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Governing Equations for Transport in Porous Electrodes

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Governing Equations for Transport in Porous Electrodes
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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 authors8-11 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.

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

* Electrochemical Society Active Member.
Volume $V$ with surface $S$

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 $B_{(i)}$ be called the local volume average of $B$ in the phase $i$

$$
\bar{B}_{(i)} = \frac{1}{V} \int_{V_{(i)}} B \, dV
$$

Let $B_{(i)}^{ii}$ be the intrinsic volume average of $B$ in phase $i$

$$
\langle B \rangle_{(i)}^{ii} = \frac{1}{V_{(i)}} \int_{V_{(i)}} B \, dV
$$

Let $\epsilon^{li}$ and $\epsilon^{gi}$ be the liquid and gas porosities, respectively

$$
\epsilon^{li} = \frac{V_{(l)}}{V}
$$

$$
\epsilon^{gi} = \frac{V_{(g)}}{V}
$$

Thus, the porosity of volume $V$ is given by

$$
\epsilon = \frac{V_{(l)} + V_{(g)}}{V} = \epsilon^{li} + \epsilon^{gi}
$$

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

$$
\bar{B}_{(i)} = \langle B \rangle_{(i)}^{ii} \quad i = l, g
$$

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

$$
\nabla \bar{B}_{(i)} = \nabla \langle B \rangle_{(i)}^{ii} + \frac{1}{V} \int_{S_{(i)}} B_{(i)}^{ii} n_{(i)} \, dS + \frac{1}{V} \int_{S_{(i)}} B_{(i)}^{ii} n_{(i)} \, dS
$$

$$
\nabla \langle B \rangle_{(i)}^{ii} = \nabla \bar{B}_{(i)} + \frac{1}{V} \int_{S_{(i)}} B_{(i)}^{ii} n_{(i)} \, dS + \frac{1}{V} \int_{S_{(i)}} B_{(i)}^{ii} n_{(i)} \, dS
$$

where $n_{(i)}$ and $n_{(i)}^{ii}$ are unit vectors normal to the surfaces $S_{(i)}$ and $S_{(i)}^{ii}$, respectively, as shown in Fig. 3. In Eq. 8, $n_{(i)}$ and $n_{(i)}^{ii}$ are unit vectors normal to the surfaces $S_{(i)}$ and $S_{(i)}^{ii}$, respectively, also shown in Fig. 3. Note that

$$
n_{(i)} = -n_{(i)}^{ii}
$$

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

$$
\nabla \cdot \bar{B}_{(i)} = \nabla \cdot \langle B \rangle_{(i)}^{ii} + \frac{1}{V} \int_{S_{(i)}} B_{(i)}^{ii} \cdot n_{(i)} \, dS
$$

$$
\nabla \cdot \langle B \rangle_{(i)}^{ii} = \nabla \cdot \bar{B}_{(i)} + \frac{1}{V} \int_{S_{(i)}} B_{(i)}^{ii} \cdot n_{(i)} \, dS
$$

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

$$
\frac{d}{dt} \int_{V_{(i)}} B \, dV = \int_{S_{(i)}} \frac{\partial b}{\partial t} \, dV + \int_{V_{(i)}} B_{(i)} \cdot n \, dS
$$

in which $V_{(i)}$ represents the space region currently occupied by a fluid system, $S_{(i)}$ is the closed bounding surface of the system, $v$ is velocity of the fluid, and $n$ is a unit normal to the surface $S_{(i)}$ pointing out of the system $V_{(i)}$. 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

$$
\frac{\partial c_{(i)}^{li}}{\partial t} + \nabla \cdot N_{(i)}^{li} = 0
$$

where $c_{(i)}^{li}$ and $N_{(i)}^{li}$ 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

$$
\int_{V_{(l)}} \frac{\partial c_{(i)}^{li}}{\partial t} \, dV + \int_{S_{(l)}} \frac{\partial b}{\partial t} \, dS + \int_{V_{(l)}} N_{(i)}^{li} \cdot n \, dS
$$

$$
\int_{V_{(l)}} \frac{\partial c_{(i)}^{li}}{\partial t} \, dV + \int_{S_{(l)}} \frac{\partial b}{\partial t} \, dS + \int_{V_{(l)}} N_{(i)}^{li} \cdot n \, dS
$$

$$
\int_{V_{(l)}} \frac{\partial c_{(i)}^{li}}{\partial t} \, dV + \int_{S_{(l)}} \frac{\partial b}{\partial t} \, dS + \int_{V_{(l)}} N_{(i)}^{li} \cdot n \, dS
$$

$$
\int_{V_{(l)}} \frac{\partial c_{(i)}^{li}}{\partial t} \, dV + \int_{S_{(l)}} \frac{\partial b}{\partial t} \, dS + \int_{V_{(l)}} N_{(i)}^{li} \cdot n \, dS
$$

$$
\int_{V_{(l)}} \frac{\partial c_{(i)}^{li}}{\partial t} \, dV + \int_{S_{(l)}} \frac{\partial b}{\partial t} \, dS + \int_{V_{(l)}} N_{(i)}^{li} \cdot n \, dS
$$

