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Voltage prediction from Coulomb potential created by atoms of spinel $LiMn_2O_4$ cathode active material for Li ion cells

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Abstract

We studied the contribution of internal energy and entropy change to cathode voltage assuming that the cathode material $Li_xMn_2O_4$ was completely ionic and only the Coulomb potential was effective. We calculated the cathode voltage of an ideal spinel structure $Li_xMn_2O_4$ (*Fd3m*) (Mn–O: 2 Å, Li–O: 1.732 Å, O–O: 2.828 Å). From this calculation, we found that $Li_xMn_2O_4$ has a multiphase co-existence for $0 < x < 1$ with a very high voltage (8.7 V versus Li), and has a negative voltage when $1 < x$. If we suppose that inserted Li^+ and electron have 40% of the formal charge, $Li_xMn_2O_4$ has a voltage from 4.55 to 4.79 V for $0 < x < 1$, and has a voltage of 1.75 V when $1 < x$.

Keywords: Lithium ion cells; Cathode voltage; Calculation; Coulomb potential; Spinel $Li_xMn_2O_4$

1. Introduction

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 [1–5]. However at present, it is not easy to calculate non-averaged voltage using the first principles quantum chemistry because of long calculation time.

We have been studying 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 versus Li/Li^+) assuming that the cathode material was completely ionic and only the Coulomb potential was effective in terms of changing the internal energy. We calculated the cathode voltage of an ideal structure Li_xMO_2 (*R3m*) (Li–O: 2 Å, Ni–O: 2 Å) [6,7], 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 $0.25 < x < 1$.

In this paper, we calculate the cathode voltage of an ideal structure spinel $Li_xMn_2O_4$ (*Fd3m*) using the same method employed for the calculation [6,7] of Li_xMO_2 (*R3m*).

2. Basic theory and model [6,7]

We assume that the 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} (Å) be the distance from a certain atom k to the surrounding atoms of species i in an ionic crystal, and Zi be the charge number of species i. Then the Coulomb potential at atom k is expressed by the following Eq. (1).

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

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

From thermodynamics, we have

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

where E is cell voltage (V), ΔG_r the reaction Gibbs function (J/mol), n the electrons per molecule oxidized or reduced, and F is the Faraday constant (C/equiv). From Eqs. (1) and (2), we have

$$E = -\frac{1}{nF}\left[\left(\frac{\partial U}{\partial \xi}\right)_{P,T} + P\left(\frac{\partial V}{\partial \xi}\right)_{P,T} - T\left(\frac{\partial S}{\partial \xi}\right)_{P,T}\right] \tag{3}$$

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where ξ is the reaction coordinate (mol), P the pressure (Pa), T the temperature (K), U the internal energy (J), V the volume (m^3), and S is the entropy (J/K). Let U_a (eV, energy change for one atom Li insertion) be the internal energy change caused by the insertion of one Li. Then we have, for the first term, $E_{int} = -U_a/ne$. We will ignore the second term, because the value is very small. The third term (E_{ent}) is the entropy term: $E_{ent} = (RT/nF)\ln((1-y)/y)$, where y is the probability of Li occupation in cathode Li sites. The electron arrangement does not contribute to the entropy term because we assumed that electron is inserted into the nearest Mn from the inserted Li^+.

We considered the energy cycle for the reaction

$$\delta\xi \mathrm{Li(crystal)} \rightarrow \delta\xi \mathrm{Li^+(g)} + \delta\xi \mathrm{e}$$

and

$$\delta\xi \mathrm{Li^+(g)} + \delta\xi \mathrm{e} + \mathrm{Li}_x\mathrm{Mn_2O_4} \rightarrow \mathrm{Li}_{x+\delta\xi}\mathrm{Mn_2O_4}$$

