

Application of Monte Carlo Simulation to Intercalation Electrochemistry I. Thermodynamic Approach to Lithium Intercalation into LiMn_2O_4 Electrode

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Abstract. The present article is concerned with the application of the Monte Carlo simulation to electrochemistry of lithium intercalation from the thermodynamic view point. This article first introduced the fundamental concepts of the ensembles, and Ising and lattice gas models in statistical thermodynamics for the Monte Carlo simulation in brief. Finally the Monte Carlo method based upon the lattice gas model was employed to analyse thermodynamics of the lithium intercalation into the transition metal oxides. Especially we dealt with the thermodynamic properties as the electrode potential curve and the partial molar internal energy and entropy of lithium ion in the case of the LiMn_2O_4 electrode, and consequently confirmed the utility of the Monte Carlo method in the field of electrochemistry of the lithium intercalation.

초 록 : 열역학적 관점에서 몬테 카를로 방법의 전기화학적 리튬 인터칼레이션에로의 응용에 대하여 다루었다. 우선 통계 열역학의 앙상블, Ising 및 lattice gas 모델의 기본 개념을 간단히 소개하였고, lattice gas 모델에 근거한 몬테 카를로 방법을 사용하여 전이금속 산화물내로의 리튬 인터칼레이션의 열역학을 해석하였다. 특히 LiMn_2O_4 전극에 대해 전극 포텐셜 곡선과 리튬 이온의 부분 몰 내부에너지와 엔트로피와 같은 열역학적 특성을 다루었고, 이로부터 리튬 인터칼레이션의 전기화학분야에서 몬테 카를로 방법의 유용성을 확인하였다.

Key words : Lattice gas model, LiMn_2O_4 electrode, Lithium Intercalation, Monte Carlo simulation

1. Introduction

The name Monte Carlo method arises from the fact that this method uses random numbers. The Monte Carlo methods started during the 1940s, developed parallel to the performance of the computers, and have become an indispensable tool in many fields of science, especially in physics.¹⁻⁴⁾ Most of the recent programming languages for computers contain the so-called pseudo-random number generators using recurrence relations which are known to have periods intrinsic to the algorithms used, but usually to satisfy the criteria for randomness.⁵⁾

The Monte Carlo methods have been used to the simulation of the thermodynamic properties of a system at an equilibrium state. The methods have allowed us to explore the methodology of statistical thermodynamics and to introduce the effect of temperature on the thermodynamic properties. Application of the methods has expanded from the traditional research areas of dense gases, liquids and solids to the studies of phase transition⁶⁻⁸⁾, growth of phases⁹⁻¹⁰⁾, adsorption on surface of solids¹¹⁻¹⁷⁾ and diffusion in solid bulks¹⁸⁻²⁰⁾. Those phenomena were theoretically analysed by using simple statistical thermodynamics based upon an Ising model or a lattice gas model with appropriate approximations.

Recently, the Monte Carlo methods based upon the lattice gas model have been also employed in the field of electrochemistry to investigate 2-dimensional adsorption of ions on the electrode surface²¹⁾ and 3-dimensional electrochemical intercalation of ions into the bulk electrodes, especially electrochemical intercalation of lithium ions into transition metal oxides where lithium ions interact strongly with each other.^{22,23)} In those works, the Monte Carlo methods have been successfully applied to theoretically derive the thermodynamic properties such as the relationship between the electrode potential and either the surface coverage or the composition of ions.

This article reviewed fundamentals of the Monte Carlo methods based upon statistical thermodynamics to analyse the electrochemical lithium intercalation from the thermodynamic view point. Basic concepts of statistical thermodynamics and the procedures of the Monte Carlo simulation to calculate the thermodynamic quantities were first introduced in brief, and then the results theoretically calculated were compared with those results experimentally measured on the LiMn_2O_4 electrode, one of the transition metal oxides as the intercalation compounds.

2. Fundamentals of Statistical Thermodynamics for Monte Carlo Method

2.1. Canonical and grandcanonical ensembles

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In order to calculate the thermodynamic properties based upon statistical thermodynamics, let us discuss the concept of an ensemble of systems. An ensemble is a collection of a very large number of microstates, each constructed to be an instantaneous replica of the macroscopic properties of the particular system of interest.

