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Pauline De Vidts

Texas A & M University - College Station

Ralph E. White

University of South Carolina - Columbia, white@cec.sc.edu

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Governing Equations for Transport in Porous Electrodes

Pauline De Vidts* and Ralph E. White*

Department of Chemical Engineering, University of South Carolina, Columbia, South Carolina 29208, USA

ABSTRACT

General governing equations for a porous electrode containing three phases (liquid, solid, and gas) are developed using the volume-averaging technique. These equations include the mass transfer in each phase, ohmic drop in the liquid and solid phases, and the equations resulting from applying the principle of conservation of charge. The electrolyte is considered to be a concentrated binary solution.

Introduction

The purpose of this paper is to present the derivation of transport equations for porous electrodes using the volume-averaging technique.¹ The application of this technique results in the representation of a porous medium with multiple phases (gas, liquid, and solid) as a continuum. This eliminates the need for the description and representation of the microscopic configuration of the medium, which in many practical cases is not known. This technique has been used extensively for deriving governing equations for mass and heat transfer in porous media.¹⁻⁷ In electrochemical applications, Prins-Jansen *et al.*⁸ used volume averaging to develop a model of a molten carbonate fuel cell. Newman and Tiedemann⁹ presented general equations for porous electrodes based on a form of averaging which is similar to the technique used here. The derivation of their equations was presented by Dunning¹⁰ and again by Trainham,¹¹ who gave a more detailed derivation. These authors⁹⁻¹¹ used an area-averaging technique to define some variables (for example, the molar-flux vector), which results in expressions that are not exactly the same as those obtained when applying the volume-averaging technique used here, as discussed below.

In this work, the equations are derived for a porous electrode consisting of three phases: solid, liquid, and gas. The equations include the material balances of ionic and neutral species in the three phases, electrical relations, and equations resulting from applying the principle of conservation of charge. In the first section of this paper we present a brief summary of the principles and theorems involved in volume averaging to make it easier for the reader to follow the derivations presented in the following sections. We begin by presenting the derivation of the equations for the material balances in the three phases, followed by Ohm's law in the liquid and solid phases, and finally, the equations obtained from applying conservation of charge to every portion of the porous electrode.

Definitions from the Volume-Averaging Technique

In this section we present a brief description of the concepts and definitions involved in the volume-averaging technique as presented by Slattery¹ for systems of two phases and later extended by Zanotti and Carbonell² to multiphase systems. The porous medium under consideration in this work consists of three phases: liquid, solid, and gas.

Consider a porous medium that consists of a solid phase with its pores filled with two fluids (liquid and gas) as shown in Fig. 1. The solid phase is considered to have no

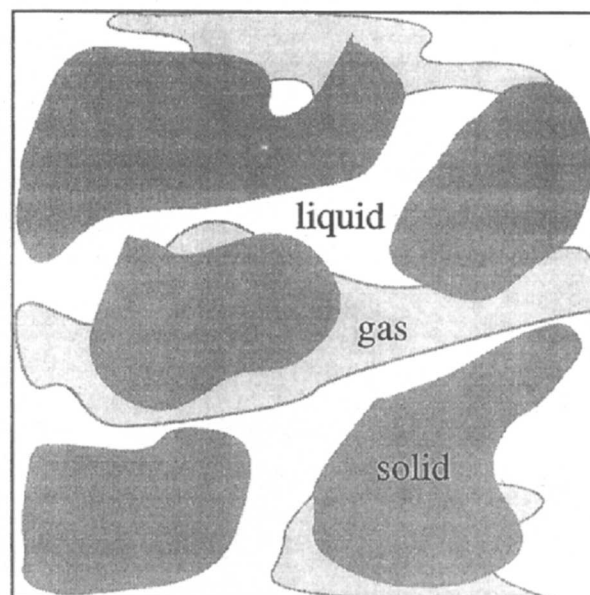


Fig. 1. Porous medium consisting of three phases: solid, liquid, and gas.

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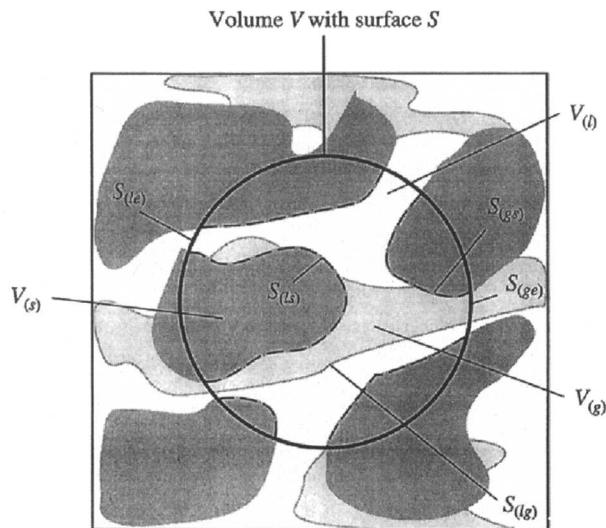


Fig. 2. The averaging volume V to be associated with every point in the porous medium. Volume V consists of a volume of liquid, V_l ; volume of gas, V_g ; and volume of solid, V_s . The surfaces of interest contained in volume V are the interface surfaces and the exits and entrances of the gas and liquid phases.

microporosity. Let V be a volume of this porous medium, as shown in Fig. 2, over which we conduct volume averaging. Volume V is located at any given point in the porous medium and is enclosed by surface S . The dimensions of the volume V must be negligible with respect to the overall dimensions of the porous medium. Yet V must be large enough to ensure that it contains parts of all three phases. Also, V must be a representative subvolume of the medium. Figure 2 shows a schematic of volume V and the surfaces inside this volume which are defined in the List of Symbols.

Let B be a quantity (either scalar, vector, or tensor) associated with the liquid or gas phases, and let the quantity $\bar{B}^{(i)}$ be called the local volume average of B in the phase i

$$\bar{B}^{(i)} = \frac{1}{V} \int_{V_i} B \, dV \quad [1]$$

Let $\langle B \rangle^{(i)}$ be the intrinsic volume average of B in phase i

$$\langle B \rangle^{(i)} = \frac{1}{V_i} \int_{V_i} B \, dV \quad [2]$$

Let $\epsilon^{(l)}$ and $\epsilon^{(g)}$ be the liquid and gas porosities, respectively

$$\epsilon^{(l)} = \frac{V_l}{V} \quad [3]$$

$$\epsilon^{(g)} = \frac{V_g}{V} \quad [4]$$

Thus, the porosity of volume V is given by

$$\epsilon = \frac{V_l + V_g}{V} = \epsilon^{(l)} + \epsilon^{(g)} \quad [5]$$

A comparison of Eq. 1-4 shows that the local and intrinsic volume average for the liquid and gas phases are related by the appropriate porosity

$$\bar{B}^{(i)} = \epsilon^{(i)} \langle B \rangle^{(i)} \quad i = g, l \quad [6]$$

The theorem of the local volume average of a gradient,¹ written for a system of multiple phases,⁴ states that

$$\nabla \bar{B}^{(l)} = \nabla \bar{B}^{(l)} + \frac{1}{V} \int_{S_{(lg)}} B^{(l)} \mathbf{n}_{(lg)} \, dS + \frac{1}{V} \int_{S_{(ls)}} B^{(l)} \mathbf{n}_{(ls)} \, dS \quad [7]$$

$$\nabla \bar{B}^{(g)} = \nabla \bar{B}^{(g)} + \frac{1}{V} \int_{S_{(lg)}} B^{(g)} \mathbf{n}_{(lg)} \, dS + \frac{1}{V} \int_{S_{(gs)}} B^{(g)} \mathbf{n}_{(gs)} \, dS \quad [8]$$

where $\mathbf{n}_{(lg)}$ and $\mathbf{n}_{(ls)}$ are unit vectors normal to the surfaces $S_{(lg)}$ and $S_{(ls)}$, respectively, as shown in Fig. 3. In Eq. 8, $\mathbf{n}_{(lg)}$ and $\mathbf{n}_{(gs)}$ are unit vectors normal to the surfaces $S_{(lg)}$ and $S_{(gs)}$, respectively, also shown in Fig. 3. Note that

$$\mathbf{n}_{(lg)} = -\mathbf{n}_{(gl)} \quad [9]$$

The theorem of the local volume average of a divergence¹ reads, for the liquid and gas phases, respectively

$$\nabla \cdot \bar{B}^{(l)} = \nabla \cdot \bar{B}^{(l)} + \frac{1}{V} \int_{S_{(lg)}} B^{(l)} \cdot \mathbf{n}_{(lg)} \, dS + \frac{1}{V} \int_{S_{(li)}} B^{(l)} \cdot \mathbf{n}_{(li)} \, dS \quad [10]$$

$$\nabla \cdot \bar{B}^{(g)} = \nabla \cdot \bar{B}^{(g)} + \frac{1}{V} \int_{S_{(lg)}} B^{(g)} \cdot \mathbf{n}_{(lg)} \, dS + \frac{1}{V} \int_{S_{(gs)}} B^{(g)} \cdot \mathbf{n}_{(gs)} \, dS \quad [11]$$

Another theorem that we use in the derivations presented below is the generalized transport theorem for a system¹

$$\frac{d}{dt} \int_{V_t} B \, dV = \int_{V_t} \frac{\partial B}{\partial t} \, dV + \int_{S_t} B \mathbf{v} \cdot \mathbf{n} \, dS \quad [12]$$

in which V_t represents the space region currently occupied by a fluid system, S_t is the closed bounding surface of the system, \mathbf{v} is velocity of the fluid, and \mathbf{n} is a unit normal to the surface S_t , pointing out of the system V_t . This theorem involves the assumption that the normal component of the velocity of the fluid at the boundary of the system is equal to the normal component of the velocity of the boundary of the system.

In this work we consider the porous medium to be a porous electrode. The electrode consists of a solid matrix with pores filled with liquid and gas. The liquid phase is a binary electrolyte with dissolved gaseous species.

