Thermodynamics for Electrochemistry and Photoelectrochemistry

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Abstract Electrochemistry and photoelectrochemistry are based on thermodynamics, especially for its equilibrium. In this chapter, the thermodynamics for the electrochemistry and photoelectrochemistry are discussed.

1 Gibbs Free Energy and Chemical Reaction

Thermodynamics is an important tool for understanding the theoretical background of electrochemical reactions. It is an established rule of thumb and defines macroscopic variables, such as internal energy, entropy, and pressure, and other textbooks should be referenced for its details [1]. This chapter focuses on thermodynamics used for electrochemical and photoelectrochemical reactions.

According to the first law of thermodynamics for a closed system, any net increase in the internal energy U is described using heat δQ entering the system and the work δW done by the system;

$$\delta Q = \mathrm{d}U + \delta W. \tag{1}$$

This shows that heat entering the system is used for the net increase in the internal energy and the work done by the system. This is the analogous to the law of energy conservation, i.e., the energy entering the system is used for the net increase in the potential energy and the work done by the system (The energy for thermodynamic "work" is accounted for by changes in the external generalized mechanical constraints on the system. The work is a generalization of the concept of mechanical work in physics.). Usually, this is expressed as follows:

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$$dU = \delta Q - \delta W. \tag{2}$$

The letter d indicates an exact differential, expressing that internal energy U is a property of the state of the thermodynamic system. The internal energy depends only on the original state and the final state, and not upon the path taken. In contrast, the Greek delta (δ) in this equation reflects the fact that the heat transfer and work transfer are not properties of the initial and final states of the system. Thus, heat and work depend on the path taken and are not state functions. (The work is changed by the path taken in the real world, that is, the existence of friction etc. This means the process in reality can be close to the reversible process but is a non-reversible process.) For a reversible process in a closed system, δW has the following relationship of differential equation using pressure (P) and volume (V) under constant pressure condition (This pressure can be changed to variable in some cases. In this chapter, the equations are treated as the chemical reaction occurring under standard conditions (25 °C, 101.3 kPa for chemical reaction).);

$$\delta W = P dV. \tag{3}$$

Enthalpy is defined as the entering heat used for the net increase of internal energy and the work done by the system, which does not depend on the path. Enthalpy (H) consists of the internal energy of the system (U) plus the work done by the system, that is the product of pressure (P) and volume (V) of the system, which are all functions of the state of the system;

$$dH = dU + P dV. \tag{4}$$

The unit of enthalpy is the energy unit like "joule." Enthalpy changes with its energy transfer, i.e., increases with receiving heat from the environment. It should be noted that enthalpy includes internal energy change, thus this change is observed as system phase changes, reactions, and heat capacitances.

The other important thermodynamic concept is entropy. It should be noted that entropy is included in internal energy U and cannot be used for the work done by the system. Entropy (S) is a measure of disorder of the system. According to statistical mechanics, entropy is defined by Boltzmann's entropy formula with the quantity Ω, which is the number of microstates corresponding to a given macrostate;

$$S = k_B \ln \Omega, \tag{5}$$

where, k_B is the Boltzmann's constant. The other definition from thermodynamics according to the Clausius theorem is;

$$dS \leq \frac{\delta Q}{T}, \tag{6}$$

where, Q is heat entering into a closed system and T is absolute temperature. This clearly shows that entropy changes upon heat transfer. The equality establishes only in a closed system at the same temperature under the reversible process. Entropy is also the state function of a system and the unit is the energy/temperature like "joule/kelvin."

Thermodynamic free energy is a state function like internal energy U and is defined as the energy converted to do work. (The free energy is the internal energy of a system minus the amount of energy that cannot be used to perform work. This unusable energy is given by the entropy of a system multiplied by the temperature of the system.) The unit is energy/amount of substance, that is, "joule/mole." Free energy can be voluntarily reduced, that is, a chemical reaction occurs spontaneously if the change in free energy is negative. Furthermore, when the free energy takes a constant value of minimum, the system is in equilibrium. Free energy is defined in particular, as Helmholtz energy (F) under constant temperature and volume;

$$\mathrm{d}F = \mathrm{d}U - T\mathrm{d}S = \mathrm{d}H - T\mathrm{d}S - p\mathrm{d}V. \tag{7}$$

Gibbs energy (G) is defined under constant temperature and pressure;

$$\mathrm{d}G = \mathrm{d}U - T\mathrm{d}S + p\mathrm{d}V = \mathrm{d}F + p\mathrm{d}V = \mathrm{d}H - T\mathrm{d}S. \tag{8}$$

Since chemical reaction is usually treated under the condition of constant temperature and pressure, Gibbs energy is used. When the chemical reaction contains its pressure change, Helmholtz energy has to be used. It should be noted that internal energy cannot be determined but free energy, enthalpy, and entropy can be measured. Thus, chemical reaction can be discussed by using free energy.

Standard formation Gibbs energy ($\Delta_f G^0$, where the ^{0} expresses the system under the standard condition; 25 °C, 101.3 kPa) is the change of Gibbs free energy that accompanies the formation of 1 mol of that substance from its component elements at their standard states (the most stable form of the element at 25 °C, 101.3 kPa). Thus, the standard molar Gibbs energy of formation of element is defined as zero (0). Standard formation Gibbs energy is defined from Eq. (8) as

$$\Delta_f G^0 = \Delta_f H^0 - T\Delta_f S^0 \tag{9}$$

where, $\Delta_f H^0$ is standard formation enthalpy and $\Delta_f S^0$ is standard formation entropy.

Standard formation Gibbs energy also tells us about the spontaneity of a reaction;

$\Delta_f G^0 < 0$, favored reaction, stabilizing direction, spontaneous, exergonic,
$\Delta_f G^0 = 0$, Neither the forward nor the reverse reaction proceeds, at equilibrium,
$\Delta_f G^0 < 0$, disfavored reaction, instabilizing direction, nonspontaneous, endergonic.

One of the simplest substance formation, water generation from hydrogen and oxygen reaction, is used as an example here. The reaction under the standard condition is described as follows:

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(\ell). \tag{10}$$

The standard formation enthalpy ($\Delta_f H^0$) is obtained due to the phase change and the reaction;

$$\Delta_f H^0 = -285.83\,[\text{kJ/mol}]. \tag{11}$$

The standard formation entropy ($\Delta_f S^0$) also exists;

$$\begin{gathered} -T\Delta_f S^0 = 48.70\,[\text{kJ/mol}] \\ (\text{in this condition}, \Delta_f S^0 = -163.34\,[\text{J/mol/K}]). \end{gathered} \tag{12}$$

As a result, the total energy change is expressed by the change of the Gibbs energy (standard formation Gibbs energy, $\Delta_f G^0$);

$$\Delta_f G^0 = \Delta_f H^0 - T\Delta_f S^0 = -237.13\,[\text{kJ/mol}]. \tag{13}$$

Since the $\Delta_f G^0$ for the stable standard substance with a singular element is defined as zero, the $\Delta_f G^0$s of H_2 and O_2 in Eq. (10) are zero. The lower Gibbs energy indicates the more stable condition. Thus, H_2O is more stable than H_2 and O_2 because the Gibbs energy of H_2O is lower than those of H_2 and O_2. The free-energy diagram associated with this reaction is shown in Fig. 1.

It should be noted here that the Gibbs energy change does not contain the activation energy (E_a). As known well, the reaction of H_2 and O_2 does not occur under the standard condition due to the existence of a large activation energy. The discussion of electrochemical reactions is based on this Gibbs energy change, which means it does not contain the activation energy. Unknown energies including activation energy for electrochemical reactions are expressed as "overpotential."

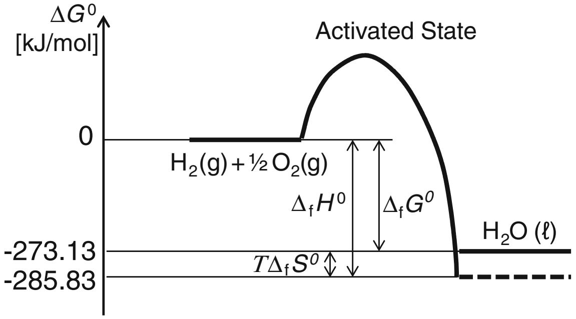


Fig. 1 Schematic diagram for H_2 and O_2 forms H_2O. The relationship of Gibbs energy ($\Delta_f G^0$), enthalpy ($\Delta_f H^0$), and entropy term ($T\Delta_f S^0$) are shown here

2 Equilibrium Criteria for Chemical and Electrochemical Systems

Ideal chemical equilibrium condition can be expressed by using standard formation Gibbs energy ($\Delta_f G^0$). An equilibrium chemical reaction is;

$$pP + qQ + \cdots \text{(reactants)} = xX + yY + \cdots \text{(products)}. \tag{14}$$

The ideal equilibrium condition of this reaction is expressed as;

$$\begin{gathered} p\Delta_f G^0(p) + q\Delta_f G^0(q) + \cdots = x\Delta_f G^0(x) + y\Delta_f G^0(y) + \cdots, \\ \sum_{\text{reactant}} p\Delta_f G^0(p) = \sum_{\text{product}} x\Delta_f G^0(x). \end{gathered} \tag{15}$$

This expresses that the sum of Gibbs energy equals between the products and the reactants when the reaction is under equilibrium.

