

Voltage prediction of nano-sized LiNiO₂ cathode for use in Li-ion cells

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Abstract

The effect of cathode particle size on cell potential was investigated using a voltage prediction method from the Coulomb potential created by the atoms of a cathode active material. LiNiO₂ was selected as a typical cathode of an ordered rock salt structure. From the calculation, it was found that the voltage changes when the size becomes less than about 10 nm. The voltage increased with decreasing in-plane size, and decreased with decreasing the number of layers.

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1. Introduction

Lithium ion cells 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 [1–4]. The internal energy was calculated using the first principles quantum chemistry, and the Gibbs function was obtained. The researchers in these studies discussed the phase separation using the Gibbs function. We studied the voltage using a more simple method [5–7], from the Coulomb potential created by the atoms of a cathode active material.

We used this simple method to investigate the effect of cathode particle size on the cell potential. LiNiO₂ was selected as a typical cathode of an ordered rock salt structure.

2. The voltage measured from Li/Li⁺

We would like to introduce our simple method briefly. The following basic equations for calculating the voltage are

derived from thermodynamics:

$$E = -\frac{\Delta G_r}{nF} \quad (1)$$

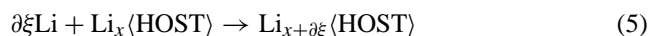
$$\Delta G_r = \left(\frac{\partial G}{\partial \xi} \right)_{P,T} \quad (2)$$

$$G = U + PV - TS \quad (3)$$

$$\left(\frac{\partial G}{\partial \xi} \right)_{P,T} = \left(\frac{\partial U}{\partial \xi} \right)_{P,T} + P \left(\frac{\partial V}{\partial \xi} \right)_{P,T} - T \left(\frac{\partial S}{\partial \xi} \right)_{P,T} \quad (4)$$

where E is the cell voltage (V), ΔG_r the reaction Gibbs function (J mol⁻¹), ξ the reaction coordinate (mol), n the electrons per molecule oxidized or reduced, F the Faraday constant (C equiv.⁻¹), G the Gibbs free energy (J), P the pressure (Pa), T the temperature (K), U the internal energy (J), V the volume (m³) and S is the entropy (JK⁻¹).

If we consider Li insertion into the host matrix (HOST), ΔG_r is obtained from the difference of G for the following reaction divided by $\partial \xi$:



From Eqs. (1)–(4), we have the following:

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

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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

$$E_{\text{int}} \equiv -\frac{1}{nF} \left(\frac{\partial U}{\partial \xi} \right)_{P,T} = \frac{U_a}{ne} \quad (7)$$

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

The second term (E_w) is a work performed against a pressure P . If we consider the volume change of the system, V is the volume of the system and P is the atmospheric pressure. In this case, the work is very small. In this paper, we assumed that the matrix does not deform by Li extraction. Therefore, there is no volume change. Then, the second term (E_w) can be ignored. The lithium ion expands the host lattice when it is inserted. Such a work is included in U_a . We then have

$$E_w \equiv \frac{P}{nF} \left(\frac{\partial V}{\partial \xi} \right)_{P,T} = 0 \quad (8)$$

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 ” the number of Li atoms inserted in the host matrix, and N_A Avogadro’s number. The number of ways that “ a ” indistinguishable from 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

$$\begin{aligned} E_{\text{ent}} &\equiv \frac{kT}{nF} \left(\frac{\partial \ln \Omega_p}{\partial \xi} \right)_{P,T} \\ &= \frac{kTN_A}{nF} \left\{ \ln \left[\frac{N!}{(N-a-1)!(a+1)!} \right] \right. \\ &\quad \left. - \ln \left[\frac{N!}{(N-a)!a!} \right] \right\} \\ &= \frac{RT}{nF} \ln \left[\frac{N-a}{a+1} \right] \approx \frac{RT}{nF} \ln \left[\frac{1-y}{y} \right] \end{aligned} \quad (9)$$

where $y = a/N$. This is a well-known result obtained from thermodynamics [8]. In this study, we examined the entropy term contribution within the framework of Eq. (9). A more accurate approximation of the insertion system is discussed by Kudo and Hibino [9]. Ultimately, the voltage is

