ELECTROCHEMICAL PROCESSING

1. Introduction

Electrochemical systems convert chemical and electrical energy through charge-transfer reactions. These reactions occur at the interface between two phases. Consequently, an electrochemical cell contains multiple phases, and surface phenomena are important. Electrochemical processes are sometimes divided into two categories: electrolytic, where energy is supplied to the system, eg, the electrolysis of water and the production of aluminum; and galvanic, where electrical energy is obtained from the system, eg, batteries (qv) and fuel cells (qv).

The industrial economy depends heavily on electrochemical processes. Electrochemical systems have inherent advantages such as ambient temperature operation, easily controlled reaction rates, and minimal environmental impact (qv). Electrosynthesis is used in a number of commercial processes. Batteries and fuel cells, used for the interconversion and storage of energy, are not limited by the Carnot efficiency of thermal devices. Corrosion, another electrochemical process, is estimated to cost hundreds of millions of dollars annually in the United States alone (see CORROSION AND CORROSION CONTROL). Electrochemical systems can be described using the fundamental principles of thermodynamics, kinetics, and transport phenomena.

2. Thermodynamics of Electrochemical Cells

Consider the cell

$$\begin{array}{c|c|c c c c c|c|c} \alpha & \beta & \gamma & \wr & & \wr & \varepsilon & \beta' & \alpha' \\ \mathrm{Pt(s)} & \mathrm{Fe(s)} & \mathrm{NaOH} & \wr & \text{membrane} & \wr & \mathrm{NaCl} & \mathrm{TiO_2(s)} & \mathrm{Pt(s)} \\ & \mathrm{H_2} & \text{in } \mathrm{H_2O} & \wr & & \wr & \text{in } \mathrm{H_2O} & \mathrm{Cl_2} & \end{array}$$

for which the electrode reactions are

$$2\,\mathrm{Cl}^- \longrightarrow \mathrm{Cl}_2 + 2\,e^- \tag{1}$$

and

$$2\,\mathrm{H_2O} + 2\,e^- \longrightarrow \mathrm{H_2} + 2\,\mathrm{OH}^- \tag{2}$$

The electrode where oxidation occurs is the anode; the electrode where reduction occurs is called the cathode. Electrons released at the anode travel through an external circuit and react at the cathode. The vertical lines denote phase separation; the squiggly lines separate a junction region. Although adjacent phases are in equilibrium, not all species are present in every phase. The membrane provides an ionic path for sodium ions that are transported from the anode to the cathode, but also separates the chlorine and hydrogen gases. Within the junction region, ie, the membrane, transport processes occur (see also Alkali and chlorine products; Membrane technology).

Determining the cell potential requires knowledge of the thermodynamic and transport properties of the system. The analysis of the thermodynamics of electrochemical systems is analogous to that of neutral systems. For ionic species, however, the electrochemical potential replaces the chemical potential (1).

$$\mu_i = RT\ln\lambda_i = RT\ln\left(c_i f_i a_i^{\theta}\right) \tag{3}$$

The electrochemical potential, μ_i, of a species is a function of the electrical state as well as temperature, pressure, and composition; λ_i is the absolute activity, which can be broken down into three parts as shown. For an electrolyte, A, which dissociates into ν_+ cations and ν_- anions, the chemical potential of the electrolyte can be expressed by

$$\mu_A = \nu_+\mu_+ + \nu_-\mu_- = \nu RT\ln\left(cf_\pm a_+^{\theta}\right) \tag{4}$$

where the subscript $\pm$ indicates a mean coefficient. For instance,

$$f_\pm^{\nu} = f_+^{\nu+} f_-^{\nu-} \tag{5}$$

At open-circuit, the current in the cell is zero, and species in adjoining phases are in equilibrium. For example, the electrochemical potential of electrons in phases α and β are identical. Furthermore, the two electrochemical reactions are equilibrated. Thus,

$$2\,\mu^{\epsilon}_{\mathrm{Cl}^-} = \mu^{\beta\prime}_{\mathrm{Cl}_2} + 2\,\mu^{\alpha'}_{e^-} \tag{6}$$

and

$$2\,\mu^{\delta}_{\mathrm{H_2O}} + 2\,\mu^{\alpha}_{e^-} = \mu^{\beta}_{\mathrm{H_2}} + 2\,\mu^{\delta}_{\mathrm{OH}^-} \tag{7}$$

