# **Chapter 3: Electrochemical Theory**

The actuators described in later chapters are activated electrochemically, with polypyrrole forming one or both electrodes of an electrochemical cell. This chapter provides a brief overview of some of the theory that has been developed to describe the kinetics and thermodynamics of electrochemical reactions (Atkins 1990). The theory presented here is used in later chapters to help elucidate the thermodynamics and the rate limiting mechanisms involved in charging and discharging polypyrrole actuators.

The rate of charge transfer (the current) in an electrochemical cell is typically limited by the speed of mass transport of ions in the electrolyte phase or by barriers restricting the rate at which electron transfer can occur at the electrodes. Theories used to describe mass transport by migration, convection and diffusion are described, as is a theory employed to model charge transfer kinetics.

The extent of a reaction or equivalently of charge transfer is determined by thermodynamics. Two thermodynamic models are presented which relate voltage and charge transfer. The first assumes that the potential energy of a molecule in a given state is independent of population and concentration, and thus that there is no significant interaction between molecules. The second describes the voltage/charge relationship for a particular type of interaction, namely the electrostatic interaction found in capacitive charging.

The theory presented in this chapter assumes a typical electrochemical cell, with two planar, non-porous metal electrodes separated by an electrolyte (a medium having ionic conductivity). The behavior of cells having polypyrrole electrodes is somewhat more

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complicated, as the electrode is porous, and its conductivity is finite and dependent on the applied potential. Nevertheless, the same basic physical mechanisms described in this chapter apply to the more complex case of polypyrrole charging.

In electrochemistry voltage and current are measured and controlled. Thus it is natural to express the thermodynamic state in terms of voltage, the rate of reaction as a current, and the extent of reaction as a charge. The equations that follow are therefore often expressed as electrical impedances.

# 3.1 Electrolyte Impedance

The impedance of the electrolyte is one potentially rate limiting factor. An electrolyte is a medium that possesses ionic conductivity – in other words charged molecules are the carriers. Salt solutions (e.g. sea water), molten salts (e.g. alumina Al<sub>2</sub>O<sub>3</sub>/cryolite Na<sub>3</sub>AlF<sub>6</sub> used in smelting), and some polymers (e.g. Nafion<sup>©</sup> and polyethylene oxide) are all electrolytes. Note that except in the cases of Nafion<sup>©</sup> and polyethylene oxide, both positive charges (cations) and negative charges (anions) are mobile, and that in all cases the net charge on the electrolyte is zero. Application of an electric field drives anions parallel and cations antiparallel, creating a current. In aqueous solutions of relatively small ions such as sodium chloride, the current density, *j*, is proportional to field, *E*, up to megahertz frequencies<sup>#</sup>:

$$\sigma = \kappa \cdot E \qquad \qquad 1$$

<sup>&</sup>lt;sup>#</sup> At Megahertz frequencies the amplitude of ionic displacement is smaller than the size of the solvation sphere, at which point conductivity rises.

where  $\kappa$  is conductivity. The ionic conductivity of an electrolyte depends on the mobilities<sup>+</sup> and concentrations<sup>&</sup> of the ions present. Ionic species with high mobilities and concentrations thus make the greatest contributions to the total current. Ion mobility is proportional to the diffusion coefficient, as might be expected, given that both are measures of the ease with which ions are transported through the electrolyte. In general, small, highly charged ions have the highest mobilities. However, very small ions such as Li<sup>+</sup> form tight solvation spheres in water, effectively increasing size and 'drag'. The diffusion coefficient of Li<sup>+</sup> is thus lower than that of Na<sup>+</sup> (Atkins 1990).

Diffusion and convection (fluid flow) also lead to ionic mass transport. These effects are important near the electrolyte/electrode interface, but typically have a negligible influence on the bulk electrical impedance<sup>\*</sup>. Equation 1 normally suffices to describe bulk electrolyte impedance. Near electrode/electrolyte interfaces diffusion and convection become relevant, as is discussed below.

