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# Relationship between Steady-State Current in Symmetric Cells and Transference Number of Electrolytes Comprising Univalent and Multivalent Ions

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We derive a general relationship between the applied potential across a binary electrolyte in a symmetric cell and steady-state current density,  $i_{ss}$ . The relationship is applicable to salts comprising ions that are either univalent or multivalent. In concentrated solutions,  $i_{ss}$  depends on the electrolyte conductivity which governs  $i_0$ , the initially recorded current density at time zero when the potential is applied, and a dimensionless parameter derived here in terms of multicomponent transport coefficients. In the dilute limit, the ratio  $i_{ss}/i_0$  is the cation transference number, irrespective of the charge on the cation or the anion.

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The relationship between the applied potential between electrodes and current density is of fundamental importance; the efficacy of electrolytes used in electrochemical devices depends crucially on this relationship. The fact that this relationship is governed by three transport properties and the concentration dependence of the salt activity coefficient is well-established.<sup>1</sup> The commonly measured transport properties are ionic conductivity,  $\kappa$ , concentration-based salt diffusion coefficient,  $D$ , and the cation transference number with respect to the solvent,  $t_+^0$ . The purpose of this paper is to derive a general relationship between applied potential across symmetric electrodes and current density obtained at steady-state. The expressions developed here are applicable to salts comprising two univalent or multivalent ions, and solvents that are either small molecules or polymers.

Bruce and Vincent<sup>2</sup> showed that the steady-state dc current density obtained in a symmetric lithium-electrolyte-lithium cell,  $i_{ss}$ , in response to an applied potential,  $\Delta\phi$ , could be used to estimate  $t_+^0$ . They showed that for salts comprising univalent ions,  $t_+^0$  is given by

$$\frac{i_{ss}}{i_0} = t_+^0, \quad [1]$$

where  $i_0$  is the initially recorded current density at time zero when the potential is applied. This relationship was derived assuming that the ionic solution is ideal, that ion diffusion follows Fick's law, and that the effective potential across the electrolyte includes any effect of induced concentration overpotential.

Bruce and Vincent used Equation 1 to estimate  $t_+^0$  of a polymer electrolyte containing a lithium salt. Unlike flammable organic solvents that are currently used as electrolytes in lithium batteries, polymer electrolytes are nonflammable. They thus have the potential to improve the safety of lithium batteries. High-modulus solid polymer electrolytes have the potential to improve the energy density of lithium batteries by enabling the use of a lithium metal anode. There is thus renewed interest in the development of polymer electrolytes.

In a more recent publication,<sup>3</sup> Archer and coworkers attempted to rederive Equation 1 under the same assumptions but arrived at a different equation:

$$\frac{i_{ss}}{i_0} = 2t_+^0. \quad [2]$$

They applied this equation to interpret data obtained from a newly developed polymer electrolyte in Ref. 3.

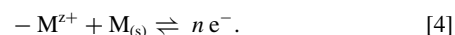
The main purpose of this paper is to present a straightforward derivation of  $i_{ss}/i_0$  based on concentrated-solution theory.<sup>1</sup> Dilute solution theory uses the electrostatic potential, a potential that is well-defined only in the limit of infinite dilution. In Ref. 2, the effective applied potential was reduced by intuitively introducing a contribution due to concentration polarization. (Concentration overpotential was overlooked in Ref. 3, resulting in the factor of 2 on the right side of Equation 2.) In contrast, the potentials measured in electrochemical cells are based on an appropriate reference electrode. Concentrated solution theory naturally incorporates potentials measured with respect to a reference electrode. In addition, equations relating current density and applied potential within concentrated-solution theory can be applied without adding or subtracting terms based on intuition.<sup>1</sup> Doyle and Newman<sup>4</sup> used concentrated solution theory to derive an expression for  $i_{ss}/i_0$ . The present work goes beyond that study, providing new expressions for  $i_{ss}/i_0$  that are useful for interpreting experiments on a much wider variety of salt solutions than covered in previous studies.<sup>2-4</sup>

