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Thermodynamics and digital simulation of intercalation processes

Abstract The insertion of guest particles into insertion and intercalation compounds is reconsidered from the viewpoint of reversible thermodynamics. A correlation between enthalpy of formation and volume changes is described, the latter being accessible from X-ray data. The phase changes caused by guest insertion are emphasized. Tungsten bronzes are used as model data.

Keywords Intercalation · Insertion · Thermodynamics · Simulation · Diffusion

Symbols

C	concentration of mobile species (mol m^{-3})
C_p	specific heat (J mol^{-1})
D	diffusion coefficient (m^2 s^{-1})
D_0	thermodynamic diffusion coefficient (m^2 s^{-1})
index M	for the guest
index H	for the host
P	pressure, a scalar, independent of surface orientation (Pa)
V	partial molar volume of the systems (m^3 mol^{-1})
x	stoichiometric ratio of sites in the lattice occupied by the guest particles to their number ($0 < x < 1$) (dimensionless)
x_{max}	maximum available value of x for certain crystalline modifications to full saturation of the lattice by the guest
x'_{in}	minimum value of x which indicates the change of crystalline modification ($x'_{in} > x_{max}$)
R	ideal-gas constant (83,145 J K^{-1} mol^{-1})
t	time (s)
T	temperature (K)
α	linear thermal expansion (taken from literature)
γ	angle of lattice between a and b crystalline lattice parameters (deg)
γ_M, γ_H	activity coefficients (dimensionless)
Γ	Grüneisen constant
δ	a parameter
ΔH^{tr}	enthalpy change for transition (kJ mol^{-1})
ΔH^*	additional change of enthalpy (kJ mol^{-1})
κ	volume isothermal compressibility (Pa^{-1})
μ	chemical potential of the inserted species (J mol^{-1})
μ^0	standard chemical potential of the reaction (J mol^{-1})
$\mu^1(x)$	additional chemical potential corresponding to non-ideal behaviour of the system (J mol^{-1})
ξ	coordinate vector of concentrations at time t_j

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Introduction

The search for new sources of electrical energy has included batteries based on the electrochemical formation of intercalation or insertion compounds. In this way, batteries with very high specific energy have been designed and brought to commercial use. The fundamentals of the principle have been described [1].

The intercalation compound is formed from a solid host substance and particles of the guest. The host lattice contains regularly spaced and mutually interconnected

voids. As a rule, the term "intercalation" is used mostly for host substances of the layered type (such as graphite, TiS_2, MoS_2 or $LiCoO_2$), while the more general term "insertion" suits better those substances with a three-dimensional framework containing cavities connected by narrow channels. The conclusions presented in this paper were tested on a typical insertion system of tungsten bronzes. They follow from reversible thermodynamics and therefore should be valid generally.

Results and discussion

Definition of insertion compounds

Let an insertion compound M_xH be formed from the host substance (marked as H) and inserted metal ions M^+ according to the electrochemical reaction:

$$H + xM^+ + xe^- \rightarrow M_xH \tag{1}$$

The stoichiometric ratio x is the ratio of the number of lattice sites occupied by the guest to all their number so that $x = 1$ would correspond to full saturation of the lattice by the guest. Its value is dependent on the activity of the guest in the surroundings under the assumption that the non-stoichiometric compound is in equilibrium with its surroundings at actual potential. The value $x = 1$ cannot be reached sometimes owing to thermodynamic reasons; the maximum value of the fraction available at reasonable conditions would then be equal to $x_{max} < 1$.

Another phenomenon appears if the system can exist in two different crystalline modifications. Then the less saturated modification can exist only to some value of x_{max} and the other modification is created at some value of $x'_{min} > x_{max}$ and the modification change is accompanied by a non-zero change of enthalpy, ΔH^{tr}. Then a "solubility gap" appears and the change is a first-order phase transition, while a continuous change without any gap and with negligibly low enthalpy change appears sometimes and has to be considered as a second-order transition. In the latter case, both the thresholds are identical (i.e. $x_{max} = x'_{min}$). Both cases are known in the system of ReO_3-perovskite tungsten bronzes.