Let I_{Li} be the ionization potential (eV) of Li metal, 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 $-\Phi_{Mn} + I_{Mn}$, where Φ_{Mn} is the Coulomb potential of the electron insertion site and I_{Mn} is the LUMO energy of an isolated Mn atom in a vacuum. When Φ_{Mn} is calculated for a cathode before the Li^+ insertion, we have to add the contribution of the inserted Li^+. Thus, we have to add $-14.399/R_{Li\text{–}Mn}$ to Φ_M, where $R_{Li\text{–}Mn}$ is the distance between the inserted Li^+ and the electron. Finally we have the following equation 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, $n = 1$.

$$\begin{aligned} E &= E_{int} + E_{ent} \\ &= -\frac{1}{ne}\left(\Phi_{Li} - \Phi_{Mn} + I_{Mn} - I_{Li} \pm \frac{e}{4\pi\varepsilon_0 R_{Li\text{–}Mn}}\right) \\ &\quad -\frac{RT}{nF}\ln\left(\frac{y}{1-y}\right) \end{aligned} \tag{4}$$

3. Calculation of cathode voltage of $Li_xMn_2O_4$

In this paper, we assume an ideal spinel $LiMn_2O_4$ which has the same nearest length of $2r$ (Å) for O–O or Mn–Mn. In this ideal material, oxygen atoms form regular tetrahedrons linked at their edges to form oxygen layers, and MnO_6 and LiO_4 form regular octahedral and tetrahedral structures, respectively. We used $r = 2^{0.5}$. Then, the oxygen layer distance of the ideal structure is 2.309 (Å), and that of the experimental value is 2.38 (Å) [8]. The distance from the experiment is 1.03 times greater than that of the ideal structure.

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

We obtained an I_{Li} value of −7.107 eV (685.78 kJ/mol) from the enthalpy change for $\mathrm{Li(cr)} \rightarrow \mathrm{Li^+(g)} + \mathrm{e}$.

Using the DV-Xα molecular orbital method (SCAT) [9], we determined that the HOMO energy of $[MnO_6]^{-1}$ cluster was −0.40627 eV, where the nominal valences of Mn and O are 3 and −2/3, respectively. The contribution of the Coulomb potential of oxygen is −28.798 eV. Therefore, $I_{Mn} = -0.40627 - 28.798 = -29.204$ eV.

The calculated voltages (E_{int}) are summarized in Table 1. When all the Li^+ atoms are moved from tetrahedral sites to octahedral sites, the spinel structure changes to a rock salt structure.

After the addition of entropy term in Eq. (4), the voltage profile is calculated using "Mathematica (Wolfram)", and shown in Fig. 1. The Li sites, where Li can be inserted or extracted, are C4-2 at $Z = 3 + 1/4$, B4-2 at $Z = 1 + 1/4$, A4-1 at $Z = 5 + 1/4$ for $0 < x < 0.25$, A4-2 at $Z = 3 + 1/4$, C4-1 at $Z = 1 + 1/4$, B4-2 at $Z = 5 + 1/4$ for $0.25 < x < 0.5$, C4-1 at $Z = 3 + 1/4$, B4-1 at $Z = 1 + 1/4$, A4-2 at $Z = 5 + 1/4$ for $0.5 < x < 0.75$, A4-1 at $Z = 3 + 1/4$, C4-2 at $Z = 1 + 1/4$, B4-1 at $Z = 5 + 1/4$ for $0.75 < x < 1$ (Fig. 2). 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 each area. Then, for E_{int}, we have a straight line connecting two voltages (E_{int}) at each end point

Table 1
The calculated voltage of $Li_xMn_2O_4$/Li cell

x in $Li_xMn_2O_4$		Li site	Mn charge		E_{int} (V)	Voltage from E_{int} (V)	$E_{bmod\,int}$ (V)	Voltage from $E_{bmod\,int}$ (V)
			Li–Mn layer	Mn charge				
Spinel								
0	Insertion	Tetrahedral	+4	+4	6.93	8.74	3.81	4.79
0.25	Extraction	Tetrahedral	+3, +4	+4	9.27		5.57	
	Insertion				9.09		4.15	
0.5	Extraction	Tetrahedral	+3	+4	9.65		5.63	
	Insertion				7.00	7.91	3.82	4.66
0.75	Extraction	Tetrahedral	+3	+3, +4	8.81		5.50	
	Insertion				6.73	7.19	3.78	4.55
1	Extraction	Tetrahedral	+3.5	+3.5	7.64		5.31	
Rock salt								
0	Insertion	Octahedral	+4	+4	2.03	5.18	–	1.75
1	Insertion	Octahedral	+3.5	+3.5	5.18	5.18	–	
2	Extraction	Octahedral	+3	+3	4.42	4.42	–	