In general, most physical systems are in thermal contact with the environment and exchange their energy with the environment. This thermal contact allows energy to be exchanged between the system and its environment in the form of heat. Since such system of interest is usually small in comparison to its environment, we assume that any change in the energy of the system does not significantly affect temperature of the environment which is referred to the heat reservoir or heat bath. The ensemble which describes the probability distribution of microstates in thermal equilibrium with the environment is known as the canonical ensemble (CE). In CE, all microstates have the same volume V , the same temperature T and the same total number of atoms or ions N with each other.

Considering an infinitely large number of microstates of the system in CE, the probability P_i of a microstate i with energy E_i is given by

$$P_i = \frac{1}{Z} \exp\left(-\frac{E_i}{k_B T}\right) \quad (1)$$

where Z is a normalisation constant; k_B , the Boltzmann's constant, and T represents the absolute temperature. Since $\sum_i P_i = 1$,

$$Z = \sum_i \exp\left(-\frac{E_i}{k_B T}\right) \quad (2)$$

which is known as the partition function or sum of state (Zustandssumme) of CE. One can obtain the ensemble average of the thermodynamic quantity of interest $\langle A \rangle$ from

$$\langle A \rangle = \sum_i A_i P_i = \frac{1}{Z} \sum_i A_i \exp\left(-\frac{E_i}{k_B T}\right) \quad (3)$$

where A_i is the thermodynamic quantity A of the microstate i .

As a matter of fact, one can generate only a finite number n of the total number of microstates N , and hence estimate the mean value $\langle A \rangle$ by

$$\begin{aligned} \langle A \rangle &= \sum_i^N A_i \exp\left(-\frac{E_i}{k_B T}\right) / \sum_i^N \exp\left(-\frac{E_i}{k_B T}\right) \\ &\approx \sum_i^n A_i \exp\left(-\frac{E_i}{k_B T}\right) / \sum_i^n \exp\left(-\frac{E_i}{k_B T}\right) \end{aligned} \quad (4)$$

In order to save a lot of time on calculation of the ensemble average, we generally use an importance sampling method by generating the configuration of microstates according to a probability distribution function π_i as

$$\langle A \rangle \approx \sum_i^n A_i \frac{1}{\pi_i} \exp\left(-\frac{E_i}{k_B T}\right) / \sum_i^n \frac{1}{\pi_i} \exp\left(-\frac{E_i}{k_B T}\right) \quad (5)$$

where π_i is generally accepted as the Boltzmann probability itself,

$$\pi_i = \exp\left(-\frac{E_i}{k_B T}\right) / \sum_i^n \exp\left(-\frac{E_i}{k_B T}\right) \quad (6)$$

In this case $\langle A \rangle$ can be written as

$$\langle A \rangle \approx \frac{1}{n} \sum_i^n A_i \quad (7)$$

The above importance sampling method is so-called Metropolis algorithm²⁴ that is described in detail as follows:

- (i) Establish an initial configuration of the system,
- (ii) Make a random trial change in the initial configuration,
- (iii) Compute the change in the energy of the system ΔE due to the trial change,
- (iv) If ΔE is less than or equal to zero in value, accept the new configuration and go to the step (vii),
- (v) If ΔE is positive in value, compute the transition probability $W_{tr} = \exp(-\Delta E/k_B T)$,
- (vi) If W_{tr} is larger in value than a random number generated between 0 and 1, accept the new configuration; otherwise, retain the previous configuration,
- (vii) Determine the value of the thermodynamic quantities of interest, and then repeat the steps (ii) through (vii) to obtain a sufficient number of the configurations of the system.