$$E \approx \frac{U_a}{ne} + \frac{RT}{nF} \ln \frac{1-y}{y} \quad (10)$$

3. Phase separation and thermodynamics

From Eqs. (2), (3), and (10), the corresponding molar Gibbs free energy [$G_m = G/(\text{moles of matrix})$] is

$$G_m = U(y) + RT[y \ln y + (1-y) \ln(1-y)] \quad (11)$$

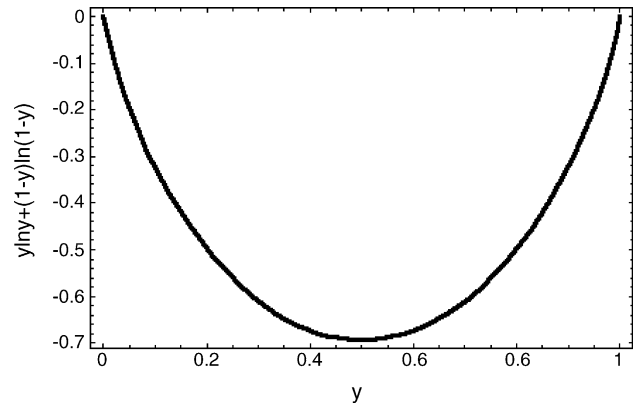


Fig. 1. Curve of $y \ln y + (1-y) \ln(1-y)$.

where $U(y)$ is the internal energy (J mol^{-1}) at a lithium occupancy of y . The curve of $y \ln y + (1-y) \ln(1-y)$ was shown in Fig. 1. The tangents at $y=0$ and $y=1$ are $+\infty$ and $-\infty$, respectively.

The relation between the cell potential, the reaction Gibbs function, and the Gibbs function are shown in Fig. 2 (left) assuming $U(y)$ is a convex function. The reaction Gibbs function is a mirror image of the cell potential. The maximum point A in Fig. 2 (left) (a) is the minimum point A in Fig. 2 (left) (b) and the inflection point A in Fig. 2 (left) (c). The minimum point B in Fig. 2 (left) (a) is the maximum point B in Fig. 2 (left) (b) and the inflection point B in Fig. 2 (left) (c). Because $y \ln y + (1-y) \ln(1-y)$ versus y curve shows a very large tangent at $y=0$ and $y=1$, and $U(y)$ is a convex function, there is a common tangential line at a lower side of G . The points of tangency are y_1 and y_2 . Let the matrix be N_m moles. When a point y on curve $G(y)$ in Fig. 2 (left) (c) is considered, it is well known that the phase is separated to the $N_m(-y+y_2)/(y_2-y_1)$ moles of the $y=y_1$ phase and the $N_m(y-y_1)/(y_2-y_1)$ moles of the $y=y_2$ phase. In this case, the total G of the two phases is $G = N_m [(-y+y_2)G(y_1) + (y-y_1)G(y_2)]/(y_2-y_1)$. This G value is on the contact line. The total G of the two phases is smaller than the original $G(y)$. Therefore, the phase separation occurs spontaneously. From this consideration, the two-phase region is at $y_1 < y < y_2$, and the single-phase regions are at $0 < y < y_1$ and $y_2 < y < 1$. Because the slope of the common tangential line is constant, the cell voltage is constant (E_0) at the two-phase region, as shown in Fig. 2 (left) (a). The integration of the reaction Gibbs function gives the Gibbs function. Therefore, the integrated value of the reaction Gibbs function from y_1 to y_1 through the original curve and through the common tangential line have the same value. This means that the area CBF and the area FAD are the same. From this relation, we can estimate the cell voltage (E_0) at the two-phase region.

When $U(y)$ is a concave function, there is no common tangential line at the lower side of G , as shown in Fig. 2 (right). The insertion electrode is in a single phase in this case.

