

CHAPTER

1

***ELECTROCHEMICAL CELLS:
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1 ELECTROCHEMICAL CELLS AND ION TRANSPORT

An electrochemical cell is a device with which electrical energy is converted into chemical energy, or vice versa. We can consider two types: *electrolytic cells*, in which electric energy is converted into chemical energy (corresponding to the charging of a battery), and *galvanic cells*, in which chemical energy is converted into electric energy (corresponding to a battery in discharge). In its most basic structure, an electrochemical cell is formed by two electrodes, one positive and one negative, separated by an ionically conductive and electronically insulating *electrolyte*, which may be a liquid, a liquid imbibed into a porous matrix, an ionomeric polymer, or a solid. At the negative electrode, an oxidation or anodic reaction occurs during discharge (e.g., the release of electrons and lithium ions from a graphite electrode: $\text{LiC}_6 \rightarrow \text{C}_6 + \text{Li}^+ + \text{e}^-$), while the process is reversed during charge, when a reduction or cathodic reaction occurs at the negative electrode (e.g., $\text{C}_6 + \text{Li}^+ + \text{e}^- \rightarrow \text{LiC}_6$). Even though the negative electrode is in principle an anode during discharge and a

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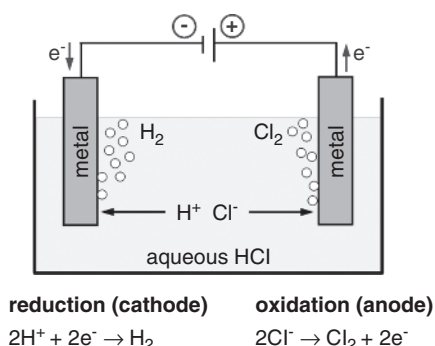


FIGURE 1 Electrolytic cell, illustrating the decomposition of aqueous hydrochloric acid into hydrogen and chlorine. Here, aqueous HCl serves as an ionically conducting and electronically insulating electrolyte, facilitating the overall reaction: $2\text{HCl} \rightarrow \text{Cl}_2 + \text{H}_2$.

cathode during charge, the *negative electrode is commonly referred to as an anode* in the battery community (i.e., the discharge process is taken as the nominal defining process). Similarly, a reduction or cathodic reaction occurs at the positive electrode during discharge (e.g., the uptake of lithium ions and electrons by iron phosphate: $\text{FePO}_4 + \text{Li}^+ + \text{e}^- \rightarrow \text{LiFePO}_4$), and thus the *positive electrode is commonly referred to as a cathode*, even though, of course, an anodic process occurs on the positive electrode during charge. Since this convention can be somewhat confusing, referring to the electrodes as a negative or positive electrode would eliminate the ambiguity introduced by using the terms *anode* and *cathode*.

Figure 1 schematizes an $\text{HCl}/\text{H}_2/\text{Cl}_2$ *electrolytic cell*. The electrochemical processes are the cathodic reduction of hydrogen ions (protons) at the negative electrode ($2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$) and the anodic oxidation of the chloride ions at the positive electrode ($2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$). These two *half-cell reactions* can be added up to the overall reaction of this electrolytic cell: namely, the evolution of chlorine and hydrogen from hydrochloric acid (used industrially to recycle waste HCl in chemical plants): $2\text{HCl} \rightarrow \text{H}_2 + \text{Cl}_2$. As illustrated in Figure 1, an electrochemical reaction leads to a flow of electrons in the external circuit which is balanced by the migration of positive ions (cations) to the cathode and of negative ions (anions) to the anode; the principle of electroneutrality demands that the external electronic current must be matched by an internal ionic current (i.e., by the sum of the cation flow to the cathode and the anion flow to the anode).

The reversible cell voltage, $E_{\text{cell,rev}}$, also referred to as the *electromotoric force* (emf), can be obtained from the Gibbs free energy change of the reaction, ΔG_R :

$$E_{\text{cell,rev}} = -\frac{\Delta G_R}{nF} \quad (1)$$

where n is the number of electrons involved in the electrochemical reaction (for Fig. 1, $n = 2$) and F is the Faraday constant, equal to 96,485 As/mol. The standard Gibbs free energy of reaction, ΔG_R^0 , can readily be obtained from the standard Gibbs free energies of formation, ΔG_f^0 , as is shown for the HCl electrolysis process above:

$$\Delta G_R^0 = \Delta G_{f(\text{H}_2)}^0 + \Delta G_{f(\text{Cl}_2)}^0 - 2 \cdot \Delta G_{f(\text{HCl})}^0 \quad (2)$$

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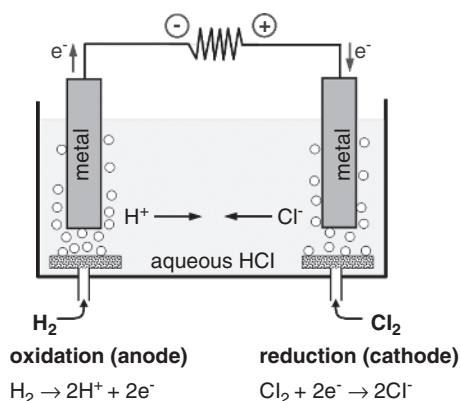


FIGURE 2 Galvanic cell, illustrating the reaction between hydrogen and chlorine to yield aqueous hydrochloric acid: $\text{Cl}_2 + \text{H}_2 \rightarrow 2\text{HCl}$.

Considering that $\Delta G_{f(\text{H}_2)}^0$ and $\Delta G_{f(\text{Cl}_2)}^0$ are defined to be zero under standard conditions (conventionally defined as 25°C and gas partial pressures of 100 kPa) and taking a value of -131.1 kJ/mol for $\Delta G_{f(\text{HCl})}^0$ at the standard condition for species dissolved in water (conventionally, 1 M solution at 25°C), one can determine the standard Gibbs free energy of reaction of 262.2 kJ/mol . If the reaction is run under these standard conditions, the reversible cell voltage can be calculated from ΔG_R^0 using equation (1):

$$E_{\text{cell,rev}}^0 = -\frac{262.2 \text{ kJ/mol}}{2 \times 96,485 \text{ As/mol}} = -1.36 \text{ V} \quad (3)$$

Since ΔG_R is greater than 0, energy is required to decompose HCl into H_2 and Cl_2 ; a negative emf value (i.e., $E_{\text{cell,rev}}$ is < 0) therefore means that electric energy is needed to drive the electrochemical reaction, as in fact is expected for an electrolytic cell, which also corresponds to a battery cell during charge.

Figure 2 schematizes an $\text{HCl}/\text{H}_2/\text{Cl}_2$ *galvanic cell*. The electrochemical half-cell reactions are the anodic oxidation of hydrogen molecules at the negative electrode ($\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$) and the cathodic reduction of chlorine molecules at the positive electrode ($\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-$), resulting in the overall formation of HCl from hydrogen and chlorine ($\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl}$), just the opposite reaction to that of an electrolytic cell. A comparison of Figures 1 and 2 once more illustrates that, for example, the hydrogen electrode is always the negative electrode and that irrespective of whether the cell is operated as an electrolytic or a galvanic cell, the half-cell reaction at the hydrogen electrode is either anodic (Fig. 2) or cathodic (Fig. 1). As discussed for the electrolytic cell (Fig. 1), the flow of electrons through the external circuit has to be exactly balanced by the flow of cations to the cathode and anions to the anode.