The well-known Faughnan-Armand equation [2, 3, 4] should be valid for the chemical potential of guest M in the compound:

$$\mu = \mu^0 + \mu^1(x) + RT \ln\left[\frac{x}{1-x}\right] \tag{2}$$

In this equation, μ is the chemical potential of the inserted species, μ^0 is the standard chemical potential of reaction 1, and $\mu^1(x)$ is the additional chemical potential corresponding to the non-ideal behaviour of the system at the guest concentration corresponding to the value of the stoichiometric ratio x. The symbols R and T have their conventional meanings.

Some standard state must be defined using similar equations. A hypothetical state with $x = 1$ and without any non-ideal behaviour (i.e. without any dependence of enthalpy change on the degree of saturation) must be considered here. Similarly, an ideal insertion compound is such that the term $\mu^1 = 0$. In other words, the energy of intercalation does not depend on x and the entropy is governed just by the randomness of guest distribution in the host.

Assumptions

The following assumptions were taken:

1. The distribution of particles M in the lattice is random (therefore, the entropy of insertion is related to the random occupation of vacant sites only).
2. The stoichiometric ratio x is defined within the range $0 < x < 1$.
3. If any phase transition appears in the process of insertion, then the enthalpy change of transition, ΔH^{tr}, is either small or virtually zero. In the latter case we can talk of a second-order transition; otherwise we assume the process is a first-order transition. The host lattice should not undergo any massive change in either type of transition.
4. The energy of free electron formation is constant and its contribution to the additional chemical potential may be neglected (i.e. as the energy of degenerated electron gas). This is valid with some approximation only; any kind of this sort of concentration-dependent energy should be included in the term μ^1 from the viewpoint of reversible macroscopic thermodynamics.
5. As in any condensed phase, the work against external pressure can be neglected. In other words, internal energy and enthalpy can be considered as equal.

Partial molar volume of metal in the compound

The insertion of guest particles M is accompanied by lattice expansion. In most cases this expansion is a linear function of the stoichiometric ratio of the guest x; this expansion does not exceed a few percent and the linear change is known as Vegard's law [5, 6]. Hence, this relation can be generalized easily to the molar volume V and its dependence on x:

$$V = V_H + xV_M \tag{3}$$

This formula can be derived from the influence of x on all lattice parameters by a simple geometric consideration; this is obvious in the case of anisotropic systems. This relation defines the partial molar volumes of the host V_H and guest particles V_M, the values of which can be evaluated from X-ray data easily.

Chemical potential of the metal in the compound

Let κ be the volume isothermal compressibility:

$$\kappa = \frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \tag{4}$$

Its value is considered as constant and independent of x as a first approximation. Moreover, it is a scalar quantity and corresponds to volume changes caused by an external pressure. Assuming formal thermodynamics to be valid, then the additional change of enthalpy associated with the insertion of the guest, ΔH^*, should be related to the volume by the relation of Eq. 5.

The additional change of enthalpy, ΔH^*, here representing the work absorbed by the cohesion or repulsion forces, can be expressed as:

$$\left(\frac{\partial^2 \Delta H^*}{\partial V^2}\right) = \frac{1}{V \cdot \kappa} \tag{5}$$

In accordance with assumptions (1) and (4), the additional chemical potential does not include any entropy contribution and can be estimated from the corresponding change of enthalpy, ΔH^*, as the first derivative $\partial \Delta H^* / \partial x$.

Introducing the molar volume of the host from Eq. 3 into Eq. 5 and performing a twofold integration of the result, both from the volume V_H to $V_H + x V_M$, we obtain the enthalpy change equal to the work spent against cohesion or repulsion forces in the lattice. Finally, the partial molar additional chemical potential $\mu^1(x)$ is obtained as the derivative of the last result by x. According to our assumptions, the entropy change does not contain any other contribution than the configuration term described by the logarithmic term in Eq. 2. Despite the chemical or physical nature of the system under investigation, this result follows from formal reversible thermodynamics and it must be valid for any kind of host-guest interaction and can therefore be generalized.