On the other hand, in case the system exchanges both heat and mass with its environment, the probability distribution of microstates of the system is described by the grandcanonical ensemble (GCE) in which all microstates have the same V , T and chemical potential μ with each other. In GCE, the probability P_i of a microstate i with energy E_i is written as

$$P_i = \frac{1}{\Xi} \exp\left(-\frac{E_i}{k_B T}\right) \exp\left(\frac{\mu N}{k_B T}\right) \quad (8)$$

where Ξ is the partition function of GCE given by

$$\Xi = \sum_N \sum_i \exp\left(-\frac{E_i}{k_B T}\right) \exp\left(\frac{\mu N}{k_B T}\right) \quad (9)$$

According to the definition of the mean value, the ensemble average of the thermodynamic quantity of interest $\langle A \rangle$ in GCE can be obtained from

$$\begin{aligned} \langle A \rangle &= \sum_N \sum_i P_i A_i \\ &= \frac{1}{\Xi} \sum_N \sum_i A_i \exp\left(\frac{\mu N}{k_B T}\right) \exp\left(-\frac{E_i}{k_B T}\right) \end{aligned} \quad (10)$$

2.2. Ising and lattice gas models

Most popular model for the systems in statistical physics is an Ising model^{1,2,6-8} which is first used to investigate the 2nd

order phase transition, for example, from a paramagnet to a ferromagnet. In order to introduce the Ising model, let us consider each site i in the lattice associated with a number s_i meaning the spin of the site i , where $s_i = +1$ for an up-spin and $s_i = -1$ for a down-spin for magnetic moment. In this case, the total number of atoms or ions N in the lattice is equal to the total number of sites N_s of the lattice in value.

In the Ising model, the total energy of the lattice as Hamiltonian H in the presence of a magnetic field h is simply given by

$$H = -J \sum_{ij} s_i s_j - h \sum_{i=1}^N s_i \quad (11)$$

where J is the exchange constant which is a measure of interaction between the nearest neighbour spins, and s_j represents the spin of the site j which is the nearest neighbour of the site i . A particular configuration of the spins is specified by a set of variables $\{s_1, s_2, \dots, s_i, s_j, \dots, s_N\}$ for all the sites of the lattice. If $J > 0$, the favorable configuration of the spins is ferromagnetic; if $J < 0$, that configuration of the spins is antiferromagnetic.⁶⁾ In Eq. (11), the first summation over all the nearest neighbour spins in the lattice corresponds to the total interaction energy of the lattice.

If we interpret the down-spin as an occupied site by an atom or ion, and the up-spin as an empty site in the lattice, we can simply transform the Ising model to a lattice gas model. The lattice gas model has been also of great importance to investigate the 2nd order phase transition of solids with critical transition behaviour. In the lattice gas model, the total energy of the lattice H in the presence of a chemical potential μ is simply written as

$$H = J \sum_{ij} c_i c_j - \mu \sum_{i=1}^N c_i \quad (12)$$

where c_i is the occupation number of the site i which is related to s_i by $c_i = (1-s_i)/2$: if the site i is occupied by an atom or ion, $c_i = 1$ at $s_i = -1$; otherwise, $c_i = 0$ at $s_i = 1$. A particular configuration of the lattice is specified by the set of variables $\{c_1, c_2, \dots, c_i, c_j, \dots, c_N\}$ for all the sites of the lattice. In the case of the lattice gas model, the positive value of J in Eq. (12) means the repulsive interaction between atoms or ions, while the negative value of J indicates the attractive interaction.

In the lattice gas model, it should be noted that the total number of atoms or ions N in the lattice is less than or equal to the total number of sites N_s of the lattice in value. The difference between the Ising model and the lattice gas model is that the total number of atoms or ions is fixed in the former, whereas that total number of atoms or ions can be changed in the latter during the Monte Carlo procedure.

The simple algorithms commonly used to change the configuration of the system are the spin-exchange dynamics and the single spin-flip dynamics as shown in Figs. 1(a) and (b), respectively. One can readily expect that the total number of atoms or ions remains as invariant in the spin-exchange dynamics, while that total number of atoms or ions can be

