

Chapter 2

Theoretical Framework of the Electrochemical Model

The basic principles of the electrochemical model for Li ion battery is developed from fundamentals of thermodynamics and transport phenomena. The evolution of the electrochemical model and the inherent assumptions are discussed. The discussions and derivations are self-consistent and complete. Mathematical model for each process in the Li-ion cell is constructed in a stepwise manner to evolve the complete electrochemical model.

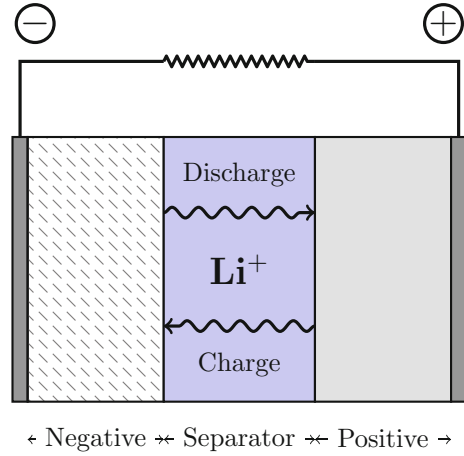
2.1 Introduction

The framework for modeling lithium-ion batteries from a physics perspective essentially involves the specification of the mass and charge conservation equations in the various regions of the battery at a sufficiently coarse scale.

The basic components of the lithium-ion cell are the solid positive and the negative electrodes sandwiching a separator which is an electron insulating material. The whole region of the battery is then filled with a liquid electrolyte (a majority of the commercial cells still use liquid electrolytes). As a matter of terminology, active components refer to those that participate in the essential physicochemical processes that convert the chemical energy to electrical energy and vice versa. Thus, the fillers or binding material are not directly considered.

The electrodes constituting the battery are porous in nature. This is an artifact of the synthesis process which grossly involves mixing of the active material in a solvent and then allowing the solvent to dry. Depending on the intensity of the crushing of the material as well as the packing density, the porous structures can have a pore size distribution typically of the order of a micron. These porous structures enhance the contact surface area of the active material with the electrolyte and increase the probability of the charge transfer reaction.

Fig. 2.1 Schematic diagram of the lithium-ion battery. During charge, the lithium ions move from the positive to the negative electrode. During discharge, the inverse direction is followed



This allows the basic framework in which the electrodes are modeled by appealing to the established porous electrode theory. Reference [32] The basic picture of an electrode is a porous solid filled with electrolyte in its interstices.

At the level of the length scale of the porous electrode theory, however, the differentiation between a pore and the solid is not made. This allows both the electrode as well as the electrolyte phase to be modeled as continuous media, implying that both the phases are assumed to exist at all points in space. Additionally, any point in space is considered electrically neutral. Thus, the model treats the system at a length scale larger than individual charge carriers, and smaller than the electrode dimensions. A schematic of a lithium-ion cells is given in Fig. 2.1.

The principal process during discharge is the transfer of lithium ion from the positive electrode to the negative electrode through the electrolyte, and in the reverse direction during charge. Each individual electrode section consists of the solid phase consisting of the active material, and the electrolyte, through which the lithium is transferred. The combined picture of a cell has a continuous electrolyte medium, interposed with solid electrode particles at the respective electrode sections. As a cell is a closed system, mass conservation is applied to the lithium that exists in the ionized state in the electrolyte. As the lithium ion carries a unit charge with it, charge is also simultaneously conserved. Similar to the electrolyte, these conservation laws also apply to the electrode. The interaction between the solid particles of the electrode and the liquid electrolyte happen at the interface, where charge is transferred. This charge transfer reaction couples the electrode and the electrolyte phases.

From the above description, it can be seen that any given electrode has to satisfy a couple of conservation laws—one for the mass of lithium and the other for the charge—in each of the solid and the electrolyte phases, with the charge transfer reaction coupling both of them. Each electrode region can, therefore, be represented by a total of five equations, and the separator region by two equations as this region is characterized by the single electrolyte phase with no charge transfer reaction.

This set of 12 equations forms the core of the electrochemical model or the macro-homogeneous model developed based on the continuum picture for the cell.

The mathematical model involves several levels of abstraction namely:

1. The solution methodology represents the porous solid phase as a collection of particles that are individually surrounded by the electrolyte phase.
2. The framework represents the electrode as a homogeneous system of electrolyte and particles at every point.
3. Due to the first abstraction, the diffusion of lithium in solid phase between particles is neglected. Diffusion in the solid phase is modeled within each particles that are typically assumed to be spheres.

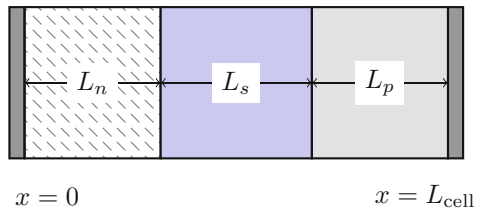
The diffusion equation, which is the mass conservation equation in the solid phase, is solved in spherical coordinates to obtain the lithium surface concentration in the spheres. As the solid phase is also continuous, the surface concentration is obtained at every point in the electrode region. The surface concentration is the driving force for charge transfer reaction. The reaction flux, in turn, appears as the boundary condition for the solid phase diffusion equation. Thus, the model results in a set of equations that are fully coupled.

It is to be noted that all the equations in the model are solved as a function of the thickness of the electrode, except the diffusion in the solid phase which is solved in the spherical coordinates. Due to this effective mapping of the output of the spherical diffusion equation onto other field equations that are solved in Cartesian coordinates, this model is also called as a Pseudo-2D (P2D) model [32].

2.2 Conservation Equations

The governing equations of the P2D model can be derived by appealing to the charge and mass conservation equations in the various regions of the battery. These are derived in the following subsections. The dimensions of the LiB model electrodes and separator are illustrated in Fig. 2.2. The thickness of positive electrode, separator, and negative electrode are given by L_p , L_s and L_n , respectively.