The standard Gibbs free energy of reaction for the galvanic cell in Figure 2 is given by

$$\Delta G_R^0 = 2 \cdot \Delta G_{f(\text{HCl})}^0 - (\Delta G_{f(\text{H}_2)}^0 + \Delta G_{f(\text{Cl}_2)}^0) = -262.2 \text{ kJ/mol} \quad (4)$$

equating to a reversible cell voltage of $E_{\text{cell,rev}} = +1.36 \text{ V}$ [see equation (1)] under standard conditions. The fact that ΔG_R is < 0 and $E_{\text{cell,rev}}$ is > 0 signifies that

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the reaction proceeds spontaneously by converting chemical energy into electrical energy, as in fact is expected for a galvanic cell or for a battery during discharge.

The rate of energy conversion in galvanic or electrolytic cells is typically expressed as current (in units of amperes, A) or as current density (in units of A/cm²). It depends on the kinetics of the half-cell reactions as well as on many other materials (e.g., ionic conductivity of the electrolyte) and design parameters (thickness of the electrolyte-gap between positive and negative electrodes). Clearly, the actual size of a galvanic or electrolytic device for a required energy or materials conversion rate decreases with increasing current density, so that the maximum power density of galvanic (e.g., fuel cells) and electrolytic (e.g., chlorine–alkaline electrolyzer) cells is an important figure of merit:

$$P_{\text{electric}}(\text{W/cm}^2) = E_{\text{cell}}(V) \times i(\text{A/cm}^2) \quad (5)$$

Power densities vary from $\approx 0.1 \text{ W/cm}^2$ for high-power lithium-ion batteries at discharge C rates of $\approx 10 \text{ h}^{-1}$ [the *C rate* is defined as the number of times the full capacity of the battery is (dis)charged per hour] to $\approx 1 \text{ W/cm}^2$ for proton-exchange membrane (PEM) fuel cells. Obviously, the higher the achievable power density, the lower the necessary electrode area and, generally, the smaller the device. The efficiency of galvanic and electrolytic cells is often given in terms of the cell voltage efficiency, η_{cell} , which relates the actual cell voltage to the reversible cell voltage of a galvanic or electrolytic cell:

$$\eta_{\text{cell,galvanic}} = \frac{E_{\text{cell}}}{E_{\text{cell,rev}}} \quad \text{and} \quad \eta_{\text{cell,electrolytic}} = \frac{E_{\text{cell,rev}}}{E_{\text{cell}}} \quad (6)$$

For all galvanic and electrolytic cells, the deviation between the actual cell voltage and the reversible cell voltage increases with increasing current density, which means that η_{cell} increases with current and power density.

The ionic conductivity, κ , of an electrolyte solution derives from the movement of anions and cations in the electrolyte solution caused by an electric field, that is, by a gradient of the electrostatic potential in the electrolyte solution phase, $\nabla\phi_s$. The flow of ions produces an electric current which can be expressed in terms of the ionic mobility u , the ion concentration c , and the charge number z :

$$i = -F(z_+c_+u_+ + |z_-|c_-u_-)\nabla\phi_s = -\kappa\nabla\phi_s \quad (7)$$

where the subscripts $+$ and $-$ refer to the cations and anions, respectively, and F is the Faraday constant; the ionic mobility quantifies the terminal velocity of an ion in an electric field and has units of (cm/s)/(V/cm). The ionic conductivity is most commonly expressed in units of S/cm (a siemens, S, is a reciprocal ohm). The conductivity of typical battery electrolytes is on the order of 1 to 10 mS/cm (see Table 1), while the conductivity of aqueous or ionomeric electrolytes used in fuel cells and electrolyzers is on the order of 100 mS/cm.

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TABLE 1 Conductivities of Typical Lithium Ion Battery Electrolytes at 25°C and 1 M Salt Concentration

Solvent	Mixing ratio (g/g)	Salt	Conductivity, κ (mS/cm)
EC/DMC	1 : 1	LiAsF ₆	11
EC/DMC	1 : 1	LiPF ₆	11
EC/DMC/DEC	1 : 1 : 1	LiPF ₆	10
EC/PC	3 : 2	LiBF ₄	2.7

EC, ethylene carbonate; DMC, dimethyl carbonate; DEC, diethyl carbonate; PC, propylene carbonate.

2 CHEMICAL AND ELECTROCHEMICAL POTENTIAL**2.1 Temperature Dependence of the Reversible Cell Voltage**

The temperature dependence of the Gibbs free energy change of a reaction under isobaric conditions is proportional to the entropy change of reaction, ΔS_R :

$$\left(\frac{\partial \Delta G_R}{\partial T} \right)_{p, n_i} = -\Delta S_R \quad (8)$$

where ΔS_R is the entropy change of the reaction. Combining equation (8) with equation (1) yields the temperature dependence of the reversible cell voltage:

$$\left(\frac{\partial E_{\text{cell, rev}}}{\partial T} \right)_{p, n_i} = \frac{\Delta S_R}{nF} \quad (9)$$

2.2 Chemical Potential

Let us consider a generic chemical reaction: $\nu_A A + \nu_B B \rightarrow \nu_C C + \nu_D D$. The Gibbs free energy change of reaction, ΔG_R , is given by

$$\Delta G_R = \nu_C \mu_C + \nu_D \mu_D - (\nu_A \mu_A + \nu_B \mu_B) \quad (10)$$

where μ_i is the chemical potential of species i . The chemical potential defines the change of the Gibbs free energy when an infinitesimal number of moles of species i is added to a mixture, with all other components remaining constant:

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{p, T, n_{j \neq i}} \quad (11)$$

The concentration dependence of the chemical potential is

$$\mu_i = \mu_i^0 + RT \ln(a_i) \quad (12)$$

where μ_i^0 is the standard chemical potential (conventionally defined at 25°C and 100 kPa_{abs}), R is the gas constant (8.314 J/(mol·K)), and T is the temperature in Kelvin. In the case of chemical activity, a_i , one has to distinguish between the activity of pure solid substances ($a_i = 1$), of gases ($a_i = f_i p_i / p^0$, where f_i is the fugacity coefficient, p_i is the partial pressure, and p^0 is the standard pressure); for ideal gases, $f_i = 1$), of dissolved species ($a_i = \gamma_i c_i / c^0$, where γ_i is the activity coefficient, c_i is the

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concentration, and c^0 is the standard concentration of 1 mol/L; for ideal solutions, $\gamma_i = 1$, and of pure solvents ($a_i = 1$; e.g., water in aqueous electrolytes).