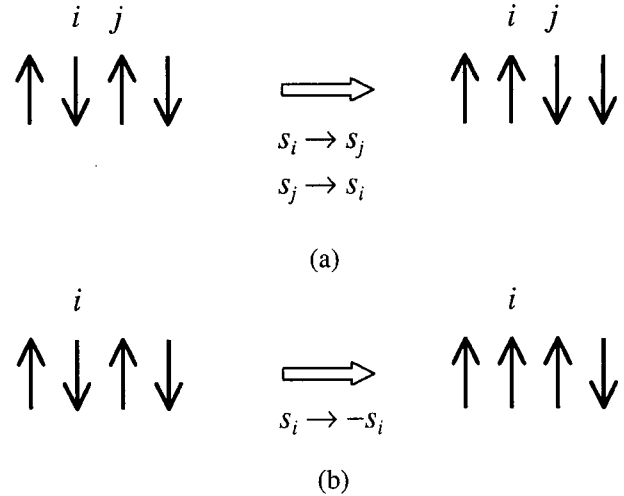


Fig. 1. Schematic diagrams of the changes in a configuration of a system by (a) spin-exchange algorithm (Kawasaki dynamics) and (b) single spin-flip algorithm (Glauber dynamics) for Monte Carlo simulation.⁴⁾

changed in the single spin-flip dynamics. Thus, these algorithms can describe two different ensembles: the former describes CE, whereas the latter does GCE.⁴⁾ Keeping in mind that the spin s_i is interpreted as the occupation number c_i , the spin-exchange and the single spin-flip dynamics can be also employed in the lattice gas model to change the configuration of the system in CE and GCE, respectively.

2.3. Monte Carlo calculation of thermodynamic quantities

Most thermodynamic studies by using the Monte Carlo method based upon the lattice gas model have focussed on determination of such thermodynamic quantities as the partial molar internal energy and entropy. Those partial quantities can be obtained by differentiation of the integral quantities given as a function of temperature or composition. In most cases, however, the integral quantities are not simply described as an analytical function of temperature or composition. It is thus necessary to evaluate the integral quantities at various temperatures and compositions by multiple Monte Carlo procedures. After that one can differentiate those integral quantities with respect to temperature and composition to obtain the partial quantities.

Instead of the crude method, we can easily calculate the partial quantities by a single Monte Carlo procedure at a given temperature²⁵⁾ according to the relationship between the partial quantities and the fluctuations in the integral quantities²⁶⁾. In GCE, the equilibrium fraction of the sites occupied by atoms or ions δ is obtained by averaging the occupation number c_i over all the sites in the lattice N_s from

$$\delta = \frac{1}{N_s} \sum_i c_i \quad (13),$$

at given μ and T with a single Monte Carlo procedure. According to Eq. (13), the plot of μ vs. δ can be obtained without multiple Monte Carlo procedures.

The partial molar internal energy \tilde{U} and entropy \tilde{S} at constant V and T can be also calculated by using the relationships between those partial quantities and the fluctuations in U and N about their mean values in GCE in a single Monte Carlo procedure. The partial molar internal energy \tilde{U} is described as a function of the independent variables μ , V and T ,

$$\tilde{U} = \left(\frac{\partial U}{\partial N}\right)_{V,T} = \left(\frac{\partial U}{\partial \mu}\right)_{V,T} / \left(\frac{\partial N}{\partial \mu}\right)_{V,T} \quad (14)$$

The partial derivatives in Eq. (14) can be obtained by differentiating the mean value of U and N with respect to μ .

According to the definition of the mean value, the average number of atoms or ions $\langle N \rangle$ in GCE is

$$\begin{aligned} \langle N \rangle &= \sum_N P_i N \\ &= \exp\left(\frac{Q}{k_B T}\right) \sum_N N \exp\left(\frac{\mu N}{k_B T}\right) \sum_i \exp\left(-\frac{E_i}{k_B T}\right) \end{aligned} \quad (15)$$

where Q is the grandcanonical ensemble potential²⁵. Differentiation of Eq. (15) with respect to μ at constant V and T gives

$$\begin{aligned} \left(\frac{\partial N}{\partial \mu}\right)_{V,T} &= \exp\left(\frac{Q}{k_B T}\right) \sum_N \left[\frac{N^2}{k_B T} + \frac{N}{k_B T} \left(\frac{\partial Q}{\partial \mu}\right) \right] \exp\left(\frac{\mu N}{k_B T}\right) \sum_i \exp\left(-\frac{E_i}{k_B T}\right) \end{aligned} \quad (16)$$

From the relationship of $dQ = -Vdp = -SdT - Nd\mu$ ²⁶, it can be readily seen that $(\partial Q/\partial \mu)_{V,T} = -\langle N \rangle$ and hence

$$\left(\frac{\partial N}{\partial \mu}\right)_{V,T} = \frac{1}{k_B T} (\langle N^2 \rangle - \langle N \rangle^2) = \frac{\text{Var}(N)}{k_B T} \quad (17)$$

where $\text{Var}(N)$ is the variance of N in GCE.

