen layers, and NiO_6 and LiO_6 form regular tetrahedral structures. Therefore, the nearest length of Ni–Ni and Li–Li is 1.414 $\times 2 = 2.828$ A.

The Coulomb potential at atom k (Eq. 1) is calculated using VIP BASIC (Mainstay) for Power Macintosh. The program is given in Appendix A.

4.1. Voltage of LiNiO₂

From the calculation, we obtain $\Phi_{Li} = -18.872$ eV and $\Phi_{Ni} = -32.1207$ eV. Using $R_{Li-Ni} = 2.828$ A, we have, $14.399/R_{Li-Ni} = 5.091$ eV. We obtained an I_{Li} value of -7.1076 eV (685.78 kJ/mol) from the enthalpy change for $Li(cr) \rightarrow Li^+(g) + e$.

We assumed that the energy level of a Ni atom is the sum of the electron energy level in vacuum and the Coulomb potential. Using DV-Xα molecular orbital method (SCAT) [8], we determined that the HOMO energy of $[NiO_6]^{-1}$ cluster was -0.30858 eV, where the nominal valences of Ni and O are 3 and $-2/3$, respectively. The contribution of the Coulomb potential of oxygen is

-28.798 eV. Therefore, $I_{Ni} = -0.30858 - 28.798 = -29.106$ (eV).

Finally, we obtained the potential with the following equation, using Eqs. (8) and (9-2).

$$E_{int} = 18.872 - 32.120 - 7.107 + 29.106 - 5.090$$
$$= 3.468\,(V)$$

4.2. Voltage of NiO₂

We assume that the cathode structure is not changed by the extraction of Li^+. From the calculation, we had $\Phi_{Li} = -12.2485$ eV (empty Li site) and $\Phi_{Ni} = -38.7447$ eV (Ni^{4+} site). Therefore, using Eqs. (8) and (9-1), we have:

$$E_{int} = 12.248 - 38.744 - 7.107 + 29.106 + 5.090$$
$$= 0.593\,(V).$$

However, the voltage is too low. Let us consider a structure in which one Li atom is inserted into each plane along the c-axis. Li^+ atoms may occupy the nearest position of the inserted Li^+ into the next layer, because the Ni valence is reduced to 3, which decreases the repulsion force against Li^+. Here, we have to add -6.73329 eV to Φ_{Li} and 6.73329 eV to Φ_{Ni}. Using Eqs. (8) and (9-2), we have:

$$E_{int} = 12.248 + 6.733 - 38.744 + 6.733 - 7.107$$
$$+ 29.106 - 5.090 = 3.879\,(V)$$

Therefore, we have to use the following equation (Eq. 11) for the structure before Li insertion instead of Eq. (9-1).

$$U_a = \Phi_{Li} - \Phi_M + I_M - I_{Li} + \frac{14.399}{R_{Li-M}} - 13.466. \qquad (11)$$

4.3. Lithium ordering in Li_x NiO₂

Li^+ ordering was assumed for $0 < x < 0.25$, $0.25 < x < 0.5$, $0.5 < x < 0.75$, and $0.75 < x < 1$ as shown in Fig. 1. The calculated results are shown in Table 1. Unfortunately,
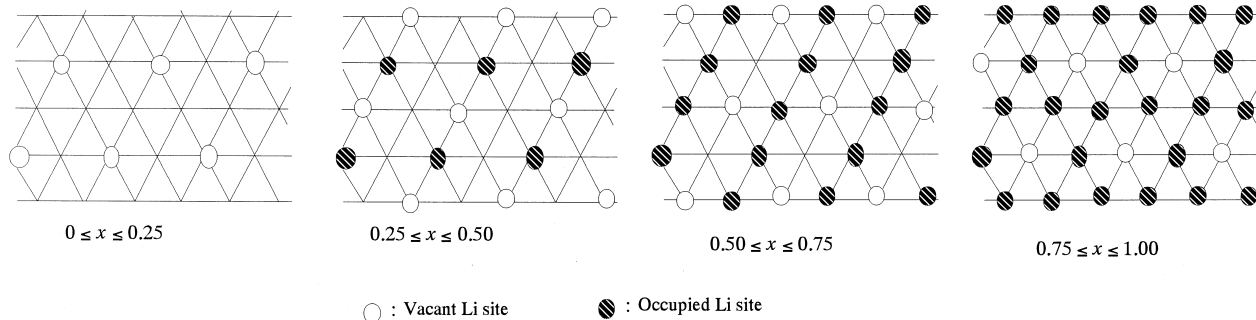

$0 \leq x \leq 0.25$ $0.25 \leq x \leq 0.50$ $0.50 \leq x \leq 0.75$ $0.75 \leq x \leq 1.00$

○ : Vacant Li site   ◉ : Occupied Li site

Fig. 1. Lithium ordering assumed for $0 < x < 0.25$, $0.25 < x < 0.5$, $0.5 < x < 0.75$, and $0.75 < x < 1$.

