

# The effect of surface transport on water desalination by porous electrodes undergoing capacitive charging

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## Abstract

Capacitive deionization (CDI) is a technology in which water is desalinated by ion electrosorption into the electric double layers (EDLs) of charging porous electrodes. In recent years significant advances have been made in modeling the charge and salt dynamics in a CDI cell, but the possible effect of surface transport within diffuse EDLs on these dynamics has not been investigated. We here present theory which includes surface transport in describing the dynamics of a charging CDI cell. Through our numerical solution to the presented models, the possible effect of surface transport on the CDI process is elucidated. While at some model conditions surface transport enhances the rate of CDI cell charging, counter-intuitively this additional transport pathway is found to slow down cell charging at other model conditions.

Keywords: desalination, capacitive deionization, surface transport, electric double layers

(Some figures may appear in colour only in the online journal)

## Introduction

Capacitive deionization (CDI) is an emerging technology typically applied to the desalination of brackish feedwaters [1], but also to organic solvent remediation [2], water softening [3], ion separations [4], microfluidic sample preparation [5], and sea water desalination [6]. The classic CDI cell consists of two microporous carbon electrodes sandwiching a porous dielectric separator, see figure 1(a). The electrodes are charged by either a constant voltage or constant current [1, 7], resulting in the migration of salt ions from the feedwater towards the oppositely charged electrode, and their storage within micropore electric double layers (EDLs). The latter process is referred to as the electrosorption of salt ions [8, 9]. The feedwater flows most often between the two charging electrodes [1], although flow can also be through the electrodes themselves [10–12]. Alternative CDI cell architectures utilize suspension electrodes, such as flow or fluidized bed electrodes [6, 13, 14], and include ion exchange membranes along the inner electrode surfaces [15]. The porous electrodes of CDI cells typically contain a multiscale pore structure, which includes a through-electrode network of macropores

which access smaller micropores [8]. The layout of the electrode's pore structure can vary for different materials, as for example, activated carbon electrodes often consist of a collection of bound micron-scale microporous carbon particles [16], while hierarchical carbon aerogel monoliths (HCAMs) have micropores etched into the walls of a macroporous monolith via thermal activation [10, 17].

Surface transport (ST) refers the movement of ions in EDLs tangentially to the charged interface due to, for example, tangential electric fields or tangential gradients in ion concentration [18]. There is an extensive literature investigating the effects of ST in electrokinetic systems employing dielectric media such as planar dielectric walls [19–23], porous dielectric media [24–28], dielectric solid–liquid colloidal suspensions [29–31], and also for electrochemical systems employing charging planar metal electrodes [32, 33]. By contrast, the literature is far sparser on the topic of ST in charging conductive porous media such as porous carbons electrodes, despite the widespread application of such electrodes in energy storage systems and in water desalination by CDI [8, 34]. To our knowledge, the latter literature consists solely of the work of Mirzadeh *et al.*, who presented theory and a numerical model capturing the effect of ST

on the charging dynamics of the porous electrodes of supercapacitors [35], and of Vol'fkovich *et al.*, who presented measurements of surface conductivity as a function of applied potential in porous carbons [36]. We know of no previous works which investigate the effect of ST in porous electrodes on desalination and charging dynamics in a CDI cell. ST (and more specifically surface conductivity) may be significant in CDI, as during cell charging the electrosorption of ions into the EDL from the bulk electrolyte can result in a high surface to bulk conductivity ratio (a high Dukhin number) [37].

Theoretical models of CDI cells typically employ macroscopic porous electrode (MPE) theory coupled to an EDL structure model [1, 16]. MPE theory involves volume averaging local (in-pore) transport equations over a suitable control volume which allows for averaging over the complex geometry present in random porous media, and MPE theory has also been applied to energy storage systems such as batteries and supercapacitors [38–40]. For CDI, MPE theory was first implemented by Johnson and Newman coupled to a simple Helmholtz-type model of the EDL along pore surfaces [41]. Several decades later, Biesheuvel and Bazant coupled MPE theory to a Gouy–Chapman EDL along pore surfaces [37], as did Gabitto and Tsouris [42]. Shortly thereafter, Biesheuvel *et al.* proposed using instead an EDL structure model which assumes a common electrostatic potential and concentration within the volume of strongly confined micropore geometry, which was termed the modified Donnan EDL model [43, 44]. The latter model captured the multiscale nature of CDI electrodes and has been fitted to experimental data using several fitting parameters such as the Stern layer capacitance and a non-electrostatic attractive potential [45–48]. In addition, Gabitto and Tsouris developed a model for CDI by multiscale porous electrodes via a two-step volume averaging technique [49]. Building upon previous CDI theoretical models, we here expand them to include the effect ST in CDI cells, and apply the theory to understand the effect of ST on desalination and cell charging dynamics in both uni- and multi-scale porous electrodes. Counter-intuitively, we find that at some model conditions, the effect of ST (an additional transport pathway for ions) is to slow down cell charging.

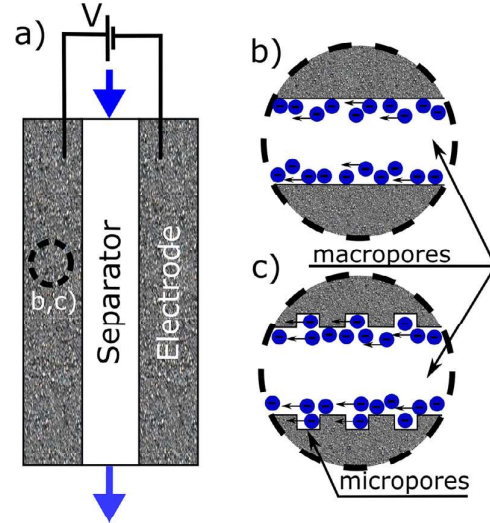
### Theory

To develop the theory of ST in CDI cells, we begin by describing transport of salt and charge in the electroneutral bulk of a macropore (see figure 1). For a binary and symmetric electrolyte with equal anion and cation diffusivities, non-dimensional salt and charge balance equations are given by:

$$\frac{\partial \hat{c}}{\partial \hat{t}} = \hat{\nabla}^2 \hat{c} \quad (1)$$

$$\hat{\nabla} \cdot (\hat{c} \hat{\nabla} \hat{\phi}) = 0 \quad (2)$$

where  $\hat{c}$  is local salt concentration in the pore bulk scaled by the initial pore bulk salt concentration,  $c_0$ , and  $\hat{\phi}$  is the local bulk electrostatic potential non-dimensionalized by the



**Figure 1.** (a) Schematic of a typical CDI cell with feedwater flow between the two electrodes. Schematics (b) and (c) show the pore structures investigated in this work, which include (b) solely through-electrode macropores, and (c) through-electrode macropores which access micropores.

