

## 17.10 Diffusion in electrolytes

We use the context of electrolytes to illustrate forced diffusion. The energy of an ion is zero when it is far away from all other ions. Work has to be done to bring it closer to other ions that repel it. Conversely, work can be extracted when it is brought closer to an ion that attracts it. Hence, energy of an ion is different when it is near other ions. If the electric potential at a location is  $\phi$ , the energy of an ion with charge  $Q$  is given by  $Q\phi$ . The total energy of an ion then is due to its chemical nature as well as its concentration in the solution, and that due to electrical potential. It is referred to as electrochemical potential in electrochemistry.

The force experienced by an ion of charge  $Q$  in any location can be obtained if  $\phi$  is known and is given by  $-Q\nabla\phi$ . This is like the action of a body force. It should be noted that the force experienced by a charge depends upon its sign and magnitude. Thus, charged species will experience different body forces. Hence, the average body force exerted on a species and the total body force experienced by the species will be different and this leads to forced diffusion.

### 17.10.1 Notation for ionic solutions

Commonly encountered ionic solutions are those of salts in water, acids in water, and so on. The compound as a whole is electrically neutral. When it is put a solvent, it dissolves and ionizes. For example, NaCl ionizes into  $\text{Na}^+$  and  $\text{Cl}^-$ . Strong electrolytes are those which ionize completely and the compound is not present in the solvent in unionized form. For example, NaCl is a strong electrolyte and, when it is dissolved in water, only  $\text{Na}^+$  and  $\text{Cl}^-$  are present, and none of it is present in the form of NaCl. A compound which gives only two ions is called a binary electrolyte. We work with a simple situation of a strong binary electrolyte in this section to clearly state the principles. Let the electrolyte be represented by



Let us explain the notation.  $z$  stands for charge, and  $\nu$  stands for the number of ions released when ionization occurs. When one mole of the above compound ionizes, it will form  $\nu_A$  moles of ionic species A, each with a charge of  $z_A$ , and  $\nu_B$  moles of ionic species B, each with a charge of  $z_B$ . Thus,  $\text{H}_2\text{SO}_4$  will form ionic species H and  $\text{SO}_4$ .  $\nu$  and  $z$  of H are 2 and 1 respectively.  $\nu$  and  $z$  of  $\text{SO}_4$  are 1 and  $-2$  respectively. Let  $C$  be the amount of the compound dissolved in a unit volume of the solvent. Since it dissociates completely, the concentration of ionic species are given by

$$C_A = \nu_A C \text{ and } C_B = \nu_B C \quad (17.30)$$

Charge neutrality of the compound dictates that

$$\nu_A z_A + \nu_B z_B = 0 \quad (17.31)$$

Generally speaking, solutions of electrolytes are also electrically neutral except near surfaces where potential gradients<sup>14</sup> are large. Electrical neutrality of a solution implies

$$C_A z_A + C_B z_B = 0$$

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<sup>14</sup>Such situation arises in a zone few tens of nanometers thick near electrodes. This zone is referred to as electrical double layer. We will not consider this complication in this text. Interested readers should refer to the book *Electrochemical systems* by Newman and Thomas-Alyea, Wiley-Interscience, 2004.

### 17.10.2 Constitutive equation for ionic solutions

We note that electrolytic solutions are multicomponent systems since there is the solvent and then at least two ions. We have to apply Stefan Maxwell equations or, if applicable, dilute solution formulae. First let us calculate the force due to electrical potential on the ions. The concentration of charge due to species A is given by  $C_A z_A \mathcal{F}$ , where  $\mathcal{F}$  is the charge on a mole of electrons or the Faraday's constant. The force due to electrical potential per unit volume is therefore given by

$$-C_A z_A \mathcal{F} \nabla \phi$$

The total force due to electrical potential on a unit volume of solution is given by

$$-(C_A z_A + C_B z_B) \nabla \phi$$

But by electrical neutrality, the term in the brackets is zero, and hence the total force due to electrical potential is therefore zero. Let us now refer to eq .17.6. The term  $\rho_i \sum_j w_j \mathbf{g}_j$  is the contribution made by the total force on  $i^{th}$  species, and hence this term is zero for electrically neutral solutions. The term  $\rho_i \mathbf{g}_i$  in eq .17.6 is the body force on  $i^{th}$  species per unit volume. For the ionic species, this is given by

$$-C_i z_i \mathcal{F} \nabla \phi$$

Hence, the left hand side of eq .17.6 for  $i^{th}$  species is given by

$$-C_i (\nabla \mu_i)_{T,P} - C_i z_i \mathcal{F} \nabla \phi$$

where we ignored the pressure diffusion term, which is not relevant here. We will consider solutions to be dilute<sup>15</sup> and take solvent as the special species. Hence, we use eq. 17.7, further specializing it to dilute solutions to obtain

$$\mathbf{J}_i^N = -\frac{D_{iN}}{\mathcal{R}T} (C_i \nabla \mu_i + C_i z_i \mathcal{F} \nabla \phi)$$

or

$$\mathbf{N}_i^N = C_i \mathbf{v}_N - \frac{D_{iN}}{\mathcal{R}T} (C_i \nabla \mu_i + C_i z_i \mathcal{F} \nabla \phi) \quad (17.32)$$

In electrochemistry literature, these are known as Nernst Planck equations.

### 17.10.3 Effective diffusivity

Consider diffusion in a dilute solution of a binary electrolyte. Let us assume that the solutions are ideal, and that the total molar concentration remains constant. Then, the constitutive relation reduces to

$$\mathbf{J}_A^N = -\mathcal{D}_{AN} \left( \nabla C_A + \frac{C_A z_A \mathcal{F}}{\mathcal{R}T} \nabla \phi \right)$$

Very often we are interested in the extent of flux of the salt. Further, the current passing through the solution is also of great interest. Thus, it is desirable to develop expression for these.

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<sup>15</sup>Readers interested in concentrated solutions should refer to the book by Newman and Thomas-Alyea referred to earlier.

## Current density

Charge is carried by ions<sup>16</sup> in an electrolyte. Current is the rate of movement of charge and is a vector. Charge has a sign, *e.g.*, electrons are negatively charged. Charge moves as ionic species move, and hence current vector is related to the sign of the charge and the velocity of the species. Thus, if  $\mathbf{I}$  is the current density, then

$$\frac{\mathbf{I}}{\mathcal{F}} = (\mathbf{N}_A z_A \mathbf{N}_B z_B) = (C_A z_A + C_B z_B) \mathbf{v} + \mathbf{J}_A^N z_A + \mathbf{J}_B^N z_B = \mathbf{J}_A^N z_A + \mathbf{J}_B^N z_B$$

since solution is electrically neutral. Hence, current density is given by

$$\mathbf{I} = -\mathcal{D}_{AN} \mathcal{F} z_A \nabla C_A - \mathcal{D}_{BN} \mathcal{F} z_B \nabla C_B - \frac{C_A z_A^2 \mathcal{D}_{AN} \mathcal{F}^2 + C_B z_B^2 \mathcal{D}_{BN} \mathcal{F}^2}{\mathcal{R}T} \nabla \phi$$

The factor multiplying the gradient of potential is the specific conductivity of the solution,  $\kappa$

$$\kappa = \frac{C_A z_A^2 \mathcal{D}_{AN} \mathcal{F}^2 + C_B z_B^2 \mathcal{D}_{BN} \mathcal{F}^2}{\mathcal{R}T}$$