Table 1
Calculated result

x in Li_xNiO_2	Coulomb potential (eV)				Cathode potential (V vs. Li/Li$^+$)
	Occupied Li$^+$ site	Ni^{3+} site	Vacant Li$^+$ site	Ni^{4+} site	
0			-12.2485	-38.7447	3.879
0.25	-19.4871	-31.5061			4.889
0.5	$-19.5706///$, $-18.7056=$	$-31,4226///$, $-32.2876=$			$5.056///$, $3.326=$, average 4.191
0.75	$-19.6541=$, $-18.8721///$	$-31.3391=$, $-32.1211///$			$5.223=$, $3.659///$, average 4.441
1.00	-18.872	-32.1207			3.659
0.25			$-11.4669=$, $-12.3320///$	$-39.5263=$, $-38.6612///$	$2.314=$, $4.044///$, average 3.179
0.5			$-11.5504///$, $-12.4154=$	$-39.4428///$, $-38.5778=$	$2.481///$, $4.211=$, average 3.346
0.75			-11.6339	-39.3593	2.648

the calculated Coulomb potential for two identical positions (shown as $=$ and $///$ in Fig. 2 and Table 1) did not converge to the same value. Therefore, we used the average value.
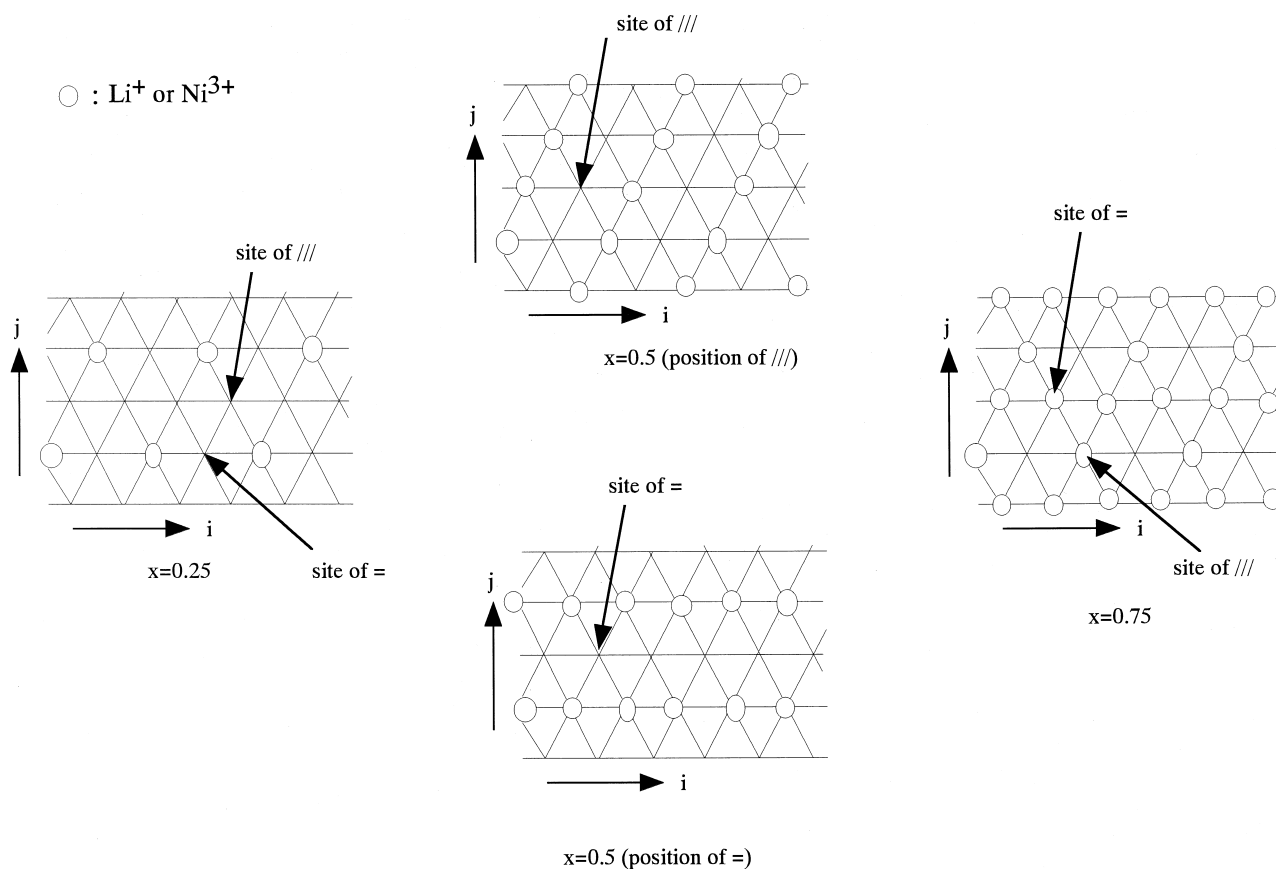

Fig. 2. In-plane position of Li or Ni, indicated by ''$=$''and ''$///$'' in Tables 1–4.