If two phases (I and II) with a common species i are brought into contact, i is exchanged between the two phases until

$$\mu_i(\text{I}) = \mu_i(\text{II}) \quad (13)$$

Thus, equation (13) is the thermodynamic condition for phase equilibrium in the absence of charge separation at the interface between the two phases.

2.3 Electrochemical Potential

When a metal (Me) electrode (e.g., Cu) is brought into contact with a solution of its Me^{z+} ions (e.g., an aqueous solution of Cu^{2+}), the following reactions will occur until equilibrium is attained:



This reaction leads to a charge separation between the electrolyte phase (s) and the metal phase (M), which occurs spontaneously when equilibrium is being established between the two phases. As can be seen in Figure 3, two different processes are conceivable when pure copper (Cu^0) is brought into contact with a dissolved copper salt (Cu^{2+}): on the left-hand side, partial dissolution of copper, leading to the accumulation of negative charges in the metal at the metal–solution interface which are counterbalanced by positive ionic charges on the solution side of the interface; on the right-hand side, partial plating of copper, leading to the accumulation of positive charges in the metal at the metal–solution interface which are counterbalanced by negative ionic charges on the solution side of the interface. The accumulation of charges on each side of the metal–solution interface can be described in terms

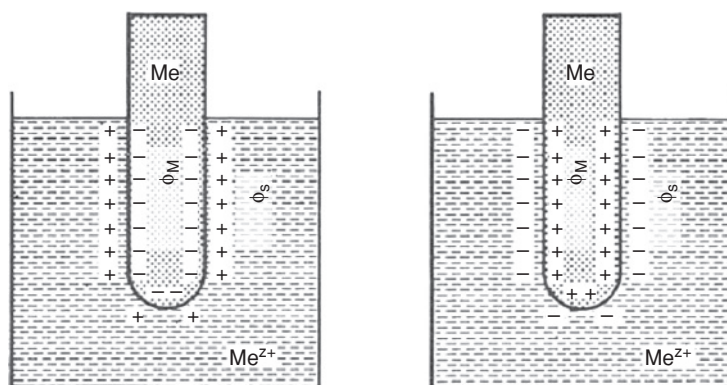


FIGURE 3 Charge separation between the electrode phase (Me phase) and the electrolyte solution phase (Me^{z+} phase) for cases of spontaneous metal dissolution (left-hand side) and of spontaneous metal deposition (right-hand side). In each case, a potential difference between the metal phase potential, ϕ_M , and the solution phase potential, ϕ_s , is being created. (Adapted from [1].)

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of the electrostatic potential in both the metal, ϕ_M , and the electrolyte solution, ϕ_s (see Fig. 3).

In contrast to the simple chemical phase equilibrium described by equation (13), which considers only the chemical equilibrium between species in the two different phases in the absence of charge separation at the interface, description of the electrochemical phase equilibrium for electrochemical reactions where a charge separation across the interface is established requires that the energy of formation of the charge accumulation or depletion at the interface be included in the chemical potential. Therefore, a complete description of the *electrochemical equilibrium* has to consider the electrostatic potential ϕ in each phase, in addition to the chemical potentials of species i in the two phases. With the definition of the electrochemical potential $\tilde{\mu}_i$,

$$\tilde{\mu}_i = \mu_i^0 + RT \ln(a_i) + z_i F \phi \quad (15)$$

the electrochemical phase-equilibrium condition reads

$$\tilde{\mu}_i(\text{I}) = \tilde{\mu}_i(\text{II}) \quad (16)$$

The electrochemical potential difference between the solid and the solution phase is illustrated in Figure 3 for the copper dissolution/plating example: (1) if $\tilde{\mu}_{\text{Cu}}^{2+}(\text{M}) = \tilde{\mu}_{\text{Cu}}(\text{M}) - 2\tilde{\mu}_{e^-}(\text{M}) > \tilde{\mu}_{\text{Cu}^{2+}}(\text{s})$ equilibrium will be established via copper dissolution (left-hand side); and (2) if $\tilde{\mu}_{\text{Cu}}(\text{M}) < \tilde{\mu}_{\text{Cu}^{2+}}(\text{s}) + 2\tilde{\mu}_{e^-}(\text{M})$, equilibrium is reached via copper plating (right-hand side). Establishing equilibrium gives rise to the charge separation illustrated in Figure 3 for both copper plating and copper dissolution, creating an electrical potential difference between the two phases which is referred to as the *Galvani potential difference*: $\Delta\phi = \phi_M - \phi_s$. Consequently, the electrochemical equilibrium condition based on equation (16) and using equation (15) for each phase can be written as

$$\begin{aligned} \mu_{\text{Cu}}(\text{M}) &= \mu_{\text{Cu}^{2+}}(\text{s}) + 2F\phi_s + 2\mu_{e^-}(\text{M}) - 2F\phi_M \\ &= \mu_{\text{Cu}^{2+}}(\text{s}) + 2\mu_{e^-}(\text{M}) - 2F\Delta\phi \end{aligned} \quad (17)$$

Inserting the activity dependence of the chemical potential, μ_i , from equation (15), equation (17) can be expanded to

$$\begin{aligned} \mu_{\text{Cu}}^0(\text{M}) + RT \ln[a_{\text{Cu}}(\text{M})] &= \mu_{\text{Cu}^{2+}}^0(\text{s}) + RT \ln[a_{\text{Cu}^{2+}}(\text{s})] + 2\mu_{e^-}^0(\text{M}) \\ &+ RT \ln[a_{e^-}(\text{M})] - 2F\Delta\phi \end{aligned} \quad (18)$$

In summary, equation (18) represents a detailed description of the electrochemical phase equilibrium between a copper metal electrode and copper ions in solution, including the Galvani potential difference which is produced during the phase equilibration process.

2.4 The Nernst Equation

Equation (18) can be simplified further by considering that the activity of a pure solid phase is 1 [i.e., $a_{\text{Cu}}(\text{M}) \equiv 1$] and that the activity of electrons in the metal phase, $a_{e^-}(\text{M})$, will not be affected by establishing the electrochemical phase equilibrium due to the high and essentially unperturbed electron concentration in the metal,

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so that we can define $a_{e^-}(\text{M}) \equiv 1$. Under these assumptions, equation (18) can be rewritten as

$$\Delta\phi - \frac{\mu_{e^-}^0(\text{M})}{F} = \frac{\mu_{\text{Cu}^{2+}}^0(\text{s}) - \mu_{\text{Cu}}^0(\text{M})}{2F} + \frac{RT}{2F} \ln[a_{\text{Cu}^{2+}}(\text{s})] \quad (19)$$

By defining the electrode potential E and the standard potential E^0 for the case when the activity of Cu^{2+} ions is 1 (i.e., under standard conditions), equation (19) becomes the well-known *Nernst equation* applied to the Cu/Cu^{2+} redox couple:

$$E \equiv \Delta\phi - \frac{\mu_{e^-}^0(\text{M})}{F} = E^0 + \frac{RT}{2F} \ln[a_{\text{Cu}^{2+}}(\text{s})] \quad (20)$$