$$
\int_{V_{(l)}} \frac{\partial c_{(i)}^{li}}{\partial t} \, dV + \int_{S_{(l)}} \frac{\partial b}{\partial t} \, dS + \int_{V_{(l)}} N_{(i)}^{li} \cdot n \, dS
$$

$$
\int_{V_{(l)}} \frac{\partial c_{(i)}^{li}}{\partial t} \, dV + \int_{S_{(l)}} \frac{\partial b}{\partial t} \, dS + \int_{V_{(l)}} N_{(i)}^{li} \cdot n \, dS
$$

$$
\int_{V_{(l)}} \frac{\partial c_{(i)}^{li}}{\partial t} \, dV + \int_{S_{(l)}} \frac{\partial b}{\partial t} \, dS + \int_{V_{(l)}} N_{(i)}^{li} \cdot n \, dS
$$

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

Downloaded on 2014-10-20 to IP 129.252.69.176 address. Redistribution subject to ECS terms of use (see ecsdl.org/site/terms_use) unless CC License in place (see abstract).
Applying the general transport theorem (Eq. 12) for \( B = c_i \) and \( V_r = V_g \), we have

\[
\frac{1}{V} \int_{V_g} \frac{\partial c_i}{\partial t} dV + \frac{1}{V} \int_{V_g} V \cdot \nabla c_i \, dV = 0 \tag{14}
\]

Applying the general transport theorem (Eq. 12) for \( B = c_i \) and \( V_r = V_g \), we have

\[
\int_{V_g} \frac{\partial c_i}{\partial t} dV = \frac{d}{dt} \int_{V_g} c_i \, dV - \int_{S_{lg}} c_i V \cdot n \, dS \tag{15}
\]

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

\[
\frac{1}{V} \int_{S_{lg}} \frac{\partial c_i}{\partial t} dV = \frac{d}{dt} \int_{V_g} c_i \, dV - \int_{S_{lg}} c_i V \cdot n \, dS - \int_{S_{gs}} c_i V \cdot n \, dS \tag{16}
\]

in which \( v_{lg} \) and \( v_{gs} \) represent the velocities of the liquid/gas and liquid/solid interfaces, respectively. Also, \( n_{lg} \) and \( n_{gs} \) 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 \( S_{go} \) be zero.

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

\[
\frac{1}{V} \int_{V_g} V \cdot \nabla c_i \, dV = \nabla \cdot \left( c_i V \right) = \frac{d}{dt} \int_{V_g} c_i \, dV - \int_{S_{lg}} c_i V \cdot n \, dS - \int_{S_{gs}} c_i V \cdot n \, dS \tag{17}
\]

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

\[
\frac{d C_i}{dt} + V \cdot \nabla c_i + \frac{1}{V} \int_{V_g} (N^{(lg)} - c_i v_{lg}) \cdot n_{lg} \, dS + \frac{1}{V} \int_{V_g} (N^{(gs)} - c_i v_{gs}) \cdot n_{gs} \, dS = 0 \tag{18}
\]

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

\[
\frac{d C_i}{dt} + V \cdot \nabla c_i + \frac{1}{V} \int_{V_g} (N^{(lg)} - c_i v_{lg}) \cdot n_{lg} \, dS + \frac{1}{V} \int_{V_g} (N^{(gs)} - c_i v_{gs}) \cdot n_{gs} \, dS = 0 \tag{19}
\]

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

\[
\frac{d C_i}{dt} + V \cdot \nabla c_i + \frac{1}{V} \int_{V_g} (N^{(lg)} - c_i v_{lg}) \cdot n_{lg} \, dS + \frac{1}{V} \int_{V_g} (N^{(gs)} - c_i v_{gs}) \cdot n_{gs} \, dS = 0 \tag{20}
\]

for the gas phase and by

\[
\frac{d C_i}{dt} + V \cdot \nabla c_i + \frac{1}{V} \int_{V_g} (N^{(lh)} - c_i v_{gh}) \cdot n_{gh} \, dS + \frac{1}{V} \int_{V_g} (N^{(sl)} - c_i v_{sh}) \cdot n_{sh} \, dS = 0 \tag{21}
\]

for the solid phase.

In Eq. 20, \( v_{lg} \) and \( v_{gs} \) are the velocities of the liquid/gas and gas/solid interfaces, respectively; and \( n_{lg} \) and \( n_{gs} \) 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 \( S_{go} \) be zero. In Eq. 21, \( v_{gh} \) and \( v_{sh} \) are the velocities of the liquid/solid and gas/solid interfaces, respectively, and \( n_{gh} \) and \( n_{sh} \) 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 \( n_{lg} \) and \( n_{gs} \).