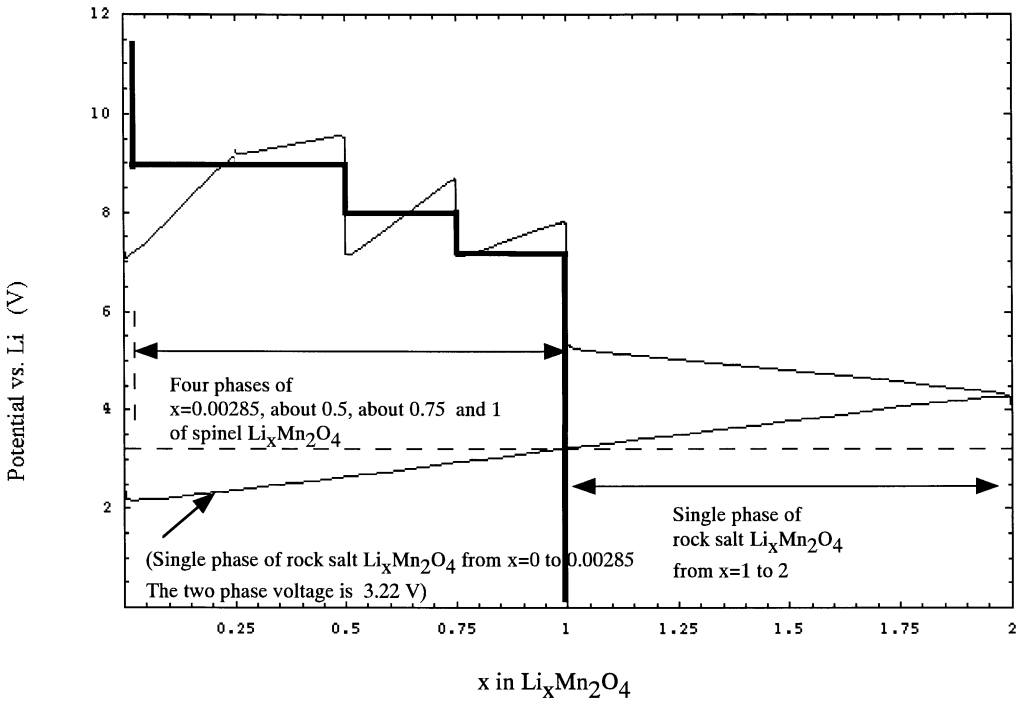

Fig. 1. The calculated voltage of $Li_xMn_2O_4$.

of the area. We obtained the following equation for spinel

$$E = E_i^0 + K_i y - \frac{RT}{F}\ln\left(\frac{y}{1-y}\right) \tag{5}$$

where

$$\begin{aligned}
&E_1^0 = 6.93\,(\mathrm{V}), \quad K_1 = 2.34\,(\mathrm{V}) \quad \text{and} \quad y = \frac{x}{0.25}, && \text{for} \quad 0 < x < 0.25 \\
&E_2^0 = 9.09\,(\mathrm{V}), \quad K_2 = 0.56\,(\mathrm{V}) \quad \text{and} \quad y = \frac{(x-0.25)}{0.25}, && \text{for} \quad 0.25 < x < 0.50 \\
&E_3^0 = 7.00\,(\mathrm{V}), \quad K_3 = 1.80\,(\mathrm{V}) \quad \text{and} \quad y = \frac{(x-0.5)}{0.25}, && \text{for} \quad 0.50 < x < 0.75 \\
&E_4^0 = 6.73\,(\mathrm{V}), \quad K_4 = 0.91\,(\mathrm{V}) \quad \text{and} \quad y = \frac{(x-0.75)}{0.25}, && \text{for} \quad 0.75 < x < 1,
\end{aligned}$$