Material Balances on the Liquid, Gas, and Solid Phases

The equation of continuity for species i in a free-stream liquid in the absence of homogeneous reactions is given by

$$\frac{\partial c_i^{(l)}}{\partial t} + \nabla \cdot \mathbf{N}_i^{(l)} = 0 \quad [13]$$

where $c_i^{(l)}$ and $\mathbf{N}_i^{(l)}$ are the concentration and molar flux of species i , respectively. If we integrate Eq. 13 over the volume of liquid, V_l , contained in V , we have

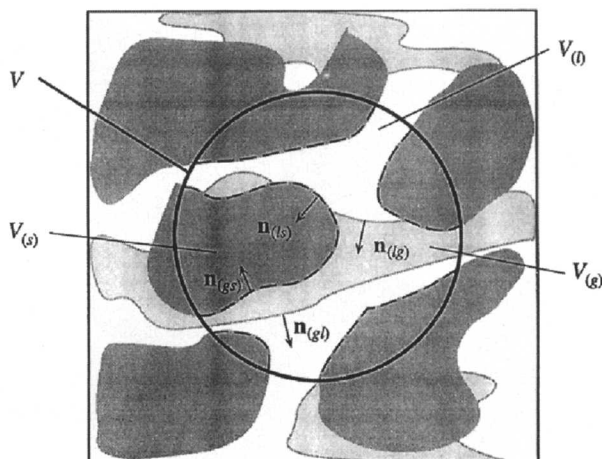


Fig. 3. The unit vectors normal to the various surfaces inside volume V .

$$\frac{1}{V} \int_{V_{(i)}} \frac{\partial c_i^{(i)}}{\partial t} dV + \frac{1}{V} \int_{V_{(i)}} \nabla \cdot \mathbf{N}_i^{(i)} dV = 0 \quad [14]$$

Applying the general transport theorem (Eq. 12) for $B = c_i^{(i)}$ and $V = V_{(i)}$, we have

$$\int_{V_{(i)}} \frac{\partial c_i^{(i)}}{\partial t} dV = \frac{d}{dt} \int_{V_{(i)}} c_i^{(i)} dV - \int_{S_{(i)}} c_i^{(i)} \mathbf{v} \cdot \mathbf{n} dS \quad [15]$$

Dividing Eq. 15 by V , which is independent of time, and considering that the surface $S_{(i)}$ consists of the sum of $S_{(ls)}$, $S_{(lg)}$, and $S_{(le)}$, Eq. 15 becomes

$$\begin{aligned} \frac{1}{V} \int_{V_{(i)}} \frac{\partial c_i^{(i)}}{\partial t} dV &= \frac{d}{dt} \left(\frac{1}{V} \int_{V_{(i)}} c_i^{(i)} dV \right) - \frac{1}{V} \int_{S_{(lg)}} c_i^{(i)} \mathbf{v}_{(lg)} \cdot \mathbf{n}_{(lg)} dS \\ &\quad - \frac{1}{V} \int_{S_{(le)}} c_i^{(i)} \mathbf{v}_{(le)} \cdot \mathbf{n}_{(le)} dS \\ &= \frac{d\bar{c}_i^{(i)}}{dt} - \frac{1}{V} \int_{S_{(lg)}} c_i^{(i)} \mathbf{v}_{(lg)} \cdot \mathbf{n}_{(lg)} dS - \frac{1}{V} \int_{S_{(ls)}} c_i^{(i)} \mathbf{v}_{(ls)} \cdot \mathbf{n}_{(ls)} dS \end{aligned} \quad [16]$$

in which $\mathbf{v}_{(lg)}$ and $\mathbf{v}_{(ls)}$ represent the velocities of the liquid/gas and liquid/solid interfaces, respectively. Also, $\mathbf{n}_{(lg)}$ and $\mathbf{n}_{(ls)}$ are the unit normals to the interfaces pointing from the liquid into the gas and solid phases, respectively. In deriving Eq. 16 we have required that the velocity of the boundary $S_{(le)}$ be zero.

Applying the theorem for the local volume average of a divergence (Eq. 10) to the second term in Eq. 14, we obtain

$$\frac{1}{V} \int_{V_{(i)}} \nabla \cdot \mathbf{N}_i^{(i)} dV = \nabla \cdot \bar{\mathbf{N}}_i^{(i)} + \frac{1}{V} \int_{S_{(lg)}} \mathbf{N}_i^{(i)} \cdot \mathbf{n}_{(lg)} dS + \frac{1}{V} \int_{S_{(ls)}} \mathbf{N}_i^{(i)} \cdot \mathbf{n}_{(ls)} dS \quad [17]$$

Substituting Eq. 16 and 17 into Eq. 14, we have

$$\begin{aligned} \frac{d\bar{c}_i^{(i)}}{dt} + \nabla \cdot \bar{\mathbf{N}}_i^{(i)} + \frac{1}{V} \int_{S_{(lg)}} (\mathbf{N}_i^{(i)} - c_i^{(i)} \mathbf{v}_{(lg)}) \cdot \mathbf{n}_{(lg)} dS \\ + \frac{1}{V} \int_{S_{(ls)}} (\mathbf{N}_i^{(i)} - c_i^{(i)} \mathbf{v}_{(ls)}) \cdot \mathbf{n}_{(ls)} dS = 0 \end{aligned} \quad [18]$$

Equation 18 has been derived for an elemental volume V inside the porous medium. Volume V can be placed at any position in the porous medium. Therefore, if we write Eq. 18 for the whole porous medium with respect to a fixed coordinate system, we have

$$\begin{aligned} \frac{d\bar{c}_i^{(i)}}{dt} + \nabla \cdot \bar{\mathbf{N}}_i^{(i)} + \frac{1}{V} \int_{S_{(lg)}} (\mathbf{N}_i^{(i)} - c_i^{(i)} \mathbf{v}_{(lg)}) \cdot \mathbf{n}_{(lg)} dS \\ + \frac{1}{V} \int_{S_{(ls)}} (\mathbf{N}_i^{(i)} - c_i^{(i)} \mathbf{v}_{(ls)}) \cdot \mathbf{n}_{(ls)} dS = 0 \end{aligned} \quad [19]$$

Following the same procedure used for the liquid phase, the material balances for the gas and solid phases are given by

$$\begin{aligned} \frac{\partial \bar{c}_i^{(g)}}{\partial t} + \nabla \cdot \bar{\mathbf{N}}_i^{(g)} + \frac{1}{V} \int_{S_{(lg)}} (\mathbf{N}_i^{(g)} - c_i^{(g)} \mathbf{v}_{(lg)}) \cdot \mathbf{n}_{(lg)} dS \\ + \frac{1}{V} \int_{S_{(gs)}} (\mathbf{N}_i^{(g)} - c_i^{(g)} \mathbf{v}_{(gs)}) \cdot \mathbf{n}_{(gs)} dS = 0 \end{aligned} \quad [20]$$

for the gas phase and by

$$\begin{aligned} \frac{\partial \bar{c}_i^{(s)}}{\partial t} + \nabla \cdot \bar{\mathbf{N}}_i^{(s)} + \frac{1}{V} \int_{S_{(ls)}} (\mathbf{N}_i^{(s)} - c_i^{(s)} \mathbf{v}_{(ls)}) \cdot \mathbf{n}_{(ls)} dS \\ + \frac{1}{V} \int_{S_{(gs)}} (\mathbf{N}_i^{(s)} - c_i^{(s)} \mathbf{v}_{(gs)}) \cdot \mathbf{n}_{(gs)} dS = 0 \end{aligned} \quad [21]$$

for the solid phase.

In Eq. 20, $\mathbf{v}_{(lg)}$ and $\mathbf{v}_{(gs)}$ are the velocities of the liquid/gas and gas/solid interfaces, respectively; and $\mathbf{n}_{(lg)}$ and $\mathbf{n}_{(gs)}$ are

the unit normals to the interfaces pointing from the gas into the liquid and solid phases, respectively, as shown in Fig. 3. We have required that the velocity of the boundary $S_{(ge)}$ be zero. In Eq. 21, $\mathbf{v}_{(ls)}$ and $\mathbf{v}_{(gs)}$ are the velocities of the liquid/solid and gas/solid interfaces, respectively, and $\mathbf{n}_{(sg)}$ and $\mathbf{n}_{(sl)}$ are the unit normals to the interfaces pointing from the solid into the gas and liquid phases, respectively. These are not shown in Fig. 3, but are the negatives of $\mathbf{n}_{(gs)}$ and $\mathbf{n}_{(ls)}$.

Jump Mass Balance for Species i at the Liquid/Gas Interface

The general form of the jump mass balance for species i at an interface is¹

$$(\mathbf{N}_i^{(+)} \cdot \mathbf{n}_{(+)} - c_i^{(+)} \mathbf{v}_{(+)} \cdot \mathbf{n}_{(+)}) + (\mathbf{N}_i^{(-)} \cdot \mathbf{n}_{(-)} - c_i^{(-)} \mathbf{v}_{(-)} \cdot \mathbf{n}_{(-)}) = R_i^{(+)} \quad [22]$$

in which $\mathbf{n}_{(+)}$ and $\mathbf{n}_{(-)}$ are unit normals to the interface pointing into phase $+$ and $-$, respectively. Also, $\mathbf{v}_{(+)} \cdot \mathbf{n}_{(+)}$ and $\mathbf{v}_{(-)} \cdot \mathbf{n}_{(-)}$ are the velocities of the interface in the $+$ and $-$ direction, respectively. $R_i^{(+)}$ is the rate at which species i is produced by heterogeneous or catalytic chemical reactions per unit area of interface.

If we apply Eq. 22 to the liquid/gas interface and assume that there are no chemical or electrochemical reactions taking place at that interface, we obtain

$$(\mathbf{N}_i^{(l)} \cdot \mathbf{n}_{(gl)} - c_i^{(l)} \mathbf{v}_{(lg)} \cdot \mathbf{n}_{(gl)}) + (\mathbf{N}_i^{(g)} \cdot \mathbf{n}_{(lg)} - c_i^{(g)} \mathbf{v}_{(lg)} \cdot \mathbf{n}_{(lg)}) = 0 \quad [23]$$

Equation 23 means that the flux of species i entering the liquid phase is equal to that leaving the gas phase.

If we integrate Eq. 23 over the surface $S_{(lg)}$ contained in volume V , we have

$$\begin{aligned} \frac{1}{V} \int_{S_{(lg)}} (\mathbf{N}_i^{(l)} - c_i^{(l)} \mathbf{v}_{(lg)}) \cdot \mathbf{n}_{(gl)} dS + \frac{1}{V} \int_{S_{(lg)}} (\mathbf{N}_i^{(g)} - c_i^{(g)} \mathbf{v}_{(lg)}) \cdot \mathbf{n}_{(lg)} dS = 0 \end{aligned} \quad [24]$$

Because $\mathbf{n}_{(lg)} = -\mathbf{n}_{(gl)}$, Eq. 24 is equivalent to

$$\begin{aligned} -\frac{1}{V} \int_{S_{(lg)}} (\mathbf{N}_i^{(l)} - c_i^{(l)} \mathbf{v}_{(lg)}) \cdot \mathbf{n}_{(lg)} dS - \frac{1}{V} \int_{S_{(lg)}} (\mathbf{N}_i^{(g)} - c_i^{(g)} \mathbf{v}_{(lg)}) \cdot \mathbf{n}_{(lg)} dS = 0 \end{aligned} \quad [25]$$

Let $\bar{F}_i^{(lg)}$ be the averaged flux of species i at the liquid/gas interface in volume V leaving the liquid phase and entering the gas phase; thus

$$\begin{aligned} \bar{F}_i^{(lg)} &= \frac{1}{V} \int_{S_{(lg)}} (\mathbf{N}_i^{(l)} - c_i^{(l)} \mathbf{v}_{(lg)}) \cdot \mathbf{n}_{(lg)} dS \\ &= -\frac{1}{V} \int_{S_{(lg)}} (\mathbf{N}_i^{(g)} - c_i^{(g)} \mathbf{v}_{(lg)}) \cdot \mathbf{n}_{(lg)} dS \end{aligned} \quad [26]$$

Jump Mass Balance for Species i at the Liquid/Solid Interface

Applying Eq. 22 to the liquid/solid interface, we obtain

$$(\mathbf{N}_i^{(l)} \cdot \mathbf{n}_{(sl)} - c_i^{(l)} \mathbf{v}_{(ls)} \cdot \mathbf{n}_{(sl)}) + (\mathbf{N}_i^{(s)} \cdot \mathbf{n}_{(ls)} - c_i^{(s)} \mathbf{v}_{(ls)} \cdot \mathbf{n}_{(ls)}) = R_i^{(ls)} \quad [27]$$

If we integrate Eq. 27 over the surface $S_{(ls)}$ contained in volume V , we have

$$\begin{aligned} -\frac{1}{V} \int_{S_{(sl)}} (\mathbf{N}_i^{(l)} - c_i^{(l)} \mathbf{v}_{(ls)}) \cdot \mathbf{n}_{(ls)} dS - \frac{1}{V} \int_{S_{(sl)}} (\mathbf{N}_i^{(s)} - c_i^{(s)} \mathbf{v}_{(ls)}) \cdot \mathbf{n}_{(sl)} dS = \frac{1}{V} \int_{S_{(sl)}} R_i^{(ls)} dS \end{aligned} \quad [28]$$

