



A model for degradation of electrochemical devices based on linear non-equilibrium thermodynamics and its application to lithium ion batteries

Anil V. Virkar*

Department of Materials Science & Engineering, 122 S. Central Campus Drive, University of Utah, Salt Lake City, UT 84112, United States

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ABSTRACT

Transport through ionic conducting membranes is examined. An equation describing the chemical potential, μ_s , of electrically neutral species, s , in the membrane is derived in terms of ionic and electronic currents, and ionic and electronic transport resistances. It is shown that the μ_s in the membrane need not be mathematically bounded by the values at the two electrodes (reservoirs) if the ionic and the electronic currents through the membrane are in the same direction. Conditions could develop under which the μ_s in the membrane may exceed the thermodynamic stability of the membrane even when exposed to stable conditions at the two electrodes. It is shown that during charging, chemical potential of lithium, μ_{Li} , in the electrolyte of a lithium-ion battery may exceed that corresponding to pure lithium thus causing lithium precipitation and/or reaction with the electrolyte. It is also shown that in a lithium ion battery pack containing several cells, degradation may occur during discharge due to cell imbalance. In unbalanced cells, the SEI layer may form at both the anode/electrolyte and the cathode/electrolyte interfaces. A bi-layer separator comprising an electronic conductor and an electronic insulator is proposed for improved stability of lithium batteries.

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1. Introduction

It is well known that many electrochemical devices such as batteries, fuel cells, and electrolyzers degrade over time and under various operating conditions. In batteries, for example, it is known that in series-connected cells, degradation often occurs if one or more cells exhibit different characteristics than the rest of the cells [1,2]. This phenomenon in batteries is attributed to ‘cell imbalance’, and great care is necessary to minimize failures. Cell imbalance has been extensively investigated, and various engineering solutions have been developed [3]. Many are based on the use of balancing circuits. Also, batteries are more prone to degradation during charging. In lithium ion batteries, the design of separator, the choice of electrolyte, additives to electrolytes, the incorporation of sensors, etc. are some of the approaches used to increase safety [4,5]. It is known that fuel cells (especially stacks) also undergo degradation during operation. There is considerable literature on solid oxide electrolyzers, which too are known to degrade under certain operating conditions [6–8]. A review of literature shows that many electrochemical devices degrade under various operating conditions. While there are several reasons for degradation, and many

depend upon the specifics of a particular system, the observation that many electrochemical devices degrade suggests that there may be a common underlying reason (or reasons) which is (are) applicable to all such electrochemical systems. The intent of this manuscript is to propose a mechanism of degradation based on fundamentals of linear non-equilibrium thermodynamics which may be applicable to virtually all active (current carrying) electrochemical devices.

An active electrochemical device such as a fuel cell, a battery, and an electrolyzer involves transport of ionic and electronic species under thermodynamic potential gradients (forces). Much of the literature on transport is based on expressing fluxes as functions of forces. The simplest case is that of transport of a species in response to a force acting on it. Many phenomena, however, involve coupling of two or more processes [9,10]. For instance, transport of two or more species may be coupled [9,10]. In many such cases, fluxes can be written as linear functions of forces and transport coefficients. The fundamental basis of linear non equilibrium thermodynamics applied to coupled processes is the classic work by Onsager, according to which the generalized flux j_i of species i is linearly related to the generalized force X_k on k , by the equations [9–11]

$$J_i = \sum_k L_{ik} X_k \quad (1)$$

* Tel.: +1 801 581 5396; fax: +1 801 5814816.

E-mail address: anil.virkar@utah.edu

Nomenclature

| | |
|---------------------|---|
| a_i | thermodynamic activity of i |
| e | electronic charge (C) |
| E_N | Nernst potential (V) |
| E_A | applied voltage (V) |
| E_{cell} | average cell voltage (V) |
| v | voltage per cell (V) |
| x | position (m) |
| I_i | ionic current density through the membrane (A m^{-2}) |
| I_e | electronic current density through the membrane (A m^{-2}) |
| L_{ik} | Onsager transport coefficients |
| R_{ik} | Onsager transport resistances |
| N | number of series connected cells in a battery pack |
| J_i | thermodynamic flux of species i |
| X_k | thermodynamic force on k |
| R_i | membrane ionic area specific resistance (including interfaces) ($\Omega \text{ m}^2$) |
| R_e | membrane electronic area specific resistance (including interfaces) ($\Omega \text{ m}^2$) |
| \vec{r} | position vector |
| s | neutral species |
| T | temperature (K) |
| $r_i(x)$ | membrane ionic area specific resistance between a point in the left reservoir (electrode) and position x in the membrane ($\Omega \text{ m}^2$) |
| $r_e(x)$ | membrane electronic area specific resistance between a point in the left reservoir (electrode) and position x in the membrane ($\Omega \text{ cm}^2$) |
| m_1, m_2 | masses of spheres (kg) |
| r_1, r_2 | radii of spheres (m) |
| v_1, v_2 | velocities of spheres (m s^{-1}) |
| g | gravitational acceleration (m s^{-2}) |
| T | tension in the string (N) |
| $d_i S/dt$ | entropy generation rate ($\text{J K}^{-1} \text{ s}^{-1}$) |
| z_i | valence of i |
| δ_{x_o} | interface thickness at x_o (m) |
| δ_{x_f} | interface thickness at x_f (m) |
| μ_i | chemical potential of i (J species^{-1}) |
| $\tilde{\mu}_i$ | electrochemical potential of i (J species^{-1}) |
| μ_{Li} | chemical potential of lithium (J species^{-1}) |
| μ_{Li}^o | standard state chemical potential of pure lithium (J species^{-1}) |
| Φ | electrostatic potential (V) |
| φ | electric potential (V) |
| σ_i | ionic conductivity (S m^{-1}) |
| σ_e | electronic conductivity (S m^{-1}) |
| η | viscosity of the fluid |
| Ψ | dissipation function |

where L_{ik} are the transport coefficients. Onsager reciprocal relations show that

$$L_{ik} = L_{ki} \quad (2)$$

The coefficients $L_{i \neq k}$ are the coupling coefficients (non-diagonal terms in the $[L_{ik}]$ matrix). For a two species transport, the equations are

$$J_1 = L_{11}X_1 + L_{12}X_2 \quad (3)$$

$$J_2 = L_{21}X_1 + L_{22}X_2 \quad (4)$$

If the forces are independent of each other and the fluxes are independent of each other, it is known that [10]

$$L_{11}L_{22} - L_{12}^2 > 0 \quad (5)$$

This inequality is called positive definite. The two limiting cases of Eq. (5) are as follows: (a) $L_{11}L_{22} - L_{12}^2 = 0$ (and thus actually not positive definite). This case corresponds to full coupling. (b) $L_{12} = 0$, which corresponds to no coupling.

In most studies, certain experimental conditions are imposed that create forces, X_k s, which drive the fluxes, J_i s. The forces X_k s are not easily measurable, but the fluxes, J_i s, are usually measurable. Thus, in the often used formulation of flux-force relationships (Eq. (1)), the easily measurable parameters are on the left hand side of the equations while those not so easy to measure are on the right hand side. Onsager gave the equations in both forms; fluxes written as functions of forces and forces written as functions of fluxes. The latter are given by

$$X_i = \sum_k R_{ik}J_k \quad (6)$$

in which the measurable parameters are on the right hand side (independent variables) and difficult to measure parameters are on the left hand side (dependent variables). The reciprocity relations give

$$R_{ik} = R_{ki} \quad (7)$$

For a two species transport, the corresponding inverted equations written with fluxes as independent variables are

$$X_1 = R_{11}J_1 + R_{12}J_2 \quad (8)$$

$$X_2 = R_{21}J_1 + R_{22}J_2 \quad (9)$$

and

$$R_{11}R_{22} - R_{12}^2 > 0 \quad (10)$$

The relationships among the various Onsager coefficients (L_{ij} s and R_{ij} s) depend upon whether all of the forces are independent, all of the fluxes are independent, or whether some of the forces and/or fluxes are dependent. Hasse [10] has discussed some specific examples for two and three species systems.

For matter transport, the forces can be related to gradients in chemical potentials. Thus, X_k is related to the chemical potential of k , μ_k by [10]

$$X_k = -\nabla\mu_k \quad (11)$$

and thus

$$J_i = -\sum_k L_{ik}\nabla\mu_k \quad (12)$$

The preceding equations for two species transport thus are

$$J_1 = -L_{11}\nabla\mu_1 - L_{12}\nabla\mu_2 \quad (13)$$

$$J_2 = -L_{21}\nabla\mu_1 - L_{22}\nabla\mu_2 \quad (14)$$

and

$$\nabla\mu_1 = -R_{11}J_1 - R_{12}J_2 \quad (15)$$

$$\nabla\mu_2 = -R_{21}J_1 - R_{22}J_2 \quad (16)$$

Both forms of these equations have been used in the literature and discussed in numerous textbooks. However, the next step which relates the chemical potentials to fluxes does not appear to have been discussed in the literature, at least not from the standpoint of stability [12]. The obvious next step is the integration of forces given as functions of fluxes to obtain the chemical potentials. While mathematically a trivial step, it is the intent of this

manuscript to propose that this next step is important from the standpoint of stability of the materials/systems 'subjected to transport'. The chemical potential of species i as a function of fluxes and spatial coordinates is then given by

$$\mu_i(\vec{r}) - \mu_i(\vec{r}_o) = \Delta\mu_i(\vec{r}, \vec{r}_o) = - \int_{\vec{r}_o}^{\vec{r}} \sum_k R_{ik} \vec{J}_k \cdot d\vec{r} \quad (17)$$

where \vec{r} and \vec{r}_o are position vectors from some arbitrarily chosen origin. Thus, Eq. (17) gives differences in chemical potentials of species i between two positions (\vec{r} and \vec{r}_o). Eq. (17) states that if the fluxes of all species are known as functions of position, if all (inverse) transport coefficients are known as functions of position, and if the chemical potentials of all species are known at one position (\vec{r}_o), then the chemical potentials of all species can be determined at any other position (\vec{r}) over which the transport parameters (L_{ij} s or R_{ij} s) are known. In this manuscript we will only discuss the steady state, thus no time dependence is involved. The approach, however, can in principle be extended to include the time dependence (transient cases).

If we know all of the fluxes, no matter what their magnitudes, we know nothing about whether or not a system is thermodynamically stable, since transport equations involve gradients in chemical potentials—not chemical potentials. However, in an integrated form, Eq. (17) provides magnitudes of the chemical potentials of various species, which is the information needed to determine stability under transport. A system (or a material) is stable over some given chemical potential range of a species (or given chemical potential ranges of more than one species)—but outside of the range, the system (material) may not be thermodynamically stable.

The objective here is to determine what may be the 'externally' imposed conditions of fluxes of the various species on a system (a separation membrane, a fuel cell membrane, a battery membrane, an electrolyzer membrane, etc.) which would force the chemical potentials of one or more (electrically neutral) species in the membrane go outside the thermodynamic stability range of the membrane. Fig. 1 shows a schematic and the significance. With reference to Fig. 1, our focus is the membrane between x_o and x_f , for the time being without discussing the details of interfaces separating the membrane and the reservoirs (electrodes). There are two transition regions at the two interfaces over which properties change sharply over a very small distance (perhaps a few nm or even a fraction of a nm). In Fig. 1, the insets show enlarged schematics of interface regions of thicknesses δ_{x_o} and δ_{x_f} . Thus on a microscopic or even on a submicroscopic scale, properties change abruptly across the interfaces.

