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Ionic Transport in Charged Porous Media

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ABSTRACT. Energy storage in capacitor porous materials, capacitive deionization (CDI) for water desalination, geophysical applications, and removal of heavy ions from waste streams are some examples of processes where understanding of ionic transport processes is very important. Most studies available in literature apply only to symmetric, binary electrolytes. A new model that computes the individual ionic concentration profiles inside porous electrodes is proposed to simulate ionic transport process. A volume averaging methodology has been used to derive the averaged equations from the point equations and appropriate boundary conditions. The transport parameters have been calculated for isotropic porous media. Finally, important issues to practically implement the proposed model are discussed.

INTRODUCTION

Most studies of ionic transport in porous media have been carried out using the assumption of binary, symmetric electrolytes ([1-5]; among others). This assumption leads to a single equation for the salt concentration instead of dealing with several equations for multiple ions of different charges and diffusivities (mobilities). Biesheuvel at al. [6] presented a porous electrode theory for the general situation of electrolytes containing mixtures of mobile ions of arbitrary charges and diffusion coefficients. The authors focused on porous electrodes comprising solid particles that are porous themselves. Biesheuvel at al. [6] proposed that the macropores operate as transport pathways while the ionic species are stored inside the micropores. The potentials and ionic concentrations between the macro and microscales are related by a modified Donnan model. This phenomenological formulation led to a set of individual ionic concentrations plus equations to calculate ionic charges and potentials. Schmuck and Bazant [7] derived effective Poisson-Nernst-Planck (PNP) equations for macroscopic ionic transport in charged porous media. The authors performed a homogenization analysis of a two-component periodic porous medium consisting of a dilute electrolyte and a continuous dielectric matrix impermeable to the ions and carrying a given surface charge. The transport coefficients in the macroscopic PNP equations were calculated from periodic reference cell problems.

The goal of this research project is to derive a system of equations to model ionic transport in porous media without the assumption of binary, symmetric salts and equal diffusivities. We will represent ionic transport using the PNP system of equations and the Poisson-Boltzmann equation for the electrostatic potential [8].

THEORETICAL SECTION
Model Development

The ion flux of species \( i \) in the bulk of the solution filling the pores is given by [3],

\[
N_i = -D_i \left( \nabla c_i + (z_i F c_i / RT) \nabla \phi \right).
\]

(1)

Here, \( N_i \) is the ion flux, \( c_i \) is the ion concentration, \( \nabla \) is the nabla operator in the \( x \) direction, \( z_i \) is the ion charge, \( D_i \) is the diffusion coefficient of ionic species \( i \), \( F \) is the Faraday constant, \( R \) is the universal gas constant, and \( \phi \) is the electrostatic potential in the pores. Equation (1) has been derived assuming that the isotropic mobility, \( u_i \), is given by the Nernst-Einstein relation [9], \( (u_i = D_i / RT) \).

![Porous medium and representative elementary volume (REV).](image)

**Figure 1.** Porous medium and representative elementary volume (REV).

We consider a two-phase medium consisting of a phase \( \alpha \) (liquid) and a phase \( \beta \) (solid) as shown in Figure 1. The point species molar continuity equation, including the Nernst-Planck expression for the molar flux for the \( \alpha \) phase, is given by:

\[
\frac{\partial c_i}{\partial t} = -\nabla \cdot N_i.
\]

(2)

We use the boundary condition at the \( \alpha-\beta \) interphase proposed by Bazant et al. [10],

\[
-n_{\alpha\beta} \cdot N_i = n_{\alpha\beta} \cdot D_i \left( \nabla c_i + z_i c_i \nabla \psi \right) = 0.
\]

(3)

Here, \( \psi \) is the dimensionless potential \( (\psi = \phi / F / R / T) \).

The relationship between liquid-phase potential and the spatial distribution of electric charges in the solution is given by the Poisson equation [11].

\[
\nabla \cdot \left( \eta \nabla \phi \right) = -F \sum_i z_i c_i.
\]

(4)

In the liquid-solid interphase \( (A_{\alpha\beta}) \) we use the boundary condition proposed by Scheiner et al. [11]:

\[
n_{\alpha\beta} \eta \nabla \phi = \sigma
\]

(5)
Here, $\eta$ is the permittivity of the electrolyte. The surface charge density ($\sigma$) represents the charge in the solid and it is assumed to be constant.