Considering the free energy for nonideal mixed substance, driving force of reaction is weakened in mixed substances compared with pure substances due to the concentration decrease. In order to express this nonideality, chemical potential (μ_i^0) of *i*th component is introduced. When pressure is constant, chemical potential in a mixture is expressed as the partial molar Gibbs energy. The pure component is estimated as 1 mol using this expression. The definition for ideal condition of n mole *i*th component in a mixture is;

$$\mu_i^{0\phi} = \frac{\partial \Delta_f G^0}{\partial n_i} = \frac{\partial}{\partial n_i} \sum_j n_j \Delta_f G^0(n_j). \tag{16}$$

where, n_i is the molar ratio of *i*th component in a mixture. This $\mu_i^{0\Phi}$ is standard chemical potential. Describing this deviation for nonideal mixed substance from the ideal one, activity (a) is introduced. Nonideal chemical potential (μ_i^0) is expressed with activity as;

$$\mu_i^0 = \mu_i^{0\phi} + RT \ln a, \tag{17}$$

where, R is gas constant. The definition of this activity (a) without any interaction between molecules is the molar ratio of a substance in the mixture. That is,

gas	partial pressure (p_i [kPa]) divided by standard pressure (p_0 = 101.3 [kPa]),
solute	molar concentration (m_i [mol/kg or mol/L]) divided by standard condition (m_0 = 1 [mol/kg or mol/L]),
solvent	solvent for diluted solution is defined as a = 1,
solid	pure solid is defined as a = 1,
electron	electrons in a material is defined as a = 1.

Using the chemical potential, the equilibrium reaction of Eq. (14) for nonideal mixed substance is expressed instead of Eq. (15) as;

$$\begin{aligned} &p\mu_p^{0\phi} + pRT\ \ln a_p + q\mu_q^{0\phi} + qRT\ \ln a_q + \cdots \\ &\quad = x\mu_x^{0\phi} + xRT\ \ln a_x + y\mu_y^{0\phi} + yRT\ \ln a_y + \cdots . \end{aligned} \tag{18}$$

From the definition of a general chemical reaction, the temperature and pressure are constant, thus;

$$\begin{aligned} &-\left(\left(xRT\ \ln a_x + yRT\ \ln a_y + \cdots\right) - \left(pRT\ \ln a_p + qRT\ \ln a_q + \cdots\right)\right) \\ &\quad = \left(x\mu_x^{0\phi} + y\mu_y^{0\phi} + \cdots\right) - \left(p\mu_p^{0\phi} + q\mu_q^{0\phi} + \cdots\right) = \Delta_r G^0, \end{aligned}$$

$$-RT\ \ln\left(\frac{a_x^x a_y^y \ldots (\text{product})}{a_p^p a_q^q \ldots (\text{reactant})}\right) = \Delta_r G^0. \tag{19}$$

where, $\Delta_r G^0$ is standard reaction Gibbs energy. Equilibrium constant (K) is defined by using Eq. (19) as;

$$\Delta_r G^0 = -RT\ \ln\left(\frac{a_x^x a_y^y \ldots (\text{product})}{a_p^p a_q^q \ldots (\text{reactant})}\right) = -RT\ \ln K. \tag{20}$$

This Eq. (20) is called “low of mass action.”

Electrode potential also plays an important role in electrochemical reaction. The basis for an electrochemical reaction is always a redox reaction (reduction and oxidation reaction), which can be broken down into two half-reactions: oxidation at anode (loss of electron) and reduction at cathode (gain of electron). The driving force of the redox reaction is the electricity due to electric potential difference between two electrodes. This potential difference is created by the applied potentials of the two metal electrodes in an electrolyte. The electron energy at an electrode under equilibrium condition can be defined for a certain half-reaction including ions and electrons as follows. The ideal half-reaction can be described as;

$$pP + qQ + \cdots (\text{reactants/oxides}) + ne^- = xX + yY + \cdots (\text{products/redactants}) \tag{21}$$

Important point of this Eq. (21) is that P, Q, X, Y, … represent not only substances but also ions. The equilibrium condition of Eq. (21) using the Faraday constant (elementary charge for 1 mol electron; $F = 96{,}485$ [°C/mol]) and standard electrode potential (oxidation reduction potential, redox potential; ϕ^0(Ox/Red) under standard condition) is;

$$p\Delta_f G^0(p) + q\Delta_f G^0(q) + \cdots + n\Delta_f G^0(e) = x\Delta_f G^0(x) + y\Delta_f G^0(y) + \cdots,$$

$$\phi^0(Ox/Red) = \frac{-n\Delta_f G^0(e)}{nF} = \frac{-\left(\sum\limits_{\text{product/Red}} x\Delta_f G^0(x) - \sum\limits_{\text{reactant/Ox}} p\Delta_f G^0(p)\right)}{nF} = \frac{-n\Delta_r G^0}{nF}. \tag{22}$$

It should be noted that the sign of ϕ and that of $\Delta_f G$ are opposite from the definition.

The electrode potential may not be obtained empirically. The galvanic cell (composed of only two electrodes, anode, and cathode) potential results from a pair of electrodes. Thus, only one empirical value is available in a pair of electrodes and it is not possible to determine the value for each electrode in the pair. A reference electrode, for which the potential is defined or agreed upon by convention, needed to be established. The most important reference electrode is the standard hydrogen electrode (SHE) (or normal hydrogen electrode (NHE)), where the half-reaction can be described as;

$$2H^+(\text{in}\,\ell) + 2e^- = \mathrm{H}_2(g). \tag{23}$$

The Gibbs energy of H^+ is defined conventionally as;

$$\Delta_f G^0(H^+) = 0.00. \tag{24}$$

The equilibrium of hydrogen gas and ion in aqueous solution is;

$$\Delta_f G^0(H^+) - 2F\phi^0(H^+/\mathrm{H}_2) = \Delta_f G^0(\mathrm{H}_2). \tag{25}$$

From definitions;

$$\Delta_f G^0(H^+) = 0.00, \Delta_f G^0(\mathrm{H}_2) = 0.00,$$

thus,

$$\phi^0(H^+/\mathrm{H}_2) = 0.00\,[\mathrm{V}]. \tag{26}$$

This standard electrode potential of Eq. (26) is used as a reference for electrochemical reactions. Any electrode, for which the electrode potential is not yet known, can be paired with SHE to form a galvanic cell. The galvanic cell potential gives the unknown electrode's potential. Using this process, any electrode with an unknown potential can be paired with either the SHE or another electrode for which the potential has already been derived and that unknown value can be established. From electrochemical notation, the potential needs to clarify the value with "+" or "−", and the unit with "V versus (reference electrode)" like "V versus SHE" due to the relative measurement method.

One simple reaction is the chemical reaction with electron transfer. The example of half-reactions are;

$$\begin{aligned} &5\mathrm{Fe(CN)}_6^{3-} + 5e^- = 5\mathrm{Fe(CN)}_6^{4-}, \\ &\phi^0\left(\mathrm{Fe(CN)}_6^{3-}\middle/\mathrm{Fe(CN)}_6^{4-}\right) = +0.36\,[\mathrm{V\ vs.\ SHE}], \\ &\mathrm{MnO}_4^- + 8\mathrm{H}^+ + 5e^- = \mathrm{Mn}^{2+} + 4\mathrm{H_2O}, \\ &\phi^0\left(\mathrm{MnO}_4^-/\mathrm{Mn}^{2+}\right) = +1.51\,[\mathrm{V\ vs.\ SHE}]. \end{aligned} \tag{27}$$

Electron moves from the lower to the higher electrode potential, thus;

$$5\mathrm{Fe(CN)}_6^{4-} + \mathrm{MnO}_4^- + 8\mathrm{H}^+ = 5\mathrm{Fe(CN)}_6^{3-} + \mathrm{Mn}^{2+} + 4\mathrm{H_2O}. \tag{28}$$

Similar to this Eq. (28), an electron in electrochemical reaction moves from/to electrode. That is, an electron moves from an electrode when the electrode potential is more negative (electrode energy is more positive) than a half-reaction under equilibrium condition (reduction), and an electron moves to electrode when the electrode potential is more positive (electrode energy is more negative) than a half-reaction under equilibrium condition (oxidation). The details is discussed in Sects. 4 and 5.

For nonideal conditions, electrochemical potential has to be introduced in order to express the nonideality similar to chemical reaction. The electrochemical potential ($\tilde{\mu}_i$) is defined using the valence of ion (z_i) as;

$$\tilde{\mu}_i^0 = \mu_i^{0\phi} + RT\ \ln a_i + z_i F\phi_i. \tag{29}$$

Electrochemical potential of electron is;

$$\tilde{\mu}_e^0 = \mu_e^{0\phi} + RT\ \ln a_e - F\phi_e. \tag{30}$$

Nonideal equilibrium condition of Eq. (21) is expressed using electrochemical potential instead of Eq. (22) as;

$$\begin{aligned} &p\mu_p^{0\phi} + pRT\ \ln a_p + pz_pF\phi^0 + q\mu_q^{0\phi} + qRT\ \ln a_q + qz_qF\phi^0 + \cdots + n\mu_e^{0\phi} + RT\ \ln a_e - nF\phi^0 \\ &\quad = x\mu_x^{0\phi} + xRT\ \ln a_x + xz_xF\phi^0 + y\mu_y^{0\phi\iota} + yRT\ \ln a_y + yz_yF\phi^0 + \cdots. \end{aligned} \tag{31}$$

