REVIEW

Chemical diffusion of electroactive species in ionic compounds: a focus on chemical equilibrium constraint

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Abstract This work aims at considering the theoretical basis of chemical diffusion of electroactive species in ionic compounds, in particular from the perspective of the chemical equilibrium constraint. For this purpose, first a variety of descriptions on diffusivity are briefly summarised from the viewpoint of driving forces. Then, the equations to stand for the chemical diffusion behaviour are theoretically derived with and without the chemical equilibrium constraint. Finally, the two different situations above are critically compared to explore the origin of chemical diffusion in ionic compounds.

Keywords Chemical diffusion · Ionic compound · Chemical diffusivity · Component diffusivity · Chemical equilibrium constraint

Introduction

In many functional electrochemical devices such as batteries, sensors and fuel cells, low internal resistance is essential for the sustained high-rate operation. Specifically speaking, in most of mixed conductor electrodes (usually ionic compounds) [1, 2], the high rate performance is quite

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dependent upon the diffusion rate, i.e. diffusivity, of the electroactive species in the compounds. There are a number of descriptions on diffusivities. In this place, we briefly explain four typical definitions of diffusivity according to the driving forces of diffusion [3–24].

First, we consider the macroscopic mass transport through ionic compounds under the concentration gradient. From the Fick's first law, the flux density ji (mol cm^{-2} s^{-1}) of species i under the concentration gradient is defined as follows [17]:

$$j_i = -D_{F,i}\nabla c_i, \tag{1}$$

where $D_{F,i}$ (cm^2 s^{-1}) and c_i (mol cm^{-3}) represent the Fickian diffusivity and concentration of species i, respectively. ∇ means the gradient operator. It is noted that the flux density is linearly proportional to the concentration gradient, with a proportionality constant, $D_{F,i}$.

Second, in case that the species i transports under the chemical potential gradient, the flux density equation is given by [24]:

$$j_i = -\frac{D_{k,i}c_i}{RT}\nabla\mu_i \tag{2}$$

where $D_{k,i}$ (cm^2 s^{-1}) and μ_i (J) denotes the component diffusivity (self diffusivity divided by correlation factor) and chemical potential of species i, respectively. The notations R and T have their common meanings. From the definition of μ_i, Eq. 2 is rearranged into

$$j_i = -D_{k,i}c_i\nabla\ln\alpha_i, \tag{3}$$

where a_i (−) is the activity of species i. From Eq. 3, it is inferred that if the concentration is fixed, ji is linearly proportional to the logarithmic activity gradient, with a proportionality constant, $D_{k,i}$.

Third, let us consider that the species i transports under the electrochemical potential gradient. The flux density

equation under the electrochemical potential gradient is given by [24]:

$$j_i = -c_i b_i \nabla \eta_i \tag{4}$$

where b_i (cm^2 J^{-1} s^{-1}) and η_i (J) are the general mobility and electrochemical potential of species i, respectively. By considering the definition of η_i, we get

$$j_i = -c_i b_i \nabla \mu_i - z_i F c_i b_i \nabla \phi \tag{5}$$

Here, z_i (−) is the charge of species i and ϕ (V) means the local electrostatic potential (Galvani potential) across the diffusion medium. The notation F has its common meaning. In Eq. 5, the first term on the right-hand side represents the chemical contribution and the second term represents the electrical contribution to total transport, respectively.

By assuming that the chemical contribution to total transport in the presence of the potential gradient just equals that transport under the chemical potential gradient, the first term on the right-hand side of Eq. 5 can be expressed by considering Eq. 2 as [25, 26]:

$$j_i = -c_i b_i \nabla \mu_i = -\frac{D_{k,i} c_i}{RT} \nabla \mu_i \tag{6}$$

Therefore, it can be said that b_i is equivalent to $D_{k,i}/RT$ and hence Eq. 5 can be written as:

$$j_i = -\frac{D_{k,i} c_i}{RT} \nabla \mu_i - \frac{z_i F D_{k,i} c_i}{RT} \nabla \phi = -\frac{D_{k,i} c_i}{RT} (\nabla \mu_i - z_i F \nabla \phi). \tag{7}$$

This means that j_i is also linearly proportional to the $D_{k,i}$ value under the electrochemical potential gradient.

Finally, let us consider a process in which the transport of all species within the transport medium is involved, which is generally called chemical diffusion. In this case, the flux density is expressed in terms of the individual kinetic and thermodynamic properties of electroactive species. If there is no external electrical field, the overall charge neutrality holds:

$$\sum_k z_k j_k = 0, \tag{8}$$

where k represents an electroactive species.