Equations (2) and (4) describe ionic transport by concentration and electrical potential gradients at the microscale inside porous media and are referred to as the Poisson-Nernst-Planck (PNP) system of equations ([8] and [12]). In order to obtain the macroscopic formulation of the PNP equations, we will use the volume averaging method developed by Prof. Whitaker and co-workers [13]. A brief description of the derivations is shown in the next sections.

**Species Concentration**

We start our derivation from eq. (2) and the boundary condition at the $\alpha$-$\beta$ interphase given by eq. (3). A variety of averages is encountered in this type of analysis [13]. The traditionally encountered averages are the *phase average* given by:

$$\langle c_{\alpha} \rangle = \frac{1}{V} \int c_{\alpha} \, dV .$$  \hspace{1cm} (6)

The *intrinsic phase average* which takes the form:

$$\langle c_{\alpha} \rangle^\alpha = \frac{1}{V_{\alpha}} \int_{V_{\alpha}} c_{\alpha} \, dV = \varepsilon_{\alpha} \langle c_{\alpha} \rangle .$$  \hspace{1cm} (7)

Here, $V$ is the volume of the REV, $V_{\alpha}$ represents the volume of the $\alpha$ phase contained within the REV, and $\varepsilon_{\alpha}$ is the volume fraction given explicitly by $\varepsilon_{\alpha} = V_{\alpha} / V$. We also use the spatial averaging theorem [14] that takes the form for a scalar variable $\psi_{\alpha}$:

$$\langle \nabla \psi_{\alpha} \rangle = \nabla \langle \psi_{\alpha} \rangle + \frac{1}{V} \int_{A_{\alpha \beta}} n_{\alpha \beta} \nabla \psi_{\alpha} \, dA .$$  \hspace{1cm} (8)

After repeated use of the averaging tools described above, plus algebraic manipulations, we obtain the following volume averaged equation:

$$\varepsilon_{\alpha} \frac{\partial \langle c_i \rangle^\alpha}{\partial t} = \nabla \cdot \left( D_i \left( \nabla \langle c_i \rangle + \frac{1}{V} \int_{V_{\alpha}} n_{\alpha \beta} \tilde{c}_i \, dV + z_i \langle c_i \nabla \psi \rangle \right) \right) .$$  \hspace{1cm} (9)

In the derivation of eq. (9), we have used Gray’s decomposition for the species i concentration [15],

$$c_i = \langle c_i \rangle^\alpha + \tilde{c}_i .$$  \hspace{1cm} (10)

The term $\langle c_i \nabla \psi \rangle$ is given by,

$$\langle c_i \nabla \psi \rangle = \varepsilon_{\alpha} \langle c_i \rangle^\alpha \nabla \langle \psi \rangle^\alpha + \langle c_i \rangle^\alpha \frac{1}{V} \int_{V_{\alpha}} n_{\alpha \beta} \tilde{c}_i \, dV + \langle \tilde{c}_i \nabla \tilde{\psi} \rangle .$$  \hspace{1cm} (11)

Here, $\langle \tilde{c}_i \nabla \tilde{\psi} \rangle$ represents the dispersion of species i produced by the electric field. Introducing eq. (11) into eq. (9) leads to,
\[
\varepsilon_a \frac{\partial \langle c_i \rangle^a}{\partial t} = \nabla \cdot \left\{ D_i \left[ \varepsilon_a \frac{\nabla \langle c_i \rangle^a}{V} + \frac{1}{V} \int_{\Lambda_{\alpha\beta}} \tilde{n}_{\alpha\beta} \tilde{c}_i dV + \frac{z_i \varepsilon_a}{V} \langle c_i \rangle^a \nabla \langle \psi \rangle^a \right] \right\}.
\]  

(12)

Closing eq. (12) requires expressions for the species concentration and potential deviations \((\tilde{c}_i, \tilde{\psi})\). These expressions are calculated in the closure section.