Using this, the above equation can be rewritten as

$$-\nabla \phi = \frac{\mathbf{I}}{\kappa} + \frac{\mathcal{D}_{AN} \mathcal{F} z_A}{\kappa} \nabla C_A + \frac{\mathcal{D}_{BN} \mathcal{F} z_B}{\kappa} \nabla C_B$$

Conductivity of the solution can be thought of as a summation of contributions made by the two ions. The fractions contributed are denoted by *transport numbers* of the ions:  $t_A$  and  $t_B$ . Thus,

$$\begin{aligned} t_A &= \frac{C_A z_A^2 \mathcal{D}_{AN}}{C_A z_A^2 \mathcal{D}_{AN} + C_B z_B^2 \mathcal{D}_{BN}} & \text{and } t_B &= \frac{C_B z_B^2 \mathcal{D}_{BN}}{C_A z_A^2 \mathcal{D}_{AN} + C_B z_B^2 \mathcal{D}_{BN}} \\ &= \frac{z_A \mathcal{D}_{AN}}{z_A \mathcal{D}_{AN} - z_B \mathcal{D}_{BN}} & \text{and } t_B &= -\frac{z_B \mathcal{D}_{BN}}{z_A \mathcal{D}_{AN} - z_B \mathcal{D}_{BN}} \end{aligned}$$

These can be used to rewrite the equation for potential gradient as

$$-\nabla \phi = \frac{\mathbf{I}}{\kappa} + \frac{\mathcal{R}T}{\mathcal{F}} \left( \frac{t_A}{z_A C_A} \nabla C_A + \frac{t_B}{z_B C_B} \nabla C_B \right)$$

This is interpreted as follows. The applied potential gradient goes to overcome the ohmic resistance in part, and the rest of it is used for diffusion of ions. Since  $C_A = C \nu_A$  and  $C_B = C \nu_B$ , the above can be rewritten as

$$-\nabla \phi = \frac{\mathbf{I}}{\kappa} + \frac{\mathcal{R}T}{C \mathcal{F}} \left( \frac{t_A}{z_A} + \frac{t_B}{z_B} \right) \nabla C \quad (17.33)$$

where  $C$  is the concentration of the salt, were it to be present in the solution. If concentration gradients are absent, the ohmic resistance of the solution fully accounts for the potential drop. More interestingly, even if current is not flowing, the potential gradient is not zero. Thus,  $\mathbf{N}_A/z_B = -\mathbf{N}_B/z_A$  or  $\mathbf{N}_A/\nu_A = \mathbf{N}_B/\nu_B$ . Both the ions must diffuse at such a rate as if the compound itself is diffusing. But the diffusivity of the two ions is different and need not be in this ratio. Potential gradient is established suitably to ensure that both diffuse at the same rate.

<sup>16</sup>Electrons are not soluble in electrolytes and hence, unlike in solids, it is the ionic species that carry current. Conversely, ions are not present in solids and it is electrons that carry current in solids. There are many exceptions to this, and solid oxides are there which conduct ions. Similarly, there are exceptions whereby solvated electrons can be present in solvents.

## Diffusivity of the salt

We can evaluate this from the constitutive relationship for either ion:

$$\mathbf{J}_A^N = -\mathcal{D}_{AN} \left( \nabla C_A + \frac{C_A z_A \mathcal{F}}{\mathcal{R}T} \nabla \phi \right)$$

We can eliminate concentration of the ion and the potential from the expression derived earlier to obtain

$$\mathbf{J}_A^N = -\mathcal{D}_{AN} \nu_A \nabla C + \frac{C_A \mathcal{D}_{AN} z_A \mathcal{F}}{\mathcal{R}T} \left( \frac{\mathbf{I}}{\kappa} + \frac{\mathcal{R}T}{C \mathcal{F}} \left( \frac{t_A}{z_A} + \frac{t_B}{z_B} \right) \nabla C \right)$$

which after some algebra and rearrangement becomes

$$\mathbf{J}_A^N = -\nu_A \frac{\mathcal{D}_{AN} \mathcal{D}_{BN} (z_A - z_B)}{z_A \mathcal{D}_{AN} - z_B \mathcal{D}_{BN}} \nabla C + \nu_A \frac{t_A}{\nu_A z_A \mathcal{F}} \mathbf{I} \quad (17.34)$$

By a similar procedure it can be shown that

$$\mathbf{J}_B^N = -\nu_B \frac{\mathcal{D}_{AN} \mathcal{D}_{BN} (z_A - z_B)}{z_A \mathcal{D}_{AN} - z_B \mathcal{D}_{BN}} \nabla C + \nu_B \frac{t_B}{\nu_B z_B \mathcal{F}} \mathbf{I}$$

Consider the case when current flow is not there. Then, as discussed earlier,  $\mathbf{J}_A^N / \nu_A = \mathbf{J}_B^N / \nu_B = \mathbf{J}^N$ , the diffusive flux of the salt. It is therefore given by

$$\mathbf{J}^N = -\frac{\mathcal{D}_{AN} \mathcal{D}_{BN} (z_A - z_B)}{z_A \mathcal{D}_{AN} - z_B \mathcal{D}_{BN}} \nabla C$$

The effective diffusivity of the compound is given by

$$\mathcal{D}_{eff} = \frac{\mathcal{D}_{AN} \mathcal{D}_{BN} (z_A - z_B)}{z_A \mathcal{D}_{AN} - z_B \mathcal{D}_{BN}}$$

## Mass balances

Before leaving this topic, we show how the expressions derived in the previous section are used in mass balances. The mass balance of  $A$  ions is given by

$$\frac{\partial C_A}{\partial t} + \nabla \cdot (\mathbf{v} C_A) = -\nabla \cdot \mathbf{J}_A^N + \dot{\mathcal{R}}_A$$

The rate of reaction that appears in the above equation is the loss due to homogeneous reactions. We can replace the concentration of ions in solution with the concentration of salt, were it to be present in the solution, to obtain,

$$\frac{\partial C}{\partial t} + \nabla \cdot (\mathbf{v} C) = -\nabla \cdot \frac{\mathbf{J}_A^N}{\nu_A} + \frac{\dot{\mathcal{R}}_A}{\nu_A}$$

Equation 17.34 is used to substitute for the diffusive flux giving an equation for the concentration of the compound.

### 17.10.4 Electrorefining

Let us consider a very simplified example of application of forced diffusion. The process of purification of impure metals electrolytically is known as electrorefining. Plates of pure metal and impure metal are used as electrodes. In this process, the positive of a power source *e.g.*, a battery, is connected to the impure metal plate while the pure metal plate is connected to the negative of the power source. These connections make the potential of the impure metal more positive while the pure metal is made more negative. Due to this polarization, electrons are removed from the impure metal and it dissolves in the form of positively charged metal ions. The metal ions diffuse through the electrolyte to the electrode made up of pure metal. As it is more negative, the metal ions pick up electrons and deposit as metal on the pure plate. The process is shown in figure 17.6. For simplicity, we have chosen the electrolyte to be  $M^+X^-$ . We assume that only the diffusional

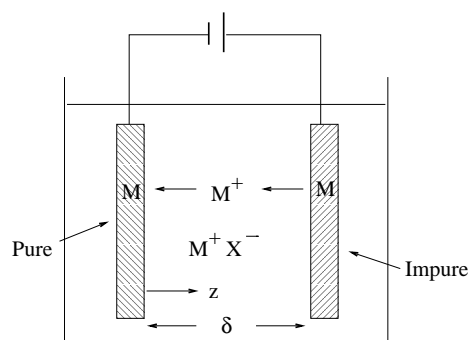


Figure 17.6: The impure metal plate is positively polarized. Hence, metal loses electrons and forms metal ions, which dissolve into the electrolyte and diffuse to the oppositely polarized plate. They gain electrons from there and deposit as pure metal.

processes are important in determining the rate<sup>17</sup> of the refining process. The rate of refining is of interest in this process.