In addition, since the average internal energy $\langle U \rangle$ is

$$\langle U \rangle = \sum_N P_i U = \exp\left(\frac{Q}{k_B T}\right) \sum_N U \exp\left(\frac{\mu N}{k_B T}\right) \sum_i \exp\left(-\frac{E_i}{k_B T}\right) \quad (18)$$

the partial derivative of U with respect to μ at constant V and T is also given by

$$\begin{aligned} \left(\frac{\partial U}{\partial \mu}\right)_{V,T} &= \exp\left(\frac{Q}{k_B T}\right) \sum_N \left[\frac{UN}{k_B T} + \frac{U}{k_B T} \left(\frac{\partial Q}{\partial \mu}\right) \right] \\ &\quad \times \exp\left(\frac{\mu N}{k_B T}\right) \sum_i \exp\left(-\frac{E_i}{k_B T}\right) \\ &= \frac{1}{k_B T} (\langle UN \rangle - \langle U \rangle \langle N \rangle) = \frac{\text{Cov}(U, N)}{k_B T} \end{aligned} \quad (19)$$

where $\text{Cov}(U, N)$ is the covariance of U and N in GCE.

From Eqs. (14), (17) and (19), the partial molar internal energy \tilde{U} at constant V and T in GCE is

$$\tilde{U} = \frac{\text{Cov}(U, N)}{\text{Var}(N)} \quad (20)$$

Since μ is given as constant in GCE, the partial molar entropy \tilde{S} at constant V and T is expressed as

$$\tilde{S} = \frac{1}{T} \left[\frac{\text{Cov}(U, N)}{\text{Var}(N)} - \mu \right] \quad (21)$$

3. Application of Monte Carlo Method to Electrochemical Lithium Intercalation into LiMn_2O_4

3.1. Relationship between electrode potential and lithium content

The Monte Carlo methods based upon the lattice gas model have played an important role in our understanding of the thermodynamic properties of 2-dimensional adsorption and 3-dimensional intercalation of ions in the field of electrochemistry. Recently, the Monte Carlo methods have successfully applied to theoretically analyse the lithium intercalation into transition metal oxides involving the disorder to order phase transition in terms of the relationship between the electrode potential and lithium content.^{22,23} Among those transition metal oxides, let us apply the Monte Carlo method to investigate thermodynamics of the electrochemical lithium intercalation into the LiMn_2O_4 electrode in rechargeable lithium batteries.

For the Monte Carlo simulation, we employed the two sub-lattice model of the LiMn_2O_4 electrode well-established in the previous works^{22,23,27}. In consideration of the first- and second-nearest interactions between lithium ions in the LiMn_2O_4 electrode, Hamiltonian H of the lattice is defined as^{22,23}

$$H = J_1 \sum_{ij} c_i c_j + J_2 \sum_{ik} c_i c_k - (\varepsilon + \mu) \sum_i c_i \quad (22)$$

where J_1 and J_2 are the effective pairwise interaction parameters for the first- and second-nearest neighbouring lithium ions, respectively; ε , the effective binding energy between lithium ion and manganese oxide matrix; μ , the chemical potential of lithium ion; c_i , the local occupation number of the site i , and c_j and c_k represent the local occupation numbers of the first- and second-nearest neighbour sites, respectively; c_i , c_j or $c_k = 1$ if the site is occupied by lithium ion, and c_i , c_j or $c_k = 0$ otherwise.