**Potential**

We start our derivation from eq. (4) and the boundary condition at the \(\alpha-\beta\) interphase given by eq. (5). The use of the phase average plus complex algebraic manipulations lead to,

\[
\nabla \cdot \left\{ \eta \varepsilon_a \left( \nabla \langle \phi \rangle^a + \frac{1}{V} \int_{\Lambda_{\alpha\beta}} \tilde{n}_{\alpha\beta} \tilde{\phi} dA \right) \right\} = -a_v \langle \sigma \rangle_{\alpha\beta} - F \varepsilon_a \sum_i z_i \langle c_i \rangle^a.
\]  

(13)

In eq. (13) we have used Gray’s decomposition for the potential and \(\langle \sigma \rangle_{\alpha\beta}\) is defined as,

\[
\langle \sigma \rangle_{\alpha\beta} = \frac{1}{A_{\alpha\beta}} \int_{A_{\alpha\beta}} \sigma dA.
\]  

(14)

A constitutive expression for the potential deviations \((\tilde{\phi})\) is calculated in next section.

**Closure Section**

**Potential**

We start by the boundary condition given by eq. (5). Gray’s decomposition for the potential and the approximation \(\sigma \approx \langle \sigma \rangle_{\alpha\beta}\) lead to,

\[
\nabla \cdot \left\{ \eta \langle c_i \rangle^a \nabla \langle \phi \rangle^a + \frac{1}{V} \int_{\Lambda_{\alpha\beta}} \tilde{n}_{\alpha\beta} \tilde{\phi} dA \right\} = a_v \langle \sigma \rangle_{\alpha\beta} - F \varepsilon_a \sum_i z_i \langle c_i \rangle^a.
\]  

(15)

Based upon eq. (15) we propose the following constitutive equation for the potential deviations:

\[
\tilde{\phi} = g \cdot \nabla \langle \phi \rangle^a + g_1 \langle \sigma \rangle_{\alpha\beta} + \zeta.
\]  

(16)

Here, \(g\) and \(g_1\) are the closure variables for the species concentrations. We obtain the equation for the potential deviation \((\tilde{\phi})\) by subtracting eq. (13) divided by \(\varepsilon_a\) from eq. (4) to obtain:

\[
\nabla \cdot \left\{ \eta \nabla \tilde{\phi} \right\} = a_v \langle \sigma \rangle_{\alpha\beta} / \varepsilon_a - F \sum_i z_i \tilde{c}_i.
\]  

(17)

The last term in the left-hand-side is negligible compared to the first and considering the permittivity constant within a unit cell leads to,
\[ \nabla^2 \tilde{\phi} = \frac{a_v \langle \sigma \rangle_{\alpha \beta}}{\varepsilon_{\alpha} \eta}. \]  \tag{18} 

Introducing eq. (16) into eqns. (15) and (18) leads to the following boundary value problems required to calculate the values of the closure variables \( g \) and \( g_1 \).

**Problem 1**

\[ \nabla^2 g = 0, \]  \tag{19} 

\[ -n_{\alpha \beta} \cdot \nabla g = n_{\alpha \beta}, \]  \tag{20} 

in the \( A_{\alpha \beta} \) and for spatially periodic porous media,

\[ g(r+l) = g(r) \text{ for } i = 1, 2, 3. \]  \tag{21} 

**Problem 2**

\[ \nabla^2 g_1 = \frac{a_v}{\varepsilon_{\alpha} \eta}, \]  \tag{22} 

\[ n_{\alpha \beta} \cdot \nabla g_1 = 1/\eta, \]  \tag{23} 

in the \( A_{\alpha \beta} \) and also for spatially periodic porous media,

\[ g_1(r+l) = g_1(r) \text{ for } i = 1, 2, 3. \]  \tag{24} 

**Species Concentration**

We start by introducing eq. (1) into the boundary condition given by eq. (2),

\[ -n_{\alpha \beta} \cdot \{ \nabla c_i + (z_i c_i) \nabla \psi \} = 0. \]  \tag{25} 

Using Gray’s decomposition [15] leads to,

\[ -n_{\alpha \beta} \cdot \{ \nabla \tilde{c}_i + z_i \tilde{c}_i \nabla \psi \} = n_{\alpha \beta} \cdot \{ \nabla \langle c_i \rangle^a + z_i \langle c_i \rangle^a \nabla \psi \}. \]  \tag{26} 

Inspection of eq. (26) allows us to propose the following equation for the deviation:

\[ \tilde{c}_i = f \cdot \nabla \langle c_i \rangle^a + f_i \langle c_i \rangle^a + \phi. \]  \tag{27} 

Here, \( f \) and \( f_i \) are the closure variables for the species concentrations.

