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Transport Equations for a Mixture of Two Binary
Molten Salts in a Porous Electrode

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Abstract

Concentrated solution theory is generalized to provide a framework for the description of isothermal transport processes in a mixture of two binary molten salts with a common ion. Electrochemical flux equations are derived for several, commonly-used reference velocities. Non-steady state material balances and conservation equations, based on the macrohomogeneous theory of porous electrodes, are also presented, together with a relationship for the ohmic potential drop in the solution. These equations can be used in conjunction with information on electrode kinetics to predict the behavior of molten salt electrolytes in porous media or in free electrolytic solutions.

Mass transfer in electrolytic solutions requires a description of the movement of mobile ionic species, together with material balances and equations for current flow and fluid mechanics. A consistent set of transport equations has been established for dilute solutions of electrolytes (1). This theory can be extended, with the use of the multicomponent diffusion equation, to treat the effects of convection, diffusion, and migration in concentrated solutions with two or more electroactive constituents (2,3). A parallel analysis, that employs the principles of irreversible thermodynamics, has considered transport phenomena in mixtures of two binary electrolytes with a common ion in a neutral solvent (4).

For porous media, a macroscopic model has been developed which can describe the essential features of porous materials in terms of readily accessible system parameters. This model can be used in conjunction with concentrated solution theory to elucidate transport processes in porous electrodes (5). With this approach, detailed studies have been made of electrodes with sparingly soluble reactants in concentrated binary electrolytes (6), and of the zinc electrode in a ternary electrolyte (7).

Recent interest in the development of high performance batteries and fuel cells with molten salt electrolytes has focused attention on the need for a rigorous analysis of transport phenomena in these systems. In particular, high temperature, lithium/iron sulfide batteries that are candidates for storage of off-peak electrical energy and for electric vehicle propulsion can use mixtures of binary molten

salts with a common ion, such as the lithium chloride/potassium chloride eutectic (8). These systems have been analyzed previously, but without due regard for the details of the transport phenomena (9). This paper presents a consistent set of transport equations for mixtures of two binary molten salts with a common ion. The equations can be applied to free electrolytic solutions or to electrolytes in porous media.

Development of flux equations

The analysis is based on the macrohomogeneous model for porous electrodes in which the solution and matrix phases are treated as superposed continua without regard for the actual geometric details of the pores (10). With this approach one can obtain a material balance for species i of the form

$$\frac{\partial(\epsilon c_i)}{\partial t} = a_{j_{in}} - \nabla \cdot \underline{N}_i \quad [1]$$

where $\underline{N}_i$ is the flux of species i in the pore solution averaged over the cross-sectional area of the electrode and where $a_{j_{in}}$ represents the transfer rate of species i from the solid phases to the pore solution per unit electrode volume. In addition, the superficial current density in the pore phase is given by

$$i_2 = F \sum_i z_i \underline{N}_i, \quad [2]$$

and the condition of electrical neutrality for each phase gives

$$\sum_i z_i c_i = 0 \quad [3]$$

for the electrolyte solution and specifies that the divergence of the total current density is zero. Explicit relationships for the fluxes in terms of the thermodynamic potential driving forces may be derived by inversion of the multicomponent diffusion equation (2)

$$c_i \nabla \mu_i = \frac{RT}{c_T} \sum_j \frac{c_i c_j}{D_{ij}} (\underline{v}_j - \underline{v}_i) \quad [4]$$

for each species in an isothermal, isobaric system with n components.

This set of $(n - 1)$ independent force balances defines the transport coefficients for binary interactions D_{ij} , which are functions of temperature, pressure, and composition only. The number of independent transport properties in Eq. [4] is $\frac{1}{2} n(n - 1)$ because D_{ii} is not defined and, by Newton's third law of motion, $D_{ij} = D_{ji}$. Specific combinations of these properties correspond to transport parameters that can be measured directly. The behavior of an electrolyte with three species can be described with a molecular diffusion coefficient, a transference number, and the bulk electrolyte conductivity, together with a single chemical potential or composition variable.