**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 is

\[
(N^{(lg)} - c_i v_{lg}) \cdot n_{lg} = (N^{(lg)} - c_i v_{lg}) \cdot n_{lg} = R_i^{(lg)} \tag{22}
\]

in which \( n_{lg} \) and \( n_{gs} \) are unit normals to the interface pointing into phase + and -, respectively. Also, \( v_{lg} \cdot n_{lg} \) and \( v_{gs} \cdot n_{gs} \) are the velocities of the interface in the + and - direction, respectively. \( R_i^{(lg)} \) 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

\[
(N^{(lg)} - c_i v_{lg}) \cdot n_{lg} = (N^{(lg)} - c_i v_{lg}) \cdot n_{lg} = 0 \tag{23}
\]

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

\[
\frac{1}{V} \int_{S_{lg}} (N^{(lg)} - c_i v_{lg}) \cdot n_{lg} \, dS = 0 \tag{24}
\]

Because \( n_{lg} = - n_{gs} \), Eq. 24 is equivalent to

\[
- \frac{1}{V} \int_{S_{lg}} (N^{(lg)} - c_i v_{lg}) \cdot n_{lg} \, dS = 0 \tag{25}
\]

Let \( F_i^{(lg)} \) 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

\[
F_i^{(lg)} = \frac{1}{V} \int_{S_{lg}} (N^{(lg)} - c_i v_{lg}) \cdot n_{lg} \, dS = \frac{1}{V} \int_{S_{lg}} (N^{(lg)} - c_i v_{lg}) \cdot n_{lg} \, dS = 0 \tag{26}
\]

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

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

\[
(N^{(ls)} - c_i v_{ls}) \cdot n_{ls} = (N^{(ls)} - c_i v_{ls}) \cdot n_{ls} = R_i^{(ls)} \tag{27}
\]

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

\[
- \frac{1}{V} \int_{S_{ls}} (N^{(ls)} - c_i v_{ls}) \cdot n_{ls} \, dS = 0 \tag{28}
\]

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

\[
- \frac{1}{V} \int_{S_{ls}} (N^{(ls)} - c_i v_{ls}) \cdot n_{ls} \, dS = \frac{1}{V} \int_{S_{ls}} R_i^{(ls)} \, dS = 0 \tag{29}
\]
Let $R_i^{(b)}$ be the averaged rate at which species $i$ is produced at the liquid/solid interface in volume $V$; thus
\[
R_i^{(b)} = \frac{1}{V} \int_{S_{sol}} R_i^{(o)} dS
\]
\[
= -\frac{1}{V} \int_{S_{sol}} (N_i^{(o)} - c_i^{(b)} \nu_{(o)}) \cdot n_{sol} dS
\]
On the other hand, if species $i$ is present in the solid phase only, $R_i^{(s)}$ is given by
\[
R_i^{(s)} = \frac{1}{V} \int_{S_{sol}} R_i^{(o)} dS
\]
\[
= -\frac{1}{V} \int_{S_{sol}} (N_i^{(o)} - c_i^{(s)} \nu_{(s)}) \cdot n_{sol} dS
\]