The equations used are (for the structure after Li insertion):

$$E_{int} = -(\Phi_{Li} - \Phi_{Ni})/e - 7.107 + 29.106 - 5.090$$

$$= (-\Phi_{Li} + \Phi_{Ni})/e + 16.909 \qquad (12)$$

where Φ_{Li} is a vacant Li site and Φ_{Ni} is a Ni^{4+} site, and (for the structure before Li insertion):

$$E_{int} = -(\Phi_{Li} - \Phi_{Ni})/e - 7.107 + 29.106 - 5.090$$

$$+ 13.466 = (-\Phi_{Li} + \Phi_{Ni})/e + 30.375 \qquad (13)$$

where Φ_{Li} is an occupied Li site and Φ_{Ni} is a Ni^{3+} site.

There are four areas of ordering, which are $0 < x < 0.25$, $0.25 < x < 0.5$, $0.5 < x < 0.75$ and $0.75 < x < 1$. In each area, Li$^+$ ions are assumed to distribute at random. This means that all the sites are occupied by Li^{y+} and e^{y-}, where y is the site occupancy in an area of ordering. Then, we have $E_{int} = E^0 + Ky$, where E^0 is the voltage at $y = 0$, and K is a constant (see Appendix B, Eqs. A-6 and A-7). For each area, we have to add the entropy term $E_{ent} = -(RT/F)\ln[y/(1-y)]$. Then, we have:

$$E = E^0 + Ky - \frac{RT}{F}\ln\frac{y}{1-y} \qquad (14)$$

where $E^0 = 3.879$ (V), $K = 1.011$ (V) and $y = x/0.25$ for $0 < x < 0.25$, $E^0 = 3.179$ (V), $K = 1.095$ (V) and $y = (x - 0.25)/0.25$ for $0.25 < x < 0.50$, $E^0 = 3.346$ (V), $K = 1.095$ (V) and $y = (x - 0.5)/0.25$ for $0.50 < x < 0.75$, and $E^0 = 2.648$ (V), $K = 1.011$ (V) and $y = (x - 0.75)/0.25$ for $0.75 < x < 1$.

Eq. (14) is shown in Fig. 3. The parameter K is positive, which means that there is an attractive interaction between the Li$^+$ ions.

Lithium intercalation compounds are sometimes unstable when their voltage exhibits a maximum value as a function of the amount of inserted Li$^+$, as pointed out by Armand [5]. They sometimes decompose into two phases
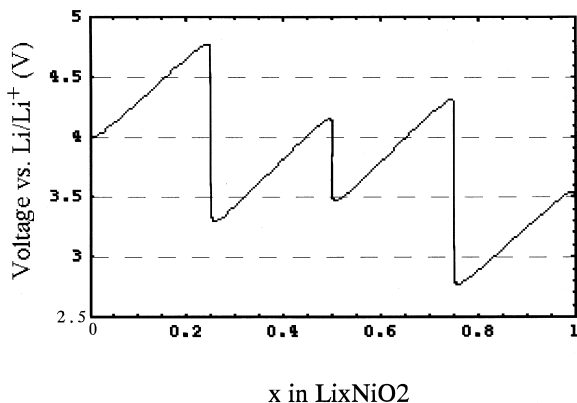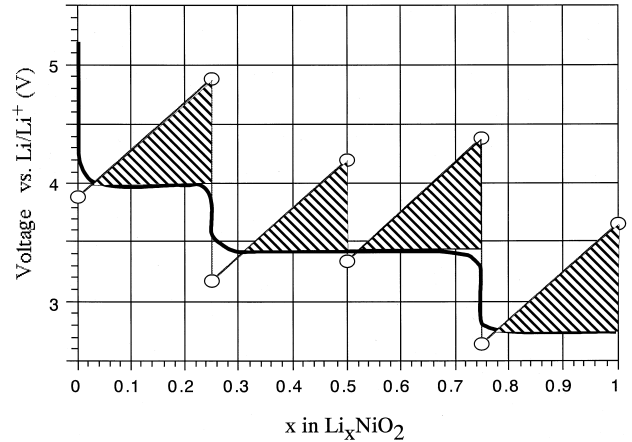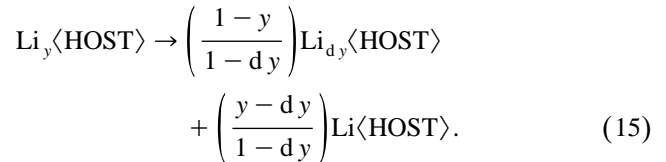

