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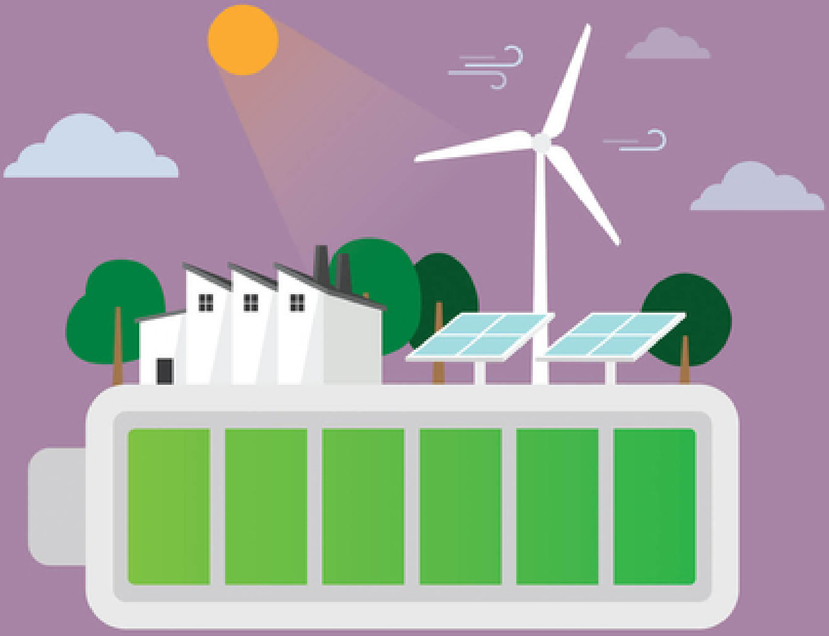
Towards Next Generation Energy Storage Technologies

From Fundamentals to Commercial Applications



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Editor

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Preface

The excessive use of nonrenewable fossil energy has triggered energy crises and environmental degradation. To address these issues, replacing nonrenewable fossil energy with renewable energy such as solar, wind, and tidal energy has been proposed and rapidly developed. However, in general, renewable energy cannot provide stable electric output due to its susceptibility to the environment. To harvest renewable energy and achieve output with the required power density, incorporating electrochemical energy storage technologies is believed to be an effective strategy that prevents the wasting of renewable energy. In addition, replacing gasoline-powered cars with electric-powered cars is a promising way to reduce dependence on nonrenewable energy sources, with their electricity supply primarily coming from electrochemical energy storage technologies. Hence, developing electrochemical energy storage technologies is critical to cope with the energy crises and environmental degradation, and hence, they have attracted ever-increasing attention in recent years.

The currently available electrochemical energy storage techniques, dominated by lead–acid batteries, lithium-ion batteries (LIBs), and supercapacitors (SCs), have greatly developed and changed our daily lives. The energy density of state-of-the-art commercial technologies (LIBs) can reach about 180~300 Wh kg^{-1}, which makes them beneficial for applications in electric vehicles and grid-scale energy storage systems. Nevertheless, safety issues (caused by lithium dendrite growth and the use of flammable electrolytes), high cost of raw materials, and the limited energy/power density hinder the widespread application of energy storage technologies in large-scale energy storage systems and long-lasting electric vehicles. To address these challenges, many novel promising energy storage technologies (e.g. solid-state batteries, lithium–sulfur batteries, and lithium–carbon dioxide batteries) based on various electrochemical redox reactions have been proposed recently. These newly emerged technologies are of high energy density, low cost, and high safety and can facilitate a wide range of applications in electric vehicles, grid-scale energy storage systems, and other devices (e.g. power supply of equipment applied in aerospace, deep sea, and polar regions). Substantial work has been devoted to exploring the potential of the aforementioned energy storage technologies, and some of them have stepped into the practical application stage.