**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
\[
\frac{\partial c_i^{(L)}}{\partial t} + \mathbf{v} \cdot \nabla c_i^{(L)} + \mathbf{F}_i^{(o)} - \mathbf{R}_i^{(o)} = 0
\]
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
\[
\sum_{k} s_{ik} M_k^{(i)} = n_{e} e^{-}
\]
where $M_k^{(i)}$ represents species $i$ participating in reaction $k$, $s_{ik}$ is the stoichiometric coefficient of species $i$ in reaction $k$, and $n_{e}$ 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
\[
R_i^{(a)} = \frac{1}{V} \int_{S_{sol}} \left( \sum_{k} \frac{s_{ik}}{n_{e} F} \mathbf{j}_k \right) dS
\]
\[
= -\sum_{k} \left( \frac{s_{ik}}{n_{e} F} \int_{S_{sol}} \mathbf{j}_k dS \right) = -\sum_{k} \frac{s_{ik}}{n_{e} F} \mathbf{j}_k^{(o)}
\]
where $\mathbf{j}_k^{(o)}$ is the pore wall surface area wet by electrolyte per unit volume of porous medium ($S_{s,w}/V$), in cm$^2$/cm$^3$, and $\mathbf{j}_k^{(o)}$ is the average reaction rate of electrochemical reaction $k$ taking place at the liquid/solid interface contained in volume $V$ and is defined as
\[
\mathbf{j}_k^{(o)} = \left( \frac{1}{S_{s,w}} \int_{S_{sol}} \mathbf{j}_k dS \right)
\]
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 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
\[
\mathbf{N}_i^{(o)} = c_i \mathbf{v} = \mathbf{J}_i + c_i \mathbf{v}
\]
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
\[
\mathbf{J}_i = \mathbf{F}_i^{(o)} + \mathbf{J}_i^{(d)}
\]
where $\mathbf{J}_i^{(o)}$ and $\mathbf{J}_i^{(d)}$ 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)
\[
\mathbf{J}_i^{(o)} = \frac{c_i}{pRT} \sum_{k=1}^{N} M_k D_{k} \left[ \mathbf{x}_k \sum_{k=1}^{N} \frac{\partial x_k}{\partial x_k} \right] V_{k,1}
\]
\[
\mathbf{J}_i^{(d)} = -\frac{c_i}{pRT} \sum_{k=1}^{N} M_k D_{k} \left[ \mathbf{x}_k M_k \left[ \mathbf{f}_k - \sum_{k=1}^{N} \mathbf{w}_k \mathbf{f}_k \right] \right]
\]
where $c_i$ and $p$ are the molar and mass densities of the solution, respectively; $M_k$ is the molecular (or ionic) mass of species $i$; $D_k$ is the multicomponent diffusion coefficient between species $i$ and $k$; $\mu_i$ is the chemical potential of species $i$; $\mathbf{x}_k$ is the mole fraction of species $k$; $\nu_i$ is the mass fraction of species $i$; $\mathbf{f}_k$ 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
\[
\mathbf{f}_k = -\frac{z_k F}{M_k} \nabla \phi^{(o)}
\]
where $g$ is the acceleration of gravity and $\phi^{(o)}$ 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
\[
\mathbf{i}^{(o)} = \mathbf{F} \sum_{i=1}^{N} n_i \mathbf{N}_i^{(o)}
\]
we obtain
\[
\mathbf{N}_i^{(o)} = -\frac{\nu_i D_{i e} c_i}{pRT} \nabla \mu_i + \frac{z_i}{z_i F} \mathbf{i}^{(o)} + \nu_i c_i \mathbf{v}^* + \frac{\nu_i}{pRT} \mathbf{v}^{*}
\]
Here $\mu_i$ is the chemical potential of the electrolyte, $c_i$ is the concentration of electrolyte, $\mathbf{v}$ is the number of ions $i$ into which a molecule of electrolyte dissociates, $\mathbf{i}^{(o)}$ is the current density in the solution, $\mathbf{v}^*$ is the molar-average velocity of the solution, and $\mathbf{v}^*$ is the transference number of species $i$ with respect to $\mathbf{v}^*$. The diffusion coefficient of the electrolyte, $D_{i e}$, is based on a thermodynamic driving force and is given by
\[
D_{i e} = \frac{D_i D_e (z_e - z_i)}{z_i D_e - z_i D_e}
\]
where $D_{i e}$ is the diffusion coefficient that describes the interaction between species $i$ and $j$ (i.e., multicomponent diffusion coefficient). The subscripts, $+$, $-$, and 0 refer to the cation, anion, and solvent, respectively. The diffusion coefficient of the electrolyte was defined as
\[
c_i = \frac{c_i}{\nu_i} = \frac{c_i}{\nu_i}
\]
This definition for the electrolyte concentration allows us to satisfy automatically the electroneutrality condition, which reads
\[ \sum_i z_i c_i = 0 \]  

[45]

The chemical potential of the electrolyte, \( \mu_e \), in Eq. 42 is given by
\[ \mu_e = \nu_e \mu_e + \nu_e \mu_e \]  

\[ = \nu_e RT \ln \left( c_f j_e \right) \]  

\[ = \nu_e RT \ln \frac{m_i \gamma_i \Lambda_i}{m_i \gamma_i \Lambda_i} \]

in which \( f_e \) and \( \gamma_i \) are the mean molar and molal activity coefficients of the electrolyte, respectively; \( \Lambda_i \) are proportionality constants independent of composition; \( m_i \) is the molality of the electrolyte; and \( \nu_e = \nu_e + \nu_e \). These equations can be used to obtain
\[ \mathbf{N}(0) = -v_i D V c_e + \frac{1}{z_i f_e} + \nu_i c_i v^* \]  

[47]

where \( D \) is the diffusion coefficient of the salt (electrolyte) based on a gradient of concentration and is related to \( D \) by
\[ D = D_i \left( 1 + \frac{d \ln f_e}{d \ln c_i} \right) \]  

[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
\[ \mathbf{N}(0) = -D(D) \sqrt{c_e} + c_i v^* \]  

[49]

in which \( D(0) \) is the diffusion coefficient of species \( i \) in the electrolytic solution.

**Volume average of the molar flux vector.**—Assuming that \( v^* \) is constant, the local volume average of the molar flux vector can be written as
\[ \mathbf{N}(0) = -v_i D V c_e + \frac{1}{z_i f_e} + \nu_i c_i v^* \]  

[50]

Using the theorem for the volume average of a gradient (Eq. 7), we have
\[ \overline{c_e} = \overline{c_e} + \frac{1}{V} \int_{V_{sol}} c_i n_{sol} dS + \frac{1}{V} \int_{V_{sol}} c_i n_{sol} dS \]  

[51]

This allows us to write
\[ \overline{c_e} = -v_i \left( D(0) \sqrt{c_e} \right) + \frac{1}{z_i f_e} + \nu_i \left( c_e \right)^{0.5} - \Delta_v^{0} \]  

[52]

where \( \Delta_v^{0} \) is the molar density tortuosity vector and is defined as
\[ \Delta_v^{0} = v_i D V c_e - v_i \left( D(0) \sqrt{c_e} \right) + v_i \left( D(0) \right) \frac{1}{V} \int_{V_{sol}} c_i n_{sol} dS \]  

\[ + v_i \left( D(0) \right) \frac{1}{V} \int_{V_{sol}} c_i n_{sol} dS + \nu_i \left( c_e \right)^{0.5} - \nu_i \left( c_e \right)^{0.5} \]  

[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 \( \Delta_v \) (see, e.g., Ref. 1).