It follows that the partial molar enthalpy should contain the non-ideal contribution:

$$\mu^1(x) = \frac{1}{2\kappa}\frac{V_M^2}{V_H}x \tag{6}$$

Note that only the compressibility and the volume changes have to be evaluated experimentally. In this model, we consider that cohesion and repulsion forces in the lattice are in equilibrium and thus equal. Further, this quantity is always positive due to the quadratic term $V_M{}^2$.

Enthalpy of phase transitions

Let V_H be the molar volume of the pure host compound and V is the molar volume of the insertion compound. Then we can compute easily the work necessary for the volume change from the compressibility by twofold integration over the volume change. Then, a similar formula can be derived for the change of enthalpy of the phase transition, ΔH^{tr}:

$$\Delta H^{tr} = \frac{1}{2\kappa}\frac{(V - V_H)^2}{V_H}x \tag{7}$$

This formula should be valid only for the enthalpy of transition of various phases if the phase formation is just a change of symmetry, such as if two values of the lattice parameters a and b are approaching mutually or at an angle γ to 90° without any essential rearrangement of atoms in the lattice (e.g. the formation of tunnel or layered structures).

Diffusion kinetics of insertion

According to Darken theory, the diffusion coefficient D has to be corrected by the activity coefficient of the diffusing species. We suppose that the activity coefficient γ_M reflects the change of additional enthalpy ΔH^* and is related to the linear term in Eq. 2 only and its value should be derived easily in following way:

$$D = D_0\left(1 + \frac{\partial \ln\gamma_M}{\partial \ln C}\right) = D_0\left(1 + \frac{1}{2\kappa RT}\frac{V_M^2}{V_H}x\right) \tag{8}$$

where D_0 is the thermodynamic diffusion coefficient, γ_M is the activity coefficient of the guest and C is the concentration of the mobile species. Here, the linear term is accessible from crystallographic data as well. The ratio D/D_0 reaches considerable values and should be considered in numerical simulations of transients, etc. [7].

Tungsten bronzes as a model system

Tungsten bronzes have been used readily as an almost ideal system of insertion compounds. We therefore used them for demonstration of our model. Tungsten bronzes are insertion compounds of a general formula M_xWO_3. Depending on the value of x, their structures vary from monoclinic, orthorhombic, tetragonal II and, finally, to cubic for $x \to 1$. First, two transitions can be described as second-order transitions. The angle γ approaches to 90° first and the monoclinic structure becomes an orthorhombic one. When the x value increases beyond that point, the parameters a and b become equal gradually and, finally, the lattice is converted into a structure named tetragonal II when $a = b$ [11]. A gap between the tetragonal II and cubic (perovskite-like) structures indicates that some non-zero enthalpy change of transition is necessary for this process. Other structures such as hexagonal and tetragonal I are of different configurations, characterized by voids arranged in tunnels (two kinds in hexagonal bronzes and three in tetragonal) and our model should be considered as a rough approximation only in their case.

The value of the compressibility, $\kappa = 1.25 \times 10^{11}$ Pa^{-1}, was found experimentally for cubic tungsten bronzes [8], while an estimate from the Grüneisen constant $\Gamma = 1$ using the semi-empirical relation:

$$\Gamma = 3V \frac{\alpha}{\kappa C_p} \approx 1 \qquad (9)$$

offered the value $\kappa = 0.95 \times 10^{11}$ Pa^{-1}. Values of the specific heat C_p and the linear thermal expansion α were taken from the literature [9]. The partial molar volume V_M, evaluated from crystallographic data, and the maximum stoichiometric ratio, x_{max}, were compiled from references which are noted in Table 1.