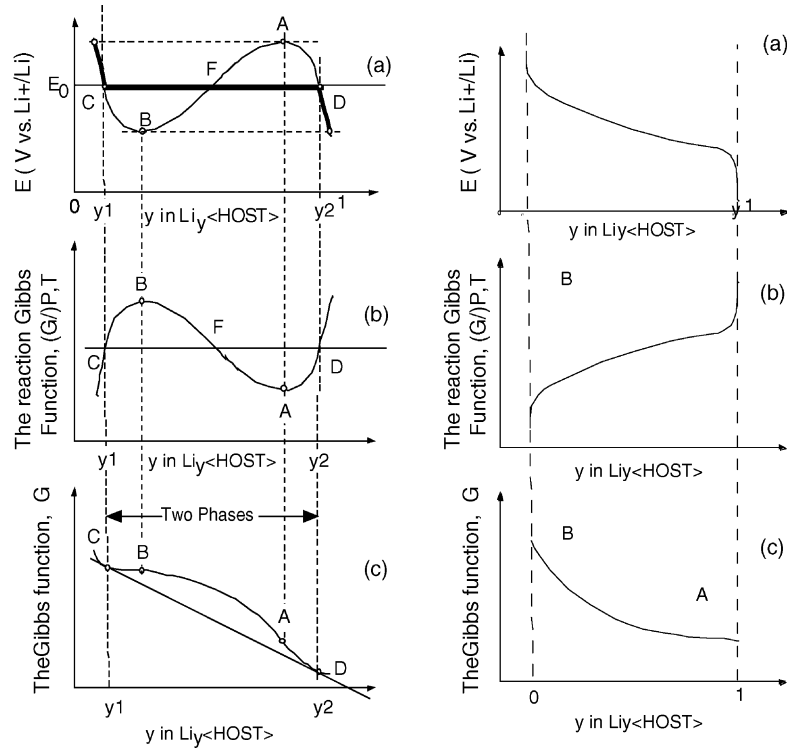


Fig. 2. Relation between (a) the cell potential, (b) the reaction Gibbs function and (c) the Gibbs function [left: $U(y)$ is a convex function, right: $U(y)$ is a concave function.].

4. Phase separation of cathode

We studied the voltage using a more simple method [5–7]. We considered the energy cycle for the reaction $\delta\xi\text{Li}(\text{crystal}) \rightarrow \delta\xi\text{Li}^+(\text{g}) + \delta\xi e$ and $\delta\xi\text{Li}^+(\text{g}) + \delta\xi e + \text{Li}_x\text{NiO}_2 \rightarrow \text{Li}_{x+\delta\xi}\text{NiO}_2$ [6]. Let I_{Li} be the ionisation potential (eV) of the Li metal ($I_{\text{Li}} = -7.107$ eV), and Φ_{Li} be the Coulomb potential at a vacant Li^+ insertion site. The increase in internal energy caused by the insertion of an electron is assumed to be $-\Phi_{\text{Ni}} + I_{\text{Ni}}$, where Φ_{Ni} is the Coulomb potential of the electron insertion site and I_{Ni} is the LUMO energy of an isolated Ni atom in a vacuum ($I_{\text{Ni}} = -29.106$ eV). When Φ_{Ni} is calculated for a cathode before the Li^+ insertion, we have to add the contribution of the inserted Li^+ . Thus, we have to add $-14.399/R_{\text{Li-Ni}}$ to Φ_{Ni} , where $R_{\text{Li-Ni}}$ is the distance between the inserted Li^+ and the electron. Finally, we have

$$E = E_{\text{int}} + E_{\text{ent}} = -\frac{1}{ne} \Phi_{\text{Li}} - \Phi_{\text{Ni}} + I_{\text{Ni}} - I_{\text{Li}} \pm \frac{e}{4\pi\epsilon_0 R_{\text{Li-Ni}}} - \frac{RT}{nF} \ln \frac{y}{1-y} \quad (12)$$

where the sign after I_{Li} is + if there is already Li at the center of k (extraction of Li) and – if there is no Li at the center of k (insertion of Li). With Li-ion cells, $n = 1$.

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 the following equation:

$$\Phi_k = 14.399 \sum \left(\frac{Z_i}{r_{ij}} \right) \quad (13)$$

On the surface of the LiNiO_2 , “ Z_i ”s at plane, edge, and corner are assumed to be $1/2Z_i$, $1/4Z_i$ and $1/8Z_i$, respectively. Φ_k was calculated using VIP BASIC (Mainstay) for Power Macintosh. The value of r_{ij} was obtained from the crystal structure of a cathode active material. The summation of r_{ij} was undertaken for all the ions until the value converged.