Fig. 2.2 Dimensions of the battery model components



2.2.1 Mass Conservation in the Electrode (Solid) Regions

In this section, the mass conservation equation in the solid phase of the active materials for both the electrodes is derived. The porous electrode constitutes of individual particles represented as spheres—that interact through the electrolyte that surrounds each particle. Lithium diffuses into the active material particles after gaining an electron by the charge transfer reaction at the electrode–electrolyte interface, it is considered as neutral lithium. During the charging or discharging processes, the lithium ion undergoes diffusion inside the solid porous electrodes. The porous electrode region is abstracted to be composed of individual particles, assumed to be spheres of finite radius, that interact with the electrolyte that surrounds each particle.

Lithium ion undergoes the charge transfer reaction at the electrode–electrolyte interface, becomes neutral by gaining an electron, and diffuses into the active material particles. Hence, the mass conservation in the solid phase, in the most simplistic representation, is provided by the Fick's law of diffusion in the spherical coordinates. This continuity equation is given by,

$$\frac{\partial c_{si}}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(D_{si} r^2 \frac{\partial c_{si}}{\partial r} \right), \quad (2.1)$$

where c_{si} is the concentration of lithium in the solid particles, with $i = p, n$ providing an index for either the positive or negative electrode. The spherical symmetry results in the boundary condition at the center of the sphere

$$\left. \frac{\partial c_{si}}{\partial r} \right|_{r=0} = 0. \quad (2.2)$$

The concentrations of the solid and the electrolyte phases are connected by the condition at the surface of the particles. At the surface, the flux of lithium is given by the pore wall flux, given by the charge transfer reaction.

$$-D_s \left. \frac{\partial c_s}{\partial r} \right|_{r=R_{pi}} = j_i. \quad (2.3)$$

2.2.2 Mass and Charge Flux from Solution Thermodynamics

A basic description of mass and charge flux in the solution phase is required to derive the mass and charge balance equations in the electrolyte region. The framework is derived in this subsection. Derivations for the mass and charge conservation equations resulting in the electrochemical model for Li-ion battery are presented in the next subsections.

Based on the concentrated solution theory, the flux is defined as

$$\mathbf{N}_i = -\mathcal{M}_i c_i \nabla \mu_i, \quad (2.4)$$

where $\mathcal{M}_i$ is the mobility of ion i , and is given by the Einstein relation to be

$$\mathcal{M}_i = \frac{D_i}{k_B T}, \quad (2.5)$$

where D_i is the mass diffusivity, k_B the Boltzmann constant, and T is the absolute temperature. Corresponding to the mass flux, a current flux can be defined as

$$\mathbf{J}_i = z_i e \mathbf{N}_i. \quad (2.6)$$

For electrochemical systems, μ_i is constructed including the contribution from the activity a_i , charge on the ion z_i and the electronic charge e , as well as the potential ϕ , as given below

$$\mu_i = k_B T \ln(a_i) + z_i e \phi \quad (2.7)$$

Activity is related to concentration c_i through the activity coefficient γ_i via the relation $a_i = c_i \gamma_i$. Thus,

$$\mu_i = k_B T (\ln(c_i) + \ln(\gamma_i)) + z_i e \phi \quad (2.8)$$

and

$$\nabla \mu_i = k_B T \nabla \ln(c_i) + k_B T \nabla \ln(\gamma_i) + z_i e \nabla \phi \quad (2.9)$$

$$\nabla \mu_i = k_B T \frac{\nabla c_i}{c_i} \left[1 + \frac{\nabla \ln(\gamma_i)}{\nabla \ln(c_i)} \right] + z_i e \nabla \phi = k_B T \frac{\nabla c_i}{c_i} \left[1 + \frac{\partial \ln(\gamma_i)}{\partial \ln(c_i)} \right] + z_i e \nabla \phi. \quad (2.10)$$

Based on this, the flux is written as

$$\mathbf{N}_i = -\mathcal{M}_i c_i \nabla \mu_i = -\frac{D_i}{k_B T} c_i \left(k_B T \frac{\nabla c_i}{c_i} \left[1 + \frac{\partial \ln(\gamma_i)}{\partial \ln(c_i)} \right] + z_i e \nabla \phi \right) \quad (2.11)$$

On simplification,

$$\mathbf{N}_i = -D_i \left[1 + \frac{\partial \ln(\gamma_i)}{\partial \ln(c_i)} \right] \nabla c_i - \frac{D_i}{k_B T} c_i z_i e \nabla \phi = D_i \nabla c_i - \frac{z_i e}{k_B T} D_i c_i \nabla \phi \quad (2.12)$$

The electric conductivity σ_i is defined as

$$\sigma_i = (z_i e)^2 \mathcal{M}_i c_i = (z_i e)^2 c_i \frac{D_i}{k_B T}. \quad (2.13)$$

Thus, the mass and charge flux can be written as

$$\mathbf{N}_i = -D_i \nabla c_i - \frac{z_i e}{k_B T} D_i c_i \nabla \phi \quad (2.14)$$

$$\mathbf{J}_i = -z_i e D_i \nabla c_i - \sigma_i \nabla \phi. \quad (2.15)$$

The total current density in the electrolyte is obtained by the sum of the current fluxes of ions

$$\mathbf{i}_e = \sum_i \mathbf{J}_i = - \sum_i z_i e D_i \nabla c_i - \sigma \nabla \phi. \quad (2.16)$$

Defining the conductivity of the electrolyte as the sum of conductivities of the ions, $\sigma = \sum_i \sigma_i$. Electro neutrality is invoked to identify that $c_i = c_+ = c_- = c$. The current density is

$$\mathbf{i}_e = -e \nabla c \sum_i z_i D_i - \sigma \nabla \phi \quad (2.17)$$

$$= -\nabla c \sum_i z_i e D_i \left[1 + \frac{\partial \ln(\gamma_i)}{\partial \ln(c_i)} \right] - \sigma \nabla \phi \quad (2.18)$$

$$= -\nabla \ln(c) \frac{k_B T}{e} \sum_i \frac{\sigma_i}{z_i} \left[1 + \frac{\partial \ln(\gamma_i)}{\partial \ln(c_i)} \right] - \sigma \nabla \phi. \quad (2.19)$$

The final result is an expression for the total current density in the electrolyte in terms of the conductivity. Please note that the same expression, in terms of the diffusivities, is

$$\mathbf{i}_e = -e \nabla c \sum_i z_i D_i - \frac{e^2 c}{k_B T} \nabla \phi \sum_i z_i^2 D_i. \quad (2.20)$$

The first expression for the current flux is used to derive the current balance equation in the electrolyte, whereas the second is used to derive the mass conservation equation.