Although the internal electrical field gradient $\nabla \phi$ is not known, it can be eliminated from Eqs. 7 and 8. Then the flux density equation of the neutral species i^* for chemical diffusion is expressed in terms of transport quantities and activity gradients related to electroactive species i and to all other species j [1].

$$j_{i^*} = -D_{k,i} \left[(1 - t_i) \frac{\partial \ln a_{i^*}}{\partial \ln c_{i^*}} - \sum_{j \neq i} t_j \frac{z_i}{z_j} \frac{\partial \ln a_j}{\partial \ln c_{i^*}} \right] \nabla c_i = \widetilde{D}_{i^*} \nabla c_i \tag{9}$$

Here, t_i (−) and $D_{k,i}$ mean the transference number and component diffusivity of the charged species i, respectively. $\widetilde{D}_{i^*}$ (cm^2 s^{-1}) is the chemical (apparent) diffusivity of the neutral form i^* for the charged species i. This equation includes the influence of the motion of species j other than species i on the motion of electroactive species i by the effect of the internal electrical field.

Among the four different diffusion equations briefly considered above, Eq. 9, containing the chemical diffusivity, is usually adopted to analyse the transport of electroactive species within the transport medium in the real electrochemical systems. It is noted that the component diffusivity $D_{k,i}$ is independent of the motion of any other species and is not influenced by the internal electrical field, whereas the chemical diffusivity $\widetilde{D}_{i^*}$ crucially depends upon the motion of any other species, as shown in Eq. 9. This indicates that the transport of electroactive species i is enhanced or retarded by the motion of the other species induced by the internal electric field [1, 3, 4].

The consideration of all of the electroactive species participating in the transport behaviour usually fails due to the complexity of the situation and the difficulty in reasonable evaluation of the parameters needed for calculation. In many electrochemical systems of practical importance, fortunately, the situation becomes simplified by the fact that two types of species dominate the transport phenomena. Under this circumstance, this work covers in the following sections the chemical diffusion behaviour in the electrochemical systems containing only two electroactive species. Specifically, the chemical diffusion equations were theoretically derived in the condition where two electroactive species with different charges diffuse under or without the chemical equilibrium constraint. Then, the experimental values of diffusivities were quantitatively compared to those theoretical values under these two constraints.

Theoretical approaches to chemical diffusion

Theoretical derivation of the chemical diffusivity without the chemical equilibrium

The general equation for the flux density of species i, j_i, is given by [27]:

$$j_i = -\frac{D_{k,i} c_i}{RT} \nabla \mu_i - \frac{z_i F}{RT} D_{k,i} c_i \nabla \phi + v c_i, \tag{10}$$

where v (cm s^{-1}) is the velocity of a volume element. Here, the first, second and third terms on the right in Eq. 10 are the contribution of diffusion, migration and convection, respectively, to total flux density. Assuming one-dimen-

sional transport and no convection flow, Eq. 10 is rearranged as follows:

$$j_i = -\frac{D_{k,i} c_i}{RT} \frac{\partial \mu_i}{\partial x} - \frac{z_i F}{RT} D_{k,i} c_i \frac{\partial \phi}{\partial x} \qquad (11)$$

Now, let us consider the following ionic compound, which consists of M^{z+} and X^{z-}.

$$M_A X_B = A M^{z+} + B X^{z-}$$
$$\text{with } A z_+ + B z_- = 0 \qquad (12)$$

where M^{z+} and X^{z-} mean cation (or hole) and anion (or electron), z_+ and z_- are the charges of M^{z+} and X^{z-}, respectively. A and B mean the stoichiometric numbers. If the neutral $M_A X_B$ species diffuses through the diffusion medium, under the electrochemical potential gradient in open-circuit condition, where the diffusion medium means ionic compound in this work, the net current of the diffusion medium should be zero, i.e. $i_{net} = i_{M^{z+}} + i_{X^{z-}} = 0$ [1, 28]. Hence, due to the relations of $i_{M^{z+}} = z_+ F J_{M^{z+}}$ and $i_{X^{z-}} = z_- F J_{X^{z-}}$, the flux of M^{z+} is correspondingly matched by an equivalent charge flux of X^{z-} in the same direction as follows:

$$A j_{M^{z+}} = B j_{X^{z-}} \text{ (charge neutrality constraint)} \qquad (13)$$