### 17.10.5 Mass balances

The process is conducted by applying a potential difference across the electrodes. Let us assume that steady state has been achieved and the process is one dimensional. Due to the applied potential difference, some current passes. Let the current density be  $I_z$ . We will assume that convection is absent.

As solutions are electrically neutral, we need to determine the concentration of only one ion. In the process, we see that  $M^+$  moves from the positive electrode to the negative, while  $X^-$  is stagnant, and so its flux is zero. Thus, it is more convenient to write the balance of this ion. Reaction occurs only at the electrode-electrolyte interface and hence the rate of homogeneous reaction  $\dot{\mathcal{R}}_B$  is zero. Thus, we have

$$0 = -\frac{dJ_{Xz}^N}{dz}$$

<sup>17</sup>Addition or removal of electrons at the electrode is a charge transfer reaction which can be written as  $M \rightleftharpoons M^+ + e$ . This reaction occurs at the electrolyte - electrode interface and requires application of some potential.

The flux of the negative ion is constant and is equal to zero.

$$J_{xz}^N = 0$$

### 17.10.6 Constitutive relation

The constitutive equation for the flux of the negative ion can be substituted into the above to obtain

$$J_{xz}^N = 0 = -\frac{2\mathcal{D}_{MN}\mathcal{D}_{XN}}{\mathcal{D}_{MN} + \mathcal{D}_{XN}} \frac{dC}{dz} - \frac{t_X}{\mathcal{F}} I_z = -\mathcal{D}_{eff} \frac{dC}{dz} - \frac{t_X}{\mathcal{F}} I_z \quad (17.35)$$

As deposition occurs at the negative electrode, we expect concentration to decrease from the positive to the negative electrode. This creates a force that makes the negative ion also to diffuse towards the negative electrode. The potential gradient however is positive and hence creates a force that drives the negative ions towards the positive plate. The two forces oppose each other and the negative ion remains stagnant.

### 17.10.7 Charge balance

Current appears in the above equation, and it is related to the applied potential. A charge balance is needed in order to formulate an equation for the potential. Solutions are electrically neutral and hence accumulation of charge is always equal to zero. Charge consuming reactions are not present. Charge balance then gives

$$\frac{dI_z}{dz} = 0$$

or the current density is a constant.

### 17.10.8 Limiting current density

Equation 17.35 can be integrated to obtain

$$-I_z = \frac{\mathcal{F}\mathcal{D}_{eff}}{t_X} \frac{C - C(0)}{z} \quad (17.36)$$

One hopes to increase the rate of refining by increasing the current density, which in turn can be achieved by applying increasingly larger potential difference between the electrodes. The above equation suggests that the current density is proportional to the concentration gradient. It is not possible to increase the concentration gradient beyond that corresponding to  $C(0) = 0$ . Thus it is interesting note that the equation suggests that current density can not be increased beyond some level no matter however large a potential one might attempt. This current density is referred to as the *limiting current density*. First we will determine its value and explain in the next section the physical reason as to how the current is stopped from increasing beyond some level. The limiting current density is given by

$$-I_z = \frac{\mathcal{F}}{t_X} \frac{\mathcal{D}_{eff}C(\delta)}{\delta}$$

The electrolyte is not consumed during refining. Hence, the amount of electrolyte remains constant and equal to what was taken before the start of the process. If the start up concentration of the

electrolyte was  $C_o$ , it must equal the average concentration of the electrolyte at steady state. Since the concentration profile is linear, we obtain

$$C(\delta) = 2C_o - C(0)$$

and hence

$$-I_z = \frac{\mathcal{F} 2\mathcal{D}_{eff}C_o}{t_x \delta}$$

### 17.10.9 Potential difference

Let us now calculate the potential difference that needs to be applied to achieve a given current density. Equation 17.33 simplifies in the present case to

$$-\frac{d\phi}{dz} = \frac{I_z}{\kappa} + \frac{\mathcal{R}T}{C\mathcal{F}}(t_M - t_x)\frac{dC}{dz}$$

The equation suggests that the potential gradient is different from that dictated by conductivity alone since the negative ion has to be kept stationary. The conductivity is proportional to concentration assuming that pure solvent has zero conductivity and that all other properties are independent of concentration. We can therefore write it as  $\kappa = \alpha C$ . Substituting these into the equation for potential, and replacing the current density from eq. 17.35 we get

$$-\frac{d\phi}{dz} = -\frac{\mathcal{D}_{eff}\mathcal{F}}{\alpha t_x} \frac{1}{C} \frac{dC}{dz} + \frac{\mathcal{R}T}{\mathcal{F}}(t_M - t_x) \frac{1}{C} \frac{dC}{dz}$$

This can be integrated to obtain

$$\phi(\delta) - \phi(0) = \frac{\mathcal{D}_{eff}\mathcal{F}}{\alpha t_x} \ln \frac{2C_o - C(0)}{C(0)} - \frac{\mathcal{R}T}{\mathcal{F}}(t_M - t_x) \ln \frac{2C_o - C(0)}{C(0)}$$

As current density increases,  $C(0)$  decreases and the potential difference needed maintain to the current density increases. As the limiting current density is approached, the potential difference tends to infinity. The first term blows up since solution's conductivity goes to zero as concentration goes to zero. This term would not go to infinity if solvent has some finite conductivity. The second term is the increase in potential difference required to keep the negative ion stagnant as the driving force generated by concentration gradient increases. This effect is referred to as *concentration polarization*. This blows up logarithmically and is the main physical cause for ever increasing potential difference required to maintain increased current densities. Concentration polarization is also observed in applications involving electrochemical power sources.

## 17.11 Mass transfer to a rotating disk

Transfer rates of a passive scalar in a convective system generally vary in the direction of flow. We have seen this in the examples in chapters 8, and 9 as well as in earlier sections of this chapter. We consider mass transfer under steady state conditions to a rotating disk since it is a special case where mass transfer rate remains constant in a convective system. As mass transfer is well characterized, it can be used with effect when it is coupled to other processes, especially heterogeneous catalytic reactions. It is widely used in electrochemistry to measure rates of charge transfer reaction and is referred to as rotating disk electrode.

items in the observed results we listed at the beginning of this section. But note that the diffusion coefficient is given by

$$D_{eff,ax} = \frac{(R\bar{V})^2}{48\mathcal{D}}$$

or the effective axial dispersion coefficient is inversely proportional to the molecular diffusivity! This explains the third item we listed in the surprising results.

A mass balance of the dye with respect to the *moving frame* is given by

$$\frac{\partial \bar{\rho}_d}{\partial t} = D_{eff,ax} \frac{\partial^2 \bar{\rho}_d}{\partial x'^2}$$

This equation was solved by Taylor and the results matched well with observations explaining the second item we listed in the surprising results. Taylor neglected molecular diffusion altogether. Aris[1] developed a more exact and beautiful theory using method of moments and showed that if molecular diffusion is also included, the result is given by

$$\frac{D_{eff,ax}}{\mathcal{D}} = 1 + \frac{Pe^2}{48}$$

The second term is the one calculated by Taylor, and is very accurate if  $Pe \gg 7$ . Aris has also written in his inimitable style about how his paper got developed. See Citation classics in Current Contents of 14 January 1991. It can be accessed from the website [www.citationclassics.org](http://www.citationclassics.org).