2.2.3 Mass Conservation in the Electrolyte (Liquid Phase)

To obtain the mass conservation equation, we start from

$$\mathbf{i}_e = -e \nabla c \sum_i z_i \tilde{D}_i - \frac{e^2 c}{k_B T} \nabla \phi \sum_i z_i^2 D_i. \quad (2.21)$$

From this equation, we can obtain expression for the electrolyte potential.

$$\nabla \phi = \frac{\mathbf{i}_e + e \nabla c \sum_i z_i \tilde{D}_i}{-\frac{e^2 c}{k_B T} \sum_i z_i^2 D_i} \quad (2.22)$$

The above expression is used to eliminate for the electrolyte potential from equation for the mass flux.

$$\mathbf{N}_i = -\tilde{D}_i \nabla c_i - \frac{z_i e}{k_B T} D_i c_i \left(\frac{\mathbf{i}_e + e \nabla c \sum_i z_i \tilde{D}_i}{-\frac{e^2 c}{k_B T} \sum_i z_i^2 D_i} \right) \quad (2.23)$$

which on simplification gives

$$\mathbf{N}_i = -\tilde{D}_i \nabla c_i + \frac{\frac{z_i e}{k_B T} D_i c}{\frac{e^2 c}{k_B T} \sum_i z_i^2 D_i} \left(\mathbf{i}_e + e \nabla c \sum_i z_i \tilde{D}_i \right) \quad (2.24)$$

The conservation equation for concentration states that the accumulation is accounted by the divergence of the flux and the rate of generation by charge transfer reaction.

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot \mathbf{N}_i + R_i \quad (2.25)$$

For a porous electrode, the conservation equation is applied to the fractional volume occupied by the electrolyte. As the concentration is defined in terms of the pure electrolyte, the conservation equation is modified to be

$$\varepsilon \frac{\partial c_i}{\partial t} = -\nabla \cdot \mathbf{N}_i + R_i \quad (2.26)$$

The corresponding equation for the mass flux is given by

$$\mathbf{N}_i = -\varepsilon \mathcal{M}_i c_i \nabla \mu_i \quad (2.27)$$

This modification eventually results in

$$\mathbf{N}_i = -\varepsilon \tilde{D}_i \nabla c + \frac{\frac{z_i e}{k_B T} D_i c}{\frac{e^2 c}{k_B T} \sum_i z_i^2 D_i} \left(\mathbf{i}_e + e \varepsilon \nabla c \sum_i z_i \tilde{D}_i \right) \quad (2.28)$$

The mass flux has the corresponding divergence given by

$$\nabla \cdot \mathbf{N}_i = -\nabla \cdot (\varepsilon \tilde{D}_i \nabla c) + \nabla \cdot \left(\frac{z_i D_i}{e \sum_i z_i^2 D_i} \mathbf{i}_e \right) + \nabla \cdot \left(\frac{\varepsilon \nabla c z_i D_i \sum_i z_i \tilde{D}_i}{\sum_i z_i^2 D_i} \right) \quad (2.29)$$

This can be further simplified for univalent ions to give

$$\nabla \cdot \mathbf{N}_i = -\nabla \cdot \left[\varepsilon \nabla c \left(\tilde{D}_i - \frac{z_i D_i \sum_i z_i \tilde{D}_i}{\sum_i D_i} \right) \right] + \nabla \cdot \left(\frac{z_i D_i}{e \sum_i z_i^2 D_i} \mathbf{i}_e \right) \quad (2.30)$$

$$\nabla \cdot \mathbf{N}_i = -\nabla \cdot \left[\varepsilon \nabla c \left(\tilde{D}_i - \frac{z_i D_i \sum_i z_i \tilde{D}_i}{\sum_i D_i} \right) \right] + \nabla \cdot \left(\frac{z_i t_i}{e} \mathbf{i}_e \right) \quad (2.31)$$

As we are interested in the Li^+ ions, the equation results in

$$\nabla \cdot N_+ = -\nabla \cdot \left[\varepsilon \nabla c \left(t_- \tilde{D}_+ + t_+ \tilde{D}_- \right) \right] + \nabla \cdot \left(\frac{t_+}{e} \mathbf{i}_e \right) \quad (2.32)$$

Defining the total chemical diffusivity to be $(t_- \tilde{D}_+ + t_+ \tilde{D}_-) = \tilde{D}$, and t_- , t_+ are the transference numbers of the ions.

$$\nabla \cdot N_+ = -\nabla \cdot (\varepsilon \tilde{D} \nabla c) + \nabla \cdot \left(\frac{t_+}{e} \mathbf{i}_e \right) \quad (2.33)$$

Substituting above equation in the mass conservation equation,

$$\varepsilon \frac{\partial c}{\partial t} = \nabla \cdot (\varepsilon \tilde{D} \nabla c) - \nabla \cdot \left(\frac{t_+}{e} \mathbf{i}_e \right) - R_+ \quad (2.34)$$

The conservation equation can be written in molar units as

$$\varepsilon \frac{\partial c_e}{\partial t} = \nabla \cdot (\varepsilon D_e \nabla c_e) - \nabla \cdot \left(\frac{t_+}{F} \mathbf{i}_e \right) - R_+ \quad (2.35)$$