The problem examined here is different from those given in books on irreversible thermodynamics (e.g. Hasse [10], Denbigh [11]). For example, Hasse [10] has examined transport across an interface (a thin membrane) separating two phases (reservoirs). The focus of most such studies is on transport between two reservoirs through a membrane but not on the 'state' of the membrane. In those studies which have focused on the membrane (and there are numerous), the emphasis has been on transport but not on membrane thermodynamics. The present focus is on membrane thermodynamics (that is the 'membrane' separating the two reservoirs or electrodes is the 'system' of interest). In studies reported to date, it has been assumed (explicitly or tacitly) that chemical potentials of relevant species in the membrane are bounded by the values in the adjacent reservoirs (electrodes) [12]. As will be demonstrated here, the intuitive notion of the chemical potentials of species in the membrane being bounded by the values in the adjacent reservoirs (electrodes) is not of general validity. There are conditions under which chemical potentials in the membrane may lie outside the range covered by the two electrodes (reservoirs).

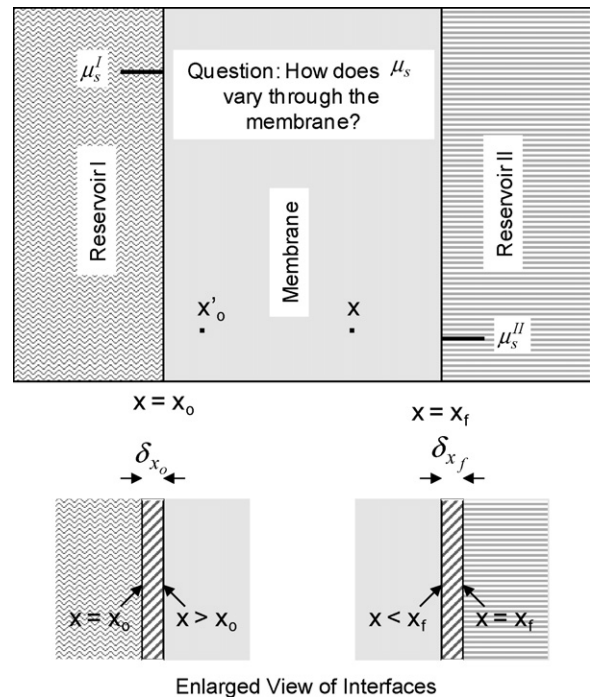


Fig. 1. A schematic of a membrane separating two electrodes (reservoirs). The chemical potentials of electrically neutral species s , μ_s , in the two electrodes are μ_s^I and μ_s^{II} . The question addressed is: how does μ_s vary through the membrane? Positions x_o and x_f are in the reservoirs (electrodes), adjacent to the membrane.

Such situations can lead to instability of the membrane and thus of the device in question.

The following discussion begins with the description of coupled processes (or chemical reactions), such as those described in textbooks on non-equilibrium thermodynamics (e.g. Kondepudi and Prigogine [9], Hasse [10], Denbigh [11]). Suppose we consider two coupled processes (reactions). One of them occurs such that its free energy decreases as the process occurs. The second process is coupled to the first. However, it occurs in a direction such that its free energy increases along the direction of reaction. This is perfectly reasonable as long as the combined two-reaction process leads to a net decrease in free energy [9]. What does this mean for transport? It means the chemical potentials of some species in a coupled transport process may increase along the direction of transport. Our interest is in determining the conditions under which the chemical potentials of one or more electrically neutral species exceed the thermodynamic stability range of the membrane. We now consider one simple but an illustrative example based on Stokes law of spheres moving through a fluid to demonstrate the role of coupling. Subsequently, an analogy between ion-electron transport through membranes and the Stokes law problem will be discussed. The illustrative example of two spheres immersed in a fluid (Stokes law) describes a case in which the two processes are fully coupled.

2. Theory

2.1. Coupled motion of spheres in a fluid: Stokes law

Fig. 2(a) shows two spheres of radii r_1 and r_2 immersed in a fluid of viscosity η , joined by a mass-less, infinitely thin string going over a frictionless pulley (pulley outside the fluid). Fig. 2(b) shows two spheres immersed in a viscous fluid connected by a string, but without a pulley. As given in Appendix A, the velocities of the two spheres in steady state (terminal velocities achieved) with a string going over the pulley (Fig. 2(a)) are given by [Eqs. (A1) and (A2)

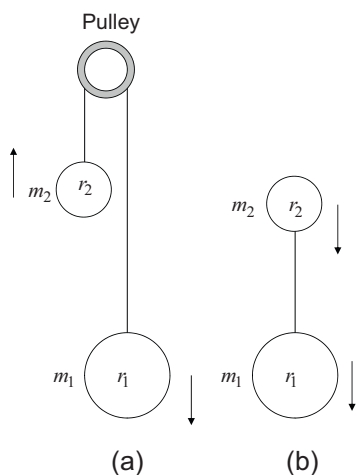


Fig. 2. (a) Two spheres of masses (corrected for buoyancy) m_1 and m_2 , of radii r_1 and r_2 immersed in a fluid, connected by a string going over a pulley (pulley outside the fluid). (b) Two spheres of masses (corrected for buoyancy) m_1 and m_2 , of radii r_1 and r_2 immersed in a fluid, connected by a string but without a pulley.

from Appendix A]

$$v_1 = -v = \frac{1}{6\pi\eta(r_1+r_2)}(-m_1g) - \frac{1}{6\pi\eta(r_1+r_2)}(-m_2g) \\ = -L_{11}\nabla\mu_1 - L_{12}\nabla\mu_2 = L_{11}X_1 + L_{12}X_2 \quad (18)$$

and

$$v_2 = v = -\frac{1}{6\pi\eta(r_1+r_2)}(-m_1g) + \frac{1}{6\pi\eta(r_1+r_2)}(-m_2g) \\ = -L_{21}\nabla\mu_1 - L_{22}\nabla\mu_2 = L_{21}X_1 + L_{22}X_2 \quad (19)$$

The coupling coefficients are negative, that is

$$L_{12} = L_{21} = -\frac{1}{6\pi\eta(r_1+r_2)} < 0 \quad (20)$$

This case corresponds to $L_{11} = L_{22} = -L_{12} = -L_{21} = L = 1/(6\pi\eta(r_1+r_2)) > 0$. For the case without a pulley (Fig. 2(b)), the velocities are [Eqs. (A7) and (A8) from Appendix A]

$$v_1 = -v = \frac{1}{6\pi\eta(r_1+r_2)}(-m_1g) + \frac{1}{6\pi\eta(r_1+r_2)}(-m_2g) \\ = -L_{11}\nabla\mu_1 - L_{12}\nabla\mu_2 = L_{11}X_1 + L_{12}X_2 \quad (21)$$

and

$$v_2 = -v = \frac{1}{6\pi\eta(r_1+r_2)}(-m_1g) + \frac{1}{6\pi\eta(r_1+r_2)}(-m_2g) \\ = -L_{21}\nabla\mu_1 - L_{22}\nabla\mu_2 = L_{21}X_1 + L_{22}X_2 \quad (22)$$

Note the coupling coefficients are positive, that is

$$L_{12} = L_{21} = \frac{1}{6\pi\eta(r_1+r_2)} > 0 \quad (23)$$

The signs of the forces are the same in both cases, but the signs of $L_{12} = L_{21}$ are different. Thus in the two cases the signs of the terms $L_{12}X_2$ and $L_{21}X_1$ are different. In one case, in which $L_{12}X_2 > 0$ and $L_{21}X_1 > 0$, an increase in energy of one sphere occurs as a result of coupling.

The example of spheres joined by a string moving in a fluid under gravity gives a simple analogy to coupling. In most systems of interest, transport is of molecular/atomic/ionic/electronic species. The origin of coupling in transport is typically Coulombic. Also, processes may or may not be fully coupled. Additionally, force $X_k = -\nabla\mu_k$ refers to that acting on a generic species

k , molecule/atom/ion/electron, at some position \vec{r} . With the passage of time, 'new' k molecules/atoms/ions/electrons arrive at \vec{r} and force $X_k = -\nabla\mu_k$ refers to that acting on new k molecules/atoms/ions/electrons at \vec{r} . The illustrative example given here is only meant to demonstrate that the coupling terms $L_{12}X_1$ and $L_{21}X_2$ can be positive or negative, and this determines if the chemical potentials of some species increase along the direction of transport during coupled transport. We will now examine atomic/ionic/electronic transport.

2.2. Transport through predominantly ionic conductors

Transport of electrically charged species occurs under electrochemical potential gradients. Even in predominantly ionic conductors, as discussed in Appendix B, local equilibrium demands that electronic conductivity while may be negligible, is not mathematically zero. For a material with mobile ions i of valence z_i , with the corresponding neutral species being s , local equilibrium at \vec{r} between the neutral species s , the corresponding constituent mobile ion i of valence z_i , and electrons, e , is given by

$$s(\vec{r}) \Leftrightarrow i(\vec{r}) + z_i e(\vec{r}) \quad (24)$$

Analysis of transport under local equilibrium, the fundamental assumption in virtually all transport theory, gives an equation for the chemical potential of the neutral species s within the membrane in terms ionic current density through membrane, I_i , electronic current density through the membrane, I_e , and ionic and electronic transport resistances, $r'_i(x)$ and $r'_e(x)$, is given by [Appendix B, Eq. (B32)]

$$\mu_s(x) = \mu_s(x'_o) - z_i e r'_i(x) I_i + z_i e r'_e(x) I_e \\ = \mu_s(x'_o) - z_i e [r'_i(x) I_i - r'_e(x) I_e] \quad (25)$$

which is in a form similar to the author's previous derivation [13].

Eq. (25) is of fundamental interest for materials exhibiting predominantly ionic transport with one ionic species transporting, typical of electrolytes with only one ion exhibiting significant conductivity.

Returning to Fig. 1 let x_o refer to a point in the left reservoir (electrode), close to the membrane. Let x_f refer to a point just outside the membrane on the other side (in the right reservoir/electrode close to the membrane). The chemical potentials of s in the two reservoirs (electrodes) adjacent to the membrane are $\mu_s(x_o)$ and $\mu_s(x_f)$. These are the *experimentally imposed* conditions; for example in a lithium ion battery, $\mu_{Li}(x_o)$ and $\mu_{Li}(x_f)$ could be the lithium chemical potentials in the anode and the cathode, respectively. The interface thicknesses are assumed to be very small. Thus, properties and thermodynamic functions vary relatively smoothly through both reservoirs (electrodes) and the membrane. However, they vary sharply across the 'interfaces' [13,14]. As properties do vary through the interfaces, however sharply, one can still define effective or average interface properties. For example, area specific resistance to ion transport across the interface at x_o may be given by

$$r_i^{x_o} = \frac{\delta_{x_o}}{\sigma_i^{x_o}} = \int_0^{\delta_{x_o}} \frac{dx}{\sigma_i^x} \quad (26)$$

where $\sigma_i^{x_o}$ is the average 'ionic conductivity' of the interface at x_o and δ_{x_o} is the thickness of the interface at x_o . Eq. (26) also gives the interface area specific resistance as an integral, if such a variation through the interface is known. This information on spatial variation through the interface is not available, and the integral in Eq. (26) is given only for completeness. The parameters, $\sigma_i^{x_o}$ and δ_{x_o} , are also not separately measurable. However, $r_i^{x_o}$ is measurable. The parameter $r_i^{x_o}$ is the area specific charge transfer resistance and thus is inversely proportional to the exchange current density

(excluding any effects of porous electrode contribution to electrocatalysis). Similarly, area specific resistance to ion transport across the interface at x_f is $r_i^{x_f}$. Some transport of electrons must also occur across both interfaces. The corresponding area specific resistances for electron transport across the two interfaces are given similarly by $r_e^{x_o}$ and $r_e^{x_f}$.