Fig. 4. Voltage profile of LiNiO$_2$ (an ideal structure, Li ordering was assumed). The hatched region is unstable.

similar to spinodal decomposition, even with an open circuit, following the equation:

$$Li_y\langle HOST\rangle \rightarrow \left(\frac{1-y}{1-dy}\right)Li_{dy}\langle HOST\rangle$$

$$+ \left(\frac{y-dy}{1-dy}\right)Li\langle HOST\rangle. \qquad (15)$$

The cathode voltage shown in Fig. 4 is unstable in the hatched region and so may follow the bold curve (see Appendix C). This means that Li-rich and Li-poor phases coexist. The plateau voltage is about 0.1 V higher than E^0 because of the effect of the entropy term. We can see the phase separation for $0 < x < 0.25$, $0.25 < x < 0.75$ and $0.75 < x < 1$.

Although we assumed that there was ordering, the condition for its appearance have to be considered. For Li$^+$ ordering to occur, the ordered state must be stable compared with the disordered state, which means that the voltage must be higher in the ordered state. We compared the voltage as shown in Fig. 5. The final voltage curve is the bold curve in Fig. 5. LiNiO$_2$ exhibits a two phase region for $0 < x < 0.25$ and is single phase for $0.25 < x < 1$.

Ohzuku et al. [9] reported experimental results on LiNiO$_2$ phase separation. From their report, the two phase region is $0.05 < x < 0.25$ and other region is single phase. Later, Arai et al. [7] obtained similar results, and the two-phase region is $0.15 < x < 0.35$. Different results were reported by Li et al. [10]. From their report, the two phase regions are $0 < x < 0.3$, $0.43 < x < 0.5$ and $0.75 < x < 0.85$. The phase separation of LiCoO$_2$ was reported by Ohzuku and Ueda [11], where the two-phase regions are $0 < x < 0.25$ and $0.75 < x < 0.90$.

All the experimental results show that the two phase region is $0 < x < 0.25$. The results are in good agreement with our calculation. The unstable phases at $x = 0.75$ and $x = 0.25$ may affect the phase separation. We believe that
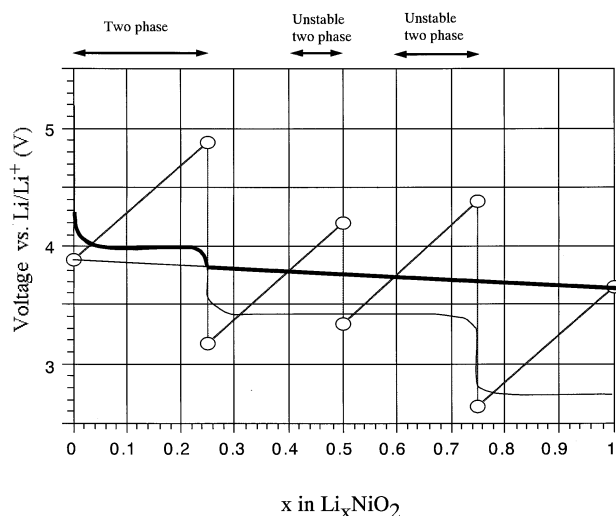

x in LixNiO2

Fig. 3. Voltage profile from Eq. (14). (The value was calculated exactly using ''Mathematica''.)

Fig. 5. Voltage profile of LiNiO$_2$ (an ideal structure, the final result).

Fig. 6. Voltage profile of LiNiO$_2$ (4% deformed structure to fit the real LiNiO$_2$).

the phase separation other than $0 < x < 0.25$ may appear from some kinetic situation of the unstable phases.

It is interesting to consider the deformation of the cathode structure during Li$^+$ extraction. The Li$^+$ ordering at $x = 0.5$ is unstable, however as mentioned above, it may deform the structure from hexagonal to monoclinic. The regular hexagon shown in Fig. 2 may deform in one direction when ordered Li$^+$ atoms are inserted. Thus, the structure must be monoclinic, although we cannot deny the contribution of the Jahn–Teller effect.

5. Fitting to real LiNiO$_2$ structure

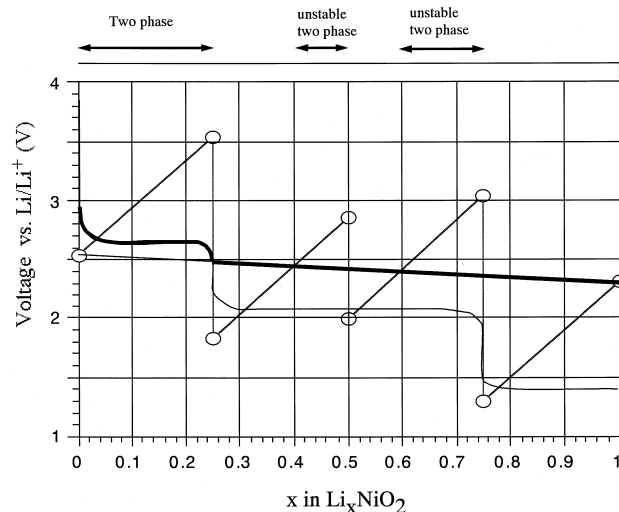The calculated cathode voltage is in good agreement with the experimental value. However, the structure we