The specific Nernst equation derived above for the Cu/Cu^{2+} redox couple can also be generalized for a generic half-cell reaction:



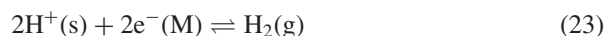
yielding the general Nernst equation:

$$E = E^0 - \frac{RT}{nF} \ln \frac{(a_{\text{C}})^{\nu_{\text{C}}}(a_{\text{D}})^{\nu_{\text{D}}} \cdots}{(a_{\text{A}})^{\nu_{\text{A}}}(a_{\text{B}})^{\nu_{\text{B}}} \cdots} = E^0 + \frac{RT}{nF} \ln \frac{\prod_{\text{oxidized}} (a_i)^{\nu_i}}{\prod_{\text{reduced}} (a_i)^{\nu_i}} \quad (22)$$

whereby the species on the reduced side of the half-cell reaction (i.e., the side where the electrons are written) are placed in the denominator in the logarithmic term and the species on the oxidized side of the half-cell reaction are placed in the numerator. The activity a_i of nonionic species is related to their concentration c_i by the activity coefficient γ_i and the standard concentration c^0 according to $a_i = \gamma_i c_i / c^0$. For ionic species, one often uses the mean ionic activity coefficient, $\gamma_{\pm}$, instead of γ ($\gamma_{\pm}$ is defined for neutral cation–anion pairs, since the activity coefficient of single ions cannot be measured). The activity of a solvent is given in terms of the mole fraction x_i and the activity coefficient, which is usually also denoted by γ_i (i.e., $a_i = \gamma_i x_i$). The activity of pure solvents (e.g., of water) is always equal to 1. Finally, for gaseous species the activity is linked to the partial pressure p_i of the species through the fugacity coefficient f_i and the standard pressure p^0 (100 kPa), $a_i = f_i p_i / p^0$. For ideal gases the fugacity becomes the partial pressure of the gas p_i . E^0 is, as described above, the *standard half-cell potential* of the reaction, that is, the potential at which each of the species involved is present at an activity equal to 1.

It is common to list standard half-cell potentials, E^0 , as to *standard reduction potentials*, that is, for half-cell reactions written as reduction reactions, as done in equation (21). A series of half-cell reactions and their standard reduction potentials are listed in Table 2.

For example, in the case of the hydrogen electrode reaction with the reduction reaction written on the left side of the electrochemical equation,



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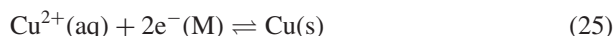
TABLE 2 Examples of the Electrochemical Standard Reduction Potentials of Some Common Half-Cell Reactions

Electrode reaction	E^0 (V)	Electrode reaction	E^0 (V)
$\text{Li}^+ + \text{e} \rightleftharpoons \text{Li}$	-3.01	$\text{Tl}^+ + \text{e} \rightleftharpoons \text{Tl}$	-0.34
$\text{Rb}^+ + \text{e} \rightleftharpoons \text{Rb}$	-2.98	$\text{Co}^{2+} + 2\text{e} \rightleftharpoons \text{Co}$	-0.27
$\text{Cs}^+ + \text{e} \rightleftharpoons \text{Cs}$	-2.92	$\text{Ni}^{2+} + 2\text{e} \rightleftharpoons \text{Ni}$	-0.23
$\text{K}^+ + \text{e} \rightleftharpoons \text{K}$	-2.92	$\text{Sn}^{2+} + 2\text{e} \rightleftharpoons \text{Sn}$	-0.14
$\text{Ba}^{2+} + 2\text{e} \rightleftharpoons \text{Ba}$	-2.92	$\text{Pb}^{2+} + 2\text{e} \rightleftharpoons \text{Pb}$	-0.13
$\text{Ca}^{2+} + 2\text{e} \rightleftharpoons \text{Ca}$	-2.84	$\text{H}^+ + \text{e} \rightleftharpoons 1/2\text{H}_2$	0.000
$\text{Na}^+ + \text{e} \rightleftharpoons \text{Na}$	-2.71	$\text{Cu}^{2+} + 2\text{e} \rightleftharpoons \text{Cu}$	0.34
$\text{Mg}^{2+} + 2\text{e} \rightleftharpoons \text{Mg}$	-2.38	$\frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2\text{e} \rightleftharpoons 2\text{OH}^-$	0.40
$\text{Ti}^{2+} + 2\text{e} \rightleftharpoons \text{Ti}$	-1.75	$\text{Cu}^+ + \text{e} \rightleftharpoons \text{Cu}$	0.52
$\text{Be}^{2+} + 2\text{e} \rightleftharpoons \text{Be}$	-1.70	$\text{Hg}^{2+} + 2\text{e} \rightleftharpoons \text{Hg}$	0.80
$\text{Al}^{3+} + 3\text{e} \rightleftharpoons \text{Al}$	-1.66	$\text{Ag}^+ + \text{e} \rightleftharpoons \text{Ag}$	0.80
$\text{Mn}^{2+} + 2\text{e} \rightleftharpoons \text{Mn}$	-1.05	$\text{Pd}^{2+} + 2\text{e} \rightleftharpoons \text{Pd}$	0.83
$\text{Zn}^{2+} + 2\text{e} \rightleftharpoons \text{Zn}$	-0.76	$\text{Ir}^{3+} + 3\text{e} \rightleftharpoons \text{Ir}$	1.00
$\text{Ga}^{3+} + 3\text{e} \rightleftharpoons \text{Ga}$	-0.52	$\text{Br}_2 + 2\text{e} \rightleftharpoons 2\text{Br}^-$	1.07
$\text{Fe}^{2+} + 2\text{e} \rightleftharpoons \text{Fe}$	-0.44	$\text{O}_2 + 4\text{H}^+ + 4\text{e} \rightleftharpoons 2\text{H}_2\text{O}$	1.23
$\text{Cd}^{2+} + 2\text{e} \rightleftharpoons \text{Cd}$	-0.40	$\text{Cl}_2 + 2\text{e} \rightleftharpoons 2\text{Cl}^-$	1.36
$\text{In}^{3+} + 3\text{e} \rightleftharpoons \text{In}$	-0.34	$\text{F}_2 + 2\text{e} \rightleftharpoons \text{F}^-$	2.87

the Nernst equation would be written

$$E_{\text{H}_2/\text{H}^+} = E_{\text{H}_2/\text{H}^+}^0 + \frac{RT}{2F} \ln \frac{(a_{\text{H}^+})^2}{a_{\text{H}_2}} = E_{\text{H}_2/\text{H}^+}^0 + \frac{RT}{F} \ln \frac{a_{\text{H}^+}}{(a_{\text{H}_2})^{0.5}} \quad (24)$$

where the H_2 fugacity coefficient is often assumed to be 1 (ideal gas behavior, i.e., $a_{\text{H}_2} = p_{\text{H}_2}/p^0$) and where the proton activity is often written in terms of pH [i.e., $\text{pH} \equiv -\log(a_{\text{H}^+})$]. In the example above of the copper electrode, the corresponding half-cell reaction reads



and the Nernst equation can be written

$$E_{\text{Cu}/\text{Cu}^{2+}} = E_{\text{Cu}/\text{Cu}^{2+}}^0 + \frac{RT}{2F} \ln(a_{\text{Cu}^{2+}}) = E_{\text{Cu}/\text{Cu}^{2+}}^0 + \frac{RT}{2F} \ln \left(\frac{\gamma_{\pm} c_{\text{Cu}^{2+}}}{c_{\text{Cu}^{2+}}^0} \right) \quad (26)$$