The expectation that some electron transport must occur across all interfaces (and through the bulk) can be understood as follows. All materials at a finite, nonzero temperature exhibit nonzero free electron concentration, which means electronic conductivity cannot be mathematically zero. Thus, some transport of electrons must occur between two points when nonzero electrochemical potential gradient of electrons is established. And therefore $r_e^{x_o}$ and $r_e^{x_f}$ may be very large compared to ion transport resistances, but are not mathematically infinite for reasons of local equilibrium. If the electronic resistances were infinite, the electronic current will be zero, and from Eq. (25), there will be terms of the type $\infty \times 0$ which are mathematically indeterminate, which means the chemical potential is undefined—violation of the local equilibrium criterion [13,15]. The very low level electronic conductivity in typical ionic conductors will likely be of hopping or a polaron type.

The chemical potential of s at x_o (in the reservoir or the electrode) is $\mu_s(x_o)$. Consider position x in the membrane such that $x > x_o$. The chemical potential of s at x is given by Eq. (25) in terms of $\mu_s(x_o)$ (with x'_o replaced by x_o) in which the net area specific ionic and electronic resistances are respectively

$$r_i(x) = r_i^{x_o} + \frac{(x - x_o)}{\sigma_i} \quad (27)$$

and

$$r_e(x) = r_e^{x_o} + \frac{(x - x_o)}{\sigma_e} \quad (28)$$

Eqs. (27) and (28) are applicable for $x_o < x < x_f$ and the $\mu_s(x)$ is given by Eq. (25) (with x'_o replaced by x_o). In order to relate the chemical potential of s , $\mu_s(x_f)$, at x_f , to $\mu_s(x_o)$, both interfaces must be taken into account. The corresponding area specific ionic and electronic resistances are

$$r_i(x_f) = r_i^{x_o} + \frac{(x_f - x_o)}{\sigma_i} + r_i^{x_f} \quad (29)$$

and

$$r_e(x_f) = r_e^{x_o} + \frac{(x_f - x_o)}{\sigma_e} + r_e^{x_f} \quad (30)$$

The corresponding $\mu_s(x_f)$ is given using Eq. (25) (with x'_o replaced by x_o) by

$$\mu_s(x_f) = \mu_s(x_o) - z_i e [r_i(x_f)I_i - r_e(x_f)I_e] \quad (31)$$

The $\mu_s(x_o)$ and $\mu_s(x_f)$ are the experimentally imposed conditions (in the electrodes or the reservoirs). Our interest is in determining the chemical potential of s , $\mu_s(x)$ within the membrane, that is for $x_o < x < x_f$ (Fig. 1). Suppose the chemical potentials of s in the two reservoirs (electrodes) adjacent to the membrane, $\mu_s(x_o)$ and $\mu_s(x_f)$, correspond to stable conditions for the membrane. An intuitively obvious conclusion that therefore the membrane must be stable 'under transport' is not of general validity, as discussed in what follows.

Let us return to Eq. (25) (with x'_o replaced by x_o) and choose the range $x_o < x < x_f$. We will consider two cases.

2.2.1. Case I

The ionic and the electronic currents are in opposite directions: That is, the signs of I_i and I_e are opposite. The term $[r_i(x)I_i - r_e(x)I_e]$ in Eq. (25) then can be written as $\pm[r_i(x)|I_i| + r_e(x)|I_e|]$. Thus the $\mu_s(x)$ for $x_o < x < x_f$ must be mathematically bounded by $\mu_s(x_o)$ and $\mu_s(x_f)$. That is, $\mu_s(x_o) \leq \mu_s(x) \leq \mu_s(x_f)$ or $\mu_s(x_o) \geq \mu_s(x) \geq \mu_s(x_f)$, depending

upon whether $\mu_s(x_o) \leq \mu_s(x_f)$ or $\mu_s(x_o) \geq \mu_s(x_f)$. In such a case, the membrane is thermodynamically stable under transport, if it is stable in the range from $\mu_s(x_o)$ to $\mu_s(x_f)$.

2.2.2. Case II

The ionic and the electronic currents are in the same direction: That is, the signs of I_i and I_e are the same and the term $[r_i(x)I_i - r_e(x)I_e]$ may be written as $\pm[r_i(x)|I_i| - r_e(x)|I_e|]$. The relative magnitudes of $r_i(x)|I_i|$ and $r_e(x)|I_e|$ now determine the sign of $[r_i(x)|I_i| - r_e(x)|I_e|]$. Thus the $\mu_s(x)$ need not be mathematically bounded by $\mu_s(x_o)$ and $\mu_s(x_f)$. Suppose we choose $\mu_s(x_o) > \mu_s(x_f)$. Then, the preceding implies that the $\mu_s(x)$ for $x_o < x < x_f$ may be higher than $\mu_s(x_o)$, or lower than $\mu_s(x_f)$, or may lie in the range covered by $\mu_s(x_f)$ and $\mu_s(x_o)$. If $\mu_s(x) < \mu_s(x_f)$ and/or $\mu_s(x) > \mu_s(x_o)$, and if the $\mu_s(x)$ lies outside the thermodynamic stability range, membrane degradation may occur even when exposed to reservoirs (electrodes) corresponding to stable conditions for the membrane. Thus, when the I_i and I_e are in the same direction, the membrane may become thermodynamically unstable under transport, even when exposed to stable conditions at the two electrodes (reservoirs) ($\mu_s(x_o)$ to $\mu_s(x_f)$).

2.3. Abrupt changes across interfaces

It is commonly assumed in much of the electrochemical literature that reversible electrodes means equilibration of the chemical potential of the neutral species (corresponding to the mobile ion in the electrolyte) across electrode/electrolyte interfaces. However, as shown in Appendix C, this is generally not true. The transport theory fundamentals based on local equilibrium show that chemical potentials of neutral species generally exhibit abrupt changes across interfaces, even when electrodes are reversible. In general, abrupt changes in chemical potential of neutral species across interfaces can be given in terms of ionic and electronic current densities, and ionic and electronic transport parameters of the interfaces [Appendix C, Eqs. (C3) and (C4)].

2.4. Implications of the analysis concerning failure of lithium metal and li-ion batteries

Implications of the above analysis concerning lithium metal and lithium ion batteries are discussed in what follows. It is well known that lithium batteries (as do other batteries) degrade under various conditions. Much of the work on lithium metal and lithium-ion batteries describes roles of electrode composition and microstructure, which are important factors. There is also considerable literature concerning the electrolyte, especially related to its reactivity with lithium and physical properties such as viscosity. Most electrolytes are unstable in contact with a lithium metal containing anode (and sometimes may also be unstable in contact with some cathode materials) and form a solid electrolyte interphase (SEI) layer. There is extensive literature on the formation, modeling and characterization of the SEI layer [16–26], and its role in dictating cycle life and durability [27]. The present work suggests that transport properties of the membrane, including the SEI layer and the interfaces, may be important in cell durability in light of the model presented here.

Lithium metal batteries often form lithium dendrites during charging which can short the battery. Since lithium exists in a metallic state in lithium metal battery anodes, the likely location for dendrite initiation is the anode/electrolyte interface. This is experimentally observed. In lithium ion batteries, the anode is typically graphite in which lithium is intercalated [28]. Thus, the chemical potential of lithium in the anode, μ_{Li}^A , is lower than that of pure lithium, μ_{Li}^o , and this should lower propensity to dendrite formation. These expectations have in general been well supported by

observations. Even so, lithium metal dendrites or lithium plating are known to occur in lithium ion batteries under certain conditions. These observations are in accord with the analysis presented here which shows that even when the chemical potential of lithium, μ_{Li} , in both electrodes may be less than μ_{Li}^o , no guarantee exists that it would so remain in the electrolyte under all conditions. The model presented here based on linear non equilibrium thermodynamics shows that μ_{Li} in the electrolyte may exceed that corresponding to pure metallic lithium, μ_{Li}^o , causing precipitation of Li as dendrites or plating, and/or lead to electrolyte destabilization by chemically reacting with lithium. *This scenario is possible if under any conditions lithium ion and electronic currents through the electrolyte are in the same direction.* This is discussed in what follows.

2.5. Discharging and charging of li-ion batteries

Fig. 3(a) is a schematic of a Li-ion cell during discharge. Fig. 3(b) is a schematic during the charging step. The simple schematics do not show the SEI layers, nor do they show the electrode details, which are assumed to be of uniform composition (ignores concentration polarization [29]). The objective here is to first present a high-level description of the differences between charge and discharge steps insofar as the chemical potential of neutral lithium, $\mu_{Li}(x)$, at x within the electrolyte is concerned. The x_o refers to the anode, close to the electrolyte. The x_f refers to the cathode, close to the electrolyte. The chemical potential of lithium in the anode is μ_{Li}^A and that in the cathode is μ_{Li}^C . For a lithium ion battery, $\mu_{Li}^C < \mu_{Li}^A < \mu_{Li}^o$. With reference to Fig. 3, note $\mu_{Li}^A = \mu_{Li}(x_o)$ and $\mu_{Li}^C = \mu_{Li}(x_f)$.

During discharge (Fig. 3(a)), lithium ions transport from the anode, through the electrolyte, to the cathode. Thus, the current due to lithium ion transport, $I_{Li} = I_i$ is from the anode through the electrolyte to the cathode. The cathode is at a higher electric potential, φ , than the anode, that is $\varphi^C > \varphi^A$ and electron transport *through the electrolyte*, however small may be the electronic conductivity in relation to the ionic conductivity, occurs from the anode through the electrolyte to the cathode. Thus, the electronic current through the electrolyte, I_e , is from the cathode through the electrolyte to the anode since electrons are negatively charged. Therefore, during discharge, I_i and I_e are in *opposite* directions, and according Eq. (25), $\mu_{Li}(x)$ in the electrolyte is bounded by the values at the electrodes, that is $\mu_{Li}^C < \mu_{Li}(x) < \mu_{Li}^A$. In such a case, lithium precipitation in the electrolyte cannot occur since $\mu_{Li}^A < \mu_{Li}^o$.