Consider a binary molten salt electrolyte with a common ion. The stoichiometries for dissociation of the individual salts, A and B, are described by

$$\begin{aligned} M_A &= v_1^A M_1^{z_1} + v_3^A M_3^{z_3} \\ M_B &= v_2^B M_2^{z_2} + v_3^B M_3^{z_3}, \end{aligned} \quad [5]$$

where M_3 is the chemical symbol for the common ion and where the electroneutrality condition dictates that

$$\sum_i z_i v_i^k = 0 \quad [6]$$

for the particular neutral salt, k . The chemical potential of each salt can then be expressed as a sum of the electrochemical potentials of the constituent charged species:

$$\mu_k = \sum_i v_i^k \mu_i. \quad [7]$$

For this system, Eq. [4] yields two independent equations which may be rearranged, with the introduction of the superficial current density from Eq. [2], to give expressions for the fluxes based on a reference velocity characteristic of the bulk motion of the electrolyte. For example, if the velocity v_3 of the common ion is chosen as the reference velocity, the superficial fluxes in a porous electrode are given by

$$\begin{aligned} \frac{N_1}{v_1} &= c_1 \frac{v_1}{v_1} = - \frac{\epsilon v_1^A v_3^B D}{RT} c_A \nabla \mu_A + \frac{t_{1-2}^c}{z_1 F} + c_1 \frac{v_1}{v_3} \\ \frac{N_2}{v_2} &= c_2 \frac{v_2}{v_2} = - \frac{\epsilon v_2^B v_3^A D}{RT} c_B \nabla \mu_B + \frac{t_{2-1}^c}{z_2 F} + c_2 \frac{v_2}{v_3} \\ \frac{N_3}{v_3} &= c_3 \frac{v_3}{v_3}, \end{aligned} \quad [8]$$

where $c_A = c_1/v_1^A$ and $c_B = c_2/v_2^B$. The effective diffusion coefficient based on a thermodynamic driving force is

$$D = \frac{z_3^2 c_T / v_1^A v_2^B}{\frac{z_1^2 c_1}{D_{23}} + \frac{z_2^2 c_2}{D_{13}} + \frac{z_3^2 c_3}{D_{12}}} \quad [9]$$

where c_T is the total concentration defined as $c_T = \sum_i c_i$. The transference numbers t_i^c relative to the common ion velocity can also be expressed in terms of the coefficients D_{ij} as,

$$t_2^c = 1 - t_1^c = \frac{\left(\frac{z_2}{D_{13}} - \frac{z_3}{D_{12}} \right)}{\left(\frac{z_2}{D_{13}} - \frac{z_3}{D_{12}} \right) + \frac{z_1 c_1}{z_2 c_2} \left(\frac{z_1}{D_{23}} - \frac{z_3}{D_{12}} \right)} \quad [10]$$

Equations [9] and [10] are directly analogous to the definitions of transport properties in concentrated binary electrolytes (1). In contrast to previous work on molten salt electrolytes (9), the transport parameters defined by the flux expressions (Eq. [8]) are measurable state properties, independent of the fluxes and driving forces for mass transfer.

In parallel with the transport theory for concentrated binary electrolytes, the molar average velocity (2), the mass average velocity (3), or the volume average velocity (11) can be used as alternative reference frames for the diffusion fluxes. With the molar average velocity,

$$\underline{v}^* = \sum_i \underline{N}_i / c_T, \text{ mole fractions of the salts, defined by } x_A = c_A / (c_A + c_B)$$

and $x_A + x_B = 1$, become a convenient way to express concentrations. The chemical potentials can be related to the composition variable by suitable definitions for activity coefficients of the salts, that are in turn linked through the Gibbs-Duhem equation. For example, if dissociation of the electrolyte is disregarded (12), one can obtain

$$\begin{aligned}\mu_A &= RT \ln \left(x_A^{v_1^A} \gamma_A^{\lambda_A^o} \right) \\ \mu_B &= RT \ln \left(x_B^{v_2^B} \gamma_B^{\lambda_B^o} \right)\end{aligned}\quad [11]$$

where the activity coefficients γ_k of the salts are based on the mole fraction of the molten salt mixture. The effective diffusion coefficient based on a gradient of mole fraction is then related to the thermodynamic diffusion coefficient by

$$D = \mathcal{D} \left(\frac{c_3}{c_A + c_B} \right) \left(v_1^A + \frac{d \ln \gamma_A}{d \ln x_A} \right). \quad [12]$$