That is;

$$\begin{aligned} &-\big(\big(xRT\ \ln a_x + yRT\ \ln a_y + \cdots(\text{redactant})\big) - \big(pRT\ \ln a_p + qRT\ \ln a_q + \cdots(\text{oxide})\big)\big) \\ &\quad -\big(\big(xz_x + yz_y + \cdots\big) - \big(pz_p + qz_q + \cdots\big)\big)F\phi^0 + \big(n\mu_e^{0\varphi} + nRT\ \ln a_e\big) - nF\phi^0 \\ &\qquad = \left(x\mu_x^{0\phi} + y\mu_y^{0\phi} + \cdots\right) - \left(p\mu_p^{0\phi} + q\mu_q^{0\phi} + \cdots\right). \end{aligned} \tag{32}$$

The charge has to be balanced in the chemical equation in Eq. (32), thus,

$$-\left(\left(xz_x + yz_y + (\text{reductants})\right) - \left(pz_p + qz_q + (\text{oxides})\right)\right)F\phi^0 - nF\phi^0 = 0. \quad (33)$$

From the relationship between chemical potentials and standard reaction of Gibbs energy in Eq. (19) and the definition of standard electrode potential of Eq. (22);

$$\left(x\mu_x^{0\phi} + y\mu_y^{0\phi} + \cdots\right) - \left(p\mu_p^{0\phi} + q\mu_q^{0\phi} + \cdots\right) = \Delta_r G^0 = -nF\phi^0(Ox/Red). \quad (34)$$

Equation (32) can be organized with the relationship of Eqs. (33) and (34),

$$RT\ \ln\frac{a_p^p a_q^q \ldots (\text{oxide})}{a_x^x a_y^y \ldots (\text{redactant})} + n\left(\mu_e^{0\phi} + RT\ \ln a_e\right) = -nF\phi^0(Ox/Red). \quad (35)$$

The definition of electrode potential and Eq. (35) derive;

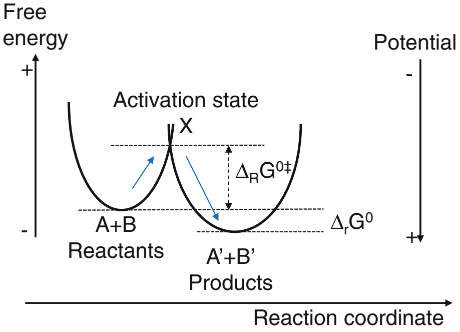
$$\phi^0 = -\frac{n\left(\mu_e^{0\phi} + RT\ \ln a_e\right)}{nF} = \phi^0(Ox/Red) + \frac{RT}{nF}\ln\frac{a_p^p a_q^q \cdots (\text{oxide})}{a_x^x a_y^y \cdots (\text{redactant})}. \quad (36)$$

This Eq. (36) indicates that the electrode potential changes when the activity of the elements in the mixture changes even under standard condition. This relationship is called Nernst equation.

3 Marcus Theory and Gerischer Model

The thermodynamic treatment of chemical reaction shows the equilibrium condition but it cannot treat the rate of chemical reaction. Activation energy is required for the discussion of the rate. Marcus theory explains the activation energy of chemical reaction and the rates of electron transfer reactions [2]. The rate at which an electron can move or jump from one chemical species (called the electron donor) to another (called the electron acceptor). It was originally explained as outer sphere electron transfer reactions, in which the two chemical species only change in their charge with an electron jumping (e.g., the oxidation of an ion like Fe^{2+}/Fe^{3+}), but do not undergo large structural changes. It was extended to include inner sphere electron transfer contributions, in which a change of distances or geometry in the solvation or coordination shells of the two chemical species is taken into account; e.g., the Fe–O distances in $Fe(H_2O)^{2+}$ and $Fe(H_2O)^{3+}$ are different. Adiabatic (continuous free energy change of reacting substance during reaction) and nonadiabatic (discontinuous free energy change existing of reacting substance during reaction) reactions are usually discussed in chemical reactions. The Marcus theory discusses adiabatic reactions, and the Gerischer model applied for electrochemical reaction can take into account nonadiabatic reactions.

Fig. 2 Schematic diagram for reaction coordinate. The direction of energy and potential are opposite



Reaction coordinate (an abstract one-dimensional coordinate to represent progress along a reaction pathway) has to be introduced for the discussion of the chemical reaction rate as shown in Fig. 2. The chemical reaction process starts from the configuration of reactants (A + B), passes through via activation state (X), and reaches to the configuration of products (A′ + B′). The reaction coordinate typically choses to follow the path along the gradient (path of shallowest ascent/deepest descent) of potential energy from reactants to products. For this configuration, energy needs to reach the activation state (X) from the configuration of reactants (A + B), and it goes naturally from activation state to the configuration of reactants (A′ + B′) with certain probability. For common chemical reaction, the energy from A + B to X is given by thermal motion. The chemical reaction probability P_{cr} from A + B to X is described with Boltzmann distribution because the fraction of A + B with the activation energy $\Delta_{\mathrm{R}} G^{0‡}$ out of entire ensemble of A + B follows Boltzmann distribution;

$$P_{\mathrm{cr}} = \exp\left(\frac{-\Delta_R G^{0‡}}{RT}\right), \tag{37}$$

where R is gas constant, and T is absolute temperature. Reaction speed (v_{ct}) from A to B is described with the concentration of reactants A + B ($c_{\mathrm{A+B}}$) and P_{cr};

$$v_{\mathrm{cr}} = kc_{A+B}, \quad k = k_0 P_{\mathrm{cr}} = k_0 \exp\left(\frac{-\Delta_R G^{0‡}}{RT}\right), \tag{38}$$

where k_0 is a constant related to the probability of the process from X to the configuration of products (A′ + B′).

For the Marcus theory, the reaction coordinate path is selected as a parabolic shape of the Gibbs energy of activation. Since the reaction coordinate describes the minimum energy path from the reactants to the products, the real path may not be simplified as parabolic shape. The activation energy of the Marcus theory is

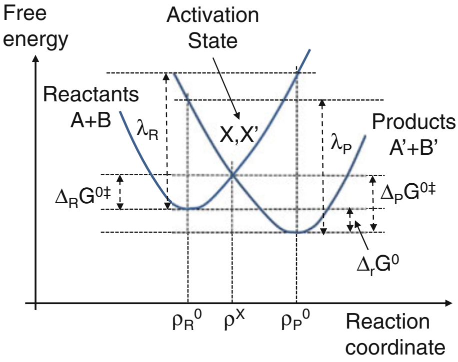


Fig. 3 Schematic diagram of chemical reaction based on Marcus Theory using reaction coordinate

calculated when the parabolic potential curves of Gibbs energy shapes have the same curvature for both reactants and products;

$$\Delta_R G^{0\ddagger} = \frac{(\Delta_r G^0 + \lambda)^2}{4\lambda} \tag{39}$$

where λ is reorganization energy and $\lambda = \lambda_R = \lambda_P$ in Fig. 3 for this case. This reorganization energy is considered the energy required for the reorganization process of the molecule after electron transfer is finished. The electron transfer occurs very fast compared with the molecular reorganization, that is, the electron transfer occurs without any nuclear motion in the molecule (Franck–Condon principle). It should be noted that the energy of activation state calculated from the Marcus theory is that for the adiabatic reaction ($\Delta_R G^{0\ddagger}$) and not for the nonadiabatic reaction (λ).

Quantum mechanical treatments considering the molecular wave function overlap were also proposed in order to develop more detailed treatment of electron transport for chemical reactions. Famous models include Dogonadze and Levich treatment, which takes into account the Landu–Zener formula of transition theory, and the theory proposed by Hopfield, which introduces the Fermi's golden rule for the transition. Detailed descriptions can be found in text books [2].

For electrochemical reaction, equilibrium condition for oxidant (*Ox*) and reductant (*Red*) is described as;

$$Ox + ne^- \leftrightarrow Red. \tag{40}$$

This equilibrium condition can be established with a certain electrode potential of electron. For this condition, the reaction speed of reduction and oxidation are the same, i.e., the minimum points of reaction coordinates for both reactants and products are the same. For the situation shown in Fig. 4, the activation energies from $Ox + ne^-$ to *Red* and *Red* to $Ox + ne^-$ are the same as;

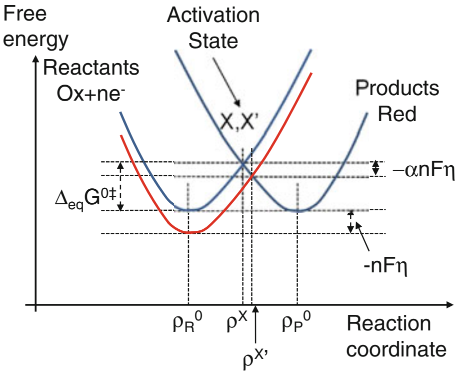


Fig. 4 Schematic diagram of electrochemical equilibrium and the changes with applied bias η

$$\Delta_{\rm eq}G^{0\ddagger} = \Delta_c G^{0\ddagger} = \Delta_a G^{0\ddagger}, \tag{41}$$

where, $\Delta_{\rm eq}G^{0\ddagger}$, $\Delta_c G^{0\ddagger}$, and $\Delta_a G^{0\ddagger}$ are equilibrium, cathodic, and anodic activation energy, respectively. As a result, the chemical reaction rate of $Ox + ne^-$ to Red (v_c) and Red to $Ox + ne^-$ (v_a) are the same. Thus;

$$v_c = k_c c_{Ox} = v_a = k_a c_{Red}, \tag{42}$$

where, k_c and k_a are cathodic (reduced) and anodic (oxidized) rate constant, $C_{\rm Ox}$ and $c_{\rm Red}$ are the concentration of oxidant and reductant. Using Eq. (38);

$$k_{\rm eq} = k_c = k_a = k_0 \exp\left(\frac{-\Delta_{\rm eq}G^{0\ddagger}}{RT}\right) \tag{43}$$

Oxidation and reduction current can be estimated from Eq. (43);

$$i_0 = nFk_{\rm eq}c_{Ox}\exp\left(\frac{-\Delta_{\rm eq}G^{0\ddagger}}{RT}\right) = nFk_{\rm eq}c_{Red}\exp\left(\frac{-\Delta_{\rm eq}G^{0\ddagger}}{RT}\right). \tag{44}$$

where, i_0 is exchange current density.