From Eq. 11, the flux densities of M^{z+} and X^{z-} are given by:

$$j_{M^{z+}} = -\frac{D_{k,M^{z+}} c_{M^{z+}}}{RT} \frac{\partial \mu_{M^{z+}}}{\partial x} - \frac{z_+ F}{RT} D_{k,M^{z+}} c_{M^{z+}} \frac{\partial \phi}{\partial x} \qquad (14)$$

$$j_{X^{z-}} = -\frac{D_{k,X^{z-}} c_{X^{z-}}}{RT} \frac{\partial \mu_{X^{z-}}}{\partial x} - \frac{z_- F}{RT} D_{k,X^{z-}} c_{X^{z-}} \frac{\partial \phi}{\partial x} \qquad (15)$$

Thus, from Eq. 13, we get

$$A\left(-\frac{D_{k,M^{z+}} c_{M^{z+}}}{RT} \frac{\partial \mu_{M^{z+}}}{\partial x} - \frac{z_+ F}{RT} D_{k,M^{z+}} c_{M^{z+}} \frac{\partial \phi}{\partial x} \right)$$
$$= B\left(-\frac{D_{k,X^{z-}} c_{X^{z-}}}{RT} \frac{\partial \mu_{X^{z-}}}{\partial x} - \frac{z_- F}{RT} D_{k,X^{z-}} c_{X^{z-}} \frac{\partial \phi}{\partial x} \right) \qquad (16)$$

By considering Eq. 12, Eq. 16 is rearranged into

$$A z_+ F \left(D_{k,M^{z+}} c_{M^{z+}} + D_{k,X^{z-}} c_{X^{z-}} \right) \left(\frac{\partial \phi}{\partial x} \right)$$
$$= -\left(A D_{k,M^{z+}} c_{M^{z+}} \frac{\partial \mu_{M^{z+}}}{\partial x} - B D_{k,X^{z-}} c_{X^{z-}} \frac{\partial \mu_{X^{z-}}}{\partial x} \right) \qquad (17)$$

Now, in addition to the flux constraint of Eq. 13, we consider two stoichiometric constraints as follows:

$$A c_{M^{z+}} = B c_{X^{z-}} \text{ (stoichiometric constraint)} \qquad (18)$$

$$A \frac{\partial c_{M^{z+}}}{\partial x} = B \frac{\partial c_{X^{z-}}}{\partial x} \text{ (stoichiometric constraint)} \qquad (19)$$

Here, Eq. 19 was directly derived by differentiating Eq. 18 with respect to the position coordinate x. Considering Eq. 18, Eq. 17 is given as:

$$A z_+ c_{M^{z+}} F \left(D_{k,M^{z+}} + \frac{A}{B} D_{k,X^{z-}} \right) \left(\frac{\partial \phi}{\partial x} \right)$$
$$= -A c_{M^{z+}} \left(D_{k,M^{z+}} \frac{\partial \mu_{M^{z+}}}{\partial x} - D_{k,X^{z-}} \frac{\partial \mu_{X^{z-}}}{\partial x} \right) \qquad (20)$$

Thus, the internal electrical field is expressed by:

$$\left(\frac{\partial \phi}{\partial x} \right) = -\frac{1}{z_+ F} \frac{1}{\left(D_{k,M^{z+}} + \frac{A}{B} D_{k,X^{z-}} \right)}$$
$$\times \left(D_{k,M^{z+}} \frac{\partial \mu_{M^{z+}}}{\partial x} - D_{k,X^{z-}} \frac{\partial \mu_{X^{z-}}}{\partial x} \right) \qquad (21)$$

Inserting Eq. 21 into Eq. 14, the flux equation yields

$$j_{M^{z+}} = -\frac{D_{k,M^{z+}} c_{M^{z+}}}{RT} \frac{\partial \mu_{M^{z+}}}{\partial x} + \frac{1}{RT}$$
$$\times \frac{D_{k,M^{z+}} c_{M^{z+}}}{\left(D_{k,M^{z+}} + \frac{A}{B} D_{k,X^{z-}} \right)}$$
$$\times \left(D_{k,M^{z+}} \frac{\partial \mu_{M^{z+}}}{\partial x} - D_{k,X^{z-}} \frac{\partial \mu_{X^{z-}}}{\partial x} \right) \qquad (22)$$