Measurements of electrolyte conductivity involve placing electrodes into the electrolyte. The measured conductance is a function both of bulk conductivity and electrode interface effects. The interface impedance includes a capacitance resulting from the build-up of ions, as discussed in the next section. At frequencies that are typically in the 1-100 kHz range for salts in liquid solution, the interface impedance becomes negligible, and the bulk conductivity is readily measured.

<sup>&</sup>lt;sup>+</sup> Mobility, *u*, relates applied field, *E*, to ion drift velocity, *v*: *v*=*u*·*E*.

<sup>&</sup>lt;sup>&</sup> One might expect conductivity to be proportional to concentration. As concentration increases, interactions between ions become significant, which is modeled by subtracting a term proportional to the square root of concentration (Atkins 1990). The model fails at high concentration.

<sup>\*</sup> Convection and diffusion influence current where concentration gradients are present. The latter tend to arise near electrode/electrolyte interfaces due to reactions, and not in the bulk electrolyte.

## **3.2 Interfacial Impedance**

In this section models of the impedance at electrode/electrolyte interfaces are described. It is assumed that electrodes are non-porous and planar. In Chapter 8, porous electrodes are discussed. The physics described here can be generalized to describe non-planar geometries (Bard and Faulkner 1980).

Electrically, the metal/electrolyte interface is a junction between ionic and electronic modes of conductivity, and is somewhat analogous to a semiconductor PN junction. In many situations the interface behaves like a capacitor, with the application of a voltage leading to a build-up of equal and opposite charges, and the excess or dearth of electrons at the metal surface being balanced by cations or anions in solution. If the potential is pushed to increasingly negative values, the potential difference eventually becomes such that it is thermodynamically more favorable for the electrons to be transferred to the ions, or to neutral species in the electrolyte. The electrode itself may also form anions. In such cases a chemical reduction occurs. Positive potentials similarly lead to transfer of electrons from ions, neutral species or the electrode atoms themselves, resulting in oxidation. The occurrence of charge transfer, leading to a change in chemical state of the electrolyte or the electrode, is referred to as a Faradaic reaction. Faradaic processes are described in Section 1.2.2, while Section 1.2.1 presents models of capacitive charging.

## 3.2.1 Double Layer Capacitance: Metal/Liquid Electrolyte

Consider the case of two electrodes in solution. The electrodes might for example be platinum, and the solution 1 M aqueous KCl. A potential is applied, and an electric field is formed between the electrodes. The field leads to a current in the electrolyte, as cations and anions are driven in opposite directions. The concentrations of cations and anions increase at the anode and cathode, respectively, balanced by charge on the electrodes. Eventually, providing that no Faradaic processes occur, the field within the bulk electrolyte drops to zero, and sum of the potential drops across each electrode equals the applied potential. The process is most simply modeled as an RC charging, with R being the sum of the electrolyte resistance plus any resistance from the remainder of the circuit and C, referred to as the double layer capacitance, generally being in the range of 0.1-0.4 Farads per square meter of electrode for aqueous electrolytes (Bard and Faulkner 1980).

The simplest model of capacitance assumes that ions sit at a fixed distance,  $\delta$ , from the electrode, as determined by their diameters. This model, proposed by Helmholtz in 1853, predicts a double layer capacitance, *C*, that is proportional to electrode surface area, *A*, and the dielectric constant,  $\varepsilon$ , and that is inversely proportional to charge separation,  $\delta$ , as in a parallel plate capacitor:

$$C = \frac{\varepsilon \cdot \varepsilon_o \cdot A}{\delta}, \qquad 2$$

where  $\varepsilon_o$  is the permittivity of free space (8.85419×10<sup>-12</sup> C<sup>2</sup>·N<sup>-1</sup>·m<sup>-2</sup>). The size of the Helmhotz double layer,  $\delta$  is typically 0.15-0.5 nm, depending on the solvent and ions.