From Eqs. (2) and (5), the corresponding Gibbs free energy is

$$G = -\frac{F}{4}\left\{E_i^0 y + \frac{K_i}{2}y^2 - \frac{RT}{F}[y\ln y + (1-y)\ln(1-y) + C_i]\right\}$$

where

$$\begin{aligned}
&C_1 = 0 \quad \text{and} \quad y = \frac{x}{0.25}, && \text{for} \quad 0 < x < 0.25 \\
&C_2 = -\left(E_1^0 + \frac{K_1}{2}\right) \quad \text{and} \quad y = \frac{(x-0.25)}{0.25}, && \text{for} \quad 0.25 < x < 0.50 \\
&C_3 = C_2 - \left(E_2^0 + \frac{K_2}{2}\right) \quad \text{and} \quad y = \frac{(x-0.5)}{0.25}, && \text{for} \quad 0.50 < x < 0.75 \\
&C_4 = C_3 - \left(E_3^0 + \frac{K_3}{2}\right) \quad \text{and} \quad y = \frac{(x-0.75)}{0.25}, && \text{for} \quad 0.75 < x < 1
\end{aligned}$$

If Li^+ ordering does not occur for rock salt, G is

$$G = -F\left\{2.03x + \frac{2.39x^2}{4} - \left(\frac{RT}{F}\right)[x\ln(x) + (2-x)\ln(2-x) - 2\ln 2]\right\}$$

The relation is shown in Fig. 3. There are three tangential lines (dotted lines in Fig. 1), which show phase separation at $0 < x < 0.5$, $0.5 < x < 0.75$, and $0.75 < x < 1$. From Eq. (2), the potential of the phase separation area is −(slope of the tangential line). Therefore, the voltage of bold curve shown in Fig. 1 is the final result from this calculation. Unfortunately, the state at $x = 1$ is the most stable phase and we could not observe the discharge curve for $1 < x < 2$.

Z	Ion	Layer pattern	site
0	O	A	32e
1/2	Mn	B1+B2+B3	16d
1	O	C	32e
1+1/4	Li	B4	8a
1+1/2	Mn	A4	16d
1+3/4	Li	C4	8a
2	O	B	32e
2+1/2	Mn	C1+C2+C3	16d
3	O	A	32e
3+1/4	Li	C4	8a
3+1/2	Mn	B4	16d
3+3/4	Li	A4	8a
4	O	C	32e
4+1/2	Mn	A1+A2+A3	16d
5	O	B	32e
5+1/4	Li	A4	8a
5+1/2	Mn	C4	16d
5+3/4	Li	B4	8a
6	O	A	32e

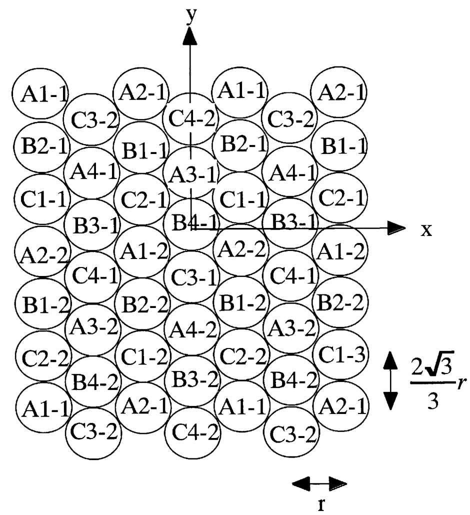

Fig. 2. The (1, 1, 1) in-plane position of $Li_xMn_2O_4$.