In order to obtain the chemical diffusivity of the neutral species $M_A X_B$, $\widetilde{D}_{M_A X_B}$, it is assumed that M^{z+} and X^{z-} show the ideal solution behaviour [28, 29]. This means that the stoichiometric compound can be regarded as an ideal solution with its molecular vacancy, and hence the activity of each species is just equal to be the concentration of each species. From this assumption and Eq. 19, the chemical potential gradient can be expressed as follows:

$$\frac{\partial \mu_{M^{z+}}}{\partial x} = RT \frac{\partial \ln a_{M^{z+}}}{\partial x} = \frac{RT}{c_{M^{z+}}} \frac{\partial c_{M^{z+}}}{\partial x} \qquad (23)$$

$$\frac{\partial \mu_{X^{z-}}}{\partial x} = RT \frac{\partial \ln a_{X^{z-}}}{\partial x} = \frac{RT}{c_{X^{z-}}} \frac{\partial c_{X^{z-}}}{\partial x} = \frac{RT}{c_{M^{z+}}} \frac{\partial c_{M^{z+}}}{\partial x} \qquad (24)$$

By considering Eqs. 23 and 24, Eq. 22 is simplified as:

$$j_{M^{z+}} = -D_{k,M^{z+}} \frac{\partial c_{M^{z+}}}{\partial x} + D_{k,M^{z+}} \frac{\left(D_{k,M^{z+}} - D_{k,X^{z-}} \right)}{\left(D_{k,M^{z+}} + \frac{A}{B} D_{k,X^{z-}} \right)} \frac{\partial c_{M^{z+}}}{\partial x} \qquad (25)$$

Thus,

$$j_{M^{z+}} = -\left[\frac{(A+B) D_{k,M^{z+}} D_{k,X^{z-}}}{\left(B D_{k,M^{z+}} + A D_{k,X^{z-}} \right)} \right] \frac{\partial c_{M^{z+}}}{\partial x} \qquad (26)$$

By assuming that chemical diffusion through the stoichiometric ionic compound may occur via vacancy mechanism satisfying the charge neutrality condition, the

flux and concentration of each species satisfies the following relationship.

$$j_{M_A X_B} = \frac{1}{A} j_{M^{z+}} = \frac{1}{B} j_{X^{z-}} \tag{27}$$

$$c_{M_A X_B} = \frac{1}{A} c_{M^{z+}} = \frac{1}{B} c_{X^{z-}} \tag{28}$$

The final flux equation of the neutral species $M_A X_B$ is

$$j_{M_A X_B} = -\left[\frac{(A+B) D_{k,M^{z+}} D_{k,X^{z-}}}{\left(B D_{k,M^{z+}} + A D_{k,X^{z-}} \right)} \right] \frac{\partial c_{M_A X_B}}{\partial x} = -\widetilde{D}_{M_A X_B} \frac{\partial c_{M_A X_B}}{\partial x} \tag{29}$$

Therefore, $\widetilde{D}_{M_A X_B}$ is determined as follows:

$$\widetilde{D}_{M_A X_B} = \frac{(A+B) D_{k,M^{z+}} D_{k,X^{z-}}}{B D_{k,M^{z+}} + A D_{k,X^{z-}}} \tag{30}$$

As an illustration of the effect of charge separation, it is instructive to consider the following two extremely limiting cases.

(First case)

$$\text{for } D_{k,M^{z+}} \gg D_{k,X^{z-}}, \text{ then } \widetilde{D}_{M_A X_B} = \frac{(A+B)}{B} D_{k,X^{z-}} \tag{31}$$

(Second case)

$$\text{for } D_{k,X^{z-}} \gg D_{k,M^{z+}}, \text{ then } \widetilde{D}_{M_A X_B} = \frac{(A+B)}{A} D_{k,M^{z+}} \tag{32}$$

Equations 31 and 32 tell us that the species with lower diffusion rate determines the chemical diffusion rate. In addition, the faster diffusing species accelerates the motion of the slower species by the factor of $(A+B)/B$ and $(A+B)/A$ for the first case and the second case, respectively.

The relation derived above, Eq. 30, has applied to the real systems to investigate the chemical diffusion through the ionic compounds via vacancy mechanism such as Al_2O_3, TiO_2, BeO and MgO during creep or the sintering process [28–34]. An exemplary study is that on the chemical diffusion of BeO during diffusional creep [30]. During diffusional creep, the defects are formed by a tensile stress, and the formation rate of the defects is determined by the chemical diffusivities of Be or O since the rate of diffusional creep is controlled by diffusion. In the case of Be defect formation, the values of and in Eq. 30 are 1 and 2, respectively. Hence, Eq. 30 is given as

$$\widetilde{D}_{Be} = \frac{3 D_{k,Be^{2+}} D_{k,e}}{2 D_{k,Be^{2+}} + D_{k,e}} \tag{33}$$

where $\widetilde{D}_{Be}$ is the chemical diffusivity of the neutral species Be, and $D_{k,Be^{2+}}$ and $D_{k,e}$ represent the component diffusivities of Be^{2+} ion and e, respectively.