Transition enthalpies

The data by Wechter et al. [6] were used for estimation of the partial molar volumes of the host in the case of cubic bronzes by the extrapolation to $x \to 0$, while Anderson's data [10] were used for monoclinic WO$_3$. The remaining data (for orthorhombic and tetragonal II bronzes) were taken from Reau et al. [11] in a similar way. The results are summarized in Table 1.

The calorimetric data were given by Dickens and Nield [12] for several x values; the ΔH^{tr} could be estimated from them by a linear extrapolation (6.5 kJ mol^{-1}). The data of Morozova and Ovcharova [13] yielded a value slightly higher in the same way (9.2 kJ mol^{-1}). Both are slightly higher than that evaluated from the partial molar volumes of pure WO$_3$ and of cubic bronzes by Wechter et al. (see Table 2). However, these values explain at least qualitatively the gap between $x_{max,tetr} < 0.1$ for the tetragonal II and $x'_{min,cub} > 0.37$ for cubic sodium bronzes.

The transition from monoclinic to orthorhombic and, finally, to tetragonal II is more or less continuous and

should be treated as a second-order phase transition, with discontinuities of the first derivatives of the fundamental thermodynamic functions (in other words, the discontinuities of partial molar quantities). There is no detectable change of partial molar volume connected with this transition. Therefore, the transition enthalpy change of these processes is small or zero.

Partial molar volume of guest particles

A collection of literature data is summarized in Table 1, where the ionic radius ρ, the change of enthalpy ΔH^* (corresponding to hypothetical $x = 1$) and the experimental value x_{max} are listed. Essentially, the elements entering tungsten oxide to create the bronze can be divided into three groups. The first two are the cubic bronzes and the bronzes possessing hexagonal tunnel structure, for which the relations should be taken with caution, as noted above. The guest in their case is denoted by an asterisk. Metals of these groups possess low electronegativity and their partial molar volume is controlled just by the geometry of their ions and the dimensions of the voids in the lattice. Therefore, their entry to the lattice is easy and rather high saturation (expressed as x_{max}) is possible. Contrary to this, metals and semimetals of the third group create bronzes with difficulty, which increases with increasing electronegativity. As a result, only very low saturation (i.e. $x_{max} << 1$) is possible in their case. The estimated enthalpy change ΔH^* for $x \to 1$ is quite high and this prevents the saturation to a higher level.

Voltammetry of insertion compounds

The theoretical description of diffusion processes in insertion compounds was given by Lovric et al. [14] recently, who introduced the idea of a concentration gap between two successive phases which depends on the value of x. Our model offers a deeper view on this topic. According to the Darken formula, the chemical diffusion coefficient should be a linear function of x. Similarly to our previous paper [7], waveforms known from experiments with insertion compounds can be obtained by numerical solution of a generalized second Fick law for the case of a variable diffusion coefficient. The modification of the Feldberg method, together with a

Table 2 Properties of host lattices of tungsten bronzes[a]

Lattice	a_0	b_0	c_0	γ_0	$V_H \times 10^6$	ΔH^{tr}	Ref.
Monoclinic	0.72885	0.7517	0.3835	90.90	31.374	–	[10]
Orthorhombic	0.72235	0.7488	0.3821	–	31.120	0.09	[11]
Tetragonal II	0.52199	–	0.3560	–	31.699	0.12	[11]
Cubic	0.37845	–	–	–	32.644	2.34	[6]

[a] a_0, b_0, c_0 (nm), γ_0 (deg) = lattice constants; V_H = partial molar volume of the host (m^3 mol^{-1}); ΔH^{tr} = enthalpy of transformation from monoclinic structure (kJ mol^{-1})

Table 1 Partial molar volumes of metal and compressibility of tungsten bronzes[a]