During charging as shown in Fig. 3(b), lithium ions transport from the cathode, through the electrolyte, to the anode. Thus, the ionic current I_i is from the cathode through the electrolyte to the anode. The cathode is still at a higher electrical potential than the anode (even more so), that is $\varphi^C > \varphi^A$ and electronic current through the electrolyte I_e is still from the cathode to the anode. Thus, during charging, I_i and I_e are in the *same* direction. The relative magnitudes of $r_i(x)I_i$ and $r_e(x)I_e$ now determine the sign of $[r_i(x)I_i - r_e(x)I_e]$ in Eq. (25) (with x_o' replaced by x_o) and determine $\mu_{Li}(x)$. Thus during the charging step, $\mu_{Li}(x)$ in the electrolyte need no longer be bounded by the values at the electrodes (by μ_{Li}^C and μ_{Li}^A). Conditions could develop under which the $\mu_{Li}(x)$ may exceed μ_{Li}^o and this will lead to the precipitation of lithium metal in the electrolyte. This precipitation would likely occur at the anode/electrolyte interface and would appear as a dendrite or as plating. An increase in $\mu_{Li}(x)$

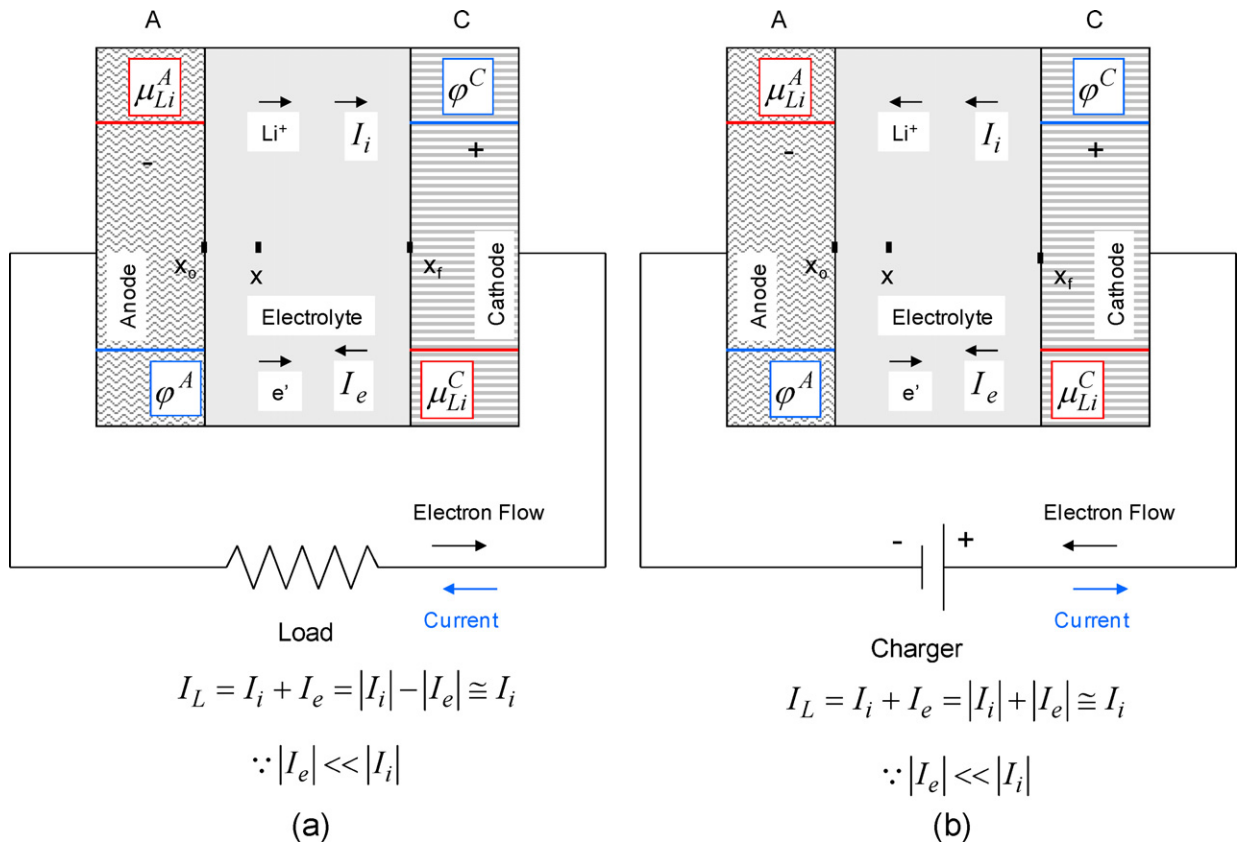


Fig. 3. (a) A schematic of a lithium-ion cell during discharge. The directions of the ionic current, I_i , and the electronic current, I_e , through the electrolyte are shown. The ionic and the electronic currents through the electrolyte are in *opposite* directions. Note that $|I_e| \ll |I_i|$. (b) A schematic of a lithium-ion cell during charge. The directions of the ionic current, I_i , and the electronic current, I_e , through the electrolyte are shown. The ionic and the electronic currents through the electrolyte are in the *same* direction. Note that $|I_e| \ll |I_i|$.

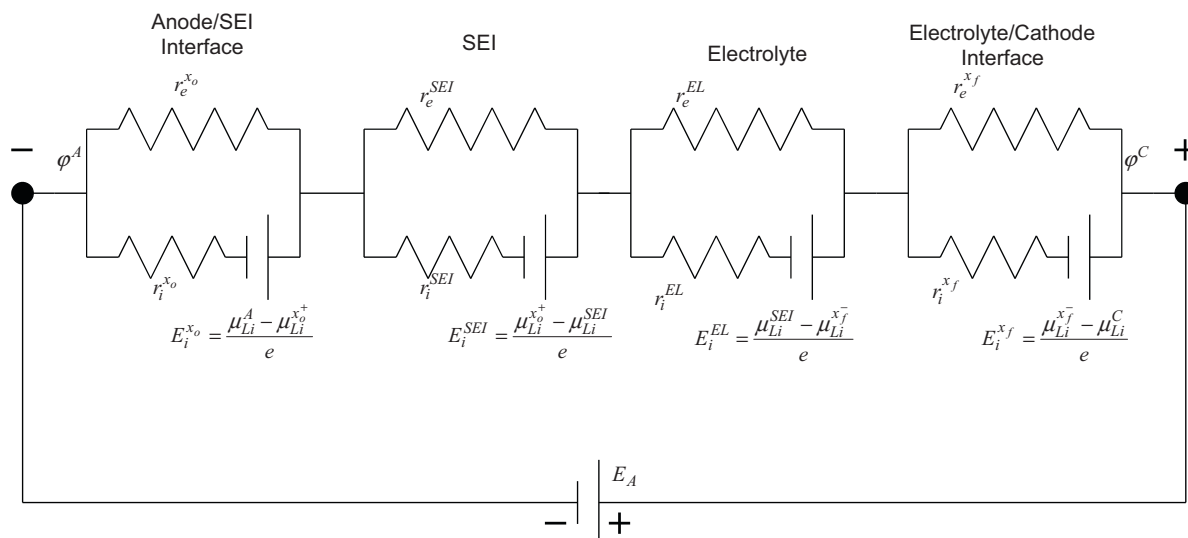


Fig. 5. An equivalent circuit during charging in steady state for the cell schematic shown in Fig. 4. The equivalent circuit contains four segments: (a) anode/SEI layer interface, (b) SEI layer, (c) electrolyte, and (d) electrolyte/cathode interface. Each segment has an ionic leg and an electronic leg in parallel. The circuit elements in between the filled circles are not physically separable. Note that $|I_e| \ll |I_i|$.

Thus, substituting in Eq. (40), the chemical potential of lithium at the SEI/EL interface, $\mu_{Li}(SEI/EL)$, is given by

$$\mu_{Li}(SEI/EL) = \mu_{Li}^A + e \left[\frac{(r_i^{x_o} + r_i^{SEI})(E_A - E_N)}{(r_i^{x_o} + r_i^{SEI} + r_i^{EL} + r_i^{x_f})} - \frac{(r_e^{x_o} + r_e^{SEI})E_A}{(r_e^{x_o} + r_e^{SEI} + r_e^{EL} + r_e^{x_f})} \right] \quad (44)$$

Eq. (44) gives the chemical potential of lithium at the SEI/EL interface during charging in terms of the Nernst voltage (E_N), the applied voltage (E_A), the chemical potential of lithium in the anode (μ_{Li}^A) and the various transport resistances.

2.8. Four cases

Many different scenarios are possible. We will now examine four cases. These are selected to illustrate the application of Eq. (44) and the resulting implications.

2.8.1. Case 1

Suppose the SEI layer exhibits very high ionic and electronic resistances such that

$$r_i^{SEI} \gg r_i^{x_o}, r_i^{EL}, r_i^{x_f} \quad \text{and} \quad r_e^{SEI} \gg r_e^{x_o}, r_e^{EL}, r_e^{x_f}$$

Then Eq. (44) reduces to

$$\mu_{Li}(SEI/EL) \approx \mu_{Li}^A - eE_N \approx \mu_{Li}^C \quad (45)$$

That is $\mu_{Li}(SEI/EL)$ is about the same as in the cathode. The μ_{Li} at the anode/SEI layer interface (in the SEI layer) is also the same, that is

$$\mu_{Li}^{x_o} \approx \mu_{Li}^A - eE_N \approx \mu_{Li}^C \quad (46)$$

Fig. 6(a) shows the corresponding schematic variation of $\mu_{Li}(x)$ through the electrolyte and the SEI layer. The μ_{Li} in the electrolyte and in the SEI layer are about the same as in the cathode, and no precipitation or plating of metallic lithium is expected nor is a reaction with the electrolyte expected (assuming the electrolyte is stable corresponding to the cathode chemical potential of Li, μ_{Li}^C). This

however comes with a penalty—the cell ionic resistance is relatively high due to high r_i^{SEI} , thus lowering the performance (current density and power density).

2.8.2. Case 2

Suppose the SEI layer is a good ionic conductor but a poor electronic conductor. Then $r_e^{SEI} \gg r_e^{x_o}, r_e^{EL}, r_e^{x_f}$ and Eq. (44) then reduces to

$$\mu_{Li}(SEI/EL) \approx \mu_{Li}^A - e \left[\frac{(r_i^{x_o} + r_i^{SEI})E_N + (r_i^{EL} + r_i^{x_f})E_A}{(r_i^{x_o} + r_i^{SEI} + r_i^{EL} + r_i^{x_f})} \right] \quad (47)$$

The term in square brackets of Eq. (47) is positive. Thus, $\mu_{Li}(SEI/EL) < \mu_{Li}^A$ and precipitation/plating of lithium or reaction with the electrolyte is not expected. The preceding implies that the SEI layer should be an excellent electronic insulator. This of course is well known. However, the previously discussed reason for the desired high electronic resistance of the SEI layer is to prevent the SEI layer from growing too fast which can shorten cell life and lower capacity. The present analysis shows that it is also important to lower the μ_{Li} in the electrolyte and lower the propensity for cell degradation during charging, which is achieved if r_e^{SEI} is large. The present work also suggests that anode purity may be an important consideration. Especially, it should be free of transition metal ions which may increase the electronic conductivity of the SEI layer.