E cannot be determined experimentally since measurement requires the use of a suitable instrument (e.g., a voltmeter) that necessarily has a second terminal to which a second electrode has to be connected. Commonly, the material of the second electrode will differ from that of the first one. In Figure 4 we assume that the two electrodes are made of metal M and M_1 , respectively, and for simplicity we assume that the electrical connections in our voltmeter are made from M_1 . Then the voltage measured is equal to the potential drop across three interfaces, the two metal solution interfaces M/S and M_1/S with potential drops $\Delta\phi(\text{M})$ and $\Delta\phi(\text{M}_1)$, respectively, and the metal–metal interface M/M'_1 , where the prime indicates that the electrostatic potential of M_1 , ϕ_{M} , at the two terminals is, in general, different.

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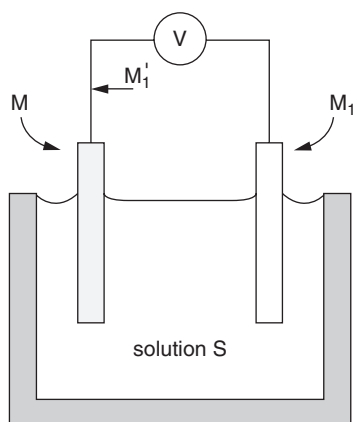


FIGURE 4 Various metal-metal and metal-solution interfaces in an electrochemical cell.

The potential read at the voltmeter is thus given by

$$V = \Delta\phi(M_1) - \Delta\phi(M) + (\phi_M - \phi_{M_1}) \quad (27)$$

At the metal-metal interface, the electrochemical potentials adjust, and hence

$$\tilde{\mu}_{e^-}(M'_1) = \mu_{e^-}(M_1) - F\phi_{M'_1} = \mu_{e^-}(M) - F\phi_M = \tilde{\mu}_{e^-}(M) \quad (28)$$

Combining equations (27) and (28), we obtain

$$V = \left[\Delta\phi(M_1) + \frac{\mu_{e^-}(M_1)}{F} \right] - \left[\Delta\phi(M) + \frac{\mu_{e^-}(M)}{F} \right] \quad (29)$$

Furthermore, when comparing equation (28) with Nernst equation (21), it is obvious that the measured voltage is equal to the difference between the Nernst potentials of the two electrodes:

$$V = E(M_1) - E(M) \quad (30)$$

Since we cannot measure individual electrode potentials, we can compare electrode potentials of two different electrodes only when they have been measured with respect to the same reference electrode (i.e., electrode M_1 in Fig. 4 would be replaced by a reference electrode).

The zero of the electrode potential scale has been chosen arbitrarily as the electrode potential of the standard hydrogen electrode (SHE), with the potential being determined by the H_2/H^+ reaction equation (23) at standard conditions. In practice, this typically involves the use of a Pt electrode immersed in a solution of unit activity of protons in equilibrium with H_2 gas bubbling at a pressure of 100 kPa (see Fig. 5). Electrode potentials given with respect to this zero point are reported “versus SHE.”

In addition to the SHE, other reference electrodes can be used. One of the most common is the saturated calomel electrode (SCE) formed by mercury in contact with an insoluble Hg_2Cl_2 paste and a saturated KCl solution (see Fig. 6). Here the electrode potential is determined by the reaction



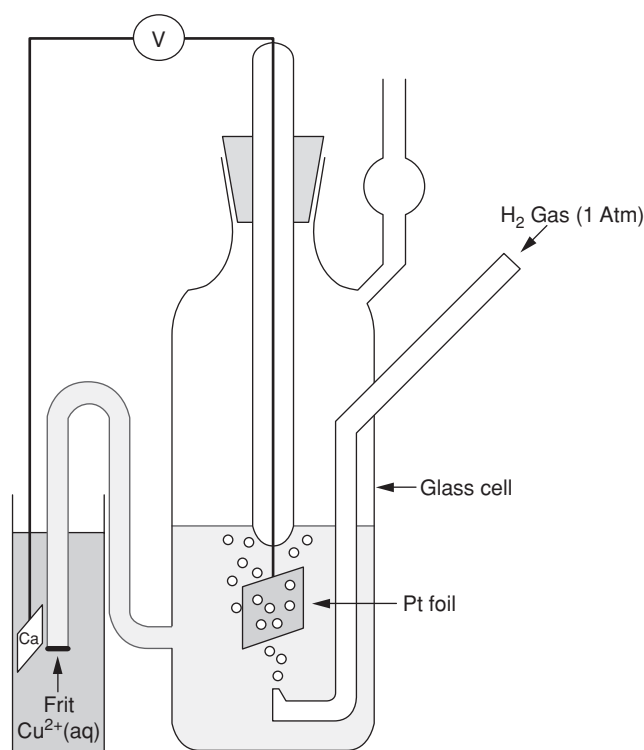


FIGURE 5 Cell for the measurement of an electrode potential (e.g., the Cu/Cu^{2+} electrode) vs. the SHE reference electrode. (From [1].)

The Hg_2^{2+} ions are in equilibrium with insoluble calomel, Hg_2Cl_2 , which, to a small extent, is dissociated in Hg_2^{2+} and Cl^- ions. The electrode potential can, therefore, be expressed through the Cl^- concentration:

$$E = E_{\text{Hg}/\text{Hg}_2\text{Cl}_2}^0 - \frac{RT}{F} \ln(a_{\text{Cl}^-}) = 0.241 \text{ V vs. SHE} \quad (32)$$

It is always possible to reconvert the electrode potential from the scale based on the chosen reference electrode (e.g., SCE) to that of the SHE:

$$E_{\text{SHE}} = E_{\text{SCE}} + 0.241 \text{ V} \quad (33)$$

2.5 Electrochemical Double Layer

The interfacial region in which the excess charges on the electrode and in the solution accumulate (see, e.g., Fig. 3) is called the *electrochemical double layer* (DL). On the metal electrode, the excess charge resides in a thin layer ($<0.1\text{\AA}$) at the electrode surface. The charge is counterbalanced by the accumulation of ion in the electrolyte close to the electrode (i.e., cations in the case of negative excess charge on the electrode, anions in the case of positive excess charge on the