**Specific example.**—Nonoriented porous solid with no convection.—The simplest form of empirical correlations for \( \Delta_v \) is that of a nonoriented porous solid when convection can be neglected. In such a case, we can expect \( \Delta_v \) to be a function of the particle size of the porous medium, \( r_i \); the liquid porosity, \( \epsilon_i \); the diffusion coefficient, \( D(0) \); and some local distribution of the electrolyte concentration, such as \( c^{0}_e \) or \( \overline{c}_e \). Following the analysis presented by Slattery, an empirical expression for \( \Delta_v \) takes the form
\[ \Delta_v^{0} = \nu_i D^{0} r(0) \sqrt{c_e^{0}} \]  

[54]

with
\[ D^{0} = D^{0} \left( \frac{1}{\tau} \frac{\overline{c}_e}{\nu_i} \right) \]  

[55]

If we substitute Eq. 54 into Eq. 6, 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
\[ \overline{c}_e^{0} = -v_i \left( D(0) \right) \left( 1 + D^{0} \right) \sqrt{c_e^{0}} + \frac{1}{z_i f_e} \]  

[56]

or using the relation between the local and the intrinsic volume average (Eq. 6), we have
\[ \overline{c}_e^{0} = -v_i \left( D(0) \right) \left( 1 + D^{0} \right) \sqrt{c_e^{0}} + \frac{1}{z_i f_e} \]  

[57]

The term \( \left( D^{0} \left( 1 + D^{0} \right) \right) \overline{c}_e \) in Eq. 56 is called the effective diffusion coefficient for species \( i \), \( D_{eff} \). In many practical applications, \( D_{eff} \) is expressed as
\[ D_{eff} = \left( D \right) \frac{\tau^{0}}{\tau} \]  

[59]

where \( \tau \) is the tortuosity factor of the porous medium. In view of Eq. 58, Eq. 59 suggests that
\[ D_{eff} = \left( 1 + D_{eff} \right) \overline{c}_e \]  

[60]

Using Eq. 60 in Eq. 58, we obtain
\[ \overline{c}_e^{0} = -v_i \left( D(0) \right) \left( \frac{\tau^{0}}{\tau} \right) \sqrt{c_e^{0}} + \frac{1}{z_i f_e} \]  

[61]

For porous electrodes, researchers often use the following expression for the effective diffusion coefficient
\[ D_{eff} = \left( D^{0} \right)^{(0.6)} \]  

[62]

where \( b \) is a constant parameter normally equal to 1.5. This expression for the effective diffusion coefficient 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
\[ \left( 1 + D_{eff} \right) = \frac{1}{\tau} \]  

[63]

Substituting Eq. 63 into Eq. 58, we obtain
\[ \overline{c}_e^{0} = -v_i \left( D^{0} \right) \left( \frac{\tau^{0}}{\tau} \right) \sqrt{c_e^{0}} + \frac{1}{z_i f_e} \]  

[64]

For the case of an oriented porous solid when convection can be neglected, we can expect the molar density tortuosity vector \( \Delta_v \) to be a function of the gradient in particle size, \( V \), in addition to the quantities considered for the nonoriented porous media. In this case \( \Delta_v \) can be expressed as
where $l$ is the particle diameter, which is a function of position. Here

$$E_n^k = E_n^k (e^{(i)}, l, \nabla l, \nabla e^{(i)}, \nabla \cdot e^{(i)}, \nabla^2 e^{(i)}, \nabla l^2)$$

for $k = 1, 2$ [66]

Applying the Buckingham-Pi theorem reduces this to

$$E_{i\kappa}^* = E_{i\kappa}^* \left( e^{(i)}, \nabla l, \frac{\nabla^2 e^{(i)}}{|\nabla l|}, \frac{\nabla \cdot e^{(i)}}{l^2} \right)$$

for $k = 1, 2$ [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 in Eq. 63. Substituting Eq. 65 into Eq. 52, we obtain an expression for the molar flux for the liquid, gas, and solid phases (please see Ref. 12).

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

$$\bar{\Delta}^{(i)} = v_i (D_n^{(i)} \nabla e^{(i)} + \{D_n^{(i)} \nabla e^{(i)} \} \nabla)}$$

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

$$\bar{\nabla}^{(i)} e^{(i)} = \frac{\nabla e^{(i)} + \left( \int_{V_{nt}} c_n^{(i)} n_{nt} dS + 1 \int_{V_{nt}} c_n^{(i)} n_{nt} dS \right)}{V}$$

and Eq. 74 becomes

$$\bar{\nabla}^{(i)} e^{(i)} + \left( \int_{V_{nt}} c_n^{(i)} n_{nt} dS + 1 \int_{V_{nt}} c_n^{(i)} n_{nt} dS \right)$$

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

$$\bar{\nabla}^{(i)} e^{(i)} + \left( \int_{V_{nt}} c_n^{(i)} n_{nt} dS + 1 \int_{V_{nt}} c_n^{(i)} n_{nt} dS \right)$$