2.8.3. Case 3

Now suppose $r_i^{SEI} \gg r_i^{x_o}, r_i^{EL}, r_i^{x_f}$ but now $r_e^{SEI}, r_e^{x_o} \ll r_e^{EL}, r_e^{x_f}$. This could be the case if some transition metal ions are present in the SEI layer or some metal or graphite particles inadvertently penetrate the SEI layer (due to defects formed during manufacturing, such as a rough anode/electrolyte interface), or impurities in the anode which could introduce localized or non-localized electronic conductivity in the SEI layer. Then Eq. (44) reduces to

$$\mu_{Li}(SEI/EL) \approx \mu_{Li}^A + e(E_A - E_N) = \mu_{Li}^C + eE_A \quad (48)$$

During charging, we must have $E_A > E_N$. This means

$$\mu_{Li}(SEI/EL) > \mu_{Li}^A \quad (49)$$

That is, now μ_{Li} in the electrolyte is not bounded by the values at the electrodes. Typically, lithium potential as intercalated in

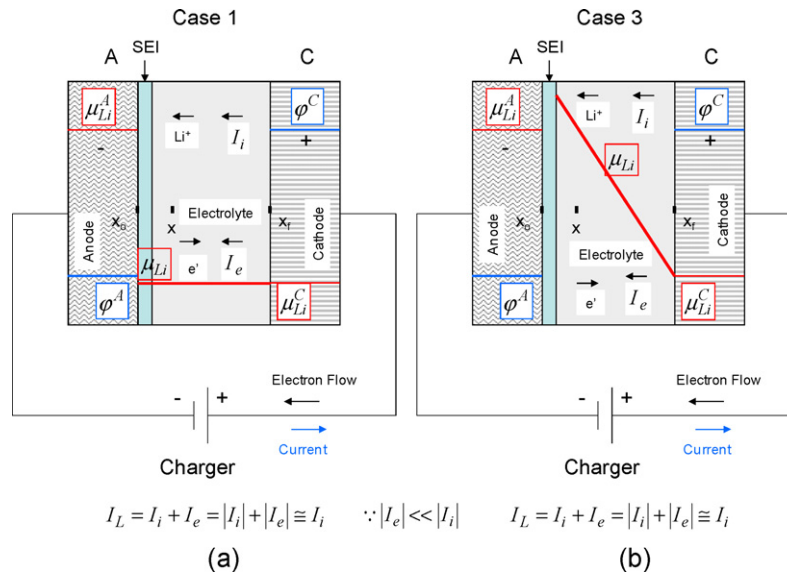


Fig. 6. (a) A schematic of a cell for Case 1: the chemical potential of lithium in the electrolyte, $\mu_{\text{Li}}(x)$, is about the same as at the cathode, $\mu_{\text{Li}}^{\text{C}}$. In such a case, precipitation of lithium within the cell is not expected. Note that $|I_e| \ll |I_i|$. (b) A schematic of a cell for Case 3: the chemical potential of lithium in the electrolyte at the SEI/EL interface can exceed that at the anode, and may even reach/exceed that corresponding to pure lithium, $\mu_{\text{Li}}^{\text{A}}$. In such a case, precipitation of lithium within the cell may occur leading to degradation of the cell. Note that $|I_e| \ll |I_i|$.

graphite is ~ 0.25 V with respect to pure lithium. This means

$$\frac{\mu_{\text{Li}}^{\text{o}} - \mu_{\text{Li}}^{\text{A}}}{e} \sim 0.25 \text{ V} \quad (50)$$

Thus, if the applied voltage E_{A} exceeds E_{N} by 0.25 V,

$$\mu_{\text{Li}}(\text{SEI/EL}) > \mu_{\text{Li}}^{\text{o}} \quad (51)$$

If this situation occurs, lithium metal can precipitate within the electrolyte, initiating at the SEI/EL interface. The cell may then degrade by various mechanisms—formation of lithium dendrites or plating, electrolyte degradation (reaction with lithium due to high chemical potential of lithium) leading to further thickening of the SEI layer or both. Fig. 6(b) shows a schematic variation of $\mu_{\text{Li}}(x)$ through the electrolyte for this case. The preceding thus shows that even a modest level of electronic conduction in the SEI layer is detrimental to cell stability and can lead to dendrite formation/plating during charging.

2.9. The proposed mechanism and implications concerning capacity loss

As discussed here, during discharge (single cell only), μ_{Li} in the membrane (electrolyte) is bounded by the values at the electrodes. Thus high values of μ_{Li} in the electrolyte are not expected. However, during charging, μ_{Li} in the electrolyte may exceed $\mu_{\text{Li}}^{\text{A}}$. The most likely location of high μ_{Li} will be at (or close to) the SEI/EL interface. Should this occur, dendrites (or plating) could occur or electrolyte may react with lithium to form (further thicken) the SEI layer, or both. The source of this lithium is the cathode during charging. During successive discharge–charge cycles less and less active lithium will be available, and the step during which capacity loss occurs will primarily be the charging step.

Recently, Zhou and Notten [31] carried out an interesting study on lithium-ion cells. They subjected a number of lithium-ion cells to discharge–charge cycles. The initial capacity was ~ 100 mAh, which degraded to ~ 80 mAh at the end of the test protocol. The last step for each cell was a full discharge. They then separated the cell components and new cells of two types were constructed. *Type 1 cell*: These cells were made with a new separator, a new anode, but a cathode from the cycled cells. *Type 2 cell*: These cells were made

with a new separator, a new cathode, but an anode from the cycled cells. Type 1 (old cathode) cells had a capacity of ~ 80 mAh, the same as the original cells at the end of cycling. Type 2 (old anode) cells, by contrast, had a capacity of ~ 100 mAh, the same as the pristine cells. These results thus demonstrated that the capacity loss could be attributed to the charging step during which loss of lithium occurred. These observations are in accord with the theory developed here showing the anticipated increase in the chemical potential of lithium within the electrolyte during the charging step and its plating or reaction with the electrolyte causing loss of capacity, the origin of which lies in the Onsager theory.

2.9.1. Case 4

An electronically conductive separator: A typical separator for a lithium-ion battery is a micro-porous polymeric material such as polyethylene or polypropylene. Both of these materials are electronic insulators [32]. A lithium salt solution in a non aqueous, organic polar liquid such as ethylene carbonate is impregnated into such a micro-porous separator. We will now examine the possible use of a micro-porous separator which has a rather *high* electronic conductivity. This is a radically different approach from the current practice [32]. As discussed in what follows, a significant benefit may be achieved in suppressing degradation and capacity fade provided the SEI layer is an excellent electronic insulator but the separator has a relatively high electronic conductivity.

Consider now that $r_{\text{e}}^{\text{EL}} \approx 0$ (the separator is a good *electronic conductor*) and also assume $r_{\text{e}}^{\text{x}} \approx 0$. Eq. (44) then becomes

$$\mu_{\text{Li}}(\text{SEI/EL}) \approx \mu_{\text{Li}}^{\text{A}} + e \left[\frac{(r_{\text{i}}^{\text{x}_0} + r_{\text{i}}^{\text{SEI}})(E_{\text{A}} - E_{\text{N}})}{(r_{\text{i}}^{\text{x}_0} + r_{\text{i}}^{\text{SEI}} + r_{\text{i}}^{\text{EL}} + r_{\text{i}}^{\text{x}_f})} - E_{\text{A}} \right] \quad (52)$$

or

$$\mu_{\text{Li}}(\text{SEI/EL}) \approx \mu_{\text{Li}}^{\text{A}} - e \left[\frac{(r_{\text{i}}^{\text{x}_0} + r_{\text{i}}^{\text{SEI}})E_{\text{N}} + (r_{\text{i}}^{\text{EL}} + r_{\text{i}}^{\text{x}_f})E_{\text{A}}}{(r_{\text{i}}^{\text{x}_0} + r_{\text{i}}^{\text{SEI}} + r_{\text{i}}^{\text{EL}} + r_{\text{i}}^{\text{x}_f})} \right] \quad (53)$$

The term in the square brackets in Eq. (53) is positive. Thus, $\mu_{\text{Li}}(\text{SEI/EL}) < \mu_{\text{Li}}^{\text{A}}$. Note Eq. (53) is the same as Eq. (47). The difference is that Eq. (47) was derived assuming the SEI layer is an *electronic insulator*. Eq. (53) is derived assuming the separator is a good *electronic conductor*. Effectively, both achieve the same result

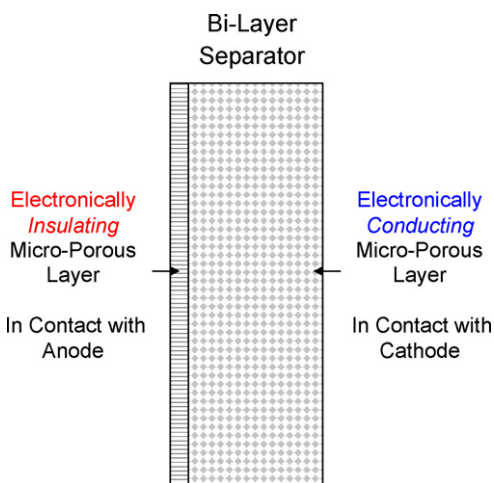


Fig. 7. A schematic of a lithium-ion cell with a bi-layer separator.

insofar as the $\mu_{\text{Li}}(\text{SEI/EL})$ is concerned. It is understood of course that the SEI layer must exhibit high electronic resistance to minimize internal leakage. What Case 4 shows is that the lowering of $\mu_{\text{Li}}(x)$ may also be achieved by using a separator of high electronic conductivity. In such a case, precipitation of lithium should not occur and also no further reaction with electrolyte should occur (except with whatever lithium that permeates from the anode through the SEI layer). Also, then the SEI layer functions as the electrolyte and the micro-porous layer with the electrolyte impregnated in it is a composite mixed ionic electronic conductor. Now, however, because of high electronic conduction through the separator, $\mu_{\text{Li}}(x) < \mu_{\text{Li}}^{\text{A}}$ which suppresses dendrite formation (or plating). The present analysis thus shows that the separator actually could be made of a reasonably good electron conducting material—and need not be an electronic insulator as has been the common practice. The analysis also suggests that the electrolyte and the anode should be essentially free of any transition metals to minimize electronic conduction through the SEI layer. An SEI layer free of transition metals should be a very good electronic insulator and, with high electronic conduction occurring through the separator will maintain $\mu_{\text{Li}}(\text{SEI/EL}) < \mu_{\text{Li}}^{\text{A}}$ and thereby suppress degradation.

2.10. Bi-layer separator

The preceding discussion suggests that an ideal separator may be a bi-layer porous structure consisting of a relatively thick porous electronic conductor and a thin porous electronic insulator. This could be achieved, for example, by applying a coating of polyethylene or polypropylene on a porous carbon paper. The anode should be in contact with the *electronically insulating* layer (polyethylene or polypropylene) while the cathode should be in contact with the *electronically conducting* layer (carbon paper). In this manner, the chances of the electronic conducting layer coming in direct contact with the anode, in the case of breach, will be minimized. Fig. 7 shows a schematic.

2.11. Battery pack failure due to cell imbalance

We have seen that for a single cell during discharge, $\mu_{\text{Li}}(x)$ is always bounded by the values at the electrodes. As discussed below, such however is not the case with battery packs containing many series-connected cells. The following discussion is restricted to discharging of a lithium ion battery containing a number of lithium-ion cells connected in series. In a typical laptop lithium-ion battery,

4–6 cells are connected in series. For higher voltage needs, several cells are connected in series, such as for automotive applications. In the Tesla Roadstar car battery the nominal operating voltage is ~ 375 V, indicating over 100 cells connected in series. The following discussion is particularly relevant to such applications.