## Theory

Following concentrated solution theory as developed by Newman (Chapter 12 of Ref. 1), we assume that a potential  $\Delta\phi$  is applied at  $t = 0$  across a symmetric cell containing a salt  $(M^{z+})_{v+}(X^{z-})_{v-}$  in the  $x$  direction. The applied external potential creates gradients in both the potential in the solution  $\phi$  and salt concentration  $c$ . We assume  $\phi$  is measured relative to a reference electrode using the reaction



where  $M^{z+}$  is the cation of interest (typically  $\text{Li}^+$ , but our treatment applies to any cation such as  $\text{Mg}^{2+}$  or  $\text{Al}^{3+}$ ), and  $M$  is a neutral solid in the probing electrode that is insoluble in the electrolyte. Following the convention in Ref. 1, we rewrite this equation as



The relationship between electric current density,  $i$ , and  $\phi$  in cases where the solvent does not participate in the probing electrode reaction [e.g., reaction 4] is given by

$$i = -\kappa \frac{d\phi}{dx} - \frac{\kappa}{F} \left( \frac{s_+}{nv_+} + \frac{t_+^0}{z_+v_+} \right) \frac{d\mu_e}{dx}, \quad [5]$$

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where  $\kappa$  is the electrolyte conductivity,  $F$  is Faraday's constant (96485 C/mol),  $s_+$  is the stoichiometric coefficient of the positive ion in the probing electrode reaction (taken to be  $-1$  in Equation 4),  $n$  is the number of electrons in the probing electrode reaction,  $\nu_+$  is the number of cations into which a molecule of the salt dissociates, and  $\mu_e$  is the chemical potential of the electrolyte. We note in passing that the electrolyte is electrically neutral and thus  $\mu_e$  is independent of  $\phi$ . Charge balance implies that  $z_+ = n$ . We apply Equation 5 to both the steady state wherein both terms on the right contribute, and the initial state wherein the second term on the right is zero because the solution initially is uniform in concentration. Thus,

$$i_0 = -\kappa \frac{d\phi}{dx}, \quad [6]$$

and potential difference across the electrolyte,  $\Delta\phi$ , is obtained by integrating Equation 6,

$$\Delta\phi = \frac{i_0 L}{\kappa}, \quad [7]$$

where  $L$  is the distance between the electrodes and  $\kappa$  is the electrolyte conductivity at the initial concentration.

The anion flux through the electrolyte,  $N_-$ , is related to the current density as given below (Equation 12.9 in Ref. 1).

$$N_- = -\frac{\mathcal{D}c_T c_{v-}}{RTc_0 v} \frac{d\mu_e}{dx} + \frac{it_-^0}{z_- F} \quad [8]$$

where  $\mathcal{D}$  is the diffusion coefficient of the electrolyte based on a thermodynamic driving force,  $v$  is the total number of moles of ions produced by dissociation of the salt ( $v = \nu_+ + \nu_-$ ),  $c_0$  is the concentration of monomers making up the polymer chain,  $c$  is salt concentration, and  $c_T$  is the total solution concentration ( $c_T = c_0 + \nu c$ ). At steady state, the anion flux is zero at all  $x$ . Setting  $N_-$  to zero gives

$$\frac{d\mu_e}{dx} = i_{ss} \frac{t_-^0}{z_- F} \frac{RTc_0 v}{\mathcal{D}c_T c_{v-}} \quad [9]$$

Substituting Equation 9 into Equation 5 at steady-state, and noting that  $z_- \nu_- = -z_+ \nu_+$ , we obtain

$$i_{ss} = -\frac{\kappa}{1 + Ne} \frac{d\phi}{dx} \quad [10]$$

where

$$Ne = a \frac{\kappa RT (t_-^0)^2}{F^2 \mathcal{D} c} \frac{c_0}{c_T}. \quad [11]$$

The parameter  $a$  in Equation 11 is related to the stoichiometry of the salt,

$$a = \frac{\nu}{(\nu_+ z_+)^2}. \quad [12]$$

Our approach shows that  $i_{ss}$  is independent of the electrochemical potential of the electrolyte,  $\mu_e$  (see Equation 10). The previous derivations of  $i_{ss}$ ,<sup>2-4</sup> all begin with expressions for  $\mu_e$ .