thermal voltage. Further,  $\hat{t}$  is time scaled by the characteristic diffusion time across the characteristic pore size, defined by  $\tau_D = h_p^2/D$ , where  $D$  is the diffusivity of both anion and cation and  $h_p$  is the pore volume divided by pore surface area [37]. The parameter  $h_p$  is used as the characteristic lengthscale for the scaled bulk coordinates  $\hat{x}$ ,  $\hat{y}$ , and  $\hat{z}$ . During cell charging, counterions electromigrate towards macropore walls (figure 1(b) and (c)) or into micropores (figure 1(c)) while coions electromigrate away. This results in the formation of non-electroneutral EDLs along the macropore wall with a characteristic thickness given by the Debye length,  $\lambda_D$ , and also within micropores where the characteristic geometric size is often on the order of  $\lambda_D$ . Including the EDLs in the model domain requires a solution of the coupled Poisson–Nernst–Planck equations, which can be numerically challenging as the EDLs and micropores are often significantly smaller than the macropore size,  $h_p$ . An alternative method for thin EDLs is to instead model the effects of EDL charging on the bulk domain via effective flux boundary conditions [32, 33, 50]. For the case of ion transport between a diffuse EDL and bulk domain, and surface (tangential) transport of ions within the diffuse EDL, Chu and Bazant presented the following general effective flux boundary conditions at the location of the EDL [32] (e.g. at  $\hat{z} = 0$ ):

$$\varepsilon \frac{\partial \tilde{w}}{\partial \hat{t}} = \varepsilon \hat{\nabla}_s \cdot \left( \hat{\nabla}_s \tilde{w} + \tilde{q} \hat{\nabla}_s \hat{\phi} + \int_0^\infty \tilde{\rho} \hat{\nabla}_s \tilde{\psi} d\tilde{z} \right) - \left( \frac{\partial \hat{c}}{\partial \hat{z}} \right) \Big|_{(\hat{x}, \hat{y}, 0)} \quad (3)$$

$$\varepsilon \frac{\partial \tilde{q}}{\partial \hat{t}} = \varepsilon \hat{\nabla}_s \cdot \left( \hat{\nabla}_s \tilde{q} + \tilde{w} \hat{\nabla}_s \hat{\phi} + \int_0^\infty \tilde{c} \hat{\nabla}_s \tilde{\psi} d\tilde{z} \right) - \left( \hat{c} \frac{\partial \hat{\phi}}{\partial \hat{z}} \right) \Big|_{(\hat{x}, \hat{y}, 0)} \quad (4)$$

where the tilde refers to variables of the EDL (inner) domain. The EDL has inner coordinates  $\tilde{x}$  and  $\tilde{y}$  parallel to the pore surface and non-dimensionalized by  $h_p$ , and  $\tilde{z}$  perpendicular to the surface and scaled by  $\lambda_D$ , with  $\tilde{z} = 0$  being the location of the solid wall. Further,  $\nabla_{\tilde{s}}$  is the surface gradient [50],  $\varepsilon$  is the ratio  $\lambda_D/h_p$ , and  $\tilde{\rho}$  is the local net charge density in the EDL, defined as  $(\tilde{c}_c - \tilde{c}_a)/2$ , where  $\tilde{c}_a$  and  $\tilde{c}_c$  are, respectively, the anion and cation concentration in the EDL non-dimensionalized by  $c_0$ .  $\tilde{c}$  is the local mean ion concentration in the EDL, defined as  $(\tilde{c}_c + \tilde{c}_a)/2$ , and  $\tilde{\psi}$  is the excess potential in the EDL [32]. Also,  $\tilde{q}$  is the non-dimensional charge density in the EDL and  $\tilde{w}$  is the non-dimensional EDL excess salt density in the EDL, defined as [33]:

$$\tilde{w} = \int_0^\infty (\tilde{c} - \hat{c}) d\tilde{z} \quad (5)$$

$$\tilde{q} = \int_0^\infty \tilde{\rho} d\tilde{z}. \quad (6)$$

Additionally, Chu and Bazant derived effective flux boundary conditions for the case of a Gouy–Chapman (GC) EDL, which were given as the following [32, 33]:

$$\tilde{w} = 4\sqrt{\tilde{c}} \sinh^2 \frac{\tilde{\zeta}}{4} \quad (7)$$

$$\tilde{q} = -2\sqrt{\tilde{c}} \sinh \frac{\tilde{\zeta}}{2} \quad (8)$$

$$\varepsilon \frac{\partial \tilde{w}}{\partial \hat{t}} = \varepsilon \nabla_{\tilde{s}} \cdot (\tilde{w} \nabla_{\tilde{s}} \ln \hat{c} + \tilde{q} \nabla_{\tilde{s}} \hat{\phi}) - \left( \frac{\partial \hat{c}}{\partial \tilde{z}} \right) \Big|_{(\tilde{x}, \tilde{y}, 0)} \quad (9)$$

$$\varepsilon \frac{\partial \tilde{q}}{\partial \hat{t}} = \varepsilon \nabla_{\tilde{s}} \cdot (\tilde{q} \nabla_{\tilde{s}} \ln \hat{c} + \tilde{w} \nabla_{\tilde{s}} \hat{\phi}) - \left( \hat{c} \frac{\partial \hat{\phi}}{\partial \tilde{z}} \right) \Big|_{(\tilde{x}, \tilde{y}, 0)} \quad (10)$$

where  $\tilde{\zeta}$  is the zeta potential, defined as the induced potential drop across the GC EDL. While a GC EDL can be used to approximate the EDL structure along macropore walls, such a model cannot describe EDL structure in micropores due to a characteristic geometric size which is on the order of  $\lambda_D$  [45]. Instead, for micropores a Donnan EDL model is used, which assumes uniform micropore electric potential and concentration, reflecting the geometric confinement and resulting strong EDL overlap in micropores [43, 44, 51]. Modified versions of the Donnan model have been used to fit model results to experimental data, where modifications include a Stern layer and an additional adsorption potential [47], or capture the amphoteric nature of the carbon electrode [52]. To model ST in CDI systems with micropores, we here derived the effective flux boundary conditions for the case of a Donnan EDL (see appendix A for detailed derivation):

$$\varepsilon_{mi} \frac{\partial (\tilde{c}_{mi} - \hat{c})}{\partial \hat{t}} = \varepsilon_{mi} \nabla_{\tilde{s}}^2 (\tilde{c}_{mi} - \hat{c}) - \left( \frac{\partial \hat{c}}{\partial \tilde{z}} \right) \Big|_{(\tilde{x}, \tilde{y}, 0)} \quad (11)$$

$$\varepsilon_{mi} \frac{\partial \tilde{\sigma}_{mi}}{\partial \hat{t}} = \varepsilon_{mi} \nabla_{\tilde{s}} \cdot (\nabla_{\tilde{s}} \tilde{\sigma}_{mi} - \hat{c} \nabla_{\tilde{s}} \hat{\phi}) - \left( \hat{c} \frac{\partial \hat{\phi}}{\partial \tilde{z}} \right) \Big|_{(\tilde{x}, \tilde{y}, 0)} \quad (12)$$

where  $\varepsilon_{mi} = l_{mi}/h_p$ ,  $l_{mi}$  is the depth of the micropores,  $\tilde{c}_{mi} \equiv (\tilde{c}_{mi,c} + \tilde{c}_{mi,a})/2$  is the micropore salt concentration, and  $\tilde{\sigma}_{mi} \equiv (\tilde{c}_{mi,c} - \tilde{c}_{mi,a})/2$  is the micropore charge density, here  $c_{mi,i}$  is the concentration of ion  $i$  in the micropore non-dimensionalized by  $c_0$ . We note that, in equations (11) and (12), all of the micropores' excess salt and charge participates in ST, and thus these equations give an upper limit of ST due to micropore EDLs. A more refined model capturing precisely micropore ST requires resolving micropore geometric features. However, such a model is beyond the scope of the current work. We note that some CDI electrode materials with long micropores (relative to micropore hydraulic diameter), such as activated carbon electrodes consisting of microporous micron-scale carbon particles, may result in most of the micropore ionic charge being unavailable for ST. However others, such as hierarchical activated carbon aerogels (HCAMs), where short micropores are etched into macropore walls, may exhibit a more significant fraction of micropore charge and salt contributing to effective tangential fluxes.