To push forward the development of these promising energy storage technologies, this book focuses on the fundamental energy storage mechanisms, critical achievements, and challenges of next-generation energy storage technologies from the perspective of practical applications. This book discusses the recent progress of commercialized energy storage technologies (LIBs and SCs) first and then comprehensively introduces the recent progress of newly emerged energy storage technologies. This book aims to help readers clarify what are the critical issues that hinder the widespread application of these energy storage technologies, translate complex scientific concepts into easily understandable language, and demonstrate the potential of these technologies in practical applications through case studies. In this rapidly evolving field, acquiring up-to-date knowledge is challenging, but we are committed to providing the most up-to-date and comprehensive information to help readers stay informed about the latest developments in energy storage technology.

Lastly, we would like to express our gratitude to all individuals and institutions who have contributed to the writing and publication of this book, as well as to all scientists who have contributed to the development of energy storage technologies. We hope that this book will contribute to the development of energy storage technologies and the goal of achieving clean, sustainable energy.

April 2024 *Minghua Chen*
Harbin, China

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The writing of this book was enriched by numerous scientific discussions. I would like to thank my colleagues for their valuable comments. Their knowledge, experience, and skills have greatly enriched this book and have advanced our understanding of next-generation energy storage technologies. We have much gratitude for the many graduate students who have worked on the examples cited and proofread the chapters.

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1

Introduction

Minghua Chen[1] *and Yu Li*[2]

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With ever-increasing concerns about limited fossil fuel reserves (e.g. oil, coal, and natural gas) and the environmental degeneration caused by the emission of harmful gases (e.g. CO_2 and SO_2), there is an urgent need to replace polluted unrenewable energy resources with clean renewable energy resources (e.g. wind and solar energy). Nevertheless, the generation of renewable energy is intermittent, and the electricity output is unstable. Harvesting renewably generated electricity using an electrochemical energy storage system is a practical way to address the intrinsic issues with renewable energy. In addition, removable electrochemical energy storage technologies play a huge role in our daily lives. For example, phones, laptops, and smartwatches we use daily are powered by high-energy-density lithium-ion batteries (LIBs). Some advanced vehicle manufacturing companies (e.g. BYD and Tesla) have launched electric vehicles, in an attempt to decrease harmful gas emissions. Nevertheless, the application of electrochemical energy storage technologies in a wide range of fields is still challenging. The properties of energy storage technologies depend on the applications and the market they are being used. For example, portable energy storage devices and energy storage systems used by people in their daily lives should be energy dense and highly safe. Outdoor energy storage systems in cold regions should possess good low-temperature energy storage performance. Energy storage devices used in regenerative braking should have both high energy density and power density.

To push forward the energy structure upgrade, numerous studies have been dedicated to the investigation of advanced energy storage technologies. Various promising energy storage technologies (e.g. high-safety solid-state batteries, aqueous lithium-ion batteries [ALIBs], aqueous zinc-ion batteries [AZIBs], high-energy-density lithium–sulfur batteries [Li-S batteries], metal–air batteries, and metal–CO_2 batteries) have been developed. These advanced energy storage technologies are designed for different requirements and markets and show

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promise for next-generation energy storage technologies. In this book, recent advances in energy storage technologies that can be commercialized are thoroughly summarized and discussed in detail, providing the landscape of the state-of-the-art electrochemical energy storage technologies and their widespread practical applications. First, the fundamental knowledge about energy storage technologies will be introduced, and then the practical progress of the existing commercial energy storage technologies and the corresponding energy storage properties, as well as critical challenges, will be presented. Subsequently, energy storage mechanisms, critical issues, design strategies, and practical progress of next-generation energy storage technologies will be discussed. Finally, future trends in these advanced energy storage technologies will be presented. We hope this book can contribute to the development of electrochemical energy storage technologies.

2

Fundamentals of Electrochemical Energy Storage Technologies

Minghua Chen[1] *and Yu Li*[2]

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2.1 Typical Battery Patterns and Corresponding Functions