For the particular case in which species i is present in the liquid phase but not in the solid phase, the second term in Eq. 28 is zero

$$-\frac{1}{V} \int_{S_{(sl)}} (\mathbf{N}_i^{(l)} - c_i^{(l)} \mathbf{v}_{(ls)}) \cdot \mathbf{n}_{(ls)} dS = \frac{1}{V} \int_{S_{(sl)}} R_i^{(ls)} dS \quad [29]$$

Let $\bar{R}_i^{(ls)}$ be the averaged rate at which species i is produced at the liquid/solid interface in volume V ; thus

$$\begin{aligned}\bar{R}_i^{(ls)} &= \frac{1}{V} \int_{S_{(sl)}} R_i^{(ls)} dS \\ &= -\frac{1}{V} \int_{S_{(sl)}} (\mathbf{N}_i^{(l)} - c_i^{(l)} \mathbf{v}_{(ls)}) \cdot \mathbf{n}_{(sl)} dS\end{aligned}\quad [30]$$

On the other hand, if species i is present in the solid phase only, $\bar{R}_i^{(ls)}$ is given by

$$\begin{aligned}\bar{R}_i^{(ls)} &= \frac{1}{V} \int_{S_{(sl)}} R_i^{(ls)} dS \\ &= -\frac{1}{V} \int_{S_{(sl)}} (\mathbf{N}_i^{(s)} - c_i^{(s)} \mathbf{v}_{(ls)}) \cdot \mathbf{n}_{(sl)} dS\end{aligned}\quad [31]$$

Jump Mass Balance for Species i at the Gas/Solid Interface

Equations similar to Eq. 30 and 31 can be derived in an analogous way for species at the gas/solid interface (see Ref. 12).

Resulting Material Balances on the Three Phases

We can now use the expressions derived for mass transfer at the interfaces in the equations of continuity derived previously. If we substitute Eq. 26 and 30 into Eq. 19, the volume averaged equation of continuity for species i in the liquid phase becomes

$$\frac{\partial \bar{c}_i^{(l)}}{\partial t} + \nabla \cdot \bar{\mathbf{N}}_i^{(l)} + \bar{F}_i^{(lg)} - \bar{R}_i^{(ls)} = 0 \quad [32]$$

Similar equations can be derived for the gas and solid phases (see Ref. 12).

Rate of Reaction of Electrochemical Reactions

Consider the case in which species i is being produced by electrochemical reactions taking place at the surface of the pore walls. An electrochemical reaction can be represented in general

$$\sum_i s_{ik} M_i^{z_i} = n_k e^- \quad [33]$$

where $M_i^{z_i}$ represents species i participating in reaction k , z_i is the ionic charge number or valence of species i , s_{ik} is the stoichiometric coefficient of species i in reaction k , and n_k is the number of electrons being released by reaction k .

The average production rate over the liquid/solid interface contained in volume V is given by

$$\begin{aligned}\bar{R}_i^{(ls)} &= -\frac{1}{V} \int_{S_{(sl)}} \left(\sum_k \frac{s_{ik}}{n_k F} j_k \right) dS \\ &= -\sum_k \left(\frac{s_{ik}}{n_k F} \frac{1}{V} \int_{S_{(sl)}} j_k dS \right) = -\sum_k \frac{s_{ik} a^{(sl)}}{n_k F} \langle j_k \rangle^{(sl)}\end{aligned}\quad [34]$$

where $a^{(sl)}$ is the pore wall surface area wet by electrolyte per unit volume of porous medium ($S_{(sl)}/V$), in cm^2/cm^3 , and $\langle j_k \rangle^{(sl)}$ is the average reaction rate of electrochemical reaction k taking place at the liquid/solid interface contained in volume V and is defined as

$$\langle j_k \rangle^{(sl)} = \left(\frac{1}{S_{(sl)}} \int_{S_{(sl)}} j_k dS \right) \quad [35]$$

Comparison of the integrand in Eq. 34 to the integrand in Eq. 30 reveals the mode of transport of species i to the solid/liquid interface where it may react in one or more electrochemical reactions. If $s_{ik} = 0$, species i does not react at the solid/liquid interface. Note that the transport of liquid-phase species i to the solid/liquid interface can be affected by the movement of the solid/liquid interface, if

appropriate. If species i is present in both the liquid and the solid phases, Eq. 28 should be used instead of Eq. 30.

Molar Flux Vector in the Liquid Phase

Free-stream molar flux for ions in an electrolytic solution.—The molar flux of species i with respect to a fixed frame of reference is defined as

$$\mathbf{N}_i^{(l)} \equiv c_i \mathbf{v}_i = \mathbf{J}_i + c_i \mathbf{v} \quad [36]$$

where \mathbf{v} is the mass-average velocity of the multicomponent system and \mathbf{J}_i is the molar flux of species i with respect to \mathbf{v} . If we neglect thermal and pressure diffusion, \mathbf{J}_i is given by

$$\mathbf{J}_i = \mathbf{J}_i^{(w)} + \mathbf{J}_i^{(f)} \quad [37]$$

where $\mathbf{J}_i^{(w)}$ and $\mathbf{J}_i^{(f)}$ are the molar fluxes due to ordinary and forced diffusion, respectively. For a mixture of N components, the molar fluxes are given by (see Ref. 1, p. 478)

$$\mathbf{J}_i^{(w)} = \frac{c_i^2}{\rho RT} \sum_{k=1}^N M_k D_{ik} \left[x_k \sum_{\substack{l=1 \\ l \neq k}}^N \left(\frac{\partial \mu_k}{\partial x_l} \right)_{T,P,x_s (s \neq k,l)} \nabla x_l \right] \quad [38]$$

$$\mathbf{J}_i^{(f)} = -\frac{c_i^2}{\rho RT} \sum_{k=1}^N M_k D_{ik} \left[x_k M_k \left(\mathbf{f}_k - \sum_{l=1}^N w_l \mathbf{f}_l \right) \right] \quad [39]$$

where c_i and ρ are the molar and mass densities of the solution, respectively; M_k is the molecular (or ionic) mass of species k ; D_{ik} is the multicomponent diffusion coefficient between species i and k ; μ_i is the chemical potential of species i ; x_k is the mole fraction of species k ; w_l is the mass fraction of species l ; \mathbf{f}_k is the external force affecting species k ; R is the universal gas constant; and T is the temperature. In an electrochemical cell, the ionic species are subject to two external forces, gravity and that attributable to the electric field

$$\mathbf{f}_i = \mathbf{g} - \frac{z_i F}{M_i} \nabla \phi^{(l)} \quad [40]$$

where \mathbf{g} is the acceleration of gravity and $\phi^{(l)}$ is the electrostatic potential in the liquid phase.

Using the above equations applied to a binary electrolytic solution and the definition of the current density in an electrolytic solution

$$\mathbf{i}^{(l)} = F \sum_{i=1}^N z_i \mathbf{N}_i^{(l)} \quad [41]$$

we obtain¹²

$$\mathbf{N}_i^{(l)} = -\frac{\nu_i D_e c_e}{\nu RT} \nabla \mu_e + \frac{t_i^*}{z_i F} \mathbf{i}^{(l)} + \nu_i c_e \mathbf{v}^* \quad [42]$$

Here μ_e is the chemical potential of the electrolyte, c_e is the concentration of electrolyte, ν_i is the number of ions i into which a molecule of electrolyte dissociates, $i^{(l)}$ is the current density in the solution, \mathbf{v}^* is the molar-average velocity of the solution, and t_i^* is the transference number of species i with respect to \mathbf{v}^* . The diffusion coefficient of the electrolyte, D_e , is based on a thermodynamic driving force and is given by¹³

$$D_e = \frac{D_{o+} D_{o-} (z_+ - z_-)}{z_+ D_{o+} - z_- D_{o-}} \quad [43]$$

where D_{ij} is the diffusion coefficient that describes the interaction between species i and j (i.e., multicomponent diffusion coefficient). The subscripts, +, −, and o refer to the cation, anion, and solvent, respectively. We have assumed here that $D_{ij} = D_{ji}$ and that the concentration of the binary electrolyte was defined as

$$c_e \equiv \frac{c_+}{\nu_+} = \frac{c_-}{\nu_-} \quad [44]$$

This definition for the electrolyte concentration allows us to satisfy automatically the electroneutrality condition, which reads

$$\sum_i z_i c_i = 0 \quad [45]$$

The chemical potential of the electrolyte, μ_e , in Eq. 42 is given by

$$\begin{aligned} \mu_e &= \nu_+ \mu_+ + \nu_- \mu_- \\ &= \nu_e RT \ln (c_e f_{\pm} a_{\pm}^0) \\ &= \nu_e RT \ln (m_e \gamma_{\pm} \lambda_{\pm}^0) \end{aligned} \quad [46]$$

in which f_{\pm} and γ_{\pm} are the mean molar and molal activity coefficients of the electrolyte, respectively; a_{\pm}^0 and λ_{\pm}^0 are proportionality constants independent of composition; m_e is the molality of the electrolyte; and $\nu_e = \nu_+ + \nu_-$. These equations can be used to obtain

$$\mathbf{N}_i^{(0)} = -\nu_i D \nabla c_e + \frac{t_i^*}{z_i F} \mathbf{i}^{(0)} + \nu_i c_e \mathbf{v}^* \quad [47]$$

where D is the diffusion coefficient of the salt (electrolyte) based on a gradient of concentration and is related to D_e by¹³

$$D = D_e \left(1 + \frac{d \ln f_{\pm}}{d \ln c_e} \right) \quad [48]$$

Finally, the molar flux vector for a neutral species dissolved in the electrolyte is treated here as a dilute species and is given by

$$\mathbf{N}_i^{(0)} = -D_i^{(0)} \nabla c_i^{(0)} + c_i^{(0)} \mathbf{v}^* \quad [49]$$

in which $D_i^{(0)}$ is the diffusion coefficient of species i in the electrolytic solution.

Volume average of the molar flux vector.—Assuming that t_i^* is constant, the local volume average of the molar flux vector can be written as

$$\begin{aligned} \overline{\mathbf{N}}_i^{(0)} &= -\overline{\nu_i D \nabla c_e^{(0)}} + \frac{t_i^*}{z_i F} \mathbf{i}^{(0)} + \overline{\nu_i c_e \mathbf{v}^*} \\ &= -\overline{\nu_i D \nabla c_e^{(0)}} + \frac{t_i^*}{z_i F} \mathbf{i}^{(0)} + \nu_i c_e \mathbf{v}^* \end{aligned} \quad [50]$$

Using the theorem for the volume average of a gradient (Eq. 7), we have

$$\overline{\nabla c_e^{(0)}} = \overline{\nabla c_e^{(0)}} + \frac{1}{V} \int_{S_{(0g)}} c_e \mathbf{n}_{(0g)} dS + \frac{1}{V} \int_{S_{(0s)}} c_e \mathbf{n}_{(0s)} dS \quad [51]$$

This allows us to write

$$\overline{\mathbf{N}}_i^{(0)} = -\nu_i \langle D \rangle^{(0)} \overline{\nabla c_e^{(0)}} + \frac{t_i^*}{z_i F} \mathbf{i}^{(0)} + \nu_i \langle c_e \rangle^{(0)} \mathbf{v}^* - \Delta_i^{(0)} \quad [52]$$

where $\Delta_i^{(0)}$ is the molar density tortuosity vector and is defined as

$$\begin{aligned} \Delta_i^{(0)} &= \nu_i \overline{\nabla c_e^{(0)}} - \nu_i \langle D \rangle^{(0)} \overline{\nabla c_e^{(0)}} + \nu_i \langle D \rangle^{(0)} \frac{1}{V} \int_{S_{(0g)}} c_e \mathbf{n}_{(0g)} dS \\ &+ \nu_i \langle D \rangle^{(0)} \frac{1}{V} \int_{S_{(0s)}} c_e \mathbf{n}_{(0s)} dS + \nu_i \langle c_e \rangle^{(0)} \mathbf{v}^* - \nu_i c_e \mathbf{v}^* \end{aligned} \quad [53]$$

The molar density tortuosity vector represents the deviations of the molar flux in a porous medium from the free-stream molar flux. These deviations are caused by the physical obstruction of the transport path in one phase by the presence of other phases. Thus, the transport of material is expected to be slower through a multiple-phase system than through a free stream. Experimental data can be used to prepare empirical correlations for $\Delta_i^{(0)}$ (see, e.g., Ref. 1).