Equations (1) and (2) with either equations (9) and (10) or equations (11) and (12) as boundary conditions can be applied to study the macropore salt and charge dynamics. However, these models require accounting for the complexity of the macropore geometry, which is often difficult for random porous media. To avoid geometric complexities, a common technique is to develop macroscopic models based on volume averaged variables [38]. As described in Biesheuvel and Bazant [37], via integrating the pore bulk transport equations, here equations (1) and (2), over a suitable representative volume, the normal flux component of the effective flux boundary conditions can be converted to volumetric source terms in a macroscopic model. The latter authors developed such volumetric source terms for the case of ion electrosorption into GC EDLs but did not include the effect of ST within the EDL [37]. We here extend the latter work to include ST via volume integrating the pore bulk transport equations and implementing the effective flux boundary conditions given by equations (9) and (10). The complete procedure is shown in appendix B, and we here present the results for the 1D form of the macroscopic transport equations:

$$\frac{\partial (\bar{c} + \varepsilon \bar{w})}{\partial \hat{t}} = \frac{\partial^2 \bar{c}}{\partial \bar{x}^2} + \varepsilon \frac{\partial}{\partial \bar{x}} \left( \bar{w} \frac{\partial \ln \bar{c}}{\partial \bar{x}} + \bar{q} \frac{\partial \bar{\phi}}{\partial \bar{x}} \right) \quad (13)$$

$$\varepsilon \frac{\partial \bar{q}}{\partial \hat{t}} = \frac{\partial}{\partial \bar{x}} \left( \bar{c} \frac{\partial \bar{\phi}}{\partial \bar{x}} \right) + \varepsilon \frac{\partial}{\partial \bar{x}} \left( \bar{q} \frac{\partial \ln \bar{c}}{\partial \bar{x}} + \bar{w} \frac{\partial \bar{\phi}}{\partial \bar{x}} \right). \quad (14)$$

We denote equations (13) and (14) as our 1D ST model, and  $\bar{c}$  and  $\bar{\phi}$  represent volume-averaged bulk concentration and potential, respectively, while  $\bar{w}$  and  $\bar{q}$  are the surface area averaged excess salt concentration and charge, respectively, see equations (B.5) and (B.6). The variables  $\bar{x}$  and  $\bar{t}$  are defined as  $\bar{x} = x/L_e$  and  $\bar{t} = tD/L_e^2$ , where  $x$  is the dimensional location, see figures 3(a) and (b),  $t$  is the dimensional time and  $L_e$  is the electrode's thickness. As shown in equations (13) and (14), the tangential flux components of the effective flux boundary conditions have been converted to volumetric flux terms in the macroscopic equations. We can compare our 1D ST model to the 1D model presented by Mirzadeh *et al* for ST

in a supercapacitor electrode (equations (12) and (13) of that work), [35] which we reproduce here:

$$\frac{\partial(\bar{c} + \varepsilon\bar{w})}{\partial\bar{t}} = \frac{\partial^2(\bar{c} + \varepsilon\bar{w})}{\partial\bar{x}^2} + \varepsilon \frac{\partial}{\partial\bar{x}} \left( \bar{q} \frac{\partial\bar{\phi}}{\partial\bar{x}} \right) \quad (15)$$

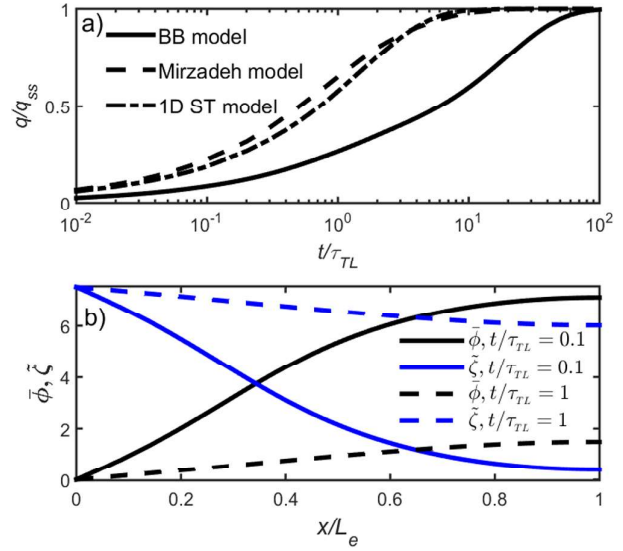
$$\varepsilon \frac{\partial\bar{q}}{\partial\bar{t}} = \varepsilon \frac{\partial^2\bar{q}}{\partial\bar{x}^2} + \frac{\partial}{\partial\bar{x}} \left( (\bar{c} + \varepsilon\bar{w}) \frac{\partial\bar{\phi}}{\partial\bar{x}} \right). \quad (16)$$

As can be seen, our 1D ST model differs from the Mirzadeh model, as the latter model did not include the effect of surface conduction driven by gradients in the excess potential. In other words, equations (15) and (16) can be derived by volume integrating the bulk equations and implementing equations (3) and (4) with  $\widehat{\nabla}_s \widehat{\psi} = 0$  as effective flux boundary conditions, as we show in appendix B. All models in this work were solved using COMSOL Multiphysics 4.4 (COMSOL Inc., Sweden).