Of late, numerous electrochemical energy storage systems have been developed to meet the demands of our daily lives, of which five are commonly used and commercialized: lead–acid batteries, lithium-ion batteries (LIBs), nickel metal hydride (Ni-MH) batteries, nickel–zinc (Ni-Zn) batteries, and supercapacitors. Lead–acid batteries are most commonly used in gasoline cars for engine ignition and running the auxiliary electronics when the engine is off. However, they are harmful to the environment, and replacing them with less expensive, safe, and energy-dense electrochemical energy storage technologies is one of the major challenges faced by researchers. Ni-MH batteries and Ni-Zn batteries are typical alkaline batteries using KOH-based electrolytes. Their energy density is slightly higher than that of lead–acid batteries; however, their output voltage is highly restricted by the limited theoretical thermodynamic stable potential (1.23 V). In addition, alkaline electrolytes will continuously etch the current collector and zinc anode, and thus, cycling lifespans of these batteries can rarely be more than 500 cycles without obvious decay [1]. LIBs have been widely used in portable devices, electric vehicles, and grid-scale energy storage systems due to their high output voltage, high energy density, and long cycling lifespans. The lifespan of advanced LIBs can be more than 10,000 cycles. Although the safety of using LIBs is ensured in various portable devices (e.g. phones and laptops), thermal runaway and explosion can occur in grid-scale energy storage systems and electric vehicles due to the growth of lithium dendrite, which induces internal short circuits and releases substantial heat to ignite flammable electrolytes. Dendrite growth is related to overcharging and over-discharging of batteries. These can be prevented by rational battery management, which can be efficiently controlled in a single

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cell and hardly controlled in the battery pack [2]. The more the number of LIBs, the higher the thermal runaway risk. Supercapacitor is a power-density-superior electrochemical energy storage device that harvests energy via a rapid physical adsorption/desorption process. However, the energy density of supercapacitors is more than tenfold lower than that of batteries, and thus, they cannot be used as a main power source for the functioning of electric equipment [3].

Nevertheless, all the abovementioned electrochemical energy storage technologies have changed our daily lives and have similar component patterns. In general, all of them have two electrodes. If the electrode materials used are different, they can be classified into cathode and anode, which will be introduced in the following sections. Materials used as electrodes should at least be good electronic conductors. Meanwhile, the cathode and anode need to be separated by electrolytes and separators to avoid direct contact between them. The energy storage mechanism of electrochemical energy storage technologies is mainly based on the electrochemical reactions (reversible redox reaction or intercalation) at cathode and anode. It is noteworthy that the redox reactions happened in electrochemical energy storage devices is quite different with chemical reactions. The primary distinction between an electrochemical reaction and a chemical redox reaction is that, in the former, reduction occurs at one electrode and oxidation occurs at the other, while in the latter, both reduction and oxidation occur at the same electrode. This distinction has several implications. In an electrochemical reaction, oxidation is spatially separated from reduction. Thus, the entire redox reaction is divided into two half-cells. The rate of these reactions can be controlled by externally applying a potential difference between the electrodes, e.g. using an external power supply, a feature that is not present in chemical reactors. Furthermore, electrochemical reactions are always heterogeneous; i.e. they always occur at the interface between the electrolyte and an electrode (and possibly a third phase, such as a gaseous or insulating reactant). Even though half-cell reactions occur at different electrodes, reaction rates are coupled by the principles of conservation of charge and electroneutrality.

2.1.1 Cathode

To date, many electrochemical battery systems have been proposed. The term "cathode" is a relative concept. A cathode in one electrochemical system can be an anode in another system. For example, MnO_2 is a cathode material in Zn-Mn batteries but an anode material in LIBs. Hence, whether a material is a cathode or anode depends on the relative redox potential of the material, which, in an electrochemical device, can be deduced based on standard reduction potential. Standard reduction potential describes the ability of a material to release electrons. The lower the standard reduction potential, the stronger the ability to release electrons. Therefore, when two materials are assembled into an electrochemical system, one with the higher reduction potential is the cathode, and the other one is the anode. Theoretically, any material can be assembled into electrochemical batteries with appropriate electrolytes. The output voltage of an electrochemical

Table 2.1 The standard reduction potential of typical materials.