Consequently, for the molar average reference velocity, we have

$$\begin{aligned}\underline{N}_1 &= - \frac{\varepsilon (c_A + c_B)^2 \mathcal{D} v_1^A v_1^B}{c_T} \nabla x_A + \frac{t_{1-2}^{\star}}{z_1 F} + c_1 \underline{v}^{\star} \\ \underline{N}_2 &= - \frac{\varepsilon (c_A + c_B)^2 \mathcal{D} v_2^B v_2^A}{c_T} \nabla x_B + \frac{t_{2-2}^{\star}}{z_2 F} + c_2 \underline{v}^{\star} \\ \underline{N}_3 &= - \frac{\varepsilon (c_A + c_B)^2 \mathcal{D} (v_3^A v_3^B - v_3^B v_3^A)}{c_T} \nabla x_A + \frac{t_{3-2}^{\star}}{z_3 F} + c_3 \underline{v}^{\star}\end{aligned}\quad [13]$$

where $v^A = v_1^A + v_3^A$, $v^B = v_2^B + v_3^B$, and where the transference numbers are given by

$$\begin{aligned} t_1^* &= \frac{(v_1^A v_3^B c_3 t_1^c - v_3^A v_2^B c_1)}{v_1^A v_3^B c_T} \\ t_2^* &= \frac{(v_2^B v_3^A c_3 t_2^c - v_1^A v_3^B c_2)}{v_2^B v_3^A c_T} \\ t_3^* &= 1 - t_1^* - t_2^* . \end{aligned} \quad [14]$$

With a mass average reference velocity defined by $\underline{v} = \sum_i \omega_i \underline{v}_i$ it is appropriate to use a mass fraction ω_i as a concentration variable. Equation [8] can then be rearranged to give

$$\begin{aligned} \underline{N}_1 &= - \frac{\epsilon \rho D v_1^A}{M_A} \nabla \omega_A + \frac{t_1 i_2}{z_1 F} + c_1 \underline{v} \\ \underline{N}_2 &= - \frac{\epsilon \rho D v_2^B}{M_B} \nabla \omega_B + \frac{t_2 i_2}{z_2 F} + c_2 \underline{v} \\ \underline{N}_3 &= - \epsilon \rho D \left(\frac{v_3^A}{M_A} - \frac{v_3^B}{M_B} \right) \nabla \omega_A + \frac{t_3 i_2}{z_3 F} + c_3 \underline{v} , \end{aligned} \quad [15]$$

where $\omega_1 = c_1 M_1 / \rho$, $\omega_A = c_A M_A / \rho$, and $\sum_{\ell=i \text{ or } k} \omega_\ell = 1$. The molecular weight of either salt is defined by $M_k = \sum_i v_i^k M_i$, and expressions for the transference numbers based on the mass average velocity, analogous to Eq. [14], are

$$\begin{aligned}
 t_1 &= \frac{(c_3^M t_1^c - v_2^B v_3^A c_A^M)}{\rho v_3^B} \\
 t_2 &= \frac{(c_3^M t_2^c - v_1^A v_3^B c_B^M)}{\rho v_3^A} \\
 t_3 &= 1 - t_1 - t_2 .
 \end{aligned}
 \tag{16}$$