used is different from the real structure, and so we tried to fit our structure to the real one. As we mentioned, the nearest lengths of Ni–O and Li–O are 1.957 and 2.126 A, respectively, for LiNiO$_2$. The mean length is 2.0415 A, and the Ni–O distance shrinks by 4% and the Li–O distance expands by 4%. We calculated such a case, and the results are shown in Table 2. The equations we used for the calculation are (for the structure after Li insertion):

$$E = 0.98(\Phi_{Li} - \Phi_{Ni})/e - 7.107$$
$$+ 29.106 - 0.98 \times 5.090$$
$$= 0.98(-\Phi_{Li} + \Phi_{Ni})/e + 17.010 \qquad (16)$$

where Φ_{Li} is a vacant Li site and Φ_{Ni} is a Ni^{4+} site with

Table 2
4% deformed LiNiO$_2$

x in Li$_x$NiO$_2$	Coulomb potential (eV)				Cathode voltage (V vs. Li/Li$^+$)
	Occupied Li$^+$ site	Ni^{3+} site	Vacant Li$^+$ site	Ni^{4+} site	
0			−11.3905	−39.6177	2.545
0.25	−18.6292	−32.379			3.535
0.5	−18.7127///, −17.8476 =, average −18.2801	−32.2955///, −33.1606* =, average −32.7280			average 2.851
0.75	−18.7961 −18.0142///	−32.2121 −32.994///			average 3.096
1.00	−18.0413	−32.9936			2.356
0.25			−10.609 =, −11.474///, average −11.0415	−40.3992 =, −39.5342///, average −39.9667	average 1.860
0.5			−10.6924///, −11.5575 =, average −11.1249	−40.3158///, −39.4507 =, average −39.8832	2.023
0.75			−10.7759	−40.2323	1.339

○ : Vacant Li site   ● and ◉ : Occupied Li site of x=0.9375   ● : Occupied Li site of x=0.75
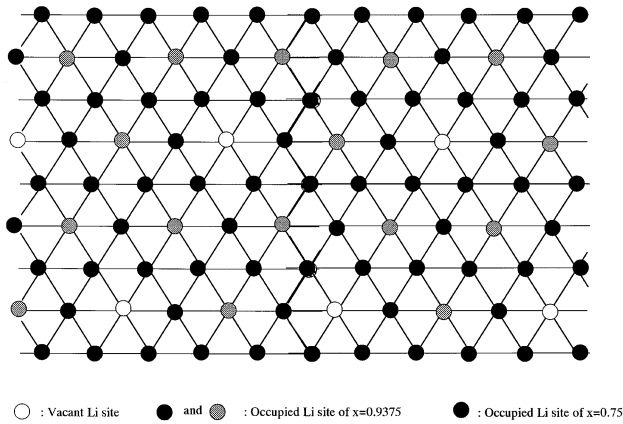
Fig. 7. In-plane position of Li at ordering of $x = 0.9375-$.

a 4% deformation from 2 A, and (for the structure before Li insertion):

$$E = -0.98(\Phi_{Li} - \Phi_{Ni})/e - 7.107 + 29.106 - 0.98$$
$$\times 5.090 + 0.98 \times 6.733 \times 2$$
$$= 0.98(-\Phi_{Li} + \Phi_{Ni})/e + 30.207 \qquad (17)$$

where Φ_{Li} is an occupied Li site and Φ_{Ni} is a Ni^{3+} site with 4% deformation from 2A.

The final result of the cathode voltage dependence on the amount of inserted Li is shown in Fig. 6 (bold line). The voltage becomes lower, and its difference from the experimental value increases. The shape in Fig. 6 is almost the same as that in Fig. 5 when the latter is shifted 1.4 V in the lower voltage direction. This means that the phase separation does not have any effect by this fitting of the structure. However, it has to be recognized that even a small cathode deformation causes a great change in the voltage. We believe that we had a lower voltage because the I_{Ni} value we used was small. If we estimate I_{Ni} from a $(NiO_6)^{-9}$ cluster, $I_{Ni} = 34.091$ eV, though the value is very large, and the voltage increases by about 5 V. We need a more precise estimation of I_{Ni}.