	Half-cell reaction		Potential
↑ Stronger pulling electron	$F_2 + 2e^- \rightleftharpoons 2F^-$	Stronger giving electron ↓	+2.87 V
	$Pb^{4+} + 2e^- \rightleftharpoons Pb^{2+}$		+1.67 V
	$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$		+1.36 V
	$Ag^+ + 1e^- \rightleftharpoons Ag$		+0.81 V
	$Fe^{3+} + 1e^- \rightleftharpoons Fe^{2+}$		+0.77 V
	$Cu^{2+} + 2e^- \rightleftharpoons Cu$		+0.34 V
	$2H_2 + 2e^- \rightleftharpoons H_2$		0.00 V
	$Fe^{3+} + 3e^- \rightleftharpoons Fe$		–0.04 V
	$Pb^{2+} + 2e^- \rightleftharpoons Pb$		–0.13 V
	$Fe^{2+} + 2e^- \rightleftharpoons Fe$		–0.44 V
	$Nz^{2+} + 2e^- \rightleftharpoons Zn$		–0.76 V
	$Al^{3+} + 3e^- \rightleftharpoons Al$		–1.66 V
	$Mg^{2+} + 2e^- \rightleftharpoons Mg$		–2.36 V
	$Li + 1e^- \rightleftharpoons Li$		–3.05 V

system depends on the potential difference between the cathode and anode. Some electrodes commonly used in diverse electrochemical energy storage technologies are $LiCoO_2$, $LiFePO_4$, $LiMn_2O_4$, $LiNiCoMnO_2$, and $Ni(OH)_2$. All these possess unique crystal structures (e.g. layer structure and sodium super ionic conductor (NASICON) structure) and have sufficient space to store ions and ensure rapid ion transportation (Table 2.1).

2.1.2 Anode

In an electrochemical system, anode is the electrode that reacts at a lower potential among the two electrodes. Metals and graphite are some of the commonly used anode materials in state-of-the-art energy storage technologies. Usually, graphite and other carbon materials are used as host materials to store energy through reversible ion intercalation. The capacity of these materials is usually less than 300 mAh g^{-1}. In metal anodes, energy storage occurs via reversible ion plating/striping. Theoretically, the capacity of metal anodes is much higher than that of carbon materials. However, in metal anodes, irreversible etching and uneven plating/striping lead to the formation of dendrites and "dead metal," thus presenting them with poor cycling stability and high safety hazard. Designing advanced electrolytes and artificial solid electrolyte interphase (SEI) for ensuring uniform ion plating/striping and protecting irreversible etching is an interesting topic in the field of electrochemical energy storage.

2.1.3 Electrolyte

The electrolyte is an essential component that ensures rapid ionic conductivity inside the battery and prevents direct contact between cathodes and anodes. Electrolytes used in various electrochemical energy storage technologies should generally meet the following basic requirements [4]: (i) high ionic conductivity, at least $1 \times 10^{-3} \sim 2 \times 10^{-2}\ \mathrm{S\,cm^{-1}}$; (ii) high thermal and chemical stability, with no separation in a wide voltage range; (iii) a wider electrochemical stability window (ESW) to keep the electrochemical performance stable in a wider voltage range; (iv) good compatibility with other parts of the battery, such as electrode materials, electrode current collectors, and separators; and (v) safe, nontoxic, and nonpolluting.

Based on the energy storage mechanism of electrode materials, various electrolytes have been developed, which can primarily be classified into three categories: aqueous electrolytes, organic electrolytes, and solid-state electrolytes. In aqueous electrolytes, water is used as the solvent. The following are the major advantages of aqueous electrolytes: low cost, high ionic conductivity (compared with organic electrolytes and solid-state electrolytes), and being nonflammable and recyclable. Their primary disadvantage is the limited thermodynamic ESW of water. Theoretically, water decomposes above a voltage of 1.23 V. Considering the overpotential of water splitting, the voltage of aqueous electrolytes is less than 2.0 V. Since energy density is highly dependent on output potential, electrochemical energy storage technologies with aqueous electrolytes usually have much lower energy density than those using organic electrolytes and solid-state electrolytes. Recently, numerous strategies have been developed to make the ESW of aqueous electrolytes wider, e.g. water-in-salt (WIS) electrolytes, deep eutectic solvents, and artificial SEI. In particular, using well-designed WIS electrolytes, the ESW of aqueous electrolytes can be extended to 3 V, as proposed in some previously published studies. However, usually, only electrolytes based on the trifluoromethanesulfonimide (TFSI) anion can barely work above 3 V, and the ESW of aqueous electrolytes using inorganic salts can rarely reach above ~2.5 V in devices. Recent studies suggest that an SEI derived by the decomposition of the TFSI anion is highly porous and dynamically soluble in electrolytes [5]. Since the SEI is not stable, water splitting continuously occurs in LiTFSI-based WIS electrolytes. The continuous generation of gases increases the pressure in the batteries, leading to rapid capacity decay and even explosion. It is proposed that even in high-cost LiTFSI-based electrolytes, electrochemical energy storage devices with aqueous electrolytes can rarely work above 2 V and do not present apparent superiorities over lead–acid batteries [6]. Gel electrolytes are a type of aqueous electrolytes that confine water molecules through strong interactions that can effectively prohibit the decomposition of water at low salt concentrations, which may be a practical way to achieve high output voltage and high energy density in energy storage technologies with aqueous electrolytes. The success of lead–acid batteries can provide a meaningful reference for the development of high-voltage energy storage technologies using aqueous electrolytes.