Finally, the volume average velocity, $\underline{v} = \sum_i \bar{V}_i \underline{N}_i$, may be used, even though the partial molar volumes of individual ionic species are not accessible to experimental determination. It is required that the quantities $\bar{V}_i$ combine to yield partial molar volumes for the salts according to

$$\bar{V}_k = \sum_i v_i^k \bar{V}_i ,
 \tag{17}$$

where k represents either salt A or salt B. The flux relations are

$$\begin{aligned}
 \underline{N}_1 &= -\epsilon D \nabla c_1 + \left(\frac{t_1^c}{z_1} - c_1 Q \right) \frac{i_2}{F} + c_1 \underline{v} \\
 \underline{N}_2 &= -\epsilon D \nabla c_2 + \left(\frac{t_2^c}{z_2} - c_2 Q \right) \frac{i_2}{F} + c_2 \underline{v} \\
 \underline{N}_3 &= -\epsilon D \nabla c_3 - c_3 Q \frac{i_2}{F} + c_3 \underline{v}
 \end{aligned}
 \tag{18}$$

where Q is taken to be the quantity

$$Q = \sum_i \frac{t_i^c \bar{V}_i}{z_i} . \quad [19]$$

This quantity cannot be measured independently but, if the transference numbers are arbitrarily chosen to satisfy

$$\frac{t_1^c \bar{V}_1}{z_1 c_1} = \frac{t_2^c \bar{V}_2}{z_2 c_2} = \frac{t_3^c \bar{V}_3}{z_3 c_3} , \quad [20]$$

it may be shown that a consistent definition for Q would be

$$Q = \frac{-t_1^c t_2^c \left(\frac{\bar{V}_A}{v_3^A} - \frac{\bar{V}_B}{v_3^B} \right)}{z_3 (t_2^c - c_B \bar{V}_B)} . \quad [21]$$

Material balances and conservation equations

The flux relations given by Eqs. [13], [15], and [18] reflect the dependence of the motion of charged species on the driving forces for diffusion, migration, and convection in porous electrodes. Each set of flux expressions, relative to a specific reference velocity can be incorporated into the general material balance, Eq. [1], to give a continuity equation for the electrolyte in the absence of thermal and pressure diffusion. For salt A, these relationships are presented in Table 1 for the mass average, molar average, and volume average reference velocities, and for a reference frame based on the velocity of the common ion. These equations describe the time-dependent behavior of the electrolyte in terms of the composition variable most appropriate for the particular reference velocity used.

Table 1. Material balance equations for a mixture of two binary molten salts with a common ion.

Mass average reference velocity:

$$\rho \left(\epsilon \frac{\partial \omega_A}{\partial t} + \underline{v} \cdot \nabla \omega_A \right) = \nabla \cdot (\epsilon \rho D \nabla \omega_A) + r_{AB} + \frac{i_2}{z_3 F} \cdot \left(\frac{\omega_B^M}{v_3^A} \nabla t_1 - \frac{\omega_A^M}{v_3^B} \nabla t_2 \right) \quad [22-A]$$

Molar average reference velocity:

$$(c_A + c_B) \left(\epsilon \frac{\partial x_A}{\partial t} + \underline{v}^* \cdot \nabla x_A \right) = \frac{c_T}{c_A + c_B} \nabla \cdot \left(\frac{\epsilon (c_A + c_B)^2}{c_T} D \nabla x_A \right) + R_{AB} + \frac{i_2}{z_3 F} \cdot \left(\frac{x_B}{v_3^A} \nabla t_1^* - \frac{x_A}{v_3^B} \nabla t_2^* \right) \quad [22-B]$$

Volume average reference velocity:

$$\epsilon \frac{\partial c_A}{\partial t} + \underline{v}^\square \cdot \nabla c_A = \nabla \cdot (\epsilon D \nabla c_A) + R_A + \frac{\bar{v}_B}{z_3 F} i_2 \cdot \left(\frac{c_B}{v_3^A} \nabla t_1^\square - \frac{c_A}{v_3^B} \nabla t_2^\square \right) + \frac{c_A \epsilon D}{c_B \bar{v}_B} \nabla c_A \cdot \nabla \bar{v}_A \quad [22-C]$$

Common ion reference velocity:

$$(c_A + c_B) \left(\epsilon \frac{\partial c_A}{\partial t} + \underline{v}_3 \cdot \nabla x_A \right) = \frac{c_3}{c_A + c_B} \nabla \cdot \left(\frac{\epsilon (c_A + c_B)^2}{c_3} D \nabla x_A \right) + R_{AB} + \frac{i_2}{z_3 F} \cdot \left(\frac{x_B}{v_3^A} \nabla t_1^c - \frac{x_A}{v_3^B} \nabla t_2^c \right) \quad [22-D]$$