6. Other Li ordering

At $x = 0.75 + (3/4) \times 0.25 \simeq 0.9375$, there is ordering as shown in Fig. 7. The results are shown in Tables 3 and

Table 3
4% deformed LiNiO$_2$

x in Li$_x$NiO$_2$	Coulomb potential (eV)		Cathode voltage (V vs. Li/Li$^+$)
	Occupied Li$^+$ site	Ni^{3+} site	
0.9375	$-17.2896///$, $-18.0699 =$, average -17.6797	$-33.7186///$, $-32.9383 =$, average -33.3284	1.674

Table 4
Ideal LiNiO$_2$

x in Li$_x$NiO$_2$	Coulomb potential (eV)		Cathode voltage (V vs. Li/Li$^+$)
	Occupied Li$^+$ site	Ni^{3+} site	
0.9375	$-18.1476///$, $-18.9279 =$, average -18.5377	$-32.8456///$, $-32.9383 =$, average -32.4554	2.991

4. The voltage is very low. Therefore, such ordering does not appear.

7. Tetrahedral Li site of ideal NiO$_2$

From the calculation, we had $\Phi_{Li} = -9.930$ eV (vacant Li tetrahedral site) and $\Phi_{Ni} = -38.7447$ eV (Ni^{4+} site). R_{Li-M} is 2.3804 A ($14.399/R_{Li-M} = 6.048$ eV). Using Eq. (11), we have:

$$E = 9.930 + 6.790 - 38.744 + 6.790 - 7.107 + 29.106$$
$$- 6.048 = 0.718 \,(V).$$

Therefore, Li$^+$ is not inserted into the tetrahedral sites but octahedral sites.

8. Conclusion

Cathode voltage can be calculated from the Coulomb potential in a cathode material, when we consider Li ordering and decomposition into two phases. Our calculation predicts a Li$_x$NiO$_2$ phase separation of $0 < x < 0.25$ and this is in good agreement with experimental results. We believe that there may be phase separation in addition to $0 < x < 0.25$ as the result of some kinetic situation of the unstable phases at around $x = 0.5$ and 0.75. The effect of the cathode deformation on the potential was very large, however, the effect was very small as regards the overall shape of the voltage profile.

We are now planning to study the voltage of spinel LiMn$_2$O$_4$ and other cathode active materials using the method described in this paper.

Acknowledgements

Appendix A

The program we used to calculate the Li site potential of the ideal LiNiO$_2$ is given here. The summation was performed for $20 \times 20 \times 20 = 8000$ unit cells. We used

the potential at an oxygen atom to check the reliability of the summation. The oxygen potential is theoretically double the Madelung constant of NaCl. The difference between the calculated and theoretical values is 0.333 V.

```
N3 = 10
N1 = 12 * N3
N = 1 * N3
N2 = 2 * N3
r = 0.5 * SQR(2)
cx = 0
qx = 0
FOR k = − N1 TO N1
  FOR j = − N2 TO N2
    N4 = abs(N − int(abs(j/2)))
    N5 = N4
    IF j mod 2 = 1 or j mod 2 = − 1 THEN
      N4 = N4 − 1
      N5 = N4 + 1
    END IF
    FOR i = − N5 TO N4
      s = 0
      p = 0
      IF j mod 2 = 1 THEN
        s = r
      END IF
      IF j mod 2 = − 1 THEN
        s = − r
      END IF
      IF k mod 3 = 1 or k mod 3 = − 2 THEN
        p = SQR(3) * 2 * r/3
      END IF
      IF k mod 3 = 2 or k mod 3 = − 1 THEN
        p = − SQR(3) * 2 * r/3
      END IF
      y1 = (p + j * SQR(3) * r) * 1
      x1 = (s + i * 2 * r) * 1.00
      z1 = k * r * SQR(2/3)
      r1 = SQR(x1 ^2 + y1 ^2 + z1 ^2)
      q = 1
      IF k mod 4 = 1 or k mod 4 = 3 or k mod
      4 = − 1 or k mod 4 = − 3 THEN
        q = − 2
      END IF
      IF k mod 4 = 2 or k mod 4 = − 2 THEN
        q = 3
      END IF
      IF (i − N4) * (i + N4) = 0 THEN
        q = q/2
      END IF
      IF (k − N1) * (k + N1) = 0 THEN
        q = q/2
      END IF
      IF (j − N2) * (j + N2) = 0 THEN
        q = q/2
      END IF

      IF (i − N4) * (i + N4) = 0 and j = 0 THEN
        q = q/2
      END IF
      IF i = 0 and j = 0 and k = 0 THEN
        m = 0
        print i, j, k
      ELSE
        m = q * 1/r1
      END IF
      cx = cx + m
      qx = qx + q
    NEXT i
  NEXT j
  IF k mod 10 = 0 THEN
    print ''k = '';k, ''cx = '';cx;
    print ''q = '';qx
  END IF
NEXT k
print ''N = '';N,''N1 = '';N1,''N2 = '';N2, ''Final
c = '';cx
print ''Total q = '';qx
f = 14.399 * cx/2
print ''potential (V) = ''; f
```