Specific example.—*Nonoriented porous solid with no convection.*—The simplest form of empirical correlations for $\Delta_i^{(0)}$ is that of a nonoriented porous solid when convection can be neglected. In such a case, we can expect $\Delta_i^{(0)}$ to be a function of the particle size of the porous medium, l_0 ; the liquid porosity, $\epsilon^{(0)}$; the diffusion coefficient, $\langle D \rangle^{(0)}$; and some local distribution of the electrolyte concentration, such as $\overline{c_e^{(0)}}$ or $\nabla \overline{c_e^{(0)}}$. Following the analysis presented by Slattery,¹ an empirical correlation for $\Delta_i^{(0)}$ takes the form

$$\Delta_i^{(0)} = \nu_i D_i^* \langle D \rangle^{(0)} \nabla \overline{c_e^{(0)}} \quad [54]$$

with

$$D_i^* = D_i^* \left(\epsilon^{(0)} \frac{l_0 |\nabla \overline{c_e^{(0)}}|}{\overline{c_e^{(0)}}} \right) \quad [55]$$

If we substitute Eq. 54 into Eq. 52, we obtain an expression for the average molar flux when convection can be neglected in a porous electrode with uniform porosity and nonoriented matrix structure

$$\overline{\mathbf{N}}_i^{(0)} = -\nu_i \langle D \rangle^{(0)} (1 + D_i^*) \nabla \overline{c_e^{(0)}} + \frac{t_i^*}{z_i F} \mathbf{i}^{(0)} \quad [56]$$

or using the relation between the local and the intrinsic volume average (Eq. 6), we have

$$\overline{\mathbf{N}}_i^{(0)} = -\nu_i \langle D \rangle^{(0)} (1 + D_i^*) \nabla (\epsilon^{(0)} \langle c_e \rangle^{(0)}) + \frac{t_i^*}{z_i F} \mathbf{i}^{(0)} \quad [57]$$

The porosity is not a function of position because we are considering the case of a nonoriented porous medium; thus, Eq. 57 becomes

$$\overline{\mathbf{N}}_i^{(0)} = -\nu_i \langle D \rangle^{(0)} (1 + D_i^*) \nabla (\langle c_e \rangle^{(0)}) + \frac{t_i^*}{z_i F} \mathbf{i}^{(0)} \quad [58]$$

The term $\langle D \rangle^{(0)} (1 + D_i^*) \epsilon^{(0)}$ in Eq. 56 is called the effective diffusion coefficient for species i , $D_{i,\text{eff}}$. In many practical applications, $D_{i,\text{eff}}$ is expressed as^{14,15}

$$D_{i,\text{eff}} = \langle D \rangle^{(0)} \frac{\epsilon^{(0)}}{\tau} \quad [59]$$

where τ is the tortuosity factor of the porous medium. In view of Eq. 58, Eq. 59 suggests that

$$(1 + D_i^*) = \frac{1}{\tau} \quad [60]$$

Using Eq. 60 in Eq. 58, we obtain

$$\overline{\mathbf{N}}_i^{(0)} = -\nu_i \langle D \rangle^{(0)} \left(\frac{\epsilon^{(0)}}{\tau} \right) \nabla (\langle c_e \rangle^{(0)}) + \frac{t_i^*}{z_i F} \mathbf{i}^{(0)} \quad [61]$$

For porous electrodes, researchers often use the following expression for the effective diffusion coefficient¹³

$$D_{i,\text{eff}}^{(0)} = \langle D \rangle^{(0)} (\epsilon^{(0)})^b \quad [62]$$

where b is a constant parameter normally equal to 1.5. This expression for the effective diffusion coefficient¹⁶ is based on findings for the electrical conductivity of fluids in porous media in which the porosity and the particle size do not depend on position (nonoriented). In view of Eq. 58, Eq. 62 suggests that

$$(1 + D_i^*) = (\epsilon^{(0)})^{b-1} \quad [63]$$

Substituting Eq. 63 into Eq. 58, we obtain

$$\overline{\mathbf{N}}_i^{(0)} = -\nu_i \langle D \rangle^{(0)} (\epsilon^{(0)})^b \nabla (\langle c_e \rangle^{(0)}) + \frac{t_i^*}{z_i F} \mathbf{i}^{(0)} \quad [64]$$

For the case of an oriented porous solid when convection can be neglected, we can expect the molar density tortuosity vector $\Delta_i^{(0)}$ to be a function of the gradient in particle size, ∇l , in addition to the quantities considered for the nonoriented porous media. In this case $\Delta_i^{(0)}$ can be expressed as

$$\Delta_i^{(l)} = \nu_i \langle D \rangle^{(l)} E_{i1}^* \nabla \bar{c}_e^{(l)} + \langle D \rangle^{(l)} \nu_i |\nabla \bar{c}_e^{(l)}| E_{i2}^* \nabla l \quad [65]$$

where l is the particle diameter, which is a function of position. Here

$$E_{ik}^* = E_{ik}^*(\epsilon^{(l)}, l, |\nabla l|, |\nabla \bar{c}_e^{(l)}|, \nabla l \cdot \nabla \bar{c}_e^{(l)}, \bar{c}_e^{(l)}) \quad \text{for } k = 1, 2 \quad [66]$$

Applying the Buckingham-Pi theorem¹⁷ reduces this to

$$E_{ik}^* = E_{ik}^* \left(\epsilon^{(l)}, |\nabla l|, \frac{|\nabla l \cdot \nabla \bar{c}_e^{(l)}|}{|\nabla l| |\nabla \bar{c}_e^{(l)}|}, \frac{|\nabla \bar{c}_e^{(l)}|}{\bar{c}_e^{(l)}} \right) \quad \text{for } k = 1, 2 \quad [67]$$

We can see that a tortuosity correction for a porous electrode in which the particle size is a function of position, in general, will not take the most commonly used form given in Eq. 63. Substituting Eq. 65 into Eq. 52, we obtain an expression for the average molar flux when convection can be neglected in a porous electrode with an oriented matrix structure

$$\bar{N}_i^{(l)} = -\nu_i \langle D \rangle^{(l)} \left(1 + E_{i1}^* \right) \nabla \bar{c}_e^{(l)} - \nu_i \langle D \rangle^{(l)} |\nabla \bar{c}_e^{(l)}| E_{i2}^* \nabla l + \frac{t_i^*}{z_i F} \bar{i}^{(l)} \quad [68]$$

or using the relation between the local and the intrinsic volume average (Eq. 6), we have

$$\bar{N}_i^{(l)} = -\nu_i \langle D \rangle^{(l)} \left(1 + E_{i1}^* \right) \nabla (\epsilon^{(l)} \langle c_e \rangle^{(l)}) - \nu_i \langle D \rangle^{(l)} \left| \nabla (\epsilon^{(l)} \langle c_e \rangle^{(l)}) \right| E_{i2}^* \nabla l + \frac{t_i^*}{z_i F} \bar{i}^{(l)} \quad [69]$$

Equation 69 should be used instead of Eq. 64 for porous electrodes in which the porosity and characteristic particle size of the solid are a function of position, unless these variations are negligible. Such cases are, for example, porous electrodes that exhibit large changes in volume of the solid phase as the active materials react, because this leads to changes in the particle size and porosity which varies with position inside the electrode.

Because Eq. 69 is valid for variable porosity, it must be also valid for the particular case in which the porosity and particle size are not functions of position. In such a case, we obtain

$$\bar{N}_i^{(l)} = -\nu_i \langle D \rangle^{(l)} \left(1 + E_{i1}^* \right) \epsilon^{(l)} \nabla (\langle c_e \rangle^{(l)}) + \frac{t_i^*}{z_i F} \bar{i}^{(l)} \quad [70]$$

Equation 70 should be equivalent to Eq. 58. And, if we assume that the effective diffusion coefficient is given by Eq. 62, the term $(1 + E_{i1}^*)$ should be given by

$$(1 + E_{i1}^*) = (\epsilon^{(l)})^{b-1} \quad [71]$$

Substituting Eq. 71 into Eq. 69, we obtain

$$\bar{N}_i^{(l)} = -\nu_i \langle D \rangle^{(l)} (\epsilon^{(l)})^{b-1} \nabla (\epsilon^{(l)} \langle c_e \rangle^{(l)}) - \nu_i \langle D \rangle^{(l)} |\nabla (\epsilon^{(l)} \langle c_e \rangle^{(l)})| E_{i2}^* \nabla l + \frac{t_i^*}{z_i F} \bar{i}^{(l)} \quad [72]$$

Equation 72 is valid for cases in which the porosity and the particle size are functions of position. For cases in which the particle size does not change with position, the second term in Eq. 72 is zero, and the molar-flux vector is given by

$$\bar{N}_i^{(l)} = -\nu_i \langle D \rangle^{(l)} (\epsilon^{(l)})^{b-1} \nabla (\epsilon^{(l)} \langle c_e \rangle^{(l)}) + \frac{t_i^*}{z_i F} \bar{i}^{(l)} \quad [73]$$

The averaged molar flux for neutral species is obtained by taking the volume average of Eq. 49

$$\bar{N}_i^{(l)} = -D_i^{(l)} \nabla \bar{c}_i^{(l)} + c_i \bar{v}^{(l)} \quad [74]$$

In Eq. 74 we have assumed that the diffusion coefficient $D_i^{(l)}$ is a constant. The theorem for the volume average of a gradient (Eq. 7) allows us to write

$$\nabla \bar{c}_i^{(l)} = \nabla \bar{c}_i^{(l)} + \frac{1}{V} \int_{S_{(lg)}} c_i \mathbf{n}_{(lg)} dS + \frac{1}{V} \int_{S_{(ls)}} c_i \mathbf{n}_{(ls)} dS \quad [75]$$

and Eq. 74 becomes

$$\bar{N}_i^{(l)} = -D_i^{(l)} \nabla \bar{c}_i^{(l)} + \langle c_i \rangle^{(l)} \bar{v}^{(l)} - \Delta_i^{(l)} \quad [76]$$

with the molar density tortuosity vector defined as

$$\Delta_i^{(l)} = \frac{D_i^{(l)}}{V} \int_{S_{(lg)}} c_i \mathbf{n}_{(lg)} dS + \frac{D_i^{(l)}}{V} \int_{S_{(ls)}} c_i \mathbf{n}_{(ls)} dS + \langle c_i \rangle^{(l)} \bar{v}^{(l)} - \bar{c}_i \bar{v}^{(l)} \quad [77]$$