It may be shown that

$$R_A = R_{AB}(c_A + c_B)\bar{v}_B = \frac{r_{AB}\rho\bar{v}_B}{M_A M_B} \quad [23]$$

and that

$$R_A = a\bar{v}_B \left[\frac{j_{1n}}{v_1^A} \left(\frac{c_2 t_3^r}{v_2^B} + \frac{c_3 t_2^r}{v_3^B} \right) - \frac{j_{2n}}{v_2^B} \left(\frac{c_1 t_3^r}{v_1^A} + \frac{c_3 t_1^r}{v_3^A} \right) + j_{3n} \left(\frac{c_2}{v_2^B v_3^A} t_1^r - \frac{c_1}{v_1^A v_3^B} t_2^r \right) \right] \quad [24]$$

is independent of the reference frame, r . (Transference numbers with no superscript are relative to the mass average reference velocity.) Equations [1], [2], and [3] can also be combined with the flux relationships to give overall conservation or "continuity" equations, which indicate how the reference velocity and porosity change as a result of electrode reactions, migration, and changes in solution composition. For the four reference velocities considered, the corresponding conservation equations are given in Table 2, where

$$S_A^r = \frac{a}{v_1^A} \left(j_{1n} - \frac{t_1^r}{z_1} \sum_i z_i j_{in} \right) \quad [26]$$

and

$$S_B^r = \frac{a}{v_2^B} \left(j_{2n} - \frac{t_2^r}{z_2} \sum_i z_i j_{in} \right) \quad [27]$$

Table 2. Continuity equations for a mixture of binary molten salts with a common ion.

Mass average reference velocity:

$$\frac{\partial \epsilon}{\partial t} + \nabla \cdot \underline{v} = \bar{v}_A S_A + \bar{v}_B S_B + \frac{i_2}{z_3 F} \cdot \left(\frac{M_A}{v_3} \nabla t_1 + \frac{M_B}{v_3} \nabla t_2 \right) \quad [25-A]$$

Molar average reference velocity:

$$\frac{\partial \epsilon}{\partial t} + \nabla \cdot \underline{v}^{\star} = \bar{v}_A S_A^{\star} + \bar{v}_B S_B^{\star} + \frac{i_2}{z_3 F} \cdot \left(\frac{\bar{v}_A}{v_3} \nabla t_1^{\star} + \frac{\bar{v}_B}{v_3} \nabla t_2^{\star} \right) + \left(\bar{v}_A v_B - \bar{v}_B v_A \right) \nabla \cdot \left(\frac{\epsilon (c_A + c_B)^2 D}{c_T} \nabla x_A \right) \quad [25-B]$$

Volume average reference velocity:

$$\frac{\partial \epsilon}{\partial t} + \nabla \cdot \underline{v}^{\blacksquare} = \bar{v}_A S_A^{\blacksquare} + \bar{v}_B S_B^{\blacksquare} + \frac{i_2}{z_3 F} \cdot \left(\frac{\bar{v}_A}{v_3} \nabla t_1^{\blacksquare} + \frac{\bar{v}_B}{v_3} \nabla t_2^{\blacksquare} \right) - \frac{\epsilon D \nabla c_A}{c_B \bar{v}_B} \cdot \nabla \bar{v}_A \quad [25-C]$$

Common ion reference velocity:

$$\frac{\partial \epsilon}{\partial t} + \nabla \cdot \underline{v}_3 = \bar{v}_A S_A^c + \bar{v}_B S_B^c + \frac{i_2}{z_3 F} \cdot \left(\frac{\bar{v}_A}{v_3} \nabla t_1^c + \frac{\bar{v}_B}{v_3} \nabla t_2^c \right) + \left(\bar{v}_A v_3^B - \bar{v}_B v_3^A \right) \nabla \cdot \left(\frac{\epsilon (c_A + c_B)^2 D}{c_3} \nabla x_A \right) \quad [25-D]$$