The cell potential U is

$$FU = -F(\Phi^{\alpha} - \Phi^{\alpha'}) = \mu^{\alpha}_{e^-} - \mu^{\alpha'}_{e^-} \tag{8}$$

By convention, U denotes the potential of the right electrode relative to the left. Substituting equations 6 and 7 gives

$$FU = \frac{1}{2}\,\mu^{\beta}_{\mathrm{H_2}} - \mu^{\gamma}_{\mathrm{H_2O}} + \frac{1}{2}\,\mu^{\beta\prime}_{\mathrm{Cl_2}} + \left(\mu^{\delta}_{\mathrm{OH^-}} - \mu^{\epsilon}_{\mathrm{Cl^-}}\right) \tag{9}$$

Because only differences in chemical potential can be measured, the chemical or electrochemical potential of each species is broken down as in equation 3. An arbitrary secondary reference state is defined for each compound. For instance, the chemical potential of chlorine gas is expressed as

$$\mu_{\mathrm{Cl_2}} = \mu^{*}_{\mathrm{Cl_2}} + RT\ln p_{\mathrm{Cl_2}} \tag{10}$$

The superscript * refers to the ideal-gas secondary reference state, and p is the fugacity. Equation 4 is used for the ionic species. Hence,

$$FU = FU^{\theta} + RT\ln\left[\frac{p^{1/2}_{\mathrm{H_2}}\,p^{1/2}_{\mathrm{Cl_2}}\,c^{\delta}_{\mathrm{OH^-}}}{a^{\delta}_{\mathrm{H_2O}}\,c^{\epsilon}_{\mathrm{Cl^-}}}\right] + 2RT\ln\left[\frac{f^{\delta}_{\mathrm{NaOH}}}{f^{\epsilon}_{\mathrm{NaCl}}}\right] + \left(\Phi^{\epsilon} - \Phi^{\delta}\right) \tag{11}$$

where the electric potential Φ of the solution has been defined by

$$\mu_{\mathrm{Na^+}} = RT\ln c_{\mathrm{Na^+}} + F\Phi \tag{12}$$

The standard cell potential U^{θ} is given by

$$FU^{\theta} = \frac{1}{2}\,\mu^{*}_{\mathrm{H_2}} - \mu^{0}_{\mathrm{H_2O}} + \frac{1}{2}\,\mu^{*}_{\mathrm{Cl_2}} + \left(\mu^{\theta}_{\mathrm{OH^-}} - \mu^{\theta}_{\mathrm{Cl^-}}\right) \tag{13}$$

In equation 11 the superscripts denoting the phases have been omitted where the meaning is clear, that is, for the fugacity of hydrogen and chlorine. U^{θ} is the composition independent part of the cell potential. The value of U^{θ}, 2.1875 V, can be obtained by looking up the values of the secondary reference-state quantities in a table of chemical thermodynamic properties (qv). It is convenient to consider the reaction as the sum of two half-cell reactions. The standard cell potentials are tabulated (2), typically at 25°C, as half-cell reactions referenced to the hydrogen electrode, the potential of which is arbitrarily set to zero. This yields 1.3595 V for the chlorine electrode and −0.828 V for the hydrogen electrode in basic media; the difference being 2.1875 V. The second term on the right side of equation 11 accounts for the principal variation of the cell potential with composition of the reactants.

The third term on the right side of equation 11 is the corresponding ratio of the mean molar activity coefficients. The fourth and last term results from transport processes in the junction region, and cannot be determined from thermodynamics. This term is often small and is not treated here. Neglecting this junction region and activity corrections leads to

$$U \approx U^{\theta} + \frac{RT}{2F}\ln\frac{p_{\mathrm{H_2}}\,p_{\mathrm{Cl_2}}\,c^{2}_{\mathrm{OH^-}}}{a^{2}_{\mathrm{H_2O}}\,c^{2}_{\mathrm{Cl^-}}} \tag{14}$$

Equation 14 is a form of the Nernst equation. The overall chemical reaction for the passage of 2 Faradays of charge in the external circuit from right to left is

$$\mathrm{Cl_2 + H_2 + 2\,OH^- \longrightarrow 2\,Cl^- + 2\,H_2O} \tag{15}$$

Each reactant and product appears in the Nernst equation raised to its stoichiometric power. Thermodynamic data for cell potentials have been compiled and graphed (3) as a function of pH. Such graphs are known as Pourbaix diagrams, and are valuable for the study of corrosion, electrodeposition, and other phenomena in aqueous solutions. From the above thermodynamic analysis, the cell potential can be related to the Gibbs energy change

$$\Delta G = -nFU \tag{16}$$

Thus, because the standard cell potential for reaction 15 is positive, the reaction proceeds spontaneously as written. Consequently, to produce chlorine and hydrogen gas, a potential must be applied to the cell that is greater than the open-circuit value. This then becomes an example of an electrolytic process.