Guest	$V_M \times 10^{-6}$	ρ	ΔH^* for $x = 1$	x_{max}	Ref.
Li	–4.3	0.071	25.7	0.5	[15]
Na	2.12	0.095	6.26	∼1	[5]
K	4.07	0.135	23.1	0.6	[16]
Al*	6.47	0.052	58.3	0.135	[17]
Y*	4.87	0.096	33.0	0.15	[18]
La*	12.4	0.122	214.0	0.19	[19]
Pr*	10.7	0.118	187.0	–	[20]
Gd*	6.53	0.111	59.3	–	[19]
Lu*	0.64	0.099	0.570	–	[19]
Cd	11.68	0.099	197.5	0.15	[20]
Ge	16.46	0.053	376.8	0.07	[21]
Sb	16.85	0.076	395.3	0.07	[22]
As	15.64	0.058	354.0	0.06	[23]
Hg	109.98	0.119	17 600.0	0.0023	[10]

[a] ρ = ionic radius (nm); V_M = partial molar volume of metal in the bronze (m^3 mol^{-1}); ΔH^* = additional enthalpy of insertion (kJ mol^{-1}); x_{max} = maximum concentration of the guest known in the bronze; M* = guest possessing hexagonal tunnel structure

"regula falsi" solution of an electrochemical modification of Eq. 2 for evaluation of the concentration from the potential, was found to be the best approach. For mathematical details, see the Appendix.

A program has been created using Quick Basic 4.5. It describes the diffusion in a thin sheet, which is divided into 100 equidistant coordinate steps, and the equal exposition to electrode reactions from both sides of the sheet is supposed. The electrochemical insertion of a univalent cationic species according to Eq. 1 was considered. In following examples, voltammetry from a starting potential of –0.5 V to a vertex potential of +0.4 V or the opposite, from +0.4 V to a vertex point of –0.5 V, were used. Equation 2 was recalculated from enthalpy units to potential. Further, the value of $\mu^1(x)$ corresponding to the potential change of +0.5 V for the stoichiometric coefficient changing from 0 to 1 was chosen as an example.

The voltammograms computed with and without the application of the Darken correction term (Eq. 8) were evaluated. Simultaneously, the concentration profile at the vertex point was also recorded. The results are depicted in Figs. 1, 2, 3. The voltammograms obtained with the Darken correction are plotted by full lines, those obtained without it are plotted by dashed and dotted lines (see Fig. 1). They are rather unsymmetrical and their shape is well known from the electrochemistry of insertion compounds. The parts describing the insertion processes differ strongly from classical ones and they are rather flat and broad. Note that the cathodic part is rather distorted and similar to a wave, while the anodic part is more similar to a peak. No great difference between the voltammograms starting at +0.4 V

and/or –0.5 V appeared. The main difference in shape is that the peak starting at positive potential is sharper in the absence of the Darken term, while the increase of the apparent diffusion coefficient influences the descending part of the saturating peak, where the overall amount of
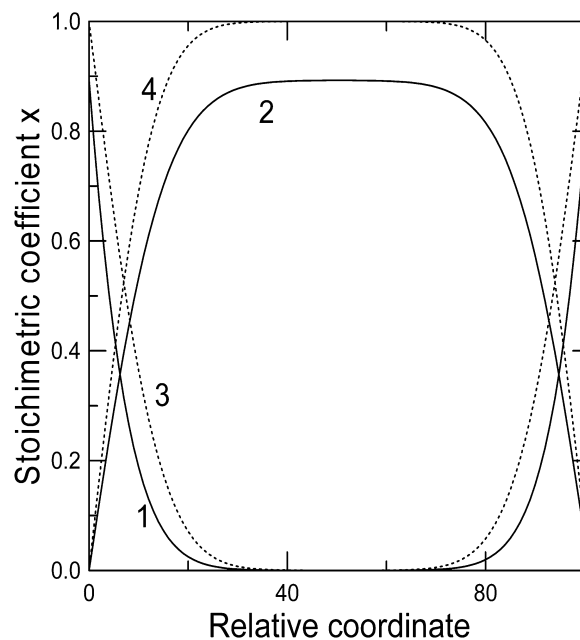