In organic electrolytes, an organic liquid is used as a solvent to dissolve salts. State-of-the-art LIBs use organic electrolytes, in which $LiPF_6$ is used as the salt and ethylene carbonate (EC)/propylene carbonate (PC)/fluoroethylene carbonate (FEC) is used as the solvent. Each component in the organic electrolytes of LIBs is carefully selected; EC/PC can provide high ionic conductivity with good electrochemical stability and large ESW, while FEC can help form LiF-rich SEI, to ensure stable and rapid ion transportation between the electrode and electrolyte. The critical challenge in using organic electrolytes is safety issues. Dendrites can form even in state-of-the-art technologies. Short circuits induced by dendrites will release a substantial amount of heat to accelerate the decomposition of organic electrolytes and form H_2/O_2 gas, leading to thermal runaway and even explosion.

Since the thermal runaway of LIBs is attributable to the decomposition and poor thermal stability of organic electrolytes, nonflammable and high-mechanical-strength solid-state electrolytes are developed to ensure the safety of LIBs and other batteries. Solid-state electrolytes can be classified into two groups: inorganic electrolytes and polymer electrolytes. Inorganic electrolytes possess sufficient mechanical strength to prevent the formation of metal dendrites and high thermal stability to achieve intrinsic safety. Their ionic conductivity is $1 \times 10^{-2} \sim 10^{-4}\ \mathrm{S\,cm^{-1}}$, which is close to that of liquid electrolytes and meets the criteria for applications in various electrochemical energy storage devices. However, solid–solid electrode–electrolyte interfaces cannot establish an intimate contact, leading to large interface impendence and poor capacity. To ensure good contact, high external pressure is usually required for batteries using solid-state electrolytes, which is hard to achieve in real-world scenarios. Furthermore, the volume expansion of electrodes results in high mechanical strength at electrode–electrolyte interfaces, which leads to the pulverization and falling off of active materials, resulting in poor cycling stability. In contrast, polymer electrolytes are usually soft and can tolerate the volume expansion of active materials and improve the electrode–electrolyte contact, which is conducive to promoting the reversible capacity and cycling lifespans. Nevertheless, polymer electrolytes do not have high enough mechanical strength to prevent short circuits induced by dendrite growth, and their ionic conductivity ($\sim 10^{-6}\ \mathrm{S\,cm^{-1}}$) is insufficient for a high ion transport pathway for electrochemical reactions. Considering all the abovementioned points, combining the advantages of inorganic electrolytes and those of polymer electrolytes can be a promising way to achieve a practicable solid-state electrolyte, and this has been widely investigated in recent years.