Predicting the cell potential requires knowledge of thermodynamic properties and transport processes in the cell. Conversely, the measurement of cell potentials can be used to determine both thermodynamic and transport properties (4).

3. Kinetics and Interfacial Phenomena

The rate of an electrochemical process can be limited by kinetics and mass transfer. Before considering electrode kinetics, however, an examination of the nature of the interface between the electrode and the electrolyte, where electron-transfer reactions occur, is in order.

Because some substances may preferentially adsorb onto the surface of the electrode, the composition near the interface differs from that in the bulk solution. If the cell current is zero, there is no potential drop from ohmic resistance in the electrolyte or the electrodes. Yet from the thermodynamic analysis it is seen that there is a measurable cell potential. The question from where this potential arises can be answered by considering the interface.

At the interface between phases, there is a region called the electrical double layer where potential variation occurs. Figure 1 shows this region. Although the electrode and electrolyte are overall electrically neutral, the metal electrode may have a net charge near the surface. The solution layer closest to the electrode contains specifically adsorbed ions and is called the inner Helmholtz plane (IHP). Ions that are hydrated, generally the cations, can approach the metal surface only to a finite distance, and comprise the outer Helmholtz plane (OHP). The nonspecifically adsorbed ions are distributed by thermal agitation; this region is called the diffuse double layer and lies just outside the OHP.

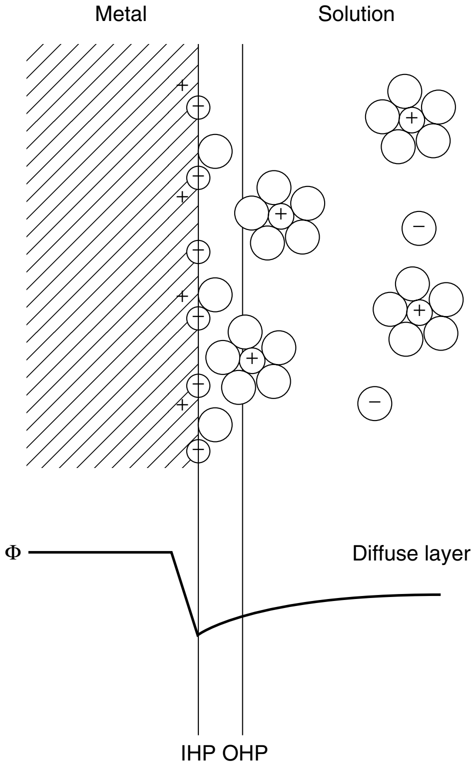


Fig. 1. The structure of the electrical double layer where ○ represents the solvent; ⊖, specifically adsorbed anions; ⊖, anions; and ⊕, cations. The inner Helmholtz plane (IHP) is the center of specifically adsorbed ions. The outer Helmholtz plane (OHP) is the closest point of approach for solvated cations or molecules. Φ, the corresponding electric potential across the double layer, is also shown.

In most electrochemical systems, the double layer is very thin (1–10 nm). The thickness is characterized by the debye length, λ,

$$\lambda = \left(\frac{\epsilon RT}{2z^2F^2c_\infty} \right)^{1/2} \tag{17}$$

In addition, the potential of the electrode can be varied, resulting in a change in the structure of the interface. If no current is passed when the potential of the electrode changes, the electrode is called an ideally polarizable electrode, and can be described using thermodynamics.

Even in the absence of Faradaic current, ie, in the case of an ideally polarizable electrode, changing the potential of the electrode causes a transient current to flow, charging the double layer. The metal may have an excess charge near its surface to balance the charge of the specifically adsorbed ions. These two planes of charge separated by a small distance are analogous to a capacitor. Thus the electrode is analogous to a double-layer capacitance in parallel with a kinetic resistance.