## 18.3 Forced diffusion: Fuel cells

Diffusion under the influences of body forces is referred to as forced diffusion. We analyse performance of a hydrogen fuel cell as an example of this. Fuel cell converts chemical energy *directly* into electrical energy. It does so through oxidation of the fuel through the electrochemical route. See figure 18.5. The most simple construction of a fuel cell consists of two electrodes, electroni-

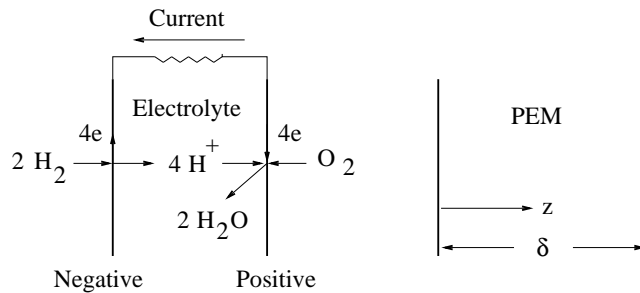


Figure 18.5: Left panel shows a schematic of a hydrogen fuel cell. Hydrogen loses electrons at the negative electrode and the protons so formed diffuse to the positive electrode through the electrolyte. Polymer electrolyte membranes (PEM) are commonly used. See text for a description. The electrons travel through an external circuit and also reach the positive electrode. There they combine with the electrons and oxygen supplied to the electrode to form water. The right panel shows the coordinate system used in the analysis.

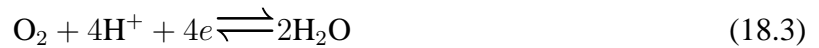
cally isolated from each other by an electrolyte. The following reaction can occur at the negative



electrode to which hydrogen is supplied.



Under some conditions, which we will discuss shortly, the negative electrode removes electrons from hydrogen to make protons, *i.e.*, the forward reaction in the scheme shown in eq. 18.2 occurs. The electrode has to be a catalyst and platinum is usually employed as the catalyst. The electrons extracted from hydrogen travel through an external circuit and reach the positive electrode while protons also diffuse towards the positive electrode through the electrolyte. Oxygen is supplied to the positive electrode and there it combines with the electrons and the protons to form water:



The overall reaction, which cannot generate electrons, is given by



### 18.3.1 Ideal performance of the cell: Thermodynamics

Thermodynamics applies to reversible processes. The rate of a reversible process is zero. If a fuel cell is operated reversibly, the current generated will be zero. If the process is carried out reversibly, thermodynamics predicts [5] that the potential difference<sup>8</sup> generated between two electrodes is related to the free energy change of the reaction:

$$-\Delta G = n\mathcal{F}U$$

where  $n$  is the number of electrons involved in the process and  $\mathcal{F}$  is Faraday's constant. It is not possible to define an equilibrium potential for a reaction occurring at a single electrode. However, one can think of the equilibrium potential difference generated by any electrode if a reference electrode is combined with it. The reference electrode is a standard, and like with the choice of standard conditions, the free energy change for the reference electrode can be assigned a value of zero. Then, the free energy change of the reaction occurring at the electrode of interest will also be the free energy change for the system consisting of the reference electrode and the electrode of interest. With the aid of this convention, one can associate a potential difference generated by any electrode. The potential difference is the *difference* between the potential of the electrode and the fluid immediately surrounding it, in which the reference electrode is assumed to be placed. If the free energy change is negative, the potential difference is positive. We can calculate the potential differences generated at the positive and negative electrodes from the free energy change for the reactions 18.2 and 18.3, respectively:

$$-\Delta G_+ = n\mathcal{F}U_+, \quad -\Delta G_- = n\mathcal{F}U_-$$

The potential difference calculated from free energy change is under equilibrium conditions when the net rate of the reaction is zero, and there is no flow of electrons into or out of an electrode. As we shall see shortly, the potential generated is less than this value due to irreversibilities. If the fuel cell operates in a reversible manner, no current flows but the best voltage is obtained!

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<sup>8</sup>This is applicable for a closed system. A fuel cell is not a closed system. But we will assume that the supply of reactants and removal of products are also carried out reversibly.

### 18.3.2 Performance under operation

At equilibrium, the rates of the forward and reverse reactions are balanced, and equal number of electrons are flowing in and out of the electrode. When equilibrium is disturbed, reaction occurs in one or the other direction, and current flows in the corresponding direction. Let us note that electrons are attracted towards regions of positive potential and repelled from regions negatively charged. Suppose we apply a potential less than  $U_+$  to the positive electrode, it will become more negative compared to equilibrium conditions. Hence electrons will move from the electrode to the electrode-fluid interface, and combine with protons and oxygen to form water. This is the reaction that occurs in a fuel cell. Conversely, if the potential is raised above  $U_+$ , electrons will be removed from water and protons and oxygen will be generated. This is the reaction that occurs at the positive plate in the reverse reaction of eq. 18.4, *i.e.*, electrolysis of water. Similar logic applies to the negative electrode also. Negative electrode becomes more positive compared to equilibrium conditions if its potential is raised above  $U_-$ , and electrons will be extracted from hydrogen into the electrode. As a result, protons will be generated. This is the reaction that occurs in a fuel cell.

If the free energy change for the overall reaction is negative, the process occurs spontaneously in the thermodynamic sense. The cell potential will be positive since the free energy change is negative, and it will generate energy. Under equilibrium conditions, when the rates of the forward and backward reaction match, the cell potential or the difference between the potentials of the positive and negative electrodes is given by  $U_+ - U_- \equiv U$ . However, since the forward and reverse processes are matched under equilibrium conditions, no current is produced by the cell. Such a situation can be realized only when the two electrodes are not connected through an external circuit. If we connect the two electrodes with a resistor in between as shown in figure 18.5, the overall reaction occurs in the forward direction, and there will be a net current flow through the resistor. The cell generates power. However, the process is irreversible in the thermodynamic sense, and the potential difference between the two electrodes falls below<sup>9</sup>  $U$ . The purpose of analysis of a fuel cell is to predict the cell potential as a function of current drawn from the cell.

### 18.3.3 Electrolyte

Hydrogen fuel cells employ *polymer electrolyte membrane* or PEM as the electrolyte. We will use this in our analysis also. Polymer electrolyte membranes are made of cross linked polymers and hence are solid in nature. Their chemical structure is like that of an ion exchange resin with the counter ions being part of the solid polymer, and the protons are bound to them by coulombic forces. The first thing to note therefore is that the concentration of the counter ions as well as the protons is therefore constant. When the membrane is hydrated, protons become mobile. Hence, protons enter and leave the membrane under the influence of a potential gradient<sup>10</sup> by conduction and not by diffusion.

### 18.3.4 Mass balance in PEM

We analyse the performance of a fuel cell under steady state conditions. The cell being analysed is as shown in figure 18.5. As protons are the only mobile species present in the membrane, mass

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<sup>9</sup>If we apply a potential greater than  $U$  across the electrodes, the reactions are reversed and electrolysis occurs.