5. Voltage prediction of LiNiO_2

We calculated the voltage of LiNiO_2 [6]. The difference between the ideal structure used for our calculations and the real structure is shown in Table 1. We assumed in-plane orderings of lithium ions as shown in Fig. 3. In each area, Li^+ -ions are assumed to be distributed at random. This means that all the sites are occupied by Li^{y+} and e^{y-} , where y is the site occupancy in each area. Then, for E_{int} , we have a straight line connecting two voltages (E_{int}) at each end point of the area. The Gibbs function and the cell voltage of LiNiO_2 are shown in Figs. 4 and 5. The experimental results of Li_xNiO_2 are two phases (R-3 m) at $0 < x < 0.25$ with 4.2 V, a single phase (R-3 m) at $0.25 < x < 0.45$ with 4.2–3.8 V, a single phase (C2/ m) at $0.45 < x < 0.75$ with 3.8–3.7 V, and a single phase (R-3 m)

Table 1
Differences between the ideal structure and the real structure

		Nearest length (Å)				
		Ni–O	Li–O	Ni–Ni	Li–Li	O layer distance
LiNiO ₂	Ideal structure	$\sqrt{2}r$	$\sqrt{2}r$	$2r$	$2r$	$(4/\sqrt{6})r$
	(): $r = \sqrt{2}\text{Å}$	(2.000)	(2.000)	(2.828)	(2.828)	(2.309)
	Real structure	1.957	2.126	2.875	2.875	2.36

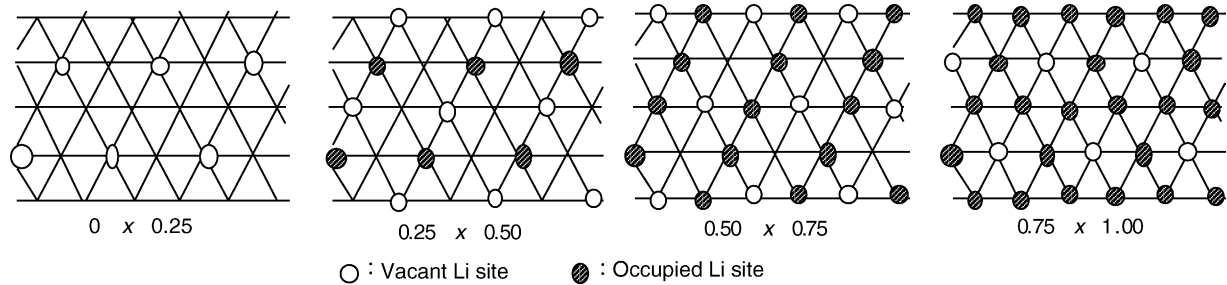


Fig. 3. In-plane orderings of lithium ions.

at $0.75 < x < 1$ with 3.7–3.5 V. Our calculated phase separation was in agreement with the experiments at $0 < x < 0.25$. This bad result probably occurred because we assumed that the matrix does not deform by the insertion of lithium ions and electrons ($w_a = 0$). The calculated voltage at $x = 1$ was in very good agreement with the experimental value, because the deformation of the matrix was very small at the beginning of the extraction of Li from the LiNiO₂ matrix.

6. Voltage prediction of nano-size LiNiO₂

Φ_k was calculated using Eq. (13). Usually, the summation of r_{ij} was undertaken for all the ions until the value converged, but when LiNiO₂ is very small, there are not enough ions around the atom k. Therefore, the Φ_k becomes a different value of the converged value. The Φ_k depends on the position

in LiNiO₂ particle. In this paper, Φ_k is calculated at the center of LiNiO₂ particle. The calculation of voltage was performed for E_{int} of LiNiO₂ and Li_{0.75}NiO₂. The two-phase voltage from $x = 1$ to 0.75 (Li_xNiO₂) was also calculated. Those three voltages are shown in Fig. 5. As already mentioned, the most reliable voltage is E_{int} of LiNiO₂. To increase the size of LiNiO₂ from a unit cell, we examined three different cases.