In practice, it is found that capacitance is a function of applied potential, V, and ion number per cubic meter,  $n^o$ . The actual double layer dimension may be up to 30 nm in aqueous solutions having ionic concentrations of greater than  $10^{-2}$  M (Bard and Faulkner

1980). These deviations from the Helmholtz model are partly due to random thermal motion of the ions, which lead to a diffuse double layer, with ion concentration at a given distance from the electrode being determined by the Boltzmann distribution. When the finite size of the ions is also taken into account, this treatment leads to an expression relating the differential double layer capacitance<sup>&</sup>,  $C_d$ , to voltage, V, absolute temperature, T, the number of charges per ion, z, the Boltzmann constant k (1.38066×10<sup>-23</sup> J·K<sup>-1</sup>) and the fundamental charge (1.60219×10<sup>-19</sup> C), e:

$$\frac{A}{C_d} = \frac{\delta}{k \cdot \varepsilon_o} + \frac{1}{\left(2 \cdot \varepsilon \cdot \varepsilon_o \cdot z^2 \cdot e^2 \cdot n^o \cdot k^{-1} \cdot T^{-1}\right)^{1/2} \cdot \cosh(z \cdot e \cdot V \cdot k^{-1} \cdot T^{-1}/2)} , \qquad 3$$

At high concentrations (>0.1 M) or large voltages (|voltage| > 0.4 V at room temperature) the equation reduces to the Helmholtz model as electrostatic potential energy is much greater than kinetic energy. Chapter 13 of Bard and Faulkner provides an excellent discussion and derivation of these models (Bard and Faulkner 1980).

A rigorous description of the double layer impedance may also require consideration of specific adsorption of species onto electrode surfaces, the structure of the dielectric, and dielectric saturation in the strong interfacial fields (Bard and Faulkner 1980). Modeling of polypyrrole double layer capacitance presented in Chapter 8 employs the Helmholtz model, which provides good agreement with the experimental observations of Chapter 10.

<sup>&</sup>lt;sup>&</sup> The differential capacitance is defined as the derivative of charge with respect to voltage, and is a function of potential and concentration.

#### **3.2.2** Electrochemical Reaction Impedance

The potential difference developed across a double layer drives an exchange of electrons between the electrolyte phase and the electrically conductive phase. Thermodynamics and kinetics help describe and model these Faradaic processes, relating the double layer potential to current and the concentration of reactants and products. Three cases are treated, namely (1) the reversible case, in which the kinetics of charge exchange and of mass transport are fast compared with the time scale of observation, (2) the mass transport limited case, and (3) the kinetics limited case.

Suppose that at the electrode of interest, called the working electrode, a species O is reduced by the transfer of n electrons to form R:

$$O + n \cdot e^{-} \rightarrow R$$
. 4

The oxidation of species R' forming O' via m electrons occurs at the counter electrode, such that the complete reaction is:

$$m \cdot O + n \cdot R' \rightarrow m \cdot R + n \cdot O'$$
. 5

The beauty of electrochemistry is that the direction, rate and extent of such reactions are determined by the electrode potentials, the current and the total charge transferred, respectively. Potential, current and charge transfer are controllable, and hence the direction, rate and extent of the chemical reaction can be set.

The double layer potential at each electrode determines the direction of the reaction (right to left or left to right) and the rate. As the potential drop between the working electrode and the electrolyte,  $V_w$ , is increased, electron energy,  $V_w \cdot e$ , decreases, increasing the likelihood that the Reaction 4 will proceed from right to left. If equilibrium is reached between the reactants and the products at some potential,  $V_w = E$ , then at a potential  $V_w = E + \eta$  the rate of reaction and the magnitude of the current increases as the absolute value  $|\eta|$  increases. Integration of the current over time tells us exactly how many moles of reactant become product, or vice-versa<sup>&</sup>.

Thus far it has been suggested that the voltage across the double layer,  $V_w$ , also drives Faradaic reactions. Thus the double layer capacitance and Faradaic impedance are in parallel, with the solution resistance acting in series. The next section describes a common form of the Faradaic impedance. Later the effect of limited rates of mass transport is modeled.