<sup>10</sup>We should qualify it with the word 'mostly' since there is another mechanism known as electro-osmosis, which we will ignore in this text.

balance and charge balance give the same equation. Reactions do not occur in the PEM and hence at steady state, the mass balance equation simplifies to

$$\frac{dN_{H^+,z}}{dz} = 0$$

where  $N_{H^+,z}$  is the mass flux of protons. The general constitutive equation is given by eq.17.32. In the absence of convection, it simplifies to

$$N_{H^+,z} = -\frac{\mathcal{D}_{H^+}}{\mathcal{R}T} \left( \frac{dC_{H^+}}{dz} + C_{H^+} z_+ \mathcal{F} \frac{d\phi}{dz} \right)$$

if we assume that protons in hydrated membranes behave as an ideal solution. The first term is zero in PEM since proton concentration is constant. Thus, we have the equivalent of Ohm's law:

$$N_{H^+,z} = -\frac{\mathcal{F}}{\mathcal{R}T} \mathcal{D}_{H^+} C_{H^+} z_+ \frac{d\phi}{dz}$$

After integration

$$N_{H^+,z} = \frac{\mathcal{F}}{\mathcal{R}T} \mathcal{D}_{H^+} C_{H^+} z_+ \frac{\phi(0) - \phi(\delta)}{\delta} \quad (18.5)$$

The concentration of protons in the membrane is related to its chemical structure and is a known quantity. Thus, we only need boundary conditions for the potential to determine the mass flux. The potential is related to the rate of charge transfer reaction and hence we must connect it to the proton flux to derive the boundary conditions. The proton flux is related to the rate of charge transfer through stoichiometry. From eqs. 18.2 and 18.3 we infer that one electron must be transferred for every proton discharged by reaction with oxygen or generated from hydrogen. Hence, if  $I$  is the current density generated by the cell, we have

$$I = z^+ N_{H^+,z} = \frac{\mathcal{F}}{\mathcal{R}T} \mathcal{D}_{H^+} C_{H^+} \frac{\phi(0) - \phi(\delta)}{\delta} \quad (18.6)$$

where we have substituted the valence value of the proton. Charge is conserved and hence, at the electrode-fluid interface, the current density must match the rate of charge transfer. Thus if we have a rate expression for the charge transfer reaction, the boundary conditions can be derived.

### 18.3.5 Rate of charge transfer

We discussed in an earlier section the direction of the reactions that occur at the electrodes or the electrodic reactions. Since there is a transfer of charge from the electrode to the fluid or *vice versa* in these reactions, they are referred to as charge transfer reactions. It can be anticipated that analysis of a fuel cell will involve these reactions and we will need their rates. We will give the expression for it, which is referred to as Butler Volmer equation in the electrochemistry literature. The reaction occurs at the electrode-fluid interface, and hence the rate is defined on 'per unit area' basis. The rate is considered positive if the net amount of charge transferred *from electrode to electrolyte* is positive. The rate of the charge transfer reaction is defined as the net amount of charge transferred across the interface per unit area per unit time, *i.e.*, the charge flux at the interface. From the discussion in the previous subsection, we expect the rate to be proportional to the potential difference between the electrode and the fluid, *over and above* the equilibrium value. From the

chemical reaction engineering view point, it also should be proportional to the concentrations of the reactants and the products. The equilibrium potential difference is also a complicated function of concentration. Readers have to refer to recent literature for realistic expressions, but we will use the following very simplified expression for the hydrogen electrode:

$$i_- = i_{-,ref}^o \frac{P_{H_2}}{P_{H_2,ref}} \left[ \exp\left(2\mathcal{F}(\phi_s - \phi - U_-)/\mathcal{R}T\right) - \exp\left(-2\mathcal{F}(\phi_s - \phi - U_-)/\mathcal{R}T\right) \right] \quad (18.7)$$

where

$i_-$  is the flux of charge *from the negative electrode into fluid*

$i_{-,ref}^o$  is an empirical constant to be determined from experiments conducted when Hydrogen is supplied at a pressure of  $P_{H_2,ref}$

$\mathcal{F}$  is Faraday's constant or charge of a mole of electrons

$\phi_s$  is the potential of the electrode and  $\phi$  is the potential of fluid adjacent to the electrode

$U_-$  is the equilibrium potential of Hydrogen electrode at the conditions at which Hydrogen is supplied to the electrode.

$\mathcal{R}$  is the gas constant and

$T$  is the temperature.

Similarly, we will use the following expression for oxygen electrode:

$$i_+ = i_{+,ref}^o \frac{P_{O_2}}{P_{O_2,ref}} \left[ \exp\left(2\mathcal{F}(\phi_s - \phi - U_+)/\mathcal{R}T\right) - \exp\left(-2\mathcal{F}(\phi_s - \phi - U_+)/\mathcal{R}T\right) \right] \quad (18.8)$$

The symbols are defined as before but stand for positive electrode.  $U_+$  is the equilibrium potential of the electrode at the conditions at which oxygen is supplied to it.

Note a few features of the expressions. The potential difference between the electrode and fluid adjacent to it can be thought of as an applied potential difference. The deviation of the applied potential difference from the equilibrium potential, namely,  $\phi_s - \phi - U$  is referred to as the *overpotential*. If the overpotential is equal to zero, the rate of charge transfer reaction is zero, as it should be. The rate increases with an increase in the overpotential or as the deviation from equilibrium state increases. This is also to be expected since the difference between the applied potential and the equilibrium potential is akin to the gradient in chemical potential. The rate has been assumed to be first order with respect to concentration of reactants only, but in general it is more complex. Finally,  $i^o$  is referred to as the exchange current density in electrochemistry literature and is similar to the reaction rate constant of chemical kinetics. It may be noted that the dependence of the rate on overpotential is exponential and hence is very sensitive. If the applied potential difference is greater than the equilibrium potential, or if the overpotential is positive, the electrode is more positive compared to state of equilibrium. Hence electrons are expected to move from the fluid into the electrode, or equivalently, direction of flow of positive charge is from the electrode into the fluid, and the rate should be positive. The rate expression confirms this. Thus, in a fuel cell, the overpotential at the hydrogen electrode must be positive and must be negative at the oxygen electrode. This is exactly like what we discussed earlier in the section on thermodynamics.

### 18.3.6 Boundary condition

#### Negative plate

Charge is conserved and hence charge flowing into the electrode must match the rate of transfer of charge from the electrode into the electrolyte. The former is related to the current density of the cell. The rate of charge transfer reaction per unit area is given by  $i$  and is the rate at which charge moves from the plate into the fluid. Butler Volmer equation can be used to calculate this. Current density  $I$  is also the current flowing into the negative electrode. Hence,

$$I = i_{-,ref}^o \frac{P_{H_2}}{P_{H_2,ref}} \left[ \exp\left(2\mathcal{F}(\phi_s(0) - \phi(0) - U_-)/\mathcal{RT}\right) - \exp\left(-2\mathcal{F}(\phi_s(0) - \phi(0) - U_-)/\mathcal{RT}\right) \right] \quad (18.9)$$

#### Positive plate

$I$  is also the rate at which charge flows *out* of a unit area of the positive plate and hence

$$I = -i_{+,ref}^o \frac{P_{O_2}}{P_{O_2,ref}} \left[ \exp\left(2\mathcal{F}(\phi_s(\delta) - \phi(\delta) - U_+)/\mathcal{RT}\right) - \exp\left(-2\mathcal{F}(\phi_s(\delta) - \phi(\delta) - U_+)/\mathcal{RT}\right) \right] \quad (18.10)$$

The above two equations form the boundary conditions for eq. 18.6. Mathematically speaking, there are four unknowns,  $\phi_s(\delta)$ ,  $\phi(\delta)$ ,  $\phi_s(0)$ ,  $\phi(0)$  in eqs. 18.6, 18.9, and 18.10. Thus, we can solve for  $\phi_s(\delta) - \phi_s(0)$ , which is the potential developed by the cell,  $V_{cell}$ , as a function of current density. Only numerical solution is possible in general, but we will illustrate the features in limiting cases.