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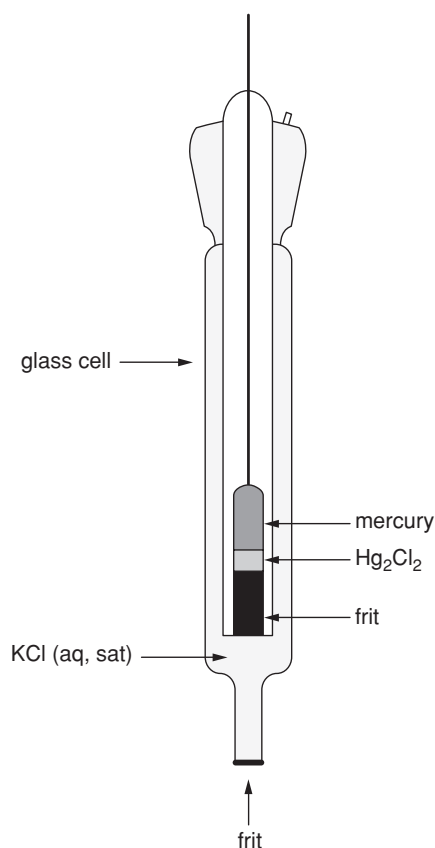
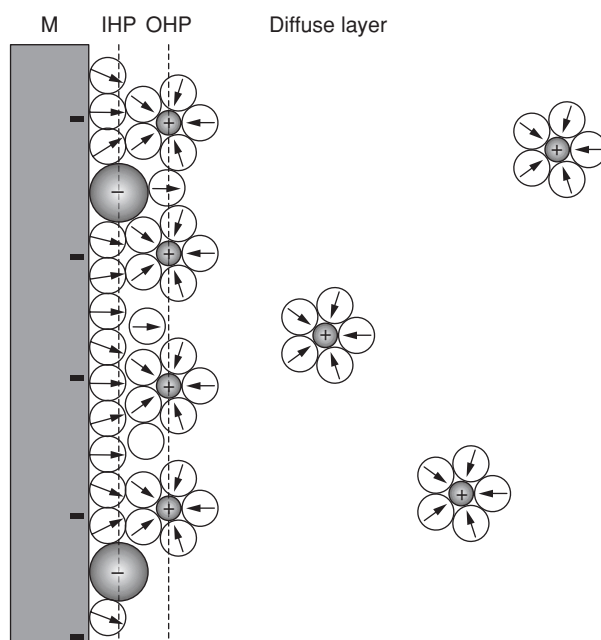


FIGURE 6 Standard calomel electrode.
(From [1].)

electrode). The driving forces for the formation of this *space charge layer* in the electrolyte are primarily coulombic forces but are also chemical interactions with the electrode surface and entropic forces which determine the distribution of ions in the DL.

Figure 7 is a model of the double layer. It can be seen that the ions in the electrolyte arrange themselves in a layered structure. The layer closest to the electrode surface is formed by ions that interact strongly with the electrode surface. These are mainly anions (e.g., halide anions) that tend to lose part of their solvation shell to adsorb directly at the electrode surface, even if the surface carries the same charge. The center of charge of these chemisorbed ions coincides approximately with the radius of the adsorbing species. The plane through the center of these specifically adsorbed ions is called the *inner Helmholtz plane* (IHP). Ions that are attracted to the electrode electrostatically (i.e., those with only minor chemical interactions with the electrode surface) keep their hydration shell. Thus, they approach the electrode at most up to a distance that corresponds to the radius of the hydrated ions. The center of charge of these hydrated ions (cations in the example in Fig. 7) is called the *outer Helmholtz plane* (OHP).

**FIGURE 7**

Electrochemical double layer. M, metal electrode (e.g., Cu); IHP, inner Helmholtz plane; OHP, outer Helmholtz plane. The solvation (hydration) shell on the cations and the dipole alignment of the solvent molecules (water) are also shown. (After [4].)

Counteracting the electrostatic force is an entropic force that entails a continuous decay of the concentration of the excess ions from the OHP into the bulk, with increasing distance to the electrode until the bulk concentration is reached. The extension of this *diffuse layer* depends on the ion concentrations of the electrolyte solution, being negligible for concentrated solutions (~ 1 M) but reaching several tens of nanometers for dilute electrolytes ($\leq 10^{-3}$ M).

The electrochemical double layer behaves like a capacitor (hence the name), whereby in concentrated solutions the metal surface and the OHP take the role of capacitor plates, with the gap between them filled by water molecules that because they possess a permanent dipole moment behave as a high-dielectric-constant medium. Due to the microscopic distance between the plates (i.e., a few tens of angstroms), the DL capacitance is much higher than that of common electronic devices, typically on the order of 10 to 40 $\mu\text{F}/\text{cm}^2$. As in a capacitor, the DL can be charged or discharged by changing the electrode–electrolyte potential difference, keeping the charge on the electrode surface always equal to that of the space charge layer in the electrolyte solution.

3 OHMIC LOSSES AND ELECTRODE KINETICS

Whereas in Section 2 we considered the thermodynamic description of electrolytic and galvanic electrochemical cells as well as of half-cell reactions, in this section we detail the various potential losses that are caused by the ion transport resistance in the electrolyte and the kinetics of the electrode reactions. Potential losses caused by

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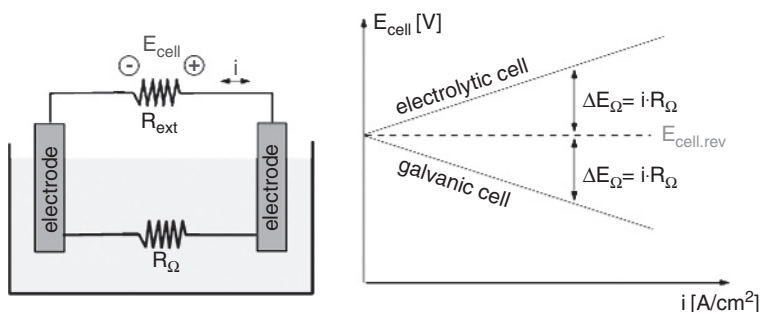


FIGURE 8 Left-hand side: simplified equivalent circuit of a galvanic or electrolytic cell in the absence of kinetic and diffusion resistances, representing the ohmic ion conduction resistance of the electrolyte by a simple resistor, R_{Ω} ; right-hand side: i vs. E curve of an idealized electrolytic and galvanic cell.

concentration gradients in the electrolyte (diffusion overpotentials) which can arise at high current densities are not discussed here.