## Results

In figure 2(a), we compare the charging dynamics predicted by the Mirzadeh model (equations (15) and (16)) to our 1D ST model (equations (13) and (14)), and to the 1D model without ST presented by Biesheuvel and Bazant (the BB model) [37]. The BB model can be obtained from equations (13) and (14) if the ST terms are neglected (the two right-most terms). In this figure,  $q$  represents the time-dependent charge stored in the electrode after applying the voltage, and  $q_{ss}$  is the charge stored at steady state. For the time axis, we non-dimensionalized time by the transmission line timescale  $\tau_{TL} = \lambda_D L_c^2 / h_p D$  [35, 53]. To contrast our 1D ST model to the Mirzadeh model, we investigate the simpler case where desalination is inhibited during cell charging by using boundary conditions of  $\bar{c} = 1$  and  $\bar{\phi} = 0$  at the inner electrode edge,  $\bar{x} = 0$ . We note that this concentration boundary condition, which was also used in the work of Mirzadeh *et al* [35, 54] is most appropriate for modeling supercapacitor systems where salt concentration in the electrode is not expected to vary during cell charging. We further used a zero flux boundary condition (both bulk and surface flux) at the outer electrode edge,  $\bar{x} = 1$ , and initial conditions of  $\bar{c} = 1$  and  $\bar{\phi} = V_{el} = 7.5$  along the length of the electrode, where  $V_{el}$  is the voltage applied to the solid phase of the electrode. As seen in figure 2(a), including ST leads to significantly faster dynamics in both the Mirzadeh model (as previously reported [35]) and our 1D ST model, when compared to the BB model. However, we can also observe that our 1D ST model demonstrates slower charging compared to the Mirzadeh model for most of the charging process. The latter is due to the inclusion in the 1D ST model of ST driven by gradients in the excess potential. The excess electric field is in the opposite direction of the bulk electric field, as is shown in figure 2(b) where we plot excess potential at  $\bar{z} = 0$ , which we denote as  $\tilde{\zeta}$  (blue lines), and also plot the bulk potential,  $\bar{\phi}$  (black lines).

We now utilize our 1D ST model to develop insight into the effect of ST on the cell charging and salt dynamics in a CDI cell, thus restricting ourselves for the moment to solely



**Figure 2.** (a) Predicted electrode charge stored,  $q/q_{ss}$ , of our 1D ST model, the Mirzadeh model [35], and the BB model [37] with supercapacitor boundary conditions and  $\varepsilon = 0.1$ ,  $V_{el} = 7.5$ . (b) Plot of the bulk potential,  $\bar{\phi}$ , and excess potential at the pore wall,  $\tilde{\zeta}$ , predicted by the 1D ST model.

macroporous CDI electrodes with GC EDLs along the pore walls (figure 1(b)). For predicting CDI cell performance, appropriate boundary conditions must be used which allow for desalination at the electrode's inner edge. Thus, we solve our 1D ST model for cells which include a porous separator layer adjacent to the porous electrode, and for two physical scenarios in the separator, see figures 3(a) and (b). For simplicity the separator layer's porosity is set to be equal to that of the electrode. The first scenario, shown schematically in figure 3(a), models the case of a stagnant diffusion layer (SDL) adjacent to the electrode, which has been used previously to model CDI cells [37]. The governing equations in the SDL are:

$$\frac{\partial\bar{c}}{\partial\bar{t}} = \frac{\partial^2\bar{c}}{\partial\bar{x}^2} \quad (17)$$

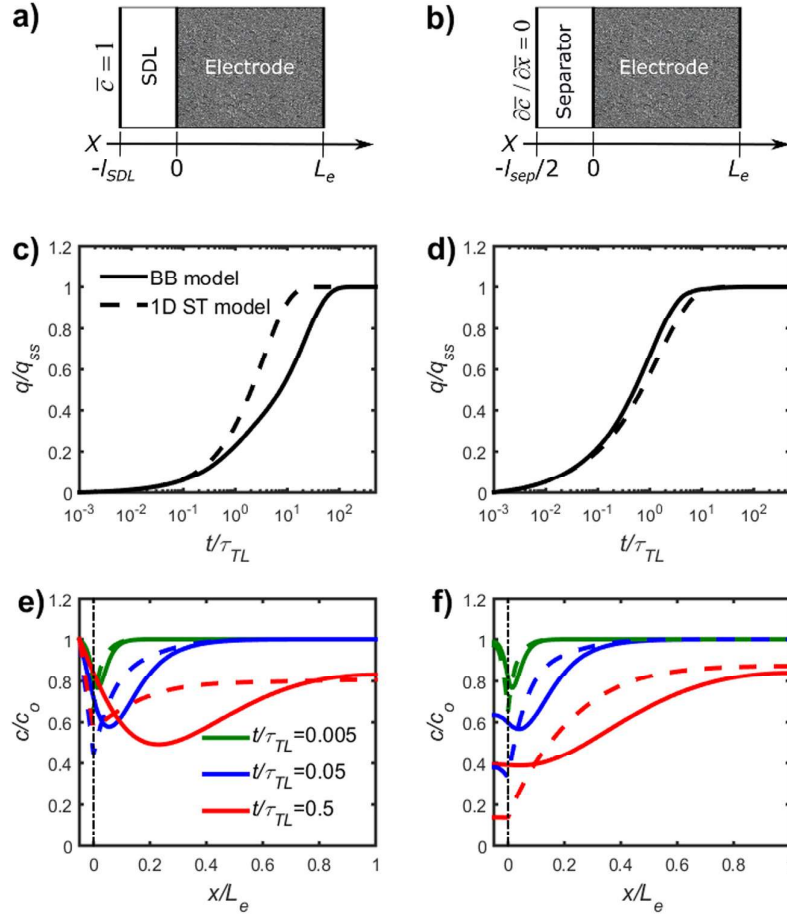
$$\frac{\partial}{\partial\bar{x}} \left( \bar{c} \frac{\partial\bar{\phi}}{\partial\bar{x}} \right) = 0 \quad (18)$$

and the boundary conditions at the edge of the separator are:

$$\bar{c}|_{\bar{x}=-l_{SDL}/L_c=-0.05} = 1, \bar{\phi}|_{\bar{x}=-0.05} = 0. \quad (19)$$

The second case, shown schematically in figure 3(b), is the case of a CDI cell which is symmetric about its midline (the midline of the separator). Such a case can approximate the physical scenario of batch mode operation whereby a batch of feedwater in the cell is desalted while flow is turned off [10]. For the symmetric cell, the boundary conditions at the midline of the separator are:

$$\frac{\partial\bar{c}}{\partial\bar{x}} \Big|_{\bar{x}=-0.05} = 0, \bar{\phi} \Big|_{\bar{x}=-0.05} = 0. \quad (20)$$