### 18.3.7 Cell voltage

#### Low current density

As discussed earlier, the overpotential increases with current density. Thus, at low current densities, the overpotential will be small. This would also be true if the 'rate constant' for the charge transfer reaction is large. We can state a more general condition for the overpotential at the hydrogen electrode to be small:

$$\frac{I}{i_{-,ref}^o} \frac{P_{H_2,ref}}{P_{H_2}} \ll 1$$

A similar condition can be formulated for the oxygen electrode. If both these are satisfied, the exponentials in the Butler Volmer expressions for the rate of charge transfer can be approximated by linear terms. Thus, eq. 18.9 can be written as

$$I = i_{-,ref}^o \frac{P_{H_2}}{P_{H_2,ref}} \frac{4\mathcal{F}}{\mathcal{RT}} (\phi_s(0) - \phi(0) - U_-)$$

and eq. 18.10 as

$$I = -i_{+,ref}^o \frac{P_{O_2}}{P_{O_2,ref}} \frac{4\mathcal{F}}{\mathcal{RT}} (\phi_s(\delta) - \phi(\delta) - U_+)$$

From eq. 18.6

$$\phi(0) - \phi(\delta) = I \frac{\mathcal{RT}}{\mathcal{F}} \frac{\delta}{\mathcal{D}_{H^+} C_{H^+}}$$

Combining the three, we obtain

$$V_{cell} = \phi_s(\delta) - \phi_s(0) = U_+ - U_- - \frac{IRT}{\mathcal{F}} \left( \frac{P_{H_2,ref}}{P_{H_2}} \frac{1}{4i_{-,ref}^o} + \frac{P_{O_2,ref}}{P_{O_2}} \frac{1}{4i_{+,ref}^o} + \frac{\delta}{\mathcal{D}_{H^+} C_{H^+}} \right) \quad (18.11)$$

$U_+ - U_-$  is the equilibrium voltage corresponding to reversible operation or at zero current density and at the pressures where hydrogen and oxygen are being supplied. This is the maximum voltage a cell can develop. As current density drawn from the cell increases, the voltage decreases from the equilibrium value. The decrease increases with increasing current density. There are three resistances contributing to the decrease in the cell voltage, and they are in brackets in eq. 18.11. The first two correspond to the charge transfer reaction at the negative and positive electrodes. These terms are referred to as *activation polarization*. These correspond to the reaction resistance encountered in our analysis of catalytic reactions in chapter 17. The last one corresponds to the voltage drop in the membrane corresponding to the conductivity of the membrane. If the exchange current densities are large, the cell voltage is determined entirely by the drop due to resistance, normally referred to as ohmic loss. Conversely, if conductivity of the membrane is large, the reaction is controlled by the charge transfer reactions. This resistance can be lowered by supplying the gases at high pressure. It is generally observed that the charge transfer reaction at the oxygen electrode is sluggish. As shown by the expression, the membrane resistance can be decreased by decreasing the thickness of the membrane. This is feasible since the membranes are made of polymers, provided they are mechanically strong to seal the electrodes from each other and do not develop pin holes.

### High current densities

As current density increases, or as the charge transfer reaction becomes sluggish, the overpotential increases and the linear approximation of exponentials is not valid. The condition for this for the hydrogen electrode is

$$\frac{I}{i_{-,ref}^o} \frac{P_{H_2,ref}}{P_{H_2}} \gg 1$$

and a similar expression can be written for the oxygen electrode. A different approximation, known as Tafel equation, has to be used here. At the negative plate, the overpotential is positive. If it is sufficiently large, the negative exponential term can be neglected, and eq. 18.9 can be written as

$$I = i_{-,ref}^o \frac{P_{H_2}}{P_{H_2,ref}} \exp \left( 2\mathcal{F}(\phi_s(0) - \phi(0) - U_-)/\mathcal{R}T \right)$$

or

$$\phi_s(0) - \phi(0) - U_- = \frac{\mathcal{R}T}{2\mathcal{F}} \ln \left( \frac{I}{i_{-,ref}^o} \frac{P_{H_2,ref}}{P_{H_2}} \right)$$

At the positive electrode, the overpotential is negative. Once again, if its magnitude is sufficiently large, the positive exponential term can be neglected and eq. 18.10 can be written as

$$I = i_{+,ref}^o \frac{P_{O_2}}{P_{O_2,ref}} \left[ \exp \left( -2\mathcal{F}(\phi_s(\delta) - \phi(\delta) - U_+)/\mathcal{R}T \right) \right]$$

or

$$\phi_s(\delta) - \phi(\delta) - U_+ = -\frac{\mathcal{R}T}{2\mathcal{F}} \ln \left( \frac{I}{i_{+,ref}^o} \frac{P_{O_2,ref}}{P_{O_2}} \right)$$

As before, from eq. 18.6

$$\phi(0) - \phi(\delta) = I \frac{\mathcal{R}T}{\mathcal{F}} \frac{\delta}{\mathcal{D}_{H^+} C_{H^+}}$$

Combining all the three, we get

$$V_{cell} = \phi_s(\delta) - \phi_s(0) = U_+ - U_- - \frac{\mathcal{R}T}{2\mathcal{F}} \left[ \ln \left( \frac{I}{i_{-,ref}^o} \frac{P_{H_2,ref}}{P_{H_2}} \right) + \ln \left( \frac{I}{i_{+,ref}^o} \frac{P_{O_2,ref}}{P_{O_2}} \right) + \frac{I\delta}{\mathcal{D}_{H^+} C_{H^+}} \right] \quad (18.12)$$

## Power of cell

The power density generated by the cell is equal to  $V_{cell}I$ . At zero current density, the power is obviously equal to zero. However, at some current density, as can be seen from eq. 18.12, the cell voltage drops to zero and hence the power generated by the cell drops to zero once again. Thus, the power density is maximum at some intermediate current density.

### 18.3.8 Porous electrode

Discussion above shows that the area of the cell has to be increased to increase the power output of the cell. A plate electrode cannot accommodate significant area per unit volume of the cell. Porous electrodes can pack a large area per unit volume and hence they have to be employed in order to increase cell's power output. However, the reactants will have to diffuse into the electrode if it is made porous. An additional resistance is therefore added, very similar to what happens in a porous catalyst pellet. Construction of a porous electrode is also complex. The charge transfer reaction is interfacial in character. In a plate electrode, the electrolyte-electrode interface is planar, and the electrons flow naturally into (or out of) the electron conducting electrode while the ions flow into (or out of) the electrolyte. In a porous electrode, electrolyte-catalyst interface is present through out the bulk of the electrode. However, current in the external circuit can only flow into or out of the outer boundaries of the electrodes. The same applies for the reactants and products as well. Hence, paths must be made from the outer boundaries of the electrode into its bulk for the conduction of ions and electrons and diffusion of reactants and products. The porous electrode is therefore is a composite made of three components: catalyst, PEM, and carbon or some other electron conducting material. See figure 18.1. The part consisting of electron conducting material forms a contiguous path to conduct electrons between the active interface and the external boundary of the electrode. The PEM part of the electrode also forms a separate contiguous path for conducting protons generated in the negative electrode to the membrane separating the two electrodes and for conducting protons from it to the active sites in the positive electrode for reduction reaction with oxygen. There are regions in each electrode where the catalyst, PEM and electron conducting materials overlap and they are referred to as triphasic regions. Additionally, the composite made of particles of catalyst, PEM and electron conducting materials is porous, and gaseous reactants diffuse through the pores to the surface of the catalyst. The complexity of construction of the electrode also makes its analysis more complex than for a planar electrode. We demonstrate in this section that the analysis of porous catalyst particles developed in the chapter 17 can be applied to Hydrogen fuel cells.