3.1 Ohmic Potential Losses

When a current is drawn from an electrochemical cell through an external load, represented by an ohmic resistor, R_{ext} , the externally flowing electronic current must be balanced by an ionic current through the electrolyte between the two electrodes. In the simplified case in which kinetic and diffusion resistances are negligible, the behavior of the electrochemical cell can be approximated by an equivalent electronic circuit as shown in Figure 8, where R_{Ω} represents the ionic electrolytic resistance and is most commonly expressed as areal resistance in units of $\Omega \cdot \text{cm}^2$. For an electrolytic cell, where external voltage has to be applied to drive the reaction (see Fig. 1), the external cell voltage that must be applied to the cell, $E_{\text{cell,electrolytic}}$, is the sum of the reversible cell voltage $E_{\text{cell,rev}}$ and the ohmic potential loss ΔE_{Ω} across the electrolyte between the electrodes:

$$E_{\text{cell,electrolytic}} = E_{\text{cell,rev}} + iR_{\Omega} = E_{\text{cell,rev}} + \Delta E_{\Omega} \quad (34)$$

where i is the current density (in units of A/cm^2 ; i.e., the total current divided by the cross-sectional area of the electrodes). For a galvanic cell (see Fig. 2), the cell voltage obtained, $E_{\text{cell,galvanic}}$, is reduced by the internal ionic resistance:

$$E_{\text{cell,galvanic}} = E_{\text{cell,rev}} - iR_{\Omega} = E_{\text{cell,rev}} - \Delta E_{\Omega} \quad (35)$$

The resulting current density/potential relationship (i vs. E curve) is illustrated in Figure 8.

Using the approximation above, we can estimate the ohmic potential loss in a lithium-ion battery at high charge–discharge rates. The latter are commonly not given in terms of current density but as a *C rate*, which describes how many times the battery capacity is being charged or discharged per hour. For high-power batteries (e.g., in hybrid electric vehicles), *C rates* can be as high as 20 h^{-1} (i.e., the battery is

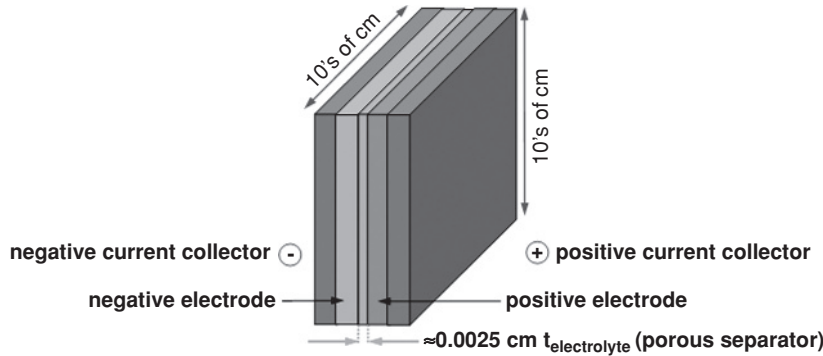


FIGURE 9 Configuration of a typical lithium battery, showing the negative and positive electrodes sandwiched between negative and positive current collectors, separated by a separator, a microporous material (usually, polypropylene and/or polyethylene) into which liquid electrolyte (solvent and salt) is imbibed.

fully charged or discharged in 1/20 of an hour). Considering a typical areal capacity of $\approx 1 \text{ mAh/cm}^2$ for high-power lithium-ion batteries, the corresponding current density would be $\approx 20 \text{ mA/cm}^2$. As illustrated in Figure 9., the electrode area of lithium-ion batteries (x/y -dimension) is very large (tens of centimeters) compared to the thickness of the electrolyte layer between the electrodes, $t_{\text{electrolyte}}$ (z -dimension; tens of micrometers), so that the ohmic resistance R_{Ω} between the two electrodes is well described by a simple one-dimensional relationship:

$$R_{\Omega} = \frac{t_{\text{electrolyte}}}{\kappa \epsilon / \tau} \approx \frac{t_{\text{electrolyte}}}{\kappa \epsilon^{1.5}} \quad (36)$$

where κ is the electrolyte conductivity, ϵ is the electrolyte volume fraction in the typically used electrolyte-imbibed porous *separator* materials used to separate the two electrodes, and τ is the tortuosity of the ionic conduction path within the separator. The latter is often approximated by the *Bruggeman relationship* ($\epsilon/\tau \approx \epsilon^{1.5}$), as shown in equation (36). For a typical electrolyte conductivity of 10 mS/cm (see Table 1), a separator thickness of 25 μm , and a electrolyte volume fraction of 0.5, equation (36) yields $R_{\Omega} \approx 0.7 \Omega \cdot \text{cm}^2$. This would result in an ohmic potential loss at 20 mA/cm² of $\Delta E_{\Omega} \approx 14 \text{ mV}$, which is rather modest compared to the average cell voltage of $\approx 4 \text{ V}$ for most lithium-ion batteries.

3.2 Kinetic Overpotential

Additional potential losses are usually caused by the fact that the electrode reactions are not infinitely fast, so that an additional driving force is required to sustain a given reaction rate. This required driving force is an additional potential loss. Let us consider first the equilibrium condition of a generic electrochemical reaction:



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The half-cell reaction above represents a dynamic state in which there is a continuous and reversible exchange between the oxidized and the reduced species, referred to as *dynamic equilibrium*. For example, for the equilibrium between copper metal and its copper ions in solution shown in equation (14), equilibrium is reached when the anodic copper dissolution ($\text{Cu} \rightarrow \text{Cu}^{+2} + 2\text{e}^-$) occurs as fast as the cathodic copper deposition ($\text{Cu}^{+2} + 2\text{e}^- \rightarrow \text{Cu}$). In this example, electrochemical equilibrium implies a flow of electrons out of the copper electrode for the copper dissolution reaction (anodic current) which is simultaneously counterbalanced by an equal flow of electrons into the copper electrode from the copper deposition reaction (cathodic current). Thus, in equilibrium, the anodic current, i_{anodic} , and the cathodic current, i_{cathodic} , are equal in magnitude and correspond to the *exchange current density*, i_0 :

$$i_0 = i_{\text{anodic}} = |i_{\text{cathodic}}| \quad (38)$$

Most commonly, anodic currents are defined as positive currents and cathodic currents are defined as negative currents (note, however, that in the older literature the opposite sign convention is often used). Since anodic (positive) and cathodic (negative) currents are equal in magnitude and opposite in sign, no externally observable net current is flowing in equilibrium. A net external current is obtained when deviating from equilibrium in either the anodic (positive current) or cathodic (negative current) direction, whereby the equilibrium in equation (37) is shifted to the right if $|i_{\text{cathodic}}| > i_{\text{anodic}}$ or to the left if $i_{\text{anodic}} > |i_{\text{cathodic}}|$.