Proceeding analogously as we did for the molar density tortuosity vector for ionic species in an oriented porous electrode when convection can be neglected (Eq. 65 and 67), we obtain

$$\Delta_i^{(l)} = D_i^{(l)} E_{i1}^* \nabla \bar{c}_i^{(l)} + D_i^{(l)} |\nabla \bar{c}_i^{(l)}| E_{i2}^* \nabla l \quad [78]$$

with

$$E_{ik}^* = E_{ik}^* \left(\epsilon^{(l)}, |\nabla l|, \frac{|\nabla l \cdot \nabla \bar{c}_i^{(l)}|}{|\nabla l| |\nabla \bar{c}_i^{(l)}|}, \frac{|\nabla \bar{c}_i^{(l)}|}{\bar{c}_i^{(l)}} \right) \quad \text{for } k = 1, 2 \quad [79]$$

Substituting Eq. 78 into Eq. 76 and using Eq. 6, we obtain

$$\bar{N}_i^{(l)} = -D_i^{(l)} (1 + E_{i1}^*) \nabla (\epsilon^{(l)} \langle c_i \rangle^{(l)}) - D_i^{(l)} |\epsilon^{(l)} \langle c_i \rangle^{(l)}| E_{i2}^* \nabla l \quad [80]$$

Again, if the effective diffusion coefficient is assumed to be of the form given in Eq. 62, Eq. 80 would become

$$\bar{N}_i^{(l)} = -D_i^{(l)} (\epsilon^{(l)})^{b-1} \nabla (\epsilon^{(l)} \langle c_i \rangle^{(l)}) - D_i^{(l)} |\nabla \bar{c}_i^{(l)}| E_{i2}^* \nabla l \quad [81]$$

And if the particle size does not depend on position, Eq. 81 becomes

$$\bar{N}_i^{(l)} = -D_i^{(l)} (\epsilon^{(l)})^{b-1} \nabla (\epsilon^{(l)} \langle c_i \rangle^{(l)}) \quad [82]$$

The equations derived in this section for the molar fluxes of species in the electrolytic solution are similar to those presented by Newman (see Eq. 22.11 of Ref. 13 or Eq. 20 and 30 of Ref. 9), but they have one important difference. The porosity that is premultiplying the average concentration in Eq. 73 and 82 appears outside the gradient operator in Newman's equations. For cases in which both the porosity and particle size of the electrode do not depend on position, the equations derived here are identical to those presented by Newman. However, for cases in which changes in porosity and particle size of the solid phase are important, one should use equations of the form given in Eq. 72 and 81. Also, one should find empirical expressions for E_{i1}^* and E_{i2}^* in view of Eq. 67 and 78 that are appropriate for the system under consideration.

Molar flux vectors for species in the gas and solid phases.—Similar flux vectors can be derived for species in the gas and solid phases (please see Ref. 12).

Summary of Equations of Continuity for the Liquid, Gas, and Solid Phases

We present here the equations that apply when variations in porosity may occur, but the variations in particle size can be neglected, that is, the terms containing ∇l in the expression for the molar fluxes for the liquid, gas, and solid are assumed to be zero.

For ionic species in the liquid phase we have

$$\frac{\partial (\epsilon^{(l)} \langle c_i \rangle^{(l)})}{\partial t} - \nu_i \nabla \cdot \left[\langle D \rangle^{(l)} (\epsilon^{(l)})^{b-1} \nabla (\epsilon^{(l)} \langle c_e \rangle^{(l)}) \right] + \frac{t_i^*}{z_i F} \nabla \bar{i}^{(l)} - \bar{R}_i^{(ls)} = 0 \quad \text{for } i = +, - \quad [83]$$

For neutral species in the liquid phase we have

$$\frac{\partial(\epsilon^{(l)}\langle c_i \rangle^{(l)})}{\partial t} - \nabla \cdot [D_i^{(l)}(\epsilon^{(l)})^{b-1} \nabla(\epsilon^{(l)}\langle c_i \rangle^{(l)})] + \bar{F}_i^{(lg)} - \bar{R}_i^{(ls)} = 0 \quad [84]$$

For species i the gas phase we have

$$\frac{\partial(\epsilon^{(g)}\langle c_i \rangle^{(g)})}{\partial t} - D_i^{(g)} \nabla \cdot [(\epsilon^{(g)})^{b-1} \nabla(\epsilon^{(g)}\langle c_i \rangle^{(g)})] + D_i^{(gl)} \nabla \cdot [(\epsilon^{(g)})^{b-1} \langle c_i \rangle^{(g)} \nabla(\epsilon^{(g)}\langle c_i \rangle^{(g)})] - \bar{F}_i^{(lg)} - \bar{R}_i^{(gs)} = 0 \quad [85]$$

And for species in the solid phase we have

$$\frac{\partial(\epsilon^{(s)}\langle c_i \rangle^{(s)})}{\partial t} - D_i^{(s)} \nabla \cdot [(\epsilon^{(s)})^{b-1} \nabla(\epsilon^{(s)}\langle c_i \rangle^{(s)})] - \bar{R}_i^{(ls)} - \bar{R}_i^{(gs)} = 0 \quad [86]$$

with the solid porosity defined as $\epsilon^{(s)} = 1 - (\epsilon^{(l)} + \epsilon^{(g)})$.

Modified Ohm's Law for the Liquid Phase

The free-stream current density for a concentrated binary electrolyte can be expressed as¹³

$$\mathbf{i}^{(l)} = -\kappa \nabla \phi^{(l)} - \frac{\kappa}{F} \left(\frac{s_+}{n\nu_+} + \left(\frac{1}{z_+} - \frac{1}{z_-} \right) \frac{c_e t_+^*}{c_o} + \frac{t_+^*}{z_+ \nu_+} + \left(\frac{1}{z_-} - \frac{s_o}{n} \right) \frac{c_e}{c_o} \right) \nabla \mu_e \quad [87]$$

where κ is the conductivity of the electrolyte. If we use the above expression for μ_e , we obtain

$$\mathbf{i}^{(l)} = -\kappa \nabla \phi^{(l)} - \frac{\kappa \nu_e RT}{F} \left(\frac{s_+}{n\nu_+} + \left(\frac{1}{z_+} - \frac{1}{z_-} \right) \frac{c_e t_+^*}{c_o} + \frac{t_+^*}{z_+ \nu_+} + \left(\frac{1}{z_-} - \frac{s_o}{n} \right) \frac{c_e}{c_o} \right) \left(1 + \frac{d \ln f_{\pm}}{d \ln c_e} \right) \frac{\nabla c_e}{c_e} \quad [88]$$

If we take the local volume average of $\mathbf{i}^{(l)}$ over the liquid phase and use the theorem for the volume average of a gradient (Eq. 7), we have

$$\bar{\mathbf{i}}^{(l)} = -\langle \kappa \rangle \nabla \phi^{(l)} - \frac{\nu_e RT}{F} \langle \kappa \rangle^{(l)} \left(1 + \left\langle \frac{d \ln f_{\pm}}{d \ln c_e} \right\rangle^{(l)} \right) \left(\frac{s_+}{n\nu_+} + \frac{t_+^*}{z_+ \nu_+} + \left(\frac{1}{z_+} - \frac{1}{z_-} \right) t_+^* \left\langle \frac{c_e}{c_o} \right\rangle^{(l)} + \left(\frac{1}{z_-} - \frac{s_o}{n} \right) \left\langle \frac{c_e}{c_o} \right\rangle^{(l)} \right) \nabla \ln c_e^{(l)} - \Psi^{(l)} \quad [89]$$

where $\Psi^{(l)}$ is defined as the current density tortuosity vector

$$\Psi^{(l)} = \kappa \nabla \phi^{(l)} - \langle \kappa \rangle^{(l)} \nabla \phi^{(l)} + \frac{\langle \kappa \rangle^{(l)}}{V} \int_{S_{(lg)}} \phi^{(l)} \mathbf{n}_{(lg)} dS + \frac{\langle \kappa \rangle^{(l)}}{V} \int_{S_{(ls)}} \phi^{(l)} \mathbf{n}_{(ls)} dS + \frac{\nu_e RT}{F} \left(\frac{s_+}{n\nu_+} + \frac{t_+^*}{z_+ \nu_+} \right) \left[\kappa \left(1 + \frac{d \ln f_{\pm}}{d \ln c_e} \right) \nabla \ln c_e - \langle \kappa \rangle^{(l)} \left(1 + \left\langle \frac{d \ln f_{\pm}}{d \ln c_e} \right\rangle^{(l)} \right) \left(\nabla \ln c_e^{(l)} - \frac{1}{V} \int_{S_{(lg)}} \ln c_e \mathbf{n}_{(lg)} dS - \frac{1}{V} \int_{S_{(ls)}} \ln c_e \mathbf{n}_{(ls)} dS \right) \right] + \frac{\nu_e RT}{F} \left(\left(\frac{1}{z_+} - \frac{1}{z_-} \right) t_+^* + \frac{1}{z_-} \right) \left(\nabla \ln c_e^{(l)} - \frac{1}{V} \int_{S_{(lg)}} \ln c_e \mathbf{n}_{(lg)} dS - \frac{1}{V} \int_{S_{(ls)}} \ln c_e \mathbf{n}_{(ls)} dS \right) \quad [90]$$

$$- \frac{s_o}{n} \left[\kappa \left(1 + \frac{d \ln f_{\pm}}{d \ln c_e} \right) \frac{c_e}{c_o} \nabla \ln c_e - \langle \kappa \rangle^{(l)} \left(1 + \left\langle \frac{d \ln f_{\pm}}{d \ln c_e} \right\rangle^{(l)} \right) \left(\frac{c_e}{c_o} \right) \left(\nabla \ln c_e - \frac{1}{V} \int_{S_{(lg)}} \ln c_e \mathbf{n}_{(lg)} dS - \frac{1}{V} \int_{S_{(ls)}} \ln c_e \mathbf{n}_{(ls)} dS \right) \right] \quad [90]$$

We can see that if $\phi^{(l)}$ and c_e were independent of position inside the volume V , $\Psi^{(l)}$ would be equal to zero. For convenience, let us define

$$A = \frac{\nu_e RT}{F} \left(1 + \left\langle \frac{d \ln f_{\pm}}{d \ln c_e} \right\rangle^{(l)} \right) \left(\frac{s_+}{n\nu_+} + \frac{t_+^*}{z_+ \nu_+} + \left(\frac{1}{z_+} - \frac{1}{z_-} \right) t_+^* \left\langle \frac{c_e}{c_o} \right\rangle^{(l)} + \left(\frac{1}{z_-} - \frac{s_o}{n} \right) \left\langle \frac{c_e}{c_o} \right\rangle^{(l)} \right) \quad [91]$$

Analogous to the molar density tortuosity vector for an oriented porous matrix, we can expect $\Psi^{(l)}$ to be a function of the solid particle size; l ; the gradient in particle size, ∇l ; the liquid porosity, $\epsilon^{(l)}$; the conductivity of the electrolyte, $\langle \kappa \rangle^{(l)}$; the quantity A defined above; and some local distribution of the electrolyte concentration and potential, such as $\nabla \ln c_e$ and $\nabla \phi^{(l)}$. Following the procedure described by Slattery,¹ we may postulate the following empirical correlation for $\Psi^{(l)}$

$$\Psi^{(l)} = \langle \kappa \rangle^{(l)} G_1^* \nabla \phi^{(l)} + \langle \kappa \rangle^{(l)} G_2^* A \nabla \ln c_e^{(l)} + \langle \kappa \rangle^{(l)} |\nabla \phi^{(l)}| G_3^* \nabla l \quad [92]$$

$$\Psi^{(l)} = \langle \kappa \rangle^{(l)} G_1^* \nabla \phi^{(l)} + \langle \kappa \rangle^{(l)} G_2^* \frac{\nu_e RT}{F} \left(1 + \left\langle \frac{d \ln f_{\pm}}{d \ln c_e} \right\rangle^{(l)} \right) \left(\frac{s_+}{n\nu_+} + \frac{t_+^*}{z_+ \nu_+} + \left(\frac{1}{z_+} - \frac{1}{z_-} \right) t_+^* \left\langle \frac{c_e}{c_o} \right\rangle^{(l)} + \left(\frac{1}{z_-} - \frac{s_o}{n} \right) \left\langle \frac{c_e}{c_o} \right\rangle^{(l)} \right) \nabla \ln c_e^{(l)} + \langle \kappa \rangle^{(l)} |\nabla \phi^{(l)}| G_3^* \nabla l \quad [93]$$

with

$$G_i^* = G_i \left(\epsilon^{(l)}, |\nabla l|, \frac{\nabla \phi^{(l)} \cdot \nabla \ln c_e^{(l)}}{|\nabla \phi^{(l)}| |\nabla \ln c_e^{(l)}|}, \frac{\nabla \phi^{(l)} \cdot \nabla l}{|\nabla \phi^{(l)}| |\nabla l|}, \frac{\nabla l \cdot \nabla \ln c_e^{(l)}}{|\nabla l| |\nabla \ln c_e^{(l)}|}, \frac{A}{|\nabla \phi^{(l)}|} \right) \quad [94]$$

for $i = 1, 2, 3$.