In order to avoid proliferation of variables $\mathbf{i}_e$ is considered to be in molar units, A/m^2 . The rate of consumption is given by the Faradays law

$$R_+ = a_{p,n} j_{p,n} = \nabla \cdot \frac{\mathbf{i}_e}{F} \quad (2.36)$$

We will discuss the relevance of $a_{p,n}$ in a later section. The mass conservation equation is, finally

$$\varepsilon \frac{\partial c_e}{\partial t} = \nabla \cdot (\varepsilon D_e \nabla c_e) + (1 - t_+) a_{p,n} j_{p,n} - \frac{\mathbf{i}_e}{F} \nabla \cdot t_+ \quad (2.37)$$

2.2.3.1 Application to Lithium-ion Cells

The analysis starts from the mass conservation, n for the electrolyte. The variable of interest is the lithium-ion concentration in the electrolyte, and c_e represents this variable. In any section of either of the electrodes, the local accumulation of lithium-ion concentration and transport due to diffusion is balanced by the rate of formation/dissipation of by the charge transfer reaction [32]. The mass balance is given by,

$$\varepsilon \frac{\partial c_e}{\partial t} = \nabla \cdot (\varepsilon D_e \nabla c_e) + (1 - t_+) a_{p,n} j_{p,n} - \frac{\mathbf{i}_e}{F} \nabla \cdot \mathbf{t}_+ \quad (2.38)$$

In Eq. 2.38, D_e is the diffusivity of the electrolyte in the bulk solution, and can be a function of the electrolyte concentration. This equation accounts for the variation in the concentration lithium ion in the x -dimension. This dimension indicates the thickness of the cell, starts at the current collector of the negative electrode (anode during discharge) and ends at the positive electrode current collector. Thus, this model is a 1D model that accounts for concentration gradients across the cell thickness. The general mass conservation equation given by Eq. 2.38 needs to be modified to be of use in battery application.

In any electrode region, a fraction of volume filled by the electrolyte is given by the porosity, μ . To account for the composite nature of the electrode region, the effective diffusivity of the electrolyte is computed from the bulk value in the following manner:

$$D_{\text{eff}} = D_e \varepsilon^b. \quad (2.39)$$

Here, ε^b the Bruggmann factor, typically assigned the value of 1.5. Although the charge transfer reaction that occurs at the surface of the electrode and the electrolyte, and should enter the mass conservation equation as a boundary term. The porous electrode treats the electrode and electrolyte as continuum, this term enters the conservation equations as a source term. The mass flux of lithium due to this reaction is defined in terms of the surface area of the particles of the active material. To introduce this quantity into the conservation equation that is defined for a unit volume of the electrode, it is multiplied by the specific surface area per unit volume of the electrode (denoted by $a_{p,n}$), computed by assuming that all the particles are spheres of the same radius r_p ,

$$a_{p,n} = \frac{4\pi r_p^2 N}{\frac{4}{3}\pi r_p^3 N} (1 - \varepsilon) = \frac{3(1 - \varepsilon)}{r_p^2}. \quad (2.40)$$

This conservation equation discussed above applies to both the positive as well as the negative electrode regions individually. For either of the electrodes, the porosity, and hence the effective diffusivity, the transference number as well as the reaction rate are different. Conventionally, subscript p and n are used for the positive and negative electrode regions respectively, and the equations for each of these sections are

$$\varepsilon \frac{\partial c_e}{\partial t} = \nabla \cdot (\varepsilon D_{\text{eff},p,n} \nabla c_e) + (1 - t_+) a_{p,n} j_{p,n} - \frac{\mathbf{i}_e}{F} \nabla \cdot \mathbf{t}_+ \quad (2.41)$$

In the above equation, $D_{\text{eff},p}$ and $D_{\text{eff},n}$ are the effective diffusivities in the positive and negative electrode regions. As no reaction takes place in the separator region, the equation simplifies to

$$\varepsilon_s \frac{\partial c_e}{\partial t} = \nabla \cdot (D_s \nabla c_e), \quad (2.42)$$

where the porosity of separator region corresponds to the partial volume occupied by the electrolyte within the pores of the separator matrix. It needs to be mentioned, however, that additional dependencies can be added to these base set of equations discussed in this section. For example, one can have a transference number or diffusivity that is dependent on concentration. Additionally, for high concentration solutions, the variation of these quantities can also be considered.

As lithium ions do not leave or enter the cell, the boundary condition for the lithium-ion mass conservation equation is zero mass flux at the current collector boundaries,

$$\left. \frac{\partial c_e}{\partial x} \right|_{x=0} = 0; \quad \left. \frac{\partial c_e}{\partial x} \right|_{x=L_{\text{cell}}} = 0, \quad (2.43)$$

where L_{cell} is the thickness of the cell. The continuity of concentrations and fluxes are also imposed at the positive electrode separator ($x = L_n$) as well as the separator-negative electrode interfaces ($x = L_n + L_s$).

2.2.4 Charge Conservation in the Electrolyte (Liquid Phase)

Corresponding to the mass flux, a current flux can be defined as

$$\mathbf{J}_i = z_i e \mathbf{N}_i. \quad (2.44)$$

The electric conductivity σ_i is defined as

$$\sigma_i = (z_i e)^2 \mathcal{M}_i c_i = (z_i e)^2 c_i \frac{D_i}{k_B T}. \quad (2.45)$$

Thus, charge flux can be written as

$$\mathbf{J}_i = -z_i e D_i \nabla c_i - \sigma_i \nabla \phi. \quad (2.46)$$

The total current density in the electrolyte is obtained by the sum of the current fluxes of ions

$$\mathbf{i}_e = \sum_i \mathbf{J}_i = - \sum_i z_i e D_i \nabla c_i - \sigma \nabla \phi. \quad (2.47)$$