A net current flow across an electrode is accompanied by deviations of the electrode potential from its equilibrium half-cell potential value, E_{rev} , described by a *kinetic overpotential*, η . To sustain a net anodic current, a positive deviation from the equilibrium potential is required, i.e., an *anodic overpotential*, η_{anodic} . On the other hand, to sustain a net cathodic current, a negative deviation from the equilibrium potential is required, i.e., a *cathodic overpotential*, η_{cathodic} . In summary, the electrode potential for an anodic net current can be described as $E_{\text{electrode}} = E_{\text{rev}} + \eta_{\text{anodic}}$ and as $E_{\text{electrode}} = E_{\text{rev}} - |\eta_{\text{cathodic}}|$ in the case of a net cathodic current. The implications of overpotentials for an electrochemical cell consisting of two electrodes can now be determined for an electrolytic cell and for a galvanic cell. For an electrolytic cell (see Fig. 1) with a net current flow, a cathodic reaction occurs on the negative electrode, and its potential is thus decreased by $|\eta_{\text{cathodic}}|$, while an anodic reaction occurs on the positive electrode, the potential of which increases by η_{anodic} . Therefore, when drawing a net current from an electrolytic cell, its potential, $E_{\text{cell,electrolytic}}$, can be described as

$$E_{\text{cell,electrolytic}} = E_{\text{cell,rev}} + \eta_{\text{anodic}} + |\eta_{\text{cathodic}}| + iR_{\Omega} \quad (39)$$

On the other hand, for a current flow in a galvanic cell (see Fig. 2), an anodic reaction occurs on the negative electrode, and its potential is thus increased by η_{anodic} , while a cathodic reaction occurs on the positive electrode, so that its potential decreases by $|\eta_{\text{cathodic}}|$. Therefore, the overall cell voltage, $E_{\text{cell,galvanic}}$, of a galvanic cell is

$$E_{\text{cell,galvanic}} = E_{\text{cell,rev}} - \eta_{\text{anodic}} - |\eta_{\text{cathodic}}| - iR_{\Omega} \quad (40)$$

The functionality between the anodic or cathodic overpotential and the current density is discussed below.

3.3 The Butler–Volmer Equation

The relation between current and kinetic overpotential for a generic reaction involving n electrons is provided by the well-known Butler–Volmer equation:

$$\begin{aligned} i &= i_0 \left(e^{\frac{\alpha n F}{RT} \cdot \eta} - e^{-\frac{(1-\alpha)n F}{RT} \cdot \eta} \right) \\ &= i_0 \left(10^{\frac{\alpha n F}{2.303 \cdot RT} \cdot \eta} - 10^{-\frac{(1-\alpha)n F}{2.303 \cdot RT} \cdot \eta} \right) \end{aligned} \quad (41)$$

where α is the *transfer coefficient*, determining what fraction of electric energy resulting from the displacement of the potential from equilibrium affects the rate of the electrochemical reaction. Often, the Butler–Volmer equation is written as a function of the base 10 [as on the right-hand side of equation (41)], in which case the terms $2.303 RT/(\alpha n F)$ and $2.303 RT/[(1 - \alpha)n F]$ in the exponents are referred to as anodic and cathodic *Tafel slopes*, respectively. The latter describe the overpotential (in mV) that is required to increase the anodic or cathodic current by a factor of 10. If $\alpha = 0.5$, the Butler–Volmer curve is inversion symmetric, and for $n = 1$, the Tafel slopes at room temperature have a value of 120 mV/decade. An example plot of the Butler–Volmer equation, including the anodic and cathodic partial currents, is shown in Figure 10.

As one can see from the figure, for small overpotentials, the i vs. η curve is approximately linear. Using a Taylor series expansion, it can be shown that the Butler–Volmer equation simplifies to a linear equation for overpotentials smaller than one-third of the value of the Tafel slope:

$$i = \frac{i_0 F}{RT} \eta \quad (42)$$

This equation resembles Ohm's law, from which one can define a *charge transfer resistance*, R_{ct} :

$$R_{ct} \equiv \frac{\eta}{i} = \frac{RT}{i_0 F} \quad (43)$$

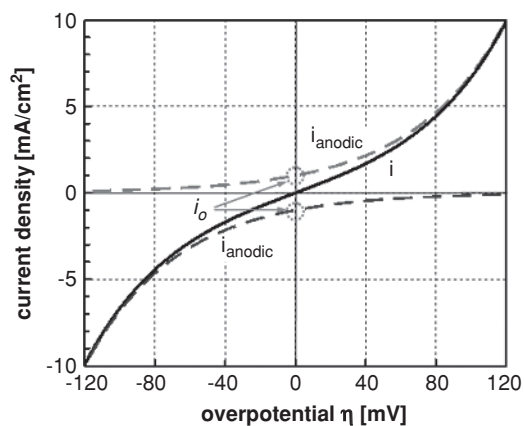


FIGURE 10 Solid curve: Butler–Volmer equation for $\alpha = 0.5$ and $n = 1$ ($\equiv 120$ mV/decade Tafel slope) and for an exchange current density of $i_0 = 1$ mA/cm². Dashed curves: anodic (top) and cathodic (bottom) partial current densities.

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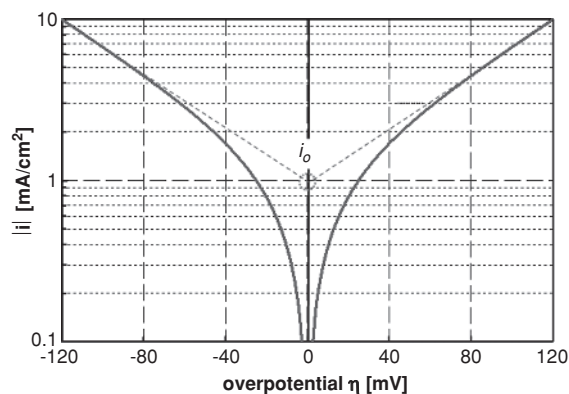


FIGURE 11 Tafel plot for the the same parameters as those used in Figure 10. The dashed lines show the linear fits at high overpotentials, with a y-axis intercept at i_0 .

This simplified relationship is frequently used in electrochemical modeling for fast electrode processes in batteries (e.g., lithium anode) and fuel cells (e.g., hydrogen anode).

For anodic (cathodic) overpotentials larger than roughly half of the value of the Tafel slope, the anodic (cathodic) current dominates the net current, i . In this case, the Butler–Volmer equation can be approximated by the *Tafel equation* for either the anodic branch at high positive overpotentials,

$$\log(i) = \log(i_0) + \frac{\alpha n F}{2.303 RT} \eta \quad (44)$$

or the cathodic branch at high negative overpotentials,

$$\log(|i|) = \log(i_0) + \frac{(1 - \alpha) n F}{2.303 RT} |\eta| \quad (45)$$

Thus, under these conditions, a plot of $\log i$ vs. η , known as the *Tafel plot*, yields a straight line (see Fig. 11). A Tafel plot is a very useful diagnostic tool to determine important kinetic parameters such as the value of α from the slope [see equation (44) and (45)] and of i_0 by interpolation of the linear segments of the Tafel plot to the equilibrium potential ($\eta = 0$; see Fig. 11). The Tafel equations above are frequently used to model slow electrochemical reactions in batteries and fuel cells (e.g., the oxygen reduction reaction).

4 CONCLUDING REMARKS

We have tried to introduce the most essential electrochemical concepts that are needed to understand the physicochemical processes controlling the performance of batteries. This includes (1) fundamental thermodynamic relationships such as reversible cell voltage and the half-cell potential and its dependence on the operating parameters (temperature, etc.); (2) the basic properties of electrolytes and the electrode–electrolyte interface; and (3) the fundamental kinetic model and its approximations. Although very restricted in scope, we hope that our brief introduction will provide

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the general reader with the background necessary to more easily comprehend the chapters that follow. For those who would like to get a deeper insight into the various aspects of electrochemistry, we refer to the monographs listed below.

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