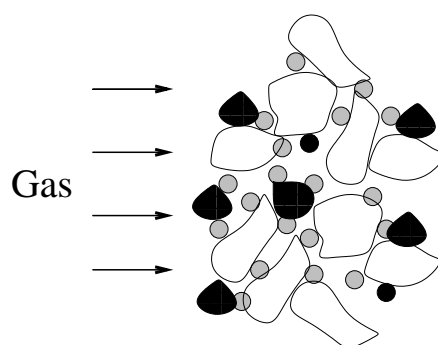


Figure 18.6: Sketch of a porous electrode using gas. The white blobs represent paste made of polymer electrolyte membrane that conduct protons. The black blobs represent electronic conductor, like carbon particles. The light colored blobs represent electrocatalyst particles, usually made of metals. The black and light colored blobs form a connected path across the entire thickness of the electrode. Electrons pass through that path. The white colored blobs form a separate connected path and it conducts protons. The pores in between all these particles allow diffusion of the gas. When the charge transfer reaction occurs on the catalyst surface, the protons and electrons will have to move into their respective conductors. Hence, charge transfer occurs at the diffuse overlapping regions of the interface where catalyst, electron conductor and PEM meet. This area is known as triphasic region or junctions.

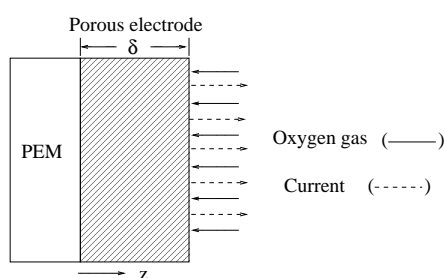


Figure 18.7: Sketch of a porous oxygen electrode using oxygen. Air may be supplied in practice. Usually there will be another porous body to the right of the electrode to ensure uniform supply of gas to the entire surface of the electrode. It is referred to as gaseous diffusion layer but is not shown in the figure. The left edge of the electrode is bonded to a slab of polymer electrolyte membrane, which separates the two electrodes. The left edge of the membrane is bonded to Hydrogen electrode, which is not shown in figure. Hydrogen electrode is similar in construction to the oxygen electrode.



## Mass balances

Consider a rectangular slab of an oxygen electrode shown in figure 18.7. Oxygen diffuses from the right edge of the electrode through the pores into the bulk of the electrode. Electrons also enter from the outer right edge of the electrode and are conducted to the site of reaction through the connected path of electron conducting particles. Protons come from the membrane separating the two electrodes, enter the electrode at the left edge the electrode and diffuse through the connected regions of PEM into the bulk of the electrode. As they diffuse, they react at the triphasic areas on the catalyst surface with oxygen and electrons to produce water. We apply the pseudo-homogeneous model of chapter 17 to the porous electrode. Let  $a$  be the interfacial area per unit volume of the electrode, *i.e.*, entire porous mass, where charge transfer reaction occurs. The charge transfer reaction given by equation



is interfacial. The rate of charge transfer reaction per unit area is given by  $i_+$ , which can be obtained from eq. 18.8. Hence, from the pseudo-homogeneous model, the rate at which charge is transferred into the PEM per unit volume of electrode is given by  $ai_+$ . The reaction stoichiometry indicates that when four moles of electrons flow into the catalyst-PEM interface, a mole of oxygen and four moles of protons are consumed and two moles of water are produced. If  $ai_+$  is the rate of charge transfer reaction, then it is equivalent to  $-ai_+$  electrons flowing into the catalyst-PEM interface. Hence, the rate of *production* of various species per unit volume are given by

$$\begin{aligned} \dot{\mathcal{R}}_{\text{O}_2} &= \frac{ai_+}{4\mathcal{F}} \\ \dot{\mathcal{R}}_{\text{H}^+} &= \frac{ai_+}{\mathcal{F}} \\ \dot{\mathcal{R}}_{\text{H}_2\text{O}} &= -\frac{ai_+}{2\mathcal{F}} \end{aligned}$$

For simplicity, we will assume that dilute solution model is applicable. Thus only an effective binary diffusion coefficient is needed to describe diffusion. The diffusion coefficient of oxygen will be denoted by  $\mathcal{D}_o$  while that of water is denoted by  $\mathcal{D}_w$ . Using all this, various mass balances can be written as follows. For Oxygen,

$$\frac{\mathcal{D}_o}{\mathcal{R}T} \frac{d^2 P_{\text{O}_2}}{dz^2} + \frac{ai_+}{4\mathcal{F}} = 0 \quad (18.13)$$

where  $P_{\text{O}_2}$  is the partial pressure of oxygen and we used ideal gas law. The mass balance for water is given by

$$\frac{\mathcal{D}_w}{\mathcal{R}T} \frac{d^2 P_{\text{H}_2\text{O}}}{dz^2} - \frac{ai_+}{2\mathcal{F}} = 0 \quad (18.14)$$

As discussed before, the flux of protons is given by

$$N_{\text{H}^+,z} = -\frac{\mathcal{F}}{\mathcal{R}T} \mathcal{D}_{\text{H}^+} C_{\text{H}^+} z_+ \frac{d\phi}{dz}$$

where  $\mathcal{D}_{\text{H}^+}$  is the effective diffusivity of protons in the electrode. The mass balance for protons gives

$$\frac{\mathcal{F}}{\mathcal{R}T} \mathcal{D}_{\text{H}^+} C_{\text{H}^+} z_+ \frac{d^2 \phi}{dz^2} + \frac{ai_+}{4\mathcal{F}} = 0 \quad (18.15)$$

Let the current density in the electronic conducting phase be  $i_s$ . This is related to the potential gradient through Ohm's law:

$$i_s = -\sigma \frac{d\phi_s}{dz}$$

where  $\sigma$  is the effective electronic conductivity of the electrode. The current density in the electronic conducting phase will change since charge flows into the PEM phase. Thus charge balance in the electron conducting phase gives

$$0 = \frac{di_s}{dz} - ai_s$$

Substituting Ohm's law into it gives

$$\sigma \frac{d^2\phi_s}{dz^2} + ai_+ = 0 \quad (18.16)$$

It is obvious that the model for a single electrode itself is fairly complex. The model for fuel cell can be arrived at by combining the above with a model for PEM and the Hydrogen electrode. The entire set of equations can be solved only numerically. For example, see Bernardi and Verbrugge [2]. The result will be a prediction of decrease of cell voltage from the thermodynamic value due to various losses. In the previous section, we have already encountered ohmic loss and loss due to the sluggishness of the charge transfer reactions. In this section, we illustrate the limitations due to diffusional resistance by taking a special case. We will make several simplifying approximations for this purpose. We list them below.