#### **3.2.3** Reversible Reactions and the Nernst Equation

Thermodynamics provides a very elegant relationship between the concentrations of the reactants and products, [O] and [R], and the equilibrium potential, E:

$$E = E_o + \frac{\Re \cdot T}{n \cdot F} \cdot \ln(\frac{[O]}{[R]}), \qquad 6$$

where *E* is the potential difference between the electrode and the electrolyte,  $\Re$  is the gas constant (8.31441 J·K<sup>-1</sup>·mol<sup>-1</sup>)<sup>@</sup>, *F* is the Faraday constant (9.64846×10<sup>4</sup> C·mol<sup>-1</sup>)<sup>@</sup>, and  $E_o$  is the potential when *O* and *R* are at equal concentration. This relationship is known as the Nernst Equation, after the German Physical Chemist Herman Walther Nernst<sup>#</sup>

<sup>&</sup>lt;sup>&</sup> provided there are no other reactions occurring, and the double layer charging current is negligible.

<sup>&</sup>lt;sup>@</sup> Note that  $F = e \cdot N_A$  and  $\Re = k \cdot N_A$ , where  $N_A$  is Avagadro's number, k is Boltzmann's constant and e is the elementary charge.

<sup>&</sup>lt;sup>#</sup> Nernst also described the dissolution of salts in water, won the 1920 Nobel prize in chemistry for proposing the third law of thermodynamics, and was the first to suggest chain reactions (Asimov 1982).

(1864-1941), who derived it in 1889. As expected, decreasing E drives Equation 4 to the right. Also note that the Nernst equation does not indicate how long it will take to reach equilibrium (zero current) state.

Batteries are examples of electrochemical cells. If the concentrations of reactants and products are held fixed, Equation 6 describes an ideal voltage source, which a battery approximates. In fact, the voltage, *V*, delivered by a battery at low current is the sum of the of the potentials across each electrode, namely:

$$V = E_o - E'_o + \frac{\Re \cdot T}{F} \cdot \ln(\frac{[O][R']}{[R][O']}), \qquad 7$$

for the case of n=m=1 in Equation 5. The Nernst equation also tells us how much of a change in voltage is required to shift between two equilibrium concentration states. Starting with [O]=1.000 M, and  $[R]=10^{-10}$  M, the change in potential required to switch to [R]=1.000 M and  $[O]=10^{-10}$  M is -0.514 V at 25 °C. The Nernst equation predicts that takes < -1.25 V change in potential to convert a 1 liter solution from containing only 1 M O to only R at room temperature.

Before describing how E and  $E_o$  are determined, and giving the limitations of the Nernst equation, a simple derivation is provided. Atkins (Atkins 1990) and Bard (Bard and Faulkner 1980) present detailed derivations based on classical thermodynamics. Here a statistical mechanics-based derivation is presented, which strips away the mystique associated with entropy and other thermodynamic functions of state.

#### **3.2.3.1** Derivation of the Nernst Equation

Thermodynamics attempts to determine the equilibrium state of a system and its surroundings given knowledge of its components and state variables (e.g. temperature, pressure, volume). Two fundamental concepts are involved, namely that the entropy of the system plus that of its surroundings cannot decrease, and that energy is conserved. An equivalent statement is that an isolated system will tend towards its most probable state, with the constraint that energy must be conserved. In this section, the latter statement is expressed mathematically for the case of non-interacting particles, from leading to the derivation of the Nernst equation.

If particles have the choice of occupying either of two states having equal energies, such as isolated nuclear spins in the absence of an applied field, then we expect half of the particles to be in the up state, and half in the down state. Similarly, in tossing a coin N times, it is most likely that half will be heads and half tails, with this becoming increasingly likely as N increases. In the presence of a magnetic field, the two nuclear spin states no longer have the same energy, those aligned with the field being in a lower energy state than those anti-parallel to it. At temperatures approaching absolute zero, nearly all the spins will be in the low energy state, whereas at room temperature, even in fields of 1.5 T or more, the spins are almost equally distributed between up and down<sup>†</sup>. This is because particle kinetic energy increases in direct proportion to temperature, and the probable population of two states becomes nearly equal when the kinetic energy is much greater than the energy difference between states.

<sup>&</sup>lt;sup>†</sup> At 1.5 T and 300 K there are  $2.6 \times 10^{-6}$  times more particles in the low energy state.