Substituting Eq. 77 into Eq. 76 and using Eq. 6, we obtain

$$\bar{\nabla}^{(i)} e^{(i)} + \left( \int_{V_{nt}} c_n^{(i)} n_{nt} dS + 1 \int_{V_{nt}} c_n^{(i)} n_{nt} dS \right)$$

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

$$\bar{\nabla}^{(i)} e^{(i)} + \left( \int_{V_{nt}} c_n^{(i)} n_{nt} dS + 1 \int_{V_{nt}} c_n^{(i)} n_{nt} dS \right)$$

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

$$\bar{\nabla}^{(i)} e^{(i)} + \left( \int_{V_{nt}} c_n^{(i)} n_{nt} dS + 1 \int_{V_{nt}} c_n^{(i)} n_{nt} dS \right)$$

The equations derived in this section for the molar fluxes of species in the electrolytic solvent 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 $E_1$ and $E_2$ 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 $\nabla$ 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

$$\frac{\partial (e^{(i)} c_n^{(i)})}{\partial t} - \nabla \cdot \left( D^{(i)} (e^{(i)}) (- \nabla e^{(i)} c_n^{(i)}) \right) + \frac{t^*}{z_i f_i} \nabla \cdot (e^{(i)} c_n^{(i)} 0) = 0$$

for $i = +, -$ [83]
For neutral species in the liquid phase we have
\[
\frac{\partial (e^0(c_i)^0)}{\partial t} - \nabla \cdot \left[ D_l^{e^0}(c_i)^0 \nabla (e^0(c_i)^0) \right] + \mathbf{F}_l^{e^0} - \mathbf{R}_l^{e^0} = 0
\]  
[84]

For species \(i\) the gas phase we have
\[
\frac{\partial (e^i(c_i)^0)}{\partial t} - D_g \nabla \cdot \left[ (e^i)^{b_1} \nabla (e^i(c_i)^0) \right] + \mathbf{F}_g^{e^i} = 0
\]

And for species in the solid phase we have
\[
\frac{\partial (e^s(c_i)^0)}{\partial t} - D_s \nabla \cdot \left[ (e^s)^{b_1} \nabla (e^s(c_i)^0) \right] - \mathbf{R}_s^{e^s} = 0
\]  
[85]

with the solid porosity defined as \(e^s = 1 - (e^0 + e^s)\).

**Modified Ohm’s Law for the Liquid Phase**

The free-stream current density for a concentrated binary electrolyte can be expressed as
\[
\mathbf{j}^0 = -\kappa \nabla \phi^0 - \frac{\nu R T}{F} \left( \frac{s_z}{n v_s} + \frac{1}{z} \frac{c_{Z^+}^*}{c_z} \right)
+ \frac{1}{z} \frac{c_{Z^+}^*}{c_z} \nabla \mu_s
\]  
[86]

where \(\kappa\) is the conductivity of the electrolyte. If we use the above expression for \(\mu_s\), we obtain
\[
\mathbf{j}^0 = -\kappa \nabla \phi^0 - \frac{\nu R T}{F} \left( \frac{s_z}{n v_s} + \frac{1}{z} \frac{c_{Z^+}^*}{c_z} \right)
+ \frac{1}{z} \frac{c_{Z^+}^*}{c_z} \nabla \mu_s
\]

If we take the local volume average of \(\mathbf{j}^0\) over the liquid phase and use the theorem for the volume average of a gradient (Eq. 7), we have
\[
\mathbf{j}^0 = -(\kappa) \nabla \phi^0 - \frac{\nu R T}{F} \left( \frac{s_z}{n v_s} + \frac{1}{z} \frac{c_{Z^+}^*}{c_z} \right)
+ \frac{1}{z} \frac{c_{Z^+}^*}{c_z} \nabla \mu_s
\]

where \(\Phi^0\) is defined as the current density tortuosity vector
\[
\Phi^0 = \kappa \nabla \phi^0 - (\kappa) \nabla \phi^0 + \frac{(\kappa)}{V} \int_{s_0} \phi^0 n_{0g} dS
+ \frac{(\kappa)}{V} \int_{s_0} \phi^0 n_{0g} dS + \frac{\nu R T}{F} \left( \frac{s_z}{n v_s} + \frac{1}{z} \frac{c_{Z^+}^*}{c_z} \right)
+ \frac{1}{z} \frac{c_{Z^+}^*}{c_z} \nabla \mu_s
\]

\[
- (\kappa) \left[ 1 + \frac{\partial (d \ln f_i)}{\partial \ln c_i} \right] \frac{\nabla \ln c_i}{V} - \frac{1}{V} \int_{s_0} \ln c_i n_{0g} dS
- \frac{1}{V} \int_{s_0} \ln c_i n_{0g} dS
+ \frac{\nu R T}{F} \left( \frac{1}{z} \frac{c_{Z^+}^*}{c_z} \right)
\]

\[
\Psi^0 = \kappa \nabla \phi^0 - (\kappa) \nabla \phi^0 + \frac{(\kappa)}{V} \int_{s_0} \phi^0 n_{0g} dS
+ \frac{(\kappa)}{V} \int_{s_0} \phi^0 n_{0g} dS + \frac{\nu R T}{F} \left( \frac{s_z}{n v_s} + \frac{1}{z} \frac{c_{Z^+}^*}{c_z} \right)
+ \frac{1}{z} \frac{c_{Z^+}^*}{c_z} \nabla \mu_s
\]

\[
\frac{1}{V} \int_{s_0} \ln c_i n_{0g} dS
\]