6.1. Increasing the size of LiNiO₂ while maintaining a similar shape of the unit cell

Shape of LiNiO₂ cathode was shown in Fig. 6, when a similar shape of the unit cell was maintained. The voltage increased as the size of LiNiO₂ decreased, as shown in Fig. 7. In this calculation, the outside layers are Li layers. E_{int} of LiNiO₂ increased very rapidly from 4.3 to 12.3 V as the size of LiNiO₂ decreased. E_{int} of LiNiO₂ was 4.3254 V

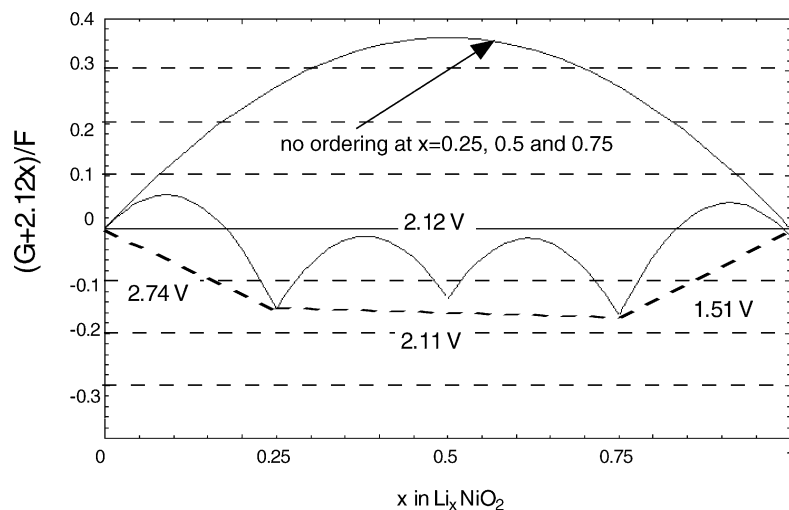


Fig. 4. Gibbs function of Li_xNiO₂.

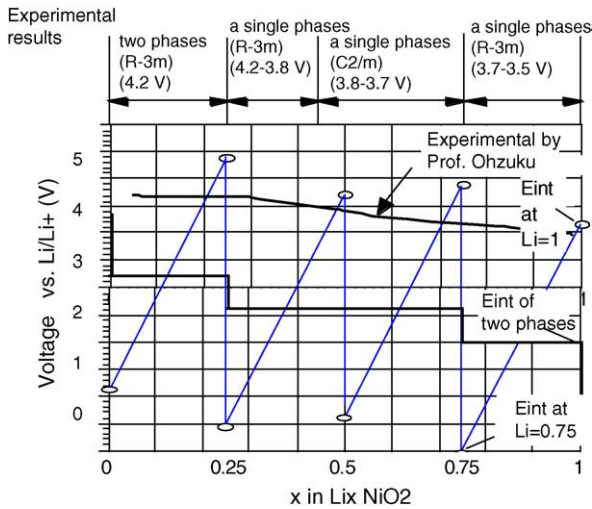


Fig. 5. Cell voltage of Li_xNiO_2 . Experimental data is from Ohzuku [10].

at $b = 139 \text{ \AA}$ and 4.3366 V at $b = 97 \text{ \AA}$. This means that E_{int} of LiNiO_2 increased for 11.2 mV by the decrease of the size from $b = 139$ to 97 \AA . It is not very difficult to measure the 10 mV difference. Therefore, if we synthesize 100 \AA ($10 \mu\text{m}$) particles of LiNiO_2 experimentally, we can check the voltage change. We are now conducting experiments to prove our theory.

The case of the outside oxygen layers was also calculated (Figs. 8 and 9), because Li must be inserted between two oxygen layers. The result was similar to the case of the Li outside layers. E_{int} of LiNiO_2 was 3.6598 V at $b = 139 \text{ \AA}$ and 3.6739 V at $b = 97 \text{ \AA}$. The difference in voltage is 14.1 mV .