Consider N lithium-ion cells connected in series. Let us assume that $N - 1$ of them have an identical internal resistance, R , but one cell has a much higher resistance, R' ; that is $R' > R$. Suppose the battery is discharged at a voltage V , with the average cell voltage $E_{\text{cell}} = V/N$. Since the cells are connected in series, the same net current, I , flows through each cell. Each cell also has the same Nernst voltage, E_N . The battery voltage is $V = NE_{\text{cell}} = NE_N - I(N - 1)R - IR'$. The voltage across each of the $N - 1$ identical cells is $v = E_N - IR$ while the voltage across the high resistance cell is $v' = E_N - IR'$. The average cell voltage is $E_{\text{cell}} = E_N - I((N - 1)/N)R + (R'/N)$. For $N \gg 1$, the voltage across each of the $N - 1$ identical cells is about $v \approx E_{\text{cell}}$, which is the average cell voltage. However, that across the unbalanced cell is $v' = E_N - IR'$. If R' is large, the voltage across this cell may become negative, that is $v' = E_N - IR' < 0$. This scenario is depicted in Fig. 8. The direction of the ionic current, I_i (the magnitude of which is about I) is the same through all cells. However, the unbalanced cell operating at a negative voltage has its electronic current, I_e , reversed in direction compared to the normal cells. That is, in the unbalanced cell, the directions of the ionic and the electronic currents are the *same*. In this cell, the $\mu_{\text{Li}}(x)$, need no longer be bounded by the values at the electrodes (by $\mu_{\text{Li}}^{\text{C}}$ and $\mu_{\text{Li}}^{\text{A}}$) and lithium metal precipitation may occur in the electrolyte. For the unbalanced cell, the chemical potential of lithium at x in the electrolyte is

$$\mu_{\text{Li}}(x) = \mu_{\text{Li}}^{\text{A}} - e[Ir'_i(x) - I_e r'_e(x)] \quad (54)$$

where $r'_i(x)$ is the ionic area specific resistance between the anode and position x in the electrolyte, $r'_e(x)$ is the electronic area specific resistance between the anode and position x in the electrolyte, and I_e is the electronic current flowing through the cell. In this unbalanced cell, the anode is at a higher electric potential than the cathode. That is, for any value of x in the electrolyte, $\varphi^{\text{A}} > \varphi(x) > \varphi^{\text{C}}$. Eq. (54) may also be given by

$$\mu_{\text{Li}}(x) = \mu_{\text{Li}}^{\text{A}} + e[(\varphi^{\text{A}} - \varphi(x)) - Ir'_i(x)] \quad (55)$$

If the term in the square brackets in Eq. (55) is positive, the $\mu_{\text{Li}}(x)$ in the electrolyte will exceed $\mu_{\text{Li}}^{\text{A}}$. If the $\mu_{\text{Li}}(x)$ exceeds $\mu_{\text{Li}}^{\text{O}}$, lithium may precipitate in the electrolyte or react with it. A schematic plot of $\mu_{\text{Li}}(x)$ vs. x in such an unbalanced cell is shown in Fig. 9. The expectation is that high μ_{Li} will occur in the electrolyte close to the electrolyte/cathode interface. Thus, in such a case, degradation may initiate at the cathode/electrolyte interface. Also, an SEI layer due to high μ_{Li} will form at the cathode (Fig. 9) in addition to that at the anode. The present work thus shows that there are some post mortem indicators one should look for in determining the possible reasons for battery degradation/failure. The present work suggests that in a battery pack unbalanced cells may exhibit SEI layers at both anode/electrolyte and cathode/electrolyte interfaces. Cells behaving normally by contrast will exhibit SEI layers only at anode/electrolyte interfaces. These statements assume that the electrolyte under normal conditions is stable with respect to the cathode. If, however, an SEI layer also forms at the cathode under normal operating conditions, then it will mean that an unbalanced cell in a battery pack will exhibit a thicker SEI layer at the cathode compared to the normal cells.

2.12. A comparison with the Stokes law problem

The analysis of two spheres connected by a string immersed in a fluid moving under gravity was conducted for two cases (Appendix A): (a) string over a pulley, and (b) no pulley. In the

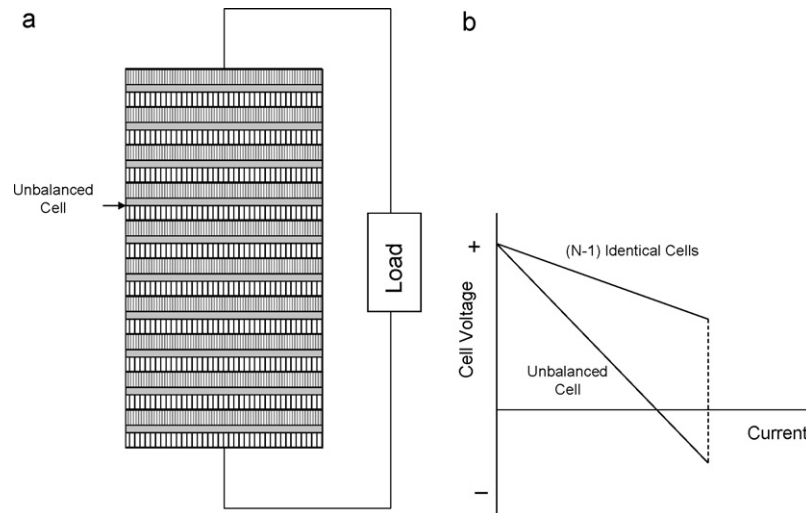


Fig. 8. (a) A schematic of a lithium-ion battery containing N cells in series of which $N - 1$ are identical and one (the unbalanced cell) has a resistance much larger than the other cells. (b) A schematic of voltage vs. current plots for the $N - 1$ identical cells and for the unbalanced cell. At a high enough current, the unbalanced cell may switch polarities. In such a case, the ionic and the electronic currents will be in the same direction in the unbalanced cell during discharge leading to cell failure, which may eventually lead to battery failure.

former, the lighter sphere moves up (moves along the direction of increasing 'chemical potential'). In the latter, both spheres move down—decrease their 'chemical potentials'.

The transport of ionic, electronic, and neutral species examined here (Appendix B) is analogous to these two cases. Note that the transport of each charged species was assumed to occur down its electrochemical potential gradient. This is a common assumption made in virtually all reported studies. This assumption naturally means that in *all* cases considered here, ionic and electronic species always move down their electrochemical potential gradients. How-

ever, such is not the case with the corresponding electrically neutral species—and therein lies the analogy.

Consider for example discharging of a lithium-ion cell shown in Fig. 3(a). The spatial variation of $\mu_{Li}(x)$ as a function position x through the electrolyte is such that it decreases from the anode to the cathode. This case is analogous to spheres joined by a string, falling under gravity (no pulley). All species move down their respective thermodynamic (chemical or electrochemical) potential gradients.

Now consider charging of a lithium-ion cell shown in Fig. 6(b). Again, lithium ions and electrons move down their respective electrochemical potential gradients (not surprising—this was the assumption made in the problem formulation, a standard assumption in virtually all reported studies on charged species transport). However, note that electrically neutral lithium is effectively transported up its chemical potential gradient through the electrolyte. Similar is the case shown in Fig. 9 for discharge through an unbalanced cell in a battery pack. These cases are analogous to spheres connected by a string going over a pulley—the lighter sphere moves up its 'chemical potential' gradient.

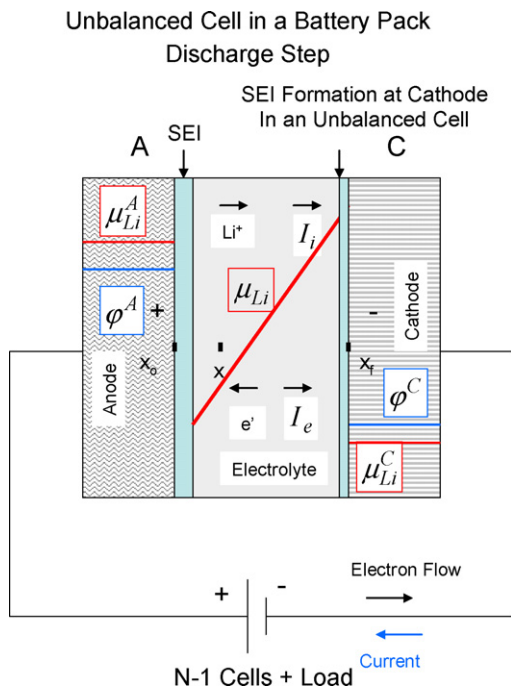


Fig. 9. A schematic showing the variation of lithium chemical potential, $\mu_{Li}(x)$, through the electrolyte during discharge in an unbalanced cell in a battery. The $\mu_{Li}(x)$ may increase with x , and may reach a high value in the electrolyte, close to the electrolyte/cathode interface (μ_{Li}^C). If μ_{Li}^C exceeds μ_{Li}^0 , lithium may precipitate or may react with the electrolyte. An SEI layer then may also form at the cathode/electrolyte interface. Note that $|I_e| \ll |I_i|$.

3. Summary

A theory of degradation of active electrochemical devices based on linear non-equilibrium thermodynamics is presented. It is shown that even in predominantly ionic conductors electronic conduction cannot be assumed to be mathematically zero since this violates the criterion of local thermodynamic equilibrium. The key conclusion of the manuscript is that the chemical potential, μ_s , of electrically neutral species, s , in a membrane need not be mathematically bounded by the values at the electrodes. Specifically, it was shown that if the ionic and the electronic currents through the membrane are in the same direction, the μ_s in the membrane may lie outside the range covered by the values at the electrodes. Under some conditions, the thermodynamic stability range of the membrane may be exceeded thus causing degradation. It was also shown that during charging of an electrochemical device, ionic and electronic currents through the electrolyte are in the same direction. Under some conditions of charging, degradation of the device may occur. In lithium-ion cells, for example during charging, the chemical potential of lithium, $\mu_{Li}(x)$, in the electrolyte may exceed that corresponding to pure lithium, μ_{Li}^0 . This will lead to the precip-

itation of lithium and/or reaction with the electrolyte, depending upon the operating conditions and the magnitudes of the various transport resistances. Capacity fading according to this model thus will primarily occur during charging. In battery packs containing several cells connected in series, a similar phenomenon can occur in an unbalanced cell even during discharge. In unbalanced cells in battery packs, SEI layers may form at both anode/electrolyte and cathode/electrolyte interfaces. If the cathode is intrinsically unstable in contact with electrolyte, then it will mean that the SEI layer at the cathode will be thicker in unbalanced cells compared to those operating normally. Thus, in unbalanced cells in a battery, capacity fade may occur during both charge and discharge. The present work also suggests that a bi-layer separator with one layer exhibiting high electronic conductivity (placed in contact with the cathode) may help lower the $\mu_{Li}(x)$ in the electrolyte, and thereby suppress degradation. This is a radically different approach from the current practice. It is suggested that by suitably tailoring transport properties of the electrolyte/separator, the SEI layer and the interfaces, incidence of degradation may be avoided or at least suppressed.

Acknowledgment

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Appendix A. Coupled motion of spheres in a fluid

Fig. 2(a) shows two spheres of radii r_1 and r_2 immersed in a fluid of viscosity η , joined by a mass-less, infinitely thin string going over a frictionless pulley (pulley outside the fluid). Fig. 2(b) shows two spheres immersed in a viscous fluid connected by a string, but without a pulley. Apparent masses of the spheres, corrected for buoyancy are $m_1 = (4\pi r_1^3/3)(\rho_M - \rho_f)g$ and $m_2 = (4\pi r_2^3/3)(\rho_M - \rho_f)g$ where ρ_M and ρ_f are specific gravities of the spheres and the fluid, respectively. Here we have chosen $m_1 > m_2$. Fig. 2 shows $r_1 > r_2$. If the specific gravities of the two spheres are different, for example if they are made of two different materials, then it is possible to have $m_1 > m_2$ but r_1 may be larger or smaller than r_2 . Note, r_1 and r_2 are contained in the transport (kinetic) coefficients; while m_1 and m_2 are contained in the thermodynamic driving forces. In Fig. 2(a) the heavier sphere moves down (lowers its potential energy) while the lighter one rises (increases its potential energy). There is a net decrease in potential energy, which is dissipated as heat lost to the reservoir (and eventually to the surroundings). The velocities of the two spheres in steady state (terminal velocities achieved) are given by

$$v_1 = -v = \frac{1}{6\pi\eta(r_1 + r_2)}(-m_1g) - \frac{1}{6\pi\eta(r_1 + r_2)}(-m_2g) \\ = -L_{11}\nabla\mu_1 - L_{12}\nabla\mu_2 = L_{11}X_1 + L_{12}X_2 \quad (A1)$$

and

$$v_2 = v = -\frac{1}{6\pi\eta(r_1 + r_2)}(-m_1g) + \frac{1}{6\pi\eta(r_1 + r_2)}(-m_2g) \\ = -L_{21}\nabla\mu_1 - L_{22}\nabla\mu_2 = L_{21}X_1 + L_{22}X_2 \quad (A2)$$

The above are velocities, so the units are ms^{-1} . The coupling coefficients are negative, that is

$$L_{12} = L_{21} = -\frac{1}{6\pi\eta(r_1 + r_2)} < 0 \quad (A3)$$

This case corresponds to $L_{11} = L_{22} = -L_{12} = -L_{21} = L = 1/(6\pi\eta(r_1 + r_2)) > 0$.