Substituting Eq. 93 into Eq. 89, we obtain

$$\bar{\mathbf{i}}^{(l)} = -\langle \kappa \rangle^{(l)} (1 + G_1^*) \nabla \phi^{(l)} - \langle \kappa \rangle^{(l)} (1 + G_2^*) \frac{\nu_e RT}{F} \left(1 + \left\langle \frac{d \ln f_{\pm}}{d \ln c_e} \right\rangle^{(l)} \right) \left(\frac{s_+}{n\nu_+} + \frac{t_+^*}{z_+ \nu_+} + \left(\frac{1}{z_+} - \frac{1}{z_-} \right) t_+^* \left\langle \frac{c_e}{c_o} \right\rangle^{(l)} + \left(\frac{1}{z_-} - \frac{s_o}{n} \right) \left\langle \frac{c_e}{c_o} \right\rangle^{(l)} \right) \nabla \ln c_e^{(l)} - \langle \kappa \rangle^{(l)} G_3^* |\nabla \phi^{(l)}| \nabla l \quad [95]$$

To find a suitable functionality for $\Psi^{(l)}$, one would have to measure the electrical conductivity of the electrolyte for various porosities and solid particle sizes. Most frequently, researchers use an effective conductivity which is proportional to the porosity of the electrode to some power,¹³ that is

$$\kappa_{\text{eff}} = \langle \kappa \rangle^{(0)} (\epsilon^{(0)})^d \quad [96]$$

where d is a constant parameter normally equal to 1.5. This expression was obtained for porous systems in which neither the porosity nor the particle size vary with position.¹⁶ Thus, if concentration effects and gradients in particle size are important for a particular system, one would have to find a better empirical expression.

Consideration of the two equations given immediately above shows that

$$1 + G_1^* = (\epsilon^{(0)})^{d-1} \quad \text{and} \quad 1 + G_2^* = (\epsilon^{(0)})^{d-1} \quad [97]$$

Thus, the current density in the electrolyte becomes

$$\begin{aligned} \bar{\mathbf{i}}^{(0)} = & -\langle \kappa \rangle^{(0)} (\epsilon^{(0)})^{d-1} \nabla \bar{\Phi}^{(0)} - \frac{\nu_e RT}{F} \langle \kappa \rangle^{(0)} (\epsilon^{(0)})^{d-1} \\ & \left(1 + \left\langle \frac{d \ln f_{\pm}}{d \ln c_e} \right\rangle^{(0)} \right) \left(\frac{s_+}{n\nu_+} + \frac{t_+^*}{z_+ \nu_+} + \left(\frac{1}{z_+} - \frac{1}{z_-} \right) t_+^* \left\langle \frac{c_e}{c_o} \right\rangle^{(0)} \right. \\ & \left. + \left(\frac{1}{z_-} - \frac{s_o}{n} \right) \left\langle \frac{c_e}{c_o} \right\rangle^{(0)} \right) \nabla \ln c_e^{(0)} - \langle \kappa \rangle^{(0)} G_3^* |\nabla \bar{\Phi}^{(0)}| \nabla l \quad [98] \end{aligned}$$

The term $\ln c_e^{(0)}$ in Eq. 98 needs to be changed to an expression in terms of $\langle c_e \rangle^{(0)}$, so that the equation will be compatible with the volume-averaged variables introduced in the equation of continuity. If we assume that the concentration in volume V is close to $\langle c_e \rangle^{(0)}$, we can use a linear approximation for $\ln c_e$ in the vicinity of $\langle c_e \rangle^{(0)}$. Using a Taylor series, we have

$$\ln c_e \approx \ln \langle c_e \rangle^{(0)} + \frac{1}{\langle c_e \rangle^{(0)}} (c_e - \langle c_e \rangle^{(0)}) \quad [99]$$

Therefore

$$\begin{aligned} \overline{\ln c_e} \approx & \frac{1}{V} \int_{V_0} \left(\ln \langle c_e \rangle^{(0)} + \frac{1}{\langle c_e \rangle^{(0)}} (c_e - \langle c_e \rangle^{(0)}) \right) dV \\ & = \epsilon^{(0)} \ln \langle c_e \rangle^{(0)} \quad [100] \end{aligned}$$

Using this approximation, we obtain

$$\begin{aligned} \bar{\mathbf{i}}^{(0)} = & -\langle \kappa \rangle^{(0)} (\epsilon^{(0)})^{d-1} \nabla (\epsilon^{(0)} \langle \Phi \rangle^{(0)}) - \frac{\nu_e RT}{F} \langle \kappa \rangle^{(0)} (\epsilon^{(0)})^{d-1} \\ & \left(1 + \left\langle \frac{d \ln f_{\pm}}{d \ln c_e} \right\rangle^{(0)} \right) \left(\frac{s_+}{n\nu_+} + \frac{t_+^*}{z_+ \nu_+} + \left(\frac{1}{z_+} - \frac{1}{z_-} \right) t_+^* \left\langle \frac{c_e}{c_o} \right\rangle^{(0)} \right. \\ & \left. + \left(\frac{1}{z_-} - \frac{s_o}{n} \right) \left\langle \frac{c_e}{c_o} \right\rangle^{(0)} \right) \nabla (\epsilon^{(0)} \ln \langle c_e \rangle^{(0)}) - \langle \kappa \rangle^{(0)} G_3^* |\nabla (\epsilon^{(0)} \langle \Phi \rangle^{(0)})| \nabla l \quad [101] \end{aligned}$$

For cases in which the variations in particle size can be neglected, the last term in Eq. 101 is zero, and the current density is given by

$$\begin{aligned} \bar{\mathbf{i}}^{(0)} = & -\langle \kappa \rangle^{(0)} (\epsilon^{(0)})^{d-1} \nabla (\epsilon^{(0)} \langle \Phi \rangle^{(0)}) - \frac{\nu_e RT}{F} \langle \kappa \rangle^{(0)} (\epsilon^{(0)})^{d-1} \\ & \left(1 + \left\langle \frac{d \ln f_{\pm}}{d \ln c_e} \right\rangle^{(0)} \right) \left(\frac{s_+}{n\nu_+} + \frac{t_+^*}{z_+ \nu_+} + \left(\frac{1}{z_+} - \frac{1}{z_-} \right) t_+^* \left\langle \frac{c_e}{c_o} \right\rangle^{(0)} \right. \\ & \left. + \left(\frac{1}{z_-} - \frac{s_o}{n} \right) \left\langle \frac{c_e}{c_o} \right\rangle^{(0)} \right) \nabla (\epsilon^{(0)} \ln \langle c_e \rangle^{(0)}) \quad [102] \end{aligned}$$

Similar to what we found for the equations for the molar flux factor in the liquid phase, the equation we have derived for Ohm's law in the electrolyte has one difference relative to that presented by Newman (see Eq. 24 of Ref. 9). The porosity that is premultiplying the average potential in Eq. 102 appears outside the gradient operator in Newman's equations. As we mentioned before, for cases in which the

porosity of the electrode and particle size do not depend on position, the equation derived here is identical to that presented by Newman. The second term in Eq. 102 cannot be compared to Newman's equation because it does not appear extended in Eq. 34 of Ref. 9; it appears just as $\nabla \mu_e$.

Ohm's Law for the Solid Phase

Ohm's law states that the electronic current density is proportional to the gradient of the electric potential; thus, the current density in a solid is given by

$$\mathbf{i}^{(s)} = -\sigma^{(s)} \nabla \Phi^{(s)} \quad [103]$$

where $\mathbf{i}^{(s)}$ and $\Phi^{(s)}$ are the current density and electric potential in the solid phase, and $\sigma^{(s)}$ is the electrical conductivity of the solid. We are interested in finding an expression for the current density in the solid at any position inside the porous electrode. If we take the local volume average of this equation over the solid phase and assume that the conductivity in the solid is constant, we have

$$\bar{\mathbf{i}}^{(s)} = -\sigma^{(s)} \nabla \bar{\Phi}^{(s)} - \Psi^{(s)} \quad [104]$$

where we have defined the current density tortuosity vector for the solid phase $\Psi^{(s)}$, as

$$\Psi^{(s)} = -\frac{\sigma^{(s)}}{V} \int_{S_{(s)}} \Phi^{(s)} \mathbf{n}_{(s)} dS - \frac{\sigma^{(s)}}{V} \int_{S_{(gs)}} \Phi^{(s)} \mathbf{n}_{(gs)} dS \quad [105]$$

By analogy with the analysis made for the molar density and current density tortuosity vectors, we may write empirical correlations for $\Psi^{(s)}$. For an oriented solid matrix $\Psi^{(s)}$ is expected to be a function of the particle size, l ; the gradient in particle size, ∇l ; the ratio between solid volume to electrode volume, $\epsilon^{(s)}$; the conductivity of the solid, $\sigma^{(s)}$; and some local distribution of the solid potential, such as $\nabla \Phi^{(s)}$. A suitable expression for $\Psi^{(s)}$ is

$$\Psi^{(s)} = \sigma^{(s)} H_1^* \nabla \bar{\Phi}^{(s)} + \sigma^{(s)} |\nabla \bar{\Phi}^{(s)}| H_2^* \nabla l \quad [106]$$

with

$$H_i^* = H_i^* \left(\epsilon^{(s)}, \frac{\nabla l \cdot \nabla \bar{\Phi}^{(s)}}{|\nabla l| |\nabla \bar{\Phi}^{(s)}|} \right) \quad \text{for } i = 1, 2 \quad [107]$$

Thus, the current density in the solid becomes

$$\bar{\mathbf{i}}^{(s)} = -\sigma^{(s)} (1 + H_1^*) \nabla \bar{\Phi}^{(s)} - \sigma^{(s)} |\nabla \bar{\Phi}^{(s)}| H_2^* \nabla l \quad [108]$$

Assuming that the tortuosity correction for the conductivity in the solid is of the same form as that for the conductivity in the liquid phase (see Eq. 98), we have

$$1 + H_1^* = (\epsilon^{(s)})^{d-1} \quad [109]$$

and

$$\bar{\mathbf{i}}^{(s)} = -\sigma^{(s)} (\epsilon^{(s)})^{d-1} \nabla (\epsilon^{(s)} \langle \Phi \rangle^{(s)}) - \sigma^{(s)} (\epsilon^{(s)} \langle \Phi \rangle^{(s)}) H_2^* \nabla l \quad [110]$$

Conservation of Charge

The equation of conservation of charge without double-layer charging reads¹³

$$\frac{\partial q}{\partial t} + \nabla \cdot \mathbf{i} = 0 \quad [111]$$

where q is the charge density at any position in a material. We require that any portion of the electrode be electrically neutral; furthermore, each separate phase must be electrically neutral.¹³ Here we consider the gas phase as an electrical insulator with no ionic species. There is no current flowing through the gas phase, and the equation of conservation of charge (Eq. 111) is identically equal to zero.