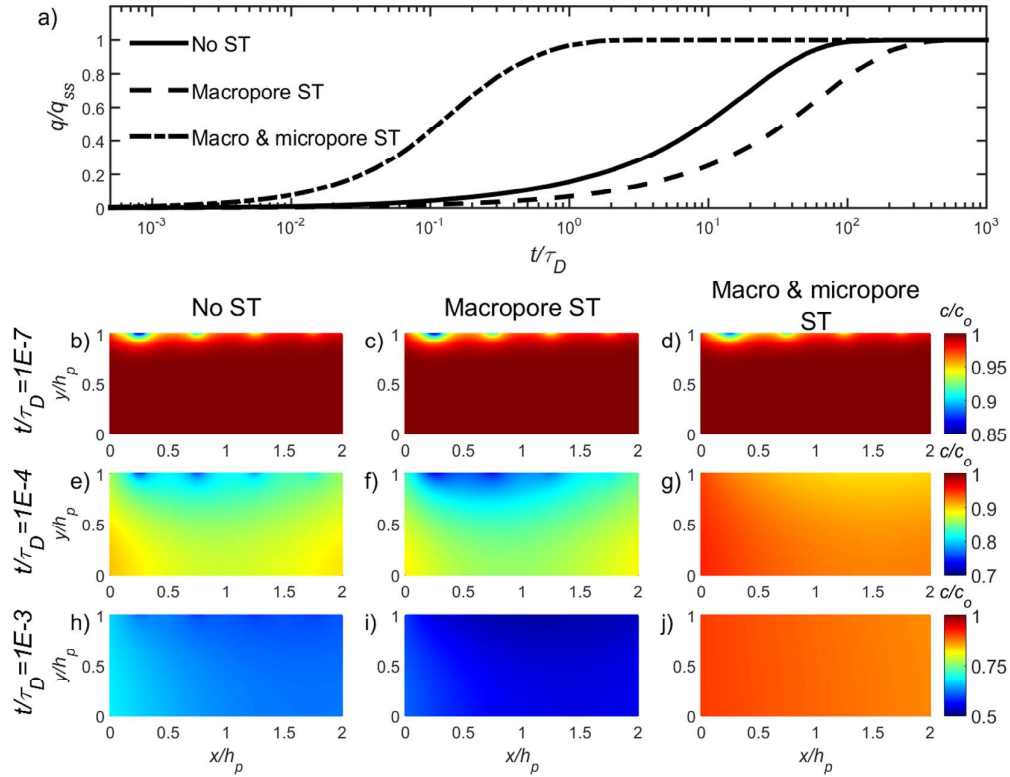


**Figure 3.** (a) A schematic of the electrode with adjacent stagnant diffusion layer (SDL). (c) and (e) Show results from the cell with an adjacent SDL layer, using either our 1D ST model or the BB model to describe the electrode. (c) Shows non-dimensional electrode charge stored,  $q/q_{ss}$ , versus time scaled by the transmission line timescale,  $\tau_{TL}$ , and (e) shows the concentration in the electrode and SDL,  $\bar{c}$ , versus non-dimensional position,  $x/L_e$ . (b) A schematic of the symmetric cell, and (d) and (f) show results using either our 1D ST model or the BB model to describe the electrode. All model results are for  $\varepsilon = 0.1$ ,  $V_{cl} = 7.5$ ,  $l_{SDL} = l_{sep}/2 = 0.05L_e$ .

For both cases (SDL and symmetric cell), at the electrode's outer edge we applied zero flux boundary conditions. The initial conditions for both cases are  $\bar{c} = 1$  throughout the electrode and separator,  $\bar{\phi} = 7.5$  in the electrode, and a linear potential profile in the separator from  $\bar{\phi} = 0$  at  $\bar{x} = -0.05$  to  $\bar{\phi} = 7.5$  at  $\bar{x} = 0$ .

For the case of a CDI electrode with an adjacent SDL, we can see from figure 3(c) that the 1D ST model's predicted charging (dashed line) is significantly faster than the BB model which does not consider ST (solid line), as might be expected given the results of figure 2(a). Figure 3(e) shows the concentration profiles and desalination dynamics at various times during cell charging for the 1D ST model (dashed lines) and the BB model (solid lines) for the cell with adjacent SDL. Here, we can observe a sharp discontinuity in the slope of the concentration profile at the separator/electrode interface (vertical dashed line) for the 1D ST model. The latter is due to the discontinuity in transport mechanisms across this interface, with ST occurring on the electrode side but not on the SDL side. For both the 1D ST and BB models, we see the expected result that EDL charging and so desalination begins

at the electrode/SDL interface and then at later times propagates deeper into the electrode [37]. Conversely, for the symmetric cell, the 1D ST model predicts slower cell charging compared to the BB model, see figure 3(d). The latter results are highly counter-intuitive, as they suggest that the inclusion of an extra transport pathway for ions (ST) results in slower cell charging. These counter-intuitive results can be understood through the concentration profiles for the symmetric cell shown in figure 3(f). Here, we can see that during charging, as no ions can enter the separator space from the boundary at  $\bar{x} = -0.05$  due to symmetry, the separator space ( $\bar{x} < 0$ ) is strongly desalted relative to results of figure 3(e). The desalination of the separator space is especially strong for the 1D ST model in figure 3(f), where concentration in the separator space can be reduced by approximately an order of magnitude (see the red dashed curve). This region of very low ion concentration acts to slow down the charging dynamics by reducing the local ionic current in the separator space, as seen by equation (18), or in other words by introducing a large resistor to ionic current into the system. In summary, the presence of ST in the symmetric cell leads to a more effective



**Figure 4.** (a) Model results for non-dimensional charge stored in EDLs,  $q/q_{ss}$ , versus time scaled by the diffusion timescale,  $\tau_D$ , for three 2D models, including the ‘No ST’ model (solid line), the ‘macropore ST’ model (dashed line), and the ‘macro and micropore ST’ model (dotted-dashed line). (b)–(d) Show model results of concentration distributions in the macropore entrance at  $t/\tau_D = 1E - 7$ , (e)–(g) show the concentration distributions for  $t/\tau_D = 1E - 4$ , and (h)–(j) show the concentration distributions  $t/\tau_D = 1E - 3$ . The parameters used for these results include  $\varepsilon = 0.001$ ,  $\varepsilon_{mi} = 0.001$ , and  $V_{el} = 12.5$ .

desalting of the separator space, which in turn significantly slows the electrode charging.

As the 1D ST model employs a GC EDL, it simulates an electrode consisting solely of macropores with thin EDLs, as depicted schematically in figure 1(b). However, CDI electrodes are typically multiscale, consisting of both through-electrode macropores which access micropores with strongly overlapped EDLs, see figure 1(c). Thus, to capture the multiscale nature of CDI electrodes, we developed a 2D model of a single slit-shaped macropore with uniform cross-sectional area, and with micropores present along the macropore wall at uniform intervals, as drawn schematically in figure 1(c). For this model, we used equations (1) and (2) to govern the macropore bulk dynamics, and used an alternating arrangement of the GC effective flux boundary conditions for macropore walls, and the Donnan effective flux boundary conditions for micropores to describe electrosorption into EDLs and ST within EDLs. We do not develop a 1D macroscopic set of equations for the case of multiscale electrodes, as such an approach would average over the serial nature of the EDL arrangement. As we show below, this local serial arrangement can have important implications in the cell charging and desalination dynamics. The importance of capturing local changes in surface conditions in charging porous electrodes was also shown by Mirzadeh *et al.*, for the case of a ‘patchy’ electrode with alternating GC EDLs and zero surface charge areas [35].