The number of spins occupying each state as a function of temperature is determined by the Boltzmann distribution, which can be applied to many systems, including electrochemical ones. The distribution is arrived at by assuming that N particles exist in an isolated system of total energy E. Each particle can exist in a number of states, where a state is labeled by the index i, and has an energy  $e_i$ . Furthermore, the particles are assumed to be independent – i.e. they do not interact. A collection of adiabatically confined molecules of an ideal gas forms such a system, for example. It is further assumed that a particle has an equal probability of residing in any state, subject only to the constraint that the sum of the energies of all particles must equal a constant, E. The most probable number of particles residing in a given energy state,  $n_i$  is then determined to be:

$$\frac{n_i}{N} = \frac{e^{-e_i/k \cdot T}}{\sum_i e^{-e_i/k \cdot T}} \,.$$
8

The intermediate steps in the derivation are presented by Atkins in Chapter 19 (Atkins 1990). The  $k \cdot T$  factor is derived from the fact that temperature, scaled by the Boltzmann constant, is a measure of average particle energy,  $E/N^{\&}$ . For a particle that exists only in two states, such as a coin and a proton spin, the Boltzmann distribution reduces to:

$$\frac{n_o}{N} = \frac{1}{1 + e^{-e_1/k \cdot T}}, \quad \frac{n_1}{N} = \frac{e^{-e_1/k \cdot T}}{1 + e^{-e_1/k \cdot T}}.$$
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<sup>&</sup>lt;sup>&</sup> Boltzmann (1844-1906) and Maxwell (1831-1879) were the first to convincingly demonstrate the link between the motions of individual particles and macroscopic thermodynamic properties such as temperature, pressure and energy.

As expected, in the limit as  $T \rightarrow 0$ , all particles are in the lowest (ground) state, whereas as  $T \rightarrow \infty$ , equal numbers in each state are expected to be equal. If the energy difference between the states,  $e_1$ , tends to zero, the probabilities tend to 1/2.

This relationship is now applied to electrochemistry. Given an aqueous solution containing both  $Fe^{2+}$  and  $Fe^{3+}$  ions, in contact with an electrode, the aim is to find a relationship between the double layer potential difference, *E*, and the ratio of numbers of iron atoms in each state. The reaction at the electrode is:

$$Fe^{3^+} + e^- \to Fe^{2^+}.$$
 10

If the potential energy difference between the two states iron is  $\alpha$ ,<sup>#</sup> then the total difference in energy between left and right is  $\alpha + E \cdot e$ . The ratio of numbers or concentrations is then:

$$\frac{n_{Fe^{3+}}}{n_{Fe^{2+}}} = e^{-(\alpha + E \cdot e)/k \cdot T},$$
11

which is equivalent to the Nernst equation, as is evident when the natural log is taken. Note that in Equations 5 and 11 the concentrations can be replaced by charge using Equation 4. The Faradaic impedance described by the Nernst equation then has the form of a non-linear capacitance, as discussed in Chapter 8.

#### **3.2.3.2** Limitations of the Nernst Equation

There are some limitations on the validity of the Nernst equation. In deriving the Boltzmann distribution, it has been assumed that there are no interactions between

 $<sup>^{\#}\</sup>alpha$  represents the energy required perform ionization plus the difference in the energies of solvation.

particles. The behaviors of gases at atmospheric pressure and of dilute solutions (<0.001 M) are fairly well modeled when this assumption is made. However, at higher concentrations and pressures, intermolecular forces (electrostatic and van der Waal's) distort the original energy level structure, resulting in deviations from the "ideal". In other words, the energy levels,  $e_i$ , are functions of density, the effect being significant beyond a certain dilution. In order to account for these deviations, the standard practice is to change the form of Equation 6, such that the molarity is replaced by a factor,  $\gamma m/m_0$ , where m is the molality, and  $m_0$  is the molality in a standard state. The  $\gamma$  factor accounts for all non-idealities of the solution. It is primarily affected by electrostatic interactions, and so to first order is a function of the solvent dielectric constant, the charge of the ions and the ionic concentration, as described by the Debye-Hückel limiting law (Atkins 1990). The  $E_o$  term is the potential difference at "standard state", which is defined to be 1 M for an aqueous solute behaving ideally (i.e. its behavior is extrapolated from measurements made at near infinite dilution, where particle interactions are negligible).  $E_o$  is referred to as the standard reduction potential, values of which are tabulated (Bard and Faulkner 1980).