The equilibrium condition of Eq. (40) can be changed by bias. When positive bias (η) is applied to the equilibrium condition, the electron energy changes by $-nF\eta$. The α of this change is applied to anodic reaction (oxidation) and $1 - \alpha$ is applied to cathodic reaction (reduction). This can be understood from Fig. 4. Thus, the anodic current (i_a) and cathodic current (i_c) change with bias;

$$\begin{aligned} i_c &= nFk_{\mathrm{eq}}c_{Ox}\exp\left(\frac{-\Delta_{\mathrm{eq}}G^{0\ddagger}-(1-\alpha)nF\eta}{RT}\right),\\ i_a &= nFk_{\mathrm{eq}}c_{Red}\exp\left(\frac{-\Delta_{\mathrm{eq}}G^{0\ddagger}+\alpha nF\eta}{RT}\right). \end{aligned} \tag{45}$$

This is called Butler–Volmar equation. The measured current (i) is the sum of cathodic and anodic currents. Considering the current direction;

$$\begin{aligned} i &= i_a - i_c\\ &= nFk_{\mathrm{eq}}\left(\exp\left(\frac{-\Delta_{\mathrm{eq}}G^{0\ddagger}}{RT}\right)\right)\left(c_{Ox}\exp\left(\frac{-(1-\alpha)nF\eta}{RT}\right)-c_{Red}\exp\left(\frac{\alpha nF\eta}{RT}\right)\right). \end{aligned} \tag{46}$$

This can be observed by Tafel plot in experiments when the applied bias is large enough. It can be described using the measured current (i);

$\eta = a - b\log|i|$, in the equation,

$$b = \frac{RT}{(1-\alpha)nF} \quad \text{or} \quad b = \frac{RT}{\alpha nF}. \tag{47}$$

Under equilibrium condition of Eq. (46), this can be expressed as;

$$\exp\left(\frac{nF\eta}{RT}\right) = \frac{c_{Ox}}{c_{Red}}, \tag{48}$$

here, $\eta = \phi^0 - \phi^0(\mathrm{Ox/Red})$, thus, Eq. (48) is;

$$\phi^0 = \phi^0(Ox/Red) + \frac{RT}{nF}\ln\left(\frac{c_{Ox}}{c_{Red}}\right). \tag{49}$$

This Eq. (49) is exactly the same as the Nernst equation of Eq. (36).

The Gerischer model uses a different approach from the Marcus theory. In this model, the charge transfer is considered in terms of electric energies in solid and of energy levels in solution. The energy level in solution is much more complex than in solid state physics because of the effect of the polar solvent surrounding the ions. As a result, the Gerischer model is only applicable for weak interactions between the redox system and the electrode, that is, mainly for nonadiabatic conditions.

The energy diagram for reduced and oxidized species in polar solvent is shown in Fig. 5. The energy levels involved in an electron transfer differ from the thermodynamic equilibrium value of $E_{F,\mathrm{redox}}$ due to the interaction with the solvent. (Electron energy is used for the Gerischer model instead of chemical potential because the model is based on an electron transfer like in solid. Thus, this electron

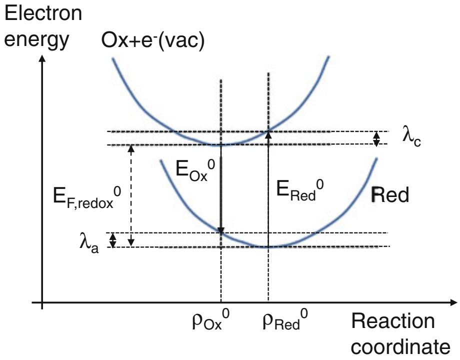


Fig. 5 Schematic diagram of the Gerischer model using reaction coordinate (*left*) and based on the electron energy of vacuum (*right*)

energy of $E_{F,\mathrm{redox}}$ is the same as the equilibrium state of electrochemical potential $(\tilde{\mu}_i)$. It should be noted here that the signs of electron energy and electrochemical energy are opposite.) The electron energy of E^0_{Red} is required to transfer an electron from the reduced state (Red) to the vacuum, and the energy is leading to the formation of the oxidation state (Ox). This electron transfer is expected to be very fast compared with the reorganization of the solvation shells and the solvent dipoles (Franck—Condon principle). Thus, the reorganization of solvation shells and solvent dipoles occur after the electron transfer step. The reorganization continues until the oxidation spices reaches its equilibrium state with changing reorganization energy λ_c. The opposite electron transfer process to capture an electron from vacuum level into the oxidation state (Ox) is similar. For this case, the electron transfer energy and reorganization energy are expressed as E^0_{Ox} and λ_a. The electron transfer energy of E^0_{Red} and E^0_{Ox} are similar to ionization energy (I^0) and electronic affinity (A^0). In addition;

$$E^0_{Red} - \lambda_c = E^0_{Ox} + \lambda_a = E^0_{F,\mathrm{redox}}. \tag{50}$$

Assuming harmonic oscillation for the fluctuation of the solvent molecules near the equilibrium position of Red and Ox, the energy curves (E_{Red} and E_{Ox}) have parabolic shapes, that is;

$$\begin{aligned} E_{Red}(\rho) &= \gamma_{Red}\left(\rho - \rho^0_{Red}\right)^2, \\ E_{Ox}(\rho) &= \gamma_{Ox}\left(\rho - \rho^0_{Ox}\right)^2, \end{aligned} \tag{51}$$

where, γ_{Red} and γ_{Ox} are force constants for Red and Ox, ρ^0_{Red} and ρ^0_{Ox} are the position at which energy takes the minimum for the Red and Ox, respectively. For simplicity, the force constants and reorganization energy are assumed to be the same ($\gamma_{\text{Red}} = \gamma_{\text{Ox}} = \gamma$, $\lambda_{\text{Red}} = \lambda_{\text{Ox}} = \lambda$). The distribution functions (W_{Red} and W_{Ox}) of solvation states are given by;

$$\begin{aligned} W_{Red}(\rho) &= W^0 \exp\left(\frac{-\left(E_{Red}(\rho) - E_{Red}(\rho^0_{Red})\right)}{kT}\right), \\ W_{Ox}(\rho) &= W^0 \exp\left(\frac{-\left(E_{Ox}(\rho) - E_{Ox}(\rho^0_{Ox})\right)}{kT}\right). \end{aligned} \tag{52}$$

Equation (52) can be converted into forms with electronic energy dependence alone using Eq. (51), here the integration over an entire energy is unity by normalizing pre-exponential factor;

$$\begin{aligned} W_{Red}(E) &= (4kT\lambda)^{-1/2}\exp\left(\frac{-\left(E - E^0_{F,\text{redox}} - \lambda\right)^2}{4kT\lambda}\right), \\ W_{Ox}(E) &= (4kT\lambda)^{-1/2}\exp\left(\frac{-\left(E - E^0_{F,\text{redox}} + \lambda\right)^2}{4kT\lambda}\right). \end{aligned} \tag{53}$$

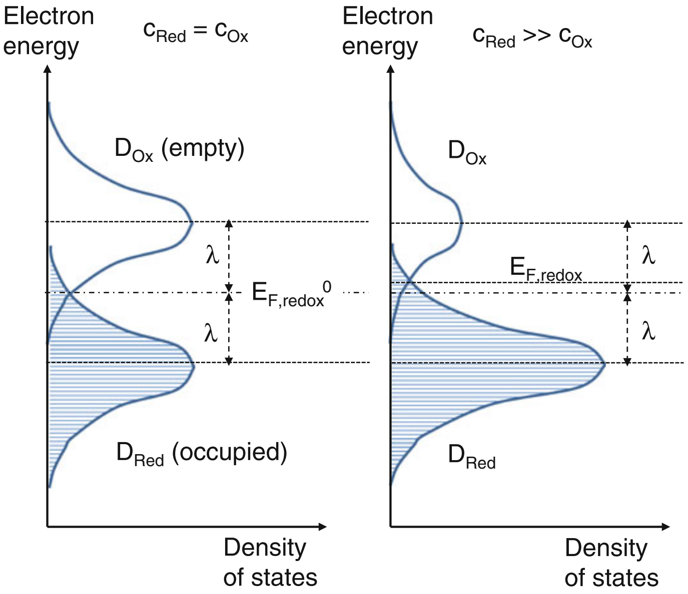


Fig. 6 Schematic electron energies of a redox system versus density of states by Gerischer model

The densities of electronic states are proportional to the concentration of the reduced (c_{Red}) and oxidized species (c_{Ox}), thus the total distribution ($D_{\mathrm{Red}}(\mathrm{E})$ and $D_{\mathrm{Ox}}(\mathrm{E})$) is;

$$D_{Red} = c_{Red} W_{Red}(E), D_{Ox} = c_{Ox} W_{Ox}(E). \tag{54}$$

The corresponding energy diagram is shown in Fig. 6.