Fig. 2 The distribution of concentration expressed as a stoichiometric coefficient x at the vertex point of the voltammetric curve. *Solid curves*: distribution of x when the parameter μ^1 corresponds to a voltage span of 0.5 V; *curve 1*: from cathodic to anodic side; *curve 2*: from anodic to cathodic side. *Dotted curves 3 and 4*: the same for $\mu^1 = 0$. No Darken correction applied
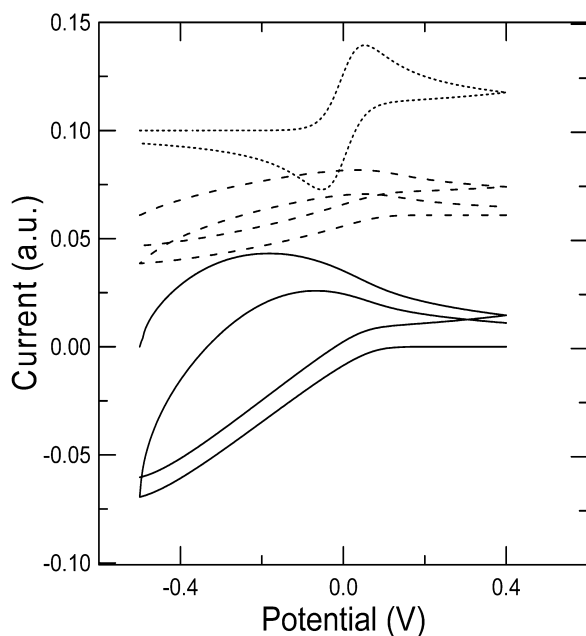

Fig. 1 The results of simulations of the diffusion processes. *Full line*: the linear term $\mu^1 = 0$. *Dashed and dotted lines*: values μ^1 corresponding to voltage shifts of 0.2 V and 0.5 V, respectively
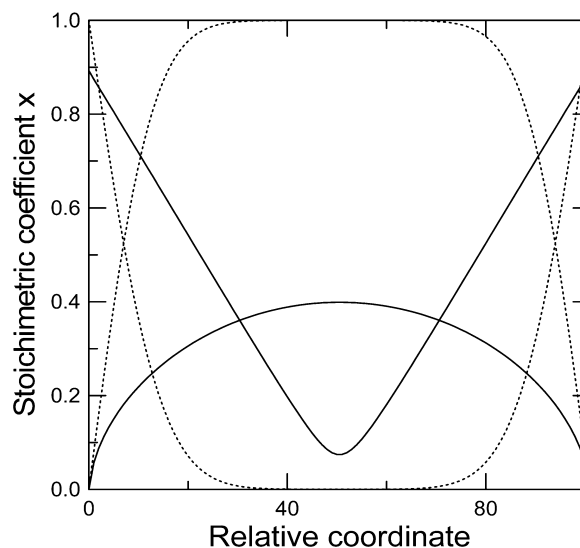

Fig. 3 The distribution of concentration expressed as the stoichiometric coefficient x at the vertex point of a voltammetric curve. *Solid curves*: distribution of x when the parameter μ^1 corresponds to a voltage span of 0.5 V; *curve 1*: from cathodic to anodic side; *curve 2*: from anodic to cathodic side. *Dotted curves 3 and 4*: the same for $\mu^1 = 0$. Darken correction according to Eq. 8 applied in computation of curves 1 and 2

inserted substance is greater. As a result, the peak is fairly broad and its maximum is shifted to more negative values. This follows from the fact that the conditions for the diffusion flow are given by the state of the sub-surface layer of the sheet. Finally, there is a marked difference in the magnitude of the current, which increased considerably by the application of the Darken term (full lines in Fig. 1) in comparison to the voltammograms not considering this correction (dashed lines in Fig. 1).

The voltammograms computed for $\mu^1(x) = 0$, which are quite similar to the classical result calculations (for example, see [24]), are given in Fig. 1 for comparison (see the dotted curve).