In electrode kinetics a relationship is sought between the current density and the composition of the electrolyte, surface overpotential, and the electrode material. This microscopic description of the double layer indicates how structure and chemistry affect the rate of charge-transfer reactions. Generally in electrode kinetics the double layer is regarded as part of the interface, and a macroscopic relationship is sought. For the general reaction

$$O + ne^- \rightleftarrows R \tag{18}$$

the cathodic and anodic reaction rates can be written as

$$r_a = k_a c_R \exp\left[(1-\beta)\frac{nF}{RT}V\right] \tag{19}$$

and

$$r_c = k_c c_O \exp\left[-\beta\frac{nF}{RT}V\right] \tag{20}$$

β is a symmetry factor equal to the fraction of the potential that promotes the cathodic reaction. The reaction rate and current are related through Faraday's law

$$\frac{i}{nF} = r_a - r_c \tag{21}$$

These two reactions may be generalized to the Butler-Volmer equation:

$$i = i_o\left\{\exp\left(\frac{\alpha_a F\eta_s}{RT}\right) - \exp\left(-\frac{\alpha_c F\eta_s}{RT}\right)\right\} \tag{22}$$

The exchange current density, i_o, depends on temperature, the composition of the electrolyte adjacent to the electrode, and the electrode material. The exchange current density is a measure of the kinetic resistance. High values of i_o correspond to fast or reversible kinetics. The three parameters, α_a, α_c, i_o, are determined experimentally. The surface overpotential, η_s, is the difference in potential of the metal and the potential of an electrode of the same kind in the electrolyte measured adjacent to the electrode, ie, just outside the double layer, but passing no current. The surface overpotential appears in the exponential terms for both the anodic and cathodic reactions, and can be considered the driving force for the electrochemical reaction. The relationship between the surface overpotential and the current is shown in Figure 2.

Two simplifications of the Butler-Volmer expression are often encountered. First, at low surface overpotentials equation 22 can be written as

$$i = (\alpha_a + \alpha_c)i_o\frac{F}{RT}\eta_s \tag{23}$$

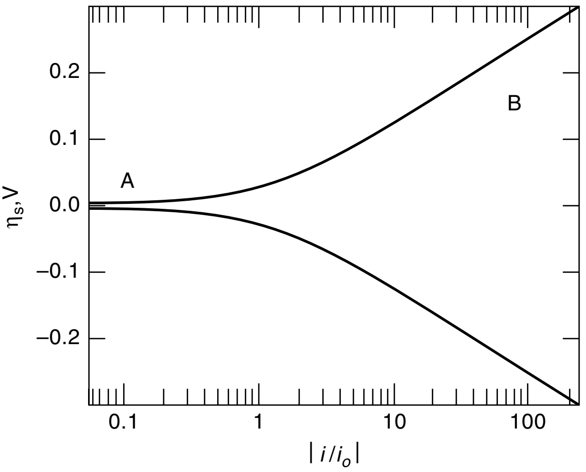


Fig. 2. Tafel plot, where α_a and α_c are both chosen to be 0.5; the temperature is 298.15 K. A indicates the linear region (eq. 23) and B the Tafel (eq. 24).

This limit is called linear kinetics. On the other hand, if the surface overpotential is large, one of the exponential terms is negligible. This limit is called Tafel kinetics. The relationship was found empirically. In the anodic Tafel region

$$\eta_s = \frac{RT}{F\alpha_a}\left(\ln i - \ln i_o\right) \tag{24}$$

The Butler-Volmer equation can be applied to many, but not all, systems. Moreover, many of the systems that do not follow the Butler-Volmer model are of great practical importance, eg, in the corrosion of passivating metals (see CORROSION AND CORROSION CONTROL).

Because of the unique nature of electron-transfer reactions, these have been of great theoretical interest. More recently, research has centered on a microscopic picture of the electron-transfer reactions and predicting reaction rate constants (5,6).

4. Transport Processes

In addition to electrode kinetics, the rate of an electrochemical reaction can be limited by the rate of mass transfer of reactants to and from the electrode surface. In dilute solutions, four principal equations are used. The flux of species i is

$$N_i = -z_i u_i F c_i \triangle\Phi - D_i \triangle c_i + c_i v \tag{25}$$

These three terms represent contributions to the flux from migration, diffusion, and convection, respectively. The bulk fluid velocity is determined from the equations of motion. Equation 25, with the convection term neglected, is frequently referred to as the Nernst-Planck equation. In systems containing charged species, ions experience a force from the electric field. This effect is called migration. The charge number of the ion is z_i, F is Faraday's constant, u_i is the ionic mobility, and Φ is the electric potential. The ionic mobility and the diffusion coefficient are related:

$$D_i = RTu_i \tag{26}$$

This relation, discovered by Nernst and Einstein, applies in the limit of infinite dilution.