2.2 Operating Mechanism of Devices

2.2.1 Potential and Thermodynamics

The working mechanism of an electrochemical battery depends on the intrinsic properties of the materials used, especially thermodynamic properties. As mentioned earlier, a redox reaction of a battery can occur separately as the oxidation reaction takes place at one electrode and the reduction reaction at another, i.e. the whole battery acting as two half-cells. The energy change of the reaction is given by the change in Gibbs free energy for each half-cell reaction:

$$\Delta G = \left(\sum_i s_i \mu_i\right)_{\text{cathode}} - \left(\sum_i s_i \mu_i\right)_{\text{anode}} \tag{2.1}$$

where G refers to the Gibbs free energy, μ_i represents the electrochemical potential of species i, and s_i is the stoichiometric coefficient of species i. If ΔG is negative, electrons will spontaneously flow from the anode to the cathode. This is the driving force for ensuring spontaneous redox reactions in electrochemical batteries. The anode side usually has a lower electrochemical potential, whereas the cathode side has a higher electrochemical potential. The electrochemical potential of different materials may have different reference potentials, e.g. Li/Li^+, Na/Na^+, Ag/AgCl, and Hg/HgO. However, these electrochemical potentials based on different reference potentials can be converted to a standard reference potential.

The maximum amount of work (W_{max}) that can be performed by an electrochemical cell is equal to the product of the cell potential (E°_{cell}) and the total charge transferred during the reaction (nF):

$$W_{\text{max}} = nFE_{\text{cell}} \tag{2.2}$$

W_{max} is expressed as a negative number because work is being done by a system (i.e. an electrochemical cell with a positive potential) on its surroundings.

The change in Gibbs free energy (ΔG) is also a measure of the maximum amount of work that can be performed during a chemical process ($\Delta G = W_{\text{max}}$). Consequently, the relationship between the potential of an electrochemical cell and ΔG can be deduced as follows:

$$\Delta G = -nFE_{\text{cell}} \tag{2.3}$$

A spontaneous redox reaction is therefore characterized by a negative value of ΔG and a positive value of E°_{cell}. When both reactants and products are in their standard states, the relationship between ΔG° and E°_{cell} can be expressed as follows:

$$\Delta G^{\circ} = -nFE^{\circ}_{\text{cell}} \tag{2.4}$$

A spontaneous redox reaction is characterized by a negative value of ΔG°, which corresponds to a positive value of E°_{cell}. Thus, equilibrium potential is a function of the intrinsic nature of the species present, as well as their concentrations and, to a lesser extent, temperature. No net current flows at equilibrium, and random thermal collisions between the reactant and product species cause the reaction to occur, sometimes in the forward direction and sometimes in the backward direction. At equilibrium, the rate of the forward reaction is equal to that of the backward reaction. The potential of the electrode at equilibrium is a measure of the electrochemical potential (i.e. energy) of electrons at equilibrium with the reactant and product species. In brief, electrochemical potential can be related to molality m_i and activity coefficient γ_i as follows:

$$\mu_i = \mu_i^\theta + RT \ln m_i\gamma_i \tag{2.5}$$

where μ^θ is independent of concentration, R is the universal gas constant (8.3143 J mol^{-1} K^{-1}), and T is the temperature in kelvin.

One can electrically control the electrochemical potential of electrons in an electrode by connecting it to an external power supply, thereby perturbing the equilibrium and driving a reaction. Applying a negative potential to an electrode increases the energy of electrons. This increase in the energy of electrons above the lowest unoccupied molecular orbital of a species in the adjacent electrolyte results in a reduction of that species. This reduction current (flow of electrons into the electrode and from there into the reactant) is also called cathodic current, and the electrode at which this occurs is called the cathode. Conversely, applying a positive potential to an electrode decreases the energy of electrons, causing them to be transferred from the reactants to the electrode. The electrode where such an oxidation reaction occurs is called the anode.

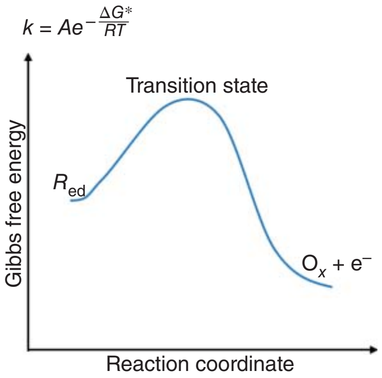
2.2.2 Kinetics of Electrode Reactions

As mentioned earlier, the redox reaction is separated into oxidation and reduction that occur in two electrodes. In galvanic cells, the reduction reaction occurs at the cathode side, and the oxidation reaction occurs at the anode side. The rate of reaction can be expressed using the transition state theory (Figure 2.1). For a reaction to occur, it needs to overcome an energy barrier (Gibbs free energy). Considering this, the rate of reaction can be expressed as follows:

$$k = Ae^{-\frac{\Delta G^*}{RT}}$$

The chemical reaction process on inert electrode surfaces involves the transportation of electrochemically active species (usually ions) from the bulk electrolyte to the region that is very close to the electrode surface, preceding chemical reactions

Figure 2.1 Rate of reaction for a chemical process.



