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# Mathematical Modeling of Ionic and Electronic Charge Transport in Electrochemical Systems

Submitted in partial fulfillment  
of the requirements for the degree of

Doctor of Philosophy  
in  
Chemical Engineering

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# Abstract

We apply mathematical methods to model diffusion and migration of ions, electrons, and holes in electrochemical and polymer semiconductor systems. When a voltage is applied across planar, blocking parallel electrodes, charge carriers redistribute in the cell to screen the electrode charge, forming electrical double layers. The structure of the double layer and the external current can be predicted via the Poisson-Nernst-Planck (PNP) equations for charge carrier flux, conservation, and electric potential. In this thesis, we employ asymptotic analysis and numerical methods to quantify charge transport in four separate electrochemical devices. In organic light-emitting diodes (OLEDs), diffusion in the disordered polymer semiconductor is significant in comparison to migration. We solve the PNP equations via asymptotic analysis and find that including diffusion leads to a large increase in current proportional to the ratio of the cell width to the double layer width, thus diffusion cannot be neglected. Mixed ionic-electronic conductors (MIECs) conduct both ions and electrons, however ion mobility is difficult to measure. We derive a similarity solution to the PNP equations for cation invasion in a planar MIEC polymer film, and find that the location of the moving front is proportional to the square-root of the product of ion mobility, applied voltage and time. However differences between these results and experimental data indicate that additional work is needed to verify the accuracy of this method to calculate ion mobility.

The net charge in a zwitterionic hydrogel is dependent on the surrounding electrolyte  $pH$ . This charge alters the electrical impedance of the hydrogel. We apply the PNP equations coupled with acid-base dissociation equations to predict the reduction in electrical impedance as  $pH$  deviates from the isoelectric point based on material parameters. This model aids in the design of low-impedance hydrogels to improve signal transmittance in biosensor encapsulation applications. Lastly, we model discharging of an electrolytic cell. At high voltage, a “reverse peak” or maximum in the current magnitude emerges. Through asymptotic analysis and numerical solutions of the PNP equations, we conclude that bulk depletion and neutral salt adsorption in the double layer during charging cause the reverse peak.

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# 1. Introduction

We applied asymptotic analysis, analytical and numerical methods to develop mathematical models for ionic and electronic transport in four electrochemical and organic electronics devices comprised of novel materials and charge carriers. Experimental research on these new materials and devices is progressing rapidly, however open questions remain that can be addressed by improved modeling. Our methodical approach to mathematical modeling has led to significant insights on the underlying physics driving charge transport in electrochemical systems and organic electronics.

The diffusion and migration of ions and electrons in response to an applied potential are fundamental to electrochemical and semiconductor systems.<sup>2-4</sup> The simplest device geometry in both cases is two blocking, parallel-plate electrodes separated by an electrolyte or semiconducting material (figure 1.1).<sup>4-6</sup> When a voltage is applied, charge carriers accumulate at the electrodes to screen the surface charge.<sup>3</sup> This region of charge accumulation is the electrical double layer, with a characteristic length scale, the Debye length

$$\lambda_D = \sqrt{\frac{\varepsilon k_B T}{2q^2 c_0}}, \quad (1.1)$$

where  $\varepsilon$  is the permittivity of the material,  $k_B$  is Boltzmann's constant,  $T$  is temperature,  $q$  is the charge of a proton, and  $c_0$  is the mean concentration of charge carriers. The Debye length  $\lambda_D$  is generally much smaller than the

device width  $L$ . For example, at  $c_0 = 1$  mM in water at  $T = 300$  K, the Debye length  $\lambda_D \approx 10$  nm. The ratio of the Debye length  $\lambda_D$  to the spacing between electrodes or width of the cell  $L$  is the dimensionless Debye length  $\epsilon$ , defined as

$$\epsilon = \lambda_D/L \ll 1, \quad (1.2)$$

at the experimentally-relevant limit of thin double layers at the electrode interfaces. In the double layer, the electric potential and concentration of charge carriers is enhanced compared to that of the bulk (figure 1.1). The transport of charge carriers in an electrochemical system can be described by the Poisson-Nernst-Planck (PNP) equations, a set of nonlinear, partial differential equations. The PNP equations include an equation for the contributions of diffusion and migration to charge carrier flux, charge conservation across the cell, and Poisson's equation relating the electric field to the charge density.<sup>7</sup> In the semiconductor community, these equations are referred to as the drift-diffusion equations, and the term "space-charge layer" is used to describe electron and hole, or electron vacancy, accumulation at an interface, where the space-charge length  $\lambda_S$  is mathematically equivalent to  $\lambda_D$ .<sup>2,8</sup> Space-charge layers are formed by charge injection from the electrode into the semiconductor,<sup>9</sup> opposed to charge separation in the case of double layer formation.

When the PNP equations are non-dimensionalized by a characteristic length-scale ( $L$ ), concentration ( $c_0$ ), and potential ( $V_T$ ), two dimensionless groups emerge:  $\epsilon$  and the dimensionless applied voltage  $V/V_T$ , where  $V$  is the applied voltage and  $V_T$  is the thermal voltage,  $V_T = k_B T/q \approx 25$  mV at  $T = 300$  K. In the systems studied in this thesis, additional dimensionless groups contribute to the dynamics, including the ratio of charge carrier mobilities or the ratio of reaction constants to  $c_0$ . The behavior of an electrochemical or semiconductor

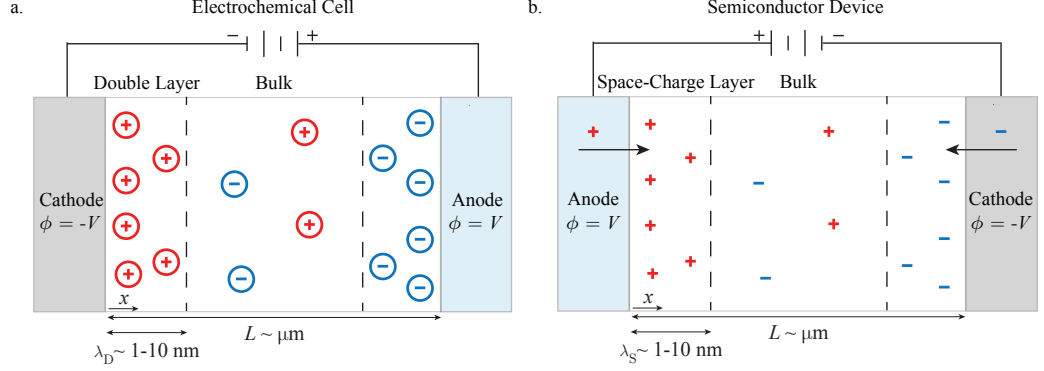


Figure 1.1: A model electrochemical cell (a) and semiconductor device (b). a) Cations (+) and anions (−) from the bulk accumulate at the counter-electrode to form double layers. b) Electrons (−) and holes (+) are injected into the polymer film from electrodes, indicated by the arrows, and accumulate in space-charge layers. The anode is the positively charged electrode, while the cathode is negatively charged.

system can be predicted by solving the PNP equations at specific values of the dimensionless groups.

At sufficiently high applied voltage  $V \gg V_T$ , strong concentration and potential gradients in the thin double layer result in sharp variations at the electrode interfaces that render the PNP equations difficult to solve numerically and impossible to solve analytically. However, we can exploit the singular nature of the PNP equations at the thin double layer limit,  $\epsilon \rightarrow 0$ , to derive asymptotic expressions for the electric potential and charge carrier concentrations in the double layer and in the bulk. The potential and charge carrier concentration are expanded around the small parameter, the dimensionless Debye length  $\epsilon$ , and inserted in the PNP equations to yield a series of asymptotic expressions in the double layer and in the bulk at each order of  $\epsilon$ .

The leading order terms reveal the dominant contributions to the charge carrier densities and potential. This insight on the physics of the system is an advantage of asymptotic analysis not accessible via a primarily numerical analysis.<sup>10</sup> A second advantage is that the asymptotic expressions are valid

for the experimentally relevant limit  $\epsilon \rightarrow 0$ , where the solution is numerically intractable due to steep gradients in potential and charge carrier concentration. In this thesis, we employ asymptotic analysis, analytical techniques such as similarity solutions and Laplace transforms, and numerical methods. Asymptotic analysis, analytical techniques, and scaling analyses are employed to simplify the PNP equations, and the results are validated by comparing to numerical solutions of the PNP equations at values of  $\epsilon$  accessible to numerical methods. Finally, we compare our models to experimental data for validation and to provide insight on the experimental findings.

Organic electronics, the focus of chapters 2 and 3, are based on solid-state polymer semiconductors that can be designed to conduct both ions and electrons and holes.<sup>5,11–13</sup> The physics of charge transport in polymer semiconductors differs from classical semiconductor theory in that diffusion, which is often neglected in crystalline semiconductors, is not negligible compared to migration, particularly in the highly concentrated space-charge layers adjacent to the electrode-semiconductor interface.<sup>9</sup> In OLEDs, the charge carriers (electrons and holes) are injected at the electrodes, accumulate in space-charge layers as depicted in figure 1.1b, and then recombine in the bulk to emit photons. The thin space-charge layers are difficult to resolve numerically, so in chapter 2 we apply asymptotic analysis to the PNP equations in order to derive a simple expression for the current resulting from an applied voltage.<sup>14</sup> This expression can be applied by experimentalists to predict the current based on material parameters, and thus device performance.

Polymer mixed ionic-electronic conductors are promising new materials for biosensor,<sup>11,15</sup> superconductor,<sup>16,17</sup> and organic lighting<sup>18,19</sup> applications. However, ion mobility in the polymer film is difficult to measure, prompting Stavriniidou *et al.*<sup>1,20</sup> to design a simple device to measure ion mobility con-

sisting of a polymer film doped with holes in contact with an electrode at one end and an electrolyte at the other. A gate electrode immersed in the electrolyte drives the injection of cations from the electrolyte into the polymer film. The positive ions displace positively charged holes, which exit and are detected at the electrode. In chapter 3, we employ the PNP equations to model the invading moving front of cations across the polymer film.<sup>21</sup> We apply a scaling analysis to simplify the PNP equations at the limit of infinite hole mobility compared to cation mobility and large voltage  $V \gg V_T$ . The simplified equations can be solved numerically via a similarity solution. We then fit our similarity solution to experimental data for cation invasion in a polymer film.<sup>1</sup> The similarity solution is valid at the thin double layer limit relevant to the experimental system, where the concentration and potential gradients in the double layer are too steep to be resolved numerically.

Biosensors for use in the brain require an electrically-conductive, mechanical barrier between the relatively hard biosensor electrode and the soft tissue of the brain to avoid damage due to mechanical strain.<sup>22,23</sup> Zwitterionic hydrogels are a promising biomaterial for this application. These hydrogels carry a charge on the hydrogel backbone at a physiological  $pH = 7.4$  that lowers the electrical impedance compared to the electrolyte, and can be designed to match the elastic modulus of the soft tissue.<sup>24,25</sup> In chapter 4, we model ion transport through zwitterionic hydrogels under the influence of a low-amplitude oscillation in the applied voltage via the PNP equations coupled with acid-base dissociation equations and predict the electrical impedance dependence on  $pH$ . When a low-amplitude oscillating voltage is applied, the resulting current responds linearly, oscillating at the same frequency as the voltage. We can exploit this linear response by linearizing the PNP equations at the limit of low amplitude  $V \ll V_T$ . The linearized equations can be solved numerically

for the spacial ion concentrations and potential at smaller  $\epsilon$  than is possible when solving the full PNP equations. The electrical impedance, equal to the ratio of the applied potential to the external current, is calculated from the solution to the linearized PNP equations. This model can aid in the design of hydrogels with desirable electrical properties for biosensor encapsulation applications such as low electrical impedance and high conductivity.

In chapter 5, we focus on charge carried by inverse micelles in nonpolar fluids. Nonpolar fluids differ from aqueous systems in that there is very little free charge available to carry a current.<sup>26</sup> Added surfactants stabilize the fluid by preventing unwanted buildup of electrical potential at interfaces.<sup>27,28</sup> Interestingly, at applied voltages  $V \sim V_T$ , the current during discharging of an electrolytic cell is asymmetric to the charging current and, at sufficiently large voltage, a “reverse peak”, or maximum, in the magnitude of the current emerges, in sharp contrast to the monotonic decay in the current during charging.<sup>29–32</sup> We apply asymptotic analysis, Laplace transforms, and numerical methods to the PNP equations to develop a mathematical model for discharging electrolytic cells that captures this asymmetry and the reverse peak in the discharging current.

Finally, in chapter 6 we conclude with a summary of major findings and future work, including mathematical models of organic electrochemical transistors and signaling molecule transport in synapses.

# **2. Asymptotic Analysis of Double-Carrier, Space-Charge-Limited Transport in Organic Light-Emitting Diodes**

## **2.1 Introduction**

Organic light-emitting diodes (OLEDs) are solid state lighting devices that convert electrical energy to light through electroluminescence.<sup>33</sup> A standard device configuration consists of a transparent anode, typically indium tin oxide, an organic semiconducting polymer film that is 10-1000 nm thick, and a metallic cathode.<sup>5,6,34,35</sup> An applied voltage drives the injection of electrons through the cathode, and electron vacancies, or holes, through the anode into the organic thin film, where they diffuse and migrate, or drift, towards the oppositely charged electrode. When in close proximity, an electron and hole recombine to form an exciton, which radiatively decays to emit a photon.

The current in an organic device is limited by charge transport across the

organic thin film<sup>36</sup> when the energy barrier to injection is lower than 0.3-0.4 eV,<sup>37</sup> as opposed to being limited by the electrode-film contacts that provide the majority of the resistance in inorganic devices.<sup>38</sup> At the electrode-organic film interface, “space-charge layers” exist where the charge carrier (electron or hole) density varies rapidly.<sup>39</sup> Quantifying the charge carrier distribution within these space-charge layers is crucial to understanding charge transport in OLEDs,<sup>39</sup> as well as in other types of organic electronics such as light-emitting electrochemical cells<sup>40</sup> and organic solar cells.<sup>41</sup>

The current and recombination rate are key parameters in analyzing OLED performance. The simplest mathematical model that relates current, charge recombination, and applied voltage is the drift-diffusion equations that account for diffusion, drift, and recombination of electrons and holes.<sup>2,3,42</sup> The drift-diffusion equations are non-linear coupled differential equations that cannot be solved exactly. However, when simplifying assumptions are made, it is possible to make analytical progress. For example, Mott & Gurney<sup>2</sup> considered diffusion-free single-carrier injection into a thin film with no intrinsic charge, for which the current is

$$\hat{J} = \frac{9\hat{\mu}\hat{\epsilon}}{8} \frac{\hat{V}^2}{\hat{L}^3}, \quad (2.1)$$

where  $\hat{V}$  is the applied voltage;  $\hat{L}$  is the width of the thin film;  $\hat{\epsilon}$  is the permittivity of the thin film;  $\hat{\mu}$  is the electric mobility,  $\hat{\mu} = \hat{D}\hat{e}/\hat{k}_B\hat{T}$ , where  $\hat{D}$  is the diffusivity of the charge carrier,  $\hat{e}$  is the magnitude of the charge of an electron,  $\hat{k}_B$  is Boltzmann’s constant, and  $\hat{T}$  is temperature. Note that all hatted variables (e.g.  $\hat{V}$ ) are dimensional. Equation (2.1) is known as the Mott-Gurney Law.<sup>2</sup>

For single-carrier injection, the Mott-Gurney law has been extended to include the effects of charge traps,<sup>43–47</sup> uneven injection barriers,<sup>38,48</sup> and intrinsic charge.<sup>45</sup> The latter is responsible for an ohmic regime ( $\hat{J} \propto \hat{V}$ ) that

precedes the space-charge limited regime described by the Mott-Gurney law.<sup>2</sup> Mark & Lampert<sup>45</sup> add a term to the Mott-Gurney law that describes the linear increase in current with voltage due to intrinsic charge. Murgatroyd<sup>49</sup> found that the current-voltage relation for single carrier, diffusion-free injection can be represented by a functional relationship between  $\hat{J}/\hat{L}$  and  $\hat{V}/\hat{L}^2$ , which is consistent with the Mott-Gurney law<sup>2</sup> and Mark & Lampert's ohmic current at low voltage.<sup>45</sup>

For double-carrier transport, Parmenter & Ruppel<sup>50</sup> obtained a solution to the drift-diffusion equations for diffusion-free, double-carrier injection and recombination into trap-free insulators, where recombination is modeled as a bimolecular reaction according to Langevin kinetics.<sup>51</sup> They<sup>50</sup> found that the Mott-Gurney law holds if the single-carrier electric mobility is replaced with an effective mobility that is a function of the individual electron and hole mobilities, and a recombination mobility. In contrast to Parmenter & Ruppel,<sup>50</sup> who neglected diffusion, Baron's<sup>52</sup> work included double-carrier diffusion, drift, and recombination. In particular, Baron used Poisson's equation to account for deviations from electroneutrality in the film, yet did not include the contribution of the gradient in charge density to the total carrier flux across the thin film. Baron found that the Mott-Gurney scaling,  $\hat{J} \propto \hat{V}^2/\hat{L}^3$ , holds.

The increase in current due to diffusion and double-carrier injection is examined in Torpey's<sup>53</sup> work. Torpey first addressed the diffusion-free case of double-carrier injection with recombination using a scaling analysis and confirmed that  $\hat{J} \propto \hat{V}^2/\hat{L}^3$ , in agreement with Parmenter & Ruppel.<sup>50</sup> Torpey then solved the drift-diffusion equations numerically and found that at small reservoir concentrations the current is limited by the inability of the contacts to provide sufficient electrons and holes. Torpey found a space-charge-limited current at large reservoir concentrations, where  $\hat{J} \propto \hat{V}^2$ . Notably, at large

reservoir concentrations, the current is much greater than the  $\hat{J} \propto \hat{V}^2/\hat{L}^3$  diffusion-free scaling (see figure 11 in Torpey<sup>53</sup>).

Lastly, when diffusion and drift are included but recombination is neglected, Neumann *et al.*<sup>54</sup> find  $\hat{J} \propto \hat{V}^3/\hat{L}^3$  at high voltage, and  $\hat{J} \propto \hat{V}/\hat{L}^3$  at low voltage compared to the thermal voltage,  $\hat{k}_B\hat{T}/\hat{e}$  (which is 26 mV at 300K). They assert that there is only one length scale in the system, the device thickness  $\hat{L}$ , to justify the scaling with  $\hat{L}^{-3}$  in the current-voltage relation at all voltages. However, as we show below, when diffusion is included an additional length scale arises: the space-charge length.

The electrode-film boundary conditions imposed in the works discussed above feature ohmic contacts,<sup>50,52,54,55</sup> or reservoir conditions that fix the concentrations at the electrodes.<sup>2,6,39,45,53</sup> The ohmic condition assumes that the electric field is zero at the electrodes, while reservoir conditions assume a fixed voltage-independent concentration. In addition to these boundary conditions, Walker *et al.*<sup>56</sup> and Malliaras & Scott<sup>38</sup> review boundary conditions that quantify the injection of charge due to thermionic emission, tunneling, and backflowing interface recombination, where injection is a function of the local electric field at the electrode-organic interface.

In this work, we derive a current-voltage relation for space-charge-limited transport in thin organic films due to diffusion and drift of electrons and holes. Although this analysis does not account for carrier recombination, the results are subsequently utilized to derive a recombination-voltage relation for low recombination rate OLEDs.

As shown below, non-dimensionalization of the drift-diffusion equations reveals an important parameter governing charge transport in the thin film:

the width of the space-charge layer,

$$\hat{\lambda}_s = \sqrt{\frac{\hat{\epsilon} \hat{k}_B \hat{T}}{2 \hat{e}^2 \hat{n}_0}}, \quad (2.2)$$

where  $\hat{n}_0$  is the charge density at the electrode. This is mathematically equivalent to the Debye screening length in electrochemical systems.<sup>57</sup> In the present case, however, the space charge develops as a result of injection of charges into a film with no intrinsic charge, while the Debye length characterizes the extent of the space charge of mobile ions intrinsic to an electrolyte near a charged surface. Importantly, for space-charge-limited transport in OLEDs, the space charge layer is often small in comparison to the width of the device, such that  $\epsilon = \hat{\lambda}_s / \hat{L} \ll 1$ .<sup>6,39,58</sup> For instance, in Pinner *et al.*'s<sup>6</sup> experiments on OLED charge transport  $\epsilon = 0.048$  for an ITO/PPV/Au device. In Torpey's<sup>53</sup> numerical simulation of small-molecule organic semiconductors, based on the material parameters used in the paper,  $\epsilon$  ranges from 0.022 to 0.049. Similarly, DeMello's<sup>39</sup> numerical work contains examples where  $\epsilon = 0.00098$  for double-carrier injection into an OLED with ohmic contacts. In Peng *et al.*'s<sup>58</sup> numerical analysis of charge transport in OLEDs,  $\epsilon = 0.0012$  for ohmic and injection limited cases.

When the space-charge layer is thin,  $\epsilon \ll 1$ , numerical solutions of the drift-diffusion equations are challenging, since the equations are singular as  $\epsilon \rightarrow 0$ .<sup>39</sup> This is manifested in the development of sharp gradients in charge carrier concentration: the charge accumulates in thin regions (space-charge layers) at each electrode and rapidly decays to a low bulk concentration. Asymptotic analysis, specifically singular perturbation methods, are ideal for such problems;<sup>10</sup> indeed they exploit the fact that  $\epsilon \ll 1$  to obtain analytic, closed-form approximations that are asymptotic as  $\epsilon \rightarrow 0$ . In this paper, we use these

techniques to derive a current-voltage relation for OLEDs with double-carrier diffusion and drift.

This paper is structured as follows. In section 2.2 we present the drift-diffusion equations that describe charge transport and recombination in an OLED. In sections 2.3 through 2.5 we apply asymptotic analysis to the drift-diffusion equations to derive a current-voltage relation for double-carrier injection into OLEDs in the thin space-charge-layer regime,  $\epsilon \ll 1$ . In section 2.6 we compare the current-voltage relation to the numerical solution of the drift-diffusion equations. In section 2.7 we derive a recombination-voltage relation for kinetically limited OLEDs and compare to the numerical solution of the drift-diffusion equations with recombination. We present conclusions in section 2.8.

## 2.2 Mathematical Model

The drift-diffusion equations describe the transport of electrons and holes in an organic film, caused by diffusion down concentration gradients and drift in an electric field. The thickness  $\hat{L}$  (10-1000 nm) of an OLED is typically much smaller than its width and depth; thus, the device is treated as one-dimensional, and charge transport occurs normal to the electrodes only, designated as the  $\hat{x}$  direction. The  $\hat{x}$ -origin is located at the anode (figure 2.1). We assume that the OLED is operating at steady-state. The net fluxes of each species are

$$\hat{j}_{\pm} = -\hat{\mu}_{\pm} \frac{\hat{k}_B \hat{T}}{\hat{e}} \frac{d\hat{n}_{\pm}}{d\hat{x}} \mp \hat{\mu}_{\pm} \hat{n}_{\pm} \frac{d\hat{\phi}}{d\hat{x}}, \quad (2.3)$$

where the  $\pm$  subscript refers to electrons (-) or holes (+),  $\hat{j}_{\pm}$  is the flux of the charge carrier,  $\hat{\mu}_{\pm}$  is the carrier mobility, and  $\hat{\phi}$  is the electric potential. The first term in (2.3) accounts for diffusion, the second drift. Poisson's equation states that the variation in electric field across the OLED is proportional to

the local charge density,

$$\frac{d^2 \hat{\phi}}{d\hat{x}^2} = -\frac{\hat{e}}{\hat{\epsilon}}(\hat{n}_+ - \hat{n}_-). \quad (2.4)$$

Charge carrier conservation equations equate the change in flux across the film to the consumption of charge carriers due to recombination,

$$\frac{d\hat{j}_{\pm}}{d\hat{x}} = -\hat{k}\hat{n}_+\hat{n}_-, \quad (2.5)$$

where  $\hat{k}$  is the reaction rate constant for the recombination of electrons and holes, with units of length cubed per time, assuming Langevin kinetics.<sup>51</sup> In (2.5) we do not account for any electron or hole generation through exciton dissociation.

We assume that electrons are injected through the cathode and holes through the anode such that the number density of charge carriers at the electrode is finite and constant,<sup>53</sup> and that the potential at the electrodes is equal to an applied potential. We assume that the concentration of a charge carrier is zero at its counter electrode.<sup>39,54</sup> These assumptions form the boundary conditions described in (4.21) and (2.15).

To non-dimensionalize the governing equations (2.3)-(2.5), the spatial coordinate,  $\hat{x}$ , is normalized by the device length,  $\hat{L}$ ; the electric potential  $\hat{\phi}$  by the thermal voltage; and the electron and hole densities by  $\hat{n}_0$ , the charge carrier density at the electrodes. The flux is normalized by  $\hat{D}\hat{n}_0/\hat{L}$ . For simplicity, we set the magnitude of the charge density at the anode and at the cathode to be equal, and set the mobility of electrons equal to the mobility of holes. In addition, we neglect the electric field-dependence of the mobility. Henceforth, all equations are in terms of dimensionless variables (unless stated otherwise)

and appear without a caret accent. From (2.3), the flux is

$$j_{\pm} = -\frac{dn_{\pm}}{dx} \mp n_{\pm} \frac{d\phi}{dx}. \quad (2.6)$$

Poisson's equation now reads

$$\frac{d^2\phi}{dx^2} = -\frac{1}{2\epsilon^2}(n_+ - n_-), \quad (2.7)$$

where  $\epsilon$  is the dimensionless space-charge length, defined as

$$\epsilon = \frac{\hat{\lambda}_s}{\hat{L}} = \frac{1}{\hat{L}} \sqrt{\frac{\hat{\epsilon} \hat{k}_B \hat{T}}{2 \hat{\epsilon}^2 \hat{n}_0}}. \quad (2.8)$$

From (2.5), the charge conservation equations are

$$\frac{d}{dx} \left( -\frac{dn_{\pm}}{dx} \mp n_{\pm} \frac{d\phi}{dx} \right) = -k n_+ n_-, \quad (2.9)$$

where the dimensionless reaction rate  $k = \hat{k} \hat{n}_0 \hat{L}^2 / \hat{D}$  is known as the Damkhöler number in engineering literature,<sup>59</sup> and is equal to the ratio of the diffusive timescale ( $\hat{L}^2 / \hat{D}$ ) to the recombination timescale ( $1 / \hat{k} \hat{n}_0$ ). When the reaction is slow in comparison to diffusion ( $k \ll 1$ ), the recombination is kinetically limited. If the inverse is true, recombination is limited by charge transport. Here, we assume that the system is kinetically limited, so the reaction term can be neglected to a first approximation ( $k = 0$ ) in (2.9) yielding

$$\frac{d}{dx} \left( -\frac{dn_{\pm}}{dx} \mp n_{\pm} \frac{d\phi}{dx} \right) = 0. \quad (2.10)$$

It is convenient to write the drift-diffusion equations (2.6-2.10) in terms of the mean charge carrier concentration,  $c = \frac{1}{2}(n_+ + n_-)$ , half the charge density,  $\rho = \frac{1}{2}(n_+ - n_-)$ , and the current,  $J = j_+ - j_-$ . Thus, Poisson's

equation becomes

$$-\epsilon^2 \frac{d^2 \phi}{dx^2} = \rho. \quad (2.11)$$

The net flux,  $j_+ + j_-$ , is zero across the film, since the flux of electrons and holes are equal in magnitude but opposite in direction, which implies

$$\rho \frac{d\phi}{dx} + \frac{dc}{dx} = 0, \quad (2.12)$$

An integration of (2.10) shows that the current  $J$  satisfies

$$c \frac{d\phi}{dx} + \frac{d\rho}{dx} = -\frac{1}{2}J. \quad (2.13)$$

The aforementioned boundary conditions, in non-dimensional form, are

$$\text{Anode, } x = 0 : n_+ = 1, n_- = 0, \text{ and } \phi = \frac{1}{2}V, \quad (2.14)$$

$$\text{Cathode, } x = 1 : n_+ = 0, n_- = 1, \text{ and } \phi = -\frac{1}{2}V, \quad (2.15)$$

where  $V$  is the applied potential (normalized by the thermal voltage,  $V = \hat{V}\hat{e}/\hat{k}_B\hat{T}$ ) minus the normalized built-in potential drop due to the difference in the work functions of the anode and cathode.<sup>60</sup> The applied potential  $V$  is equal to the integral of the electric field  $E$  across the device,

$$V = -\int_0^1 E \, dx, \quad (2.16)$$

where

$$E = -d\phi/dx. \quad (2.17)$$

A schematic of the device configuration is shown in figure 2.1. In the proceeding analysis, we solve for the electric field, hole and electron density, and

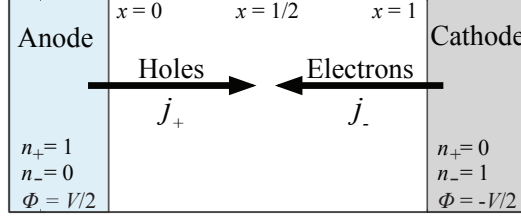


Figure 2.1: Holes are injected through the anode with a flux  $j_+$ , while electrons are injected through the cathode with a flux  $j_-$ ; the fluxes will be determined in the proceeding analysis. The boundary conditions are shown at the anode ( $x = 0$ ) and at the cathode ( $x = 1$ ).

electric potential in the anodic half ( $0 \leq x \leq 1/2$ ) of the OLED. The electric field is symmetric around  $x = 1/2$ , while the electric potential is antisymmetric. The electron density is symmetric to the hole density, so asymptotic expressions for the electron density in the cathodic region ( $1/2 \leq x \leq 1$ ) can be derived from the expressions for the hole density in the anodic region by replacing  $x$  with  $1 - x$ , and vice versa.

In the absence of recombination the problem presented here is mathematically similar to ion transport across a permeable membrane at the interface between two reservoirs of fixed electrolyte concentrations,<sup>61–63</sup> relevant to ionic channels in biological systems. Note, however, that in<sup>61–63</sup> it is assumed that the concentrations of both species (cation and anion) are non-zero in each reservoir. In the case of OLEDs, the appropriate boundary conditions set the concentration of electrons (holes) to zero at the anode (cathode). Another related electro-diffusion problem is that of current passage across a cation-selective surface, which is relevant to electrodialysis at over limiting currents in thin-gap cells.<sup>64</sup> In that problem, the anions do not react at the electrodes; hence, their concentration within the cell is subject to an integral constraint. For an OLED, there are no such constraints on the concentrations of electrons and holes in the semiconductor film.