It is well-known that electron diffusion is much faster than Be^{2+} diffusion and hence the diffusion of Be is controlled by Be^{2+} diffusion process. However, the chemical diffusivity of Be, $\widetilde{D}_{Be}$ is far from the $D_{k,e}$ value, but is close to be three times greater than the $D_{k,Be^{2+}}$ value, as expected in Eq. 33. This result indicates that the rate of diffusional creep is controlled by the component diffusivity of the slower Be^{2+}, but the diffusion of Be^{2+} is accelerated by the higher rate of e movement.

Theoretical derivation of the chemical diffusivity with the chemical equilibrium

In the previous section, to derive the transport equation for $M_A X_B$, it is assumed that the electroactive species of M^{z+} and X^{z-} show the ideal solution behaviour. In the real situation, however, this assumption is not always satisfied. For this reason, to quantitatively derive the relation between the chemical potential gradient of M^{z+}, $\partial \mu_{M^{z+}} / \partial x$, and the chemical potential gradient of neutral species $M_A X_B$, $\partial \mu_{M_A X_B} / \partial x$, the chemical equilibrium constraint is frequently introduced by researchers to explain the real situation [1, 35]. Let us consider the following electrochemical reaction (Eq. 12) in the same manner as described in the preceding section, "Theoretical derivation of the chemical diffusivity without the chemical equilibrium".

If the electrochemical species is locally in the equilibrium with the diffusion medium during chemical diffusion, the general relationship of the chemical equilibrium constraint is given by [36]:

$$\eta_{M_A X_B} = A \eta_{M^{z+}} + B \eta_{X^{z-}} \tag{34}$$

From the definition of the electrochemical potential, Eq. 34 is rearranged to

$$\mu_{M_A X_B} = A(\mu_{M^{z+}} + z_+ F\phi) + B(\mu_{X^{z-}} + z_- F\phi) = A\mu_{M^{z+}} + B\mu_{X^{z-}} \tag{35}$$

Considering its differentiation form

$$\frac{\partial \mu_{M_A X_B}}{\partial x} = A \frac{\partial \mu_{M^{z+}}}{\partial x} + B \frac{\partial \mu_{X^{z-}}}{\partial x} \tag{36}$$

the flux equation of Eq. 22 can be written as

$$j_{M^{z+}} = -\frac{D_{k,M^{z+}} c_{M^{z+}}}{RT}$$
$$\times \left[\frac{\partial \mu_{M^{z+}}}{\partial x} + \frac{B}{B D_{k,M^{z+}} + A D_{k,X^{z-}}} \left(D_{k,M^{z+}} \frac{\partial \mu_{M^{z+}}}{\partial x} - D_{k,X^{z-}} \frac{\partial \mu_{X^{z-}}}{\partial x} \right) \right] \tag{37}$$

By inserting Eqs. 27, 28 and 36 into Eq. 37, the flux equation in the ionic compound is then

$$j_{M_A X_B} = -\frac{c_{M_A X_B}}{RT} \frac{D_{k,M^{z+}} D_{k,X^{z-}}}{B D_{k,M^{z+}} + A D_{k,X^{z-}}} \left(\frac{\partial \mu_{M_A X_B}}{\partial x} \right) \quad (38)$$

Here, the $c_{M_A X_B}$ value means the concentration of neutral species $M_A X_B$, which can diffuse through the ionic compound via vacancy mechanism.

Now, considering the following definition of the chemical potential

$$\frac{\partial \mu_{M_A X_B}}{\partial x} = RT \frac{\partial \ln a_{M_A X_B}}{\partial x} = \frac{RT}{c_{M_A X_B}} \frac{\partial \ln a_{M_A X_B}}{\partial \ln c_{M_A X_B}} \frac{\partial c_{M_A X_B}}{\partial x} \quad (39)$$

Equation 38 is finally given by:

$$j_{M_A X_B} = -\frac{D_{k,M^{z+}} D_{k,X^{z-}}}{B D_{k,M^{z+}} + A D_{k,X^{z-}}} \frac{\partial \ln a_{M_A X_B}}{\partial \ln c_{M_A X_B}} \left(\frac{\partial c_{M_A X_B}}{\partial x} \right) \quad (40)$$

Accordingly, we get

$$\widetilde{D}_{M_A X_B} = -\frac{D_{k,M^{z+}} D_{k,X^{z-}}}{B D_{k,M^{z+}} + A D_{k,X^{z-}}} \frac{\partial \ln a_{M_A X_B}}{\partial \ln c_{M_A X_B}} \quad (41)$$

Similar to the section "Theoretical derivation of the chemical diffusivity without the chemical equilibrium," let us consider the following two extremely limiting cases.