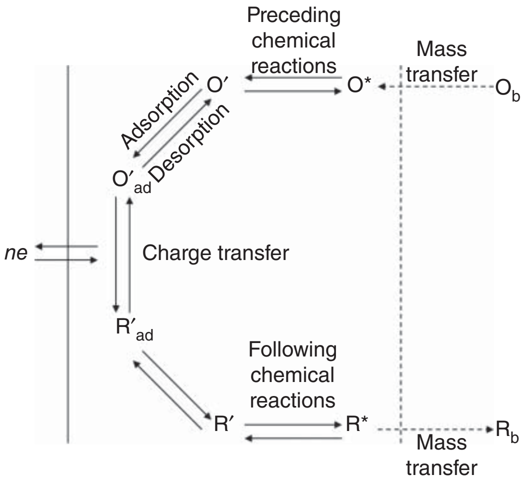


Figure 2.2 Typical charge transfer process at an inert electrode surface.

(not applicable for all electrochemical reactions however), adsorbing on the electrode surface, ensuring charge transfer, desorbing from the electrode surface, following chemical reactions (not applicable for electrochemical reactions however), and migrating to the bulk electrolyte (Figure 2.2). Adsorption, charge transfer, and desorption processes occur rapidly and cannot be separated based on the existing electrochemical technologies or structural characterization technologies. As for an active electrode, the chemical reaction process is different from that of an inert electrode. The charge transfer process can occur at the internal of the electrode. In addition, ions are solvated and undergo a desolvation process before entering the electrode, which kinetically slows down the reaction rate. To make things more complicated, some side reactions occur before the reversible energy storage reaction, which lead to continuous consumption of electrolytes or the formation of SEI.

In addition to the chemical reaction process, the bias voltage acts as a driving force to initiate electrochemical reactions at electrodes and is another essential parameter that affects reaction kinetics. This driving force is termed “surface overpotential” and is denoted as η_s. The rate of a reaction can often be related to surface overpotential using the Butler–Volmer equation, as follows:

$$i = i_0 \left[\exp\left(\frac{\alpha_{\text{ox}} nF}{RT}\eta_s\right) - \exp\left(\frac{\alpha_{\text{red}} nF}{RT}\eta_s\right)\right] \tag{2.6}$$

The first term on the right-hand side of the equation is the rate of the oxidation reaction, whereas the second term is the rate of the reduction reaction. The difference between these rates is the net rate of reaction. The parameter i_0 is the exchange current density and is analogous to the rate constant used in chemical kinetics. Based on the above equation, the Tafel $I - \eta$ relationship at very large $|\eta|$ can be expressed as follows:

$$\eta_s = \frac{RT}{\alpha_{\text{red}} nF} \ln \frac{-i}{i_0} \tag{2.7}$$

$$\eta_s = -\frac{RT}{\alpha_{ox} nF} \ln \frac{i}{i_0} \tag{2.8}$$

This relationship is also called a semi-logarithm relationship. A reaction with a high i_0 value is often called fast or reversible, and $I - \eta$ usually follows a linear relation. In contrast, a low i_0 value approaching disappearance indicates the highly polarized electrode and that the chemical reaction is hardly reversible. The $I - \eta$ relation of a low i_0 value usually is a semi-logarithm relation or similar to the charging behavior of a RC circuit. For a high i_0 value, a high current density can be obtained with a low surface overpotential. In a reaction involving high exchange current density, both the forward and backward reactions occur rapidly, and the net direction of the reaction depends on the sign of the surface overpotential. The exchange current density of the reaction depends on the concentrations of reactants and products, temperature, the nature of the electrode–electrolyte interface, and impurities that may contaminate the surface. Each of these factors can change the value of i_0 by several orders of magnitude; i_0 can range from over $1\,\text{mA}\,\text{cm}^{-2}$ to less than $10^{-7}\,\text{mA}\,\text{cm}^{-2}$. The parameters α_{ox} and α_{red}, called apparent transfer coefficients, are additional kinetic parameters that inform how an applied potential favors one direction of the reaction over the other. The values of these parameters usually range between 0.2 and 2.