A material balance on an element of the fluid gives

$$\frac{\partial c_i}{\partial t} = -\triangle \cdot N_i + R_i \tag{27}$$

where R_i is the homogeneous reaction rate. Except near the diffuse double layer, to a good approximation the solution is electrically neutral

$$\sum_i z_i c_i = 0 \tag{28}$$

The current density is given by

$$i = F \sum_i z_i N_i \tag{29}$$

These four equations, using the appropriate boundary conditions, can be solved to give current and potential distributions, and concentration profiles. Electrode kinetics would enter as part of the boundary conditions. The solution of these equations is not easy and often involves detailed numerical work.

Electroneutrality (eq. 28) is not strictly correct. More properly, equation 28 should be replaced with Poisson's equation

$$\triangle^2 \Phi = -\frac{F}{\epsilon} \sum_i z_i c_i \tag{30}$$

Although the assumption of electroneutrality is appropriate for many systems, electroneutrality does not imply that Laplace's equation holds for the potential. Further details are given in the literature (7).

When concentration gradients in the solution can be ignored, equations 25 through 29 show that the electric potential is governed by Laplace's equation

$$\triangle^2 \Phi = 0 \tag{31}$$

Laplace's equation is applicable to many electrochemical systems, and solutions are widely available (8). The current distribution is obtained from Ohm's law

$$i = -\kappa \triangle \Phi \tag{32}$$

where κ is the conductivity of the solution. For dilute solutions the conductivity is given by

$$\kappa = F^2 \sum_i z_i^2 u_i c_i \tag{33}$$

Both the anions and cations can contribute to the current. In the absence of concentration gradients, the transference number relates the fraction of current carried by each species

$$t_j = \frac{z_j^2 u_j c_j}{\sum_i z_i^2 u_i c_i} \tag{34}$$

The distribution of current (local rate of reaction) on an electrode surface is important in many applications. When surface overpotentials can also be neglected, the resulting current distribution is called primary. Primary current distributions depend on geometry only and are often highly nonuniform. If electrode kinetics is also considered, Laplace's equation still applies but is subject to different boundary conditions. The resulting current distribution is called a secondary current distribution. Here, for linear kinetics the current distribution is characterized by the Wagner number, Wa, a dimensionless ratio of kinetic to ohmic resistance.

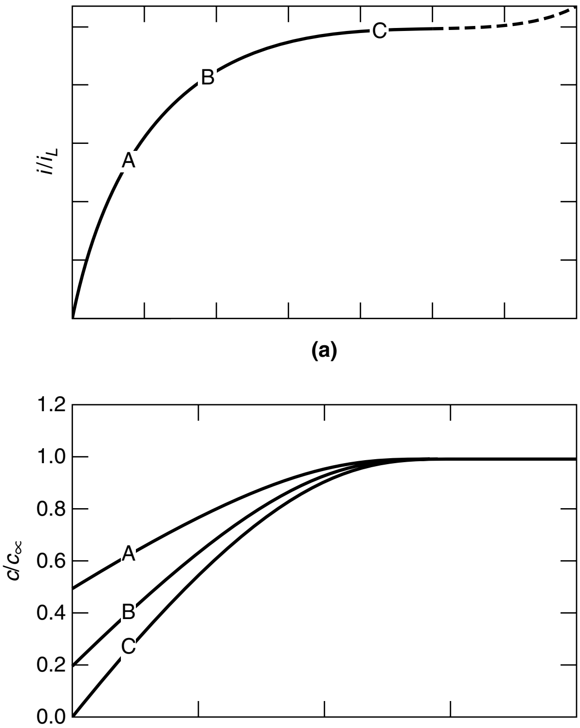
$$\mathrm{Wa} = \frac{\kappa RT}{i_o(\alpha_a + \alpha_c)FL} \tag{35}$$

For large Wa, the current distribution is uniform. For example, when electroplating (qv) an object, usually a uniform deposit is desirable. Equation 35 suggests that a larger piece, ie, low Wa, would be more difficult to plate uniformly than a smaller one.