We obtain the equation for the salt concentration deviation (\( \tilde{c} \)) by subtracting eq. (12) divided by \( \varepsilon_{\alpha} \) from eq. (2) to obtain:

\[ \frac{\partial \tilde{c}_i}{\partial t} = \nabla \cdot \{ D \nabla \tilde{c}_i - \frac{D}{V_{\alpha}} \int n_{\alpha \beta} \tilde{c}_i dA + D z_i \tilde{c}_i \nabla \psi + D z_i \langle c_i \rangle^a \nabla \tilde{\psi} \}. \]  \tag{28} 

An order of magnitude analysis shows that the second and third terms on the right-hand-side of eq. (28) are negligible compared to the first. The dispersion term is also negligible. The local process in the REV is quasi-stationary when the following restriction holds:
\[ t^* D / l_\alpha^2 \gg 1. \quad (29) \]

Here \( t^* \) is the characteristic time for the mass transport process and \( l_\alpha \) is a characteristic length of the microscale. The derivation of the closure problem is complicated because the charging process presents two very different transport regimes [3]. At very short times, supercapacitor regime, there is a fast charging of the EDLs and we can say that the predominant transport process is the migration step. At long times, the diffusive flow from outside the electrode predominates over the charging process and, from that point on, the concentration increases (desalination regime).

After long algebraic manipulations, the following boundary value problems to calculate the closure variables \( f \) and \( f_1 \) can be written:

**Problem 3**

\[ \nabla^2 f = 0 \]

\[ n_{\alpha\beta} \cdot \nabla f + z_i f \sigma^* = -n_{\alpha\beta}, \quad (31) \]

in the \( A_{\alpha\beta} \) and for spatially periodic porous media.

**Problem 4**

\[ \nabla^2 f_1 = -z_i \frac{a_i \sigma^*}{\varepsilon_\alpha}, \quad (32) \]

\[ -n_{\alpha\beta} \cdot \nabla f_1 - z_i f_1 \sigma^* = z_i \sigma^*. \quad (33) \]

in the \( A_{\alpha\beta} \) and also for spatially periodic porous media.

Here, \( \sigma^* \) is the cell’s dimensionless charge density, \( \sigma^* = \frac{\sigma r_2}{\eta V_T} \), \( f \) and \( f_1 \), are the dimensionless closure variables (\( f_i = f_i / r_2 \)), and \( r_2 \) is the unit cell characteristic length (\( r_2 \approx l_\alpha \)). More will be said about the calculation of the effective diffusivities for co- and counter-ions in the results section.

**Closed Equations Section**

**Potential**

Introducing eq. (16) into eq. (13) leads to,

\[ \nabla \cdot \left\{ \eta \varepsilon_\alpha \nabla \langle \phi \rangle^\alpha \right\} + \nabla \cdot \left\{ \varepsilon_\alpha \langle \sigma \rangle_{\alpha\beta} \frac{\eta}{V_\alpha} \left[ n_{\alpha\beta} g_1 dA \right] \right\} = -a_\alpha \langle \sigma \rangle_{\alpha\beta} - F \varepsilon_\alpha \sum_i z_i \langle c_i \rangle^\alpha. \quad (34) \]