As a matter of fact, the interaction parameters J_1 , J_2 and ε can not simply represent the direct interactions between lithium ions and oxide matrix. In the previous works^{22,23,27}, for the sake of simplicity, the effective values of those parameters were generally determined by fitting the electrode potential curve theoretically calculated by the Monte Carlo simulation to that curve experimentally measured, under the assumption that those parameters are invariant with lithium content during the lithium intercalation. In those works, the values of the effective interaction parameters were similarly taken as $J_1 = 37.5$ meV (the repulsive interaction), $J_2 = -4.0$ meV (the attractive interaction) and $\varepsilon = 4.12$ eV which allowed us to successfully approximate the thermodynamic properties of

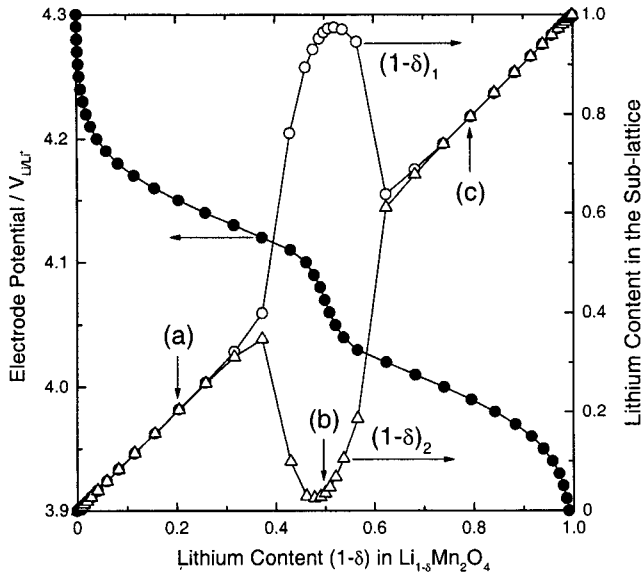


Fig. 2. Electrode potential vs. lithium content curve (●) and the plots of $(1-\delta)_1$ (○) and $(1-\delta)_2$ (△) with respect to $(1-\delta)$, theoretically obtained by the Monte Carlo method at $T = 298$ K. The average lithium content $(1-\delta)$ at the points (a), (b) and (c) are equal to 0.2, 0.5 and 0.8, respectively.

the LiMn_2O_4 electrode.^{22,23,27)}

Fig. 2 presents the electrode potential vs. lithium content curve and the plots of lithium content in one sub-lattice $(1-\delta)_1$ and lithium content in the other sub-lattice $(1-\delta)_2$ with respect to average lithium content $(1-\delta)$ in the lattice, theoretically obtained from Eq. (13) by the Monte Carlo method based upon the lattice gas model, noting that the electrode potential E is written as $E = -\mu/e$. The simulation was performed in GCE by using the Metropolis algorithm and the single spin-flip dynamics under the periodic boundary condition to minimise the finite size effect⁴⁾. In Fig. 2, as lithium content increased, the electrode potential curve showed a steep potential drop at $(1-\delta) = 0.5$, which is typical of the ordering of lithium ions in the electrode. The electrode potential curve theoretically calculated was well consistent in value and shape with that electrode potential curve experimentally measured^{23,27)}.

The ordering of lithium ions can be envisaged by considering the difference between $(1-\delta)_1$ and $(1-\delta)_2$ in value at the same $(1-\delta)$ in Fig. 2 with the aid of the local cross-sectional snapshots of the equilibrium configurations of the cubic lattice in Figs. 3(a), (b) and (c). At the point (a) in Fig. 2, $(1-\delta)_1$ and $(1-\delta)_2$ were the same in value. From the equilibrium configuration of the lattice in Fig. 3(a), which was simulated at the lithium content corresponding to the point (a) in Fig. 2, it is readily seen that lithium ions are randomly distributed over the lattice. This indicates that the lithium intercalation proceeds in the presence of the disordered phase.