## 2.3 Master Equation for the Electric Field

Equations (2.11) - (2.13) can be combined into a single master equation in terms of the electric field  $E$ . First, (2.11) is substituted into (2.12), yielding

$$\frac{d}{dx} \left( -\frac{\epsilon^2}{2} E^2 + c \right) = 0. \quad (2.18)$$

Equation (2.18) is readily integrated, resulting in

$$-\frac{\epsilon^2}{2} E^2 + c = A, \quad (2.19)$$

where the constant of integration

$$A = \frac{-\epsilon^2}{2} E_\star^2 + c_\star, \quad (2.20)$$

where  $E_\star$  and  $c_\star$  are the electric field and mean concentration, respectively, at the midpoint of the device. These two quantities are not known *a priori*, but must be determined as part of the asymptotic analysis. From (2.19) and (2.20), the carrier concentration can be written as

$$c = \frac{\epsilon^2}{2} (E^2 - E_\star^2) + c_\star. \quad (2.21)$$

Poisson's equation (2.11) is inserted into (2.13) resulting in

$$\epsilon^2 \frac{d^2 E}{dx^2} = cE - \frac{1}{2} J. \quad (2.22)$$

Equation (2.21) is combined with (2.22) to yield the master equation for the electric field across the OLED,

$$\epsilon^2 \frac{d^2 E}{dx^2} - \left[ \frac{\epsilon^2}{2} (E^2 - E_\star^2) + c_\star \right] E = -\frac{1}{2} J. \quad (2.23)$$

Similar master equations have been derived to analyze charge transport in liquid-state electrochemical systems<sup>63,65</sup> and in OLEDs without diffusion.<sup>53</sup>

## 2.4 Asymptotic Analysis

In the operation of an OLED, a potential difference between the anode and the cathode drives a current across the organic thin film. The applied voltage must be high enough to overcome the energy barriers for the injection of charge carriers. Typically, the potential difference is much greater than the thermal voltage,  $V \gg 1$  (or  $\hat{V} \gg \hat{k}_B \hat{T}/e \simeq 26$  mV).<sup>34</sup> Therefore, we prescribe the voltage

$$V = \mu(\epsilon) V_\star, \quad (2.24)$$

where  $V_\star$  is an  $O(1)$  constant and  $\mu(\epsilon) \gg 1$ . The bulk field,  $E_B$ , arises from the  $O(\mu)$  drop in potential across the  $O(1)$ -width bulk region. Due to symmetry of the field about  $x = 1/2$ , the integral (2.16) can be written as

$$\frac{1}{2} \mu V_\star = - \int_0^{\frac{1}{2}} E(x) dx, \quad (2.25)$$

where we have used  $\phi(1/2) = 0$ , and  $\phi(0) = V/2 = \mu V_\star/2$ . Hence, the bulk field is

$$E_B = \mu(\epsilon) V_\star + o(\mu), \quad (2.26)$$

which is spatially uniform to leading order. Therefore, the electric field at the midpoint is  $E_\star = \mu(\epsilon) V_\star$  to leading order. The majority of the injected

charge carriers in the device are concentrated at the space-charge layers near each electrode, so the concentration in the electroneutral bulk is expected to be asymptotically small in  $\epsilon$ ,

$$c_B = \delta(\epsilon)c_a + o(\delta) \quad (2.27)$$

where  $\delta(\epsilon) \ll 1$  is an *a priori* unknown function and  $c_a$  is an  $O(1)$  coefficient. Thus,  $c_\star = \delta(\epsilon)c_a$  to leading order. In the bulk, where  $x \sim O(1)$ , one can simply set  $\epsilon = 0$  in the master equation (2.23) to derive the leading order current  $J$  as

$$J = 2c_BE_B = 2\mu\delta c_a V_\star + o(\mu\delta). \quad (2.28)$$

The charge density is zero in the electroneutral bulk, to leading order. However, at the anode-thin-film interface ( $x = 0$ ) the charge density  $\rho = 1/2$ , and  $\rho = -1/2$  at the cathode ( $x = 1$ ), according to (4.21) and (2.15). The bulk solution (2.26)-(2.28) does not satisfy these boundary conditions. This indicates the existence of an asymptotically small region near each electrode, a space-charge layer, where electroneutrality is violated. We derive an asymptotic approximation for the electric field in the space-charge layer next.

### 2.4.1 Space-Charge Layer

Due to symmetry, we focus on the hole-rich space-charge layer near the anode ( $x = 0$ ). In this region, the concentration of charge carriers varies rapidly; hence, we define a stretched “inner” coordinate  $\bar{x} = x/\epsilon$ , such that  $\bar{x} \sim O(1)$  as  $\epsilon \rightarrow 0$ . The electric field in the space-charge layer is expected to be  $O(1/\epsilon)$ , resulting in an  $O(1)$  potential drop across the space-charge-layer (the majority of the  $O(\mu)$  applied potential drops across the bulk of the OLED). We define  $\bar{E} = E\epsilon$ , where  $\bar{E} \sim O(1)$ . Applying these scalings to the master equation

(2.23) yields:

$$\frac{1}{\epsilon} \frac{d^2 \bar{E}}{d\bar{x}^2} - \left[ \frac{1}{2\epsilon} \bar{E}^2 - \frac{\epsilon}{2} E_\star^2 + \frac{c_\star}{\epsilon} \right] \bar{E} = -\frac{J}{2}. \quad (2.29)$$

Recall that the midpoint concentration  $c_\star$  (2.27) is small,  $\delta \ll 1$ , and the midpoint field  $E_\star$  (2.26) is  $O(\mu)$ . Thus, to ensure that the space-charge layer is in quasi-equilibrium to a first approximation, we choose  $\mu \ll 1/\epsilon$  so that terms proportional to the midpoint field  $E_\star$  and current  $J$  ( $\sim \mu\delta$ ) in (2.29) do not enter the leading order balance. That leading  $O(1/\epsilon)$  balance is therefore

$$\frac{d^2 \bar{E}}{d\bar{x}^2} = \frac{1}{2} \bar{E}^3, \quad (2.30)$$

with the boundary conditions

$$\frac{d\bar{E}}{d\bar{x}} = \frac{1}{2}, \text{ and } \frac{d^2 \bar{E}}{d\bar{x}^2} = \frac{1}{2} \bar{E} \text{ at } \bar{x} = 0, \quad (2.31)$$

derived from (2.11), (4.21), and (2.23). The solution to (2.30) and (2.31) is

$$\bar{E}(\bar{x}) = -\frac{2}{\bar{x} + 2}, \quad (2.32)$$

which represents the leading order solution for the electric field in the space-charge layer. This expression was also found by Chu & Bazant<sup>66</sup> for the electric field in the Debye layer of an electrochemical cell at the diffusion-limited current.

The decay to zero of the  $O(1/\epsilon)$  space-charge field as  $\bar{x} \rightarrow \infty$  is consistent with the prescribed  $O(\mu)$  bulk field, where  $\mu \ll 1/\epsilon$ . We look to (2.29) for the scaling of the next term of the space-charge layer field. After the terms included in (2.30), the next largest term in (2.29) is  $c_\star \bar{E}/\epsilon \sim \delta c_a \bar{E}/\epsilon$  from (2.27) since  $c_a$  and  $\bar{E}$  are  $O(1)$ , and  $\mu \ll 1/\epsilon$ . Thus, the expansion of electric

field in the space-charge layer is

$$E(\bar{x}) = \frac{1}{\epsilon} (\bar{E}_0(\bar{x}) + \delta \bar{E}_1(\bar{x}) + o(\delta)), \quad (2.33)$$

where  $\bar{E}_0$  is the previously-calculated leading order term (2.32). An equation for the next,  $O(\delta/\epsilon)$ , term of the electric field in the space-charge layer,  $\bar{E}_1(\bar{x})$ , is derived by inserting (2.33) into (2.29). Since  $\mu \ll 1/\epsilon$ , the current  $J$  does not enter the  $O(\delta/\epsilon)$  balance. The term  $c_\star \bar{E}/\epsilon$  is to leading order  $\delta c_a \bar{E}_0/\epsilon$  from (2.27). The term containing the midpoint field,  $\epsilon E_\star^2 \bar{E}$  is  $O(\epsilon \mu^2)$  to leading order in  $\bar{E}$ . When  $\mu$  is restricted to  $\mu \ll \delta^{1/2}/\epsilon$ , this term does not enter into the  $O(\delta/\epsilon)$  balance. With this restriction, the  $O(\delta/\epsilon)$  field is governed by

$$\frac{d^2 \bar{E}_1}{d\bar{x}^2} - \frac{3}{2} \bar{E}_0^2 \bar{E}_1 = c_a \bar{E}_0, \quad (2.34)$$

with the boundary conditions

$$\frac{d\bar{E}_1}{d\bar{x}} = 0, \quad \text{and} \quad \frac{d^2 \bar{E}_1}{d\bar{x}^2} = \frac{1}{2} \bar{E}_1 \quad \text{at} \quad \bar{x} = 0. \quad (2.35)$$

Substituting the result for  $\bar{E}_0$  (2.32) into (2.34) and solving the resulting equation yields

$$\bar{E}_1(\bar{x}) = c_a \frac{12 + 12\bar{x} + 6\bar{x}^2 + \bar{x}^3}{3(2 + \bar{x})^2}. \quad (2.36)$$

The  $O(\delta/\epsilon)$  field (2.36) diverges as  $\bar{x} \rightarrow \infty$  and hence clearly does not match the bulk, indicating that a transition, or intermediate, region exists between the electroneutral bulk and the space-charge layer.

## 2.4.2 Intermediate Layer

The device length and the width of the space-charge layer are clear choices for the characteristic length of the bulk,  $x \sim O(1)$ , and the space-charge

layer,  $x \sim O(\epsilon)$ , respectively; however there is no obvious length scale for the intermediate layer. Through a scaling analysis, the intermediate layer field and width are found to scale as

$$E = \frac{\delta^{\frac{1}{2}}}{\epsilon} \tilde{E}, \text{ and } x = \frac{\epsilon}{\delta^{\frac{1}{2}}} \tilde{x}, \quad (2.37)$$

where  $\tilde{E}$  and  $\tilde{x}$  are  $O(1)$ . The width of the intermediate layer is  $\epsilon/\delta^{\frac{1}{2}}$ , and the magnitude of the field within it is  $\delta^{\frac{1}{2}}/\epsilon$ , which fit the criteria  $\epsilon \ll \epsilon/\delta^{\frac{1}{2}} \ll 1$  and  $\mu \ll \delta^{\frac{1}{2}}/\epsilon \ll 1/\epsilon$ . Therefore, the leading order equation that results in the intermediate layer from (2.23) is

$$\frac{d^2 \tilde{E}}{d\tilde{x}^2} = \frac{1}{2} \tilde{E}^3 + c_a \tilde{E}. \quad (2.38)$$

A solution to (2.38) that decays to zero as  $\tilde{x} \rightarrow \infty$  is<sup>67</sup>

$$\tilde{E}(\tilde{x}) = -\frac{2\sqrt{c_a}}{\sinh(\sqrt{c_a}\tilde{x})}. \quad (2.39)$$

The behavior of the asymptotic expansion for the intermediate field must match that of the space-charge field as  $\tilde{x} \rightarrow 0$  and the bulk field as  $\tilde{x} \rightarrow \infty$ . As  $\tilde{x} \rightarrow 0$ ,  $\tilde{E} \rightarrow -2/\tilde{x}$ ; as  $\tilde{x} \rightarrow \infty$ , the leading order space-charge field (2.32), rewritten in terms of  $\tilde{x}$  and  $\tilde{E}$ , approaches  $\tilde{E} = -2/\tilde{x}$ . Therefore the behavior of the intermediate field as  $\tilde{x} \rightarrow 0$  matches that of the space-charge field. Since we require  $\mu \ll \delta^{\frac{1}{2}}/\epsilon$ , the decay of (2.39) at large  $\tilde{x}$  is consistent with the  $O(\mu)$  bulk field (2.26). To determine a relation between  $\mu$ ,  $\delta$ , and  $\epsilon$ , we need a second term for the field in the intermediate layer that scales by  $\mu$  to match to the leading order bulk electric field  $E_B = \mu V_\star$ . The expansion for the field

in the intermediate region is thus written as

$$E(\tilde{x}) = \frac{\delta^{\frac{1}{2}}}{\epsilon} \tilde{E}_0(\tilde{x}) + \mu \tilde{E}_1(\tilde{x}) + O(\mu), \quad (2.40)$$

where the leading order term  $\tilde{E}_0$  is given by (2.39). From (2.23), the equation for  $\tilde{E}_1$  is

$$\frac{d^2 \tilde{E}_1}{d\tilde{x}^2} - \frac{3}{2} \tilde{E}_0^2 \tilde{E}_1 - c_a \tilde{E}_1 = c_b \tilde{E}_0 - c_a V_\star, \quad (2.41)$$

where  $c_b$  is the next order of the expansion of the midpoint concentration, that is

$$c_\star = \delta c_a + \mu \epsilon \delta^{\frac{1}{2}} c_b + o\left(\mu \epsilon \delta^{\frac{1}{2}}\right), \quad (2.42)$$

which is added to account for a possible higher order bulk concentration contribution to  $\tilde{E}_1$ . An exact solution to (2.41) cannot be obtained. However, only the behavior of  $\tilde{E}_1$  as  $\tilde{x} \rightarrow \infty$  and as  $\tilde{x} \rightarrow 0$  is needed for matching with the bulk and the space-charge layer, respectively. As  $\tilde{x} \rightarrow \infty$  it is clear that  $\tilde{E}_1 \rightarrow V_\star$  since  $\tilde{E}_0$  decays exponentially, thereby matching the bulk field, but the behavior as  $\tilde{x} \rightarrow 0$  needs to be examined carefully.

A power series expansion around  $\tilde{x} = 0$  reveals two homogeneous solutions to (2.41):

$$f_{h1} = \frac{a_0}{\tilde{x}^2} + \frac{a_0 c_a}{6} - \frac{7a_0 c_a^2}{120} \tilde{x}^2 + O(\tilde{x}^3), \quad (2.43)$$

and

$$f_{h2} = b_0 \tilde{x}^3 + O(\tilde{x}^4), \quad (2.44)$$

where  $a_0$  and  $b_0$  are constants, as well as a particular solution,

$$f_p = \frac{c_b}{3} \tilde{x} + \frac{c_a V_\star}{4} \tilde{x}^2 - \frac{c_a^2 V_\star}{24} \tilde{x}^4 + o(\tilde{x}^4). \quad (2.45)$$

The series approximation of the  $O(\mu)$  correction to the intermediate field as

$\tilde{x} \rightarrow 0$  is thus

$$\tilde{E}_1 = \frac{a_0}{\tilde{x}^2} + \frac{a_0 c_a}{6} + \frac{c_b}{3} \tilde{x} + \left( \frac{-7a_0 c_a^2}{120} + \frac{c_a V_\star}{4} \right) \tilde{x}^2 + b_0 \tilde{x}^3 + O(\tilde{x}^3). \quad (2.46)$$

We now proceed to match the intermediate field, (2.39) and (2.46), to the electric field in the space-charge layer, (2.32) and (2.36), according to van Dyke's matching procedure,<sup>10</sup> in order to obtain  $a_0$  and  $\delta$ . This is detailed in Appendix 2.A.1. The results of the matching procedure are

$$a_0 = 4 \text{ and } \delta = \mu\epsilon. \quad (2.47)$$

However, we have not yet found an expression for  $c_a$ , which can only be determined by matching to higher-order space-charge-field terms.

### 2.4.3 Higher Order Space-Charge-Field Terms

To determine an expression for  $c_a$ , where  $c_B \sim \delta c_a$  is the leading order bulk concentration, we need to determine the next two terms in the space-charge layer field, which include the contribution of current. The order of these terms in the space-charge layer expansion can be determined from the higher order terms in the correction to the intermediate field (2.46), as  $\tilde{x} \rightarrow 0$ . Equation (2.46) implies the expansion

$$E(\bar{x}) = \frac{1}{\epsilon} \bar{E}_0(\bar{x}) + \frac{\delta}{\epsilon} \bar{E}_1(\bar{x}) + \frac{\delta^{\frac{3}{2}}}{\epsilon} \bar{E}_2(\bar{x}) + \frac{\delta^2}{\epsilon} \bar{E}_3(\bar{x}) + o\left(\frac{\delta^2}{\epsilon}\right). \quad (2.48)$$

Substituting (2.48) into (2.29), the differential equation for  $\bar{E}_2$  is

$$\frac{d^2 \bar{E}_2}{d\bar{x}^2} - \frac{3}{2} \bar{E}_0^2 \bar{E}_2 = c_b \bar{E}_0, \quad (2.49)$$

subject to the boundary conditions

$$\frac{d\bar{E}_2}{d\bar{x}} = 0, \text{ and } \frac{d^2\bar{E}_2}{d\bar{x}^2} = \frac{1}{2}\bar{E}_2 \text{ at } \bar{x} = 0. \quad (2.50)$$

This differential equation has the same form as (2.34); the solution has the same form as  $\bar{E}_1$  (2.36), except that  $c_a$  is replaced by  $c_b$ . Thus,

$$\bar{E}_2(\bar{x}) = c_b \frac{12 + 12\bar{x} + 6\bar{x}^2 + \bar{x}^3}{3(2 + \bar{x})^2}. \quad (2.51)$$

This term matches to the  $O(\tilde{x})$  term in (2.46), however this does not provide the value of  $c_a$ . Another term of the expansion of the space-charge layer field is needed here to determine  $c_a$ . For the next term,  $\bar{E}_3(\bar{x})$ , we first extend the expansion of the midpoint concentration  $c_\star$  by an additional term

$$c_\star = \delta c_a + \delta^{\frac{3}{2}} c_b + \delta^2 c_c + o(\delta^2), \quad (2.52)$$

where we have applied  $\mu = \delta/\epsilon$  from (2.47). The equation for the fourth term in the space-charge layer electric field expansion is

$$\frac{d^2\bar{E}_3}{d\bar{x}^2} - \frac{3}{2}\bar{E}_0\bar{E}_3 = \frac{3}{2}\bar{E}_0\bar{E}_1^2 - \frac{1}{2}V_\star\bar{E}_0 + c_a\bar{E}_1 + c_c\bar{E}_0 - c_aV_\star, \quad (2.53)$$

subject to

$$\frac{d\bar{E}_3}{d\bar{x}} = 0, \text{ and } \frac{d^2\bar{E}_3}{d\bar{x}^2} = \frac{1}{2}\bar{E}_3 - c_aV_\star \text{ at } \bar{x} = 0. \quad (2.54)$$

Equations (2.53) and (2.54) can be solved in closed form, however we are only interested in the behavior as  $\bar{x} \rightarrow \infty$ . A power series expansion of the solution to (2.53) and (2.54) as  $\bar{x} \rightarrow \infty$  yields

$$\bar{E}_3(\bar{x}) = \frac{4c_a^2 - 21c_aV_\star}{60}\bar{x}^2 + \frac{c_a^2 - 9c_aV_\star}{90}\bar{x}^3 + O(\bar{x}^2). \quad (2.55)$$

Next, we match the first four terms in the expansion for the space-charge field to the first two terms in the intermediate solution. This matching procedure, in contrast to the last, matches the terms in each expansion that are larger than  $O(\delta^2/\epsilon)$  in the space-charge field expansion and  $O(\delta/\epsilon)$  in the intermediate field expansion according to van Dyke's rule.<sup>10</sup> This procedure, detailed in Appendix 2.A.1, yields

$$c_a = 2V_\star. \quad (2.56)$$

When (2.24) and (2.47) are inserted into (2.56), the bulk concentration is recovered to leading order as

$$c_B \sim 2\epsilon V, \quad (2.57)$$

which is indeed small as  $V = \mu V_\star$  where  $\mu \ll 1/\epsilon$ .

## 2.5 Current-Voltage Relation

From (2.26), (2.28), and (2.57), the leading order current is

$$J \sim 4\epsilon V^2. \quad (2.58)$$

The first correction to (2.58) can be found through a higher-order analysis of the integral constraint (2.16). The details of the analysis are given in Appendix 2.A.2, where it is shown that the constraint yields a logarithmic correction to the leading order bulk electric field,

$$E_B = V - 2 \ln 2\epsilon V + o(\ln \delta). \quad (2.59)$$

Substituting (2.57) and (2.59) into (2.28) yields the improved current-voltage relation,

$$J = 8\epsilon V \left( \frac{V}{2} - \ln 2\epsilon V \right) + o(\delta \ln \delta). \quad (2.60)$$

From (2.59) and (5.9), for the analysis to be valid the applied voltage must be sufficiently large such that  $\mu \gg \ln 1/\delta$ . An upper bound on the applied voltage,  $\mu \ll \delta^{\frac{1}{2}}/\epsilon$ , is necessary to calculate the first correction to the space-charge field (2.46). The current-voltage relation (5.9) is therefore valid over the range

$$\ln \frac{1}{\delta} \ll \mu \ll \frac{\delta^{\frac{1}{2}}}{\epsilon}, \quad (2.61)$$

where  $\mu$  is prescribed by the magnitude of the applied voltage  $V$ . The current (5.9), in dimensional form, reads

$$\hat{J} = 4\hat{\epsilon}\hat{\mu} \frac{1}{\hat{L}^2\hat{\lambda}_s} \left( \frac{\hat{V}^2}{2} - \frac{\hat{V}\hat{k}_B\hat{T}}{\hat{e}} \ln \frac{2\hat{e}\hat{\lambda}_s\hat{V}}{\hat{L}\hat{k}_B\hat{T}} \right), \quad (2.62)$$

where  $\hat{\lambda}_s$  is given by (2.2). To leading order, the current exhibits a quadratic dependence on the applied voltage  $\hat{V}$  and the reciprocal of the film width  $\hat{L}$ ,  $\hat{J} \propto \hat{V}^2/\hat{L}^2\hat{\lambda}_s$ , in contrast to the Mott & Gurney law for diffusion-free single carrier injection, where  $\hat{J} \propto \hat{V}^2/\hat{L}^3$ .

## 2.6 Comparison between Asymptotic Analysis and Numerical Solution of the Drift-Diffusion Equations

Our analysis has furnished asymptotic approximations for the field and carrier densities across the OLED. To validate our analysis, we solved the drift-diffusion equations (2.6), (5.4), and (2.10) numerically using the MATLAB BVP4C solver. The asymptotic results for the electric field are compared against the numerical results for  $\epsilon = 0.001$  (figure 2.2), showing good agreement.

The density of holes  $n_+$  and electrons  $n_-$  in the anodic region are easily

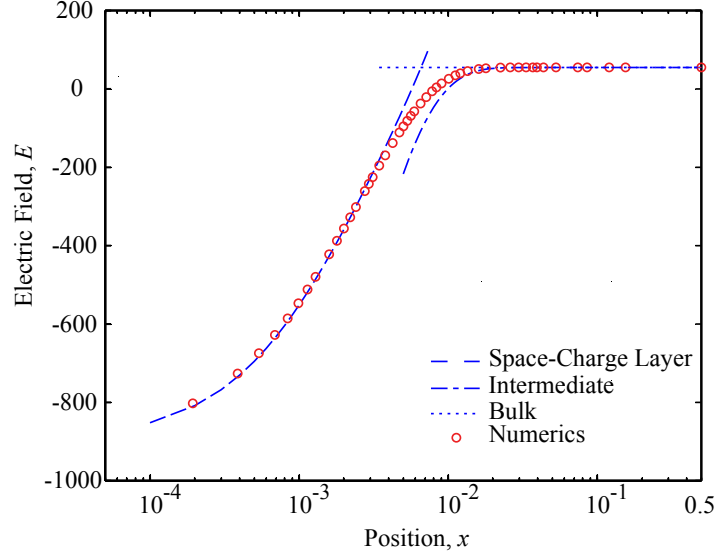


Figure 2.2: Asymptotic solutions for the electric field in the space-charge layer (dash), the intermediate layer (dash-dot) and in the bulk (dot) are compared to the numerical solution (open circles) of the electric field in the anodic region ( $0 \leq x \leq 1/2$ ) for  $\epsilon = 0.001$  and  $V = 50$ . The asymptotic solutions plotted include two terms of the asymptotic series for the field in the space-charge layer, (2.32) and (2.36), the leading order intermediate field (2.39) and the bulk field (2.59).

calculated from the asymptotic expressions for the electric field. In figure 2.3, the hole and electron densities in the anodic region are plotted on a semilog axis. The solution for the hole density in the space-charge layer includes the first correction to the density, calculated from (2.36). The asymptotic expansion for the electron density in the intermediate region decays to zero as  $\tilde{x} \rightarrow 0$  (figure 2.3), as expected; in fact, from (2.32), (2.36), and (2.51), it can be shown that the electron density is zero through  $O(\delta^{\frac{3}{2}})$ . The discrepancy between the asymptotic bulk electron and hole densities and the numerics can be attributed to the fact that only the leading order term for the bulk concentration (2.57) was calculated. This error is seen in both the electron and hole density asymptotic expansions.

The steep gradient in hole density in figure 2.3 results in a diffusive current that must be balanced by a negative electric field to conserve charge in (2.10).

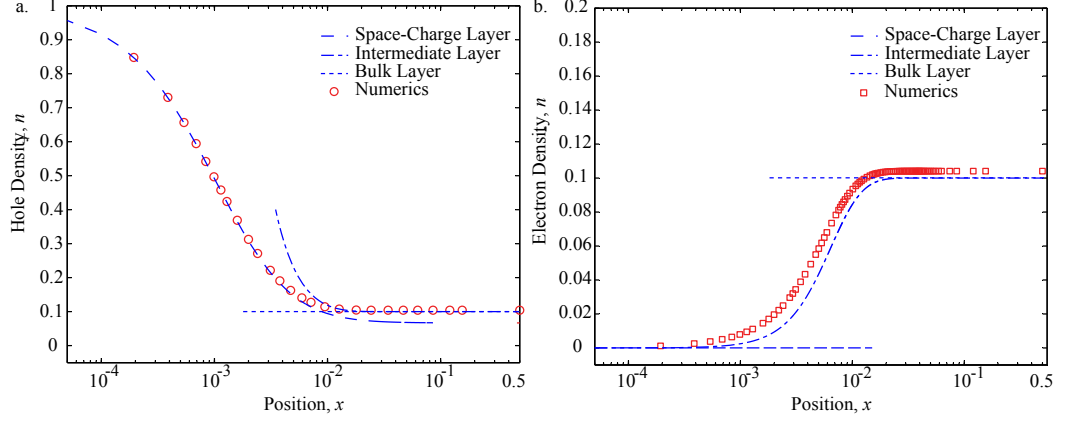


Figure 2.3: Numerical solutions for the A) hole density (circle) and B) electron density at  $\epsilon = 0.001$  and  $V = 50$  are compared to asymptotic expressions for the hole and electron densities in the space-charge layer (dash), intermediate layer (dash-dot), and bulk (dot). Note, the vertical scales of (A) and (B) are different.

From the definition of the space-charge width (2.8),  $\epsilon \propto 1/\sqrt{\hat{n}_0}$ . Hence, as the charge density in the electrode approaches infinity, as in the case of ohmic contacts without diffusion,  $\epsilon \rightarrow 0$ . A plot of the potential at several values of  $\epsilon$  is useful (figure 2.4) to elucidate the increase in current due to diffusion. The leading order potential  $\phi$  is calculated from (2.17) and the electric field across the space-charge layer (2.32), the intermediate layer (2.39), and the bulk (2.59).

As  $\epsilon \rightarrow 0$ , a maximum in potential develops, resulting in “virtual ohmic contacts”<sup>53</sup> near the electrodes. The maximum results from the negative electric field near the anode that develops to balance diffusion in the charge conservation equation (2.10). The virtual contacts are located at the point where the electric field is zero. Between the virtual contacts near the anode and the cathodes, the voltage drops linearly. The potential at the virtual contact increases as  $\epsilon$  decreases, and is larger than the applied potential at the electrode. Hence, the voltage drop across the bulk is larger than the naive estimate  $\hat{V}/\hat{L}$ , resulting in a higher current. This is reflected in the current-voltage relation (2.62), where  $\hat{J} \propto 1/\hat{\lambda}_s$ . If diffusion is neglected this increase in current due

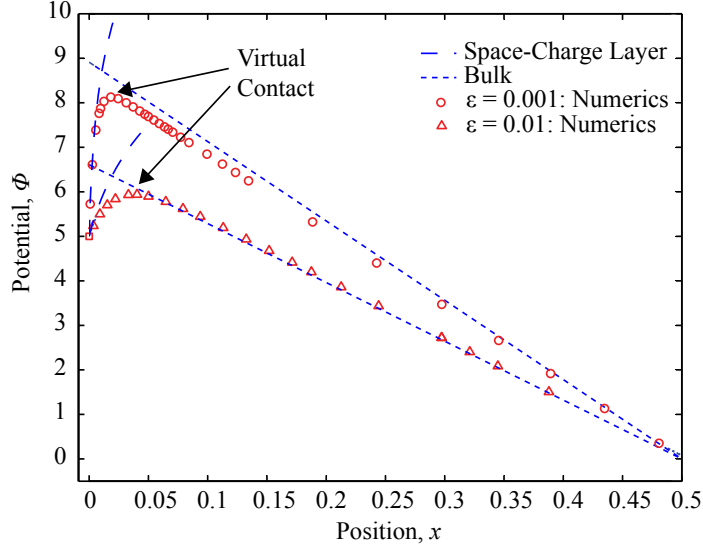


Figure 2.4: The asymptotic solutions (dash) for electric potential are compared to the numerical solution (symbols). The electric potential at  $\epsilon = 0.001$  has a maximum (indicated by arrow), or virtual contact, closer to the anode than the potential at  $\epsilon = 0.01$  (triangle). As  $\epsilon \rightarrow 0$ , the potential increases at the virtual contact, effectively increasing the voltage drop across the bulk. In this figure, the applied voltage is  $V = 10$ .

to an interior “virtual contact” across the OLED is not accounted for.

The current-voltage relation (5.9) is compared to the numerical results in figure 2.5 at three values of  $\epsilon$ . As  $\epsilon$  decreases, the accuracy of the asymptotic expression increases. The current-voltage relation (5.9) is fundamentally different from the Mott-Gurney law for diffusion-free injection into insulators. The major difference is the additional characteristic length scale, the space-charge length  $\hat{\lambda}_s$ , that results from including diffusion: instead of  $\hat{J} \propto \hat{V}^2/\hat{L}^3$ , we find that  $\hat{J} \propto \hat{V}^2/\hat{L}^2\hat{\lambda}_s$  to leading order. Since the space-charge layer is much thinner than the film,  $\epsilon = \hat{\lambda}_s/\hat{L} \ll 1$ , this predicts a large  $O(\hat{L}/\hat{\lambda}_s)$  increase in the current that passes through the film for double-carrier injection with diffusion (figure 2.5). This can be interpreted in terms of the virtual ohmic contacts as discussed above.

The increase in current is consistent with experimental results for double-

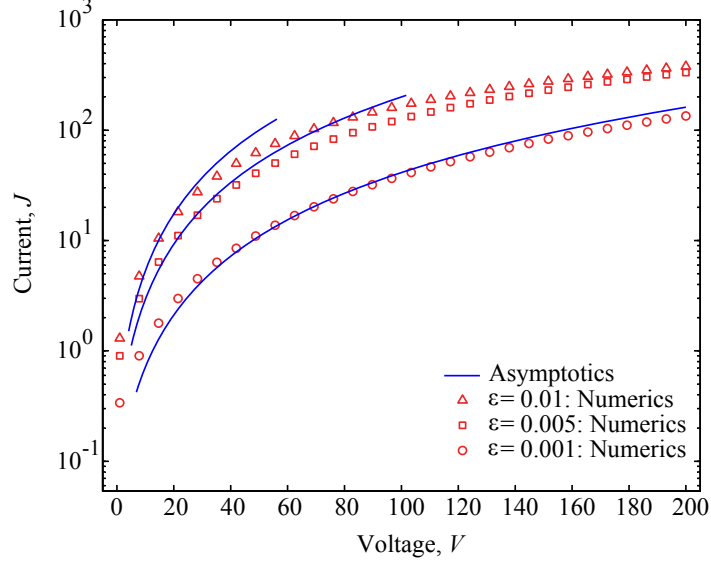


Figure 2.5: The asymptotic expression for current (5.9) (dashed line) are compared to the numerical results at  $\epsilon = 0.001$  (circle),  $\epsilon = 0.005$  (square), and  $\epsilon = 0.01$  (triangle). The asymptotics perform well as  $\epsilon \rightarrow 0$ .

carrier injection into an ITO/MEH-PPV/Ca OLED performed by Parker.<sup>68</sup> The energy barrier to injection across the MEH-PPV/Ca interface is approximately 0.1 eV, which indicates a space-charge-limited OLED.<sup>37</sup> Specifically, Parker reports current-voltage curves for OLEDs for varying widths of the polymer thin film,  $\hat{L}$ . When the macroscopic electric field across the film,  $\hat{V}/\hat{L}$ , is plotted against the current, the curves for the various widths collapse onto a single current-voltage curve, indicating that the current-voltage relation should be a function of the ratio  $\hat{V}/\hat{L}$ , as seen in (2.62), where  $\hat{J} \propto \hat{V}^2/\hat{L}^2$ , as opposed to  $\hat{J} \propto \hat{V}^2/\hat{L}^3$  for diffusion-free transport. In terms of the charge density at the electrode,  $\hat{J} \propto \sqrt{\hat{n}_0}$ ; the current increases with the reservoir density, as expected. When the charge density in the electrode is small, the current is small since it is limited by the electrons and holes available in the electrode for transfer to the thin-film.