(First case)

for $D_{k,M^{z+}} \gg D_{k,X^{z-}}$, then $\widetilde{D}_{M_A X_b} = \frac{D_{k,X^{z-}}}{B} \frac{\partial \ln a_{M_A X_B}}{\partial \ln c_{M_A X_B}}$

$$(42)$$

(Second base)

for $D_{k,X^{z-}} \gg D_{k,M^{z+}}$, then $\widetilde{D}_{M_A X_B} = \frac{D_{k,M^{z+}}}{A} \frac{\partial \ln a_{M_A X_B}}{\partial \ln c_{M_A X_B}}$

$$(43)$$

Equations 42 and 43 imply that the species with slower diffusion rate has a great effect on the rate of chemical diffusion. Nevertheless, as compared with the case where the chemical equilibrium constraint is not considered, the role of the slower species in the $M_A X_B$ diffusion is not so decisive. In other words, the diffusion rate of $M_A X_B$ can be higher or lower than the rate of slower species, which crucially depends upon the value of $\partial \ln a_{M_A X_B} / \partial \ln c_{M_A X_B}$. In the first case, the $M_A X_B$ diffusion is more facile/sluggish than the diffusion of slower species X^{z-} when the $\partial \ln a_{M_A X_B} / \partial \ln c_{M_A X_B}$ value is higher/lower than B. The similar argument is valid for the second case.

The diffusion mechanism in a number of ionic compounds has been analysed on the basis of the above concept [1, 37–43]. The study on the kinetics of lithium intercalation into transition metal oxides such as $Li_\delta V_2 O_5$ [44, 45],

$Li_{1-\delta} Mn_2 O_4$ [46, 47], $Li_{1-\delta} CoO_2$ [48] and $Li_{1-\delta} N_{1-y} Co_y O_2$ [49] is a typical example. For the diffusion of Li through $Li_\delta V_2 O_5$ [2, 44, 45], Eq. 41 can be written as

$$\widetilde{D}_{Li} = \frac{D_{Li^+} D_e}{D_{Li^+} D_e} \frac{\partial \ln a_{Li}}{\partial \ln c_{Li}} \quad (44)$$

Since electrons move very fast in typical intercalation compounds, the rate of chemical diffusion of Li is critically dependent on the diffusion of Li^+. Accordingly, Eq. 44 can be rearranged by considering the Nernst–Einstein relation as follows [1]

$$\widetilde{D}_{Li} = D_{Li^+} t_e \frac{\partial \ln a_{Li}}{\partial \ln c_{Li}} \quad (45)$$

Comparing the chemical diffusivity of Eq. 45 with that chemical diffusivity for ideal system, two extra parameters are introduced: (1) the transference number of electron t_e and (2) $\partial \ln a_{Li} / \partial \ln c_{Li}$. The former and the latter may be experimentally determined by the polarisation (or transference) and the emf measurement as a function of the composition, respectively. The experimental methods were detailed elsewhere [1, 47, 49].

From the analysis of the experimental results under the assumption of purely electronic conductor, i.e. $t_e \approx 1$ [2, 44, 45], it is suggested that the rate of chemical diffusion of Li is controlled by the component diffusivity of the slower diffusing ion Li^+ and the diffusion of Li^+ is accelerated by the diffusion of the faster electron. Also, the degree of acceleration depends critically on the $\partial \ln a_{Li} / \partial \ln c_{Li}$ value, which varies with the composition and temperature.
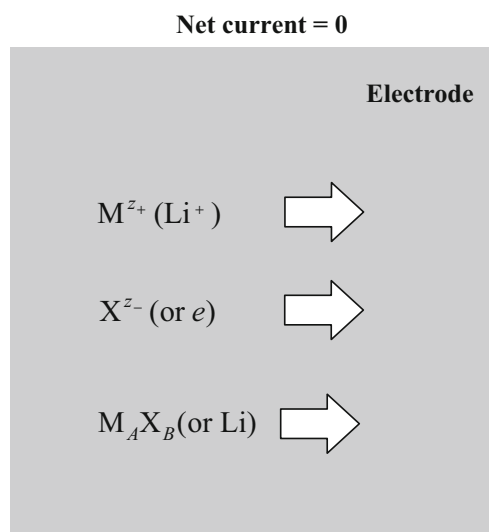