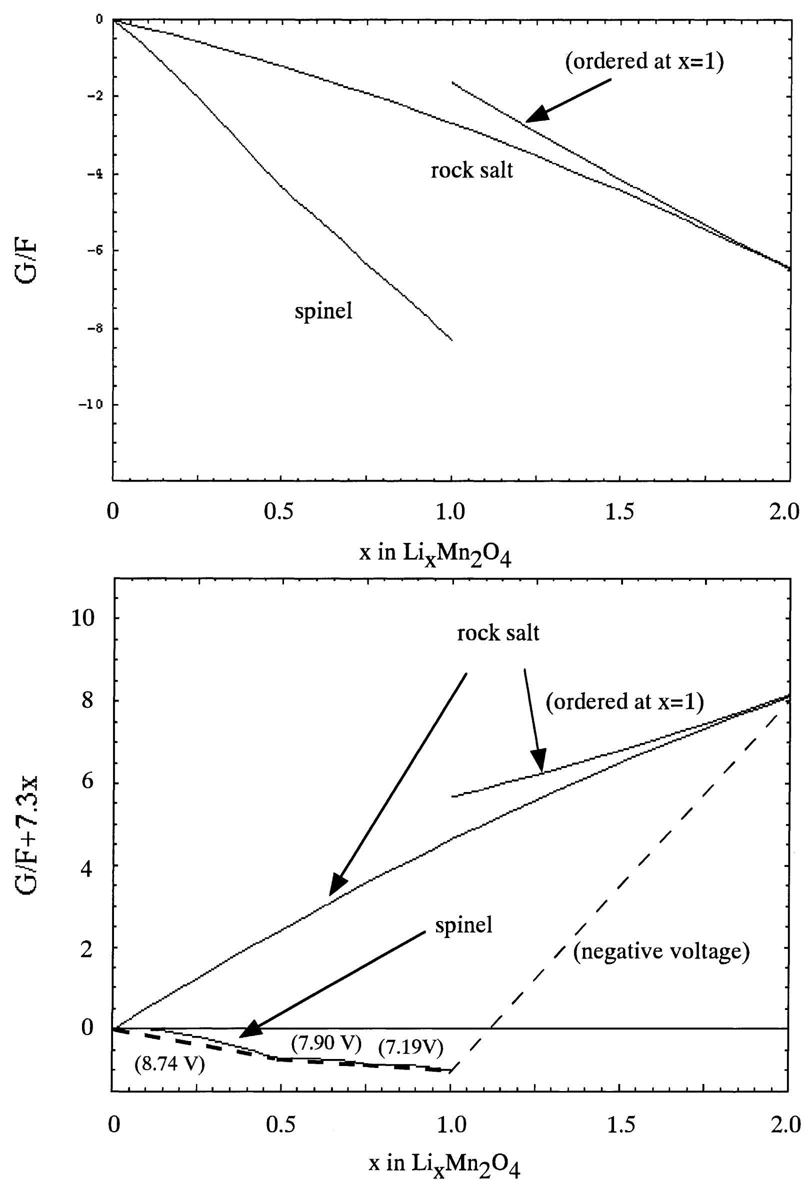

Fig. 3. The Gibbs free energy of $Li_xMn_2O_4$.

Our calculated voltage is too high compared with the experimental value (about 4.5 V ($0 < x < 1$) and 3 V ($1 < x < 2$)) [8]. We used 40% of the formal charge of inserted Li^+ and electron for spinel to improve the calculated value. The improved voltage ($E_{\mathrm{bmod\,int}}$) is shown in Table 1. We used the equation; $E_{\mathrm{bmod\,int}} = 0.16E_{\mathrm{int}} + 2.07$ (for insertion) and $E_{\mathrm{bmod\,int}} = 0.16E_{\mathrm{int}} + 4.09$ (for extraction). We assumed 100% of the formal charge of inserted Li^+ and electron for rock salt because good fitting of $LiNiO_2$ voltage using this assumption. We obtained $G/F(\mathrm{spinel}) = -4.70$ eVat $x = 1$, and $G/F(\mathrm{rock\ salt}) = -6.45$ eV at $x = 2$. Therefore, there is a two-phase region at $1 < x < 2$, and the voltage is 1.75 (V). The result is also shown in Table 1.

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