## 2.7 The First Effects of Carrier Recombination

Thus far, we have set the recombination rate constant  $k$  equal to zero, thereby neglecting recombination of carriers. The results reported in section 2.6 for the electric field, hole and electron densities, and electric potential, can be viewed as the leading order terms in an asymptotic expansion in terms of the recombination rate. That is, the leading order local recombination rate is

$$r(x; \epsilon, k) = kn_+(x; \epsilon)n_-(x; \epsilon), \quad (2.63)$$

where  $n_+(x; \epsilon)$  and  $n_-(x; \epsilon)$  are the hole and electron profiles calculated for  $k = 0$ . In the space-charge layer adjacent to the anode, the electron density is zero to  $O(\delta^{\frac{3}{2}})$ ; thus the local recombination rate in the space-charge layer is zero through  $k\delta^{\frac{3}{2}}$ . In the intermediate region, the leading order recombination rate is equal to the leading order bulk recombination rate. The total recombination rate across the OLED is the integral of the local recombination rate,  $R = \int_0^1 kn_+(x)n_-(x) dx$ . Since the space-charge layers are thin, the bulk recombination rate  $r \sim 4k\epsilon^2V^2$ , from (2.57), is the dominant contribution to the total recombination rate. The leading order asymptotic expression for the total recombination rate,

$$R \sim 4k\epsilon^2V^2, \quad (2.64)$$

is compared to numerical results in figure 2.6. In this figure, the numerics solve the full drift-diffusion equations, including recombination, at  $\epsilon = 0.001$  and  $V = 50$ , for a variety of recombination rate constants,  $k$ . The asymptotic solution matches well to the numerics through  $O(1)$  values of  $k$ , indicating that the simple expression  $R \sim 4k\epsilon^2V^2$  may be applied to OLEDs to approximate

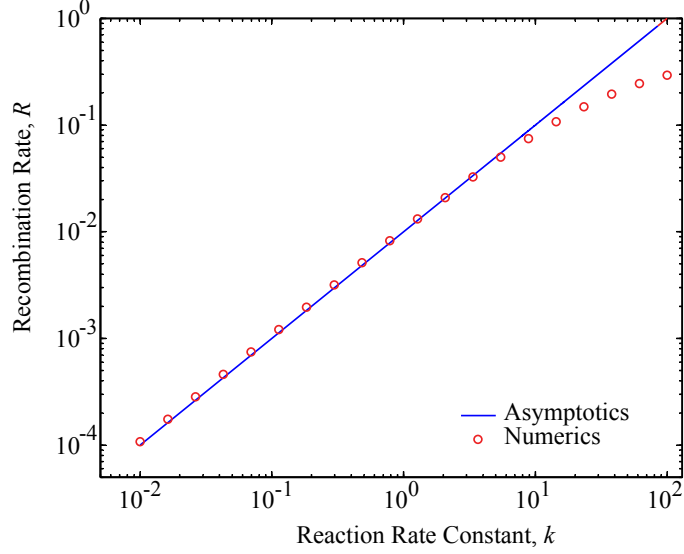


Figure 2.6: The leading order total recombination rate  $R = 4k\epsilon^2V^2$  (line) is compared to the numerical solution of the drift-diffusion equations (circle) as a function of recombination rate constant  $k$  at  $V = 50$  and  $\epsilon = 0.001$ .

the total recombination rate for low to moderate recombination rate constants.

## 2.8 Conclusions

We have quantified double-carrier drift, diffusion, and recombination in OLEDs via asymptotic analysis of the drift-diffusion equations. For space-charge-limited OLEDs, the carrier densities vary rapidly near the electrodes. We have shown this variation in carrier densities occurs on the length-scale of the space-charge width  $\hat{\lambda}_s$ , which is much smaller than the device thickness. Thus, the ratio  $\epsilon = \hat{\lambda}_s/\hat{L}$  is a small parameter exploited in our analysis to yield asymptotic approximations to the current-voltage relation and the electric field, carrier densities, and electric potential across the OLED. Chiefly, we found that the leading order current across the OLED is  $\hat{J} \propto \hat{V}^2/\hat{L}^2\hat{\lambda}_s$ , in contrast to diffusion-free single-carrier injection, where  $\hat{J} \propto \hat{V}^2/\hat{L}^3$ .<sup>2</sup> The difference is due to the characteristic length scale, the space-charge width  $\hat{\lambda}_s$  that emerges when the drift-diffusion equations are non-dimensionalized. This

space-charge width is much thinner than the width of the device, so we predict a higher current than a diffusion-free analysis would, which can be interpreted as an increased potential drop between virtual ohmic contacts that result from diffusion. The scaling for the current derived here,  $\hat{J} \propto \hat{V}^2 / \hat{L}^2 \hat{\lambda}_s$ , is consistent with experimental data for ITO/MEH-PPV/Ca OLEDs by Parker,<sup>68</sup> which shows that the current scales as  $\hat{J} \propto \hat{V}^2 / \hat{L}^2$ .

We assumed that the charge carrier densities at the electrode were equal, and the electrons and holes have the same mobility in the organic film. In addition, we assumed that the charge carrier mobility does not depend upon the electric field. These assumptions can be relaxed; we plan to do so in future work. For example, the mobility can be adjusted to account for the electric field through the functional form  $\hat{\mu} = \hat{\mu}_0 \exp \sqrt{\hat{E} / \hat{E}_0}$ , where  $\hat{\mu}_0$  and  $\hat{E}_0$  are material parameters.<sup>37</sup>

Lastly, we analyzed kinetically-limited OLEDs with small recombination rates ( $k < 1$ ). We derived an approximate expression for the recombination rate across the OLED that compares well with numerics for low to moderate reaction rate constants  $k$ . A solution extended to apply at larger  $k$  is desirable to accurately predict the recombination in an OLED beyond the kinetically-limited regime.

## 2.A Appendix

### 2.A.1 Matching

To determine the value of  $a_0$  in (2.46), we match the field in the space-charge layer to that of the intermediate layer in the domain of overlap,  $\bar{x} \rightarrow \infty$  and

$\tilde{x} \rightarrow 0$ . As  $\bar{x} \rightarrow \infty$ , from (2.32) and (2.36) we have

$$\bar{E}_0(\bar{x}) \sim \frac{-2}{\bar{x}} + \frac{4}{\bar{x}^2} - \frac{8}{\bar{x}^3} + O\left(\frac{1}{\bar{x}^4}\right), \quad \text{and} \quad \bar{E}_1(\bar{x}) \sim \frac{c_a}{3}\bar{x} + \frac{2c_a}{3} + \frac{4c_a}{3\bar{x}^2} + O\left(\frac{1}{\bar{x}^3}\right). \quad (2.65)$$

The expansion of the leading order intermediate field (2.39) as  $\tilde{x} \rightarrow 0$  is

$$\tilde{E}_0(\tilde{x}) \sim \frac{-2}{\tilde{x}} + \frac{c_a}{3}\tilde{x} - \frac{7c_a^2}{180}\tilde{x}^3 + O(\tilde{x}^4), \quad (2.66)$$

while the next term  $\tilde{E}_1$  has the expansion (2.46). Next, we rewrite the space-charge layer expansions (2.65) in terms of the intermediate coordinate  $\tilde{x}$ , collect terms, and then rewrite the intermediate expansion in terms of space-charge layer coordinate  $\bar{x}$ . This matching procedure is discussed by van Dyke.<sup>10</sup> The space-charge layer expansions (2.65) in terms of  $\tilde{x}$ , where  $\tilde{x} = \bar{x}\delta^{\frac{1}{2}}$ , are

$$\bar{E}(\tilde{x}) = \frac{\delta^{\frac{1}{2}}}{\epsilon} \left( \frac{-2}{\tilde{x}} + \frac{c_a}{3}\tilde{x} \right) + \frac{\delta}{\epsilon} \left( \frac{4}{\tilde{x}^2} + \frac{2c_a}{3} \right) + o\left(\frac{\delta}{\epsilon}\right). \quad (2.67)$$

Recall,  $\delta \ll 1$ . The expansion of the intermediate field, (2.46) and (2.66), in terms of the inner variable is,

$$\tilde{E}(\bar{x}) = \frac{\delta^{\frac{1}{2}}}{\epsilon} \left( \frac{-2}{(\delta^{\frac{1}{2}}\bar{x})} + \frac{c_a}{3}(\delta^{\frac{1}{2}}\bar{x}) \right) + \mu \left( \frac{a_0}{(\delta^{\frac{1}{2}}\bar{x})^2} + \frac{a_0 c_a}{6} \right) + o\left(\frac{\delta}{\epsilon}\right) \quad (2.68)$$

For (2.67) and (2.68) to be equal

$$a_0 = 4, \text{ and } \delta = \mu\epsilon. \quad (2.69)$$

To determine  $c_a$  we match the four terms in the space-charge layer expansion (2.32), (2.36), (2.51), and (2.55) to the two-term intermediate expansion (2.39) and (2.46). The series approximations for  $\bar{E}_0$  and  $\bar{E}_1$  as  $\bar{x} \rightarrow \infty$  and  $\tilde{E}_0$  as  $\tilde{x} \rightarrow 0$  are (2.67) and (2.68), respectively. The  $O(\delta^{\frac{3}{2}}/\epsilon)$  correction to the

space-charge field,  $\overline{E}_2$ , as  $\bar{x} \rightarrow \infty$  is

$$\overline{E}_2(\bar{x}) \sim \frac{c_b}{3}\bar{x} + \frac{2c_b}{3} + \frac{4c_b}{3\bar{x}^2} + o\left(\frac{1}{\bar{x}^3}\right), \quad (2.70)$$

while the  $O(\delta^2/\epsilon)$  correction,  $\overline{E}_3$ , is approximated as (2.55) as  $\bar{x} \rightarrow \infty$ . The first four terms in the expansion for the space-charge layer field ( $\overline{E}_0$ ,  $\overline{E}_1$ ,  $\overline{E}_2$ , and  $\overline{E}_3$ ) are rewritten as functions of the intermediate spatial variable,  $\tilde{x}$ , through the relation,  $\bar{x} = \tilde{x}/\delta^{\frac{1}{2}}$ , which gives

$$\begin{aligned} \overline{E}(\tilde{x}) &= \frac{\delta^{\frac{1}{2}}}{\epsilon} \left( \frac{-2}{\tilde{x}} + \frac{c_a}{3}\tilde{x} + \frac{c_a^2 - 9c_a V_\star}{90}\tilde{x}^3 \right) \\ &+ \frac{\delta}{\epsilon} \left( \frac{4}{\tilde{x}^2} + \frac{2c_a}{3} + \frac{c_b}{3}\tilde{x} + \frac{4c_a^2 - 21c_a V_\star}{60}\tilde{x}^2 \right) + o\left(\frac{\delta}{\epsilon}\right) \end{aligned} \quad (2.71)$$

The power series expansion of the first two terms representing the intermediate field as  $\tilde{x} \rightarrow 0$  are given by (2.66) and (2.46). These terms are rewritten in terms of the space-charge layer spatial coordinate  $\bar{x}$  as

$$\begin{aligned} \tilde{E}(\bar{x}) &= \frac{\delta^{\frac{1}{2}}}{\epsilon} \left( \frac{-2}{(\delta^{\frac{1}{2}}\bar{x})} + \frac{c_a}{3}(\delta^{\frac{1}{2}}\bar{x}) - \frac{7c_a^2}{180}(\delta^{\frac{1}{2}}\bar{x})^3 \right) \\ &+ \frac{\delta}{\epsilon} \left( \frac{4}{(\delta^{\frac{1}{2}}\bar{x})^2} + \frac{2c_a}{3} + \frac{c_b}{3}(\delta^{\frac{1}{2}}\bar{x}) + \frac{15c_a V_\star - 14c_a^2}{60}(\delta^{\frac{1}{2}}\bar{x})^2 \right) + o\left(\frac{\delta}{\epsilon}\right) \end{aligned} \quad (2.72)$$

After rewriting (2.71) and (2.72), it is clear that the following matching conditions result:

$$\frac{c_a^2 - 9c_a V_\star}{90} = -\frac{7}{180}c_a^2, \quad \text{and} \quad \frac{4c_a^2 - 21c_a V_\star}{60} = \frac{15c_a V_\star - 14c_a^2}{60}. \quad (2.73)$$

Both of these conditions yield the same expression for  $c_a$ ; namely,

$$c_a = 2V_\star. \quad (2.74)$$

## 2.A.2 Integral Constraint

An integral constraint (2.25) relates the applied potential to the integral of the electric field across the thin film. The integral (2.25) is broken up into three regions, corresponding to the electric field profiles in the space charge layer, intermediate layer, and in the bulk. Thus,

$$\frac{1}{2}\mu V_{\star} = \int_0^{\frac{\eta}{\epsilon}} \bar{E}(\bar{x}) d\bar{x} + \int_{\frac{\eta\delta^{\frac{1}{2}}}{\epsilon}}^{\frac{\gamma\delta^{\frac{1}{2}}}{\epsilon}} \tilde{E}(\tilde{x}) d\tilde{x} + \int_{\gamma}^{\frac{1}{2}} E_B(x) dx. \quad (2.75)$$

In the space charge layer, the lower bound is zero at the anode, while the upper bound is a regularization variable  $\eta$  normalized by the space-charge layer width  $\epsilon$ , where  $\epsilon \ll \eta \ll \epsilon/\delta^{\frac{1}{2}}$ . In the intermediate layer, the bounds are the variables  $\eta$  and  $\gamma$  normalized by the intermediate layer width  $\epsilon/\delta^{\frac{1}{2}}$ , where  $\epsilon/\delta^{\frac{1}{2}} \ll \gamma \ll 1$ . The purpose of  $\eta$  and  $\gamma$  are to avoid diverging contributions from the space-charge layer and intermediate integrals as  $\bar{x} \rightarrow \infty$ ,  $\tilde{x} \rightarrow 0$ , and  $\tilde{x} \rightarrow \infty$  respectively. The final result cannot depend on  $\eta$  or  $\gamma$ . The integral of the space-charge field is

$$\int_0^{\frac{\eta}{\epsilon}} \bar{E}(\bar{x}) d\bar{x} \sim \int_0^{\frac{\eta}{\epsilon}} \bar{E}_0(\bar{x}) d\bar{x} + \int_0^{\frac{\eta}{\epsilon}} \delta \bar{E}_1(\bar{x}) d\bar{x} + O\left(\frac{\delta^{\frac{3}{2}}\eta^2}{\epsilon^2}\right), \quad (2.76)$$

where the error originates from the integral of the next term,  $\delta^{\frac{3}{2}}\bar{E}_2(\bar{x})$ , across the space charge layer. The integral of the leading order field (2.32) is

$$\int_0^{\frac{\eta}{\epsilon}} \bar{E}_0(\bar{x}) d\bar{x} = \int_0^{\frac{\eta}{\epsilon}} \frac{-2}{\bar{x} + 2} d\bar{x} \sim -2 \ln \frac{\eta}{\epsilon} + 2 \ln 2 + O\left(\frac{\epsilon}{\eta}\right), \quad (2.77)$$

while the integral of the first correction (2.36) is

$$\int_0^{\frac{\eta}{\epsilon}} \delta \bar{E}_1(\bar{x}) d\bar{x} = \int_0^{\frac{\eta}{\epsilon}} \delta c_a \frac{12 + 12\bar{x} + 6\bar{x}^2 + \bar{x}^3}{3(2 + \bar{x})^2} d\bar{x} \sim \frac{c_a}{6} \frac{\delta \eta^2}{\epsilon^2} + O\left(\frac{\delta \eta}{\epsilon}\right). \quad (2.78)$$

In the intermediate layer, the integral of the leading order field (2.39) is

$$\int_{\frac{\eta\delta^{\frac{1}{2}}}{\epsilon}}^{\frac{\gamma\delta^{\frac{1}{2}}}{\epsilon}} \tilde{E}_0(\tilde{x}) d\tilde{x} \sim \int_{\frac{\eta\delta^{\frac{1}{2}}}{\epsilon}}^{\infty} \frac{-2\sqrt{c_a}}{\sinh \sqrt{c_a}\tilde{x}} d\tilde{x} \sim \ln \delta + 2 \ln \frac{\eta}{\epsilon} + \ln c_a - 2 \ln 2 - \frac{c_a}{6} \frac{\delta \eta^2}{\epsilon^2} + O\left(\frac{\delta^2 \eta^4}{\epsilon^4}\right). \quad (2.79)$$

Finally, the integral of the bulk field, whose lower limit  $\gamma$  is replaced by 0 since the bulk field is a constant to leading order, is

$$\int_0^{\frac{1}{2}} E_B(x) dx \sim \frac{1}{2} \frac{\delta}{\epsilon} V_{\star} + O\left(\frac{\delta}{\epsilon}\right). \quad (2.80)$$

The contributions (2.77)-(2.80) are summed, resulting in

$$\frac{1}{2} \mu V_{\star} + \ln c_a \delta + \dots \quad (2.81)$$

Thus, (2.75) is asymptotic to (2.81) to  $O(\mu)$ ; however, there is an  $O(\ln \delta)$  mismatch. Therefore, the bulk field is adjusted to  $E_B = \mu V_{\star} - 2 \ln \delta c_a$ . Note, this adjustment of  $E_B$  does not affect any of the preceding analysis.

The new expression for the bulk electric field, after substituting for  $\mu V_{\star}$ ,  $\delta$ , and  $c_a$  according to (2.24), (2.47), and (2.56), respectively, is thus

$$E_B = V - 2 \ln 2 \epsilon V + o(\ln \delta). \quad (2.82)$$

# 3. Moving Ion Fronts in Mixed Ionic-Electronic Conducting Polymer Films

## 3.1 Introduction

Mixed ionic-electronic conductors (MIECs) are materials that conduct both electronic (electrons or holes) and ionic charge carriers.<sup>69</sup> Certain organic semiconductors are MIECs; the ability to transport ionic and electronic charge carriers opens up organic electronics to a wide range of promising applications including gas sensors,<sup>70,71</sup> light-emitting electrochemical cells,<sup>18,19</sup> superconductors,<sup>16,17</sup> and transistors.<sup>15,72</sup>

MIECs based on organic semiconductors are used in biosensors to detect the presence of ions in biological tissue.<sup>13</sup> An example biosensor device is the Organic Electrochemical Transistor<sup>73</sup> (OECT), which consists of a gate electrode immersed in an electrolyte, in contact with an organic semiconductor film sandwiched between a grounded source electrode and a drain electrode where the voltage is applied.<sup>74</sup> The applied voltage drives the injection of ions from the electrolyte into the polymer film. The ions displace electronic charge carriers that evacuate the thin film across the source electrode, resulting in the con-

version of an ionic current to an electrical signal. For example, Bernards *et al.*<sup>75</sup> employed an OECT to measure glucose concentrations in the blood stream, while Tarabella *et al.*<sup>76</sup> designed an OECT to monitor micelle formation in an electrolyte. The conjugated polymer poly(3,4-ethylenedioxythiophene) doped with negatively charged poly(styrenesulfonate) (PEDOT:PSS) is an organic biocompatible MIEC commonly used in biosensors due to its high ion and hole mobilities, flexibility, and stability.<sup>77</sup>

The electrical mobility is defined as the ratio of the drift velocity of a charged species to the magnitude of the applied electric field.<sup>78</sup> Accurate prediction and measurement of the mobility of ionic species in an organic MIEC is key to characterizing ion transport. However, the mobility is challenging to determine because standard techniques to measure charge carrier mobility, such as time of flight measurements,<sup>79</sup> are difficult to implement in organic MIECs.<sup>1</sup> Stavrinidou *et al.*<sup>1</sup> designed a device to measure ion mobility in organic MIECs, which is depicted in figure 3.1. Their device is comprised of a gold cathode adjacent to a PEDOT:PSS polymer thin film in contact with an electrolyte. A reference electrode in the electrolyte completes the circuit. The

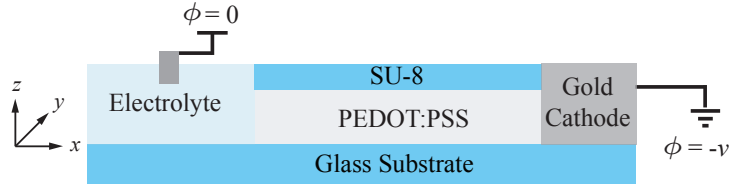


Figure 3.1: Schematic of the planar organic semiconductor device designed by Stavrinidou *et al.*<sup>1</sup> The device consists of a 32 mm  $\times$  16 mm  $\times$  400 nm ( $x \times y \times z$ ) PEDOT:PSS film in contact with a gold cathode and an electrolyte reservoir, sandwiched between an SU-8 ion barrier layer and a glass substrate. The potential is  $\phi$ . The magnitude of the applied voltage,  $v$ , is around 2 volts.

polymer thin film is enriched in holes compensated by the fixed negative charge on the functional groups of PSS. When a constant voltage is applied across the electrodes the cations displace the positively charged holes, which exit at the cathode resulting in an electric signal indicating the presence of invading ions. The PEDOT:PSS is electrochromic, so the film changes color based on the density of electrons and holes. As the holes evacuate, transmittance of light through the device increases. The measured change in transmittance  $\Delta T$  is the change in transmittance relative to the transmittance in the absence of an applied field. Stavrinidou *et al.*<sup>1</sup> measured the transmittance along the film with time in order to determine the profile of the invading cations. They define the cation drift length  $\delta$  as the location where  $\Delta T$  is one half of its maximum value. Stavrinidou *et al.*<sup>1</sup> find that the drift length increases as the square-root of time,  $\delta \sim t^{1/2}$ , for a range of electrolytes. Thus, it is inferred that the moving cation front also advances as  $t^{1/2}$ .

In an earlier paper, Stavrinidou *et al.*<sup>20</sup> analyzed the invasion of cations via a circuit model comprised of two resistors in series. The holes are far more mobile than the ions, hence the voltage drops primarily across the cation-rich region, or resistor. They found that the drift length  $\delta = \sqrt{2\mu_p vt}$  where  $\mu_p$  is the cation mobility, and  $v$  is the applied voltage. Stavrinidou *et al.*<sup>1</sup> combined this result with the measurement of the change in drift length with time to determine the cation mobility,  $\mu_p$ , assumed to be a constant (i.e. no field dependence). They also solved the governing differential equations for charge carrier transport numerically to confirm the  $\delta = \sqrt{2\mu_p vt}$  relation.

The square-root-of-time front scaling is intriguing for several reasons. First, this scaling is typically associated with a diffusive process, yet in this case electro-migration is expected to dominate ion transport due to the large applied voltage. We define “large” as an applied voltage much greater than the

thermal voltage,  $k_B T/q \approx 26$  mV, where  $k_B$  is the Boltzmann constant,  $T$  is temperature, and  $q$  is the charge of a proton. However, diffusion presumably plays a role as the measured and calculated cation density profiles are not sharp fronts, as would be expected if ion transport were solely due to electromigration. Moreover, the spatial cation profiles noticeably broaden in time due to diffusion. What is the relative importance of diffusion versus migration? Additionally, the invading cations eventually reach the cathode, so the  $\delta \sim t^{1/2}$  scaling cannot persist indefinitely. When does the scaling break down? Here, we answer these questions by constructing and analyzing a mathematical model for the front invasion dynamics.

Moving front dynamics of charged species also appear during redox reactions and electrical switching in conjugated polymer thin films,<sup>80–83</sup> and in electrophoretic separations in aqueous media.<sup>84–87</sup> The advancement of the moving front can be linear in time  $t^{81,85,86}$  or proportional to  $t^{1/280,82,83,87}$  depending on the material properties and device geometry. Mani *et al.*<sup>88</sup> and Zangle *et al.*<sup>89</sup> demonstrated that ion concentration polarization fronts at a microchannel-nanochannel junction can propagate as enrichment and depletion shocks. Under a constant current, these shocks advance linearly in time; for a fixed potential difference, the shocks advance as  $t^{1/2}$  and the shock thickness increases as  $t^{1/2}$ .<sup>90</sup> Mani and Bazant<sup>91</sup> demonstrated that a variety of scalings for the shock advancement and thickness can be obtained in microchannels with a power-law growth in width; moreover, the evolution of the shock is self-similar. It will be shown that the present problem shares certain similarities to the propagation of concentration polarization under constant voltage.

In the following section, we present the governing drift-diffusion equations for ion invasion across an MIEC film. Next, we simplify the drift-diffusion

equations in the experimentally relevant limits of large applied voltage, a high hole mobility to cation mobility ratio, and local electroneutrality. We apply a similarity transformation to the simplified drift-diffusion equations governing the cation invasion and hole displacement. The results section includes comparisons between the similarity solutions and numerical solution of the full drift-diffusion equations. We then compare our results to the experiments of Stavrinidou *et al.*<sup>1</sup>

## 3.2 Governing Equations

The invasion of cations and displacement of holes in a planar MIEC device is depicted in figure 3.2. Figure 3.2(a) shows the device at time  $t = 0$  when the electric field is applied. Initially, the polymer film is enriched in holes compensated by fixed anions supplied by the polymer backbone. We assume that the initial hole and fixed anion densities are uniform. In figure 3.2(b), at a later time  $t > 0$ , cations are injected at the electrolyte-polymer interface and invade the film, displacing holes that evacuate across the cathode. The electrolyte is assumed to be a well-mixed reservoir. The cathode accepts holes but is a blocking electrode for the ions; similarly, holes do not enter the electrolyte reservoir. To model ionic and electronic charge transport in this device,

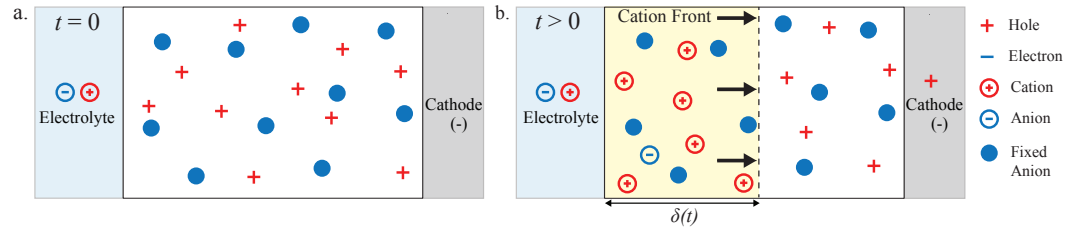


Figure 3.2: Cation invasion schematic: a) Initially, the thin film includes uniformly distributed fixed anions and holes. b) After a potential is applied, cations (and some anions) enter the film, displacing holes. The invasion length is  $\delta(t)$ .

we turn to the drift-diffusion equations, which consist of an equation for car-

rier flux that accounts for both diffusion and migration of charged species, a charge conservation equation, and Poisson's equation that relates the electric field to the local charge density. Note, the drift-diffusion equations are mathematically equivalent to the Poisson-Nernst-Planck equations: the former is typically used as a moniker for electronic charge transport, the later for ionic transport. Here, we refer to the governing equations for ionic and electronic transport as the drift-diffusion equations uniformly. Given the device dimensions,  $32 \text{ mm} \times 16 \text{ mm} \times 400 \text{ nm}$  ( $x \times y \times z$ ),<sup>1</sup> we assume that the ion and hole transport is predominately one-dimensional along the  $x$ -direction between the electrolyte and the electrode.

The flux of a charged species is equal to the sum of the fluxes due to diffusion and migration. The cation flux  $j_p$  is

$$j_p = -\mu_p \frac{k_B T}{q} \frac{\partial p}{\partial x} + \mu_p p e, \quad (3.1)$$

where  $p$  is the cation density,  $e = -\partial\phi/\partial x$  is the electric field,  $\phi$  is the electric potential, and  $x$  is the position in the direction of the width of the thin film. Similarly, the flux of holes  $j_h$  is

$$j_h = -\mu_h \frac{k_B T}{q} \frac{\partial h}{\partial x} + \mu_h h e, \quad (3.2)$$

where  $h$  is the hole density and  $\mu_h$  is the hole mobility. The flux of mobile anions from the reservoir is

$$j_n = -\mu_n \frac{k_B T}{q} \frac{\partial n}{\partial x} - \mu_n n e, \quad (3.3)$$

where  $n$  is the mobile anion density and  $\mu_n$  is the anion mobility. Poisson's

equation relates the variation in electric field to the local space charge density,

$$\frac{\partial e}{\partial x} = \frac{q}{\varepsilon}(p + h - n - a), \quad (3.4)$$

where  $a$  is the density of the uniform, fixed anions on the polymer backbone, and  $\varepsilon$  is the permittivity of the film. The final set of equations are charge conservation equations,

$$\frac{\partial p}{\partial t} = -\frac{\partial j_p}{\partial x}, \quad \frac{\partial h}{\partial t} = -\frac{\partial j_h}{\partial x}, \quad \text{and} \quad \frac{\partial n}{\partial t} = -\frac{\partial j_n}{\partial x}, \quad (3.5)$$

where  $t$  is time.

At the electrolyte-polymer film interface, we assume that the reservoir concentration of ions is equal to the concentration of fixed anions on the polymer backbone. At the electrode, we assume that there are no faradaic reactions between the ions and the electrode, regardless of the applied voltage. This assumption is dependent on the ion and electrode material selected. The corresponding boundary condition is a no-flux condition for the ions. Initially, the cation density in the film is zero. The boundary and initial conditions for cations are expressed mathematically as

$$p(0, t) = a, \quad \frac{k_B T}{q} \frac{\partial p(l, t)}{\partial x} = p(l, t)e(l, t), \quad \text{and} \quad p(x, 0) = 0, \quad (3.6)$$

where  $l$  is the width of the polymer film. Similarly, the boundary and initial conditions for anions are

$$n(0, t) = a, \quad \frac{k_B T}{q} \frac{\partial n(l, t)}{\partial x} = -n(l, t)e(l, t), \quad \text{and} \quad n(x, 0) = 0. \quad (3.7)$$

The boundary conditions for the holes include a no-flux condition at the

electrolyte-polymer interface, because the electrolyte does not conduct holes, and a reservoir condition at the electrode. Initially the hole density is assumed to be equal to the fixed anion density. These conditions are

$$\frac{k_B T}{q} \frac{\partial h(0, t)}{\partial x} = h(0, t)e(0, t), \quad h(l, t) = a, \quad \text{and} \quad h(x, 0) = a. \quad (3.8)$$

The boundary conditions for the electric potential are

$$\phi(0, t) = 0, \quad \text{and} \quad \phi(l, t) = -v, \quad (3.9)$$

corresponding to a fixed potential difference  $v$  across the film.