One other limit of interest is that as the rate of an electrochemical reaction increases (increasing surface overpotential), the concentration of reactants at the surface of the electrode decreases. When the concentration reaches zero, further changes in the overpotential do not increase the rate of reaction, ie, the reaction is mass-transfer limited. This condition is called limiting current. Current densities and concentration profiles for this condition are shown schematically in Figure 3. After plateauing, the current density often increases further in experimental systems as a result of the occurrence of a second Faradaic reaction at sufficiently high overpotential, eg, hydrogen evolution. This is shown in Figure 3**a**.

Under conditions of limiting current, the system can be analyzed using the traditional convective-diffusion equations. For example, the correlation for flow between two flat plates is

$$\mathrm{Nu}(x) = 1.2325\left(\frac{\mathrm{ReSc}d_e}{x}\right)^{1/3} = \frac{s_i i(x) d_e}{nFDc_\infty} \tag{36}$$



(b)

Fig. 3. Conditions of limiting current. (**a**) Current density on the electrode surface as a function of surface potential, showing points A, B, and C. The dashed line is for a second Faradaic reaction. (**b**) The concentration profiles corresponding to points A, B, and C.

where d_e, the equivalent diameter of the flow channel, is equal to $2h$ for the flat-plate geometry. A number of mass-transfer correlations for systems relevant to electrochemistry are available (9).

As the Nernst equation suggests, concentration variations in the electrolyte lead to potential differences between electrodes of the same kind. These potential differences are concentration polarizations or concentration overpotentials. Concentration polarizations can also affect the current distribution. Predicting these is considerably more difficult. If concentration gradients exist, equations 25 and 27 through 29 must generally be solved simultaneously.

Electrochemical systems are found in a number of industrial processes. In addition to the subsequent discussions of electrosynthesis, electrochemical techniques are used to measure transport and kinetic properties of systems (see ELECTROANALYTICAL TECHNIQUES); to provide energy (see BATTERIES; FUEL CELLS); and to produce materials (see ELECTROPLATING). Electrochemistry can also play a destructive role (see CORROSION AND CORROSION CONTROL). The fundamentals necessary to analyze most electrochemical systems have been presented. More details of the fundamentals of electrochemistry are contained in the general references.

Nomenclature Symbol	Definition	Units
a	activity	
c_i	concentration of species i	mol/m^3
d_e	equivalent diameter of annulus	m
$\mathbf{D_i}$	diffusion coefficient	m^2/s
f_i	molar activity coefficient of species i	
F	Faraday's constant	96,487 C/eq
G	Gibbs energy	J/mol
h	distance between wall of flow channel	cm
$\boldsymbol{i}$	current density	A/m^2
i_o	exchange-current density	A/m^2
k	reaction rate constant	
L	characteristic length	m
$\mathbf{N}_i$	molar flux of species i	mol/(m^2·s)
n	number of electrons transferred in reaction	
Nu	Nusselt number	
p	fugacity or pressure	kPa
r	heterogeneous reaction rate	mol/(m^2·s)
R_i	homogeneous reaction rate for species i	mol/(m^3·s)
R	universal gas constant	8.3143 J/ (mol·K)
Re	Reynolds number	
s_i	stoichiometric coefficient	
Sc	Schmidt number	
t	time	s
T	temperature	K
U	open-circuit potential	V
u_i	mobility of species i	m^2·mol/(J·s)
$\boldsymbol{v}$	velocity	m/s
V	cell potential	V
Wa	Wagner number	
x	distance from entrance of channel	m
z_i	charge number of species i	
α	transfer coefficient	
β	symmetry coefficient	
ε	permittivity	F/m
η_s	surface overpotential	V
κ	electrical conductivity	S/m
λ	debye length	m
λ_i	absolute activity of species i	
μ_i	electrochemical potential of species i	J/mol
	total number of moles from electrolyte dissociation	
ν_+	number of moles of cations from electrolyte dissociation	
ν_-	number of moles of anions from electrolyte dissociation	
Φ	electrical potential	V
Subscripts		
∞	far from the electrode surface	
O	oxidized species	
R	reduced species	
a	anodic	
c	cathodic	
L	limiting current	
$+$	cation	
$-$	anion	
Superscripts		
$*$	ideal gas	
θ	secondary reference state at infinite dilution	

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