The coupling tension in the string is

$$T = \left(\frac{r_2}{r_1 + r_2}\right) m_1g + \left(\frac{r_1}{r_1 + r_2}\right) m_2g \quad (A4)$$

We can also write for the forces

$$X_1 = -\nabla\mu_1 = -\nabla\mu_2 - \frac{v}{L} = X_2 - \frac{v}{L} = X_2 - Rv \quad (A5)$$

Note that $L_{11}L_{22} - L_{12}^2 = 0$ and not $L_{11}L_{22} - L_{12}^2 > 0$, and represents fully coupled processes (naturally, as the spheres are connected by a string). In this case, the forces are independent but the fluxes are dependent. This means we may choose X_1 and X_2 independently (by independently choosing the masses of the two spheres), but the fluxes (dependent) are given by $v_1 = -v = -v_2$.

The dissipation function is [10]

$$\Psi = T \frac{d_i S}{dt} = \sum_i J_i X_i = -v_1 \nabla\mu_1 - v_2 \nabla\mu_2 = \frac{g^2}{6\pi(r_1 + r_2)}(m_1 - m_2)^2 > 0 \quad (A6)$$

where $d_i S/dt$ is the entropy generation rate.

Now consider a case in which there is no pulley and both spheres (still joined by a string) are falling under gravity in the fluid (Fig. 2(b)). Now the velocities are

$$v_1 = -v = \frac{1}{6\pi\eta(r_1 + r_2)}(-m_1g) + \frac{1}{6\pi\eta(r_1 + r_2)}(-m_2g) \\ = -L_{11}\nabla\mu_1 - L_{12}\nabla\mu_2 = L_{11}X_1 + L_{12}X_2 \quad (A7)$$

and

$$v_2 = -v = \frac{1}{6\pi\eta(r_1 + r_2)}(-m_1g) + \frac{1}{6\pi\eta(r_1 + r_2)}(-m_2g) \\ = -L_{21}\nabla\mu_1 - L_{22}\nabla\mu_2 = L_{21}X_1 + L_{22}X_2 \quad (A8)$$

Again the forces are independent but the velocities (fluxes) are dependent. Now

$$L_{11} = L_{22} = L_{12} = L_{21} = \frac{1}{6\pi\eta(r_1 + r_2)} = L \quad (A9)$$

Note the coupling coefficients are positive, that is

$$L_{12} = L_{21} = \frac{1}{6\pi\eta(r_1 + r_2)} > 0 \quad (A10)$$

Again $L_{11}L_{22} - L_{12}^2 = 0$, consistent with fully coupled processes. Coupling tension in the string is

$$T = \left(\frac{r_2}{r_1 + r_2}\right) m_1g - \left(\frac{r_1}{r_1 + r_2}\right) m_2g \quad (A11)$$

We can also write for the forces

$$X_1 = -\nabla\mu_1 = \nabla\mu_2 - \frac{v}{L} = -X_2 - \frac{v}{L} = -X_2 - Rv \quad (A12)$$

The dissipation function is

$$\Psi = T \frac{d_i S}{dt} = \sum_i J_i X_i = -v_1 \nabla\mu_1 - v_2 \nabla\mu_2 \\ = \frac{g^2}{6\pi(r_1 + r_2)}(m_1 + m_2)^2 > 0 \quad (A13)$$

In this case, both spheres move down (both reduce their potential energies). The coupling tension is zero if $(r_2/(r_1 + r_2))m_1 = (r_1/(r_1 + r_2))m_2$.

The signs of the forces are the same in both cases, but the signs of $L_{12} = L_{21}$ are different. Thus in the two cases the signs of the terms $L_{12}X_2$ and $L_{21}X_1$ are different. In one case, in which $L_{12}X_2 > 0$ and $L_{21}X_1 > 0$, an increase in energy of one sphere occurs as a result of coupling.

Appendix B. Transport through predominantly ionic conductors

In liquid electrolytes containing ionic salts dissolved in polar liquids, there is at least one mobile cation, and at least one mobile anion. For an electrolyte M_mZ_n , a salt of metal M and a nonmetal Z , local equilibrium gives

$$M_mZ_n(\bar{r}) \Leftrightarrow mM^{n+}(\bar{r}) + nZ^{m-}(\bar{r}) \quad (B1)$$

and

$$\mu_{M_mZ_n}(\bar{r}) = m\mu_{M^{n+}}(\bar{r}) + n\mu_{Z^{m-}}(\bar{r}) = m\tilde{\mu}_{M^{n+}}(\bar{r}) + n\tilde{\mu}_{Z^{m-}}(\bar{r}) \quad (B2)$$

where $\tilde{\mu}_i(\bar{r}) = \mu_i(\bar{r}) + z_i e \Phi(\bar{r})$ is the local electrochemical potential of i , z_i is the valence of i , e is the electronic charge, and $\Phi(\bar{r})$ is the local electrostatic potential. Local equilibrium also implies

$$M(\bar{r}) \Leftrightarrow M^{n+}(\bar{r}) + ne(\bar{r}) \quad (B3)$$

which gives

$$\mu_M(\bar{r}) = \tilde{\mu}_{M^{n+}}(\bar{r}) + n\tilde{\mu}_e(\bar{r}) \quad (B4)$$

and

$$Z(\bar{r}) + me(\bar{r}) \Leftrightarrow Z^{m-}(\bar{r}) \quad (B5)$$

which gives

$$\mu_Z(\bar{r}) = \tilde{\mu}_{Z^{m-}}(\bar{r}) - m\tilde{\mu}_e(\bar{r}) \quad (B6)$$

where $\tilde{\mu}_e(\bar{r}) = \mu_e(\bar{r}) - e\Phi(\bar{r})$ is the electrochemical potential of electrons. In salt solutions in polar liquids, free electron concentration is very small (which could be present as solvated electrons). Thus, negligible electron current transports through the solution. An important point is that chemical and electrochemical potentials of electrons are still well-defined quantities in salt solutions, some concentration of free or solvated electrons always exists, and some electron transport must also occur when nonzero electrochemical potential gradient of electrons exists. Finally, for local equilibrium to exist, differential forms of the above equations must also be valid, that is,

$$\begin{aligned} \delta\mu_{M_mZ_n}(\bar{r}) &= m\delta\mu_{M^{n+}}(\bar{r}) + n\delta\mu_{Z^{m-}}(\bar{r}) = m\delta\tilde{\mu}_{M^{n+}}(\bar{r}) + m\delta\tilde{\mu}_{Z^{m-}}(\bar{r}) \\ &= m\delta\mu_M(\bar{r}) + n\delta\mu_Z(\bar{r}) \end{aligned} \quad (B7)$$

and

$$\delta\mu_M(\bar{r}) = \delta\tilde{\mu}_{M^{n+}}(\bar{r}) + n\delta\tilde{\mu}_e(\bar{r}) \quad (B8)$$

where $\delta\mu$ or $\delta\tilde{\mu}$ denote differential variations in chemical potential μ or electrochemical potential $\tilde{\mu}$. For a line compound (a very narrow range of stoichiometry), $\delta\mu_{M_mZ_n}(\bar{r}) \cong 0$. Even then, individual chemical potentials of neutral metal and neutral nonmetal species may exhibit large variations.

For differentials to satisfy local equilibrium, relevant species must exhibit some transport; that is a sufficient number of species comprising the system must exhibit nonzero conductivities or diffusivities. In typical solid electrolytes, there often exists only one substantially mobile ion. Even so the assumption of local equilibrium implies some mobility for a sufficient number of species to satisfy local equilibrium. For example, consider yttria-stabilized zirconia (YSZ) which is a predominantly oxygen ion conductor. Local equilibrium for neutral Zr is given by

$$Zr(\bar{r}) \Leftrightarrow Zr^{4+}(\bar{r}) + 4e(\bar{r}) \quad (B9)$$

For local equilibrium to be satisfied, we must have

$$\mu_{Zr}(\bar{r}) = \mu_{Zr^{4+}}(\bar{r}) + 4\mu_e(\bar{r}) = \tilde{\mu}_{Zr^{4+}}(\bar{r}) + 4\tilde{\mu}_e(\bar{r}) \quad (B10)$$

and

$$\delta\mu_{Zr}(\bar{r}) = \delta\mu_{Zr^{4+}}(\bar{r}) + 4\delta\mu_e(\bar{r}) = \delta\tilde{\mu}_{Zr^{4+}}(\bar{r}) + 4\delta\tilde{\mu}_e(\bar{r}) \quad (B11)$$

Thus, if electrons and Zr^{4+} (or Zr) exhibit nonzero conductivities (diffusivities), local equilibrium criterion can be satisfied. In general, we expect sufficient (nonzero) mobilities of the various species to satisfy local equilibrium.

We now consider local equilibrium at \bar{r} between neutral species s , the corresponding constituent mobile ions i of valence z_i , and electrons, e , namely

$$s(\bar{r}) \Leftrightarrow i(\bar{r}) + z_i e(\bar{r}) \quad (B12)$$

with

$$K = \frac{a_i(\bar{r})(a_e(\bar{r}))^{z_i}}{a_s(\bar{r})} \quad (B13)$$

as the equilibrium constant and a 's are local thermodynamic activities of species in Eq. (B12).

The valence z_i can be positive (cation) or negative (anion). Local equilibrium at \bar{r} gives

$$\mu_s(\bar{r}) = \mu_i(\bar{r}) + z_i \mu_e(\bar{r}) = \tilde{\mu}_i(\bar{r}) + z_i \tilde{\mu}_e(\bar{r}) \quad (B14)$$

where $\mu_s(\bar{r})$, $\mu_e(\bar{r})$ and $\mu_i(\bar{r})$ are respectively the chemical potentials of neutral species (s), electrons (e), and ions (i) at \bar{r} ; and $\tilde{\mu}_i(\bar{r})$ and $\tilde{\mu}_e(\bar{r})$ are respectively the electrochemical potentials of ions and electrons.