We now non-dimensionalize the governing equations by normalizing  $p$ ,  $n$ , and  $h$  by  $a$ , the uniform negative backbone density;  $x$  by  $l$ , the width of the thin film; and  $e$  by  $v/l$ , the applied voltage divided by the width of the film. Time  $t$  is normalized by the time for cations to migrate across the film at a given applied voltage,  $t \sim l^2/\mu_p v$ . There is evidence that the carrier mobility is field-dependent in disordered polymers,<sup>92,93</sup> however for simplicity we assume that all carrier mobilities are constant.

The dimensionless charge conservation equations for cations and anions (3.5), when the equations for flux (3.1)-(3.3) are inserted, are

$$\frac{\partial \hat{p}}{\partial \hat{t}} = \frac{1}{\hat{v}} \frac{\partial^2 \hat{p}}{\partial \hat{x}^2} - \frac{\partial}{\partial \hat{x}}(\hat{p}\hat{e}), \quad \text{and} \quad \frac{\partial \hat{n}}{\partial \hat{t}} = \frac{1}{\hat{v}} \frac{\partial^2 \hat{n}}{\partial \hat{x}^2} + \frac{\partial}{\partial \hat{x}}(\hat{n}\hat{e}), \quad (3.10)$$

where the caret superscript indicates a dimensionless variable or parameter. The parameter  $\hat{v}$  is the dimensionless group  $\hat{v} = vq/k_B T$ , where  $k_B T/q$  is the thermal voltage. The dimensionless charge conservation equation for holes is

$$\frac{\partial \hat{h}}{\partial \hat{t}} = \frac{\hat{m}}{\hat{v}} \frac{\partial^2 \hat{h}}{\partial \hat{x}^2} - \hat{m} \frac{\partial}{\partial \hat{x}}(\hat{h}\hat{e}), \quad (3.11)$$

where  $\hat{m} = \mu_h/\mu_p$  is the ratio of the hole mobility to the cation mobility. The dimensionless Poisson equation is

$$\epsilon^2 \hat{v} \frac{\partial \hat{e}}{\partial \hat{x}} = \frac{1}{2}(\hat{p} + \hat{h} - \hat{n} - 1), \quad (3.12)$$

where  $\hat{\epsilon}$  is the ratio of the Debye length  $\lambda_d = \sqrt{\epsilon k_B T / 2q^2 a}$  to the width of the film, defined as  $\hat{\epsilon} = \lambda_d / l$ . The Debye length characterizes the width of the screening layer adjacent to a charged surface, such as the polymer-electrolyte or polymer-cathode interfaces. In the device designed by Stavrinidou *et al.*,<sup>1</sup>  $\hat{\epsilon} \approx 10^{-9}$  based on a PEDOT:PSS dielectric constant of  $\epsilon_r = 3.5$ ,  $l = 32$  nm,  $T = 300$  K and  $a = 3 \times 10^{20}$  cm<sup>-3</sup>.<sup>1</sup> In the numerical solution to the full drift-diffusion equations, the dimensionless Debye length is taken to be  $\hat{\epsilon} = 0.001$ . This value of  $\hat{\epsilon}$  was selected because the experimental value is numerically intractable with the solvers used here. However, note that the larger value of  $\hat{\epsilon}$  should not affect the dynamics as the majority of the film is electroneutral. The dimensionless boundary and initial conditions for cations are

$$\hat{p}(0, \hat{t}) = 1, \quad \frac{\partial \hat{p}(1, \hat{t})}{\partial \hat{x}} = \hat{v} \hat{p}(1, \hat{t}) \hat{e}(1, \hat{t}) \text{ and } \hat{p}(\hat{x}, 0) = 0. \quad (3.13)$$

Similarly, the dimensionless boundary and initial conditions for anions are

$$\hat{n}(0, \hat{t}) = 1, \quad \frac{\partial \hat{n}(1, \hat{t})}{\partial \hat{x}} = -\hat{v} \hat{n}(1, \hat{t}) \hat{e}(1, \hat{t}) \text{ and } \hat{n}(\hat{x}, 0) = 0. \quad (3.14)$$

The dimensionless boundary and initial conditions for holes are

$$\frac{\partial \hat{h}(0, \hat{t})}{\partial \hat{x}} = \hat{v} \hat{h}(0, \hat{t}) \hat{e}(0, \hat{t}), \quad \hat{h}(1, \hat{t}) = 1 \text{ and } \hat{h}(\hat{x}, 0) = 1. \quad (3.15)$$

Finally, the dimensionless boundary conditions for the electric potential are

$$\hat{\phi}(0, \hat{t}) = 0 \text{ and } \hat{\phi}(1, \hat{t}) = -1. \quad (3.16)$$

The dimensionless equations (3.10)- (3.12) and boundary conditions (3.13)- (3.16) are the basis for our analysis of moving front dynamics in a planar MIEC device. In the following section, we consider a simplified description of front dynamics at large voltages, which is followed by numerical solution of the full equations in the results section.

### 3.3 Large Voltage Analysis: Similarity Solution

The governing equations (3.10)-(3.16) presented above can be simplified by considering the experimentally relevant case of a large voltage, a high hole-to-cation mobility ratio, and local electroneutrality. At large voltages  $\hat{v} \gg 1$  the flux of anions from the electrolyte into the film can be neglected, since the strongly biased voltage prevents their entry. The smallness of the Debye length  $\hat{\epsilon} \approx 10^{-9}$  in Stavriniidou *et al.*'s<sup>1</sup> experiments indicates that the charge density is confined to extremely thin regions immediately adjacent to the electrolyte- and electrode- polymer film interfaces, while the bulk of the film is electroneutral. When we assume electroneutrality and neglect the presence of anions in the film, Poisson's equation (3.12) is replaced by the algebraic constraint

$$\hat{p} + \hat{h} = 1. \quad (3.17)$$

Lastly, a mobility ratio of  $\hat{m} \sim 100$  is expected.<sup>20</sup> As the mobility ratio increases to infinity, the potential drop is confined to the cation-rich region be-

hind the moving front, and the electric field in the hole-rich region approaches zero. Effectively, the resistance of the hole region is negligible in comparison to that of the cation region. Henceforth, we assume the limit  $\hat{m} \rightarrow \infty$ .

Under the above assumptions, the drift-diffusion equations (3.10)-(3.12) can be transformed from partial differential equations to ordinary differential equations via a similarity transformation. The similarity transformation asserts that the relevant length scale in the problem is the (unknown *a priori*) invasion length  $\delta$ , rather than the film width  $l$ . This is reasonable at the above conditions ( $\hat{v} \gg 1$ ,  $\hat{m} \gg 1$ ) since the voltage is effectively dropped across  $\delta$  rather than  $l$ .

An expression for  $\delta$  can be found via the following argument. Assuming that electro-migration is the dominant transport mechanism for ions, the velocity of the front,  $d\delta/dt \sim \mu_p e$ . The field exists primarily in the cation-rich region, hence  $e \sim v/\delta$ , giving  $d\delta/dt \sim \mu_p v/\delta$ , and thus  $\delta \sim \sqrt{\mu_p v t}$ . For ease of algebra, we multiply the right-hand-side by  $\sqrt{2}$  and define

$$\delta(t) = \sqrt{2\mu_p v t}. \quad (3.18)$$

The invasion length  $\delta$  is normalized by the film width  $l$ ; and time by  $l^2/\mu_p v$ , the cation migration timescale. The dimensionless invasion length is

$$\hat{\delta}(\hat{t}) = \sqrt{2\hat{t}}. \quad (3.19)$$

This result is consistent with the invasion length given by the circuit model of Stavrinidou *et al.*<sup>20</sup> A similarity variable  $\hat{\eta}$  is defined as

$$\hat{\eta} = \frac{\hat{x}}{\sqrt{2\hat{t}}}. \quad (3.20)$$

To transform the governing equations, we first redefine the dependent variables in terms of the similarity variable,  $\hat{\eta}$ . The cation density is  $\hat{p}(\hat{x}, \hat{t}) = \hat{P}(\hat{\eta})$ , and the hole density is  $\hat{h}(\hat{x}, \hat{t}) = \hat{H}(\hat{\eta})$ . The electric field scales as the potential,  $\hat{\phi}(\hat{x}, \hat{t})$ , divided by  $\hat{\delta}$ , since the bulk of the potential drop is confined to the cation-rich region of width  $\hat{\delta}$ . The electric field scaling is therefore  $\hat{e}(\hat{x}, \hat{t}) = \hat{E}(\hat{\eta})/\hat{\delta}$ .

The cation density at the electrode ( $\hat{x} = 1$ ) satisfies a no-flux condition (3.13). It is expected that the similarity solution should be valid at early times when the moving front is far from the electrode and unaffected by its presence; that is, the front effectively advances into a semi-infinite half-space. Hence, this no-flux condition is replaced by the requirement that the cation density is equal to zero far ahead of the front,  $\hat{p}(\infty, \hat{t}) = 0$ . This new boundary condition and the initial condition  $\hat{p}(\hat{x}, 0) = 0$  collapse into a single boundary condition as  $\hat{\eta} \rightarrow \infty$ . The two boundary conditions for the cation density are thus

$$\hat{P}(0) = 1 \text{ and } \hat{P}(\infty) \rightarrow 0. \quad (3.21)$$

Assuming that the potential drop occurs in the cation-rich region and that the potential is constant in the hole-rich region, the electric field beyond the moving front is zero. In terms of the similarity variable, then

$$\hat{E}(\infty) \rightarrow 0. \quad (3.22)$$

The transformed cation conservation equation (3.10) is thus

$$\hat{\eta} \frac{d\hat{P}}{d\hat{\eta}} = -\frac{1}{\hat{v}} \frac{d^2\hat{P}}{d\hat{\eta}^2} + \frac{d}{d\hat{\eta}}(\hat{P}\hat{E}). \quad (3.23)$$

The transformed hole equation (3.11) is

$$\frac{\hat{\eta}}{\hat{m}} \frac{d\hat{H}}{d\hat{\eta}} = -\frac{1}{\hat{v}} \frac{d^2\hat{H}}{d\hat{\eta}^2} + \frac{d}{d\hat{\eta}}(\hat{H}\hat{E}). \quad (3.24)$$

The similarity solution is only valid when the mobility ratio  $\hat{m} \rightarrow \infty$ , indicating that there is no potential drop across the hole-rich region. At this limit, the left-hand side of (3.24) is negligible in comparison to the right-hand side. Thus, the hole density satisfies the equation

$$0 = -\frac{1}{\hat{v}} \frac{d^2\hat{H}}{d\hat{\eta}^2} + \frac{d}{d\hat{\eta}}(\hat{H}\hat{E}). \quad (3.25)$$

Equation (3.25) implies that the holes evolve in a quasi-steady manner. Since they are infinitely more mobile than the cations, they respond instantaneously to the slow cation front dynamics. The electroneutrality equation (3.17),  $\hat{H} = 1 - \hat{P}$ , is inserted into (3.25) to eliminate  $\hat{H}$ , yielding after rearrangement

$$-\frac{1}{\hat{v}} \frac{d^2\hat{P}}{d\hat{\eta}^2} + \frac{d}{d\hat{\eta}}(\hat{P}\hat{E}) = \frac{d\hat{E}}{d\hat{\eta}}. \quad (3.26)$$

The left-hand side of (3.26) is equal to the right-hand side of (3.23). Combining these two equations yields

$$\hat{\eta} \frac{d\hat{P}}{d\hat{\eta}} = \frac{d\hat{E}}{d\hat{\eta}}. \quad (3.27)$$

Equations (3.23) and (3.27) and the boundary conditions (3.21) and (3.22) are solved simultaneously to give the cation density and electric field profiles. These equations are ordinary differential equations and thereby easier to solve numerically than the full partial differential drift-diffusion equations. Moreover, the similarity transformation yields considerable insight into the physics of the cation invasion process, revealing the self-similarity of the moving front dynamics.

### 3.4 Results

We solve the self-similar differential equations (3.23) and (3.27) with Matlab's bvp4c function, a collocation code for boundary value problems.<sup>94</sup> The semi-infinite domain  $\eta = [0, \infty)$  is truncated at a finite value  $\eta_f$ ; the similarity equations are solved at progressively larger values of  $\eta_f$  to ensure convergence. Here, we present comparisons between the similarity solution and the solution to the full drift-diffusion equations (3.10)-(3.16), which are solved numerically by Matlab's pdepe function. The parameters used in comparing the similarity solution to the numerical solution of the full drift-diffusion equations and the experiments are summarized in table 4.1.

|                                | Full Drift-Diffusion | Similarity Solution | Experiments        |
|--------------------------------|----------------------|---------------------|--------------------|
| Debye Length, $\hat{\epsilon}$ | $10^{-3}$            | 0                   | $2 \times 10^{-9}$ |
| Applied Voltage, $\hat{v}$     | 40                   | 40 and 76.92        | 76.92              |
| Mobility Ratio, $\hat{m}$      | $10^2$               | $\infty$            | $10^2$             |

Table 3.1: Summary of the parameters used in the solution to the full drift-diffusion equations and the similarity solution in comparison to the dimensionless experimental parameters. The dimensional experimental parameters are as follows:  $\lambda_d = 2 \times 10^{-11}$  m,  $v = 2$  V, and  $\mu_p = 0.144$  mm<sup>2</sup>/Vs. The similarity solution is compared to both the full drift-diffusion equations and the experiments, so two applied voltages are listed.

Figure 3.3 compares the evolution of the ionic charge density and electric field across the film from the similarity solution and full drift-diffusion equations. The dimensionless voltage is  $\hat{v} = 40$ , which corresponds to a voltage of 1.02 volts, an experimentally relevant voltage. In the solution to the full drift-diffusion equations,  $\hat{\epsilon} = 0.001$ . Admittedly, this value of  $\hat{\epsilon}$  is much larger than in experiments, where  $\hat{\epsilon} \approx 10^{-9}$ ; at smaller values of  $\hat{\epsilon}$  sharp gradients in the ion profiles develop in the screening layers at the electrolyte-film and film-electrode interfaces that render the solution to the full drift-diffusion equations numerically intractable. This underscores the utility of the similarity solution,

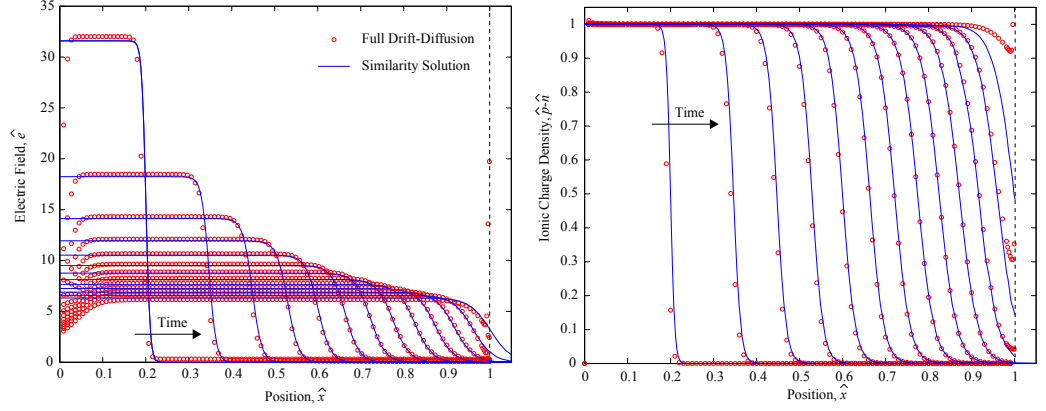


Figure 3.3: Comparison of the similarity solution (line) to the solution of the full drift-diffusion equations (circles) for a) the electric field  $\hat{e}$  and b) the ionic charge density  $\hat{p} - \hat{n}$ . Note that in the similarity solution  $\hat{n} = 0$ , so that the charge density is equal to the cation density  $\hat{p}$ . The dimensionless applied voltage is  $\hat{v} = 40$  which corresponds to a dimensional voltage of 1.02 volts, the mobility ratio  $\hat{m} = 100$ , and the dimensionless Debye length is  $\hat{\epsilon} = 0.001$ . The first curve from left to right is at  $\hat{t} = 0.02$ , and each successive curve corresponds to a time increment of 0.04. After the front reaches the wall in (b), the charge accumulates in a Debye layer, leading to a spike in the electric field in (a).

which is much easier to solve numerically yet evidently compares very well with the full drift-diffusion equations. In order to obtain converged solutions to the full drift at smaller values of  $\hat{\epsilon}$ , the pdepe solver could be replaced with more powerful numerical schemes. Another approach would be to combine numerical solution with singular perturbation analysis of the rapid variation in concentration and electric potential within the Debye (or boundary) layers. We selected the pdepe solver in Matlab because it is simple to implement. The fact that the solution of the full drift-diffusion equations agrees well with the similarity solution validates our comparison of the similarity solution to the experimental results.

At early times the electric field is extremely large (figure 3.3(a)), because the potential drop is confined to the narrow region behind the moving front that has barely infiltrated the film. As the front progresses, the electric field

weakens as the potential drops over a widening cation-rich region. This evolution is reflected in the ionic charge density profile, given in figure 3.3(b). Specifically, the cation front is sharp at early times, indicating the dominance of electro-migration under the initially strong field. The front then broadens diffusively as it is driven to the electrode by the weakening field. The most significant deviation between the similarity solution and the full drift-diffusion equations occurs at the electrolyte-film interface ( $x = 0$ ), where the full drift-diffusion equations capture charge accumulation in the thin Debye layer (figure 3.3 (b)) and a spike in the electric field (figure 3.3 (a)). Recall, the similarity solution assumes electroneutrality and hence neglects the presence of the Debye layer. Nevertheless, the overall agreement between the similarity solution and the full numerical solution is excellent, which lends confidence to the assertion that invasion dynamics are self-similar.

To quantify the persistence of the  $t^{1/2}$  scaling of the front location, we calculated the moving front location at each time-step, defined as the  $x$ -position where the ionic charge density  $\hat{p} - \hat{n} = 0.5$ . This plot is shown in figure 3.4. At large voltages, the similarity solution prediction of the front location is accurate up until the point where the moving front reaches the electrode. This is a surprising result given that the similarity solution is formally valid at early times, when the front is far from the electrode,  $\delta \ll l$  (in dimensionless terms  $\hat{x} \ll 1$ ). To explain this, recall that the position of the front advances under the applied voltage as  $\delta \sim \sqrt{\mu_p v t}$ . The thickness  $\Delta$  of the front broadens diffusively as  $\Delta \sim (t\mu_p k_B T/q)^{1/2}$ , independent of the voltage. The ratio of the front thickness to front location is then  $\Delta/\delta \sim (k_B T/vq)^{1/2}$ , which decreases with increasing voltage as  $v^{-1/2}$ . Hence, at low voltages the diffusive thickening of the front causes the ions at the leading edge of the front to reach the electrode well before the bulk of the front, as seen in the inset of figure

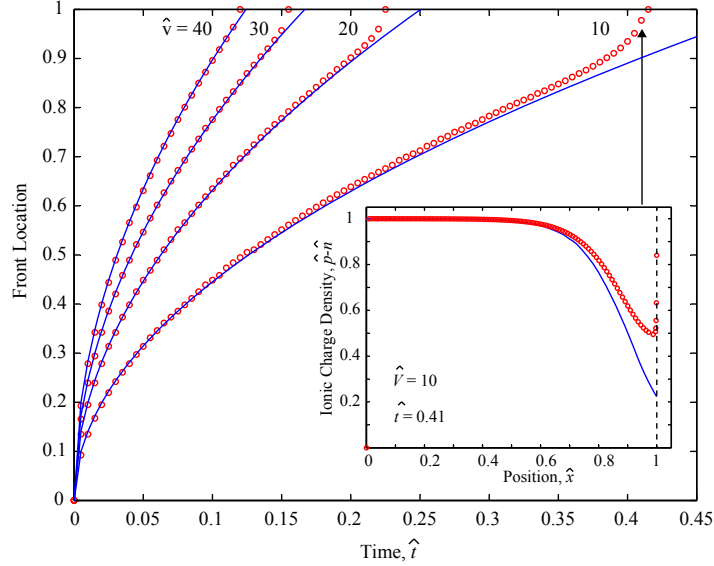


Figure 3.4: The time dependence of the location of the moving front (the position where  $\hat{p} - \hat{n} = 0.5$ ) from the similarity solution (3.19) for the dimensionless moving front location (solid line) is compared to the solution of the full drift-diffusion equations (circles) at various voltages,  $\hat{v} = 10, 20, 30, 40$ . Time  $\hat{t}$  is dependent upon voltage; here  $\hat{t}$  is scaled by  $\hat{v} = 10$ . Inset: the ionic charge density profile at  $\hat{v} = 10$  after the front reaches the electrode ( $\hat{t} = 0.41$ ). The full drift-diffusion equations capture the formation of a Debye layer, while the similarity solution does not.

3.4. Those leading ions then form a Debye layer at the electrode which causes the disparity between the front location predicted by the similarity solution and full solution. At larger voltages the front does not have the opportunity to thicken before it reaches the electrode. Consequently, the bulk of the ions reach the electrode very shortly after the ions at the leading edge, thereby reducing the disparity between the full drift-diffusion solution and the similarity solution.

Stavrinidou *et al.*<sup>1</sup> measured the change in transmittance of an electrochromatic PEDOT:PSS polymer film during potassium invasion. Assuming that the transmittance is equal to the normalized cation density, in figure 3.5 we digitized the transmittance data given in figure 1(c) of Stavrinidou *et al.*<sup>1</sup> and compared it to the similarity solution. The applied voltage in the experiment is

2 volts, or  $\hat{v} = 76.92$ , and the potassium mobility is  $\mu_p = 0.14 \pm 0.02 \text{ mm}^2/\text{V s}$ , as calculated by Stavriniidou *et al.*<sup>1</sup> In the inset, figure 3.5c, we fit the square of the front location with (3.19) and find that the data do not pass through the origin, indicating that there is a time lag between the time that the voltage is applied and the invasion of the cations. To account for this, we modified (3.19) to include a time lag term  $t_{lag}$ . We fit the modified expression,  $\delta^2 = 2\mu_p v(t - t_{lag})$ , to the data and estimated the time lag to be  $t_{lag} = 2.73 \text{ s}$ . The value of  $t_{lag}$  does not affect the similarity solution, aside from a shift in the cation density profiles with respect to time.

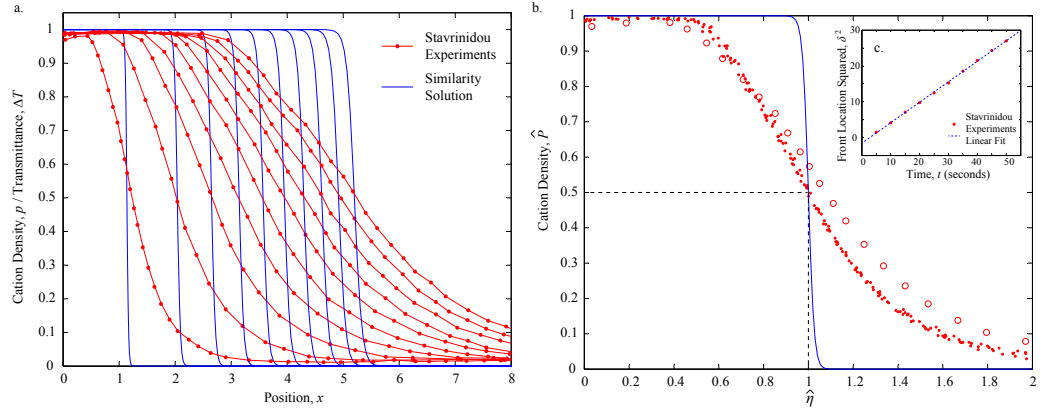


Figure 3.5: a) Comparison between transmittance data by Stavriniidou *et al.*<sup>1</sup> (symbols joined by line) and the similarity solution for the cation density (line) at an applied voltage of 2 V ( $v = 76.92$ ),  $\mu_p = 0.14 \text{ mm}^2/\text{Vs}$ , and a time lag of  $t_{lag} = 2.73 \text{ s}$ . The transmittance profiles are shown at 5 second increments. b.) The  $x$ -position of the experimental data (red dots) is transformed to the similarity variable  $\eta$ . The experimental data collapse to a single curve, indicating self-similarity, with the exception of the data from the first time step (red open circle). c.) The square of the front location where  $p = 0.5$  (circles) is plotted against time and fitted (solid line) to determine the mobility  $\mu_p$  and the time lag  $t_{lag}$ .

These experiments are conducted at an early time, when the moving front is between 0 and 8 mm from the electrolyte in a 32 mm thick film. In figure 3.5(a), we plot our similarity solution for the cation density against the transmittance data and find that while the expression for  $\delta$  (3.18) accurately

predicts the location of the moving front, the similarity solution for the cation density profile is much steeper than that of the experiments. This begs the question: do the experiments exhibit self-similar front dynamics? To answer this, in figure 3.5(b) we transformed the experimental transmittance data from  $\Delta T(x, t)$  to  $\hat{\Delta} T(\hat{\eta})$  by dividing the  $x$ -position by  $\delta$ , given by (3.18). After the transformation, the transmittance data collapse to a single curve, with the exception of the transmittance at the first time step, indicating that the invasion process is self-similar, and that the front scaling is in fact given by (3.18). However, qualitative differences in the spatial profiles are seen in figure 3.5, suggesting that additional physical effects are at play in the experiments.

We investigate this discrepancy further by relaxing several assumptions. First, we assumed that the cation and hole mobilities are constant, despite the large variations in the electric field (figure 3.3(a)). To relax this assumption, we endow the mobility with a simple power-law dependence on the electric field,  $\mu_p = \mu_{p0}(e/e_0)^s$ , where  $s$  is the power law index,  $e_0 = k_B T / ql$ , and  $\mu_{p0}$  is the mobility at  $e_0$ . We look for similarity solutions of the drift-diffusion equations with the generalized similarity variable  $\hat{\eta} = (\hat{x} + \hat{B}\hat{t}^\alpha) / \hat{A}\hat{t}^\beta$ , where  $\hat{B}\hat{t}^\alpha$  ( $B$  is a constant) controls the advancement of the front and  $\hat{A}\hat{t}^\beta$  ( $A$  is a constant) dictates the thickening of the front.<sup>91</sup> Our hope is to find similarity solutions with  $\alpha = 1/2$  and  $\beta > 1/2$  to capture the broader (or thicker) density profile seen in the experiments as compared to our existing similarity solution with a field-independent mobility ( $s = 0$ ). It can be shown that  $\alpha = \beta = 1/(s + 2)$  is required for a similarity solution to exist, revealing that the drift-diffusion equations exhibit a family of self-similar solutions for a power-law dependent mobility. Interestingly, when  $s = -1$  (the mobility increases with decreasing electric field) the front advances and thickens linearly in time. However, the experiments clearly show that the front advances as  $t^{1/2}$ ,

consistent with  $\alpha = 1/2$ . The slope of the experimental transmittance data points within  $0.2\eta$  of the midpoint in figure 3.5 is a constant, calculated to be approximately  $-1$ . Thus, the slope of the front  $dp/dx$  scales as  $t^{-1/2}$ . The thickness of the moving front is inversely proportional to the slope, so it follows that the thickness scales with the  $t^{1/2}$  and  $\beta = 1/2$ . This implies that the simple power-law dependent mobility cannot yield a similarity solution with a front that advances as  $t^{1/2}$  while thickening at a greater rate.

A second issue may be voltage losses in the electrolyte and at the electrolyte-film and film-electrode interfaces, leading to a reduced driving voltage across the film. To test this hypothesis, we fit the similarity solution to the experimental data<sup>1</sup> with two adjustable parameters: the applied voltage  $v$  and cation mobility  $\mu_p$ . The best fit between the similarity solution and the experimental data requires an order of magnitude decrease in the applied voltage and an order of magnitude increase in the cation mobility from the reported values,<sup>1</sup> which does not seem plausible.

Another effect involving the electric potential is the possibility of a Donnan potential difference between the electrolyte and the negatively charged polymer film.<sup>95</sup> The existence of such a potential difference would cause an increase in cation concentration at the electrolyte-polymer interface relative to its value in the electrolyte reservoir. We have examined whether such an increase in ion concentration alters the shape of the moving ion front as follows. The ratio of the cation concentration at the interface to the hole concentration was varied from 1:1 to 1.5:1 and 0.5:1 in our numerical solution, by adjusting the ion boundary conditions (3.13-3.14). Deviations from the 1:1 ratio hitherto assumed result in a change in the moving front location, but there is no significant change in the slope of the cation density profiles. It is therefore unlikely that a local increase in ion concentration at the electrolyte-polymer film

interface due to a Donnan potential difference is responsible for the mismatch in front shape between theory and experiment.

Third, our assumption of one-dimensional ion transport neglects the possible existence of screening layers due to surface charges at the interfaces of the film with the glass substrate and the Su-8 ion barrier. These layers could provide another path for (surface) conductivity of the cation front. A more sophisticated analysis could be performed by depth-averaging the drift-diffusion equations to arrive at effective one-dimensional transport equations that account for these screening layers.<sup>88</sup> Another reason for the discrepancy may be a delay before the applied field is switched on, allowing for cations and anions to diffuse into the film and altering the initial condition. We tested this idea and found that while the front location increases, the shape of the cation density profile does not change significantly. Finally, there is the possibility that the change in transmittance is not a precise proxy for the cation density profile. We hope that the present work will inspire additional experimental and modeling efforts. For example, an alternative method for measuring the cation density across the film would provide verification of the transmittance as an accurate measure of cation density. Experiments reporting invasion dynamics across the entire film as opposed to the initial stages would enable a verification of the persistence of the  $t^{1/2}$  scaling provided by our analysis.

### 3.5 Conclusion

Motivated by the recent experiments of Stavriniidou *et al.*,<sup>1</sup> we have analyzed the moving front dynamics of cations invading a MIEC polymer film. Our work demonstrates that the invasion process is self-similar at the large driving voltages used in the experiments, and confirms that the front location advances with a square-root-of-time scaling,  $t^{1/2}$ . The thickness of the cation

front also grows as  $t^{1/2}$ . Remarkably, at large voltages,  $\hat{v} \gg 1$ , the similarity solution is in excellent agreement with the numerical solution of the full drift-diffusion equations until the point that the front reaches the end of the film. The agreement between solutions of the full drift-diffusion equations and the similarity solution validates the reliability of the numerical methods. We compared our similarity solution to the above-mentioned experiments: although both display self-similar evolution of the ion front with a  $t^{1/2}$  advancement, the experimental ion density profile (which we assumed to be equal to the reported transmittance data) is considerably broader than we predict. We hope the discrepancy between theory and experiment will motivate further work on this subject.

The present problem is similar to that of ion concentration polarization shocks in microchannel-nanochannel systems under constant voltage.<sup>90</sup> A cation-selective nanochannel acts as a junction between two microchannels. The application of a fixed voltage results in a depleted ion concentration polarization zone in one microchannel and an enriched zone in the other. Under certain conditions the zones can propagate as shocks; the depletion shock advances with a  $t^{1/2}$  scaling, and its thickness grows as  $t^{1/2}$ . This depletion zone is equivalent to the cation front in the present problem: namely, both are low-conductivity regions displacing a region of higher conductivity. In our problem, the high-conductivity region is the hole-rich region of the film, whereas in the concentration polarization problem it is the electroneutral electrolyte ahead of the depletion shock. Importantly, in both problems the majority of the potential drop occurs across the low-conductivity region behind the advancing front. At constant current, a concentration polarization depletion shock propagates linearly in time;<sup>88,90</sup> hence, it is expected that cation front invasion would also advance linearly with  $t$  if the device of Stavriniidou *et al.*<sup>1</sup> were operated at

constant current conditions. This mode of operation may also provide another method to measure the ion mobility in MIEC films.