We assume that the applied potential is small, which, in turn, results in small concentration gradients. We thus ignore the concentration-dependence of  $\kappa$ , and Equation 10 can be rewritten as

$$i_{ss} = \frac{\kappa}{1 + Ne} \frac{\Delta\phi}{L} \quad [13]$$

Combining Equations 7 and 13, we obtain,

$$\frac{i_{ss}}{i_0} = \frac{1}{1 + Ne} \quad [14]$$

It can be shown that  $Ne$  can be rewritten as

$$Ne = \frac{t_-^0}{\varepsilon + t_+^0} \quad [15]$$

where

$$\varepsilon = \frac{c}{c_0} \frac{\nu_- \mathcal{D}_{0+}}{\mathcal{D}_{+-}} \quad [16]$$

This expression can be used to show that Equation 14 can be rewritten as

$$\frac{i_{ss}}{i_0} = \frac{t_+^0 + \varepsilon}{1 + \varepsilon} \quad [17]$$

The multicomponent diffusion coefficients,  $\mathcal{D}_{+0}$ ,  $\mathcal{D}_{-0}$ , and  $\mathcal{D}_{+-}$ , describe diffusion of the cation relative to the solvent, the anion relative to the solvent, and the cation relative to the anion based on thermodynamic driving forces. Standard relationships between multicomponent transport coefficients<sup>1</sup> are used to obtain Equations 15-17:

$$\mathcal{D} = \frac{\mathcal{D}_{0+}\mathcal{D}_{0-}(z_+ - z_-)}{z_+\mathcal{D}_{0+} - z_-\mathcal{D}_{0-}} \quad [18]$$

$$t_+^0 = 1 - t_-^0 = \frac{z_+\mathcal{D}_{0+}}{z_+\mathcal{D}_{0+} - z_-\mathcal{D}_{0-}} \quad [19]$$

$$\frac{1}{\kappa} = \frac{-RT}{F^2 c_T z_+ z_-} \left( \frac{1}{\mathcal{D}_{+-}} + \frac{c_0 t_-^0}{c_+ \mathcal{D}_{0-}} \right) \quad [20]$$

Equation 16 is particularly useful for determining the ratio  $i_{ss}/i_0$  in the dilute limit ( $c \rightarrow 0$ ) where the  $\varepsilon$  term in the equation can be set to zero. In the dilute limit, we obtain,

$$\frac{i_{ss}}{i_0} = t_+^0 \quad [21]$$

It is worth noting that the expression originally proposed by Bruce and Vincent<sup>2</sup> for dilute electrolytes comprising univalent salts is applicable to all binary salts, irrespective of the charge on the cation or the anion.

Finally, since  $\mathcal{D}_{ij}$  cannot be measured directly, we recast Equation 11 in terms of  $D$ , the salt diffusion coefficient that is measured in a restricted diffusion experiment,<sup>5</sup>

$$Ne = a \frac{\kappa RT (t_-^0)^2}{F^2 D c} \left( 1 + \frac{d\ln\gamma_{\pm}}{d\ln m} \right) \quad [22]$$

where  $\gamma_{\pm}$  is the mean molal activity coefficient of the electrolyte,  $m$  is the molality, and we have used the relationship.<sup>6</sup>

$$D = \mathcal{D} \frac{c_T}{c_0} \left( 1 + \frac{d\ln\gamma_{\pm}}{d\ln m} \right) \quad [23]$$

Equation 22 is nearly identical to Equation 16 of Doyle and Newman,<sup>4</sup> differing in the last term on the right which should be expressed in terms of mean molal activity coefficients, as given here.