At $(1-\delta) = 0.5$, corresponding to the point (b) in Fig. 2, $(1-\delta)_1$ and $(1-\delta)_2$ deviated most strongly from $(1-\delta)$. As shown in Fig. 3(b), the highly ordered phase appears, *i.e.* lithium ions mainly reside within one sub-lattice. It should be noted that most of lithium ions have purely the attractive second-nearest

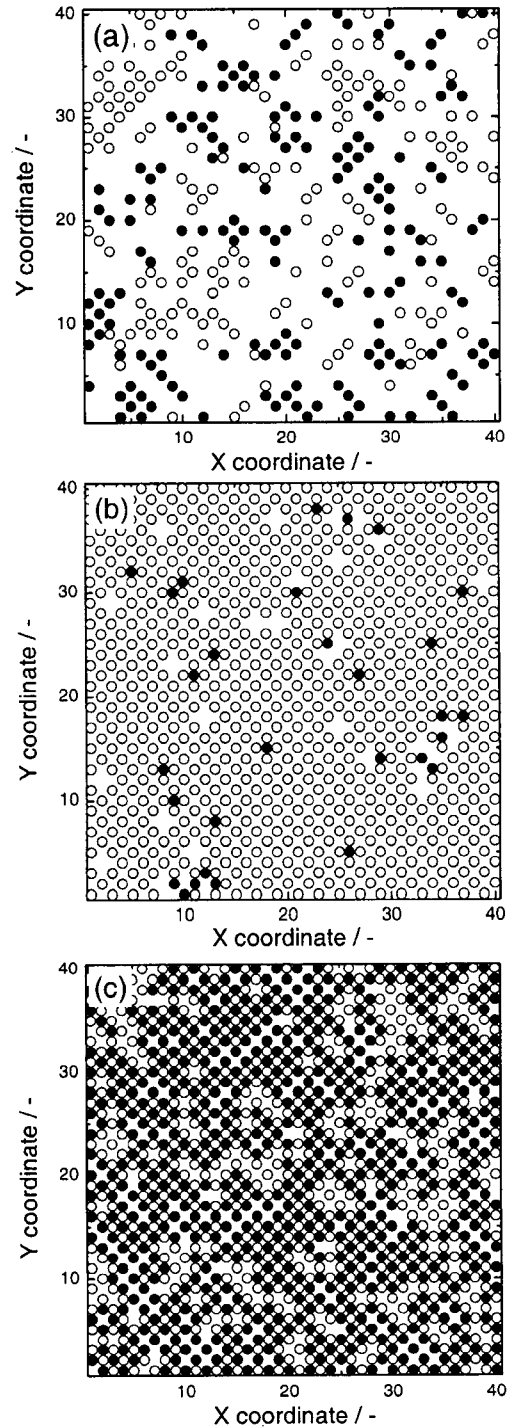


Fig. 3. Local cross-sectional snapshots of the equilibrium configurations of the cubic lattice obtained by the Monte Carlo method at (a) $(1-\delta) = (1-\delta)_1 = (1-\delta)_2 = 0.2$, (b) $(1-\delta) = 0.5$, $(1-\delta)_1 = 0.96$ and $(1-\delta)_2 = 0.04$, and (c) $(1-\delta) = (1-\delta)_1 = (1-\delta)_2 = 0.8$. The open and closed circles represent lithium ions at the sites of the sub-lattice 1 and 2, respectively.

neighbours to avoid the repulsive interaction that increases the ensemble energy of the lattice. As the concentration of lithium ion increases further, the order to disorder transition occurs because the random site occupation of lithium ions with both the first- and second-nearest neighbours (Fig. 3(c))