We can see that if \(\Phi^0\) and \(c_i\) were independent of position inside the volume \(V\), \(\Psi^0\) would be equal to zero. For convenience, let us define
\[
A = \frac{\nu R T}{F} \left( 1 + \left( \frac{d \ln f_i}{d \ln c_i} \right) \frac{s_z}{n v_s} + \frac{1}{z} \frac{c_{Z^+}^*}{c_z} \right)
+ \frac{1}{z} \frac{c_{Z^+}^*}{c_z} \nabla \mu_s
\]

[90]

Analogous to the molar density tortuosity vector for an oriented porous matrix, we can expect \(\Phi^0\) to be a function of the solid particle size; \(l_1\); the gradient in particle size, \(V_1\); the liquid porosity, \(e^0\); the conductivity of the electrolyte, \(K^e\); the quantity \(A\) defined above; and some local distribution of the electrolyte concentration and potential, such as \(V\) in \(c_i\) and \(V_4^0\). Following the procedure described by Slattery, we may postulate the following empirical correlation for \(\Psi^0\)
\[
\Psi^0 = (\kappa)^0 G_1 \nabla \phi^0 + (\kappa)^0 G_2 (\nu R T)^0 \frac{d \ln f_i}{d \ln c_i} \frac{s_z}{n v_s} + \frac{1}{z} \frac{c_{Z^+}^*}{c_z} \nabla \mu_s
\]

[92]

with
\[
G_i^* = G_i \left( \frac{V_1}{V} \frac{\nabla \phi^0 \cdot V \ln c_i}{V \nabla \phi^0 \cdot V_1} - \frac{V_4^0}{V} \frac{\nabla \phi^0 \cdot V \ln c_i}{V \nabla \phi^0 \cdot V_1} \right)
\]

[94]

for \(i = 1, 2, 3\).

Substituting Eq. 93 into Eq. 89, we obtain
\[
\mathbf{j}^0 = -(\kappa)^0 \left( 1 + G_i^* \right) \nabla \phi^0 - (\kappa)^0 \left( 1 + G_i^* \right) \frac{\nu R T}{F} \left( \frac{s_z}{n v_s} + \frac{1}{z} \frac{c_{Z^+}^*}{c_z} \right)
+ \frac{1}{z} \frac{c_{Z^+}^*}{c_z} \nabla \mu_s
\]

[95]

To find a suitable functionality for \(\Psi^0\), 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, that is
Thus, the current density in the electrolyte becomes

\[ 1 + G^* = (e^{\phi_0})^{d-1} \quad \text{and} \quad 1 + G^*_s = (e^{\phi_0})^{d-1} \]  \[ \text{[97]} \]

Thus, the current density in the electrolyte becomes

\[ \bar{I}^0 = -(e^{\phi_0})^{d-1}V\bar{c}^0 - \frac{\nu RT}{F}\left(e^{\phi_0}\right)^{d-1} \]

\[ \left(1 + \left(\frac{d \ln f}{d \ln c_e}\right)^0\right) + \frac{r^*}{n c_e} + \frac{1}{z_c} \frac{1}{z_c} \frac{z_c}{c_e} \]

\[ \left(1 \quad - \frac{z_c}{n} \right) \right) V \bar{c}^0 \ln (c_e) \quad \text{[101]} \]

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

\[ \bar{I}^0 = -(e^{\phi_0})^{d-1}V\bar{c}^0 - \frac{\nu RT}{F}\left(e^{\phi_0}\right)^{d-1} \]

\[ \left(1 + \left(\frac{d \ln f}{d \ln c_e}\right)^0\right) + \frac{r^*}{n c_e} + \frac{1}{z_c} \frac{1}{z_c} \frac{z_c}{c_e} \]

\[ \left(1 \quad - \frac{z_c}{n} \right) \right) V \bar{c}^0 \ln (c_e) \quad \text{[101]} \]

Similar to what we found for the expressions for the molar density and current density tortuosity vectors, we may write empirical correlations for \( \bar{I}^0 \). For an oriented solid matrix \( \bar{I}^0 \) is expected to be a function of the particle size, \( l \), the gradient in particle size, \( V_l \); the ratio between solid volume to electrode volume, \( e_0 \); the conductivity of the solid, \( \sigma^0 \); and some local distribution of the solid potential, such as \( \bar{V} \bar{c}^0 \). A suitable expression for \( \bar{I}^0 \) is

\[ \bar{I}^0 = \sigma^0 H^* \bar{V} \bar{c}^0 + \sigma^0 \left(\bar{V} \bar{c}^0\right) H^* \bar{V} \]

\[ \text{for } i = 1, 2 \]  \[ \text{[107]} \]