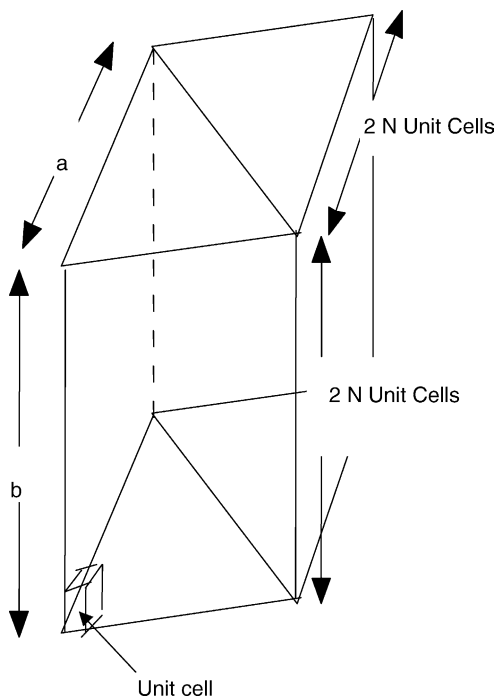


Fig. 6. Shape of LiNiO_2 cathode when a similar shape of the unit cell was maintained.

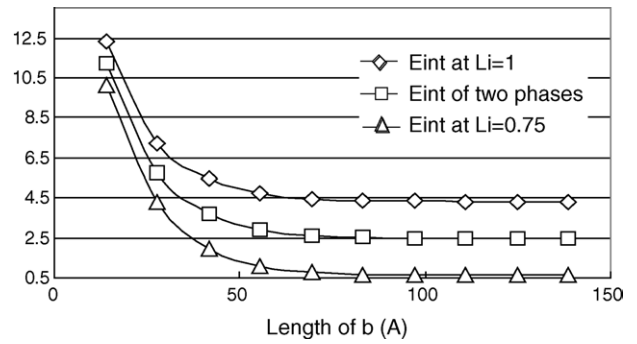


Fig. 7. E_{int} of LiNiO_2 (Li layer is outside maintaining a similar shape of the unit cell).

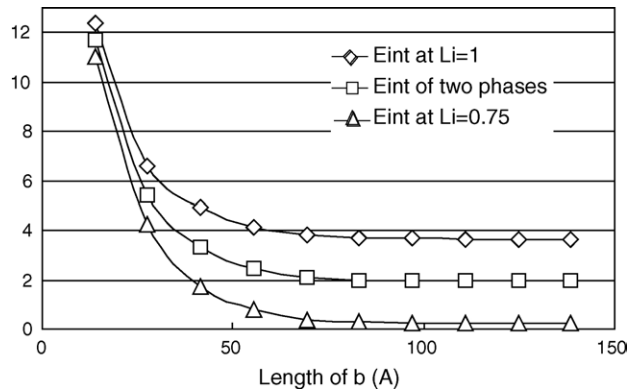


Fig. 8. E_{int} of LiNiO_2 (oxygen layer is outside maintaining a similar shape of the unit cell).

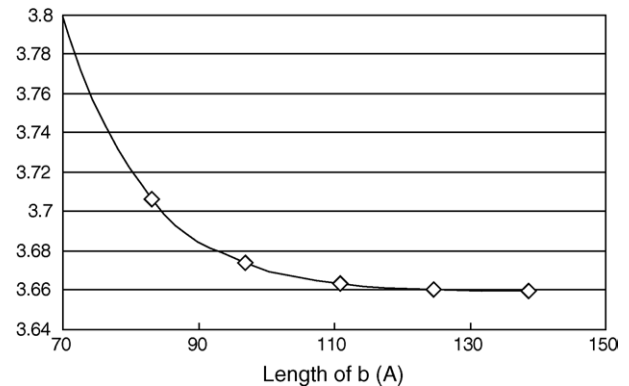


Fig. 9. E_{int} at $\text{Li} = 1$ of LiNiO_2 (oxygen layer is outside maintaining a similar shape of the unit cell).

6.2. Increasing the size of LiNiO_2 while changing the in-plane area and keeping the number of layers (20 layers)

The voltage increased as the size of LiNiO_2 decreased, as shown in Fig. 10. In this calculation, the outside layers are Li layers. E_{int} of LiNiO_2 increased very rapidly from 4.6 to 12.6 V as the size of LiNiO_2 decreased.