4 Equilibrium and Non-equilibrium in Electrochemical Reactions

Electrochemistry is one of the chemistry branches that studies chemical reactions which take place at the interface of an electron conductor and an ionic conductor. The electron conductor is an electrode and is usually made of a metal or a semiconductor. The ionic conductor is an electrolyte and is usually made of an ionic solution or an ionic liquid. The reaction involves electron transfer between the electrode and the electrolyte. Electrochemical reaction is both a chemical reaction driven by an external voltage as in electrolysis and a voltage created by a chemical reaction as in battery. A chemical reaction where electrons are transferred between molecules are called oxidation/reduction (redox) reaction. In general, the situations of electrochemistry are that the oxidation and reduction reactions are separated in space or time with connections of external electric circuit. The oxidation and reduction reactions are paired and cannot be isolated under real situation.

Equilibrium between an electrode and an electrolyte is important to understand the electrochemical reaction. The equilibrium condition for chemical reactions is usually discussed using chemical potential but the definition of equilibrium is different in electron conductor. In order to connect the equilibrium condition between chemical reaction and electron conductor, the discussion is started from the concept of the Fermi level. The Fermi level is the hypothetic potential energy for an electron inside an electron conductor.

In solid state physics, work function is the minimum thermodynamic work needed to remove an electron from a solid surface to a point in the vacuum immediately outside the solid surface as shown in Fig. 7. That is, "work" is an energy. Here "immediately" means that the final electron position is far from the surface on the atomic scale, but still so close to the solid that the energy of an electron is influenced by ambient electric fields in the vacuum. The work function is not a characteristic of a bulk material, but rather a property of the surface of the material (depending on crystal facet and contamination). When the total energy of the solid with $N + 1$ electrons is defined as $E_{\mathrm{tot}}(N + 1)$, the energy of the solid with one electron removed can be described as $E_{\mathrm{tot}}(N) + E_{\mathrm{vac}}$, where E_{vac} is the energy of the removed electron. The work function W_F is;

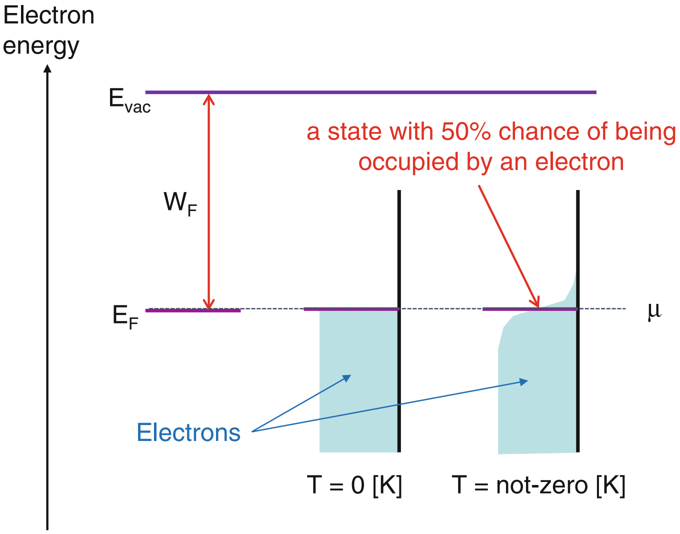


Fig. 7 Relationship among vacuum level (E_{vac}), the Fermi level (E_F), chemical potential (μ), and work function (W_F)

$$W_F = (E_{\text{tot}}(N) + E_{\text{vac}}) - E_{\text{tot}}(N+1) = -\frac{\partial E_{\text{tot}}(N)}{\partial N} + E_{\text{vac}}. \tag{55}$$

The total energy of the solid ($E_{\text{tot}}(N)$) can be treated as the Gibbs energy in the discussion of chemical reaction. Thus, in the case of $N \gg 1$, from the definition of chemical potential (Eq. (16));

$$\frac{\partial E_{\text{tot}}(N)}{\partial N} = \mu. \tag{56}$$

The electron energy which is defined as the work function can be treated as the Fermi energy (E_F), which is the free energy of a single electron in solid under equilibrium. The energy defined as the work function at the temperature of 0 K is;

$$W_F = -\mu_{\text{at}\,0\,\text{K}} = -E_{F\,\text{at}\,0\,\text{K}}. \tag{57}$$

The chemical potential is almost the same as the Fermi energy even around room temperature.

For the strict definition for the finite temperature is little different. For a system of identical fermions (like electrons), the average number of fermions in a single-particle state i (n_i), is given by the Fermi–Dirac (F–D) distribution as shown in Fig. 7,

$$n_i = \frac{1}{1 + \exp\left(\frac{\varepsilon_i - \mu}{k_B T}\right)} \tag{58}$$

where k_B is the Boltzmann's constant, T is the absolute temperature, ε_i is the energy of the single-particle at state i, and μ is the chemical potential [3]. For the case of electrons in an electron conductor, μ, which is the point of symmetry, is typically called the Fermi level (E_F) or total electrochemical potential ($\tilde{\mu}$). That is, the average number of fermions (n_i) is 0.5 when the $\varepsilon_i = E_F = \tilde{\mu}$.

As we discussed, the standard point of electrode potential is standard hydrogen electrode (SHE), which is the equilibrium between proton (H^+) and hydrogen molecule (H_2) as shown in Eqs. (23)–(26). The electrochemical potential is measured using the unit of "V" with the applied bias. For work function, the standard point is the vacuum level (E_{vac}) and it is measured by the unit of "eV" due to the definition for one electron energy. The positive/negative directions of electrode potential and work function are opposite due to the definition. Although the vacuum level is of no practical reference, the question arises where the SHE can be quantitatively related to the vacuum level. Although many reports exist for the value, the value of $E_{\text{SHE}} = -4.5$ eV for the SHE is used mostly [4].

Work function (W_F) depends on the configurations of atoms at the surface of the material. For example, the work function for polycrystalline silver is 4.26 eV, but it varies for different crystal faces as (100) surface: 4.64 eV, (110) surface: 4.52 eV, (111) surface: 4.74 eV for silver crystals [5]. Examples of work function is shown in Fig. 8. Standard hydrogen electrode is also shown in Fig. 8.

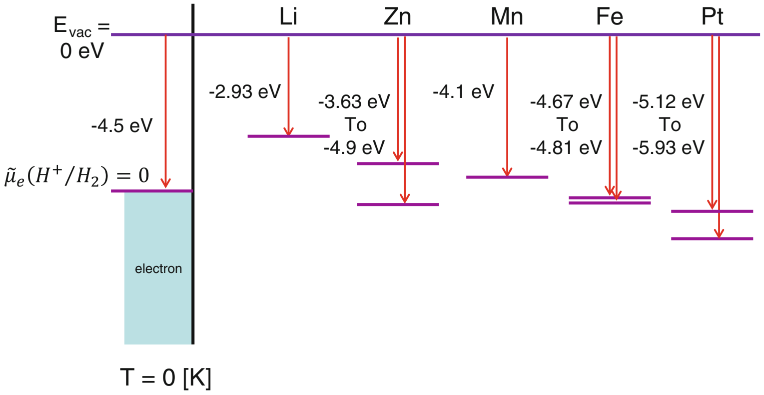


Fig. 8 Examples of work functions. Work function has positive value for the definition but the energy shown here is the value versus the electron energy of vacuum level as zero in order to compare the standard hydrogen electrode. The position for standard hydrogen electrode (SHE) is also shown

The work function (W_F) with existing electrostatic potential can be defined as;

$$W_F = -e\phi - E_F, \tag{59}$$

where, e is elementary charge, ϕ is the electrostatic potential in the vacuum nearby the surface, and E_F is the Fermi level (electrochemical potential of electrons) inside the material. The term $-e\phi$ is the energy of an electron in the vacuum nearby the surface which is almost the same as the electrostatic potential of inside the material. The work function is thus defined as the thermodynamic work required to remove an electron from the material to a state in the vacuum nearby the surface.

The chemical potentials or the Fermi levels are the same when the materials are in equilibrium. This means that the electrostatic potential in the vacuum near the surface changes at the interface when two different material are contacted. Thus, charge accumulation occurs at the interface. This charge accumulation forms to prevent charged carrier flow of the electron energies before contact, that is, electrons flow from high to low energy states of electron, for example. This is because a small amount of charged particles (electrons) move from its relatively high energy metal to relatively low energy metal. The thickness of the spatial distribution of the charges (space charge region) are defined by the Poisson equation. Two different kinds of metal contacts for example are shown in Fig. 9. The space charge region for metals are negligible because a huge number of charged particle exist in metals. This means the electrostatic potential at the interface changes abruptly.