Another analogy to cation invasion is capillary filling, in which a viscous liquid is drawn into a capillary by a pressure difference, displacing the air in the tube. The location of the advancing liquid front (or meniscus) again increases with a square-root-of-time scaling, a result referred to as Washburn's law.<sup>96</sup> Once more, this is a situation where a low conductivity region (the liquid) invades a high conductivity region (the inviscid air). The pressure difference across the capillary plays the role of the driving voltage, and the liquid and air regions are analogous to the cation and hole regions, respectively. It is well known that the displacement of a low viscosity fluid by a high viscosity fluid is stable, whereas the opposite scenario is susceptible to viscous fingering (Saffman-Taylor) instability.<sup>97</sup> Therefore, the cation invasion front should also be stable and remain uniform against perturbations transverse to the propagation direction, which could be caused by, for example, variation in the MIEC film morphology. On a related note, Mani and Bazant<sup>91</sup> demonstrated that depletion concentration polarization (or deionization) shocks at constant current evolve via the process of inverse Laplacian growth, which also yields stable and uniform fronts in disordered microstructures. We leave the interesting subject of front invasion dynamics in inhomogenous MIEC films to future work.

# 4. A Predictive Model for Electrical Impedance Spectroscopy of Zwitterionic Hydrogels

## 4.1 Introduction

Organic biosensors are promising devices for monitoring and detecting ions and small molecules at low concentrations in the body.<sup>13</sup> These devices are based on a class of materials, mixed ionic electronic conductors (MIECs), that conduct both ions and electrons and holes (electron vacancies).<sup>69</sup> Polymer MIECs are promising for biosensor applications due to their flexibility, biocompatibility, high ion and hole mobilities, and potential for functionalization.<sup>77</sup> The organic electrochemical transistor (OECT) is a device commonly applied to biological applications.<sup>13,15</sup> The OECT is comprised of a polymer semiconducting thin film between source and drain electrodes in contact with an electrolyte. A gate electrode immersed in the electrolyte completes the circuit.<sup>98</sup> Ions injected from the electrolyte into the semiconducting thin film displace electrons and holes, which then migrate and diffuse to the electrodes,

driving an electronic current. The transistor design amplifies the electrical signal, resulting in a sensitive detection method for target ions.

Tang *et al.*<sup>99</sup> designed an OECT capable of detection of the neurotransmitter dopamine at the nanomolar level. An OECT designed by Bernardis *et al.*<sup>75</sup> incorporated an enzyme, glucose oxidase, into the electrolyte to detect glucose concentration. *In vivo*, Khodagholy *et al.*<sup>100,101</sup> recorded local brain activity via an OECT at a spatial resolution and signal to noise ratio high enough to identify microseizures, a necessary step for epilepsy diagnosis. In this application, the OECT is directly in contact with the soft tissue of the brain. The OECT is bio-conformable due to the flexible nature of the semi-conducting polymer used here, poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS). However, the PEDOT:PSS thin film is still much harder than the soft tissue, with a Young’s modulus of  $\sim 2$  GPa,<sup>102,103</sup> while the magnitude of the complex modulus for the soft grey matter in the brain is  $\sim 3$  kPa.<sup>104</sup> This mechanical mismatch can lead to adverse effects caused by the strain induced by relative motion of the brain and the device.<sup>22–24,105</sup>

A hydrogel barrier between the soft tissue and the relatively hard device can be added to alleviate this mechanical strain. The hydrogel is designed to match the elastic modulus of the soft tissue while preserving electrical properties of the electrolyte such as conductivity and capacitance,<sup>25</sup> and can be endowed with additional functionality, including device encapsulation to improve device lifetime and prevent loss of molecules necessary for sensing, such as enzymes for glucose sensing.<sup>106,107</sup> The lifetime and performance of biosensors are significantly impacted by the “foreign body effect”: the biosensors illicit an immune response and the immune cells encapsulate the device in a collagen network.<sup>108,109</sup> Zwitterionic hydrogels such as poly(carboxybetaine methacrylate) (PCBMA) are ultra-low fouling: PCBMA was shown to resist

the buildup of a collagen network for up to three months<sup>109</sup> and maintain device performance.<sup>110</sup> The functional groups on a zwitterionic polymer are acidic and basic. At the isoelectric point, the monomer is neutral: the negatively charged acidic group offsets the positive charge on the basic functional group. Below the isoelectric point, the monomer is positively charged: the basic functional group is positively charged and the acidic functional group is neutralized by the high hydrogen concentration in the electrolyte. Above the isoelectric point, the polymer is negatively charged. The isoelectric point  $pI$  is calculated from the dissociation constants for acidic and basic residues,  $K_a$  and  $K_b$ , respectively as<sup>111</sup>

$$pI = \frac{-\log K_a - \log K_b}{2}. \quad (4.1)$$

For use in biosensor applications, hydrogels must be electronically active to promote electronic and ionic charge transport.<sup>112</sup> Desirable electrical properties include high ion conductivity and low electrical impedance.<sup>24</sup> The electrical impedance  $Z$  is the ratio of the applied voltage to the current, and comprises both real (in phase with voltage) and imaginary (out of phase with voltage) contributions which are frequency dependent. The real part of impedance at low frequencies is a measure of the resistance of the fluid while the imaginary part at low frequencies is the capacitance of the double layer at the hydrogel-electrode interface. The frequency of neural electrical signals is 1 kHz,<sup>113</sup> so impedance is often measured at 1 kHz for biosensors designed for use in the skull.<sup>77,112,114</sup> Electrical impedance spectroscopy (EIS) is a valuable characterization tool for measuring capacitance and resistance. EIS is performed by applying a low amplitude, sinusoidal oscillation in the voltage between two electrodes of the form  $\phi = -\frac{v}{2} \exp(i\omega t)$ , where  $i = \sqrt{-1}$ ,  $v$  is the voltage am-

plitude and  $\omega$  is the angular frequency. The oscillating voltage is expressed here as a complex number where the real part of  $\phi$  gives the physical applied voltage. At sufficiently low voltages the measured current is  $I = I_m \exp(i\omega t)$ , where  $I_m$  is a complex coefficient and the current oscillates at the same frequency as the applied voltage. The real part of  $I$  gives the physical impedance. Low voltage amplitude is defined as  $v \ll k_B T/q$ , where  $v_T = k_B T/q$  is the thermal voltage,  $k_B$  is Boltzmann's constant,  $T$  is temperature, and  $q$  is the charge of a proton. In this linear regime, the current, ion concentration and potential in the hydrogel oscillate at the frequency of the applied potential, but can be out of phase.<sup>115</sup> The electrical impedance can be calculated from the oscillating applied potential and current as  $Z = v \exp(i\omega t)/I_m \exp(i\omega t)$ , where impedance  $Z$  is independent of time and frequency in the linear regime. The phase angle between the applied potential and the measured current is  $\tan[\theta(\omega)] = \text{Im}[Z(\omega)]/\text{Re}[Z(\omega)]$ . When the current is in phase with the applied potential,  $\theta(\omega) = 0$ , the system behaves as a resistor. Conversely, a system with a current completely out of phase with the applied potential  $\theta(\omega) = \pi/2$  behaves as a capacitor. To determine the resistance and capacitance of the hydrogel and the diffusivity of the charge carriers, the current can be further analyzed by applying an equivalent circuit model.<sup>116</sup> These models are useful for interpreting EIS data, but limited in scope since they do not provide information about the micro-scale dynamics of the system, such as spatio-temporal ion densities.

The Poisson-Nernst-Planck (PNP) equations are partial, nonlinear differential equations that describe charge transport in electrochemical systems.<sup>7</sup> In the present work, the PNP equations are employed to model ion transport in zwitterionic hydrogels and to subsequently predict the current resulting from an oscillating applied potential and the electrical impedance. At a pH

not equal to the isoelectric point, the zwitterionic hydrogel carries a non-zero charge on the polymer backbone due to dissociation and association of the acidic and basic functional groups. The  $pH$  dependent charge density in the hydrogel will be incorporated into Poisson’s equation relating charge density to the electric field.

Yates *et al.*<sup>117</sup> modeled an electrochemical cell with a four-step  $pH$  dependent surface reaction using the Gouy-Chapman-Stern model<sup>118–120</sup> for the electrical double layer, a region of counter-ion accumulation next to a charged surface. Bousse *et al.*<sup>121</sup> define an equivalent circuit model where the capacitance of the double layer according to the Gouy-Chapman-Stern model is in parallel with the capacitance of adsorbed charge due to  $pH$  dependent surface reactions in series with the Warburg impedance, the impedance due to changes in the surface  $pH$  with the oscillating potential. Bousse *et al.*<sup>122</sup> apply this model to a field-effect transistor and derive an expression for the relation between  $pH$ , surface charge density, and potential. Landheer *et al.*<sup>123</sup> begin with this expression and the Poisson-Boltzmann equations to model the effect of  $pH$  on a field-effect transistor functionalized with biological macromolecules. Via an equivalent circuit model, Landheer *et al.*<sup>123</sup> calculate the capacitance of each component of the device and find that the biosensor sensitivity is highest at low electrolyte concentrations. In these previous works, the  $pH$  affected the reaction rate on the surface of the electrode, and was used to calculate the capacitance of the double layer.<sup>122,123</sup> In the case of a zwitterionic hydrogel, the  $pH$  changes the charge density throughout the cell and must be included in Poisson’s equation relating the spatial variation in the electric field to the volumetric space charge density.

In section 4.2, we propose a model for charge transport in zwitterionic hydrogels based on the PNP equations and equilibrium acid-base association

relations. We then linearize the PNP equations in section 4.3 and solve for the electrical impedance. In section 4.4 we apply an equivalent circuit model to the numerical solution of the PNP equations to calculate the conductivity, resistance, and capacitance of a model PCMBA hydrogel. We conclude in section 4.5 with a possible extension of this model to account for steric resistance due to hydrogel mesh spacing. Our findings can be applied to predict the impedance in zwitterionic hydrogels to aid in design for biosensor encapsulation.

## 4.2 Mathematical Model

We present a model for the transport of cations, anions, hydrogen and hydroxide in a zwitterionic hydrogel immersed in electrolyte and sandwiched between two planar, parallel, blocking electrodes (figure 4.1). The equations describing ion transport are the Poisson-Nernst-Planck (PNP) equations, consisting of equations for the ion conservation and Poisson's equation relating the charge density to spatial variations in the electric field. The zwitterionic hydrogel system requires four sets of ion conservation equations, one for each charged species. The four species are hydrogen ions, hydroxide ions, and dissociated cations and anions. The mean concentration of hydrogen and hydroxide depends on the  $pH$  of the electrolyte and the association and dissociation rate constants of the functional groups on the zwitterionic hydrogel backbone. The  $pH$  is determined by the composition of the electrolyte; for example, the  $pH$  of blood is  $pH = 7.4$ . The extent of dissociation of the acidic and basic functional groups depends directly on the  $pH$  according to the expressions (4.8) for the acidic  $[A^-]$  and basic  $[HB^+]$  functional group concentrations developed below. We assume that the hydrogel is a thin film, with transport in the  $x$  direction and infinite dimensions in  $y$  and  $z$  compared to  $x$ . The equations

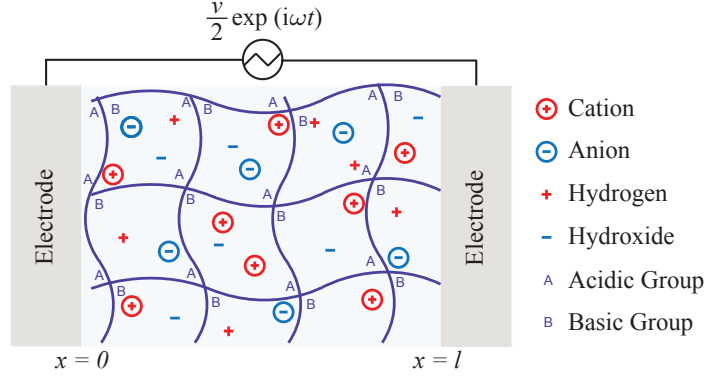


Figure 4.1: Zwitterionic hydrogel sandwiched between two electrodes immersed in an electrolyte. The system contains two functional groups on the polymer backbone and four mobile ion species: cations, anions, hydrogen, and hydroxide. The current resulting from a low amplitude oscillating applied voltage  $\frac{v}{2} \cos(\omega t)$  is calculated.

presented here are thus one-dimensional in  $x$ . The ion conservation equation is

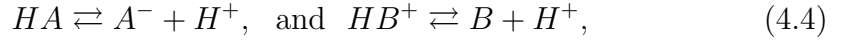
$$\frac{\partial n_i}{\partial t} = \mu_i v_T \frac{\partial^2 n_i}{\partial x^2} + z_i \mu_i \frac{\partial}{\partial x} \left( n_i \frac{\partial \phi}{\partial x} \right), \quad (4.2)$$

where  $n_i$  is the ion concentration with the following naming convention for the subscript  $i$ : H = hydrogen, X = hydroxide, C = cation, and A = anion. Additional ionic species, *e.g.* for a multi-component electrolyte, could easily be incorporated by adding additional ion concentrations to (4.3) and solving (4.2) for each additional species. Time is  $t$ ,  $x$  is position,  $\mu_i = D_i/v_T$  is the ion mobility for each species,  $D_i$  is the diffusivity, and  $z_i$  is the charge of each ion. The electric potential is  $\phi$ . Poisson's equation is

$$\frac{\partial^2 \phi}{\partial x^2} = -\frac{q}{\varepsilon} (n_H - n_X + z_C n_C + z_A n_A + \rho_{gel}), \quad (4.3)$$

where  $\rho_{gel}$  is the charge density of the hydrogel and  $\varepsilon$  is the permittivity of the hydrogel. The charge on the hydrogel backbone is determined by the equilibrium reactions for the association and dissociation of hydrogen from

the functional groups on the polymer backbone,



where  $A$  is the acidic functional group,  $B$  is the basic functional group, and  $H$  is hydrogen. The dissociation constants for these reactions are

$$K_a = \frac{[A^-]n_H}{[HA]}, \text{ and } K_b = \frac{[B]n_H}{[HB^+]}, \quad (4.5)$$

where  $[]$  indicates the concentration of the designated species. The concentration of the charged functional groups  $A^-$  and  $HB^+$  are calculated from an expression for the concentration of hydrogen ions as a function of  $pH$  and a mole balance for the total moles of monomers in the system. The  $pH$  is defined as

$$pH = -\log n_{H0}, \quad (4.6)$$

where  $n_{H0}$  is the equilibrium ( $v = 0$ ) hydrogen concentration. The mole balance on the total concentration of monomers  $N$  can be written for the acidic or basic functional groups as

$$N = [A^-] + [HA] = [HB^+] + [B]. \quad (4.7)$$

Equations (4.5-4.7) can be rearranged to eliminate  $[HA]$  and  $[B]$ , then solved for  $[A^-]$  and  $[HB^+]$ :

$$[A^-] = \frac{NK_a}{K_a + n_H}, \text{ and } [HB^+] = \frac{Nn_H}{K_b + n_H}. \quad (4.8)$$

If the  $pH$  is known, the hydrogen concentration can be calculated according to (4.6). The concentration of charged functional groups is then given by (4.8),

with the known values of the dissociation constants  $K_a$  and  $K_b$ , and the total concentration of monomer  $N$ . At low  $pH$  compared to the isoelectric point,  $pH < pI$ , the excess of hydrogen associates with the acidic group, forming  $HA$  and reducing the concentration  $[A^-]$ . Similarly, the basic group accepts a hydrogen at low  $pH$  (4.4), forming  $HB^+$ . Thus, at low  $pH < pI$ , the hydrogel is positively charged. The converse is true at  $pH > pI$ . The charge density of the hydrogel is

$$\rho_{gel} = \frac{Nn_H}{K_b + n_H} - \frac{NK_a}{K_a + n_H}. \quad (4.9)$$

When  $pH = pI$  at the isoelectric point, the charge density of the hydrogel is  $\rho_{gel} = 0$  according to (4.9). The equilibrium ion concentrations and potential at  $v = 0$  are necessary to complete the model:

$$\text{At } v = 0, \phi(x) = 0, n_i(x) = n_{i0}, \text{ and } n_{C0} = -\frac{z_A}{z_C}n_{A0}, \quad (4.10)$$

where the expression for  $n_{A0}$  gives the anion concentration based on the cation concentration  $n_{C0}$  and the stoichiometry of the electrolyte. The appropriate boundary conditions for the ion concentrations are no flux at the electrodes in the absence of Faradaic reactions,

$$\frac{\partial n_i}{\partial x} = -z_i n_i \frac{\partial \phi}{\partial x} \quad \text{at } x = 0, l. \quad (4.11)$$

The applied potential at the electrodes oscillate in time according to

$$\phi(x = 0, t) = -\frac{v}{2}e^{i\omega t} \quad \text{and} \quad \phi(x = l, t) = \frac{v}{2}e^{i\omega t}. \quad (4.12)$$

Thus the maximum total applied potential drop is  $v$ .

### 4.3 Linearized PNP Equations

Electrical impedance spectroscopy is performed by measuring the time-varying current response to an AC voltage for a sweep in frequencies. The electrical impedance is then calculated from the ratio of the applied voltage to the measured current. This technique requires a linear current response, proportional to the applied voltage. In the nonlinear regime, the impedance is dependent on the amplitude of the applied voltage.<sup>115</sup> A linear current response is achieved by applying a low-amplitude applied voltage in comparison to the thermal voltage,  $v \ll v_T$ .<sup>116</sup> The PNP equations can be linearized by perturbing the ion concentration and potential in proportion to the small-amplitude oscillations in applied voltage. Thus the ion densities are expanded as

$$n_i = n_{i0} + n_{i1}e^{i\omega t}, \quad (4.13)$$

and the potential as

$$\phi = \phi_1 e^{i\omega t}. \quad (4.14)$$

where  $n_{i1}$  and  $\phi_1$  are  $O(v)$ . Note that the physical ion densities and potential can simply be found by taking the real part of (4.13) and (4.14) after solving the linearized PNP equations. This is valid as we only consider linear departures from equilibrium. The leading order term  $\phi_0 = 0$  in the absence of an equilibrium surface charge. When these expressions are inserted into (4.2) and (4.3), the resulting linearized charge conservation equation is

$$\frac{i\omega}{\mu_i} n_{i1} = v_T \frac{d^2 n_{i1}}{dx^2} + z_i n_{i0} \frac{d^2 \phi_1}{dx^2}. \quad (4.15)$$

The equilibrium terms for the ion density  $n_{i0}$  are constants, so they do not appear in the derivatives. Poisson's equation (4.3) requires an additional step

before linearization. The hydrogel charge density  $\rho_{gel}$  is not linearly dependent on the perturbed hydrogen concentration  $n_{H1}$ . We perform a regular expansion on (4.8) for  $[A^-]$  and  $[HB^+]$  in  $v$  to yield expressions that are valid for low amplitude voltages in comparison to the thermal voltage  $k_B T/q$ . The series expansion of (4.8) for the concentration of the dissociated acidic functional group is

$$[A^-] = \frac{NK_a}{K_a + (n_{H0} + n_{H1}e^{i\omega t})} \sim \frac{NK_a}{n_{i0} + K_a} - n_{H1}e^{i\omega t} \frac{NK_a}{(n_{H0} + K_a)^2}. \quad (4.16)$$

The concentration of the dissociated basic functional group can be similarly written as

$$[HB^+] = \frac{N(n_{H0} + n_{H1}e^{i\omega t})}{K_b + (n_{H0} + n_{H1}e^{i\omega t})} \sim \frac{Nn_{H0}}{n_{i0} + K_b} + n_{H1}e^{i\omega t} \frac{NK_b}{(n_{H0} + K_b)^2}. \quad (4.17)$$

Expressions (4.16) and (4.17) are inserted into (4.9), which is combined with Poisson's equation (4.3) to yield

$$\begin{aligned} \frac{\varepsilon}{q} e^{i\omega t} \frac{d^2 \phi_1}{dx^2} = & - \left( \frac{Nn_{H0}}{n_{H0} + K_b} - \frac{NK_a}{n_{H0} + K_a} + n_{H0} - n_{X0} \right) \\ & - e^{i\omega t} \left( \frac{NK_b n_{H1}}{(n_{H0} + K_b)^2} + \frac{NK_a n_{H1}}{(n_{H0} + K_a)^2} + n_{H1} - n_{X1} + z_C n_{C1} + z_A n_{A1} \right). \end{aligned} \quad (4.18)$$

The term independent of time in (4.18), the first term on the right-hand side, must be zero since it is voltage-independent. Hence,

$$0 = \frac{Nn_{H0}}{n_{i0} + K_b} - \frac{NK_a}{n_{i0} + K_a} + n_{H0} - n_{X0}. \quad (4.19)$$

Equation (4.19) states that in the absence of an applied field, the charge density on the hydrogel backbone is equal to the difference in concentration of the

dissociated hydrogen and hydroxide in the electrolyte. The time-dependent equation for the perturbed potential  $\phi_1$  is then

$$-\frac{\varepsilon}{q} \frac{d^2 \phi_1}{dx^2} = \frac{NK_b n_{H1}}{(n_{H0} + K_b)^2} + \frac{NK_a n_{H1}}{(n_{H0} + K_a)^2} + n_{H1} - n_{X1} + z_C n_{C1} + z_A n_{A1}. \quad (4.20)$$

We can now solve equations (4.15) and (4.20) together with the linearized form of the boundary conditions (4.11),

$$\frac{dn_{i1}}{dx} = -z_i n_{i0} \frac{d\phi_1}{dx} \text{ at } x = 0, l, \quad \phi_1(0, t) = -v/2 \text{ and } \phi_1(l, t) = v/2, \quad (4.21)$$

to yield numerical solutions for the perturbed ion densities and applied potentials.

The electrical impedance is equal to the ratio of the voltage difference between the electrodes to the electrical current. The former equals  $\Delta V = v \exp i\omega t$  in dimensional variables. The current  $I(t)$  is equal to the derivative of the surface charge at the electrode,  $I(t) = dQ/dt = d(\varepsilon S E)/dt$ ,  $S$  is the constant surface area of the electrode and  $E = -\partial\phi/\partial x$  is the electric field.<sup>115</sup> Together with the expansion for potential (4.14), this yields,

$$Z = \frac{v \exp i\omega t}{\varepsilon S \frac{\partial^2}{\partial t \partial x} (\phi_1 \exp i\omega t)}. \quad (4.22)$$

After taking the mixed partial derivative, the expression for impedance  $Z$  is

$$Z = \frac{v}{\varepsilon S i \omega \frac{d\phi_1}{dx} \big|_{x=0}}. \quad (4.23)$$

The impedance  $Z$  is a complex number, comprised of a real and imaginary part. The real part of impedance corresponds to the resistivity of the hydrogel and electrolyte, while the imaginary part is proportional to the inverse of the

capacitance of the hydrogel and the double layers at the electrode-electrolyte interfaces.

## 4.4 Impedance Analysis

In order to calculate the electrical impedance at a sweep of frequencies, we solved equations (4.15) and (4.20) along with the boundary conditions (4.21) for each of the four charged species (hydrogen, hydroxide, cations, and anions) with Matlab's bvp4c method, a boundary value problem solver for systems of ordinary differential equations based on collocation methods.<sup>94</sup> We then calculated the impedance according to (4.23).

At a  $pH$  unequal to the isoelectric point, the zwitterionic hydrogel carries a net charge. Figure 4.2 is a Bode plot of the real and imaginary parts of impedance for a sweep of frequencies. The material parameters selected here, listed in table 4.1, correspond to a model PCBMA hydrogel immersed in a symmetric binary electrolyte at a cation and anion concentrations of  $n_{C0} = n_{A0} = 10^{-4}$  M and a monomer concentration of  $N = 0.1$  M.<sup>124</sup> This model electrolyte could be replaced with an asymmetric electrolyte by adjusting the ratio of the anion to cation mobility and the charge of each ion  $z_C$  and  $z_A$ . We choose a symmetric electrolyte to clearly show the impact of the hydrogel on electrical impedance. At the isoelectric point of the PCBMA polymer,  $pI = 6.4$ , the impedance is larger for all frequencies than at  $pH = 5, 7.4$ , or  $8$ . Deviations from the isoelectric point reduce both the real and imaginary portions of the electrical impedance due to the presence of a charge on the hydrogel backbone as well as an increase in the concentration of mobile hydrogen or hydroxide ions. The increase in the total number of charge carriers reduces the resistance of the hydrogel and increases the capacitance of electrical double layers at the electrode-electrolyte interface. The resistivity of the fluid corre-

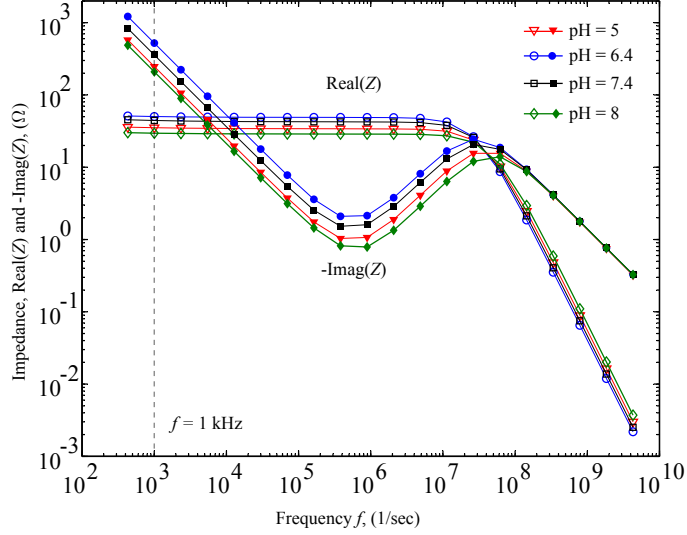


Figure 4.2: The real (open symbols) and imaginary (filled symbols) parts of impedance are plotted for a range of frequencies and an equilibrium cation concentration of  $n_{C0} = 10^{-4}$  M. In comparison to the isoelectric point,  $pH = 6.4$ , any deviation results in a decrease in impedance. Lines through computed points are included to guide the eye.

sponds to the real part of impedance at low frequencies,<sup>?</sup> which decreases in figure 4.2. The imaginary part of impedance at high frequency relates to the capacitance of the bulk fluid (a dielectric solvent), which is not dependent on the concentration of charge carriers. The double layer capacitance is inversely related to the limit of the imaginary part of impedance at low frequencies, so a decrease in  $\text{Im}(Z)$  as  $f \rightarrow 0$  corresponds to an increase in the double layer capacitance due to the increase in the concentration of charge carriers in the cell. These limits are discussed in more detail below. The physiological frequency of electrical signals in the brain,  $f = 1$  kHz as indicated in figure 4.2, falls at the low-frequency limit at which the hydrogel behaves as a resistor in series with double layer capacitance. The impact of the hydrogel is significant here compared to the high-frequency limit. For biosensor encapsulation applications, a low impedance at  $f = 1$  kHz is likely desirable, which requires an electrolyte  $pH$  unequal to the isoelectric point.

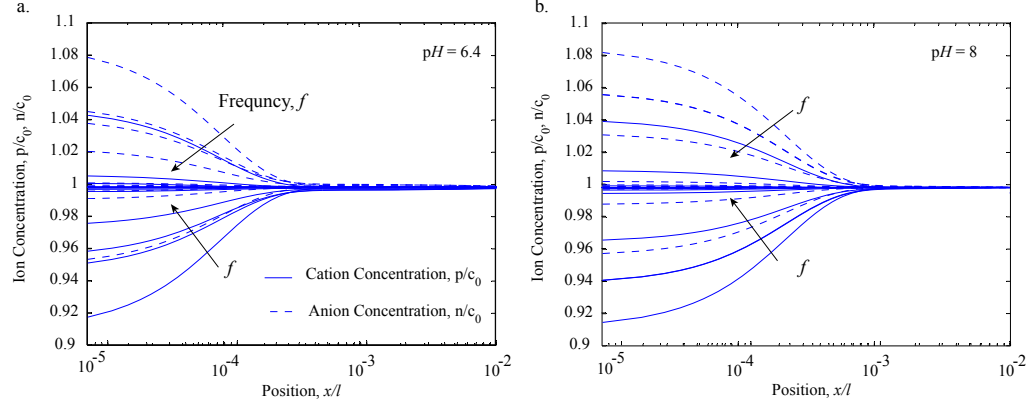


Figure 4.3: The cation (solid line) and anion (dashed line) concentrations are shown for a)  $pH = 6.4$  and b)  $pH = 8$  at frequencies ranging from  $f = 440$  to  $4.4 \times 10^9$  Hz and an equilibrium cation concentration of  $n_{C0} = 10^{-4}$  M. The ion concentration in the double layer increases as  $pH$  deviates from  $pH = 6.4$ . This is plotted for  $t = 4$  ms, the time of the first peak in current at  $f = 440$  Hz. The arrows indicated increasing frequency. At  $pH = 8$ , the width of the double layer scaled by  $l$  is  $\lambda_D/l = 3.09 \times 10^{-4}$ , beyond which the bulk is uniform in concentration. Only one electrode is shown; the behavior is symmetrical at the other electrode.

Figure 4.3 shows the cation and anion concentration profiles at  $pH = 6.4$  and  $pH = 8$  scaled by the ionic strength of the electrolyte  $c_0 = 1/2(n_H + n_X + z_C^2 n_C + z_A^2 n_A)$ . The cation and anion densities are antisymmetric around  $x = l/2$ . The anions and cations accumulate at the electrode ( $x = 0, l$ ) interfaces forming electrical double layers. The capacitance of the double layer at  $pH = 8$  is larger than at  $pH = 6.4$ . The charge on the hydrogel backbone at  $pH = 8$  is immobile, so the mobile ions in the electrolyte are free to migrate and diffuse towards the electrode interfaces to screen the surface charge. This charge screening layer is the electrical double layer with a width  $\lambda_D = \sqrt{\epsilon k_B T / 2q^2 c_0}$ . The  $RC$  timescale,  $\tau_{RC} = l\lambda_D/D$ , is the characteristic timescale for double layer charging.<sup>4</sup> For the conditions in figure 4.2, at a  $pH = 8$ , the frequency of oscillations in the applied potential is equal to the rate of double layer charging at  $f_{RC} = 1/\tau_{RC} = 4.3 \times 10^3$  Hz, which is the frequency corresponding to  $\text{Re}(Z) = \text{Im}(Z)$ . At low frequencies  $f < 1/\tau_{RC}$ , the double layer charges with

ions. As frequency increases, ion migration and diffusion is slower than the fast oscillations in the polarity of the charged electrode, reducing the capacitance of the electrical double layer.