#### 3.2.3.3 Reference Electrodes as Ideal Voltage Sources

If the potential across the double layer,  $V_d$ , can be determined at equilibrium, then *E* can be measured. In measuring cell potential, the total voltage, *V*, is the sum of the double layer potential drops at each electrode plus any *I*·*R* drop across the electrolyte, and thus the value of  $V_d$  is unclear. Furthermore, as current is driven through the cell, the equilibrium potential at each electrode changes, so it is not possible to determine how much of the relative change in cell potential is the result of changes at the working electrode. If the counter electrode is acting as a capacitor it will charge and discharge, the nature of the charging and discharging depending on the electrolyte composition. Even if the capacitance is enormous, so that very little charging occurs as current flows, preferential physical adsorption of ions<sup>#</sup> can lead to a double layer charging, and the development of an offset potential dependent on solution and electrode compositions. Thus such an electrode does not provide an absolute reference. What is desired is a universal reference potential, in essence an electrochemical ground.

The "electrochemical ground" is a third electrode added to the cell, which has high impedance and a fixed composition. The potential of the working electrode is measured relative to this reference electrode. The high impedance assures negligible current flow, and the constant composition fixes the reference double layer potential. (Recall that the Nernst equation predicts that an electrode in the presence of two reactants at fixed concentrations is an constant voltage source, providing that the current passed is small.) A silver wire in the presence of saturated aqueous silver chloride solution forms one such reference<sup>&</sup>. Another is the normal hydrogen electrode, consisting of a platinum wire in the presence of H<sub>2</sub> gas at atmospheric pressure and 1 M aqueous HCl at 25 °C. The normal hydrogen electrode (NHE) is defined to have a standard reduction potential,  $E_o$ , of

<sup>&</sup>lt;sup>#</sup> This can be due to preferential attraction of ions to their mirror charges on the electrode, for example.

<sup>&</sup>lt;sup>&</sup> In a silver chloride reference electrode, the presence of undissolved AgCl salt helps ensure that the concentration of  $Ag^+$  remains constant, even if some current is passed and  $Ag^+$  is transformed to Ag or vice-versa. A glass frit separates the controlled reference electrode from the cell, helping maintain the balance of concentrations.



Figure 1: Diagram representing the changes to the activation barrier at the electrode/electrolyte interface resulting from the application of a voltage,  $\Delta V$ .

0 volts, relative to which all other potentials listed in the standard reduction table are measured<sup>@</sup>.

# 3.2.4 Non-equilibrium Electrode Processes: Kinetics and Mass transport

The Nernst equation describes, with some limitations, the behavior at equilibrium. By equilibrium it is implied that no net change in concentration of either species is occurring. There are, nevertheless, equal and opposite currents, one driving Equation 4 left to right, the other right to left. Suppose that the voltage drop across an electrode is shifted from equilibrium by an amount,  $\eta$ , then what happens? The Nernst equation tells us what final state to expect, but not how quickly that state will be reached. Two factors affect the rate. The first is the speed at which electrons can be transferred between reactants in the

<sup>&</sup>lt;sup>@</sup> Note that there is a potential drop across the NHE double layer, but because voltage is a relative and not an absolute measure, it is convenient to define its potential as 0 volts.

vicinity of the electrode, and the second is how quickly reactants can reach the electrode from the bulk solution. These cases are referred to, respectively, as kinetics and mass transport limited reactions, and are described in the following two sections.