For the 2D model, the macropore length used was  $L_e = 100h_p$ , and the alternating arrangement of Donnan (micropore) and GC (macropore wall) effective flux boundary conditions was located along the  $\hat{y} = 1$  boundary. The first micropore was positioned at  $\hat{x} = 0.2$ , the width of all micropores was  $\Delta\hat{x} = 0.1$ , and the distance between neighboring micropores was  $\Delta\hat{x} = 0.4$ . Thus, micropores were equally spaced along the macropore wall for simplicity. We added an SDL layer adjacent to the pore inlet with thickness  $L_e/20$ , used a symmetry condition along the macropore midline ( $\hat{y} = 0$ ), and imposed no flux boundary conditions at the pore closed end. The initial conditions used were  $\hat{c} = 1$  throughout the system,  $\hat{\phi} = V_{el} = 12.5$  in the macropore, and a linear potential profile in the SDL along the  $\hat{x}$  axis from  $\hat{\phi} = 0$  at  $\hat{x} = -0.05$  to  $\hat{\phi} = 12.5$  at  $\hat{x} = 0$ . In figure 4(a), we show the charging dynamics of three 2D models versus time non-dimensionalized by the diffusion time  $\tau_D = L_e^2/D$ . The three models include the ‘macropore and micropore ST’ model where the macropore wall and micropore EDLs were modeled using the boundary conditions (9)–(12), the ‘macropore ST’ model where the terms including the surface gradient,  $\widehat{\nabla}_s$ , were dropped out of equations (11) and (12), and the ‘no ST’ model where the terms including  $\widehat{\nabla}_s$  were dropped out of equations (9)–(12). As can be seen, the ‘macropore and micropore ST’ model predicts the fastest charging, which is consistent

with the results of figure 3(c) where it was demonstrated that ST enhances CDI cell charging kinetics when including an adjacent SDL. Counter-intuitively, the ‘macropore ST’ model shows slower cell charging than the ‘no ST’ model. Here, the salt dynamics can shed insight into the observed counter-intuitive behavior. To this end, figures 4(b)–(j) show the 2D concentration fields in the macropore inlet ( $0 \leq \hat{x} \leq 2$ ) for each model at various charging times. As can be seen in figures 4(b)–(d), at the time  $t/\tau_D = 1E - 7$  desalination zones appear associated with the location of the micropores in all three model cases, with the strongest desalination occurring closest to the pore entrance. Figures 4(e)–(g) demonstrate that at a later time  $t/\tau_D = 1E - 4$ , significant differences between the three models can be observed, where a large depletion region is seen near to  $\hat{y} = 1$  for the ‘macropore ST’ model relative to that of the other two model cases. This latter depletion region can act to slow down the macropore charging, due to the introduction of local areas of high ionic resistance within the macropore, explaining the counter-intuitive results of figure 4(a). In figures 4(h)–(j), we see that at the even later time  $t/\tau_D = 1E - 3$ , we can see that the pore entrance is now more uniformly desalted, with the lowest concentration again observed for the ‘macropore ST’ model.

### Conclusions

In conclusion, we developed theory which includes ST in describing the charge and salt dynamics in a CDI cell. We presented an effective flux boundary condition for micropore Donnan EDLs, a set of 1D macroscopic transport equations for macroporous CDI electrodes, and a 2D model for a multi-scale CDI electrode. Through these models, the possible effect of ST on the CDI process is elucidated. It was observed that at some model conditions ST enhances cell charging rates, but counter-intuitively this additional transport pathway is found to slow down the cell charging at other model conditions. While we here begin to explore the effects of ST in CDI cells, future models should include additional complexities necessary to accurately predict data from CDI cells, such as the effect of the Stern layer, and geometric as well as steric effects in the highly constrained micropores.

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### Appendix A

In this appendix, we derive effective flux boundary conditions for the case of micropores described by a Donnan EDL. The Donnan model assumes a spatially uniform potential within the micropore. Via a Boltzmann distribution, the Donnan potential drop between the micropore and macropore can be related to the micropore concentration [44]:

$$\tilde{c}_{mi,i} = \hat{c} e^{-z_i \Delta \hat{\phi}_D}. \quad (\text{A.1})$$

Here  $\tilde{c}_{mi,i}$  is the concentration of ion  $i$  in the micropore non-dimensionalized by  $c_0$ ,  $z_i$  is the valance of ion  $i$ , and  $\Delta \hat{\phi}_D$  is the Donnan potential non-dimensionalized by the thermal voltage. Next, we introduce the parameters  $\tilde{c}_{mi}$  and  $\tilde{\sigma}_{mi}$  representing, respectively, micropore salt concentration and charge density:

$$\tilde{c}_{mi} \equiv \frac{\tilde{c}_{mi,c} + \tilde{c}_{mi,a}}{2} = \hat{c} \cosh \Delta \hat{\phi}_D \quad (\text{A.2})$$

$$\tilde{\sigma}_{mi} \equiv \frac{\tilde{c}_{mi,c} - \tilde{c}_{mi,a}}{2} = -\hat{c} \sinh \Delta \hat{\phi}_D \quad (\text{A.3})$$

where the expressions developed in (A.2) and (A.3) are valid for the case of monovalent ions. We also notice that in the micropores:

$$\tilde{\psi} = \Delta \hat{\phi}_D. \quad (\text{A.4})$$

In order to substitute micropore quantities into the general effective flux boundary conditions given by Chu and Bazant [32], and here as equations (3) and (4), we notice that:

$$\varepsilon \tilde{w} = \frac{\lambda_D}{h_p} \int_0^\infty (\tilde{c} - \hat{c}) d\tilde{z} = \frac{1}{h_p} \int_0^{l_{mi}} (\tilde{c} - \hat{c}) d\tilde{z} = \varepsilon_{mi} (\tilde{c}_{mi} - \hat{c}) \quad (\text{A.5})$$

$$\varepsilon \tilde{q} = \frac{\lambda_D}{h_p} \int_0^\infty \tilde{\rho} d\tilde{z} = \frac{1}{h_p} \int_0^{l_{mi}} \tilde{\rho} d\tilde{z} = \varepsilon_{mi} \tilde{\sigma}_{mi} \quad (\text{A.6})$$

$$\varepsilon \int_0^\infty \tilde{\rho} \widehat{\nabla}_s \tilde{\psi} d\tilde{z} = \varepsilon_{mi} \tilde{\sigma}_{mi} \widehat{\nabla}_s (\Delta \hat{\phi}_D) \quad (\text{A.7})$$

$$\varepsilon \int_0^\infty \tilde{c} \widehat{\nabla}_s \tilde{\psi} d\tilde{z} = \varepsilon_{mi} \tilde{c}_{mi} \widehat{\nabla}_s (\Delta \hat{\phi}_D). \quad (\text{A.8})$$

Substituting (A.5)–(A.8) into (3) and (4) lead to:

$$\varepsilon_{mi} \frac{\partial(\tilde{c}_{mi} - \hat{c})}{\partial \hat{t}} = \varepsilon_{mi} \widehat{\nabla}_s \left[ \widehat{\nabla}_s (\tilde{c}_{mi} - \hat{c}) + \tilde{\sigma}_{mi} \widehat{\nabla}_s (\hat{\phi} + \Delta \hat{\phi}_D) \right] - \left( \frac{\partial \hat{c}}{\partial \tilde{z}} \right) \Big|_{(\hat{x}, \hat{y}, 0)} \quad (\text{A.9})$$

$$\varepsilon_{mi} \frac{\partial \tilde{\sigma}_{mi}}{\partial \hat{t}} = \varepsilon_{mi} \widehat{\nabla}_s \left[ \widehat{\nabla}_s \tilde{\sigma}_{mi} + \tilde{c}_{mi} \widehat{\nabla}_s (\hat{\phi} + \Delta \hat{\phi}_D) - \hat{c} \widehat{\nabla}_s \hat{\phi} \right] - \left( \hat{c} \frac{\partial \hat{\phi}}{\partial \tilde{z}} \right) \Big|_{(\hat{x}, \hat{y}, 0)}. \quad (\text{A.10})$$