In case of the equilibrium contact between a metal and an electrolyte, the situation of the space charge region is different form that for the two-metal contacts as shown in Fig. 10. The depletion layer thickness (the thickness of the space charge

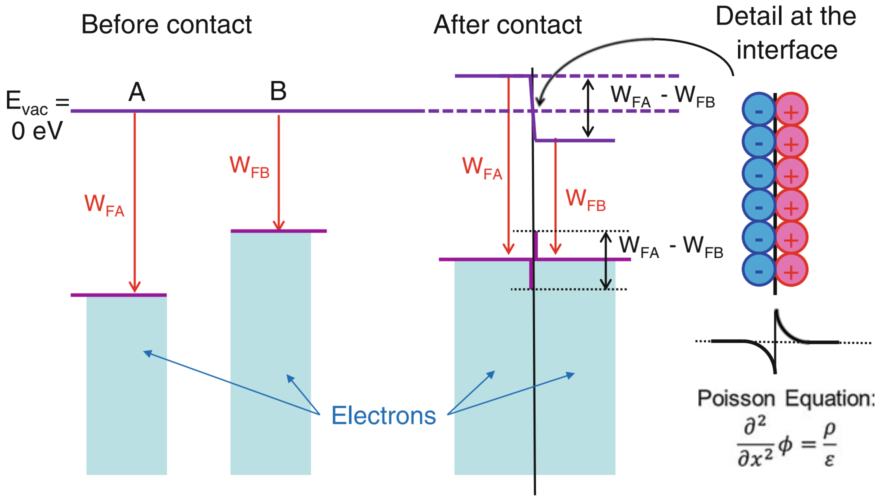


Fig. 9 Schematic diagram of contact between two different metals (*A* and *B*) contact. The Fermi levels (electrochemical potentials) become to be the same and the electrostatic potentials in the vacuum nearby the surfaces change to be different after the contact

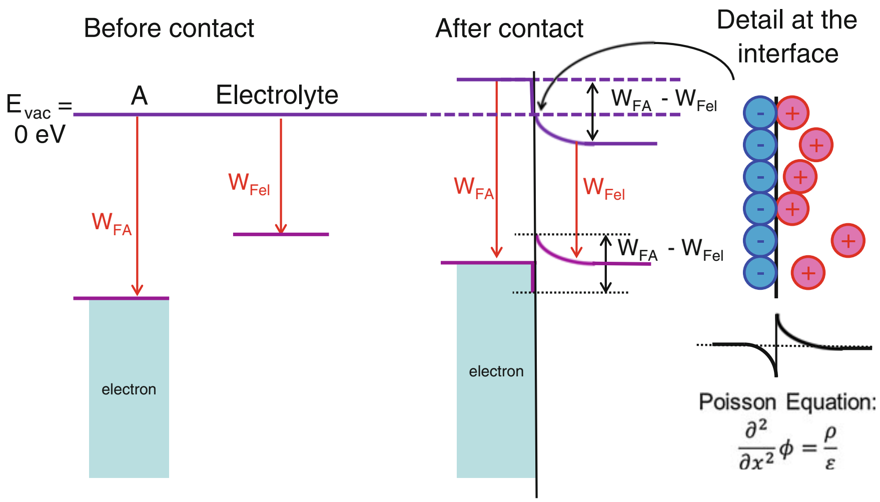


Fig. 10 Schematic diagram for metal and electrolyte (A and el) contact. The space charge region for the electrolyte is much larger than that for the metal due to the difference of the number of charged particles

region) for the electrolyte can be observed due to the density of charged particles in an electrolyte is much smaller than that in a metal. The charged particle concentration in an electrolyte is about 10^{20} cm^{-3} for 1 mol/L solvent ionic solution whereas that for the metal is over 10^{22} cm^{-3}. The Mott–Schottky plot ($1/C^2$ vs. bias where; C is the capacitance of the interface) is useful technique to know the characteristics of the depletion layer in the electrolyte.

The surface potential of a metal is generally pinned due to absorbed molecules of an electrolyte on the surface of the metal for the case of metal–electrolyte contact. (This means that the surface potential does not move as long as the surface ion condition does not change because the surface potential is defined by the coulomb interaction of the absorbed ions and the charges in the metal.) The effect is negligible, however, due to the huge number of charged particles in the metal as discussed. This means that the thickness of the depletion layer of metal is negligible thin, thus the potential of the metal is the same from the inside to very close to the surface, that is, the Fermi level. The surface orientation of a metal affects the ion absorption due to its surface structure change, however, the surface potential change of the metal is also negligible in the same way.

The chemical potential of an electrolyte was defined by the electrolyte composition, whereas the Fermi level of a metal can proceed when an appropriate bias is applied to the metal. Thus, electrochemical reaction can be occurred with the bias. Since the space charge region of a metal is too thin and can be neglected, it looks like surface potential change when bias is applied to a metal. When the anodic potential is more positive than the oxidized reaction in an electrolyte and the cathodic potential is more negative than the reduced reaction in an electrolyte,

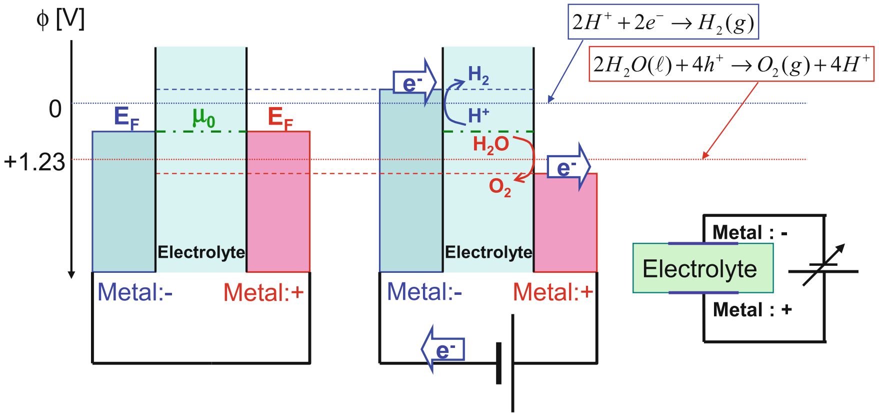


Fig. 11 Schematic diagram for electrochemical reaction. Water splitting is as an example for the reaction. The depletion layer is not shown in this graph

electrochemical reaction start as shown in Fig. 11. During the reaction, ion moves in the electrolyte and keeps the charge balance. This is electrochemical reaction (electrolysis) driven by an external bias. The characteristic of the electrochemical reaction is the high chemical reaction driving energy. The potential at 298 K for standard condition for chemical reaction is about 26 meV. A few volts for electrochemical reaction is commonly used for an electrochemical reaction. When spontaneous electrochemical reactions occur due to the difference of the redox potential, voltage is applied to the electrode, which is called battery.

5 Electrochemical and Photoelectrochemical Reactions

For energy conversion processes, not only electrochemical reaction but also photoelectrochemical reaction is important [6]. Photoelectrochemical reaction is basically the same as the electrochemical reaction but it is much more complicated due to the usage of semiconductor electrode which has a band gap between the valence band and conduction band [6]. The difference among metal, semiconductor, and insulator based on the electron energy is shown in Fig. 12. The conductivity of the metal comes from the overlap of conduction band and valence band. Semiconductor and insulator have gaps between the conduction band and valence band, thus, the conductivity is much lower than that of metal. The difference of the semiconductor and insulator is just the band gap size, that is, a large band gap material is generally called as a insulator.

The most important elements for semiconductors are silicon (Si) and germanium (Ge). The Si and Ge have four valence electrons in their outermost shell (s^2p^2 electron configuration) which gives them the ability to generate sp^3 orbital hybridisation. The

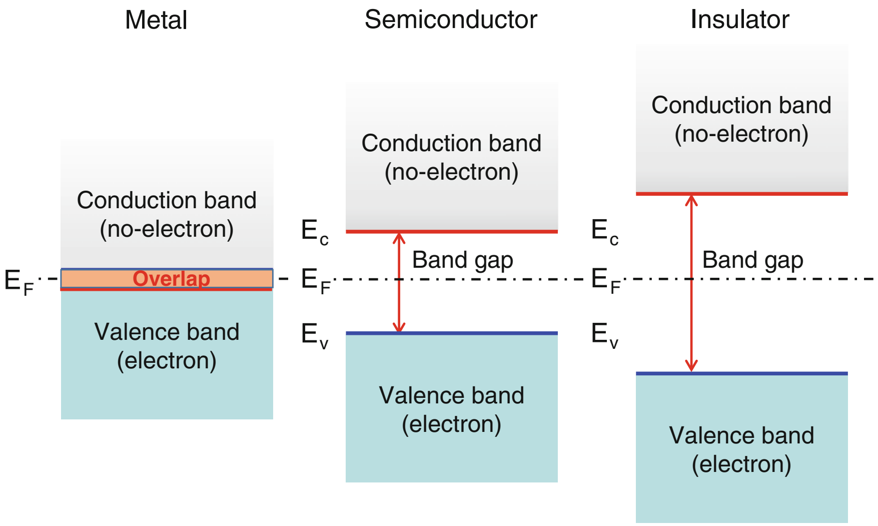


Fig. 12 Schematic electron energy diagram for metal, semiconductor, and insulator. The E_F shows the Fermi level, and that for semiconductor is an intrinsic case

sp^3 hybridisation has the lowest energy in sp^x hybridisation and the four bonds are equivalent. This allows the formation of diamond-like crystal structure with pure covalent bonds. This also results in the gaining or loss of electrons of the constituent atoms equally at the same time. Binary compounds, particularly between elements in Groups III and V such as gallium arsenide (GaAs), groups II and VI such as zinc serenade (ZnSe), and between different group IV elements such as silicon carbide (SiC) can be form covalent crystals in the same manner. Some oxide, organics, and amorphous materials also have semiconductor-like properties.

A pure semiconductor is a poor electrical conductor due to the right number of electrons filling in the valence band. Through doping technique (adding a small amount of impurity), a semiconductor can be modified to have excess electrons (becoming an n-type semiconductor) or a deficiency of electrons (becoming a p-type semiconductor). This is equivalent to adding an excess of electrons to the covalent bond in a crystal or to make a deficiency of electrons in the covalent bonds in the crystal as shown in Fig. 13. Doping an element with excess electron(s) (donor) makes n-type semiconductor and doping an element with deficient electron (s) (acceptor) makes p-type semiconductor. Group-V elements are donors and group-III elements are acceptors for the semiconductor consisting of group-VI elements for example. In both cases, the semiconductor becomes much more conductive. Electrons in conduction band are an origin of conductivity for n-type semiconductors and holes (deficient of electrons) has an origin of conductivity for p-type semiconductors. The polarity of n- and p-type and doping control of semiconductor electrode affect photoelectrochemical properties.