for a specified reference frame, r . The parameters S_A^r and S_B^r might be regarded as effective rates of production of the salts per unit volume with due account for the influence of migration. The combination $S_A^{\bar{r}} + S_B^{\bar{r}}$ that appears in Eqs. [25-A] to [25-D] is not independent of reference frame, in contrast to the modified production terms R_A , R_{AB} , and r_{AB} in the material balance equations. On the other hand, R_{AB} can be expressed in terms of S_A^r and S_B^r in the form

$$R_{AB} = x_B S_A^r - x_A S_B^r \quad [28]$$

which is equivalent to Eq. [24] and which involves a combination of S_A^r and S_B^r that is independent of the choice of reference frame.

The equations in Tables 1 and 2 can be compared with the corresponding relationships for concentrated binary electrolytes (5,6) and with the equations of change for multicomponent, nonelectrolytic systems (13). The equations presented reduce to simpler forms under various special conditions. For example, for a free electrolytic solution (outside a porous electrode), the conservation equation will only depend on time indirectly, through changes in composition, and transport properties for the bulk electrolyte should be used. If either the current density is zero or the transference numbers are independent of composition then Eqs. [22-A] and [22-C] reduce to forms analogous to the binary diffusion equations for nonelectrolytes. The term R_{AB} in Eq. [28] could be regarded as an effective difference in rates of production of species A and B which takes the influence

of migration into account. If Eqs. [22-A] and [22-B] are rewritten for the mole fraction and mass fraction of salt B, it may be shown that $R_{BA} = -R_{AB}$ and that $r_{BA} = -r_{AB}$. By analogy with Eq. [23], it follows that the ratio

$$\frac{R_A}{R_B} = - \frac{\bar{V}_B}{\bar{V}_A} \quad [29]$$

does not depend directly on the stoichiometries for either dissociation of the salts or the electrode reactions.

Several factors can dictate the choice of reference frame for a given application of the material balance equation. The relative complexity of the equations, the form in which data are available for transport properties and activity coefficients, the appropriateness of the composition variable, and the nature of any other equations in the stated problem can all be important criteria. For example, the volume average reference velocity would enable concentration units to be used directly, but there is an ambiguity in the definition of $\underline{v}$ associated with the parameter Q and Eq. [22-C] is in a non-canonical form. Fluid mechanical equations are invariably written in terms of the mass average velocity, but the molar average may be preferred if the velocity is determined from stoichiometry alone or if pertinent data are correlated with the mole fraction. However, with a mole fraction scale one must decide how to treat the dissociated electrolyte. The non-canonical diffusion terms in Eqs. [22-B] and [25-B] result from the divergent definitions for the mole fraction and the molar

average velocity. The sum $c_A + c_B$, as distinct from the total concentration c_T , is equal to the inverse of the molar volume of the salt mixture $\tilde{V}$ where $\tilde{V} = \sum_k x_k \bar{V}_k$. Transference numbers are usually measured relative to the solvent velocity and, for binary molten salt mixtures, this gives some support for the use of a common ion reference velocity.

Ohmic potential drop

The potential in the pore electrolyte can be measured with a suitable reference electrode with an electrode reaction defined by

This potential can be used as a driving force for the current, and combination of Eqs. [2], [3], and [4] with the thermodynamic relation

$$\sum_i s_i \nabla \mu_i = -nF \nabla \phi_2 \quad [31]$$

yields a modified Ohm's law expression for the superficial current density in the pore phase. This is given by

$$\frac{i_2}{\kappa} = -\nabla \phi_2 - \frac{1}{F} \left[\left(\frac{s_1}{nv_1^A} + \frac{t_1^c}{z_1 v_1^A} \right) \left(1 + \frac{v_3^A c_A}{v_3^B c_B} \right) - \frac{s_3 c_A}{nc_B v_3^B} \right] \nabla \mu_A , \quad [32]$$

where the second term includes the diffusion potential. Integration of this equation across the electrode shows that the ohmic potential drop in the solution phase is directly related to the distributions

of concentration and reaction rate. The effective conductivity within the pores may be written in terms of the binary interaction parameter $\bar{D}_{ij}$, as