For the case where we neglect the Stern layer, we can simplify by noting that the Donnan potential drop equals the potential drop between the electrode surface and the macropore, such that:

$$\widehat{\nabla}_s (\hat{\phi} + \Delta \hat{\phi}_D) = \widehat{\nabla}_s (\hat{\phi} + \hat{\phi}_{el} - \hat{\phi}) = \widehat{\nabla}_s (\hat{\phi}_{el}) = 0 \quad (\text{A.11})$$

where  $\hat{\phi}_{el}$  is the non-dimensional solid phase potential of the electrode, which we assume is held constant throughout the charging process. Substituting (A.11) into (A.9) and (A.10) lead to:

$$\varepsilon_{mi} \frac{\partial(\tilde{c}_{mi} - \hat{c})}{\partial \hat{t}} = \varepsilon_{mi} \widehat{\nabla}_s^2 (\tilde{c}_{mi} - \hat{c}) - \left( \frac{\partial \hat{c}}{\partial \tilde{z}} \right) \Big|_{(\hat{x}, \hat{y}, 0)} \quad (\text{A.12})$$

$$\varepsilon_{mi} \frac{\partial \tilde{\sigma}_{mi}}{\partial \hat{t}} = \varepsilon_{mi} \widehat{\nabla}_s [\widehat{\nabla}_s \tilde{\sigma}_{mi} - \hat{c} \widehat{\nabla}_s \hat{\phi}] - \left( \hat{c} \frac{\partial \hat{\phi}}{\partial \hat{z}} \right) \Big|_{(\hat{x}, \hat{y}, 0)} \quad (\text{A.13})$$

## Appendix B

We here derive the macroscopic transport equations of the 1D ST model, equations (13) and (14). We begin by the volume integration of the local transport equations, equations (1) and (2), over the non-dimensional pore volume,  $\widehat{V}_p$ , of the characteristic volume element presented in figure B1. The volume element consists of a solid phase and a liquid phase with a bulk electrolyte and thin EDL. We begin by integrating equations (1) and (2) over  $\widehat{V}_p$ , and applying the Divergence theorem [37, 38]:

$$\int_{\widehat{V}_p} \frac{\partial \hat{c}}{\partial \hat{t}} d\widehat{V} = \int_{\widehat{V}_p} \widehat{\nabla}^2 \hat{c} d\widehat{V} = \left[ \int_{\widehat{A}_v} \hat{n} \cdot (\widehat{\nabla} \hat{c}) d\widehat{A} + \int_{\widehat{A}_p} \hat{n} \cdot (\widehat{\nabla} \hat{c}) d\widehat{A} \right] \quad (\text{B.1})$$

$$0 = \int_{\widehat{V}_p} \widehat{\nabla} \cdot (\hat{c} \widehat{\nabla} \hat{\phi}) d\widehat{V} = \left[ \int_{\widehat{A}_v} \hat{n} \cdot (\hat{c} \widehat{\nabla} \hat{\phi}) d\widehat{A} + \int_{\widehat{A}_p} \hat{n} \cdot (\hat{c} \widehat{\nabla} \hat{\phi}) d\widehat{A} \right] \quad (\text{B.2})$$

where  $\hat{n}$  is the inwards direction normal to a surface, the dimensionless areas and volumes are defined by  $\widehat{A} = A/h_p^2$ , and  $\widehat{V} = V/h_p^3$ , and  $\widehat{A}_v$  represents the cross-sectional area of the pores and  $\widehat{A}_p$  the pore surface area.

Next we define volume-averaged bulk concentration  $\bar{c}$  and potential,  $\bar{\phi}$ , as:

$$\bar{c} = \frac{1}{\widehat{V}_p} \int_{\widehat{V}_p} \hat{c} d\widehat{V} \quad (\text{B.3})$$

$$\bar{\phi} = \frac{1}{\widehat{V}_p} \int_{\widehat{V}_p} \hat{\phi} d\widehat{V}. \quad (\text{B.4})$$

We also define area-averaged EDL quantities, such as surface area-averaged excess salt concentration,  $\bar{w}$ , and charge,  $\bar{q}$  [37]:

$$\bar{w} = \frac{1}{\widehat{A}_p} \int_{\widehat{A}_p} \tilde{w} d\widehat{A} \quad (\text{B.5})$$

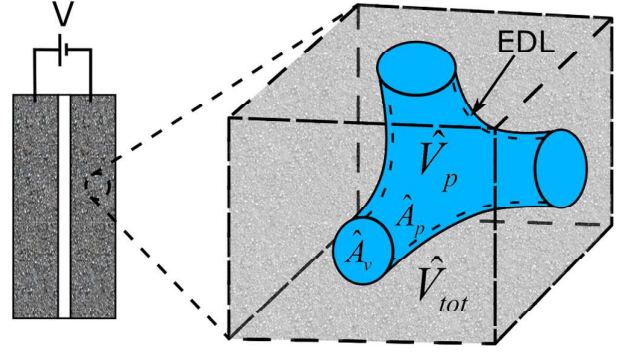
$$\bar{q} = \frac{1}{\widehat{A}_p} \int_{\widehat{A}_p} \tilde{q} d\widehat{A}. \quad (\text{B.6})$$

We can then rewrite the first term of equation (B.1) using (B.3) and re-scaling time to the electrode diffusion time,  $\bar{t} = tD/L_e^2$ :

$$\int_{\widehat{V}_p} \frac{\partial \hat{c}}{\partial \hat{t}} d\widehat{V} = \widehat{V}_p \frac{\partial \bar{c}}{\partial \bar{t}} = \frac{h_p^2 \widehat{V}_p}{L_e^2} \cdot \frac{\partial \bar{c}}{\partial \bar{t}}. \quad (\text{B.7})$$

The cross-sectional flux terms of equations (B.1) and (B.2) can be rewritten using volume averaged parameters in the following way:

$$\int_{\widehat{A}_v} \hat{n} \cdot (\widehat{\nabla} \hat{c}) d\widehat{A} = \int_{\widehat{A}_v + \widehat{A}_s} \hat{n} \cdot (\widehat{\nabla} \hat{c}) d\widehat{A} = \int_{\widehat{V}_{tot}} \widehat{\nabla}^2 \hat{c} d\widehat{V} = \frac{h_p^2 \widehat{V}_p}{L_e^2} \nabla^2 \bar{c} \quad (\text{B.8})$$



**Figure B1.** Schematic of a representative volume element used in the volume averaging process, with non-dimensional parameters shown.  $\widehat{A}_v$  is the non-dimensional cross-sectional area of the pores,  $\widehat{V}_p$  is the pore volume,  $\widehat{A}_p$  is the pore surface area, and  $\widehat{V}_{tot}$  is the total volume of the element including the solid phase [37].