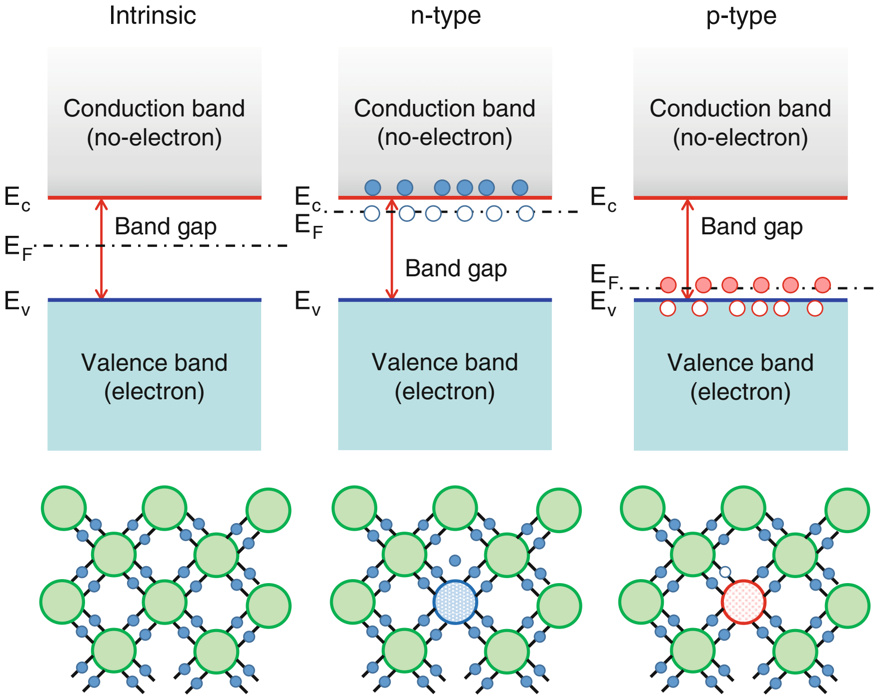


Fig. 13 Schematic diagram for intrinsic, n-type, and p-type semiconductors. The E_c, E_F, E_v show the *bottom* of conduction band, the Fermi level, and the *top* of valence band, respectively. The crystal structure model is also shown with a doped impurity to make n- and p-type are also shown

For metal, the Fermi level is located inside the conduction band, indicating that the band is partially filled. This means the Fermi level of metal can be controlled by external bias. For an insulator and a semiconductor, the Fermi level is located in the band gap, indicating that an empty conduction band is located at far above the Fermi energy as shown in Fig. 12. The definition of work function of semiconductor is the same as the other materials but the position is in the band gap, where electron cannot be allowed to exist. Therefore, the treatment of semiconductor electrode for electrochemical reaction is inevitably different from a metal electrode.

The electron affinity of a semiconductor (E_{ea}) is defined as the energy obtained by moving an electron from the vacuum just outside the semiconductor (E_{vac}) to the bottom of the conduction band (E_c) just inside the semiconductor. Here “just outside” means that the initial electron position is far from the surface on the atomic scale, but still close to the solid to be influenced by the ambient electric field in the vacuum, which is similar to the “immediately” for the work function. (It has to be noted that the definition of “electron affinity” for molecule or atom is different.) The electron affinity can be contrasted with the work function (W_F). The work function is the thermodynamic work that can be obtained by reversibly, isothermally moving an electron from the material surface to the vacuum immediately outside the solid

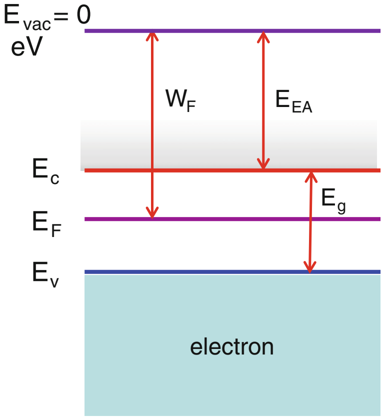


Fig. 14 Relationship among vacuum level (E_{vac}), the Fermi level (E_F), work function (W_F), electron affinity (E_{ea}), the *bottom* of the conduction band (E_c), the *top* of the valence band (E_v), and the band gap of semiconductor (E_g)

surface. The location is the Fermi level as discussed, not the conduction band edge. While the work function of a semiconductor can be changed by doping, the electron affinity ideally does not change with doping. Thus, it is almost an intrinsic value for a material. However, the electron affinity depend on the surface condition (e.g., crystal surface and surface chemical bonds).

For a semiconductor, the ideal energy for an electron from the surface to the vacuum immediately outside the semiconductor surface is "electron affinity (E_{ea}) plus band gap of semiconductor (E_g)." This is the case for intrinsic semiconductor. (It is much more complicated in reality because of the existence of the doping atoms for example.) The relationship is shown in Fig. 14.

The situation of the equilibrium at the contact between a semiconductor and an electrolyte is different from the contact between a metal and an electrolyte. It is the same that the chemical potentials or the Fermi levels are the same when the materials are in equilibrium. It is also the same that the charge accumulation forms to prevent charged carrier flow. The charged carrier in semiconductor is electron for n-type and hole for p-type, and is excited from neutral electron or hole trap (neutral donor or acceptor) thermally. The charged carrier can move in semiconductor, however, the donor or acceptor cannot move. Thus, the charge to form depletion layer is decided to be positive-charged donor for n-type and negative-charged acceptor for p-type semiconductors. As a result, the polarity of depletion layer is defined by this charged donor or acceptor. This situation is completely different from the metal case. In addition, the depletion layer thickness inside the semiconductor is significant because the number of charged particles in a semiconductor is much smaller than that in an electrolyte. The charged particle concentration in an electrolyte is about 10^{20} cm^{-3} for 1 mol/L ionic solution whereas that for the semiconductor is typically at the level of 10^{17} cm^{-3} depending on doping concentration. It has to be noted that for the contact between a metal and an electrolyte,

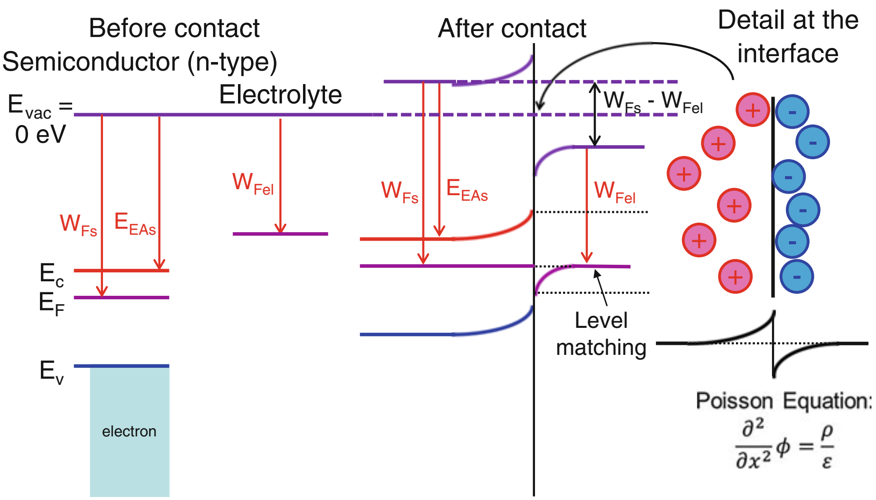


Fig. 15 Schematic diagram for n-type semiconductor and electrolyte (s and el) contact. The space charge region for the semiconductor is much larger than that for the electrolyte due to the difference of the number of charged particles

the depletion layer can be observed only in the electrolyte region. It is caused by the difference of the density of charged particles.

The position of the band edge energies of a semiconductor at the semiconductor/electrolyte interface is generally pinned due to absorbed molecules of an electrolyte on the surface of the semiconductor. This affects much of the depletion layer of the semiconductor because the density of charged particle is not high, whereas the pinned surface energy for a metal does not affect so much owning to a very thin depletion layer. The Mott-Schottky plot ($1/C^2$ vs. bias where C is the capacitance of the interface) is useful technique to know the characteristics of the depletion layer in the semiconductor [7]. This measurement indicates that not only the depleted donor/acceptor concentration but also the flatband potential, which is associated with the band bending in the depletion region inside the semiconductor.

The equilibrium contact condition of a semiconductor and an electrolyte is shown in Fig. 15. This graph displays the case for n-type semiconductor. The depletion layer curve is opposite where p-type semiconductor is used. It should be noted here that the carrier for n-type semiconductor is electrons in conduction band (not the electrons in valence band) and that for p-type semiconductor is holes in valence band (not the holes in conduction band). The current–bias characteristic for semiconductor–electrolyte electrode interface shows diode-like characteristics due to this carrier distribution.

An interesting property of the electrochemical reaction using semiconductor electrode is photoelectrochemical reaction without bias. The photoelectrochemical reaction occurs under illuminated light, where the energy is larger than the band gap energy of semiconductor, even without external bias as shown in Fig. 16.