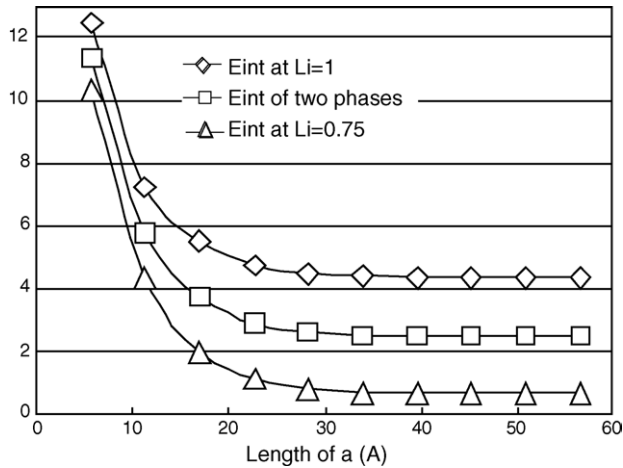


Fig. 10. E_{int} of LiNiO_2 (Li layer is outside changing the in-plane area and keeping the number of layers).

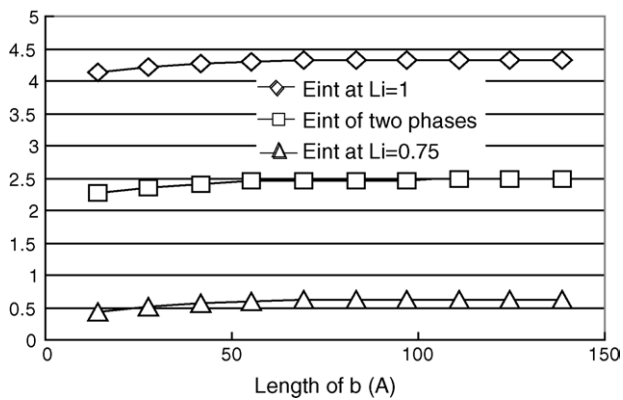


Fig. 11. E_{int} of LiNiO_2 (Li layer is outside maintaining the in-plane area).

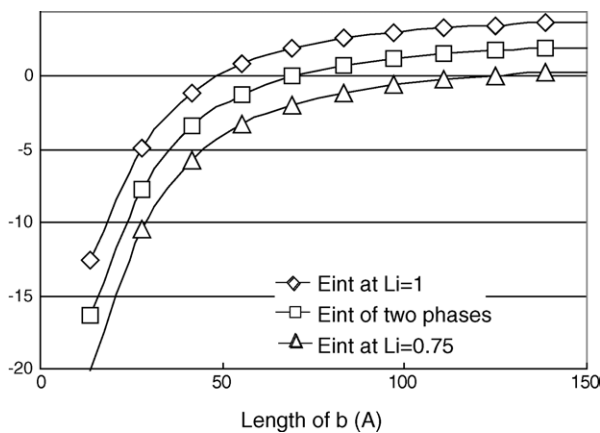


Fig. 12. E_{int} of LiNiO_2 (oxygen layer is outside. maintaining the in-plane area).

6.3. Increasing the size of LiNiO_2 while maintaining the in-plane area (20×20 unit cells) and changing the number of layers

The voltage decreased slightly as the size of LiNiO_2 decreased, as shown in Fig. 11. In this calculation, the outside layers are Li layers. E_{int} of LiNiO_2 decreased from 4.3 to 4.1 V as the size of LiNiO_2 decreased.

We also calculated the case of outside oxygen layers (Fig. 12). E_{int} of LiNiO_2 decreased very rapidly from 4.3 to -12.6 V as the size of LiNiO_2 decreased.

From a practical point of view, the decrease of the voltage is not good. We conclude, therefore, that reducing the number of layers is not a good way to synthesize nano-sized LiNiO_2 . However, we have to find a new electrolyte which have a higher oxidation potential, when the high voltage cathode is used.

7. Conclusion

Based on the results of this study, we conclude that the voltage changes when the size of LiNiO_2 becomes less than about 10 nm. The voltage increased as we decreased the in-plane size and decreased as we decreased the number of layers. However, Φ_k depends on the position in LiNiO_2 particle. And the matrix may easily deform during Li extraction when the size of LiNiO_2 particle becomes very small. We are now studying the contribution of these factors.

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