Fig. 1 Schematic representation of chemical diffusion in open-circuit condition

Comparative discussion on two different approaches

The equation for the chemical diffusivity determined without considering the chemical equilibrium constraint, i.e. Eq. 30, can be used only when the ionic compound M_AX_B shows the ideal solution behaviour. On the other hand, in the real electrochemical system, Eq. 41 might be a more appropriate form to analyse the chemical diffusion phenomena. Now, it would be very interesting to compare these two cases in the same situation.

In case that M_AX_B shows the ideal solution behaviour, the value of $\partial \ln a_{M_AX_B} / \partial \ln c_{M_AX_B}$ equals unit, and hence Eq. 41 can be rearranged to
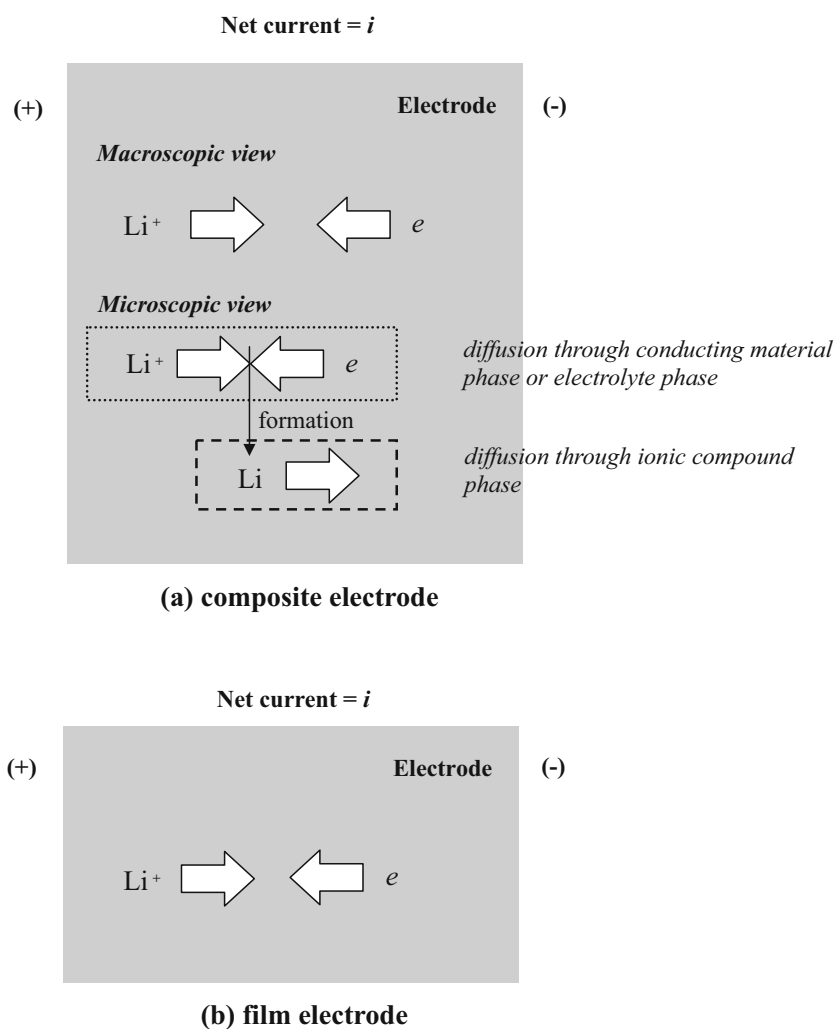
$$\widetilde{D}_{M_AX_B} = \frac{D_{k,M^{z+}} D_{k,X^{z-}}}{B D_{k,M^{z+}} + A D_{k,X^{z-}}} \quad (46)$$

It is noted that the expression of the chemical diffusivity in Eq. 46 is not the same as Eq. 30, which is derived under the assumption of the ideal solution behaviour. The difference between two equations might originate from the applica-bility of the chemical equilibrium constraint throughout the ionic compounds.