Thus, the current density in the solid becomes

\[ \bar{I}^0 = -(\bar{c}_e)^{d-1}V\bar{c}_e^0 - \frac{\nu RT}{F}\left(\bar{c}_e^0\right)^{d-1} \]

\[ \left(1 + \left(\frac{d \ln f}{d \ln c_e}\right)^0\right) + \frac{r^*}{n c_e} + \frac{1}{z_c} \frac{1}{z_c} \frac{z_c}{c_e} \]

\[ \left(1 \quad - \frac{z_c}{n} \right) \right) V \bar{c}_e^0 \ln (c_e) \quad \text{[102]} \]

Conservation of Charge

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

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

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. 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

\[ \frac{\partial q}{\partial t} + \nabla \cdot \mathbf{i} = \frac{1}{V} \int_0^1 \frac{\partial q}{\partial t} dV + \frac{1}{V} \int_0^1 \nabla \cdot \mathbf{i} dV = 0 \]  \[ \text{[112]} \]
Applying the general transport theorem (Eq. 12) to the first term, we have

\[
\frac{1}{V} \int_{V(0)} \frac{\partial q}{\partial t} dV = \frac{d}{dt} \left( \frac{1}{V} \int_{V(0)} q^0 dV \right) - \frac{1}{V} \int_{\Sigma_a} q^0 v \cdot \mathbf{n} dS [113]
\]

\[
\frac{1}{V} \int_{V(0)} \frac{\partial q}{\partial t} dV = \frac{dq}{dt} \left( V \right) - \frac{1}{V} \int_{V(0)} q^0 v_{(0)} \cdot \mathbf{n}_{(0)} dS
\]

\[-\frac{1}{V} \int_{\Sigma_a} q^0 v_{(0)} \cdot \mathbf{n}_{(0)} dS - \frac{1}{V} \int_{V(0)} q^0 v_{(0)} \cdot \mathbf{n}_{(0)} dS [114]\]

The averaged local transfer current for reaction \( k \), \( j_{(k)} \), is defined in Eq. 33.

**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

\[
\frac{dq}{dt} + \nabla \cdot \bar{i}^0 + \frac{1}{V} \int_{V(0)} (i^0 - q^0 v_{(0)}) \cdot \mathbf{n}_{(0)} dS
\]

\[+ \frac{1}{V} \int_{V(0)} (i^0 - q^0 v_{(0)}) \cdot \mathbf{n}_{(0)} dS = 0 [123]\]

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

\[\nabla \cdot \bar{i}^0 + \frac{1}{V} \int_{V(0)} (i^0 - q^0 v_{(0)}) \cdot \mathbf{n}_{(0)} dS = 0 [124]\]

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

\[\frac{1}{V} \int_{V(0)} (i^0 - q^0 v_{(0)}) \cdot \mathbf{n}_{(0)} dS + \frac{1}{V} \int_{S_{(0)}} (i^0 - q^0 v_{(0)}) \cdot \mathbf{n}_{(0)} dS = 0 [125]\]

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

\[j = \frac{1}{V} \int_{V(0)} (i^0 - q^0 v_{(0)}) \cdot \mathbf{n}_{(0)} dS [126]\]

and Eq. 124 becomes

\[\nabla \cdot \bar{i}^0 = -j [127]\]

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

\[\nabla \cdot \bar{i}^0 + i^0 = 0 [128]\]

**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.

**LIST OF SYMBOLS**

\( q^{(0)} \) specific surface area of the liquid/solid interface per unit volume of porous media, \( \text{cm}^2/\text{cm}^3 \)

\( B^{(0)} \) local volume average of quantity \( B \) in phase \( k \) (\( k = g, l, s \))

\( (B)^{(0)} \) intrinsic volume average of quantity \( B \) in phase \( k \) (\( k = g, l, s \))

\( c_e \) concentration of electrolyte, \( \text{mol/cm}^3 \)

\( c_o \) concentration of solvent, \( \text{mol/cm}^3 \)
Oxide Film Formation on a Microcrystalline Al Alloy in Sulfuric Acid

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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, 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 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.2 As is characteristic for rapidly solidified Al-Fe-V-Si alloys, the microstructure of the matrix composition of Al0.1Fe0.5V0.5Si0.1 consists of very fine, nearly spherical, intermetallic “dispersoids” uniformly distributed throughout a matrix phase.3 The microcrystalline matrix grain size typically varies from 0.5 to 2 μm in diameter.5 The matrix composition is primarily Al supersaturated with Fe [ca. 0.5 atom percent (at %) and Si (ca. 0.1 at %)].5 The nanosized dispersoids, of nominal composition of Al0.1Fe0.5V0.5Si0.1, are 0.05 ± 0.01 μm in diameter and occupy ca. 27 volume percent (v/v) of the alloy.5,6

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.8 This was verified by scanning electron microscopy which showed that, in contrast to a conventional 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 AlFe 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>
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<tr>
<th>Element</th>
<th>Atomic percent</th>
<th>Weight percent</th>
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