The electric field in the double layer, shown in figure 4.4a scaled by  $v_T/l$ , is strongly dependent on the  $pH$  of the electrolyte. The magnitude of the electric field is much larger at  $pH = 8$  than  $pH = 6.4$  due to the increased charge density in the double layer (figure 4.3). The asymmetry around  $E = 0$  results from changes in the polarity of the electrode potential at  $t = 4$  ms depending on the frequency, where  $t = 4$  ms is the time of first maximum in current at  $f = 430$  Hz, an arbitrary selection. At large frequencies, the electric field in the bulk is equal for both  $pH = 6.4$  and 8 due to absence of an appreciable double layer formation; *i.e.* electroneutrality persists throughout the cell. In

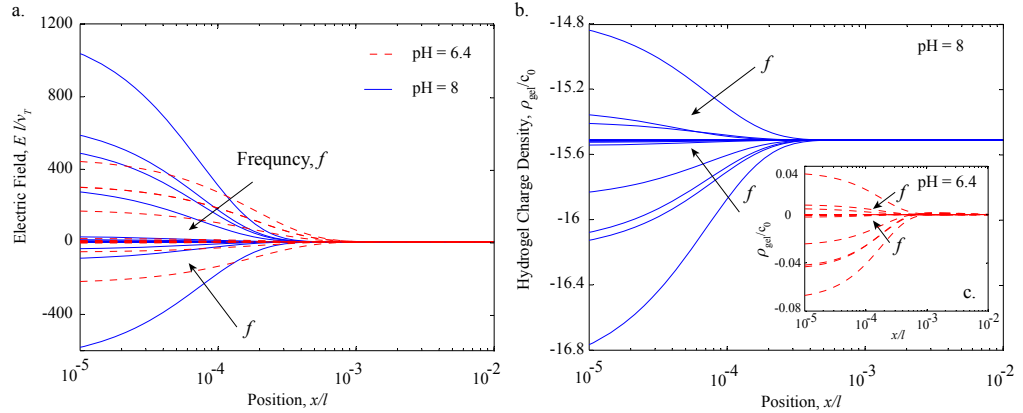


Figure 4.4: a) The electric field in the double layer at  $pH = 8$  (line) is larger than the field at  $pH = 6.4$  (dashed) due to the charge on the hydrogel backbone when the  $pH$  does not equal the isoelectric point. The hydrogel charge density scaled by the ionic strength of the electrolyte  $N_{gel}/c_0$  for b)  $pH = 8$  and c)  $pH = 6.4$ . In this figure, frequencies range from  $f = 440$  to  $4.4 \times 10^9$  Hz, the equilibrium cation concentration  $n_{C0} = 10^{-4}M$ , and time  $t = 4$  ms.

figure 4.4b, the hydrogel charge density scaled by the ionic strength of the electrolyte  $\rho_{gel}/c_0$  is plotted against position  $x/l$  at  $pH = 8$ . The hydrogel charge density in the bulk is  $\rho_{gel} = -15.5c_0$ , while at  $pH = 6.4$   $\rho_{gel} = 0$  (figure 4.4c). This significant hydrogel charge density accounts for the drop

in electrical impedance from  $pH = 6.4$  to  $pH = 8$ . Interestingly, the hydrogel charge density responds to the higher electric field (figure 4.4a) in the double layer, which is also reflected in the hydrogen and hydroxide concentrations. This results in a local change in the  $pH$  in the double layer compared to the bulk.

|                         |                                |                                                |
|-------------------------|--------------------------------|------------------------------------------------|
| Voltage                 | Cation Concentration           | Cation Charge                                  |
| $v = 5 \text{ mV}$      | $n_{C0} = 10^{-4} \text{ M}$   | $z_C = 1$                                      |
| Anion Charge            | Hydrogel Monomer Concentration | Surface Area                                   |
| $z_A = 1$               | $N = 0.1 \text{ M}$            | $S = 10^{-4} \text{ m}^2$                      |
| Association Rate        | Dissociation Rate              | Mobility Ratios                                |
| $K_a = 10^{-3}$         | $K_b = 10^{-9.8}$              | $m = [0.1, 0.1, 1, 1]$                         |
| Hydrogel Width          | Permittivity                   | Cation Diffusivity                             |
| $l = 10^{-4} \text{ m}$ | $\varepsilon_r = 80.4$         | $D = 1.33 \times 10^{-8} \text{ m}^2/\text{s}$ |

Table 4.1: Material parameters for a model PCBMA hydrogel immersed in a symmetric binary electrolyte.

The mean cation concentration in figure 4.2 is  $n_{C0} = 10^{-4} \text{ M}$ . However, in experiments the ion concentration in the electrolyte may be much higher, on the order of  $n_{C0} = 1 \text{ M}$ .<sup>124</sup> In figure 4.5, the impedance curves are shown for mean concentrations of 1 M, 0.1 M, and 0.01 M at a physiological  $pH = 7.4$  and cell width  $l = 1 \mu\text{m}$ . An order of magnitude increase in concentration decrease the real and imaginary parts of impedance by an order of magnitude at low amplitude. This decrease stems from the addition of mobile ions to carry the current in the electrolyte, reducing the resistivity of the fluid. The imaginary part of impedance converges at a higher frequency than the frequency range plotted here.

The electrical impedance can be analyzed via a four element circuit model,<sup>?</sup> depicted in figure 4.6, consisting of the geometric capacitance of the cell  $C_g$

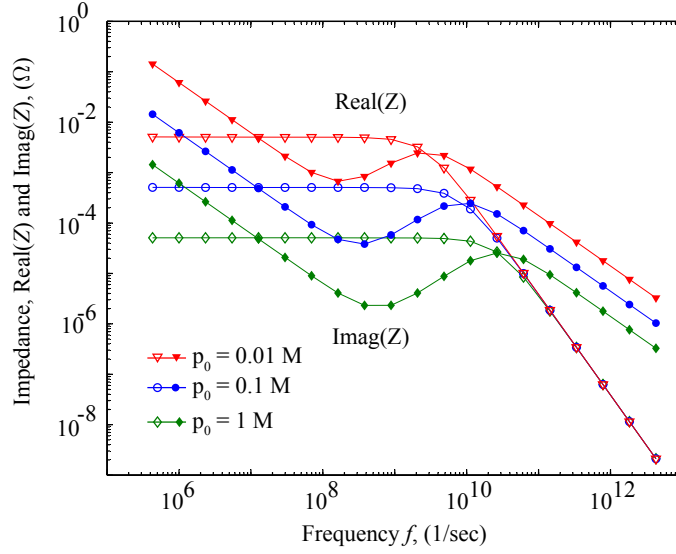


Figure 4.5: The real (open symbols) and imaginary (filled symbols) parts of impedance are plotted for a range of dimensionless frequencies. The cation concentration varies from  $10^{-2}$  M to 1 M. As the concentration increases, the impedance decreases at low frequencies.

in parallel with the three elements in series: the resistance of the hydrogel  $R_g$  and the capacitance of the double layers  $C_{dl}$ . This unit is in series with the resistance of the external circuit,  $R_e$ , which is measurable in experiments at high frequency but not included in the PNP equation-based model presented in this work. The impedance derived for this four-element circuit model can

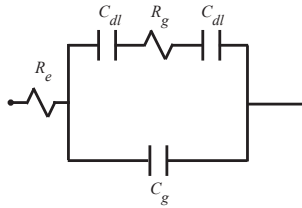


Figure 4.6: Four-element circuit model consisting of the resistance of the external circuit  $R_e$  in series with the geometric capacitance of the cell  $C_g$  in parallel with the capacitance of each double layer  $C_{dl}$  and the resistance of the hydrogel  $R_g$ .

be expressed as,<sup>?</sup>

$$Z = R_e + \left[ \left( R_g + \frac{2i}{\omega C_{dl}} \right)^{-1} + \left( \frac{i}{\omega C_g} \right)^{-1} \right]^{-1}, \quad (4.24)$$

where  $\omega = 2\pi f$  is the angular frequency. The real part of impedance is

$$\text{Re}(Z) = R_e + \frac{R_g}{a + \omega^2 R_g^2 C_g^2}, \quad (4.25)$$

where  $a = 1 + 4c + 4c^2$  and  $c = C_g/C_{dl}$ . The imaginary part of impedance is

$$\text{Im}(Z) = R_g \frac{(2c + 4c^2)(\omega R_g C_g)^{-1} + \omega R_g C_g}{a + \omega^2 R_g^2 C_g^2}. \quad (4.26)$$

The asymptotic limits of these equations as  $\omega \rightarrow 0$  and  $\omega \rightarrow \infty$  can be used to calculate the resistances and capacitances to leading order in  $\omega$ . These asymptotic limits are depicted on a Bode plot<sup>?</sup> in figure 4.7 showing  $\text{Re}(Z)$  and  $\omega \text{Im}(Z)$  plotted against frequency  $f$  at the isoelectric point  $\text{pH} = 6.4$  and cation concentration  $n_{C0} = 10^{-4}$  M. The asymptotic limits of (4.25) and (4.26) to leading order in  $\omega$  as  $\omega \rightarrow \infty$  are<sup>?</sup>

$$\lim_{\omega \rightarrow \infty} \text{Re}(Z) = R_e + O(\omega^{-2}) \quad \text{and} \quad \lim_{\omega \rightarrow \infty} \omega \text{Im}(Z) = \frac{1}{C_g} + O(\omega^{-2}). \quad (4.27)$$

The asymptotic limits as  $\omega \rightarrow 0$  are

$$\lim_{\omega \rightarrow 0} \omega \text{Im}(Z) = \frac{2}{C_{dl} + 2C_g} + O(\omega^2) \quad \text{and} \quad \lim_{\omega \rightarrow 0} \text{Re}(Z) = \frac{R_g}{a} + O(\omega^2). \quad (4.28)$$

The resistances  $R_e$  and  $R_g$  and capacitances  $C_g$  and  $C_{dl}$  can be solved for by first calculating  $R_e$  and  $C_g$  from the limits of  $\text{Re}(Z)$  and  $\omega \text{Im}(Z)$  as  $\omega \rightarrow \infty$  according to (4.27). The limits as  $\omega \rightarrow 0$  along with  $R_e$ ,  $C_g$ , and the definitions of  $c$  and  $a$  yield the double layer capacitance  $C_{dl}$  and finally the

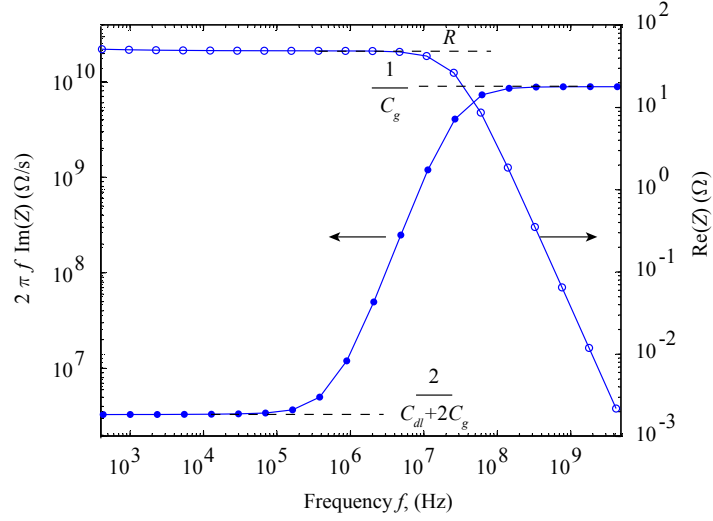


Figure 4.7: The real (open circles) part of impedance  $\text{Re}(Z)$  and imaginary (filled circles) part of impedance multiplied by the angular frequency  $\omega \text{Im}(Z)$  at  $\text{pH} = 6.4$  and  $n_{C0} = 10^{-4}$  M are plotted against frequency. The dashed lines indicate the asymptotic limits of (4.25) and (4.26).

hydrogel resistance  $R_g$ . We applied this method to the impedance spectrum at  $n_{C0} = 10^{-4}$  and  $\text{pH} = 5, 6.4, 7.4, 8$  (figure 4.2) to calculate the resistances and capacitances in figure 4.8.

The resistance  $R_g$  decreases as the  $\text{pH}$  deviates from  $\text{pH} = 6.4$  due to an increase in the total concentration of charge in the cell, including dissociated salt, the charged functional groups on the hydrogel backbone, and dissociated hydroxide and hydrogen ions. The capacitance of the double layers increases, as shown in figure 4.3, with the concentration of charge carriers, and is four orders of magnitude larger than the geometric capacitance of the cell  $C_g$ , which is independent of charge carrier concentration. The calculated capacitance  $C_g$  in figure 4.5 is  $C_g = 13.3$  nF.  $C_g \sim 1/L$ ,<sup>?</sup> so the change in the width of the cell from  $L = 10^{-4}$  m to  $L = 10^{-6}$  m is responsible for the two order of magnitude increase in  $C_g$  compared to the capacitance  $C_g = 0.133$  nF in figure 4.8.

The effect of  $\text{pH}$  on impedance is significant when the electrolyte ion concentration is  $n_{C0} = 10^{-4}$  M. However, at higher concentrations the increase in

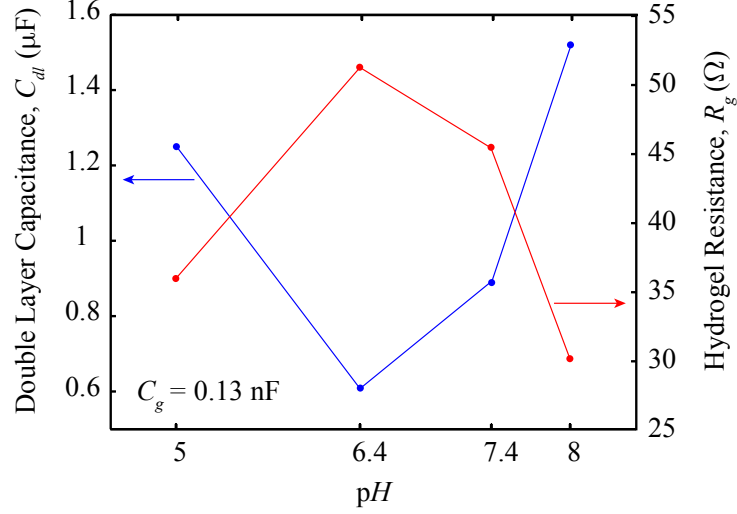


Figure 4.8: The double layer capacitance  $C_{dl}$  and hydrogel resistance  $R_g$  are plotted as a function of  $pH$ . At the isoelectric point,  $C_{dl}$  is at a minimum and increases with deviations from the isoelectric point.  $R_g$ , conversely, decreases as  $pH$  deviates from the isoelectric point. The capacitance  $C_g$  is independent of  $pH$ .

the total concentration of mobile ions due to a change in  $pH$  is minimal. At  $n_{C0} = 1$  M, the impedance decrease is  $O(10^{-9}\Omega)$  as the  $pH$  increases from  $pH = 6.4$  to  $pH = 7.4$ . The impact of the charge on the hydrogel backbone on impedance is limited to low ion concentration for this model PCBMA hydrogel. The effect of  $pH$  would be more pronounced for a zwitterionic hydrogel with divalent or trivalent functional groups due to the increase in charge per functional group from  $z = \pm 1$  to  $z = \pm 2$  or 3 when completely dissociated. Our model can be readily adapted to analyze multi-valent functional groups.

## 4.5 Discussion and Conclusions

We have developed a mathematical model for ion transport in swelled zwitterionic hydrogels based on the PNP equations and equilibrium equations for acid-base association and dissociation. This model incorporates the effect of  $pH$  on the charge of the functional groups on the hydrogel backbone by adding

a term for the charge density of the hydrogel to Poisson’s equation (4.3). The nonlinear, partial differential PNP equations were linearized for low-amplitude oscillations in the applied voltage and solved with Matlab’s `bvp4c` boundary value problem solver. The electrical impedance was calculated according to (4.23). The predicted impedance curves at a sweep of frequencies were analyzed via a four-element circuit model to extract parameters including resistivity, double layer capacitance, and the geometric capacitance to characterize the expected electrical properties of an electrolyte-hydrogel system. We have shown that the impedance decreases as the  $pH$  deviates from the  $pH$  at the isoelectric point of PCBMA hydrogel,  $pH = 6.4$ . The decrease in resistance of the hydrogel and increase in the double layer capacitance at the electrode-hydrogel interface are due to an increase in the concentration of mobile ions in the hydrogel and charged functional groups on the zwitterionic hydrogel backbone. At high electrolyte ion concentrations, we find that the total charge on the hydrogel backbone is small in comparison to the total salt concentration, thus the impedance does not change significantly with  $pH$  at those concentrations.

This model can be used to improve the design of the hydrogel for biosensor encapsulation applications. For example, the zwitterionic hydrogel will not give anomalous electrical measurements in systems with high salt concentration, since the electrolyte ion concentration dominates the impedance. However, if the electrical signal is weak, a hydrogel with a large charge density on the polymer backbone compared to the ionic strength of the electrolyte may aid in device performance due to reduced electrical impedance and increased conductivity of the electrical signal.

The charge transport model presented in this paper is modular in nature; the boundary conditions, equilibrium conditions, and parameters can be al-

tered to include additional physics. For example, to account for spatial variation in the density of the hydrogel, the total concentration of the hydrogel  $N$  can be replaced with a function of position  $x$ . This change does not impact the analysis because the PNP equations are linearized with respect time, not position. If the mesh size of the hydrogel is on the order of the hydrodynamic radius of the ion, the ion mobility is impeded. The ion mobility  $\mu_i$  can be adjusted by a Brinkman factor<sup>125</sup> to account for the reduction in mobility. The hydrogel here is sandwiched between two electrodes, as per the typical electrical impedance spectroscopy setup. For use as a mechanical barrier for biosensors, the hydrogel is in contact with soft tissue and a polymer-coated electrode.<sup>109,112</sup> The method presented to incorporate acid-base dissociation into the PNP equations can be applied to hydrogel encapsulated biosensors by altering the boundary conditions to allow for time-dependent ion concentration at the soft tissue-hydrogel interface and ion injection from the hydrogel into the polymer film driven by an applied potential. For example, in Feicht *et al.*,<sup>21</sup> we modeled ionic and electronic charge transport in a polymer coated electrode via the PNP equations numerically and analytically. The hydrogel and polymer charge transport models are compatible and can be incorporated into a device-level model for a zwitterionic hydrogel-encapsulated organic biosensor to aid in the design of a biosensor for use in the body.

# 5. Discharging Dynamics of Diffuse Charge in an Electrolytic Cell

## 5.1 Introduction

Charge carriers accumulate at a charged interface, forming electric double layers comprising a diffuse layer and fixed charge on a surface.<sup>126</sup> Electrical double layers are a key component of electrochemical systems. For example, capacitive desalination exploits double layers adjacent to high surface area electrodes to separate ions from the bulk solution.<sup>127–129</sup> Electrochemical capacitors store charge at the electrode-electrolyte interface for energy storage applications, and are notable for their high power compared to batteries and energy density compared to conventional capacitors.<sup>130–133</sup> A simple device exhibiting charge separation is an electrolytic cell, *e.g.* parallel plate blocking electrodes that charge and discharge in response to cycling the applied voltage.<sup>4</sup> An applied voltage leads to a separation of ionic charge in solution that generates a non-uniform electric field across the device, with a higher electric field in the double layers and a lower electric field in the electroneutral bulk of the cell. The ions accumulate in double layers adjacent to the electrode surface

that are typically thin compared to the width of the cell. The width of the diffuse double layer is characterized by the Debye length,  $\hat{\lambda}_D = \sqrt{\hat{\epsilon}\hat{k}_B\hat{T}/2\hat{q}^2\hat{c}_0}$  where  $\hat{\epsilon}$  is the permittivity,  $\hat{k}_B$  is Boltzmann’s constant,  $\hat{T}$  is temperature,  $\hat{q}$  is the charge of a proton and  $\hat{c}_0$  is the initial concentration of ions. Variables and parameters with a carat superscript are dimensional, while those without a carat are dimensionless. When the applied voltage is switched off, the cell discharges as the ions eventually return to a uniform concentration distribution. The external current spikes in response to the step changes in voltage, and then eventually decays in magnitude to zero. This spike and decay in the magnitude of the external current is seen during both the charging and discharging process.

One might expect that given the globally cyclic nature of the charging and discharging process, the temporal evolution of the external current during charging would be antisymmetric (i.e. opposite in sign but equal in magnitude) to the current during discharging. However, experiments at high voltages compared to the thermal voltage  $V_T$  in nonpolar fluids doped with surfactant<sup>29–32</sup> show that while the current during charging monotonically decays, the discharging current is nonmonotonic, resulting in a maximum and minimum in the current. The maximum in the magnitude of the current is referred to as the “reverse peak”.<sup>32</sup> Nonpolar fluids are doped with surfactant that self-assemble into inverse micelles to stabilize charges, thereby preventing undesirable buildup of large electric potentials,<sup>28</sup> in systems ranging from petroleum<sup>26,27</sup> to electronic inks.<sup>29,134</sup> Novotny and Hopper<sup>30</sup> reported a reverse peak in the external current while measuring the current response to a field applied to xylene doped with Aerosol OT. They suggest that the non-monotonic current response stems from dissociation and recombination of the charge carriers, in this case surfactant micelles. Novotny<sup>31</sup> performed similar

experiments for blocking and nonblocking electrodes, and compared to numerical solutions of the Poisson-Nernst-Planck (PNP) equations describing the diffusion and migration of charge carriers in a fluid. Novotny included a term for bulk dissociation and recombination of the micellar charge carriers, as well as Faradaic reactions at the electrode interfaces to account for nonblocking electrodes. Novotny found that the blocking electrode model matches experiments when dissociation and recombination are included, to account for charge transfer between micellar charge carriers.

Kornilovitch and Jeon<sup>32</sup> measured the current carried by poly-isobuthylene succinimide inverse micelles in IsoparM during charging and discharging of parallel plate electrodes and also compared the results to the numerical solution of the PNP equations. They did not include a term for dissociation and recombination, yet observed a reverse peak; thus recombination is not necessary to the formation of a reverse peak. Kornilovitch and Jeon<sup>32</sup> proposed a relation between the time the reverse peak occurs  $\hat{t}_p$ , measured from the time when the voltage is turned off, to the diffusivity of the charge carriers,  $\hat{D} \sim 0.1(\hat{L}^2/\hat{t}_p)$ , accurate to 50%, where  $\hat{L}$  is the width of the device. Their analysis assumes that the charge carriers are monodisperse and have equal diffusivities. This effort to provide an estimate of the charge carrier diffusivity can supplement existing characterization methods for charge transport in doped nonpolar fluids, including measuring conductivity as a function of dopant concentration<sup>135</sup> and performing dynamic light scattering for charge carrier mobility.<sup>29</sup> The transient, frequency-dependent current measured during electrical impedance spectroscopy (subjecting material to small amplitude AC voltage) can also be fit to standard circuit models to calculate the double layer capacitance and Debye length of doped nonpolar fluids.<sup>136,137</sup> Further, in a discharging experiment the total concentration of the charge carriers in the cell can be cal-

culated by integrating the current with respect to time at high voltage.<sup>32,138</sup> The charge carrier mobility can be calculated from the initial current during charging and discharging,<sup>138</sup> however this is challenging due to the initial spike in the current.

At high voltages  $V \gg V_T$ , the dynamics during discharging are fundamentally different from the dynamics during charging.<sup>30,32</sup> Bazant *et al.*<sup>4</sup> performed asymptotic analysis and numerical computations to model the charging dynamics of an electrolytic cell at the experimentally-relevant limit of thin Debye lengths,  $\hat{\lambda}_D \ll L$ . They solved the PNP equations for charge transport in three regimes based on the magnitude of the applied voltage  $\hat{V}$  compared to the thermal voltage,  $\hat{V}_T = \hat{k}_B \hat{T} / \hat{q}$ . The “linear regime” where the applied voltage is less than the thermal voltage, formally  $\hat{V} \ll \hat{V}_T$ , is characterized by a uniform bulk salt concentration profile everywhere in the cell, where the salt concentration is equal to the mean of the cation and anion concentration. The double layers behave as linear (voltage-independent) capacitors here, and the charging dynamics is on the  $RC$  timescale. The “weakly nonlinear” regime occurs at an applied voltage  $1 \lesssim \hat{V} < \hat{V}_T \ln 1/\epsilon$ . Here, at the limit of thin double layers  $\hat{\lambda}_D \ll \hat{L}$ , the salt concentration is uniform in the bulk electroneutral electrolyte, but the double layers behave as nonlinear capacitors, meaning that the total charge stored increases nonlinearly with the applied voltage. Again, charging is on the charging  $RC$  timescale, but now capacitance is a function of voltage. In the “strongly nonlinear” regime,  $\hat{V} \gtrsim \hat{V}_T \ln 1/\epsilon$ , the bulk is depleted of ions due to neutral salt adsorption by the double layers, where depletion refers to a bulk salt concentration lower than the initial concentration  $\hat{c}_0$ . In contrast to the linear and weakly nonlinear regimes, here charging occurs on the diffusion timescale. Bazant *et al.*<sup>4</sup> report asymptotic and numerical solutions for the linear and weakly nonlinear regimes, and de-

rive effective macro-scale equations for the strongly nonlinear regime. Beunis *et al.*<sup>139</sup> solved the PNP equations at specific limits of the dynamics of charging, including an extreme case of full charge separation at very large voltage  $\hat{V} \gg \hat{V}_T \ln 1/\epsilon$ , resulting in transient space charge layers and a power-law decay in the external current. The possibility of a transient space-charge was also suggested by Bazant *et al.*<sup>4</sup>

We adapt the analysis of Bazant *et al.*<sup>4</sup> to solve for the current during discharging in the linear and weakly nonlinear regime. The initial condition for each of these analyses is the steady-state solution derived by Bazant *et al.*<sup>4</sup> after the system has fully charged. In the linear regime, the charging and discharging current are found to be antisymmetric, although the potential and charge density are not. In the weakly nonlinear regime, the magnitude of the discharging current decays to zero over a longer period of time than the charging current, breaking the antisymmetry between current during charging and discharging. However, the current in the weakly nonlinear regime monotonically decays in magnitude, indicating that an analysis of the strongly nonlinear regime, where neutral salt is transferred between the double layer and the bulk, is necessary to capture the reverse peak in the current. At applied voltages several times larger than the thermal voltage during charging, the bulk is depleted of ions due to the large capacitance of the double layers. This bulk depletion and subsequent replenishment during discharging is a characteristic feature of the strongly nonlinear regime that is not included in the weakly nonlinear analysis.

This paper begins with a presentation of the governing Poisson-Nernst-Planck equations and boundary conditions. Numerical calculations used to verify our asymptotic results are presented in section 5.3. In section 5.4, we solve the linear regime equations via a Laplace transform for small voltages. In

section 5.5, we compare the discharging current to the charging current in the weakly nonlinear regime. We present numerical solutions to the PNP equations for the strongly nonlinear regime in section 5.6 and analyze the dynamics of discharging at three relevant timescales. We then provide discussion on the physics behind the reverse peak. In section 5.7, we note the saturation of the reverse peak at very large voltage and provide semi-analytic expressions for the reverse peak current and time. The charge carrier diffusivity and concentration can be estimated from these expressions. Finally, we conclude in section 5.8 with a summary of our findings and suggestions for future work.

## 5.2 Mathematical Model

We consider a binary, symmetric electrolyte containing ions of equal diffusivity sandwiched between planar, parallel, blocking electrodes. In the absence of an applied field or a charged electrode surface at steady state, the ionic concentration within the electrolyte is uniform. When a potential difference is applied across the electrodes, ions migrate leading to an external current that charges the electrodes. The system reaches steady state when the ion flux decays to zero throughout the cell. This redistribution of ions is reflected in the external current, which spikes when the applied voltage is suddenly switched on then decays to zero at steady state. There are no Faradaic reactions so the ion flux at the electrodes is always zero. We use the variable  $\hat{t}$  to denote time during the discharging process, whereas time is denoted as  $\hat{s}$  during charging. The applied voltage is switched on at  $\hat{s} = 0$  and switched off at  $\hat{t} = 0$ . Figure 5.1 depicts the moment when the applied voltage is switched off. The ions initially pinned in the double layer redistribute into the electroneutral bulk, discharging the parallel plate electrodes. As  $\hat{t} \rightarrow \infty$ , the ions return to a uniform concentration profile and the external current again reaches zero. Our

goal is to quantify the external current dynamics during discharging of the electrolytic cell.

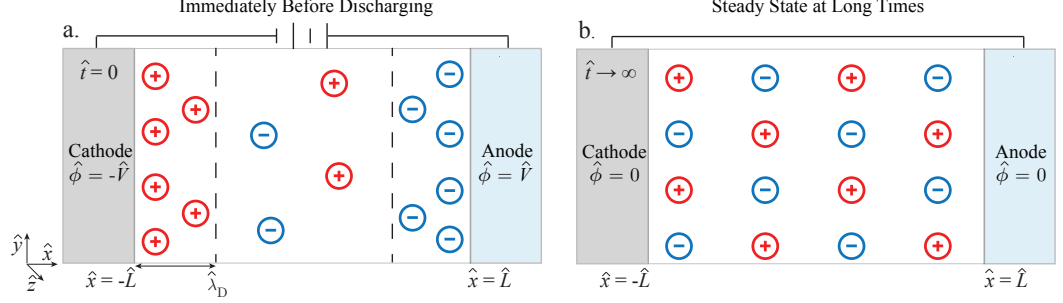


Figure 5.1: Schematic of discharging dynamics in an electrolytic cell. a) Initially, at  $\hat{t} = 0$  ions are concentrated in double layers at the electrodes and uniformly distributed in the bulk. At  $\hat{t} = 0$ , the applied field is switched off and b) the ions eventually redistribute to a uniform concentration profile.

We apply the PNP equations to model the discharging dynamics. We neglect the presence of a Stern layer at the electrode surfaces to focus on the simplest case of discharging dynamics. The PNP equations consist of equations for the flux of ions driven by diffusion and migration, a charge conservation equation, and Poisson's equation relating the gradient of the electric field to the local charge density. The cell is thin in the  $\hat{x}$  direction (figure 5.1) but wide and long in the  $\hat{y}$  and  $\hat{z}$  directions. Hence, we assume that the transport is one dimensional in the  $\hat{x}$  direction. The flux of cations,  $\hat{j}_p$ , is

$$\hat{j}_p = -\hat{D} \frac{\partial \hat{p}}{\partial \hat{x}} - \frac{\hat{D} \hat{q}}{\hat{k}_B \hat{T}} \hat{p} \frac{\partial \hat{\phi}}{\partial \hat{x}}, \quad (5.1)$$

where  $\hat{p}$  is the cation concentration,  $\hat{\phi}$  is the electric potential, and  $\hat{D}$  is the diffusivity of the ions, assuming equal diffusivity. The flux of anions  $\hat{j}_n$  is

$$\hat{j}_n = -\hat{D} \frac{\partial \hat{n}}{\partial \hat{x}} + \frac{\hat{D} \hat{q}}{\hat{k}_B \hat{T}} \hat{n} \frac{\partial \hat{\phi}}{\partial \hat{x}}. \quad (5.2)$$

The charge conservation equations are

$$\frac{\partial \hat{p}}{\partial \hat{t}} = -\frac{\partial \hat{j}_p}{\partial \hat{x}}, \quad \text{and} \quad \frac{\partial \hat{n}}{\partial \hat{t}} = -\frac{\partial \hat{j}_n}{\partial \hat{x}}. \quad (5.3)$$

Poisson's equation is

$$\frac{\partial^2 \hat{\phi}}{\partial \hat{x}^2} = -\frac{\hat{q}}{\hat{\epsilon}}(\hat{p} - \hat{n}). \quad (5.4)$$

The boundary conditions include no flux conditions for the ions at the electrode-electrolyte interface,

$$\frac{\partial \hat{p}}{\partial \hat{x}} = -\frac{\hat{q}}{\hat{k}_B \hat{T}} \hat{p} \frac{\partial \hat{\phi}}{\partial \hat{x}} \quad \text{and} \quad \frac{\partial \hat{n}}{\partial \hat{x}} = \frac{\hat{q}}{\hat{k}_B \hat{T}} \hat{n} \frac{\partial \hat{\phi}}{\partial \hat{x}}, \quad \text{at } \hat{x} = \pm \hat{L}. \quad (5.5)$$

The electric potential  $\hat{\phi}(\hat{x} = \pm \hat{L}) = 0$  at the electrode interfaces for  $\hat{t} > 0$ . At  $\hat{t} < 0$ , the cell is at steady state following the charging process driven by a voltage  $\hat{V}$ , so the charging steady state solution is the initial condition for discharging. In the linear and weakly nonlinear regime, we use Bazant *et al.*'s<sup>4</sup> steady state solutions as the initial condition. In the strongly nonlinear regime, we solve the PNP equations during charging numerically and use the numerical solution when the current reaches zero (within an error tolerance) as the initial condition for discharging.