For the derivation of Eq. 41, it is assumed that the chemical potential of the neutral species M_AX_B is the sum of two chemical potentials of the charged species M^{z+} and X^{z-}. This assumption proves to be always proper at the entry and exit sides, but it is still open to discussion whether Eq. 36 is valid or not within the diffusion medium. This means that if the electroactive species might be locally activated during chemical diffusion through the diffusion medium, the chemical equilibrium constraint is no longer valid within the diffusion medium. In this case, the electroactive species is not thermodynamically in equilibrium with the diffusion medium and hence the expression of chemical diffusivity, Eq. 41, is no longer effective. From this argument, it is suggested that the expression of the chemical diffusivity is not uniquely defined, but it depends upon the thermodynamic or electrochemical condition of the diffusion media. Nevertheless, the origin of the difference still needs to be clarified.

Fig. 2 Schematic representation of chemical diffusion in current-flowing condition (current-consuming or current-producing condition) through **a** composite electrode composed of conducting material such as carbon, Li$^+$ containing electrolyte and ionic compound such as Li$_{1-\delta}$MO$_2$ (M=transition metal) and **b** film electrode composed of single ionic compound phase

Net current $= i$

(+)   Electrode   (-)

Macroscopic view

Li$^+$ ⟹   ⟸ e

Microscopic view

Li$^+$ ⟹✕⟸ e *diffusion through conducting material phase or electrolyte phase*

formation

Li ⟹   *diffusion through ionic compound phase*

(a) composite electrode

Net current $= i$

(+)   Electrode   (-)

Li$^+$ ⟹   ⟸ e

(b) film electrode

Over the several decades, the studies on chemical diffusion through the ionic compounds have been done extensively. They can be categorised into two different approaches: (1) analysis of the chemical diffusion using Eq. 30 out of consideration of the chemical equilibrium constraint [28–34] and (2) analysis of the chemical diffusion using Eq. 41 with consideration of the chemical equilibrium constraint [37–43]. However, the chemical diffusivities determined by two different approaches are very close to each other in value. This is presumably due to the small variation of the $(A+B)$ value. In general, the chemical diffusivity ranges from 10^{-10} to 10^{-5} cm^2 s^{-1}, but the $(A+B)$ value usually varies from 1 to 5. Hence, the measured chemical diffusivities are in the same order of magnitude, irrespective of the consideration of the $(A+B)$ value.

Concluding remarks and suggestions for future perspective

The present article first provides the brief overview of the chemical diffusion behaviour and then describes the theoretical derivations of two chemical diffusion equations with and out of consideration of the chemical equilibrium constraint. Finally it discusses comparatively two different diffusion equations. This article shows that one can construct a mathematical framework for modelling the chemical diffusion behaviour by adopting the appropriate charge neutrality and stoichiometric constraints. Nevertheless, it is yet to be clarified that two chemical diffusivities derived with and out of consideration of the chemical equilibrium constraint are different under the assumption of the ideal solution.

In addition, it should be mentioned that in this work the diffusion equation for chemical diffusion was derived in open-circuit condition where the net current equals zero, which makes Eqs. 13 and 19 valid. On the other hand, Eqs. 13 and 19 are no longer suitable in current-flowing condition and hence the different constraints need to be considered to derive the diffusion equation. It might be a challenge in this field to find out what constraints are appropriate for current-flowing condition, which means either the self-driven galvanic cell operating condition or the externally driven electrolysis cell-operating condition.

However, the types of electrode give us another task to be solved. That is, the approach to the composite and film electrode could be quite different. In the case of composite electrode, the electrode consists of the ionic compound, conducting material and electrolyte. In this case, chemical diffusion through the ionic compound in current-flowing condition is virtually identical to that in open-circuit condition, as shown in Figs. 1 and (2a), and hence the

charge neutrality constraints (Eqs. 13 and 19) and the chemical diffusivity of the neutral species (Eqs. 30, and 41) can be valid. This gives an example of Li diffusion through the Li$_{1-\delta}$CoO$_2$ composite electrode. The chemical diffusion of neutral Li through the Li$_{1-\delta}$CoO$_2$ composite electrode in current-flowing condition occurs just in the same way as the chemical diffusion in open-circuit condition.

On the contrary, in the case of film electrode, the cation moves in opposite direction of the electron flux due to the net current flow (Fig. 2b). Accordingly, Eq. 13 is no longer valid and at the same time Eq. 19 is not uniquely defined in current-flowing condition. This can be exemplified with an example of Li atom diffusion through the Li$_{1-\delta}$CoO$_2$ film electrode.

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