Defining the conductivity of the electrolyte as the sum of conductivities of the ions, $\sigma = \sum_i \sigma_i$. Electro neutrality is invoked to identify that $c_i = c_+ = c_- = c$. The current density is

$$\mathbf{i}_e = -e \nabla c \sum_i z_i D_i - \sigma \nabla \phi \quad (2.48)$$

$$= -\nabla c \sum_i z_i e D_i \left[1 + \frac{\partial \ln(\gamma_i)}{\partial \ln(c_i)} \right] - \sigma \nabla \phi \quad (2.49)$$

$$= -\nabla \ln(c) \frac{k_B T}{e} \sum_i \frac{\sigma_i}{z_i} \left[1 + \frac{\partial \ln(\gamma_i)}{\partial \ln(c_i)} \right] - \sigma \nabla \phi. \quad (2.50)$$

The final result is an expression for the total current density in the electrolyte in terms of the conductivity. Now

$$\mathbf{i}_e = -\nabla \ln(c) \frac{k_B T}{e} \sum_i \frac{\sigma_i}{z_i} \left[1 + \frac{\partial \ln(\gamma_i)}{\partial \ln(c_i)} \right] - \sigma \nabla \phi. \quad (2.51)$$

The transference number is defined in terms of conductivities as $t_i = \sigma_i / \sigma$ and satisfies the relation $t_+ + t_- = 1$. The current density can be rewritten as

$$\mathbf{i}_e = -\nabla \ln(c) \frac{k_B T}{e} \sum_i \frac{t_i}{z_i} \left[1 + \frac{\partial \ln(\gamma_i)}{\partial \ln(c_i)} \right] - \sigma \nabla \phi. \quad (2.52)$$

For a binary electrolyte, like in the case of lithium-ion cells, $z_+ = z_- = 1$.

$$\mathbf{i}_e = \nabla \ln(c) \frac{k_B T \sigma}{e} \left((1 - t_+) \left[1 + \frac{\partial \ln(\gamma_-)}{\partial \ln(c_i)} \right] - t_+ \left[1 + \frac{\partial \ln(\gamma_-)}{\partial \ln(c_i)} \right] \right) - \sigma \nabla \phi. \quad (2.53)$$

On simplification

$$\mathbf{i}_e = \nabla \ln(c) \frac{k_B T \sigma}{e} \left(1 + \frac{\partial \ln(\gamma_-)}{\partial \ln(c)} - 2t_+ - t_+ \left[\frac{\partial \ln(\gamma_+)}{\partial \ln(c)} + \frac{\partial \ln(\gamma_-)}{\partial \ln(c)} \right] \right) - \sigma \nabla \phi. \quad (2.54)$$

The activity coefficient of the electrolyte can be defined in terms of the respective ionic values using $\gamma_{\pm} = \sqrt{\gamma_+ \gamma_-}$. This leads to further simplification as given below

$$\mathbf{i}_e = \nabla \ln(c) \frac{k_B T \sigma}{e} \left(2(1 - t_+) \left[1 + \frac{\partial \ln(\gamma_{\pm})}{\partial \ln(c)} \right] - \left[1 + \frac{\partial \ln(\gamma_+)}{\partial \ln(c)} \right] \right) - \sigma \nabla \phi. \quad (2.55)$$

This results in the final expression for the current density in the electrolyte

$$\mathbf{i}_e = -\sigma \nabla \phi + 2(1 - t_+) \frac{k_B T \sigma}{e} \left[1 + \frac{\partial \ln(\gamma_{\pm})}{\partial \ln(c)} \right] \nabla \ln(c) - \frac{k_B T \sigma}{e} \left[1 + \frac{\partial \ln(\gamma_+)}{\partial \ln(c)} \right] \nabla \ln(c). \quad (2.56)$$

The last term can be written in terms of the mass diffusivity as

$$\mathbf{i}_e = -\sigma \nabla \phi + 2(1 - t_+) \frac{k_B T \sigma}{e} \left[1 + \frac{\partial \ln(\gamma_{\pm})}{\partial \ln(c)} \right] \nabla \ln(c) - e \nabla c \frac{D_+}{t_+} \left[1 + \frac{\partial \ln(\gamma_+)}{\partial \ln(c)} \right]. \quad (2.57)$$

For binary electrolytes with unit charges, the transference number can also be defined as $t_i = D_i / \sum D_i = D_i / D$. Hence

$$\mathbf{i}_e = -\sigma \nabla \phi + 2(1 - t_+) \frac{k_B T \sigma}{e} \left[1 + \frac{\partial \ln(\gamma_{\pm})}{\partial \ln(c)} \right] \nabla \ln(c) - e \nabla c D \left[1 + \frac{\partial \ln(\gamma_+)}{\partial \ln(c)} \right]. \quad (2.58)$$

Defining a chemical potential to be $\tilde{\mu}_i = k_B T \ln(\gamma_i c_i)$, following simplification,

$$\mathbf{i}_e = -\sigma \nabla \phi + 2(1 - t_+) \frac{k_B T \sigma}{e} \left[1 + \frac{\partial \ln(\gamma_{\pm})}{\partial \ln(c)} \right] \nabla \ln(c) - \frac{ec}{k_B T} D \nabla \tilde{\mu}_i. \quad (2.59)$$

In obtaining the electrolyte current balance [32], one needs to assume that the flux generated due to coupling between the total mass diffusivity of the electrolyte and the chemical potential gradients are neglected, in comparison to the other contributions. Thus, the equation simplifies to

$$\mathbf{i}_e = -\sigma \nabla \phi + 2(1 - t_+) \frac{k_B T \sigma}{e} \left[1 + \frac{\partial \ln(\gamma_{\pm})}{\partial \ln(c)} \right] \nabla \ln(c). \quad (2.60)$$

The above equation is written for the electrolyte, either in the electrode region or the separator. This equation is further refined on identifying $e/(k_B T) = F/(R_G T)$,

$$\mathbf{i}_e = -\sigma \nabla \phi + 2(1 - t_+) \frac{R_G T \sigma}{F} \left[1 + \frac{\partial \ln(\gamma_{\pm})}{\partial \ln(c)} \right] \nabla \ln(c). \quad (2.61)$$