$$\kappa = \frac{\epsilon F^2 c_T}{RT} \frac{\left(\frac{z_1^2 c_1}{\bar{D}_{23}} + \frac{z_2^2 c_2}{\bar{D}_{13}} + \frac{z_3^2 c_3}{\bar{D}_{12}} \right)}{\left(\frac{c_1}{\bar{D}_{12} \bar{D}_{13}} + \frac{c_2}{\bar{D}_{12} \bar{D}_{23}} + \frac{c_3}{\bar{D}_{13} \bar{D}_{23}} \right)} \quad [33]$$

Conclusions

The macroscopic transport equations derived for a mixture of two binary molten salts with a common ion provide a consistent framework for the description of mass transfer of electrolytes of this type in free solutions or in porous media. The analysis also provides rational definitions for the transport properties that characterize the system behavior. The results presented, together with information on electrode kinetics, can be used to predict the time-dependent and position-dependent behavior of electrolyte concentration, porosity, current, and reaction rate within porous electrodes.

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List of Symbols

a	interfacial area per unit electrode volume (cm^{-1})
c_i	concentration of species i (mol/cm^3)
c_T	total ionic concentration (mol/cm^3)
D	effective diffusion coefficient of electrolyte in porous medium based on concentration gradient (cm^2/s)
$\mathcal{D}$	effective diffusion coefficient of electrolyte in porous medium for thermodynamic driving force (cm^2/s)
$\mathcal{D}_{ij}$	transport coefficient for binary interactions (cm^2/s)
F	Faraday's constant (95,487 c/equiv)
$\underline{i}_2$	superficial current density in pore phase (A/cm^2)
j_{in}	pore wall flux of species i ($\text{mol}/\text{cm}^2 \cdot \text{s}$)
M_i	molecular weight of species i (g/mol)
M_i	symbol for the chemical formula of species i
n	number of electrons transferred in electrode reaction
n	number of components in electrolyte solution
$\underline{N}_i$	superficial flux of species i ($\text{mol}/\text{cm}^2 \cdot \text{s}$)
Q	parameter defined by Eq. [19]
r_{AB}	parameter defined by Eq. [23]
R	universal gas constant (8.3143 J/mol.K)
R_A	} parameters defined by Eqs. [22], [24], and [33]
R_{AB}	
R_B	
s_i	stoichiometric coefficient of species i in electrode reaction
S_A^r	} parameters defined by Eqs. [30] and [31]
S_B^r	

t	time(s)
t_i	transference number of species i with respect to the mass average velocity
t_i^r	transference number of species i with respect to reference frame, r
T	absolute temperature (K)
$\underline{v}$	mass average velocity (cm/s)
$\underline{v}^\star$	molar average velocity (cm/s)
$\underline{v}^\square$	superficial volume average velocity (cm/s)
$\underline{v}_3$	velocity of common ion in molten salt mixture (cm/s)
$\bar{V}_i$	partial molar volume of species i (cm ³ /mol)
$\bar{V}_k$	partial molar volume of salt k (cm ³ /mol)
$\tilde{V}$	molar volume of salt mixture (cm ³ /mol)
x_k	mole fraction of salt k
z_i	valence or charge number of species i

Greek letters

γ_k	activity coefficient of salt k
ϵ	porosity or void volume fraction
κ	effective solution conductivity (mho/cm)
λ_k^o	property that expresses the secondary reference state for salt k
μ_i	electrochemical potential of species i
μ_k	chemical potential of salt k
ν^k	total number of ions produced by dissociation of a mole of salt k
ν_i^k	number of ions of species i produced by dissociation of a mole of salt k
ρ	density of electrolyte (g/cm ³)

Φ_2 electric potential in the solution (V)

ω_i mass fraction of species i

ω_k mass fraction of salt k

Subscripts

A salt A

B salt B

i species i (numbered 1, 2, 3)

k salt A or B

Superscripts

A salt A

B salt B

c relative to common ion reference velocity

r relative to reference frame r

■ relative to volume average reference velocity

★ relative to molar average reference velocity

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