$$\begin{aligned} \int_{\widehat{A}_v} \hat{n} \cdot (\hat{c} \widehat{\nabla} \hat{\phi}) d\widehat{A} &= \int_{\widehat{A}_v + \widehat{A}_s} \hat{n} \cdot (\hat{c} \widehat{\nabla} \hat{\phi}) d\widehat{A} \\ &= \int_{\widehat{V}_{tot}} \widehat{\nabla} \cdot (\hat{c} \widehat{\nabla} \hat{\phi}) d\widehat{V} \sim \frac{h_p^2 \widehat{V}_p}{L_e^2} \nabla \cdot (\bar{c} \nabla \bar{\phi}) \end{aligned} \quad (\text{B.9})$$

where we rescaled the gradient, divergence and Laplacian operators with the electrode thickness,  $L_e$ . Further, in equation (B.9) we assumed that variables are slowly varying at the pore-scale, and thus  $\int_{\widehat{V}_{tot}} \widehat{\nabla} \cdot (\hat{c} \widehat{\nabla} \hat{\phi}) d\widehat{V} \sim \widehat{V}_p \bar{\nabla} \cdot (\bar{c} \nabla \bar{\phi})$  [37].

Next we rewrite the last term in the right hand side of equations (B.1) and (B.2) using the effective flux boundary conditions, equations (9) and (10), and again assume slowly-varying variables to obtain:

$$\int_{\widehat{A}_p} \hat{n} \cdot (\widehat{\nabla} \hat{c}) d\widehat{A} \sim \frac{\varepsilon \widehat{A}_p h_p^2}{L_e^2} \left[ \nabla_s \cdot (\bar{w} \nabla_s \ln \bar{c} + \bar{q} \nabla_s \bar{\phi}) - \frac{\partial \bar{w}}{\partial \bar{t}} \right] \quad (\text{B.10})$$

$$\int_{\widehat{A}_p} \hat{n} \cdot (\hat{c} \widehat{\nabla} \hat{\phi}) d\widehat{A} \sim \frac{\varepsilon \widehat{A}_p h_p^2}{L_e^2} \left[ \nabla_s \cdot (\bar{q} \nabla_s \ln \bar{c} + \bar{w} \nabla_s \bar{\phi}) - \frac{\partial \bar{q}}{\partial \bar{t}} \right]. \quad (\text{B.11})$$

We can now place equations (B.7)–(B.11) into (B.1) and (B.2), and formulate our 1D macroscopic transport equations:

$$\widehat{V}_p \frac{\partial \bar{c}}{\partial \bar{t}} = \widehat{V}_p \frac{\partial^2 \bar{c}}{\partial \bar{x}^2} + \varepsilon \widehat{A}_p \left[ \frac{\partial}{\partial \bar{x}} \left( \bar{w} \frac{\partial \ln \bar{c}}{\partial \bar{x}} + \bar{q} \frac{\partial \bar{\phi}}{\partial \bar{x}} \right) - \frac{\partial \bar{w}}{\partial \bar{t}} \right] \quad (\text{B.12})$$

$$0 = \widehat{V}_p \frac{\partial}{\partial \bar{x}} \left( \bar{c} \frac{\partial \bar{\phi}}{\partial \bar{x}} \right) + \varepsilon \widehat{A}_p \left[ \frac{\partial}{\partial \bar{x}} \left( \bar{q} \frac{\partial \ln \bar{c}}{\partial \bar{x}} + \bar{w} \frac{\partial \bar{\phi}}{\partial \bar{x}} \right) - \frac{\partial \bar{q}}{\partial \bar{t}} \right]. \quad (\text{B.13})$$

Using the definition  $h_p \equiv V_p/A_p$ , we find that:

$$\frac{\widehat{A}_p}{\widehat{V}_p} = \frac{A_p}{h_p^2} \cdot \frac{h_p^3}{V_p} = 1. \quad (\text{B.14})$$



Thus, we can re-write (B.12) and (B.13) as:

$$\frac{\partial(\bar{c} + \varepsilon\bar{w})}{\partial t} = \frac{\partial^2\bar{c}}{\partial \bar{x}^2} + \varepsilon \frac{\partial}{\partial \bar{x}} \left( \bar{w} \frac{\partial \ln \bar{c}}{\partial \bar{x}} + \bar{q} \frac{\partial \bar{\phi}}{\partial \bar{x}} \right) \quad (\text{B.15})$$

$$\varepsilon \frac{\partial \bar{q}}{\partial t} = \frac{\partial}{\partial \bar{x}} \left( \bar{c} \frac{\partial \bar{\phi}}{\partial \bar{x}} \right) + \varepsilon \frac{\partial}{\partial \bar{x}} \left( \bar{q} \frac{\partial \ln \bar{c}}{\partial \bar{x}} + \bar{w} \frac{\partial \bar{\phi}}{\partial \bar{x}} \right) \quad (\text{B.16})$$

where equations (B.15) and (B.16) are identical to equations (13) and (14).

We here also briefly explain how to obtain the Mirzadeh model [35], equations (15) and (16), via volume averaging and utilizing effective flux boundary conditions. To begin, we re-write the effective flux boundary conditions, equations (3) and (4), but neglecting the excess potential term:

$$\varepsilon \frac{\partial \tilde{w}}{\partial \hat{t}} = \varepsilon \nabla_s \cdot (\nabla_s \tilde{w} + \tilde{q} \nabla_s \hat{\phi}) - \frac{\partial \hat{c}}{\partial \hat{z}} \Big|_{(\bar{x}, \bar{y}, 0)} \quad (\text{B.17})$$

$$\varepsilon \frac{\partial \tilde{q}}{\partial \hat{t}} = \varepsilon \nabla_s \cdot (\nabla_s \tilde{q} + \tilde{w} \nabla_s \hat{\phi}) - \left( \hat{c} \frac{\partial \hat{\phi}}{\partial \hat{z}} \right) \Big|_{(\bar{x}, \bar{y}, 0)} \quad (\text{B.18})$$

Beginning with volume integrated bulk equations (B.1) and (B.2), but instead using equations (B.17) and (B.18) as the effective flux boundary conditions, we can derive the model presented by Mirzadeh *et al* [35]:

$$\frac{\partial(\bar{c} + \varepsilon\bar{w})}{\partial t} = \frac{\partial^2\bar{c}}{\partial \bar{x}^2} + \varepsilon \frac{\partial}{\partial \bar{x}} \left( \frac{\partial \bar{w}}{\partial \bar{x}} + \bar{q} \frac{\partial \bar{\phi}}{\partial \bar{x}} \right) \quad (\text{B.19})$$

$$\varepsilon \frac{\partial \bar{q}}{\partial t} = \frac{\partial}{\partial \bar{x}} \left( \bar{c} \frac{\partial \bar{\phi}}{\partial \bar{x}} \right) + \varepsilon \frac{\partial}{\partial \bar{x}} \left( \frac{\partial \bar{q}}{\partial \bar{x}} + \bar{w} \frac{\partial \bar{\phi}}{\partial \bar{x}} \right) \quad (\text{B.20})$$

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