2.2.4.1 Application to Lithium-Ion Cells

The electrolyte current is computed using the concentrated solution theory as discussed above. Conventionally, Eq. 2.61 is written as

$$i_e = -\kappa_i \nabla \phi_e + \kappa_i \frac{2R_G T}{F} (1 - t_i) \left(1 + \frac{\ln f_i}{\ln c_e} \right) \nabla \ln c_e, \quad (2.62)$$

where κ_i is the effective conductivity of the electrolyte computed from the porosities of either the positive or the negative electrode region, using the Bruggmann relation (Eq. 2.39). This equation is applied for each of the electrodes to solve for the electrolyte potential, ϕ_e . As cell potential is arbitrary up to a constant, a boundary condition is to ground the negative end of the cell ($x = 0$), i.e., $\phi_e = 0$. As the current enters and leaves the cell through the solid particles in contact with the current collectors, an insulation boundary condition is set at the other end of the cell,

$\left. \frac{\partial \phi_e}{\partial x} \right|_{x=L_{\text{cell}}} = 0$. Alternate is to set insulation boundary condition at both $x = 0$ and $x = L_{\text{cell}}$.

Since all the current flows right through the separator region, the equation becomes

$$I = -\kappa_s \nabla \phi_e + \kappa_s \frac{2R_G T}{F} (1 - t_s) \left(1 + \frac{\ln f_s}{\ln c_e} \right) \nabla \ln c_e, \quad (2.63)$$

where I is the total current that enters or leaves the cell.

2.2.5 Charge Conservation in the Electrode (Solid) Region

The conservation of current in the solid phase of the electrode region is provided by the generalized Ohm's law written as

$$\mathbf{i}_s = -\sigma_s \nabla \phi_s. \quad (2.64)$$

Throughout the negative electrode lithium ions are generated due to the charge transfer reaction and are consumed in the positive electrode. Faradays law gives the equivalent current generated due the production of lithium ions. For one mole of univalent lithium ion, the following relation between the divergence of the solid phase current and the rate of generation of lithium ions holds

$$\nabla \cdot \mathbf{i}_s = F a_i j_i. \quad (2.65)$$

Combining the Faradays law with the Ohms law relates the potential in the electrode phase with the rate of reaction.

$$-\sigma_i \nabla^2 \phi_s = F a_i j_i. \quad (2.66)$$

The above equation is solved for the positive and negative electrodes to obtain the potential of the solid phase in the electrode. As the current enters the cell at $x = 0$ and leaves at $x = L_{\text{cell}}$, boundary conditions are

$$-\sigma_n \nabla \phi_s|_{x=0} = I; \quad -\sigma_n \nabla \phi_s|_{x=L_{\text{cell}}} = I. \quad (2.67)$$

An alternate boundary condition for the solid potential is

$$\phi_s|_{x=0} = 0. \quad (2.68)$$

This boundary condition can be used to set the datum in the potential, if insulation boundary conditions at used for the electrolyte potential, ϕ_l are $x = 0$ and $x = L_{\text{cell}}$. At $x = L_n$, the current leaves the solid phase and is the total applied current is carried

through the electrolyte in the separator, and the reverse happens at $x = L_n + L_s$. Thus, the solid phase current is zero at these interfaces

$$-\sigma_n \nabla \phi_s|_{x=L_n} = 0; \quad -\sigma_p \nabla \phi_s|_{x=L_n+L_s} = 0. \quad (2.69)$$

The solid phase current conservation equation is solved for both the electrodes to obtain the potential in the solid phase at both the electrodes. The solution also enables to study the variation of this quantity at various cell thickness. Solution of this equation is of special significance, as the cell voltage, the final output of any mathematical model for the battery is defined as the difference in solid phase potential between the ends of the cell.

$$V_{\text{cell}} = \phi_s|_{x=L_{\text{cell}}} - \phi_s|_{x=0}. \quad (2.70)$$

2.3 The Charge Transfer Reaction

The charge transfer reaction involves an equilibrium component as well as a dynamic component. The equilibrium component based on thermodynamics relates the open-circuit potential to the activity or equivalently the concentrations, and is given by the Nernst equation. The dynamic component relates the driving force for the charge transfer reaction to the reaction flux or the current transferred. We will start with the discussion of the Nernst equation.

2.3.1 Nernst Equation: Equilibrium Component and its Thermodynamic Connect

For any charge transfer reaction at equilibrium,



The Nernst equation relates the equilibrium electrode potential V_0 to the standard cell potential V'_0 and the compositions of the reactants and the products.

$$V_0 = V'_0 + \frac{R_G T}{nF} \ln Z \quad (2.72)$$

The compositions are adequately represented Z , the ratio of the activities of the products to the reactants, or simply, the ratio of their concentrations,

$$Z = \frac{a_p}{a_R} = \frac{c_P}{c_R}. \quad (2.73)$$

To obtain the Nernst equation, the first step is to identify the fundamental connection between electrochemical and thermodynamic quantities. Once this is identified, fundamental thermodynamic relations are subsequently used. The most intriguing thermodynamic quantity is the Gibbs free energy, G . This quantity being defined under conditions of constant temperature and pressure, easily achievable experimental conditions, makes it the most used (and misunderstood!) thermodynamic variable. The Gibbs free energy is defined as

$$G = H + TS. \quad (2.74)$$

We will go through a simple thermodynamic relation and see what measure G corresponds to. The enthalpy H is related to internal energy E , and pressure P and volume V , via

$$H = E + PV. \quad (2.75)$$

The change in enthalpy for a constant pressure process is given by,

$$\Delta H = \Delta E + \Delta(PV) = \Delta E + P\Delta V. \quad (2.76)$$

The change in internal energy can also be related to heat transfer and the reversible work,

$$\Delta E = \Delta Q - \Delta W = T\Delta S - \Delta W_{\text{rev}}, \quad (2.77)$$

with S being the entropy.