An order of magnitude analysis proves that the second term in the left-hand-side is negligible compared to the first in the right-hand-side; consequently, the closed potential equation can be written as,

\[ \nabla \cdot \left\{ \eta \varepsilon_\alpha \nabla \langle \phi \rangle^\alpha \right\} = -a_\alpha \langle \sigma \rangle_{\alpha\beta} - F \varepsilon_\alpha \sum_i z_i \langle c_i \rangle^\alpha. \quad (35). \]
Here, the effective permittivity tensor ($\eta_{\text{eff}}$) can be expressed as,

$$\eta_{\text{eff}} = \eta \varepsilon_\alpha (1 + \frac{1}{V_\alpha} \int_{A_{\alpha}} n_{\alpha\beta} g dA). \quad (36)$$

**Species Concentration**

Introducing eq. (27) into eq. (12) leads, after algebraic manipulations, to,

$$\varepsilon_\alpha \frac{\partial (c_i)^\alpha}{\partial t} = \nabla \cdot \left( D_{i,\text{eff}} \varepsilon_\alpha (1 + \frac{1}{V_\alpha} \int_{A_{\alpha}} n_{\alpha\beta} f dA) \right) \varepsilon_\alpha \frac{\partial (c_i)^\alpha}{\partial x} + z_i U_{i,\text{eff}} \varepsilon_\alpha (c_i)^\alpha \nabla \langle \psi \rangle^\alpha + D_{i,\text{eff}} (c_i)^\alpha \psi \right), \quad (37)$$

Here, the effective diffusivity tensor ($D_{\text{eff}}$), the effective mobility tensor ($U_{\text{eff}}$), and the vector ($v$) are given, respectively, by,

$$D_{i,\text{eff}} = D_i \varepsilon_\alpha (1 + \frac{1}{V_\alpha} \int_{A_{\alpha}} n_{\alpha\beta} f dA), \quad (38)$$

$$U_{i,\text{eff}} = D_i \varepsilon_\alpha (1 + \frac{1}{V_\alpha} \int_{A_{\alpha}} n_{\alpha\beta} g dA), \quad (39)$$

$$v = \frac{1}{V_\alpha} \int_{A_{\alpha}} n_{\alpha\beta} f dA. \quad (40)$$

Assuming that the constraints discussed in the closure section hold the terms containing the vector $v$ are negligible with respect to the first and second on the right-hand-side during most of the charging period; therefore, eq. (37) can be written as,

$$\varepsilon_\alpha \frac{\partial (c_i)^\alpha}{\partial t} = \nabla \cdot \left( D_{i,\text{eff}} \varepsilon_\alpha \frac{\partial (c_i)^\alpha}{\partial x} + z_i U_{i,\text{eff}} \varepsilon_\alpha \langle c_i \rangle^\alpha \nabla \langle \psi \rangle^\alpha \right). \quad (41)$$

Inspection of closure problems 1 and 3 shows that the vector field $f$ is a function of the geometry and electrode charge while the vector field $g$ is a function of the geometry only; therefore, the effective diffusivity and mobility tensors are not equal.

**RESULTS**

**Closure Section**

The effective permittivity ($\eta_{\text{eff}}$) and the effective mobility ($U_{\text{eff}}$) are calculated by solving boundary value problem 1 and then, calculating the integral given by eqns. (36) and (39). Closure problem 1 has been solved numerically many times in literature for isotropic porous media ([16-20]; among others). Quintard and Whitaker [19] showed that solving this closure problem in Chang’s unit cells [21-22] leads to Rayleigh’s [23] equation for the effective diffusivity.

$$\frac{\varepsilon_\alpha D_{i,xx}}{D_i} = \frac{\varepsilon_\alpha}{(2 - \varepsilon_\alpha)}, \quad (42)$$
In order to calculate the effective diffusivity tensor we have to solve boundary value problem 3. In the case of isotropic porous media only one component of the effective diffusivity tensor is needed (\(D_{i,xx}\)). In this work, we will use Chang’s unit cells [21-22], see Figure 2, to obtain analytical solutions for isotropic beds of cylinders ([18, 19, and 24]; among others).