Conservation of charge in the liquid phase.—If we take the local volume average of Eq. 111 over the liquid phase, we have

$$\frac{\partial \bar{q}}{\partial t} + \bar{\nabla} \cdot \bar{\mathbf{i}}^{(0)} = \frac{1}{V} \int_{V_0} \frac{\partial q^{(0)}}{\partial t} dV + \frac{1}{V} \int_{V_0} \nabla \cdot \mathbf{i}^{(0)} dV = 0 \quad [112]$$

Applying the general transport theorem (Eq. 12) to the first term, we have

$$\frac{1}{V} \int_{V_{(l)}} \frac{\partial q^{(l)}}{\partial t} dV = \frac{d}{dt} \left(\frac{1}{V} \int_{V_{(l)}} q^{(l)} dV \right) - \frac{1}{V} \int_{S_{(l)}} q^{(l)} \mathbf{v} \cdot \mathbf{n} dS \quad [113]$$

$$\begin{aligned} \frac{1}{V} \int_{V_{(l)}} \frac{\partial q^{(l)}}{\partial t} dV &= \frac{d\bar{q}^{(l)}}{dt} - \frac{1}{V} \int_{S_{(ls)}} q^{(l)} \mathbf{v}_{(ls)} \cdot \mathbf{n}_{(ls)} dS \\ &\quad - \frac{1}{V} \int_{S_{(lg)}} q^{(l)} \mathbf{v}_{(lg)} \cdot \mathbf{n}_{(lg)} dS - \frac{1}{V} \int_{S_{(le)}} q^{(l)} \mathbf{v}_{(le)} \cdot \mathbf{n}_{(le)} dS \quad [114] \end{aligned}$$

The velocity of the boundary $S_{(le)}$ is zero, thus

$$\begin{aligned} \frac{1}{V} \int_{V_{(l)}} \frac{\partial q^{(l)}}{\partial t} dV &= \frac{d\bar{q}^{(l)}}{dt} - \frac{1}{V} \int_{S_{(ls)}} q^{(l)} \mathbf{v}_{(ls)} \cdot \mathbf{n}_{(ls)} dS \\ &\quad - \frac{1}{V} \int_{S_{(lg)}} q^{(l)} \mathbf{v}_{(lg)} \cdot \mathbf{n}_{(lg)} dS \quad [115] \end{aligned}$$

Applying the theorem for the volume average of a divergence (Eq. 10) to the second term in Eq. 112, we have

$$\begin{aligned} \frac{1}{V} \int_{V_{(l)}} \nabla \cdot \mathbf{i}^{(l)} dV &= \nabla \cdot \bar{\mathbf{i}}^{(l)} + \frac{1}{V} \int_{S_{(ls)}} \mathbf{i}^{(l)} \cdot \mathbf{n}_{(ls)} dS \\ &\quad + \frac{1}{V} \int_{S_{(lg)}} \mathbf{i}^{(l)} \cdot \mathbf{n}_{(lg)} dS \quad [116] \end{aligned}$$

Substituting Eq. 115 and 116 into Eq. 112, we obtain

$$\begin{aligned} \frac{d\bar{q}^{(l)}}{dt} + \nabla \cdot \bar{\mathbf{i}}^{(l)} + \frac{1}{V} \int_{S_{(ls)}} (\mathbf{i}^{(l)} - q^{(l)} \mathbf{v}_{(ls)}) \cdot \mathbf{n}_{(ls)} dS \\ + \frac{1}{V} \int_{S_{(lg)}} (\mathbf{i}^{(l)} - q^{(l)} \mathbf{v}_{(lg)}) \cdot \mathbf{n}_{(lg)} dS = 0 \quad [117] \end{aligned}$$

Since we have assumed that the condition of electroneutrality applies everywhere in the liquid, there must not be an accumulation of charge in the liquid or any portion of the liquid. Thus, the first term of Eq. 117 is zero, and it becomes

$$\begin{aligned} \nabla \cdot \bar{\mathbf{i}}^{(l)} + \frac{1}{V} \int_{S_{(ls)}} (\mathbf{i}^{(l)} - q^{(l)} \mathbf{v}_{(ls)}) \cdot \mathbf{n}_{(ls)} dS \\ + \frac{1}{V} \int_{S_{(lg)}} (\mathbf{i}^{(l)} - q^{(l)} \mathbf{v}_{(lg)}) \cdot \mathbf{n}_{(lg)} dS = 0 \quad [118] \end{aligned}$$

The integral terms in Eq. 118 represent the flux of charge from the liquid phase into the other phases. Here we assume that there is no charge flux into the gas phase; thus the second term on the right of Eq. 118 is zero

$$\nabla \cdot \bar{\mathbf{i}}^{(l)} + \frac{1}{V} \int_{S_{(ls)}} (\mathbf{i}^{(l)} - q^{(l)} \mathbf{v}_{(ls)}) \cdot \mathbf{n}_{(ls)} dS = 0 \quad [119]$$

The flux of charge from the liquid phase into the solid phase is caused by the electrochemical reactions taking place at the liquid/solid interface. This leads to the definition of the local transfer current per unit, j , as follows

$$j = -\frac{1}{V} \int_{S_{(ls)}} (\mathbf{i}^{(l)} - q^{(l)} \mathbf{v}_{(ls)}) \cdot \mathbf{n}_{(ls)} dS \quad [120]$$

which allows us to write Eq. 119 as

$$\nabla \cdot \bar{\mathbf{i}}^{(l)} = j \quad [121]$$

The local transfer current is equal to the sum of the local transfer currents due to all the electrochemical reactions at the fluid/solid interface

$$j = a_{(sl)} \sum_k \langle j_k \rangle^{(sl)} \quad [122]$$

The averaged local transfer current for reaction k , $\langle j_k \rangle^{(sl)}$, is defined in Eq. 35.

Conservation of charge in the solid phase.—If we take the local volume average of Eq. 111 over the solid phase and follow the same steps described for the liquid phase, we have

$$\begin{aligned} \frac{d\bar{q}^{(s)}}{dt} + \nabla \cdot \bar{\mathbf{i}}^{(s)} + \frac{1}{V} \int_{S_{(ls)}} (\mathbf{i}^{(s)} - q^{(s)} \mathbf{v}_{(ls)}) \cdot \mathbf{n}_{(sl)} dS \\ + \frac{1}{V} \int_{S_{(sg)}} (\mathbf{i}^{(s)} - q^{(s)} \mathbf{v}_{(sg)}) \cdot \mathbf{n}_{(sg)} dS = 0 \quad [123] \end{aligned}$$

Assuming that there is no accumulation of charge in the solid (electrically neutral) and no charge flow from the solid into the gas phase, we have

$$\nabla \cdot \bar{\mathbf{i}}^{(s)} + \frac{1}{V} \int_{S_{(ls)}} (\mathbf{i}^{(s)} - q^{(s)} \mathbf{v}_{(ls)}) \cdot \mathbf{n}_{(sl)} dS = 0 \quad [124]$$

The integral term represents the flux of charge from the solid into the liquid phase. If we assume that there must not be accumulation of charge at the liquid/solid interface, the sum of fluxes from the solid and liquid phases has to be equal to zero, that is

$$\begin{aligned} \frac{1}{V} \int_{S_{(ls)}} (\mathbf{i}^{(l)} - q^{(l)} \mathbf{v}_{(ls)}) \cdot \mathbf{n}_{(ls)} dS \\ + \frac{1}{V} \int_{S_{(ls)}} (\mathbf{i}^{(s)} - q^{(s)} \mathbf{v}_{(ls)}) \cdot \mathbf{n}_{(sl)} dS = 0 \quad [125] \end{aligned}$$

Using the definition of the local transfer current per unit volume given in Eq. 120, we have

$$j = \frac{1}{V} \int_{S_{(ls)}} (\mathbf{i}^{(s)} - q^{(s)} \mathbf{v}_{(ls)}) \cdot \mathbf{n}_{(sl)} dS \quad [126]$$

and Eq. 124 becomes

$$\nabla \cdot \bar{\mathbf{i}}^{(s)} = -j \quad [127]$$

If we add Eq. 127 and 119, we find the condition for any portion of the electrode to be electrically neutral

$$\nabla \cdot (\bar{\mathbf{i}}^{(l)} + \bar{\mathbf{i}}^{(s)}) = 0 \quad [128]$$

Conclusions

The equations derived here can be used to model mass transport in porous electrodes with multiple phases: solid, liquid, and gas (see Ref. 12 and 18). The equations are readily applicable to electrodes consisting of two phases. We have presented a full description of the derivation of the transport equations using the volume-averaging technique with the goal of giving the reader a clear understanding of the assumptions and important factors to be considered when applying these equations or when developing new equations based on this same averaging technique. Also, the derivations presented here give insight into the nature of the definition of effective properties (diffusion coefficients and electrical conductivity) commonly used in modeling porous electrodes. This gives a theoretical basis for determining effective properties experimentally or for evaluating the appropriateness of empirical expressions developed by others when one is applying them to a different system.