### Diffusion controlled performance

1. If the conductivity of the electronic and ionic conductors is large, the potential drop in both phases across the electrode will be small. Therefore, the potentials in both phases will be constant but not equal to each other. Let them be denoted by  $\phi_s(+)$  and  $\phi(+)$ .
2. The equilibrium potential is a function of concentration of oxygen, but to demonstrate our solution, we will assume that it can be approximated by the value at the pressure of Oxygen being supplied to the electrode. Let it be denoted by  $U_+$ . From our assumptions, the overpotential is a constant through out the electrode and is equal to  $\phi_s(+)-\phi(+)-U_+$ .
3. We will assume that the overpotential in the hydrogen electrode and the ohmic losses in the membrane are negligible. The former implies that  $\phi(-)$ , the potential in the fluid phase in the negative electrode, is equal to  $\phi_s(-)$ , the potential in the electron conducting phase in the negative electrode, minus  $U_-$ , the equilibrium potential in the negative electrode. Thus,  $\phi(-)$  is equal to  $\phi_s(-)-U_-$ . As ohmic losses in PEM are also negligible, it implies that  $\phi(-)=\phi(+)$ . Thus we have the result that

$$\phi_s(+)-\phi(+)-U_+=\phi_s(+)-\phi_s(-)-(U_+-U_-)=V_{cell}-(U_+-U_-)$$

In view of the assumptions, the mass balance for water and oxygen become decoupled. Let us look at the oxygen balance. Combining eqs. 18.13 and 18.8, we obtain

$$\frac{\mathcal{D}_o}{\mathcal{R}T} \frac{d^2 P_{O_2}}{dz^2} + \frac{1}{4\mathcal{F}} ai_{+,ref}^o \frac{P_{O_2}}{P_{O_2,ref}} \left[ \exp\left(2\mathcal{F}(V_{cell}-U_++U_-)/\mathcal{R}T\right) - \exp\left(-2\mathcal{F}(V_{cell}-U_++U_-)/\mathcal{R}T\right) \right] = 0 \quad (18.17)$$

We need boundary conditions to solve the above second order differential equation. Let us take the pressure at which oxygen is being supplied at the reference pressure. Let us assume that the permeability of oxygen in PEM is zero. The boundary conditions are then given by

$$\frac{dP_{O_2}}{dz} = 0 \text{ at } z = 0, \text{ and } P_{O_2} = P_{O_2,ref} \text{ at } z = \delta$$

Making note that in the oxygen electrode the overpotential is negative, the solution is easily found for this and is given by

$$\theta = \frac{P_{O_2}}{P_{O_2,ref}} = \frac{\cosh\left(z\sqrt{ak^s/\mathcal{D}_{eff}}\right)}{\cosh\left(\delta\sqrt{ak^s/\mathcal{D}_{eff}}\right)}$$

where

$$k^s = \frac{i_{+,ref}^o}{4\mathcal{F}} \left[ \exp\left(2\mathcal{F}(U_+ - U_- - V_{cell})/\mathcal{R}T\right) - \exp\left(-2\mathcal{F}(U_+ - U_- - V_{cell})/\mathcal{R}T\right) \right]$$

and

$$\mathcal{D}_{eff} = \mathcal{D}_o \frac{P_{O_2,ref}}{\mathcal{R}T}$$

Now we need to connect the flux of oxygen to the current density. All the oxygen entering the electrode must react since none enters the membrane. Since four moles of electrons are consumed for every mole of oxygen, we have

$$\begin{aligned} I &= -4\mathcal{F}N_{z,O_2} = 4\mathcal{F}\mathcal{D}_{eff} \frac{d\theta}{dz} \Big|_{z=\delta} \\ &= a\delta i_{+,ref}^o \left[ \exp\left(2\mathcal{F}(U_+ - U_- - V_{cell})/\mathcal{R}T\right) - \exp\left(-2\mathcal{F}(U_+ - U_- - V_{cell})/\mathcal{R}T\right) \right] \eta \end{aligned} \quad (18.18)$$

where

$$\eta = \frac{\tanh\left(\delta\sqrt{ak^s/\mathcal{D}_{eff}}\right)}{\delta\sqrt{ak^s/\mathcal{D}_{eff}}} \quad (18.19)$$

If diffusional resistance was absent, the oxygen pressure would have been equal to  $P_{O_2,ref}$  through out the electrode, and the term multiplying  $\eta$  in eq. 18.18 would have been the current density.  $\eta$  defined in 18.19 is the effectiveness factor of the electrode, which accounts for the decrease in current density due to the diffusional limitations. It is indeed difficult to miss the similarity between this solution and the one derived for the performance of a porous catalyst!

Equations 18.18 and 18.19 may be viewed as an implicit equation for the cell voltage for a given current density. As current density increases,  $(U_+ - U_- - V_{cell})$ , the overpotential, has to increase to meet the demand for oxygen consumption. This corresponds to a decrease in the cell potential from the equilibrium value. The maximum value the overpotential can reach is the equilibrium potential itself when the cell potential becomes zero. It occurs at the maximum current density that can be drawn from the cell. At this current density, the concentration of oxygen is zero every where in the electrode. Diffusion is unable to supply oxygen demand for current densities beyond this value. The electrode's performance is limited by diffusion of oxygen.

### 18.3.9 Overview

As we mentioned, a complete model for a unit<sup>11</sup> of a fuel cell must incorporate both the electrodes and the PEM separator. The general characteristics are shown in fig. 18.8. The curve is referred

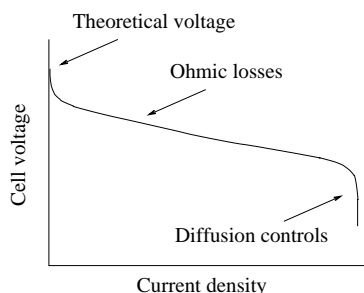


Figure 18.8: Typically observed cell voltage as a function of current density drawn from the fuel cell. The initial drop is controlled by the rate of the charge transfer reactions. The next to control the decrease in the cell voltage is the ohmic resistance. The final controlling step is diffusion of the reactants.

to as the polarization curve. In general, at low current densities, the potential drop is entirely due to charge transfer reaction or is the activation polarization. As current density is increased, the overpotentials increase and hence the rate of charge transfer reaction increases, and other steps become the limiting ones. Once again, generally speaking, at moderate current densities, oxygen and hydrogen concentrations in the electrode do not decrease from the surface values significantly. Hence, decrease in cell potential at intermediate values of current density is due to ohmic losses. At even higher current densities, diffusion becomes the limiting factor.

We make one comment in passing. We did not solve the water mass balance. Such a solution can suggest whether PEM parts remain hydrated are not. It turns out that this is very important since protons can not diffuse through if PEM is not hydrated. We did not attempt it here since a realistic solution of this is fairly complex since water may condense, and is also affected by temperature profiles.

## 18.4 Membrane separation processes

Membranes are thin sheets, which can withstand mechanical stresses when suitably supported. Membranes can be polymeric and non-porous or ceramic and microporous. Due to their structural features, solutes diffuse through them at different rates, and also dissolve to different extents in polymeric membranes. Selectivity in separations can be achieved due to these features. More detailed descriptions can be found in text by Cussler [4] and other more advanced books cited in the text [3].

We consider ultrafiltration as an example here. It is a process used to filter proteins from aqueous solutions or in general filter solutes from solvents. The ultrafiltration membranes may be considered to offer large resistance to permeation of solutes through them. Such membranes are referred to as semi-permeable membranes since they mostly permit the solvent to pass through

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<sup>11</sup>Several such units are connected in series to make a stack. Several such stacks may be arranged in series and parallel to meet practical demand for power supply.