We non-dimensionalize the above equations by normalizing length  $\hat{x}$  by  $\hat{L}$ ; the electric potential  $\hat{\phi}$  by  $\hat{V}_T$ ; and ion density  $\hat{p}$  and  $\hat{n}$  by  $\hat{c}_0$ , the initial uniform ion concentration before charging. Bazant *et al.*<sup>140</sup> show that the relevant timescale for the exponential decay in the current during charging in the linear regime is the RC time,  $\hat{t} \sim \hat{L} \hat{\lambda}_D / \hat{D}$ , where  $\hat{\lambda}_D$  is the Debye length. Two dimensionless groups emerge: the dimensionless Debye length  $\epsilon = \hat{\lambda}_D / \hat{L}$  and the dimensionless applied voltage  $V = \hat{V} / \hat{V}_T$ . These two groups fully characterize the charging and discharging dynamics, and remain constant throughout the

charging-discharging cycle. Recall, all un-hatted variables are dimensionless. The resulting dimensionless charge conservation equations (5.3), rewritten in terms of the mean salt concentration  $c = \frac{1}{2}(p + n)$  and half the charge density  $\rho = \frac{1}{2}(p - n)$  are

$$\frac{\partial c}{\partial t} = \epsilon \frac{\partial^2 c}{\partial x^2} + \epsilon \frac{\partial}{\partial x} \left( \rho \frac{\partial \phi}{\partial x} \right) \quad \text{and} \quad \frac{\partial \rho}{\partial t} = \epsilon \frac{\partial^2 \rho}{\partial x^2} + \epsilon \frac{\partial}{\partial x} \left( c \frac{\partial \phi}{\partial x} \right), \quad (5.6)$$

where  $\epsilon = \lambda_D/L \ll 1$  at the experimentally relevant thin double layer limit. The dimensionless form of Poisson's equation (5.4) is

$$-\epsilon^2 \frac{\partial^2 \phi}{\partial x^2} = \rho. \quad (5.7)$$

The dimensionless boundary conditions are

$$\frac{\partial \rho}{\partial x} = -c \frac{\partial \phi}{\partial x}, \quad \frac{\partial c}{\partial x} = -\rho \frac{\partial \phi}{\partial x}, \quad \text{and} \quad \phi = 0 \quad \text{at} \quad x = \pm 1. \quad (5.8)$$

After solving for the concentration, charge density, and potential, the external current can be calculated from Gauss' law.<sup>140</sup> The external current is equal to the change in the electric field with time at the electrode surface, and can be calculated at either electrode due to symmetry in the electric field about  $x = 0$ . The dimensionless expression for the current  $J$  in the external circuit is

$$J = \epsilon \frac{\partial^2 \phi}{\partial x \partial t} \Big|_{x=-1}, \quad (5.9)$$

where  $J$  is scaled by  $2\hat{A}\hat{D}\hat{c}_0\hat{q}/\hat{L}$ , and  $\hat{A}$  is the surface area of the electrode.

### 5.3 Numerical Solution to the PNP Equations

The dimensionless PNP equations (5.6)-(5.7) along with the boundary conditions (5.8) are solved numerically using MATLAB's pdepe solver, a finite-

difference based, initial-value problem solver. The numerical solution provides insight on the behavior of the system at a range of applied voltages  $V$  and Debye lengths  $\epsilon$  to guide our asymptotic analyses. The experimental and numerical results from Kornilovitch and Jeon<sup>32</sup> indicate that as the applied voltage increases for a fixed value of  $\epsilon \ll 1$ , the dynamics transition from linear to nonlinear, indicated by the appearance of a reverse peak in the magnitude of the current. We solved the PNP equations for  $\epsilon = 0.01$  and voltages ranging from  $V = 0.5 - 40$  in figure 5.2.

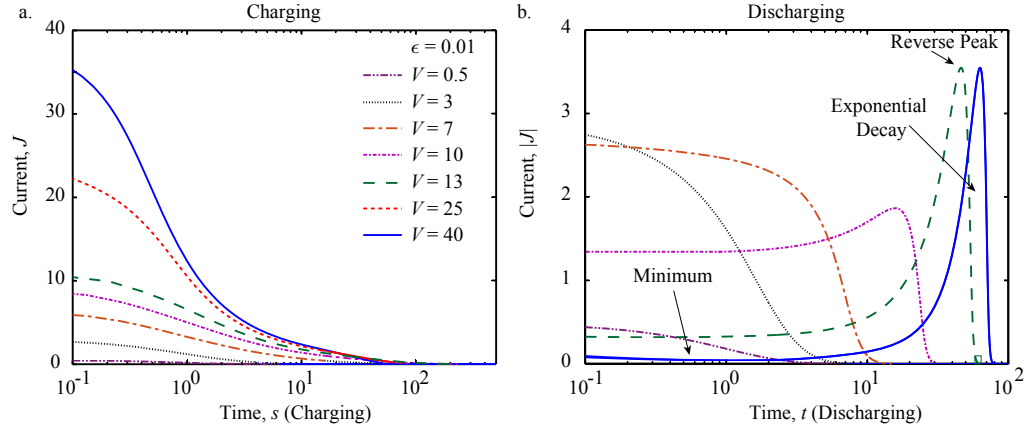


Figure 5.2: A) Magnitude of the current resulting from step changes in voltage at  $\epsilon = 0.01$ . Time is scaled by the  $RC$  timescale. a) The applied voltage is turned on at  $s = 0$ . The current decays monotonically towards zero. b) The applied field is switched off at  $t = 0$ . At low voltages  $V = 0.5, 3, 7$ , the magnitude of the current decreases monotonically towards zero. At larger voltages,  $V = 10, 13, 25, 40$ , the magnitude of the current decreases to a minimum, then reverses and increases to reach a maximum, the reverse peak, followed by a monotonic decay towards zero. At large voltage,  $V = 25, 40$  the current appears to saturate; the curves for  $V = 25, 40$  overlap.

Here, the time during charging is  $s$ , where the applied voltage undergoes a step change from  $\phi(\pm 1) = 0$  to  $\phi(\pm 1) = \pm V$  at  $s = 0$ . The current during charging decays monotonically for all  $V$ . The time variable during discharging is  $t$ , where the applied voltage is switched off at  $t = 0$ , so that  $\phi(\pm 1) = 0$  for  $t > 0$ . After the applied voltage is switched off, the external current ulti-

mately decays in magnitude towards zero at steady state. However, the decay is only monotonic at lower applied voltages ( $V = 0.5, 3, 7$ ). At  $V \geq 10$ , the magnitude of the current reaches a minimum before reversing towards a maximum referred to as the reverse peak. As the applied voltage increases further ( $V = 25, 40$ ), the current appears to saturate, meaning that the reverse peak does not shift with increasing voltage. After the reverse peak, the current decays exponentially in time for all voltages, with a similar slope. This indicates that the time scale for the decay in the current at a specific value of  $\epsilon$  is constant across a range of applied voltages. We aim to identify the charge transport dynamics that result in the asymmetry between charging and discharging in the nonlinear regimes, and the limiting factor leading to saturation of the reverse peak.

## 5.4 Linear Dynamics

We follow the analysis of Bazant *et al.*<sup>4</sup> describing the ion dynamics during charging to solve for the charge density and potential profiles during the discharging process. At low applied voltages where the applied voltage is less than the thermal voltage, formally  $V \ll 1$ , all quantities are written as a regular expansion in  $V$ , resulting in  $c = c_0 + Vc_1 + O(V^2)$ ,  $\rho = V\rho_1 + O(V^2)$ , and  $\phi = V\phi_1 + O(V^2)$ . The expansions are inserted in (5.6), yielding

$$\frac{\partial^2 c_1}{\partial x^2} = 0. \quad (5.10)$$

Integrating (5.10) results in  $c_1(x) = a(t)x + b(t)$ . The no-flux boundary conditions (5.8) to  $O(V)$ ,  $\frac{\partial c_1}{\partial x} = 0$  at  $x = \pm 1$ , require that  $a = 0$ . Finally, the integral of the concentration  $\int_0^1 c_1 dx = 0$ , as the total ion concentration is conserved in the absence of Faradaic reactions, thus  $b = 0$  and  $c_1 = 0$ . The concentration is thus equal to the initial concentration in the electrolyte,  $c_0$  through  $O(V)$ .

The  $O(V)$  charge density evolves according to the linear Debye-Falkenhagen equation,<sup>141</sup> written in terms of  $\rho = V\rho_1$  as

$$\frac{1}{\epsilon} \frac{\partial \rho}{\partial t} = \frac{\partial^2 \rho}{\partial x^2} - \frac{1}{\epsilon^2} \rho. \quad (5.11)$$

The initial condition for this equation is the steady state charge density  $\rho_{ss}$  after charging,<sup>4</sup>

$$\rho_{ss}(x) = -V \frac{\sinh(x/\epsilon)}{\sinh(1/\epsilon)}. \quad (5.12)$$

The linearized boundary conditions (5.8) are

$$\frac{\partial \rho}{\partial x} = -\frac{\partial \phi}{\partial x}, \quad \text{at } x = \pm 1. \quad (5.13)$$

We solve (5.11) by a Laplace transform  $\mathcal{L}$  in time, where  $\mathcal{L}(f(t)) = \check{f}(T)$  and  $T$  denotes the Laplace variable. The Laplace-space quantities are denoted by a check superscript. The Laplace transformed Debye-Falkenhagen equation is

$$\left( \frac{T}{\epsilon} \check{\rho} + \frac{V}{\epsilon} \frac{\sinh(x/\epsilon)}{\sinh(1/\epsilon)} \right) = \frac{\partial^2 \check{\rho}}{\partial x^2} - \frac{1}{\epsilon^2} \check{\rho}, \quad (5.14)$$

Assuming antisymmetry in the charge density about  $x = 0$ , the solution is

$$\check{\rho} = A \sinh(mx) - \frac{V\epsilon}{m^2\epsilon^2 - 1} \frac{\sinh(x/\epsilon)}{\sinh(1/\epsilon)}, \quad (5.15)$$

where  $m = \sqrt{T/\epsilon + 1/\epsilon^2}$  and  $A(T)$  is an as yet unknown function of  $T$ . Inserting (5.15) into the Laplace transform of Poisson's equation (5.7) and integrating once yields

$$\frac{\partial \check{\phi}}{\partial x} = -\frac{A}{m\epsilon^2} ((m^2\epsilon^2 - 1) \cosh(m) + \cosh(mx)) + \frac{V}{m^2\epsilon^2 - 1} \frac{\sinh(x/\epsilon)}{\sinh(1/\epsilon)}. \quad (5.16)$$

By requiring the potential  $\phi(t, 0) = 0$  due to antisymmetry, and applying the boundary conditions (5.13) we find that

$$A(T) = \frac{m^2 \epsilon^3 V}{(m^2 \epsilon^2 - 1)(m(m^2 \epsilon^2 - 1) \cosh(m) + \sinh(m))}. \quad (5.17)$$

Integrating (5.16) yields the Laplace transform of the electrical potential,

$$\check{\phi} = -\frac{A}{m^2 \epsilon^2} [m(m^2 \epsilon^2 - 1)x \cosh(m) + \sinh(x/\epsilon)] + \frac{V \epsilon}{m^2 \epsilon^2 - 1} \frac{\sinh(x/\epsilon)}{\sinh(1/\epsilon)}. \quad (5.18)$$

At long times,  $T \rightarrow 0$ , the charge density (5.15) decays exponentially. Specifically, at this limit, the charge density can be expanded as

$$\check{\rho}_{S \rightarrow 0} = \frac{\frac{V}{2} \operatorname{csch}(1/\epsilon) [x \cosh(x/\epsilon) + (2\epsilon - 3 \coth(1/\epsilon)) \sinh(x/\epsilon)]}{1 + T \coth(1/\epsilon)} + O(T). \quad (5.19)$$

This Laplace-space equation for the charge density at long times can be inverted to yield

$$\rho_{t \rightarrow \infty} = \frac{V}{2} \operatorname{sech}(1/\epsilon) [x \cosh(x/\epsilon) + (2\epsilon - 3 \coth(1/\epsilon)) \sinh(x/\epsilon)] \exp(-t \tanh(1/\epsilon)). \quad (5.20)$$

This reveals that the time scale for charge density relaxation in the linear regime is

$$\tau = \coth(1/\epsilon), \quad (5.21)$$

where time is scaled by the RC time,  $\hat{L}\hat{\lambda}_D/\hat{D}$ . This agrees with the timescale found by Bazant *et al.*<sup>4</sup> for the charging process. For comparison, in the charging case, the Laplace transform of the charge density is  $\check{\rho}_{charge} = T A \sinh mx$  where  $A$  is given in (5.17).

Equations (5.15) and (5.18) for the charge density and electric potential in Laplace space, alongside (5.17) for the parameter  $A$ , can be inverted numeri-

cally using an Euler summation method.<sup>142</sup> The numerically inverted solution for charge density is compared to the long-time solution (5.20) and numerical solution to equations (5.6-5.8) in figure 5.3 for  $V = 0.5$  and  $\epsilon = 0.05$ . The agreement between numerics and the Laplace transform solutions indicates that the assumption that the concentration is uniform and equal to one throughout the cell is valid at low voltages.

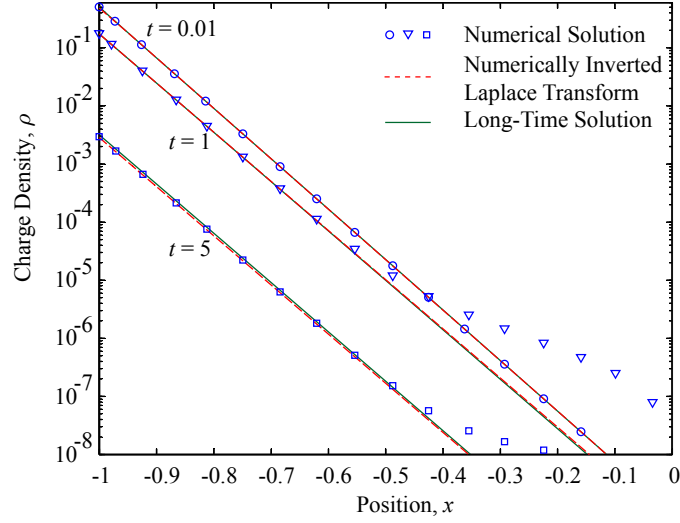


Figure 5.3: The numerically inverted Laplace transform solution (5.15) (dash) for the charge density and the long-time solution for the charge density (5.20) (line) at  $V = 0.5$  and  $\epsilon = 0.05$  are compared to the numerical solution of the PNP equations (5.6-5.8) (circle) at  $t = 0.01, 1, 5$ . Only the cathodic half of the cell is shown.

In the linear regime, the external current during charging and discharging is antisymmetric. However, the potential and charge density profiles are not. In figure 5.4, we show the potential and charge density during charging and discharging. At  $s_1$  and  $t_1$ , the magnitude of the current  $|J| = 0.25$ ; at  $s_2$  and  $t_2$ ,  $|J| = 0.05$ . The two pairs of curves show that, at the same current magnitude in the charging and discharging cycle, the potential and charge density profiles are not equivalent. This is counterintuitive given the antisymmetry of the external current (figure 5.4c). At  $t_1 = s_1$ , the current is equal to

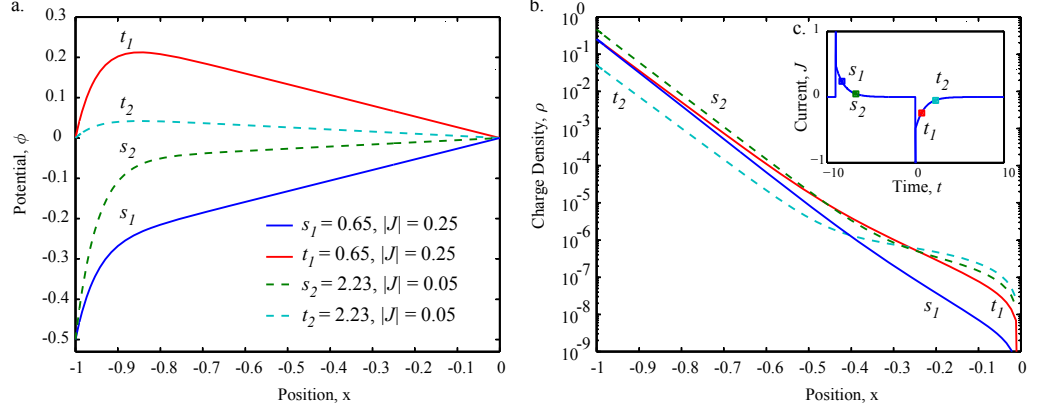


Figure 5.4: The potential and charge density, from the numerical solution to the PNP equations, are plotted during charging and discharging at two pairs of times at which the current is equal in magnitude. Here,  $\epsilon = 0.05$  and  $V = 0.5$ . At  $s_1$  and  $t_1$  (line), the current (c) is  $|J| = 0.25$ , while  $|J| = 0.05$  at  $s_2$  and  $t_2$  (dash). Neither the potential (a) nor charge density (b) profiles match at a given magnitude of the current. Only the cathodic half of the cell is shown.

$|J| = V/2$ , or half of its maximum value  $|J(t = 0)| = V$ , indicating that the charging and discharging processes are at the halfway point. As time continues the charge density during charging increases, while the discharging charge density decreases, emphasizing the asymmetry of the charging and discharging dynamics. When the applied voltage at the electrode switches to zero, the potential profile rapidly switches in response (figure 5.4a), to the potential profile shown in the schematic in figure 5.5. The maximum in potential is located at an  $O(\epsilon)$  distance from the electrode, where the charge density in the double layer causes curvature in the potential according to Poisson's equation (5.7). In the double layer, the migration of cations is directed towards the electrode due to the negative electric field, while cation diffusion is toward the midpoint of the cell driven by the steep drop in concentration from the double layer to the bulk. The potential is linear in the electroneutral bulk, where cation migration is towards the center. The potential profile also holds in the weakly nonlinear regime. In the strongly nonlinear regime, charge density in the bulk leads to curvature in the bulk potential (figure 5.9b) during

discharging according to Poisson's equation (5.7).

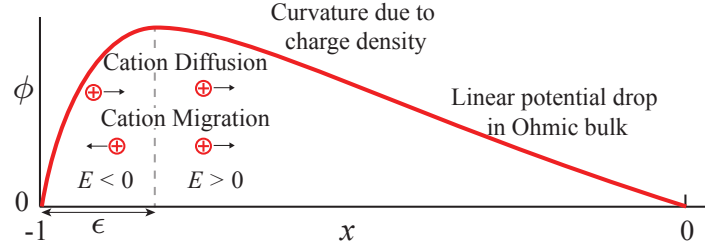


Figure 5.5: During discharging, the potential is zero at the electrode and the midpoint. The curvature in the potential is due to the charge density in the double layer according to Poisson's equation (5.7). The electric field is negative in the double layer and positive in the bulk. Cation migration and diffusion oppose each other in the double layer, whereas they do not in the bulk.

## 5.5 Weakly Nonlinear Dynamics

When the applied voltage is on the order of the thermal voltage, the salt concentration is not uniform throughout the cell. In order to screen the surface charge on the electrodes, the thin double layers adsorb neutral salt from the bulk<sup>141</sup> at a concentration that depends nonlinearly on the applied voltage.<sup>143</sup> This nonlinear capacitance is characteristic of the weakly nonlinear regime.<sup>4</sup> To a first approximation, accumulation of ions in the thin double layer does not significantly deplete the bulk of ions, so the bulk salt concentration is  $c = 1$  to leading order in  $\epsilon$ . Bulk diffusion, accordingly, is negligible in this regime. To solve for the external current during discharging in this weakly nonlinear regime, we address the PNP equations (5.6-5.8) in the thin Debye limit,  $\epsilon \rightarrow 0$ . The equations (5.6-5.8) are singular as  $\epsilon \rightarrow 0$ , motivating the use of matched asymptotic expansions.<sup>10</sup> In the weakly nonlinear regime, the electrolytic cell comprises the double layer, or inner region of width  $x \sim O(\epsilon)$ , adjacent to the electrode and the bulk, or outer region of width  $x \sim O(1)$ , centered around the midpoint of the cell. The boundary conditions (5.8) apply at the literal electrode-electrolyte interface.

Bazant *et al.*<sup>4</sup> apply matched asymptotics to the PNP equations (5.6-5.7) for charging in the weakly nonlinear regime. In the bulk, the position  $x \sim O(1)$  as  $\epsilon \rightarrow 0$ . Bazant *et al.*<sup>4</sup> perform regular expansions in  $\epsilon$  in the bulk, and coordinate rescaling in the inner region, the Debye layer. The Debye layer is shown to have a quasi-equilibrium Gouy-Chapman structure. Regular expansions in  $\epsilon$  in the bulk are inserted into (5.6-5.7), yielding the leading order bulk concentration,  $c_c = 1$ , an asymptotically small charge density  $\rho_c$ , and bulk potential

$$\phi_c = j_c(s)x, \quad (5.22)$$

where  $j_c$  is the current density to leading order in  $\epsilon$ . The subscript  $c$  refers to the charging process. The position,  $x$  is the outer coordinate where  $x = \pm 1$  corresponds to the outer edge of the inner region. Matching between the double layer and the bulk shows that the current density  $j_c$  is asymptotic to the external current  $J$  and is given by the solution to the differential equation<sup>4</sup>

$$C_c \frac{dj_c}{ds} = -j_c, \quad \text{and} \quad j_c(s=0) = V. \quad (5.23)$$

where  $C_c$  is the capacitance of the double layer,

$$C_c = \cosh((j_c - V)/2). \quad (5.24)$$

The capacitance (5.24) is a function of the total voltage and the flux of ions  $j_c$  from the bulk to the double layer. As ions flow from the bulk to the double layer during charging, the capacitance increases. It can be shown that the current density  $j_d$  during discharging is similarly given by the solution of

$$C_d \frac{dj_d}{dt} = -j_d, \quad \text{and} \quad j_d(t=0) = V, \quad (5.25)$$

where  $C_d = \cosh(j_d/2)$  is the differential capacitance of the double layer. The initial condition for discharging can be calculated from  $\phi_d = j_d(t)x$  where the potential is  $\phi_d(0, -1) = -V$  at  $x = -1$ . This shows that the potential drop in the bulk is linear, which is consistent with the applied potential at  $V = 0.5$  in figure 5.4. The initial current is thus  $j_d(0) = V$ . With this initial condition, the implicit solution to (5.25) is

$$t = F_d(j_d) - F_d(V), \quad \text{where} \quad F_d(u) = - \int_0^u \frac{\cosh z/2}{z} dz. \quad (5.26)$$

For comparison, the current in the charging case  $j_c$ , is given by the implicit solution to<sup>4</sup>

$$s = F_c(j_c - V), \quad \text{where} \quad F_c(u) = - \int_0^u \frac{\cosh z/2}{z + V} dz. \quad (5.27)$$

The current during charging  $j_c$  is not antisymmetric to the discharging current  $j_d$  in the weakly nonlinear regime. As stated previously, the current density  $j_d$  is asymptotic to the external current  $J$ . In figure 5.6 we compare the numerical solution to (5.26) for the current density  $j_d$  to the numerical solution to (5.6)-(5.8) for the external current  $J$  and the numerical solution to (5.27) for the current density during charging  $j_c$  at  $V = 0.5, 1, 3$  and  $\epsilon = 0.05$ . At low applied voltages  $V \ll 1$  (linear regime), the current density during charging, discharging and the external current match, as expected. However, deviations arise at  $V = 1$ , and are strongly apparent at  $V = 3$ . First, when comparing the charging and discharging current densities in figure 5.6, the discharging process occurs at a more rapid pace than charging. During charging, migration and diffusion oppose each other during the formation of the double layers. Conversely, during discharging the bulk potential and diffusion fluxes both promote the movement of cations from the electrode to the bulk, as depicted

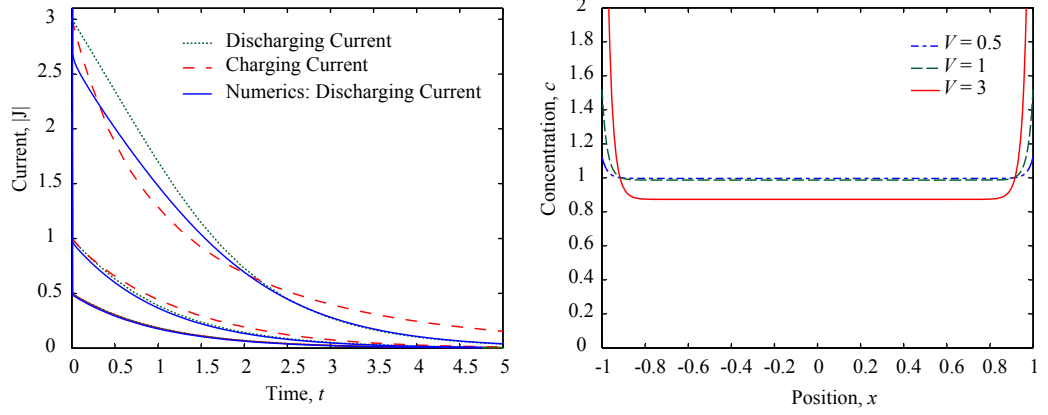


Figure 5.6: A) Current during discharging  $j_d$  (dot), given by (5.25), compared to the current during charging  $j_{0c}$  (dash), given by (5.27), and the numerically calculated current  $J$  (line) during discharging for three applied voltages,  $V = 0.5, 1, 3$  and  $\epsilon = 0.05$ . B) Concentration at time  $t = 0$  for  $V = 0.5, 1, 3$ . At  $V = 3$ , the bulk concentration is not equal to unity due to salt adsorption in the double layer and ion depletion in the bulk, which invalidates the weakly nonlinear analysis.

in figure 5.5. Secondly,  $J \neq V$  at  $t = 0$ . Instead, the current  $J < 3$  initially for  $V = 3$ . To leading order, the flux  $j_d = c_0 V$  and  $c_0(x) = 1$  for all  $x$  at  $t = 0$ . Figure 5.6b shows that the bulk concentration at  $V = 3$  and  $t = 0$  is lower than 1,  $c_0 \sim 0.87$ . If we insert this bulk concentration  $c_0 = 0.87$  and  $V = 3$  into  $j_d = c_0 V$ , we find  $j_d = 2.61$ . At  $t = 0$ ,  $|J| = 2.68$ , according to the numerical solution for  $J$  at  $V = 3$ , so the correction in the bulk concentration  $c_0$  captures the decrease in current at  $t = 0$ . At long times for  $V = 3$ , the external current  $J$  matches  $j_d$  because  $c_0 \rightarrow 1$  as  $t \rightarrow \infty$ , thus the effect of initial bulk depletion on  $j_d$  does not play a role as  $t \rightarrow \infty$ . We conclude that the drop in the magnitude of the external current at  $t = 0$  is due to an increase in the adsorption of ions in the double layer, balanced by depletion of ions in the bulk.

The weakly nonlinear analysis breaks down when the total concentration in the double layer,  $c_D \sim c_0 \epsilon \exp V$  to  $O(\epsilon)$  according to the Gouy-Chapman model,<sup>118, 119</sup> is on the order of the concentration in the bulk,  $c_0$ . This occurs at

an applied voltage (normalized by  $V_T$ )  $V \sim \ln 1/\epsilon$ . At  $\epsilon = 0.05$ , the breakdown is predicted at  $V = 3$ , in agreement with the results in figure 5.6. Bazant *et al.*<sup>4</sup> define a similar limit for the weakly nonlinear analysis during charging; namely,  $4\epsilon \sinh^2(V/4) \ll 1$ .

The weakly nonlinear analysis presented here captures the asymmetry in the current between charging and discharging stemming from nonlinear capacitance in the double layer. However, the analysis does not predict a reversal in the current during discharging. Indeed, the current is monotonic. We must therefore conclude that the non-monotonic current at higher voltages is due to neutral salt adsorption and bulk diffusion, indicating that the reversals in the current must occur on the diffusion timescale. In the following section, we numerically investigate the effects of bulk depletion and diffusion on the current at large voltages.

## 5.6 Strongly Nonlinear Dynamics

When the applied voltage is larger than  $V \sim \ln 1/\epsilon$ , the double layers adjacent to the electrodes deplete the bulk of ions during charging. The weakly nonlinear analysis assumed that the bulk concentration was equal to the initial uniform concentration; at larger voltages, this assumption breaks down, indicating a transition to the strongly nonlinear regime. The strongly nonlinear regime is characterized by the development of a “reverse peak”, or a maximum in the magnitude of the current during the discharging process, due to neutral salt desorption from the double layer to the bulk.

Recall, before the electric field is switched on, the ions are uniformly distributed throughout the cell. After the field is applied, the ions separate to form double layers adjacent to the electrodes. Once the system reaches steady state, the external current decays to zero, and the applied field is switched

off. After an initial spike, the magnitude of the current decays to a minimum. After this point, ions from the double layer diffuse and migrate into the bulk, leading to an acceleration in the current to a reverse peak, before the current magnitude decays to zero. The current during discharging is shown in figure 5.7 for  $\epsilon = 0.01$  and applied voltages between  $V = 3$  and  $V = 13$ , from which this behavior is clearly observed. The  $V = 3$  case is in the weakly nonlinear regime. The current is compared to the current density  $j_d$  (5.26) calculated from the weakly nonlinear analysis, which qualitatively matches the numerical results. The weakly nonlinear asymptotics deviate from the numerical solution at short times due to bulk depletion, as discussed in section 5.5. As the voltage increases to  $V = 7$ , the weakly nonlinear analysis no longer matches the current, but the latter is still monotonic (figure 5.7). As the voltage increases further ( $V = 10, 13$ ), the reverse peak emerges and becomes more pronounced in comparison to the minimum in the magnitude of the current.

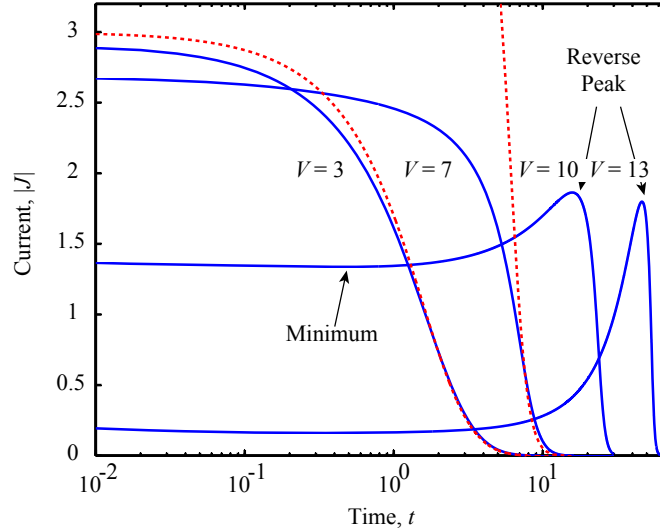


Figure 5.7: The current at a fixed double layer thickness,  $\epsilon = 0.01$ , shows the development of the reverse peak as  $V$  increases. The current calculated from the numerical solution to the PNP equations is compared to the weakly nonlinear current  $j_d$  (dash) for  $V = 3$  and  $V = 7$ . The transition from weakly to strongly nonlinear occurs at  $V \sim -\ln 0.01 = 4.7$ .