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LIST OF SYMBOLS

$a_{(ls)}$	specific surface area of the liquid/solid interface per unit volume of porous media, cm^2/cm^3
$\bar{B}^{(k)}$	local volume average of quantity B in phase k ($k = g, l, s$)
$\langle B \rangle^{(k)}$	intrinsic volume average of quantity B in phase k ($k = g, l, s$)
c_e	concentration of electrolyte, mol/cm^3
c_o	concentration of solvent, mol/cm^3

- c_i molar density of the solution, mol/cm³
 $\langle c_i \rangle^{(k)}$ volume averaged concentration of species i in phase k ($k = g, l, s$) mol/cm³
 D free-stream diffusion coefficient of a concentrated binary electrolyte based on a concentration gradient, cm²/s
 $\langle D \rangle^{(l)}$ volume averaged diffusion coefficient of a binary electrolyte, cm²/s
 D_e diffusion coefficient of the electrolyte based on a thermodynamic driving force, cm²/s
 D_{ij} multicomponent diffusion coefficient of i into j , cm²/s
 $D_i^{(k)}$ diffusion coefficient of species i in phase k ($k = g, l, s$), cm²/s
 D_i^* function of dimensionless numbers for an empirical correlation to represent the molar density tortuosity vector for a nonoriented porous matrix
 E_{ik}^* function of dimensionless numbers for an empirical correlation to represent the molar density tortuosity vector for an oriented porous matrix
 F Faraday's constant, 96,487 C/eq
 f_i external force per unit mass acting upon species i , cm/s²
 f_{\pm} mean molar activity coefficient of the electrolyte
 $\bar{F}_i^{(lg)}$ averaged flux of species i from the liquid phase into the gas phase, mol/cm² s
 g acceleration of gravity, cm/s²
 \mathbf{i} current density vector, A/cm²
 $\mathbf{i}^{(l)}$ current density in the liquid, A/cm²
 $\mathbf{i}^{(s)}$ current density in the solid, A/cm²
 $\bar{\mathbf{i}}^{(l)}$ average current density in the liquid phase, A/cm²
 $\bar{\mathbf{i}}^{(s)}$ average current density in the solid phase, A/cm²
 \mathbf{j} local transfer current per unit volume, A/cm³
 \mathbf{j}_k local transfer current per unit surface area for reaction k , A/cm²
 $\langle \mathbf{j}_k \rangle^{(ls)}$ averaged local current density due to reaction k taking place at the liquid/solid interface, A/cm²
 \mathbf{J}_i molar flux of species i with respect to \mathbf{v} , mol/cm² s
 $\mathbf{J}_i^{(w)}$ molar flux due to ordinary diffusion, mol/cm² s
 $\mathbf{J}_i^{(f)}$ molar flux due to forced diffusion, mol/cm² s
 l characteristic size of the solid particles in an oriented porous matrix, cm
 l_o characteristic size diameter of the solid particles in a nonoriented porous matrix, cm
 m molality of the electrolyte, mol/kg
 M_i molecular (or ionic) mass of species i , g/gmol
 n number of electrons released by electrochemical reaction in the reference electrode
 n_k number of electrons released by reaction k
 \mathbf{n} unit normal to S , defined for the generalized transport theorem (Eq. 12)
 $\mathbf{n}_{(gl)}$ unit vector normal to the surface $S_{(gl)}$, pointing out of the gas phase into the liquid phase
 $\mathbf{n}_{(gs)}$ unit vector normal to the surface $S_{(gs)}$, pointing out of the gas phase into the solid phase
 $\mathbf{n}_{(lg)}$ unit vector normal to the surface $S_{(lg)}$, pointing out of the liquid phase into the gas phase
 $\mathbf{n}_{(ls)}$ unit vector normal to the surface $S_{(ls)}$, pointing out of the liquid phase into the solid phase
 $\mathbf{n}_{(sg)}$ unit vector normal to the surface $S_{(sg)}$, pointing out of the solid phase into the gas phase
 $\mathbf{n}_{(sl)}$ unit vector normal to the surface $S_{(sl)}$, pointing out of the solid phase into the liquid phase
 \mathbf{N}_i molar flux vector, mol/cm² s
 $\bar{\mathbf{N}}_i^{(k)}$ volume averaged molar flux of species i in phase k ($k = g, l, s$), mol/cm² s
 q charge density, C/cm³
 R universal gas constant, 8.3143 J/mol K
 $R_i^{(ls)}$ rate of production of species i per unit surface area at the liquid/solid interface, mol/cm² s
 $\bar{R}_i^{(ls)}$ average rate of production of species i at the liquid/solid interface, mol/cm³ s
 $\bar{R}_i^{(gs)}$ average rate of production of species i at the gas/solid interface, mol/cm³ s
 s_{ik} stoichiometric coefficient of species i in reaction k
 s_+ stoichiometric coefficient of the cation participating in the reaction at a reference electrode, used to define the current density in the electrolyte (modified Ohm's law)
 s_o stoichiometric coefficient of the neutral species (solvent) participating in the reaction at a reference electrode, used to define the current density in the electrolyte (modified Ohm's law)
 $S_{(l)}$ closed boundary surface of $V_{(l)}$ and is the sum of $S_{(le)}$, $S_{(ls)}$, and $S_{(lg)}$, cm²
 $S_{(ls)}$ surface that coincides with the liquid/solid interface inside volume V , cm²
 $S_{(lg)}$ surface that coincides with the liquid/gas interface inside volume V , cm²
 $S_{(le)}$ portion of surface $S_{(l)}$ that coincides with S (exit and entrance of the liquid phase in V), cm²
 $S_{(lg)}$ closed boundary surface of $V_{(g)}$ and is the sum of $S_{(ge)}$, $S_{(gs)}$, and $S_{(lg)}$, cm²
 $S_{(gs)}$ surface that coincides with the solid/gas interface inside volume V , cm²
 $S_{(ge)}$ portion of surface $S_{(g)}$ that coincides with S (exit and entrance of the gas phase in V), cm²
 S closed surface that contains volume V , cm²
 t time, s
 T temperature, K
 t_i^* transference number of species i with respect to \mathbf{v}^*
 V total averaging volume that contains solid and fluid phases of the porous medium, cm³
 $V_{(l)}$ volume of liquid contained in volume V , cm³
 $V_{(g)}$ volume of gas contained in volume V , cm³
 $V_{(s)}$ volume of solid contained in volume V , cm³
 V volume occupied by a fluid system, used in the definition of the generalized transport theorem (Eq. 12), cm³
 \mathbf{v} mass-average velocity of the multicomponent system
 \mathbf{v}^* molar-average velocity of the solution, cm/s
 $\mathbf{v}_{(gs)}$ velocity of the gas/solid interface, cm/s
 $\mathbf{v}_{(lg)}$ velocity of the liquid/gas interface, cm/s
 $\mathbf{v}_{(ls)}$ velocity of the liquid/solid interface, cm/s
 w_i mass fraction of species i
 x_i mole fraction of species i
 z_i ionic charge number or valence of species i , eq/mol
- Greek**
 γ_{\pm} mean molal activity coefficient of the electrolyte
 $\Delta_i^{(k)}$ molar density tortuosity vector in phase k ($k = g, l, s$), mol/cm² s
 ϵ porosity of the electrode, fraction of volume occupied by gas and liquid in the porous electrode
 $\epsilon^{(k)}$ fraction of volume occupied by phase k in the porous electrode ($k = g, l, s$)
 κ free-stream conductivity of the electrolyte, S/cm
 $\langle \kappa \rangle^{(l)}$ averaged conductivity of the electrolyte, S/cm
 μ_e chemical potential of the electrolyte, J/mol
 μ_i chemical potential of species i , J/mol
 v_e number of moles of ions into which a mole of electrolyte dissociates
 v_+ number of moles of cations into which a mole of electrolyte dissociates
 v_- number of moles of anions into which a mole of electrolyte dissociates
 ρ mass density of the solution, g/cm³
 $\sigma^{(s)}$ electrical conductivity of the solid phase in the porous electrode, S/cm
 τ tortuosity factor
 $\phi^{(l)}$ electric potential in the liquid phase, V
 $\phi^{(s)}$ electric potential in the solid phase, V
 $\langle \phi \rangle^{(l)}$ averaged electric potential in the liquid phase, V
 $\langle \phi \rangle^{(s)}$ averaged electric potential in the solid phase, V
 $\Psi^{(l)}$ current density tortuosity vector in the liquid phase, A/cm²
 $\Psi^{(s)}$ current density tortuosity vector in the solid phase, A/cm²

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Oxide Film Formation on a Microcrystalline Al Alloy in Sulfuric Acid

S. C. Thomas* and V. I. Birss*

Department of Chemistry, The University of Calgary, Calgary, Alberta, Canada T2N 1N4

ABSTRACT

The differences in the electrochemical behavior of a rapidly solidified, two-phase (matrix and dispersoid) Al-based alloy containing Fe, V, and Si (FVS0812 alloy) and the bulk form of its matrix and dispersoid phases were investigated in sulfuric acid. FVS0812 exhibited generally higher electrochemical activity than the matrix material due to the presence of the very active dispersoid phase in the alloy. Impedance studies indicated that the properties of thin films formed on the FVS0812 and matrix substrates during only 5 min of anodization are similar, whereas the film formed on the alloy during 2.5 h of anodization was substantially less resistive and contained a thinner and/or damaged underlying barrier oxide compared to a comparable film formed on the matrix. Compared to the classical structure of porous Al oxide films with underlying barrier oxide, the oxide film on FVS0812, as seen by TEM, was thinner, with an intermittent barrier oxide underlying a porous oxide of contorted morphology. Evidence is seen for the loss of dispersoids from the oxide film, leaving voids throughout its structure, perhaps the reason for its lack of physical adherence and its limiting thickness.

Introduction

A recent advance in both the science and technology of metallurgy has been the application of rapid solidification techniques to Al alloy production resulting in alloys with structures and enhanced properties that are unobtainable by conventional casting methods.^{1,2} The alloy under research, designated as FVS0812 by its developer, Allied Signal Incorporated, is a microcrystalline Al-based alloy which has been rapidly solidified by planar flow casting. Table I summarizes the atomic and weight percentages of the elemental components of alloy FVS0812, which contains Fe, V, and Si in addition to Al.³ As is characteristic for rapidly solidified Al-Fe-V-Si alloys, the microstructure of alloy FVS0812 consists of very fine, nearly spherical, intermetallic "dispersoids" uniformly distributed throughout a matrix phase.⁴ The microcrystalline matrix grain size typically varies from 0.5 to 2 μm in diam.⁵ The matrix composition is primarily Al supersaturated with Fe [ca. 0.5 atom percent (a/o)] and Si (ca. 0.1 a/o).^{3,6} The nanosized dispersoids, of nominal composition of $\text{Al}_{13}(\text{Fe,V})_3\text{Si}$, are $0.05 \pm 0.01 \mu\text{m}$ in diameter and occupy ca. 27 volume percent (v/o) of the alloy.^{4,7-9}

In practice, it was known that significant difficulties exist in forming an adherent and sufficiently thick, porous oxide film on the alloy surface using regular anodizing methods.¹⁰ This was verified by scanning electron microscopy which showed that, in contrast to a conven-

tional Al alloy, such as AA-6061, at which anodizing yielded a film of ca. 25 μm , the oxide film formed on the FVS0812 alloy surface under identical conditions resulted in a corresponding thickness of ca. 3.4 μm , as shown in Fig. 1.¹¹ Moreover, this oxide contained damaged segments and could be removed relatively easily. An oxide thickness of 2.5 μm is considered to be adequate for general corrosion resistance, but the film should be at least 25 μm thick to protect the substrate against abrasion.¹² Thus, the thin oxide film formed on FVS0812 provided inadequate abrasion resistance.

A search of the literature indicates that growth of anodic films on Al alloys containing phases of differing reactivity is extremely dependent on the intermetallic phase. The behavior of intermetallic compounds during anodizing in sulfuric acid has been generally classified into three categories,¹³ those intermetallics which are unchanged and incorporated into oxide films, those which are oxidized and incorporated or dissolved at a rate slower than the surrounding Al matrix, and those which are oxidized and incorporated or dissolved at a rate faster than Al. In addition, particle size is an important factor as the extent of oxidation of the intermetallic particles will decrease with increase in size. Thus, the variability in size and distribution of intermetallic particles within the alloy as well as the anodizing conditions can explain disagreement in the literature for the seemingly same material. For example, various studies of the anodization of Al alloys containing dispersed Al_3Fe in sulfuric acid have indicated that the discrete intermetallic particles fall out or pass into the oxide film unchanged, and form a porous oxide film with an interlying barrier layer.^{14,15}

Al alloys supporting oxide films with a range of morphologies have been reported. For example, anodization of a rapidly solidified Al-10% Si alloy in phosphoric acid resulted in the development of a regular fine featured porous anodic film above the Al matrix and a Si product which grew upward from the substrate and then spread laterally parallel to the alloy/film interface.¹⁶ Therefore it

Table I. Composition of alloy FVS0812.

Element	Atomic percent	Weight percent
Al	93.2	88.5
Fe	4.3	8.5
V	0.8	1.3
Si	1.7	1.7

* Electrochemical Society Active Member.