**Figure 2.** Chang’s approximate unit cell for spatially periodic porous media.

In this case the problem becomes independent of the axial direction (\(z/r_2\)) and, following the relationships presented by Ochoa-Tapia et al. [18], we can rewrite the closure problem 3 in dimensionless form as,

\[
\frac{1}{r^2} \frac{\partial F_x}{\partial r^2} + \frac{\partial^2 F_x}{\partial \theta^2} + \frac{1}{r^2} \frac{\partial^2 F_x}{\partial \theta^2} = 0
\]

\(\text{Eq. (43)}\)

\[- \frac{\partial F_x}{\partial r^*} + z_i \sigma^* F_x = \cos \theta, \text{ at } r^* = r_1/r_2\]

\(\text{Eq. (44)}\)

\(F_x = 0, \text{ at } r^* = 1\)

\(\text{Eq. (45)}\)

Here, \(F_x\) is the x component of \(f (f_i/r_2)\), and \(r^* = r/r_2\). The solution procedure presented by Ochoa-Tapia et al. [18] leads to,

\[
\frac{\varepsilon_a}{D_{i,xx}} = \varepsilon_a \left\{ \frac{1 + z_i \sigma^* (1 - \varepsilon_a)^{0.5}}{(2 - \varepsilon_a) + z_i \sigma^* (1 - \varepsilon_a)^{0.5}} \right\}.
\]

\(\text{Eq. (46)}\)

Eq. (46) shows that the value of the effective diffusivity is a function of the charge in the electrolyte-solid interface. Figure 3 depicts the variation of co- and counter-ion effective diffusivity values at a fixed porosity value.

Figure 3 shows that different behavior is predicted for counter- and co-ions. In the case of co-ions, there is a continuous increase of the dimensionless effective diffusivity from the uncharged value, predicted by Raleigh’s equation, until the effective diffusivity approaches the ionic diffusivity value in free solution. The counter-ion behavior predicts that at low charge a singular point will appear. The value of the effective diffusivity tends to -\(\infty\) and \(\infty\) in a neighborhood of the singular point. At high charge values, the counter-ion transport coefficient approaches the value of the free solution ionic diffusivity. The location of the singular point is a function of the void fraction and interface charge values. The behavior in the neighborhood of the singular point is, obviously, non-physical. It reveals that the system behaves in different ways before and after
the singular point. Biesheuvel and Bazant [3] proposed that for small charge values, below the thermal voltage, a weak nonlinear solution is valid in the supercapacitor regime. In this linearized problem, at low voltages or early times, the porous electrode acts as a “transmission line” in series with the mass transfer layer resistor outside. However, in the desalination regime the authors stated that this linearized approximation is not valid and the full nonlinear problem has to be solved. Biesheuvel and Bazant [3] also stated that especial mathematical tools are required to match both limiting solutions.

**Figure 3.** Variation of the effectivity diffusivity with interface charge ($\varepsilon_\alpha = 0.3$).

Typical capacitive deionization experiments are carried out at high charge; therefore, under normal operating conditions both ions will be have effective diffusivity values approaching the free electrolyte solution values.

**Model Implementation**

Sharma et al. [25] reported that the left-hand-side of eq. (35) is negligible compared to the two terms in the right-hand-side. After making the equation dimensionless the left-hand-side term is multiplied by the square of the ratio of the microscopic over the macroscopic length scales, $\lambda_{\alpha}/L$. The microscopic length scale ($\lambda_{\alpha}$) is typically of the order of magnitude of the EDL Debye length, while the macroscopic length scale ($L$) is estimated by the electrode thickness; therefore, eq. (35) becomes,

$$F \sum_i z_i \langle c_i \rangle^\alpha + a_v \langle q \rangle_{\alpha\beta} = 0$$

(47)

Equation (47) states that, at the macroscopic level, the charge on the solid electrode is balanced by the charge in the solution. It is important to notice that this global electroneutrality condition results naturally from the different length scales used and not from any arbitrary assumption. MacGillivray [26] used an asymptotic expansion method to show that under certain
assumptions eq. (47) is the upscaled form of the Poisson equation. The replacement of eq. (35) by the electroneutrality condition makes the mathematical problem open as there are more variables than equations. In order to overcome this problem, Sharma et al. [25] proposed a model to calculate the average potential at the macroscopic level. The authors assumed highly overlapping EDLs in slit-shaped pores following the treatment presented by Yang et al. [27]. These authors proposed that a representative pore can be viewed as a slit formed by two planar plates with a separation distance $2L$ between them, more details are given in Sharma et al. [25]. A simple model can be also used to calculate the macroscopic potential inside the pores. We can assume that the EDL functions as a parallel plate capacitor with a distance between the plates equal to the Debye length. This model predicts an EDL capacitance equal to the Debye-Hückel linear approximation of the Poisson equation problem (Debye and Hückel [28]). The advantage of this model is the simplicity to implement and the fact that produces very robust numerical schemes.