From the earlier relations, the change in Gibbs free energy at constant temperature is

$$\Delta G = \Delta H - \Delta(TS) = P\Delta V - \Delta W_{\text{rev}}. \quad (2.78)$$

Total reversible work consists of expansion work given by $P\Delta V$ and all other types of work. Thus, the difference between the quantities in the right side of the above equations gives the net non-expansion work that is derived out of the system.

In the case of the lithium-ion cell it is electrical work, ΔW_{ec} . Thus, it can be seen that

$$\Delta G = -\Delta W_{\text{ec}}. \quad (2.79)$$

Change in Gibbs free energy gives the reversible electrical work in a lithium-ion cell. Electrical work is also defined in terms of transferring nF electrons across an equilibrium voltage of V_0 as,

$$\Delta W_{\text{ec}} = nFV_0. \quad (2.80)$$

Thus, we arrive at the fundamental relationship between thermodynamics and electrochemistry that relates the equilibrium potential and Gibbs free energy,

$$\Delta G = -nFV_0. \quad (2.81)$$

For chemical reaction thermodynamics, change in Gibbs free energy is related to concentrations as,

$$\Delta G = \Delta G(0) + R_G T \ln \frac{c_P}{c_R}. \quad (2.82)$$

which again can be derived from identifying that ΔG is the difference of chemical potentials of the product and the reactant.

$$\Delta G = \mu_P - \mu_R. \quad (2.83)$$

As seen earlier, chemical potential is defined for moderate concentrations as

$$\begin{aligned} \mu_P &= \mu'_P + R_G T \ln c_P, \\ \mu_R &= \mu'_R + R_G T \ln c_R. \end{aligned} \quad (2.84)$$

Substituting this in the earlier equation, one gets the relation for change in Gibbs free energy in terms of concentrations.

Using our newfound relation between Gibbs free energy and equilibrium potential and dividing the above equation by nF , we get the Nernst equation,

$$V_0 = V_0(0) + \frac{R_G T}{nF} \ln \frac{c_P}{c_R}. \quad (2.85)$$

The Nernst equation is the basis for obtaining any dependence of equilibrium potential of positive or negative electrode with the concentrations. This equation, however, obtained from thermodynamics, gives only an ideal case. However, material variations impart unique features in the OCV curve. For realistic scenarios, various modifications are proposed. In Figs. 2.3 and 2.4, the open-circuit potentials of common materials are shown. The present crop of commercial batteries predominantly use some blend of carbon (graphite, coke, hard carbon, or mesocarbon microbeads (MCMB)). There are more variety for the cathode electrodes and it is dependent on the application and the requisite energy density. With this subsection, we obtain the equilibrium part in the charge transfer reaction. The dynamic part is subsequently derived.

Fig. 2.3 The open-circuit potential of commonly used anode materials

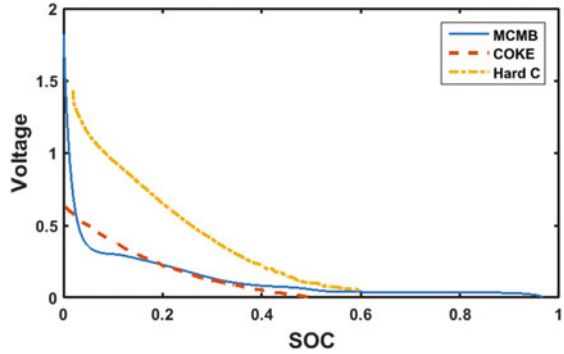
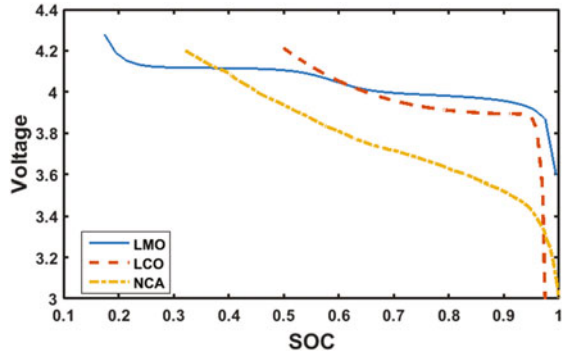


Fig. 2.4 The open-circuit potential of commonly used cathode materials



2.3.2 Butler–Volmer Equation: The Dynamic Component

For a charge transfer chemical reaction as shown below, R is reduced and P is oxidized. The former is termed as an anodic process, and the latter cathodic. The chemical reaction results in an equivalent current density given by,

$$\begin{aligned} j_c &= k_c c_R \quad \text{and,} \\ j_a &= k_a c_P. \end{aligned} \quad (2.86)$$

where j_c and j_a are termed as the cathodic and anodic current densities, k_c and k_a are the rate constants for the respective reactions. These reactions happen at the electrode surfaces, and the net reaction rate determines if the reversible process is oxidation or reduction. In the negative electrode, the net reaction during discharge is oxidation and the net reaction at the positive electrode is reduction. During charging however, the processes are reversed. As a result reduction reaction occurs at the negative electrode and oxidation at the positive electrode. The net reaction rate that results in the net current density is given by

$$i = Fj_a - Fj_c = Fk_a c_P - Fk_c c_R \quad (2.87)$$

Each of these processes is activated process. This means that the processes are triggered once the molecules undergo a threshold internal energy change required at a given temperature. Thus

$$k = k'_0 \exp \{-\Delta E/R_G T\} = k'_0 \exp \{-\Delta H/R_G T\} \quad (2.88)$$

Because, from first law of thermodynamics, $\Delta H \equiv \Delta E$, with negligible change in P or V . This equation is modified and using the second law, Gibbs free energy again appears

$$k = k'_0 \exp \{-(\Delta H - T \Delta S)/R_G T\} = k'_0 \exp \{-\Delta G/R_G T\}. \quad (2.89)$$

Thus, the rate constants of both the electrodic process can be expressed in terms of Gibbs free energy as,

$$\begin{aligned} k_c &= k'_{c0} \exp \{-(\Delta G_c)/R_G T\}, \\ k_a &= k'_{a0} \exp \{-\Delta G_a/R_G T\}. \end{aligned} \quad (2.90)$$

It can be inferred from our earlier discussion earlier, Gibbs free energy pertains to the electrical work needed to switch on these processes. The net current density at any electrode is given by

$$i = Fk'_{a0} \exp \{-\Delta G_a/R_G T\} c_P - Fk'_{c0} \exp \{-(\Delta G_c)/R_G T\} c_R. \quad (2.91)$$

The above equation, the net rate of a reversible reaction that is activated, is the basic form of Butler–Volmer reaction. The reactions are however, not at equilibrium, which was our basic premise for moving beyond Nernst type equation.