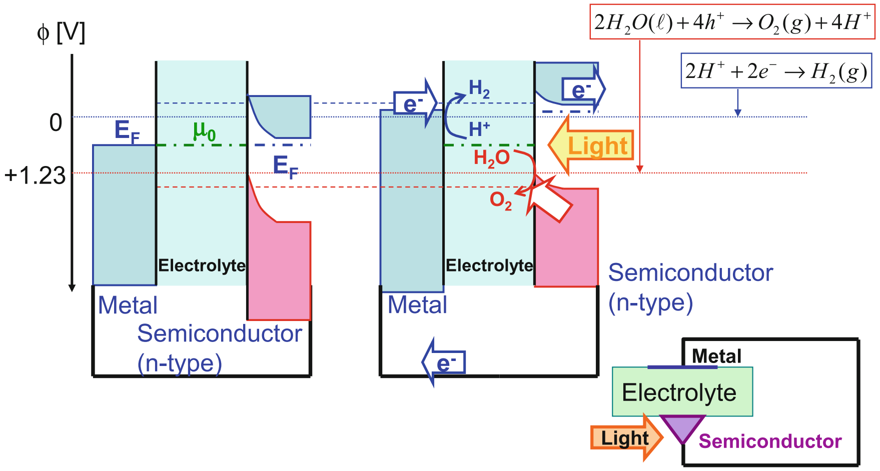


Fig. 16 Schematic diagram for photoelectrochemical reaction using n-type semiconductor

The keypoint of this reaction is the generated minority carrier by light absorption, that is, holes for n-type semiconductor and electrons for p-type semiconductor, respectively. The minority carrier in semiconductors can move to the interface between a semiconductor and electrolyte due to the electric field in the depletion layer, which is formed by the semiconductor–electrolyte contact. The minority carrier promotes photoelectrochemical reaction at the surface of the semiconductor, that the reaction is oxidation for n-type semiconductor and reduction for p-type

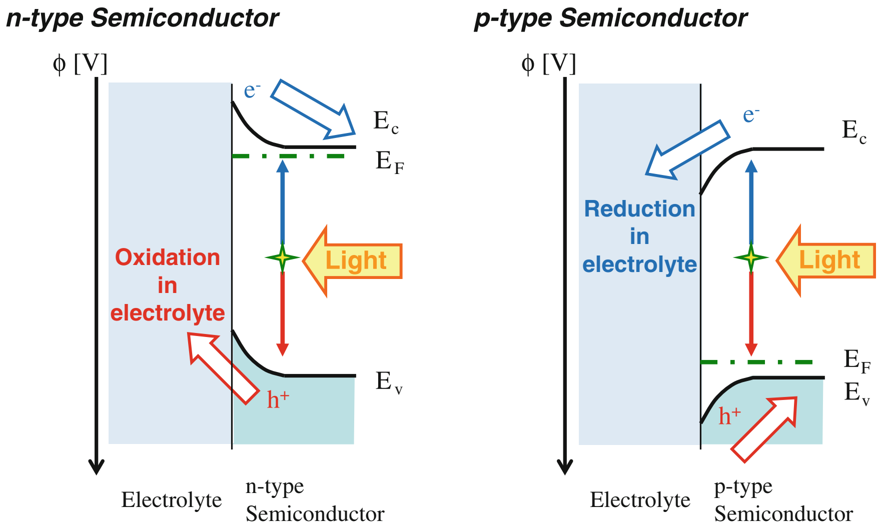


Fig. 17 Schematic diagram for photoelectrochemical reaction for n-type and p-type semiconductor electrode without bias

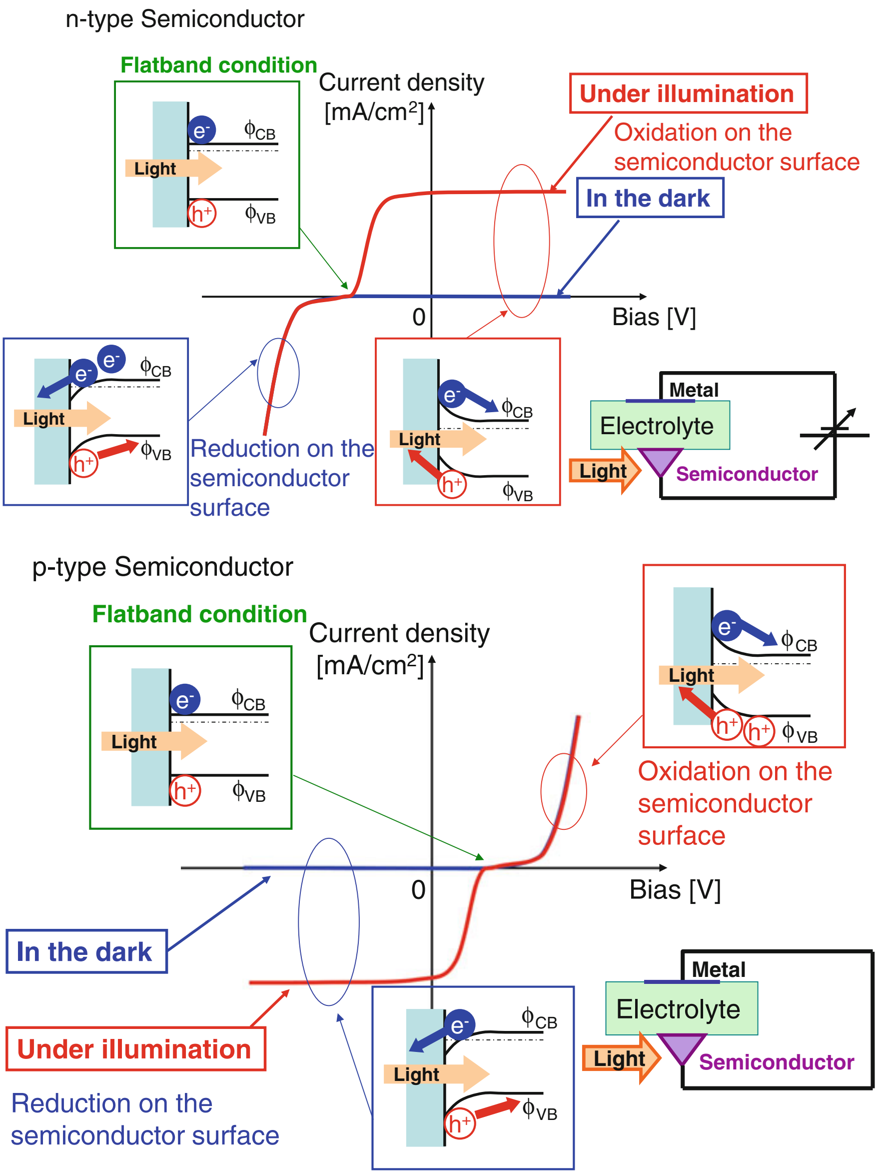


Fig. 18 Schematic current–bias diagram for semiconductor–electrolyte–metal configuration. The difference for n-type and p-type semiconductors are also shown

semiconductor, respectively. The differences in the photoelectrochemical reaction between the n-type and p-type semiconductors are shown in Fig. 17. This reaction without bias is the basic reaction for the energy conversion by photoelectrochemical reaction.

The current–bias characteristics is opposite between an n-type semiconductor and a p-type semiconductor as shown in Fig. 18. Current is not observed at the reverse bias region without light illumination. Photocurrent is observed in this reverse bias region when the light, where the energy exceeds the band gap energy, is illuminated. Band diagrams corresponding to the applied bias are also illustrated in Fig. 18. The band bending inside the semiconductor can be changed by the applied bias but the energies of conduction/valence band edges at the surface of the semiconductor cannot be changed generally because the existence of the absorbed molecule at the semiconductor surface is not changed by the applied bias. As a result, band bending in the depletion layer is changed by the applied bias. This is the cause of the dependence of current density on the applied bias. The flatband condition, where the band edges are flat, corresponds to the bias at which current density is zero.

References

1. Reference for Thermodynamics. For example Fermi E (1956) Thermodynamics. Dover Books on Physics, Dover Publications. ISBN: 0-486-60361-X; Prigogine I, Defay R (1954) Chemical thermodynamics. Prentice Hall Press, Englewood Cliffs. ISBN: 0-582-46283-5)
2. For example Marcus RA (1956) On the theory of oxidation-reduction reactions involving electron transfer I. J Chem Phys **24**:966–978; Marcus RA (1956) Electrostatic free energy and other properties of states having nonequilibrium polarization I. J Chem Phys 24:979–989; Memming R (2001) Semiconductor electrochemistry, Chap. 6. Wiley-VCH, New York, pp 112–150. ISBN: 3-527-30147-X
3. Sze SM (1981) Physics of semiconductor devices, Chap. 1, 2nd edn. Wiley, New York, pp. 7–60. ISBN: 0-471-05661-8
4. Lohmann F (1967) Fermi-Niveau und Flachbandpotential von Molekülkristallen aromatischer Kohlenwasserstoffe. Z Naturforsch a 22:843–844 (in German); Memming R (2011) Semiconductor eectrochemistry, Chap. 3. Wiley-VCH, New York, pp. 46–60. ISBN: 3-527-30147-X
5. Dweydari AW, Mee CHB (1975) Work function measurements on (100) and (110) surfaces of silver. Phys Stat Sol A 27:223–230
6. Memming R (2011) Semiconductor electrochemistry, Chap. 7. Wiley-VCH, New York, pp. 151–40. ISBN: 3-527-30147-X
7. Nozik AJ, Memming R (1996) Physical chemistry of semiconductor-liquid interfaces. J Phys Chem 100:13061–13078