The explanation of these effects is given in Figs. 2 and 3, where the concentration profiles at the vertex potential are plotted for voltammograms computed without and with the Darken correction term and starting anodically as well as cathodically. In Fig. 2 we see that the concentration profile is similar for saturation and depletion if no Darken term is applied. The profiles correspond to the vertex point of the voltammetric curve. Owing to the values of the potentials and $\mu^1(x)$, the potential 0.4 V does not ensure complete removal of the guest from the sheet. Nevertheless, the profile is very similar to the inverse process. The profiles computed for $\mu^1 = 0$ are given for comparison (dotted line in Fig. 2).

The influence of the Darken term is shown in Fig. 3. Owing to the point-by-point change of the apparent diffusion coefficient, the diffusion flow changes considerably. Therefore, both curves differ considerably. For a saturation process (i.e. from $+0.4$ V to $–0.5$ V) the concentration distribution (expressed here as the stoichiometric coefficient x) at the vertex point is undoubtedly very different from the opposite case. Correspondingly, the profile inside the sheet must reflect this difference.

As was shown in our previous paper [7], general features of processes controlled by diffusion are not much influenced by the Darken term (for example, the proportionality of the current to $D^{1/2}$). However, absolute values of the current reflect this term and a correction coefficient should be used for estimation of the rate of diffusion.

The distortion of the concentration profiles shown in Fig. 3 should be taken into consideration, for example in the explanation of incomplete charging and discharging of intercalation electrodes in lithium batteries.

Any existence of a phase transition (both first order and second order) must be treated in a similar way. More thorough calculations of insertion processes will be the subject of a future paper. Several models of phase transitions in intercalation processes should be emphasized in a way that was indicated previously [14].

Conclusions

The formation of insertion compounds by insertion of atoms or ions into the host substance is accompanied by a change of thermodynamic parameters of the system. This change can be described as the influence of a stoichiometric ratio on the enthalpy of insertion. From formal reversible thermodynamics, this influence is correlated to volume changes if the volume compressibility is considered. In this way, volume changes as estimated by X-ray diffraction can be correlated to the electrochemical isotherm of insertion, to the changes of the diffusion coefficient, and to the stability of the insertion compounds.

The diffusion-controlled voltammetric curves were computed by the finite difference method and consideration of the distortion of the diffusion coefficient by the Darken correction was shown to be rather essential.

Appendix

The numerical solution of Eq. 2

The computation of value of x from the potential E or from the value of the chemical potential μ is based on following method. For a chemical potential sufficiently outside the interval $<\mu^0; \mu^0 + \mu^1>$, Eq. 2 can be approximated by a simple Nernstian form. For example, if the solution should be close to unity, then Eq. 2 can be replace by $\mu = \mu^0 + \mu^1 - RT\ln(1 - x)$, which can be solved easily and will yield a value of sufficient precision.

For other values, the well-known method "regula falsi" offers a solution which is stable numerically. We can select two approximations x_0 and x_1, compute corresponding values of μ, and obtain a secant to the function on the right-hand side of Eq. 2. When equating it to the value of the potential, we obtain a new approximation and replace one of the original values by it. We repeat the procedure until two successive approximations do not differ by more than some estimated precision.

Implicit solution of the second Fick law

We suppose a one-dimensional case (the diffusion in a finite sheet was used in this paper). The coordinate ξ is divided into n equidistant intervals $\Delta\xi$. Let $y(i)$ ($i = 0, ..., n$) be the vector of concentration y at time t_j. The corresponding vector $y'(i)$ valid for time $t_{j+1} = t_j + \Delta t$ is given by a series of equations:

$$y(i) = y'(i) - \delta[y'(i + 1) - 2y'(i) + y'(i - 1)] \qquad (A1)$$

The parameter $\delta = D\Delta t/\Delta\xi$ can be varied for each point. First, the values $y'(0)$ and $y'(n)$ are computed from the potential at time t_{j+1}. Then a set of n linear equations is formed and expressed as a tri-diagonal matrix, the

inversion of which by elimination is possible and stable enough for any reasonable value of the parameter δ. As usual, the current is evaluated by as $x(0) - x(1)$. For details, see Appendix B in [24].

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