In lithium-ion batteries, a lithium-ion takes up only one electron during charge transfer reaction, the reaction is like, $R + e \rightleftharpoons P$. If the reaction involves a change of potential given by $\Delta \Phi = V - V(0)$, the extra electrical work required, the Gibbs free energy change is given by

$$\Delta G = \Delta G(0) + F \Delta \Phi. \quad (2.92)$$

If the energy state at the initial state (denoted as '0') is itself enough for the reaction to occur, however, $\Delta G = \Delta G(0)$. In a realistic scenario, the energy change required is taken as an average of these two extremes, and the constant, a transfer coefficient α is introduced,

$$\Delta G = \Delta G(0) + \alpha F \Delta \Phi. \quad (2.93)$$

The anodic and cathodic processes are the forward and reverse reactions of the reversible electrode reaction. If we consider the above scenario for the cathodic process, corresponding equation for the anodic process gives

$$\Delta G = \Delta G(0) - (1 - \alpha) F \Delta \Phi. \quad (2.94)$$

Inserting the above expressions for our net rate of reaction, and absorbing the terms involving $\Delta G(0)$ into the constant,

$$i = Fk_{a0} \exp \{(1 - \alpha)F \Delta \Phi / R_G T\} c_P - Fk_{c0} \exp \{-\alpha F \Delta \Phi / R_G T\} c_R. \quad (2.95)$$

For a system at equilibrium, $\Delta \Phi = V_0 - V(0)$, and the net current is zero. This results in both the current densities being the same, termed as the exchange current density, i_0 . Let us also introduce $f = F / R_G T$

$$i_0 = Fk_{a0} \exp \{(1 - \alpha)F \Delta \Phi / R_G T\} c_{P,EQ} = Fk_{c0} \exp \{-\alpha F \Delta \Phi / R_G T\} c_{R,EQ}. \quad (2.96)$$

At this state of equilibrium, one can use Nernst equation to see the dependence between concentrations,

$$\begin{aligned} \exp \{f(V_0 - V(0))\} &= \frac{C_{P,Eq}}{C_{R,Eq}}, \\ \exp \{-\alpha f(V_0 - V(0))\} &= \left(\frac{C_{P,Eq}}{C_{R,Eq}} \right)^{-\alpha}. \end{aligned} \quad (2.97)$$

Thus, the exchange current density is written as

$$i_0 = Fk_0 c_{P,Eq}^\alpha c_{R,Eq}^{(1-\alpha)} \quad (2.98)$$

To eliminate the effect of the datum potential, the net rate is divided by the exchange current,

$$\frac{i}{i_0} = \left[\frac{Fk_{a0} c_P \exp \{(1 - \alpha)f(V_0 - V(0))\}}{Fk_{a0} c_{P,Eq} \exp \{(1 - \alpha)f(V_0 - V(0))\}} - \frac{Fk_{c0} c_R \exp \{-\alpha f(V_0 - V(0))\}}{Fk_{c0} c_{R,Eq} \exp \{-\alpha f(V_0 - V(0))\}} \right] \quad (2.99)$$

Eventually, the most common form of the Butler–Volmer reaction flux is obtained as

$$i = i_0 \left[\frac{c_P}{c_{P,Eq}} \exp \{(1 - \alpha)f(V_0 - V(0))\} - \frac{c_R}{c_{R,Eq}} \exp \{-\alpha f(V_0 - V(0))\} \right]. \quad (2.100)$$

In many cases, a local equilibrium of concentration is considered, which further simplifies the equation to give,

$$i = i_0 [\exp \{(1 - \alpha)f(V_0 - V(0))\} - \exp \{-\alpha f(V_0 - V(0))\}] \quad (2.101)$$

2.3.2.1 Application to Lithium-Ion Cells

Lithium ions in the electrolyte with concentration c_e , and potential ϕ_e intercalate into the electrode particles. In this case, the concentration of the free active sites also determines the rate of reaction. In an electrode particle with solid concentration c_s ,

and the solubility $c_{s,max}$, the concentration of unoccupied sites is given by $c_{s,max} - c_s$. Also, due to the electrolyte potential, $\Delta\phi = \phi_s - \phi_e - V(0)$. Accounting for these factors, the final form of Butler–Volmer equation that is used to solve the electrochemical model reads as,

$$i = i_0 \left[\exp \{ (1 - \alpha) f (\phi_s - \phi_e - V(0)) \} - \exp \{ -\alpha f (\phi_s - \phi_e - V(0)) \} \right], \quad (2.102)$$

With the exchange current density given by,

$$i_0 = F k_0 c_s^\alpha (c_{s,max} - c_s)^{1-\alpha} c_e^{(1-\alpha)}. \quad (2.103)$$

To incorporate in the electrochemical model, this equation has to be solved for both the electrodes. While solving for realistic case scenarios, the rate constants of the electrodes are often adjusted to match the experimental results.

Mathematical Modeling of Lithium Batteries
From Electrochemical Models to State Estimator
Algorithms

Hariharan, K.S.; Tagade, P.; Ramachandran, S.

2018, XIV, 211 p. 73 illus., 34 illus. in color., Hardcover

ISBN: 978-3-319-03526-0