Results for a charge-discharge capacitive deionization (CDI) cycle calculated using the two models are presented in Figures 4 and 5.

![Figure 4. CDI charge-discharge cycle using small pores electrodes (2 nm).](image)

In Figures 4 and 5 we show values of ionic concentrations averaged throughout the electrode. The broken line in both figures represents the free solution ionic concentration. During the charging step the counter-ion concentration increases continuously while the co-ion concentration decreases. The discharge step starts when the applied potential is set to zero; therefore, the counter-ions held inside the EDL by the source potential diffuse back into the bulk of the solution. The charge of the freed ions also creates a ‘reverse’ potential that transport by migration the counter-ions into the solution bulk and the co-ions into the EDL, i.e., migration and diffusion transport the co-ions inside the EDL and the counter-ions outside. Sharma et al. [25] reported that in the case of small pores the two combined transport processes can produce an
increase of co-ion concentration inside the electrode above the concentration in the solution bulk. The authors also determined this phenomenon experimentally using a neutron imaging technique.

![Diagram showing CDI charge-discharge cycle using big pores electrodes (60 nm).](image)

**Figure 5.** CDI charge-discharge cycle using big pores electrodes (60 nm).

Figure 4 depicts results for small pores (2 nm width). We can see in the figure that, during the discharge step, both the co-ions and counter-ions concentrations have values above the free solution ones (broken line). We can also see that both models predict very similar values for small pores. Equivalent results for the dimensionless potential, not shown here, showed that Sharma’s et al. model predicts very similar values for \( \phi_D \) and \( \phi_{bulk} \). In the case of bigger pores, Figure 5 shows that the Debye-Hückel model significantly overestimated the concentration of the counter-ions and underestimated the concentration of co-ions compared to Sharma’s et al. [25] model. The reason is that there is significant difference in the \( \phi \) values calculated using both models. In the case of macropores (\( d_p > 50 \text{ nm} \)) the bulk of the electrolyte is a neutral region with uniform ionic concentration and no net charge. This fact is reflected in the results calculated using Sharma’s et al. model. The model predicts slightly different ionic concentrations because it averages the dimensionless concentrations in the thin EDLs (\( C_i \gg 1 \) or \( C_i << 1 \)) with the wider bulk (\( C_i \approx 1 \)).

In conclusion, we can say that the model presented by Sharma et al. [25] describes well the qualitative behavior of the system for all pore sizes while the parallel plate capacitor model describes well qualitative behavior in the CDI cycle only for meso and microporous electrodes.

**CONCLUSIONS**

The volume averaging method has been used to derive the averaged equations describing ionic transport phenomena in charged porous electrodes. We have derived individual ionic
volume averaged equations starting from the PNP point equations and the appropriate boundary
conditions. Our derivations show that the effective diffusivity and mobility tensors are not equal
as they are in the point equations. We have also derived the macroscopic Poisson-Boltzmann
averaged equation. However, at the macroscopic scale this equation is transformed into a global
electron neutrality condition. This condition leads to an open problem due to the loss of
microscopic information during the averaging process. In order to deal with this problem we
used the model presented by Sharma et al. [25]. This model represents the transport behavior of
counter and co-ions in pores of all sizes. We have also calculated effective diffusivities for
isotropic porous media of cylindrical particles by solving the closure problem in Chang’s unit
cells following the procedure presented by Ochoa-Tapia et al. [18]. The solution of the
appropriate closure problems shows that the effective diffusivity is a function of the electric
charge density in the solid-solution interphase. In the case where the porous media is uncharged
the effective diffusivity values are given by Rayleigh’s [23] equation while for high charge
values the effective diffusivity values approach the free solution bulk diffusivity values.

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