The asymmetry between the charging and discharging processes is highlighted by the development of the reverse peak. In order to better understand the origin of the reverse peak, we investigate the current on three timescales relevant to the discharging dynamics. The largest of these is the diffusion time,  $\hat{t}_D = \hat{L}^2/\hat{D}$ , followed by the RC time  $\hat{t}_{RC} = \hat{L}\hat{\lambda}_D/\hat{D}$ , and finally the double layer relaxation time,  $\hat{t}_\lambda = \hat{\lambda}_D^2/\hat{D}$ .

In figure 5.8, the current is plotted for pairs of  $V$  and  $\epsilon$  that fall within the strongly nonlinear regime but do not completely deplete the bulk of salt during charging. The emergence of the reverse peak in cases where the concentration in the bulk is larger than  $O(\epsilon)$ , as shown in figure 5.9c for  $V = 13$  and  $\epsilon = 0.01$ , indicates that total charge separation is not required for a reverse peak in the current. Figure 5.8a, scaled on the double layer relaxation time, shows the initial spike in current, followed by a minimum in the current that occurs at an  $O(1)$  time. Time is plotted on a log-log scale here. On this scale, the current is approximately linear leading up to the minimum in current magnitude.

In figure 5.8b, time is scaled by the RC time  $\hat{t}_{RC}$  for three values of  $\epsilon$  and applied voltage  $V$ . When plotted on a log-lin scale, the decay in current after the reverse peak is linear, corresponding to an exponential decay in the current at long times. The timescale  $b$  for the exponential decay  $J \sim \exp(-bt)$  is  $O(1)$ , indicating that the decay is occurring on the RC time  $\hat{t}_{RC}$ . This is consistent with the exponential decay in the current in the linear regime (5.21), where  $b = \coth(1/\epsilon) \sim 1$  for small  $\epsilon$ . Finally, the current is rescaled on the diffusion time  $\hat{t}_D$  in figure 5.8c. The time at which the reverse peak occurs is on the order of the diffusion time, indicating that the rapid growth in the current before the reverse peak is driven by the diffusion of ions from the double layer to the bulk (figure 5.9). The exponential increase in the current magnitude is on the timescale  $a$ , where  $J \sim \exp(at)$  and  $a \sim O(1)$  preceding the reverse

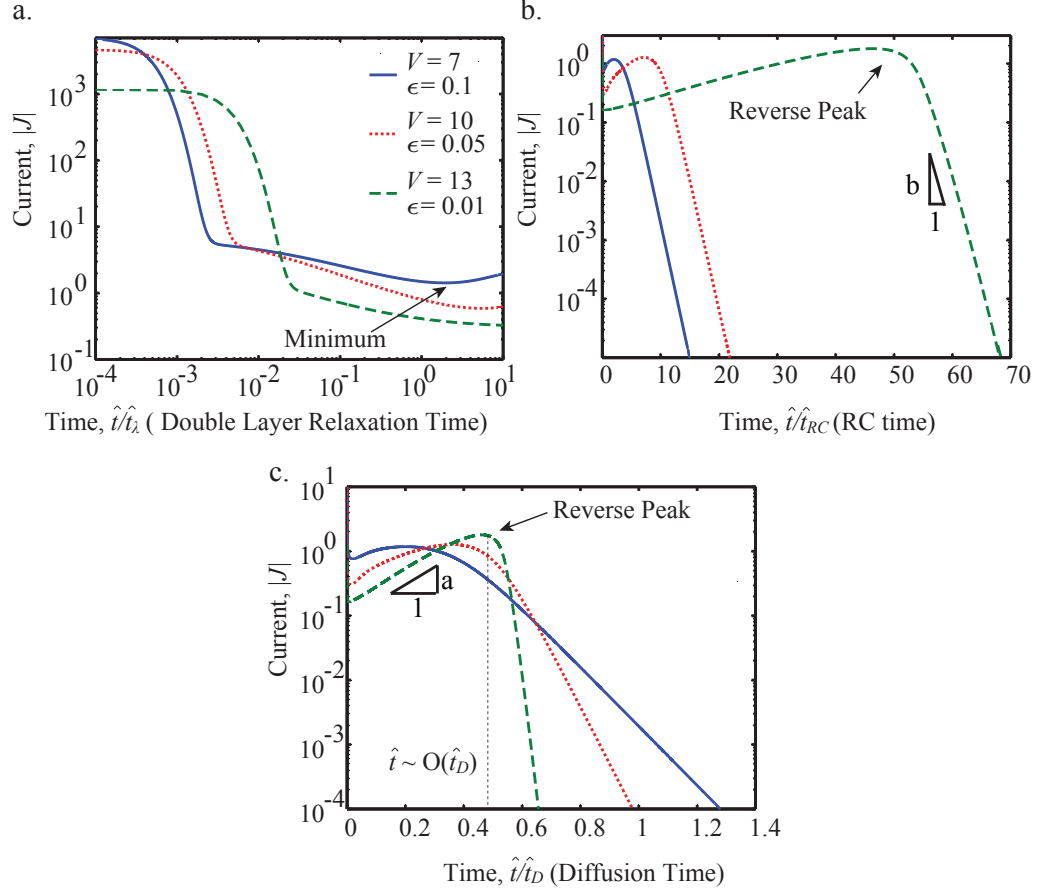


Figure 5.8: The current during discharging is scaled by three timescales: a) the double layer relaxation timescale, b) the RC timescale, and c) the diffusion timescale. The three cases shown here,  $\epsilon = 0.1$  and  $V = 7$ ,  $\epsilon = 0.05$  and  $V = 10$ ,  $\epsilon = 0.01$  and  $V = 13$ , are in the strongly nonlinear regime after the development of the reverse peak.

peak.

While the current during discharging provides insight into the dynamics of the cell, the concentration and potential profiles enable a closer look. Figure 5.9 shows the evolution of the current magnitude  $|J|$ , the potential,  $\phi$ , concentration  $c$ , and charge density  $\rho$  for  $\epsilon = 0.01$  and  $V = 13$  initially, at the minimum and maximum in current. The cathodic half of the cell is shown in figure 5.9; equivalent dynamics occur in the anodic half.

Immediately after the applied field is switched off, the potential at the elec-

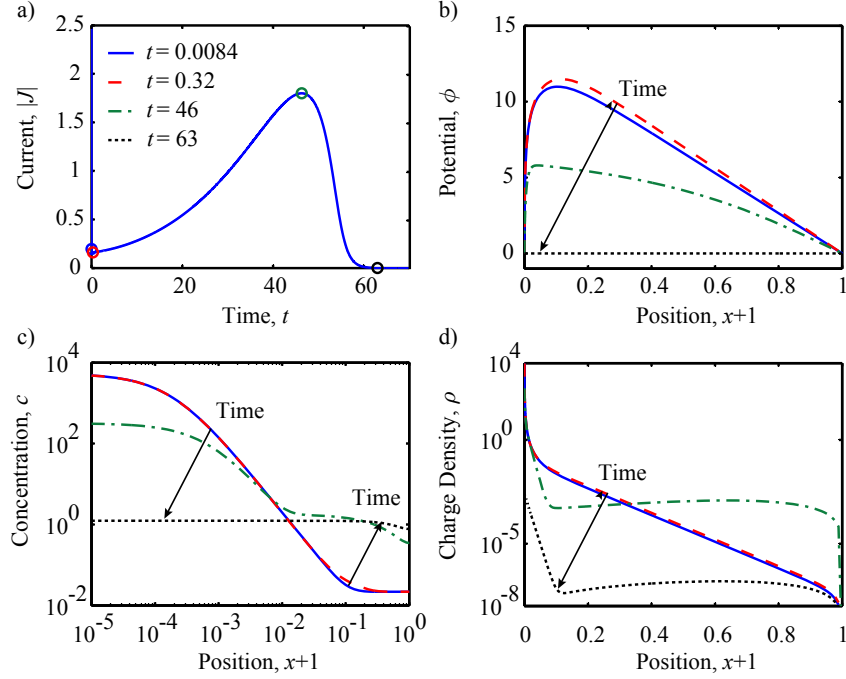


Figure 5.9: The discharging dynamics for  $V = 13$  and  $\epsilon = 0.01$  are shown at multiple times corresponding to the extrema in the current: current (a), electric potential (b), concentration (c), and charge density (d). Position is plotted as  $x + 1$  to allow for a log scale in  $x$  in b,c and d.

trode switches from  $-V$  to 0. Charge density causes curvature in the potential, according to Poisson's equation (5.7). At  $t = 0$ , the large, positive charge density in the double layer is reflected in an increase in potential. As depicted in figure 5.5, the maximum in potential is outside of the double layer, where the charge density rapidly decays to zero. Initially, cations are concentrated in the double layers and depleted in the bulk (figure 5.9c). From the first time-point to the second time-point, the latter corresponding to a minimum in the magnitude of the current, anions from the bulk of the cell migrate towards the maximum in potential, briefly increasing the charge density and potential, as indicated by the small arrowheads in figure 5.9b,d. From the minimum in current ( $t = 0.32$ ) to the reverse peak ( $t = 46$ ), cations from the double layer diffuse and migrate into the bulk driven by strong concentration gradients, de-

creasing the concentration at the electrode, increasing the bulk concentration, and yielding an exponential rise in the magnitude of the current with time (figure 5.9a,c). The charge density decreases in the bulk as both cations and anions enter, leading to a drop in the potential. As time approaches  $t = 46$ , the concentration gradient weakens, and the bulk concentration reaches  $O(1)$ . Following the reverse peak, the cell behavior can be described by a linear RC circuit: the bulk resembles an Ohmic resistor in series with the double layer, represented as a linear capacitor. Accordingly, at times after the reverse peak, the current decays exponentially on the RC timescale, as shown in figure 5.8, until the concentration profile is uniform and the current reaches zero. This is akin to the linear dynamics in section 5.4. It is evident that the reverse peak is due to the onset of bulk depletion.

## 5.7 Reverse Peak Saturation at Very Large Voltage

At larger voltages,  $V \geq 25$  at  $\epsilon = 0.01$ , the discharging current appears to saturate (figure 5.2). This saturation is due to total charge separation and complete bulk depletion of salt during charging. In figure 5.10, the magnitude of the current at the reverse peak and the time of the reverse peak scaled by the diffusion time are plotted against  $\ln \epsilon$  at voltages  $V = 15, 20, 30, 40$ , and  $55$ . It is evident from the overlap in data points at  $V \geq 30$  that the reverse peak has saturated in time and current magnitude, whereas at  $V = 15$  and  $20$  the peak is shifting in time despite saturation in the magnitude of the current at the reverse peak. The current magnitude  $J_p$  and time of the reverse peak  $t_p$  scale as  $\ln 1/\epsilon$ . Therefore, we fit  $J_p$  and  $t_p$  for  $V = 55$  to the expression  $a \ln 1/\epsilon + b$  using the data points for  $\epsilon = 0.001$  through  $0.01$ . The resulting expressions

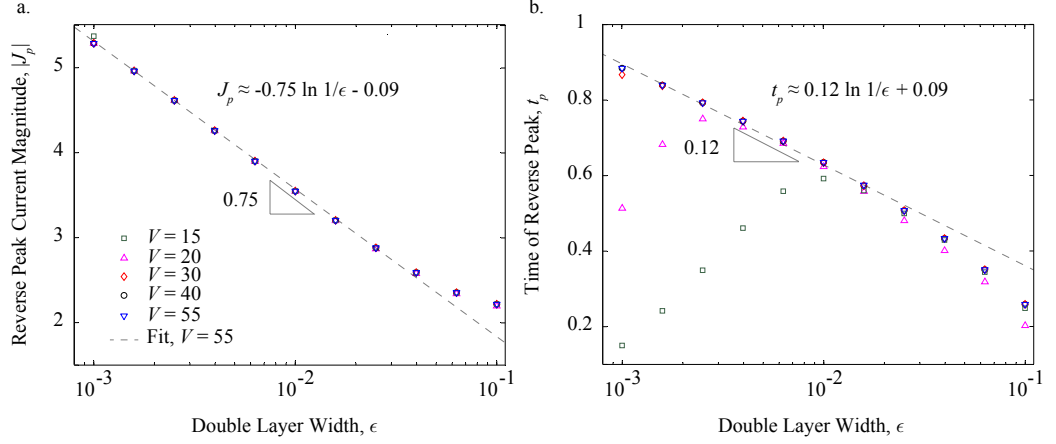


Figure 5.10: The magnitude of reverse peak in the current (a) and the time of the reverse peak (b) scaled on the diffusion time are plotted at  $V = 15, 20, 30, 40$ , and  $55$  on a log scale in  $\epsilon$ , demonstrating that both scale as  $\ln 1/\epsilon$  to leading order. The line of best fit (dash) is fit to the peak current and time at  $V = 55$  for  $\epsilon = 0.001$  through  $0.01$ .

for the peak current  $J_p$  and peak time  $t_p$  are

$$J_p = -a_j \ln 1/\epsilon - b_j \quad \text{and} \quad t_p = a_t \ln 1/\epsilon + b_t, \quad (5.28)$$

where  $a_j = 0.755 \pm 0.005$ ,  $b_j = 0.085 \pm 0.03$ ,  $a_t = 0.116 \pm 0.004$  and  $b_t = 0.093 \pm 0.02$ . The error in these constants is the standard deviation of the points from the fitted expressions. The expression for the peak current (5.28) can be re-dimensionalized as

$$\hat{J}_p = (-a_j \ln 1/\epsilon - b_j) \frac{\hat{A}_0 \hat{D}}{\epsilon^2}, \quad (5.29)$$

where  $\hat{A}_0 = \hat{A} \hat{\epsilon} \hat{k}_B \hat{T} / \hat{q} \hat{L}^3$ . The dimensional peak time is

$$\hat{t}_p = (a_t \ln 1/\epsilon + b_t) \frac{\hat{L}^2}{\hat{D}}. \quad (5.30)$$

The correlations (5.29) and (5.30) can be used to infer the charge carrier diffusivity  $\hat{D}$  and concentration  $\hat{c}_0$  from experiments. To perform this experiment,

the electrolytic cell should be discharged at a sufficiently large voltage  $\hat{V}$  such that the reverse peak saturates in current and time. Equation (5.30) can be solved for diffusivity,

$$\hat{D} = (a_t \ln 1/\epsilon + b_t) \frac{\hat{L}^2}{\hat{t}_p}. \quad (5.31)$$

This expression can be inserted into (5.29), which is solved for  $\epsilon$ . The result for  $\epsilon$  is inserted into (5.31) to obtain  $\hat{D}$ . The charge carrier concentration  $\hat{c}_0$  can be calculated from  $\epsilon = 1/L\sqrt{\hat{\epsilon}\hat{k}_B\hat{T}/2\hat{q}^2\hat{c}_0}$ . This is a single-point measurement to estimate diffusivity and charge carrier concentration; one only needs the value of  $\hat{t}_p$  and  $\hat{J}_p$ .

We applied this method to Kornilovitch and Jeon's<sup>32</sup> experimental results for the saturated reverse peak in current in an OLOA 11000- doped, Isopar M system. Those experiments were performed in a 10  $\mu\text{m}$  thick cell, with 0.5 wt.% OLOA 11000 at temperature  $T = 10$  C. Figure 1D in their paper show a peak time of  $\hat{t}_p = 1.63$  s and a peak current of  $\hat{J}_p = -6.3 * 10^{-8}$  A, at  $\hat{V} = 8$  V. These values were inserted into (5.29) and (5.30) to yield a diffusivity  $\hat{D} = 3.2*10^{-11}$  m<sup>2</sup>/s, dimensionless Debye length  $\epsilon = 0.024$ , and charge carrier concentration  $\hat{c}_0 = 37$  nmol/L. These values are consistent in magnitude with values predicted by Kornilovitch and Jeon's<sup>32</sup> method,  $\hat{D} = 7 * 10^{-12}$  and  $\hat{c}_0 = 12.15$  nmol/L at  $V = 1.16$  V. Their method was based firstly on estimating the skewness of the reverse peak for a range of charge carrier concentrations, and secondly integrating the discharging current over all times to obtain the charge carrier concentration. We emphasize that our approach requires only a single-point measurement.

## 5.8 Conclusions

This work was motivated by the asymmetry between the current during charging and discharging of an electrolytic cell, which has been experimentally ob-

served.<sup>29–32</sup> This asymmetry arises when the applied voltage is on the order of the thermal voltage or larger. We analyzed the discharging process in three regimes defined by the applied voltage magnitude via asymptotic analysis and numerical methods. We derived asymptotic solutions for the current in the linear and weakly nonlinear regimes that can be directly applied to analyzing experimental data. For the strongly nonlinear regime, we identified three relevant timescales for discharging dynamics and the impact of bulk depletion on the emergence and ultimate saturation of the reverse peak.

The discharging dynamics are linear when the applied voltage is smaller than the thermal voltage. We solved the charge transport equations via Laplace transforms in the linear regime, where the concentration is uniform throughout the cell to leading order. We find that the timescale for the exponential decay in the current during discharging is the RC timescale, and that the current is anti-symmetric to the charging current. Interestingly, the electric potential and charge density are not antisymmetric between charging and discharging. This can be attributed to a complementary diffusion and migration fluxes during discharging (figure 5.5), where both point towards the midpoint of the cell, compared to opposing diffusion and migration flux during charging.

At an applied voltage on the order of the thermal voltage, nonlinear capacitance in the double layers results in weakly nonlinear dynamics. We analyzed the weakly nonlinear dynamics via matched asymptotics for thin double layers and derived an asymptotic expression for the external current. The asymptotic current matches the current calculated from the numerical solution to the PNP equations provided  $V \lesssim \ln 1/\epsilon$ . At  $V \sim \ln 1/\epsilon$ , the asymptotic current deviates from the numerical solution at early times due to neutral salt adsorption in the double layers and depletion in the bulk, indicating a breakdown

in the weakly nonlinear analysis. Our work shows that bulk depletion results in the emergence of the reverse peak in current. The reverse peak occurs on the diffusion timescale, indicating that the diffusion of ions from the double layer to the bulk drives the acceleration in current. The timescale for the exponential decay in the magnitude of the current following the reverse peak is the  $RC$  timescale. At long times, the discharging cell behaves as a linear  $RC$  circuit, and mimics the behavior of the linear regime. At very large voltage ( $V \gg \ln 1/\epsilon$ ), the reverse peak saturates due to total depletion of the bulk salt during charging. We fit the current and time of the saturated reverse peak to develop expressions (5.29) and (5.30) correlating the peak current and time to  $\epsilon$  and the charge carrier diffusivity  $\hat{D}$ . These correlations can be used to infer the value of these two parameters as well as the charge carrier concentration  $\hat{c}_0$  from experiment, as we have demonstrated.

In this work, we solved the PNP equations for a binary, symmetric electrolyte. When the diffusivities of the ions are unequal, it can be shown that the decay in the external current in the linear regime is on the ambipolar  $RC$  time,  $\hat{\lambda}_D \hat{L} / \hat{D}_a$ . Here,  $\hat{D}_a$  is the ambipolar diffusivity,  $\hat{D}_a = 2D_1 D_2 / (D_1 + D_2)$ , where  $D_1$  and  $D_2$  are the cation and anion diffusivities. Recall, the reverse peak occurs on the diffusion timescale. When the ions have unequal diffusivities, it is likely that multiple reverse peaks in the current will be observed at timescales corresponding to the diffusivity of the two species and the ambipolar diffusivity. This is an interesting problem for future work; charge carriers of opposite sign are not necessarily of equal size in surfactant doped non-polar fluids.

The PNP equations assume a dilute solution of non-interacting ions. This can lead to an unphysically large concentration of ions in double layers at large voltages. Kilic *et al.*<sup>144,145</sup> analyze the dynamics of a charging electrolytic

cell at large voltage by incorporating the effects of steric hindrance of ions, via Bikerman's model.<sup>146</sup> Steric hindrance can be especially important for charge transport in doped nonpolar fluids as the charges are encapsulated in micelles. For reference, OLOA 1100 inverse micelles in dodecane are around 7 nm in diameter.<sup>137</sup> Kilic *et al.*<sup>144,145</sup> show that including steric hindrance limits the concentration in the double layers, which grows exponentially with voltage in the standard PNP equations. With steric hindrance, the weakly nonlinear regime thus extends to higher voltage than  $V_T \ln 1/\epsilon$ . The emergence of the reverse peak would likely be shifted to higher voltage using Bikerman's model.<sup>146</sup> This is an interesting problem for future work.

## 6. Conclusion

The electrochemical systems studied in this thesis involve novel materials, charge carriers and devices. We developed a framework for incorporating the physics of these unconventional materials into mathematical models based on the PNP equations for charge transport at the limit of thin double layers and space-charge layers. Our predictive models can be included in device-scale models for use by experimentalists to aid in the design and advancement of organic electronics and electrochemical systems.

In chapter 2, we analyzed electron and hole transport in organic light-emitting diodes (OLEDs) via the PNP equations.<sup>14</sup> In OLEDs, electrons and holes are injected at the electrodes, diffuse and migrate through the polymer semiconductor and then recombine in the bulk to form photons, which are emitted through the transparent anode. The current across an OLED, proportional to the rate of recombination, is an important measure of device performance. We focused on space-charge limited transport, in which migration and diffusion point in opposite directions in the space-charge layer, leading to accumulation of injected charge that limits the current. These rapid variations in charge carrier density and electric field in the space-charge layer motivated our application of singular asymptotic analysis to the PNP equations. In the absence of electron-hole recombination, our analysis revealed three regions within the OLED: (i) “space-charge layers” near each electrode whose width

$\lambda_s$  are much smaller than the device width  $L$ , wherein carrier densities decay rapidly and the electric field is intense; (ii) a “bulk” region whose width is on the scale of  $L$ , where carrier densities are small; and (iii) intermediate regions bridging (i) and (ii). We solved the PNP equations in each layer, and found that the current  $J$  scales as  $V^2/L^2\lambda_S$ , where  $V$  is the applied voltage. This scaling is in contrast to the diffusion-free scaling  $V^2/L^3$ ,<sup>2</sup> and agrees with the scaling for the current across ITO/MEH-PPV/Ca OLEDs in experiments by Parker.<sup>68</sup> Thus, we found that diffusion leads to a large  $O(L/\lambda_S)$  increase in current and must be included to accurately predict the current across an OLED for given material parameters. This finding emphasizes the importance of both diffusion and the space-charge layer to the current and device performance. Finally, we derived an asymptotic recombination-voltage relation for a kinetically-limited OLED, in which charge recombination occurs on a much longer timescale than diffusion and migration.

The ion mobility in mixed ionic-electronic conducting polymer films is difficult to measure directly. A simple device designed to measure ion mobility consists of a polymer film doped with holes in contact with an electrode and an electrolyte. A gate electrode immersed in the electrolyte completes the circuit.<sup>1</sup> The film contains a fixed negative charge density supplied by the polymer backbone, which is initially compensated by a uniform density of holes (electron vacancies). As the cations invade the film driven by an applied voltage, the holes evacuate across the electrode to maintain overall electroneutrality; thus, an ionic current is converted to an electronic signal. Recent experiments on ion injection into the polymer film have shown that the location of the advancing ion front increases as the square-root of time,<sup>1</sup> a scaling typically associated with diffusive transport. However, the potential difference across the film is on the order of volts; hence, one would expect that ion transport is dominated

by migration as opposed to diffusion. We modeled the ionic and electronic transport via the PNP equations.<sup>21</sup> Under the assumptions that the driving voltage is strong and that the holes are infinitely more mobile than the cations, a similarity transformation reduced the governing partial differential equations to coupled nonlinear ordinary differential equations that can be readily solved numerically. The similarity transformation clearly elucidates the square-root of time front scaling,  $\delta = \sqrt{2\mu V t}$ , where  $\delta$  is the front location,  $\mu$  is the cation mobility, and  $t$  is time. We compared the similarity solution to the numerical solution of the full drift-diffusion equations, finding excellent agreement. When compared to experimental data, our model captures the front location, confirming that the cation invasion process is self-similar at large driving voltages. However, qualitative differences between the ion profiles are observed. We suggest that potential losses at the polymer interfaces, 2-D transport along the glass substrate or ion barrier, or a nonlinear relationship between the hole concentration and transmission through the chromatographic polymer film indicating de-doping may lead to error in the mobility measurement.

In chapter 4, we reported a mathematical model for ion transport and electrical impedance in zwitterionic hydrogels. The zwitterionic hydrogel has acidic and basic functional groups that carry a net charge at a  $pH$  not equal to the isoelectric point. Such hydrogels can be used as a mechanical interface between a relatively hard biosensor and soft tissue in the body. For this application, the electrical impedance of the hydrogel must be characterized to ensure that ion transport to the biosensor is not significantly impeded. The electrical impedance is the ratio of the applied voltage to the measured current. We considered a model system, wherein an oscillating voltage is applied across an electrochemical cell comprising a hydrogel immersed in an electrolyte sandwiched between parallel, planar blocking electrodes. We employed the

PNP equations coupled with acid-base dissociation equations for the charge on the hydrogel backbone to model the transport of ions through the hydrogel. The electrical impedance was calculated from the numerical solution to the PNP equations and analyzed via a four-element circuit model comprised of the resistance of the hydrogel, the geometric capacitance of the cell, and the capacitance of the electrical double layers at the electrode-hydrogel interface. We found, for example, that an increase in  $pH$  from the isoelectric point,  $pH = 6.4$  for a model hydrogel, to  $pH = 8$  reduces the resistance of the hydrogel by  $\sim 40\%$  and increases the double layer capacitance by  $\sim 250\%$  at an equilibrium cation concentration of  $0.1 \text{ mM}$ . The significant impact of charged functional groups on the hydrogel to the resistance and capacitance is damped at higher electrolyte ion concentrations. This model can be used to improve the design of zwitterionic hydrogels for biosensor applications. For instance, if the electrical signal detected by the biosensor is weak, our model predicts that low impedance can be achieved for a hydrogel isoelectric point far from the  $pH$  of the electrolyte, increasing transmission of the electrical signal through the hydrogel.

In chapter 5, we analyzed the electrochemical dynamics of a discharging electrolytic cell comprised of a binary symmetric electrolyte between two planar, parallel blocking electrodes. This analysis is applicable to doped nonpolar fluids in which the charge is carried by inverse micelles. When a voltage is initially applied, charge carriers diffuse and migrate towards the electrodes, forming electrical double layers. After the system reaches steady state and the external current decays to zero, the applied voltage is switched off and the cell discharges, with the charge carriers eventually returning to a uniform spatial concentration. At voltages on the order of the thermal voltage  $V_T$ , experiments on doped nonpolar fluids observe that the temporal evolution of the external

current during charging and discharging is not symmetric.<sup>30,32</sup> In fact, at sufficiently large voltages,  $V > V_T \ln(1/\epsilon)$ , the current during discharging displays a “reverse peak” before decaying in magnitude to zero. We analyzed the dynamics of discharging by solving the PNP equations via asymptotic and numerical techniques in three regimes. In the “linear regime”, when the applied voltage is formally much less than the thermal voltage, the charging and discharging current is antisymmetric in time; however, the potential, charge density and concentration profiles during charging and discharging are asymmetric. When the applied voltage  $V_T \lesssim V \lesssim V_T \ln(1/\epsilon)$  in the “weakly nonlinear” regime, the current during charging and discharging is asymmetric. The bulk salt concentration is still uniform in the weakly nonlinear regime at the thin-Debye-layer limit; however nonlinear capacitance is responsible for the asymmetry of the current. The reverse peak in the discharging current develops in the “strongly nonlinear” regime at an applied voltage  $V \sim V_T \ln(1/\epsilon)$ , driven by neutral salt adsorption by Debye layers and consequent bulk depletion during charging. Our analysis provides a framework for analyzing the dynamics of an electrolytic cell during discharging and elucidates the underlying physics of the reverse peak.

## 6.1 Future Work

The organic electrochemical transistor (OECT) is a device consisting of a mixed ionic-electronic conducting polymer film in contact with source and drain electrodes at each end. The length of the polymer film is covered in an electrolyte containing an immersed gate electrode.<sup>73</sup> A potential difference between the gate and source electrodes drives the injection of cations from the electrolyte into the polymer film below. The cations, injected perpendicular to the polymer film, displace doped holes which evacuate the film at the

source electrode, resulting in an electric current. This device has been applied to measure glucose concentration<sup>75</sup> and monitor micelle formation.<sup>76</sup> The dynamics in this device are similar to the 1-D transport modeled in chapter 3, however in this case the cation flux is perpendicular to hole flux, requiring 2-D PNP equations. I am interested in developing a mathematical model for cation injection and hole transport in the polymer film via the PNP equations and numerical methods. This problem is ripe for modeling due to the complex physics of cation injection. Our hypothesis is that injection of cations results in a thin space-charge layer in the film at the polymer-electrolyte interface, similar to the space-charge layer that develops due to electron and hole injection in OLEDs.<sup>14</sup> If this is the case, the flux of holes in the film is driven by three effects: an applied potential difference between the drain and source electrodes, maintaining electroneutrality in response to cation injection, and migration due to the electric field established by the charge density in the space-charge layer. The interplay of these three effects can be captured by the PNP equations but would be difficult to observe experimentally. In future work, I am interested in determining the impact of a space-charge layer on cation and hole transport in OECTs.

In a departure from the electronic device oriented nature of this thesis, my second thought for future work lies firmly in biology. The nervous system serves as the wiring between the brain and the body, directing motion and relaying feedback. The information is relayed through electrical and electrochemical signals along the system of nerves, which are bundles of neurons.<sup>147</sup> The signal travels along a neuron and is transmitted from a neuron to a target cell via the release of neurotransmitters into the synapse, a junction between two cells that is generally between 15-25 nm wide.<sup>148</sup> The neurotransmitters are contained within vesicles that fuse to the cell membrane triggering exocy-

tosis, releasing the neurotransmitters into the synapse. The neurotransmitters then diffuse and migrate across the thin gap. In the case of direct synaptic transmission, the neurotransmitters bind to ligand-gated receptors to open ion channels selective to  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , or  $\text{Cl}^-$ . For example, acetylcholine is a positively-charged neurotransmitter that binds to the nicotinic acetylcholine receptor in the nervous system specific to  $\text{Na}^+$  and  $\text{K}^+$ .<sup>147</sup> These receptors are located directly across the gap from the neurotransmitter release point. Conversely, negatively charged glutamate often escapes the synapse due to the negative charge on the surface of the cell membranes, thus glutamate transporters are located outside of the synaptic cleft.<sup>149,150</sup> The escape of glutamate compared to acetylcholine can be attributed to the charge of the neurotransmitter,<sup>151</sup> indicating that electrostatics play an important role in the synaptic cleft. I propose modeling the transport of acetylcholine in the synapse. The transport of neurotransmitters in the synaptic cleft is best modeled via the cylindrical PNP equations. Through the use of a detailed mathematical model, I intend to study the relationship between the width of the synaptic cleft, the number of neurotransmitter molecules released, the binding kinetics and receptor concentration. This results of this work could provide valuable insight on the physics of neural signaling.

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