Appendix B

We estimate the Coulomb potential change caused by the insertion of Li^+ ions and electrons into the site shown in Fig. 1. Because Li^+ is assumed to distribute at random, the probability of site occupancy is y. After averaging the position with time, we can derive the structure in which all the sites are occupied and Li and Ni charge numbers are y and $4 - y$, respectively. We separate the Coulomb potential into the contributions from Li, Ni and O. Using Eq. (1), we have:

$$\Phi_{Li,y} = A_{Li}^0 + yA_{Li} + 4A_{Ni}^0 + (4 - y) A_{Ni} + A_O \qquad (A-1)$$

$$\Phi_{Ni,y} = B_{Li}^0 + yB_{Li} + 4B_{Ni}^0 + (4 - y) B_{Ni} + B_O \qquad (A-2)$$

where $\Phi_{Li,y}$ is the Coulomb potential when the Li occupancy is y at the Li site, $\Phi_{Ni,y}$ is that of the Ni site, A_{Li}, A_{Li}^0, A_{Ni} A_{Ni}^0 and A_O are the contributions from Li, Ni and O at the Li site, respectively, and B_{Li}, B_{Li}^0, B_{Ni}, B_{Ni}^0 and B_O are those at the Ni site. X_M^0 indicates the contribution from occupied sites, and X_M is the contribution from vacant sites (X: A, B; M: Li, Ni.).

Let $\Phi_{Li,0}$ and $\Phi_{Li,0}$ be the potential at $y = 0$, then we have:

$$\Phi_{Li,y} = \Phi_{Li,0} + y(A_{Li} - A_{Ni}) \qquad (A-3)$$

$$\Phi_{Ni,y} = \Phi_{Ni,0} + y(B_{Li} - B_{Ni}). \qquad (A-4)$$

Thus, we have:

$$\Phi_{Li,y} - \Phi_{Ni,y}$$
$$= \Phi_{Li,0} - \Phi_{Ni,0} + y(A_{Li} - A_{Ni} - B_{Li} + B_{Ni}). \qquad (A-5)$$

We consider the Li^+ ordering along the *c*-axis. Li^{y+} ions are already ordered. Thus, the remaining $Li^{(1-y)+}$ ions have to arrange themselves along the *c*-axis. The contribution to U_a is $-13.466(1-y)$.

From (Eqs. (8), (11) and (A-5)), we derive:

$$E_{int} = E^0 + yK \qquad (A-6)$$

where:

$$K = -(A_{Li} - A_{Ni} - B_{Li} + B_{Ni} + 13.466)/e. \qquad (A-7)$$

For ideal Li_xNiO_2, $A_{Li} = B_{Ni}$ and $A_{Ni} = B_{Li}$. In this case, $K = -[2(A_{Li} - A_{Ni}) + 13.466]/e$.

As shown in Fig. 1, the shapes of the vacant sites, in each ordering, are congruent. Therefore, A_{Li}, A_{Ni}, B_{Li} and B_{Ni} have the same value in each ordering in Fig. 1.

Fig. 9. Estimation of ΔG_t to judge the spontaneity of the phase separation.

This means that K has the same value theoretically for each ordering.

Appendix C

We consider a case where a cell voltage has its maximum at point A, between points B and C, as shown in Fig. 8(a). From Eq. (2), we can show the reaction Gibbs function (ΔG_r) (Fig. 8(b)) and the Gibbs function (G) (Fig. 8(c)). When the cathode material shows no phase separation, a spontaneous reaction occurs from point B, through point A, to point C, because $\Delta G_r < 0$. This is a cell discharge, and it does not occur when the cell is in open circuit. We studied the phase separation of the cathode at point A into those of points A1 and A2, which reaction may occur even in open circuit. The reaction is written as:

$$Li_x\langle HOST \rangle \to n_1 Li_{x1}\langle HOST \rangle + n_2 Li_{x2}\langle HOST \rangle \qquad (A-8)$$

where $n_1 + n_2 = 1$, $x = n_1 x1 + n_2 x2$ and $x1 < x < x2$. The reaction can be considered as the following two reactions occurring at once.

$$n_1 Li_x\langle HOST \rangle - n_1(x - x1)Li \to n_1 Li_{x1}\langle HOST \rangle \qquad (A-9)$$

$$n_2 Li_x\langle HOST \rangle + n_2(x2 - x)Li \to n_2 Li_{x2}\langle HOST \rangle. \qquad (A-10)$$