Experimentally measurable electric potential is given by [33,34]

$$\varphi(\bar{r}) = -\frac{\tilde{\mu}_e(\bar{r})}{e} = -\frac{\mu_e(\bar{r})}{e} + \Phi(\bar{r}) \quad (B15)$$

The chemical potential of neutral species s is thus also given by

$$\mu_s(\bar{r}) = \tilde{\mu}_i(\bar{r}) + z_i \tilde{\mu}_e(\bar{r}) = \tilde{\mu}_i(\bar{r}) - z_i e \varphi(\bar{r}) \quad (B16)$$

The above refers to local equilibrium, which means

$$\Delta\mu_s(\bar{r}, \bar{r}_0) = \mu_s(\bar{r}) - \mu_s(\bar{r}_0) = \mu_i(\bar{r}) - \mu_i(\bar{r}_0) + z_i \{ \tilde{\mu}_e(\bar{r}) - \tilde{\mu}_e(\bar{r}_0) \} \quad (B17)$$

or

$$\Delta\mu_s(\bar{r}, \bar{r}_0) = \mu_s(\bar{r}) - \mu_s(\bar{r}_0) = \tilde{\mu}_i(\bar{r}) - \tilde{\mu}_i(\bar{r}_0) - z_i e \{ \varphi(\bar{r}) - \varphi(\bar{r}_0) \} \quad (B18)$$

as the difference in chemical potentials of s between \bar{r} and \bar{r}_0 .

Eqs. (B17) and (B18) are the result of local equilibrium. But we also have from the Onsager equations

$$\begin{aligned} \Delta\mu_s(\bar{r}, \bar{r}_0) &= \mu_s(\bar{r}) - \mu_s(\bar{r}_0) \\ &= - \int_{\bar{r}_0}^{\bar{r}} \sum_k R_{sk} \bar{J}_k \cdot d\bar{r} \quad \text{where } k = s, i, e \end{aligned} \quad (B19)$$

which means

$$\begin{aligned} \Delta\mu_s(\bar{r}, \bar{r}_0) &= \mu_s(\bar{r}) - \mu_s(\bar{r}_0) \\ &= - \int_{\bar{r}_0}^{\bar{r}} R_{ss} \bar{J}_s \cdot d\bar{r} - \int_{\bar{r}_0}^{\bar{r}} R_{si} \bar{J}_i \cdot d\bar{r} - \int_{\bar{r}_0}^{\bar{r}} R_{se} \bar{J}_e \cdot d\bar{r} \end{aligned} \quad (B20)$$

Strictly, Eqs. (B19) and (B20) should include all other species in the system also. The neglect of the other species is an approximation. The ionic and electronic fluxes are respectively $\bar{J}_i(\bar{r})$ and $\bar{J}_e(\bar{r})$ in $\#m^{-2} s^{-1}$ and can be written in terms of the respective current densities as

$$\bar{J}_i(\bar{r}) = \frac{\bar{I}_i(\bar{r})}{z_i e} \quad (B21)$$

and

$$\bar{J}_e(\bar{r}) = -\frac{\bar{I}_e(\bar{r})}{e} \quad (B22)$$

Substituting for fluxes in terms of current densities in Eq. (B20) gives

$$\Delta\mu_s(\bar{r}, \bar{r}_0) = \mu_s(\bar{r}) - \mu_s(\bar{r}_0)$$

$$= - \int_{\vec{r}_0}^{\vec{r}} R_{ss} \vec{J}_s \cdot d\vec{r} - \frac{1}{z_i e} \int_{\vec{r}_0}^{\vec{r}} R_{si} \vec{I} \cdot d\vec{r}_i + \frac{1}{e} \int_{\vec{r}_0}^{\vec{r}} R_{se} \vec{I}_e \cdot d\vec{r} \quad (B23)$$

We will now assume that the concentration of the neutral species, s , within the material is negligible. This means a very high equilibrium constant for the reaction $s \rightleftharpoons i + z_i e$. Thus, there is hardly any concentration of neutral s ; that is $C_s(\vec{r}) \approx 0$ and thus hardly any transport of neutral s (as *neutral s*) occurs through the material; that is, $\vec{J}_s(\vec{r}) \cong 0$. If the material is a predominantly ionic conductor, it also means free electron concentration is very small. However, we still cannot set I_e identically zero to ensure that local equilibrium is satisfied. Thus, Eq. (B23) reduces to

$$\begin{aligned} \Delta \mu_s(\vec{r}, \vec{r}_0) &= \mu_s(\vec{r}) - \mu_s(\vec{r}_0) \\ &= - \frac{1}{z_i e} \int_{\vec{r}_0}^{\vec{r}} R_{si} \vec{I} \cdot d\vec{r} + \frac{1}{e} \int_{\vec{r}_0}^{\vec{r}} R_{se} \vec{I}_e \cdot d\vec{r} \end{aligned} \quad (B24)$$

The R_{ss} is finite, nonzero, positive. However, by making the usual measurements such as currents and voltages, we cannot determine R_{ss} , the parameter related to the transport of neutral s . It can in principle be determined if in addition to the measurements of ionic and electronic currents, one also accurately measures loss/gain of s at the two electrodes (reservoirs) which would require the experiments to be conducted for a sufficiently long time. Tubandt used this approach some 90 years ago to study transport through silver halides [35].

We now consider one dimensional transport and assume that the transport coefficients are independent of position. Referring to Fig. 1, we will initially choose reference point x'_0 within the membrane. Then, Eq. (B24) becomes

$$\mu_s(x) - \mu_s(x'_0) = \Delta \mu_s(x, x'_0) = - \frac{R_{si} I_i (x - x'_0)}{z_i e} + \frac{R_{se} I_e (x - x'_0)}{e} \quad (B25)$$

or

$$\mu_s(x) = \mu_s(x'_0) - \frac{R_{si} I_i (x - x'_0)}{z_i e} + \frac{R_{se} I_e (x - x'_0)}{e} \quad (B26)$$

Since we are considering a one dimensional steady state problem, I_i and I_e are position independent. Units of R_{si} and R_{se} are erg cm s or J m s (with chemical potential given per species—per ion, per electron, per atom, per molecule).

No assumptions concerning the relationships between current densities and thermodynamic potential gradients (such as electrochemical potential gradients) have been made so far. Let us now assume that the flux of a charged species occurs down its electrochemical potential gradient. That is,

$$\vec{I}_i(\vec{r}) = - \frac{\sigma_i}{z_i e} \nabla \tilde{\mu}_i(\vec{r}) \quad \text{and} \quad \vec{I}_e(\vec{r}) = \frac{\sigma_e}{e} \nabla \tilde{\mu}_e(\vec{r}) = - \sigma_e \nabla \varphi(\vec{r}) \quad (B27)$$

where σ_i and σ_e are respectively the ionic and the electronic conductivities. Eq. (B27) represents an important assumption made in virtually all transport studies of electrically charged species [36]. Substitution in Eq. (B18) for a one dimensional problem gives

$$\frac{\mu_s(x) - \mu_s(x'_0)}{x - x'_0} = - \frac{z_i e}{\sigma_i} I_i + \frac{z_i e}{\sigma_e} I_e \quad (B28)$$

or

$$\mu_s(x) - \mu_s(x'_0) = - \frac{z_i e (x - x'_0)}{\sigma_i} I_i + \frac{z_i e (x - x'_0)}{\sigma_e} I_e \quad (B29)$$

Now

$$r'_i(x) = \frac{(x - x'_0)}{\sigma_i} \quad (B30)$$

is the ionic area specific resistance between x'_0 and x , and

$$r'_e(x) = \frac{(x - x'_0)}{\sigma_e} \quad (B31)$$

is the electronic area specific resistance between x'_0 and x .

Thus,

$$\begin{aligned} \mu_s(x) &= \mu_s(x'_0) - z_i e r'_i(x) I_i + z_i e r'_e(x) I_e \\ &= \mu_s(x'_0) - z_i e [r'_i(x) I_i - r'_e(x) I_e] \end{aligned} \quad (B32)$$

which is in a form similar to the author's previous derivation [13].

Comparison of Eqs. (B26) and (B29) gives relations between the Onsager coefficients and conductivities as

$$R_{si} = \frac{z_i^2 e^2}{\sigma_i} \quad (B33)$$

and

$$R_{se} = \frac{z_i e^2}{\sigma_e} \quad (B34)$$

These are the Onsager coupling coefficients which relate forces (treated as dependent variables) to fluxes (treated as independent variables). Note also $R_{si} \neq \infty$ and $R_{se} \neq \infty$ (finite), indicating a coupling of fluxes.

Appendix C. Abrupt changes across interfaces

Let us consider points just inside the membrane adjacent to the electrodes (reservoirs) given by $x = x_0 + \delta_{x_0}$ and $x = x_f - \delta_{x_f}$, as in Fig. 1. Note that $\delta_{x_0}, \delta_{x_f} \ll |x_f - x_0|$. The chemical potentials of s in the membrane close to the interfaces are given by [using Eq. (B32)]

$$\mu_s(x_0 + \delta_{x_0}) = \mu_s(x_0) - z_i e [r_i^{x_0} I_i - r_e^{x_0} I_e] = \mu_s(x_0^+) \quad (C1)$$

and

$$\mu_s(x_f - \delta_{x_f}) = \mu_s(x_f) + z_i e [r_i^{x_f} I_i - r_e^{x_f} I_e] = \mu_s(x_f^-) \quad (C2)$$

where $x_0^+ = x_0 + \delta_{x_0}$ is slightly greater than x_0 and $x_f^- = x_f - \delta_{x_f}$ is slightly less than x_f . The corresponding (abrupt) changes in μ_s across the interfaces are

$$\Delta \mu_s^{x_0} = z_i e [r_i^{x_0} I_i - r_e^{x_0} I_e] \quad (C3)$$

and

$$\Delta \mu_s^{x_f} = z_i e [r_i^{x_f} I_i - r_e^{x_f} I_e] \quad (C4)$$

Note in general, $\Delta \mu_s^{x_0} = z_i e [r_i^{x_0} I_i - r_e^{x_0} I_e] \neq 0$ and $\Delta \mu_s^{x_f} = z_i e [r_i^{x_f} I_i - r_e^{x_f} I_e] \neq 0$. With $\mu_s(x_f) \neq \mu_s(x_0)$ (experimentally imposed conditions), the only situation for which $\Delta \mu_s^{x_0} = 0$, corresponds to both $r_i^{x_0} = 0$ and $r_e^{x_0} = 0$; and the only situation for which $\Delta \mu_s^{x_f} = 0$, corresponds to both $r_i^{x_f} = 0$ and $r_e^{x_f} = 0$. These are very unlikely situations since they imply perfect reversibility for the transfer of *both* ions and electrons across interfaces. Thus, $\Delta \mu_s^{x_0}$ and $\Delta \mu_s^{x_f}$, which represent sharp changes in μ_s across electrode (reservoir)/electrolyte interfaces are nonzero. Let us assume that the electrodes are perfectly (electrochemically) reversible, a terminology commonly used in electrochemical literature. This means $r_i^{x_0} = 0$ and $r_i^{x_f} = 0$. Even in such a case note that

$$|\Delta \mu_s^{x_0}| = |z_i e I_e r_e^{x_0}| \neq 0 \quad (C5)$$

and

$$|\Delta \mu_s^{x_f}| = |z_i e I_e r_e^{x_f}| \neq 0 \quad (C6)$$

The preceding shows that a perfectly reversible electrode in an electrochemical sense does not imply the equilibration of μ_s , the chemical potential of neutral species, across an electrode/electrolyte interface (when $\mu_s(x_f) \neq \mu_s(x_0)$), and that there

will in general be abrupt changes in μ_s across interfaces. Perfectly reversible electrode in an electrochemical sense only means the electrochemical potential, $\tilde{\mu}_i$, of the mobile ion equilibrates across the interface even at finite, nonzero current densities. There is considerable literature in electrochemistry which incorrectly assumes the equilibration of the chemical potential of neutral species, μ_s , across electrode/electrolyte interfaces when electrodes are reversible in an electrochemical sense.

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