#### **3.2.4.1** The Kinetics of Electron Transfer

For an electron to be transferred to or from an electrode to a species in solution, the species must approach the electrode, displacing solvent and absorbed molecules in the process. Also, it may be that the reactant must take on a particular conformation relative to the electrode. These factors lead to an activation energy - in other words the species must have a certain minimum energy to overcome these 'barriers' to reaction. The Boltzmann distribution tells us that the probability of overcoming the barrier is proportional to  $e^{-U/(k \cdot T)}$ , where U is the activation energy. The potential across the double layer modifies the activation energy, as shown in Figure 1. A constant,  $\alpha$ , accounts for location of the peak of the activation energy barrier relative to the thickness of the double layer, and has a values of between 0 and 1, where  $\alpha=0$  indicates that the peak of the activation barrier is at the solution edge of the double layer,  $\alpha=1$  places the peak at the electrode, and  $\alpha = \frac{1}{2}$  (typical) has the activation barrier peak in the middle of the double layer. As demonstrated by Atkins (Atkins 1990), the rate of reaction, represented by a current density, *j*, is given in terms of the overpotential,  $\eta$ , by the Butler-Volmer equation:

$$j = j_o \cdot \left(e^{\frac{(1-\alpha)\eta \cdot e}{k \cdot T}} - e^{\frac{\alpha \cdot \eta \cdot e}{k \cdot T}}\right),$$
12

where  $j_o$  is known as the exchange current density, and represents the magnitude of current in each direction at equilibrium.

Overpotentials result in an exponential increase in reaction rate. As overpotential is increased, eventually the reaction becomes limited by the rate at which reactant is able to reach the electrode from the bulk, and not by the reaction kinetics.

#### **3.2.4.2 Mass Transport**

Ions and molecules can travel from the electrolyte to the electrode as a result of random motions (diffusion), electrolyte flow (convection) or electrophoretic forces (migration). Diffusion of species, *i*, occurs in response to a concentration gradient<sup>‡</sup>,  $\nabla C_i$ . Convective flux is simply proportional to the product of electrolyte velocity, *v*, and the concentration of species *i*,  $C_i$ . Migration current is described by Ohm's law<sup>§</sup>. The resulting current density, *j*, at any point in the electrolyte, is:

$$j = \sum_{i} -D_{i} \cdot \nabla C_{i} - \frac{n_{i} \cdot F}{R \cdot T} \cdot D_{i} \cdot C_{i} \cdot \nabla V + C_{i} \cdot \mathbf{v} .$$
 13

In the second term on the right the Einstein relation between the diffusion coefficient and electrolyte conductivity is employed (Atkins 1990).

<sup>&</sup>lt;sup>‡</sup> providing that the mean free path is short compared to the characteristic length of the region over which the concentration is changing.

<sup>&</sup>lt;sup>§</sup> providing that the ionic mean free path is short compared to the characteristic length of the electric field.

If the kinetics are similar in rate or faster than the mass transport, then the concentration of the reacting species is depleted at the electrode/electrolyte interface, producing a concentration gradient. The concentration gradient leads to a diffusion current. The concentration as a function of position and time is given by:

$$\frac{\partial C_i}{\partial t} = D_i \cdot \nabla^2 C \,. \tag{14}$$

The current density at planar electrodes in response to a step change in concentration at the interface is described by the Cottrell Equation:

$$j_i = n_i \cdot F \cdot C_i \cdot \sqrt{\frac{D_i}{\pi \cdot t}} \,. \tag{15}$$

Note that the rate of reaction slows over time, corresponding to an increase in the size of the depletion region, and a reduction in the concentration gradient. In liquid electrolytes the depletion layer generally reaches a finite extent due to natural convection currents developed in response to density gradients. Forced convection (e.g. stirring or rotation of the electrode) is often used to minimize the size of the depletion layer thereby increasing mass transport, for example, to speed electroplating<sup>#</sup>, or to allow for the identification of slow kinetics.

In conclusion, this chapter provides a brief overview of the models used to describe the impedances of electrolytes, Faradaic reactions, and double layer capacitances. The basic principles described here are used in analyzing data obtained in subsequent chapters and in developing a model of polypyrrole electrochemical behavior.

<sup>&</sup>lt;sup>#</sup> IR lasers, electrolyte jets and localized high frequency currents are used to create local micro-convection currents at electrode surfaces, thereby producing localized deposits.

# 3.3 Reference List

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