Let ΔG_1 be the change in the Gibbs function caused by the reaction of Eq. (A-9) and ΔG_2 be that caused by the
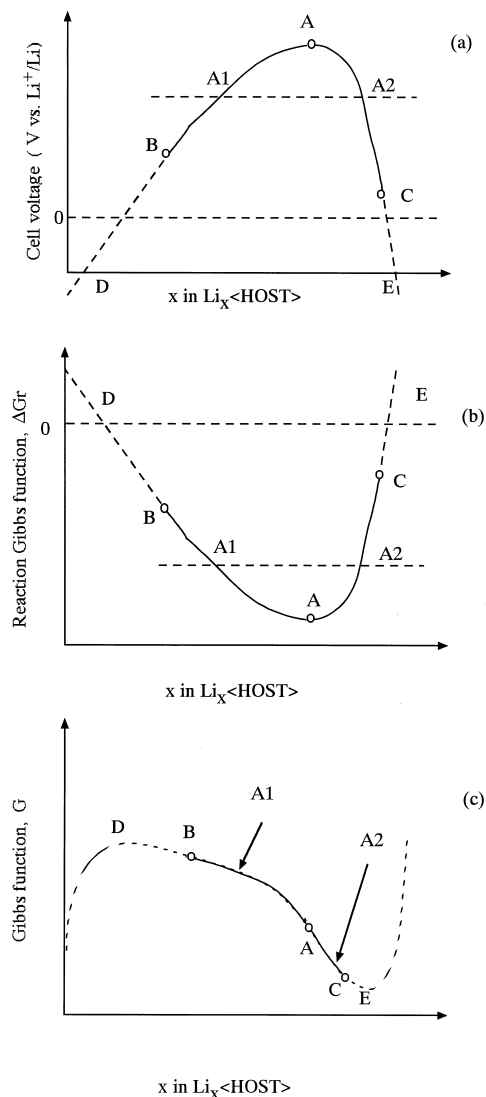
Fig. 8. The shape of the reaction Gibbs function and the Gibbs function derived from the cell voltage with a maximum point. (a) Cell voltage, (b) reaction Gibbs function, (c) Gibbs function.
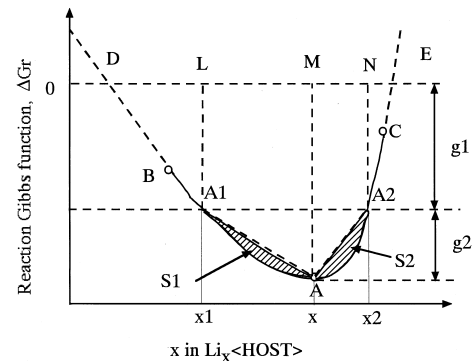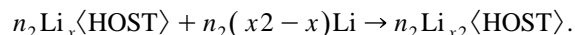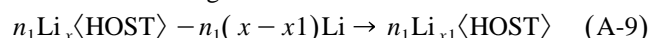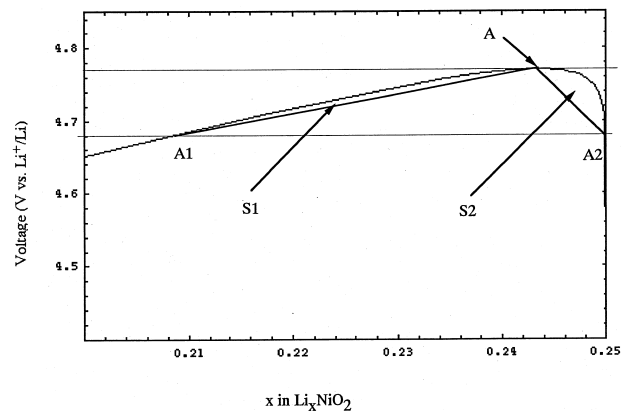
Fig. 10. Estimation of ΔG_t calculated by using Eq. (14).

reaction of Eq. (A-10). If $\Delta G_1 + \Delta G_2 < 0$, the phase separation is spontaneous.

From Fig. 9 and Eq. (1), we obtain:

$$\Delta G_1 = n_1 \left[(x - x1) g1 + 0.5 (x - x1) g2 + S1 \right] \quad \text{(A-11)}$$

$$\Delta G_2 = -n_2 \left[(x2 - x) g1 + 0.5 (x2 - x) g2 + S2 \right]. \quad \text{(A-12)}$$

Then, using the relations $n_1 + n_2 = 1$ and $x = n_1 x1 + n_2 x2$, we have:

$$\Delta G_t = \Delta G_1 + \Delta G_2 = n_1 S1 - n_2 S2.$$

Thus, the phase separation is spontaneous, if $n_1 S1 < n_2 S2$.

The profile of Eq. (14) is shown in Fig. 10. Because $n_1 = (x2 - x)/(x2 - x1)$ and $n_2 = (x - x1)/(x2 - x1)$, n_2 is very large compared with n_1. The actual values are $n_1 = 0.175$ and $n_2 = 0.825$ from Fig. 10. At the end point of the phase separation, the values must be $n_1 = 0.029$ and $n_2 = 0.971$. And $S2$ is larger than $S1$ from Fig. 10. Therefore, the phase separation occurs spontaneously.

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