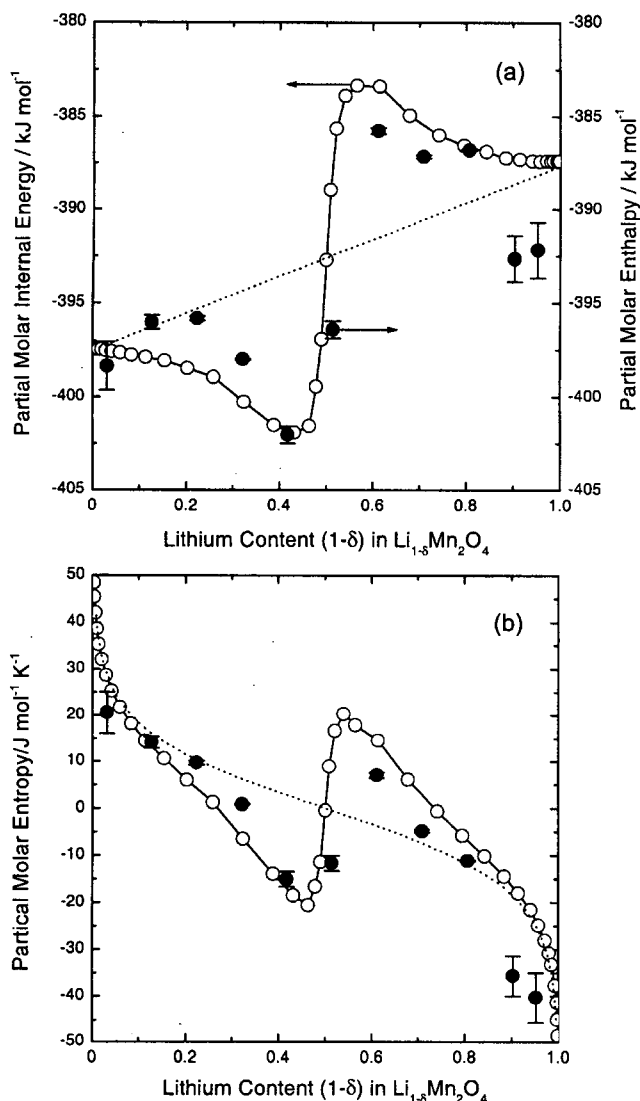


Fig. 4. Plots of (a) the partial molar internal energy \tilde{U}_{Li} and (b) entropy \tilde{S}_{Li} of lithium ion at constant volume V and temperature T with respect to $(1-\delta)$, theoretically calculated by the Monte Carlo method (○) at $T = 298$ K. The partial molar enthalpy and entropy experimentally determined at constant pressure P and temperature T from the measured temperature dependence of the electrode potential²³⁾ (●) are also plotted in figures. The dashed lines represent the partial molar internal energy and entropy calculated for the ideal solution.

reduces the ensemble energy of the lattice.

3.2. Partial molar thermodynamic quantities

Figs. 4(a) and (b) demonstrate the plots of the partial molar internal energy \tilde{U}_{Li} and entropy \tilde{S}_{Li} with respect to lithium content $(1-\delta)$, calculated from Eqs. (20) and (21), respectively, by the Monte Carlo method. The partial molar quantities experimentally measured from the temperature dependence of the electrode potential²³⁾ are also presented in figures. The partial molar quantities theoretically calculated by the Monte Carlo method well coincided in value and shape with the results experimentally measured.

All the partial molar quantities alike showed a negative

deviation below $(1-\delta) = 0.5$ and a positive deviation above $(1-\delta) = 0.5$ from those values calculated for an ideal solution. Here, the ideal solution means that the lithium intercalation proceeds into the disordered phase in the whole range of $(1-\delta)$. Below $(1-\delta) = 0.5$ the negative deviation is due to the attractive interaction energy between lithium ions in the same sub-lattice, as equivalent to a non-ideal solution with the attractive interaction, whose mixing enthalpy deviates negatively from that mixing enthalpy of the ideal solution. By contrast, above $(1-\delta) = 0.5$ the positive deviation is caused by the repulsive interaction energy between lithium ions in the other sub-lattice, as equivalent to a non-ideal solution with the repulsive interaction.

From the results theoretically calculated in the case of the LiMn₂O₄ electrode, one can easily expect that the Monte Carlo method based upon the lattice gas model is strongly applicable to theoretically investigate such thermodynamic properties as the electrode potential curve and the partial molar internal energy and entropy of the intercalation compounds.

4. Conclusions

The present article first introduced the basic concepts of the canonical and grandcanonical ensembles, and the Ising and lattice gas models in statistical physics for the Monte Carlo simulation, and then applied the Monte Carlo method based upon the lattice gas model to analyse thermodynamics of the lithium intercalation in the field of electrochemistry. From the comparison between the results theoretically calculated and experimentally measured on the LiMn₂O₄ electrode, it was found that the Monte Carlo method with appropriate algorithms is a reliable and powerful tool to analyse the intercalation of lithium ions interacting with each other from the thermodynamic view point.

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