While it is widely recognized that complete characterization of electrolytes requires measurement of three transport properties, this is seldom done in practice. A large fraction of the literature on characterization of ion transport in polymer electrolytes is restricted to determination of the ionic conductivity. The ability of an electrolyte to function in a battery is, however, closely related to the steady-state current generated in a symmetric cell. Our analysis shows that this depends fundamentally on two parameters:  $\kappa$ , which determines  $i_0$ , and  $Ne$ . We suggest that augmenting the vast experimental literature on the conductivity of electrolytes by values of the dimensionless parameter  $Ne$  will provide better insight into how electrolytes will function in full cells. For electrolytes with identical conductivities, the one with the lower value of  $Ne$  is preferred. The ideal value of  $Ne$  is zero; this is the case for a single-ion-conductor. Of course, quantitative prediction of full cell performance will require measurement of all three independent transport properties (as well as the activity coefficient). One might do this by measuring  $D$  by restricted diffusion and  $Ne$  from  $i_{ss}/i_0$  if the dependence of  $\gamma_{\pm}$  on  $m$  is known. A limitation of this approach is that it will only enable determination of the magnitude of  $t_-^0$ ; note that the square of this parameter is related to  $Ne$  (Equation 21), as recognized by Doyle and Newman.<sup>4</sup>

### Conclusions

Concentrated solution theory is used to derive a general relationship between the applied potential across a binary electrolyte and steady-state current density that is applicable to salts comprising both univalent and multivalent ions. In concentrated solutions,  $i_{ss}$  depends on a dimensionless parameter that we refer to as  $N_e$ . Explicit expressions for this parameter in terms of multicomponent transport coefficients are provided. In the dilute limit, the ratio  $i_{ss}/i_0$  gives the cation transference number, irrespective of the charge on the cation or the anion. In future work, we will apply the framework developed here to interpret steady-state current measurements on polymer electrolytes.

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### List of Symbols

$a$	dimensionless parameter that depends on salt stoichiometry defined by Equation 12.
$c$	salt concentration, mol/cm <sup>3</sup>
$c_0$	solvent concentration, mol/cm <sup>3</sup> (moles of monomers per unit volume for polymeric solvents)
$c_T$	total solution concentration, mol/cm <sup>3</sup>
$D$	salt diffusion coefficient based on concentration, cm <sup>2</sup> /s
$\mathcal{D}$	diffusion coefficient of the salt based on a thermodynamic driving force, cm <sup>2</sup> /s
$\mathcal{D}_{ij}$	diffusion coefficient for interaction of species $i$ and $j$ , cm <sup>2</sup> /s
$F$	Faraday's constant, 96485 C/mol
$i$	current density, A/cm <sup>2</sup>
$i_0$	initial current density when potential is applied, A/cm <sup>2</sup>

$i_{ss}$	steady-state dc current density, A/cm <sup>2</sup>
$m$	molality of electrolyte, mol/kg
$n$	number of electrons in the probing electrode reaction
$N_-$	anion flux, mol/(cm <sup>2</sup> s)
$N_e$	dimensionless number defined by Equation 11
$R$	Universal gas constant, 8.3143 J/(mol K)
$s_+$	stoichiometric coefficient of the positive ion in the probing electrode reaction
$t_+^0, t_-^0$	cation and anion transference number
$T$	absolute temperature, K
$z_+, z_-$	charge number of cation and anion

### Greek

$\Delta\phi$	applied potential, V
$\varepsilon$	dimensionless parameter proportional to salt concentration defined by Equation 16
$\gamma_{\pm}$	mean molal activity coefficient of the electrolyte
$\kappa$	ionic conductivity of electrolyte, S/cm
$\mu_e$	electrochemical potential of the electrolyte, J/mol
$\nu_+$ and $\nu_-$	the number of cations and anions into which the salt dissociates
$\nu$	total number of cations and anions into which the salt dissociates

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