Overpotential is the potential difference above the equilibrium potential that is required to overcome the activation energy of the cell reaction to produce a specified current. Hence, the activation energy can also affect the electrode reaction kinetics. As discussed previously, for a reaction to occur, it needs to overcome an energy barrier (Gibbs free energy). The charge transfer process of electrochemical reactions should overcome an energy barrier as well, and this energy barrier is affected by bias voltage. Considering the half-cell of the reduction reaction as an example, the free energy of reduction species (denoted as R_{ed}) is invariant with voltage, whereas the reduction product (denoted as $O_x + e^-$) is highly affected by voltage. To determine the impact of voltage on electrode reaction kinetics, it is assumed that the effect of voltage on free energy change follows a linear relationship (this is undoubtedly an oversimplification). Using this linear relationship, the activation free energies for reduction and oxidation will be considered to vary as a function of the applied voltage (V) as follows:

$$\Delta G'_{\text{red}} = \Delta G'_{\text{red no voltage}} + \alpha FV \tag{2.9}$$

$$\Delta G'_{\text{ox}} = \Delta G'_{\text{ox no voltage}} + (1 - \alpha)FV \tag{2.10}$$

The parameter α is called the transfer coefficient, which typically has a value of 0.5. Physically, this provides an insight into the way the transition state is influenced by the voltage. A value of 0.5 means that the transition state behaves midway between the reactants' and products' response to the applied voltage. The free energy on the right-hand side of Eqs. (2.9) and (2.10) can be considered the chemical component of the activation free energy change. It is dependent only on the species involved and not on the applied voltage. Substituting these activation free energy terms into the expressions for the oxidation and reduction rate constants gives the following:

$$k_{\text{red}} = Z\ \exp\left[\left(\frac{-\Delta G'_{\text{red no voltage}}}{RT}\right)\left(\frac{-\alpha FV}{RT}\right)\right] \tag{2.11}$$

$$K_{\text{ox}} = Z\ \exp\left[\left(\frac{-\Delta G'_{\text{red no voltage}}}{RT}\right)\left(\frac{-\alpha FV}{RT}\right)\right] \tag{2.12}$$

These results suggest that the rate constants for a charge transfer process are proportional to the exponential of the applied voltage. So the electrode reaction kinetics can be changed by simply varying the applied voltage. This result provides the fundamental basis for the experimental technique called voltammetry.

Now that the effects of overpotential and activation energy on electrode reaction kinetics are discussed, the following text introduces the effects of mass transfer. Mass transfer is the movement of species in a medium (liquid, gas, or solid). The rate of mass transfer denotes the number of species passing through a unit area within an interval of unit time. Three processes are related to mass transfer, namely diffusion, migration, and convection. Diffusion is the movement of a charged species derived by a gradient of chemical potential (e.g. concentration gradient), which is also called Fick's first law of diffusion. This can be expressed as follows:

$$J_i^{\text{D}} = -D_i \nabla c_i \tag{2.13}$$

Migration refers to the movement of a species driven by a gradient of electric potential, which can be represented as follows:

$$J_i^{\text{M}} = -\frac{Z_i F}{RT} c_i D_i \nabla \phi \tag{2.14}$$

Convection refers to the movement of a species in the fluid flow. Natural convection is induced by density gradient, whereas forced convection is caused by stirring or other hydrodynamic means, as shown below:

$$J_i^{\text{C}} = v c_i \tag{2.15}$$

Hence, mass transfer in an electrochemical cell can be expressed as follows:

$$J_i = J_i^{\text{D}} + J_i^{\text{M}} + J_i^{\text{C}} \tag{2.16}$$

Usually, some measures can be taken so that only one kind of mass transfer contributes predominantly and others are negligible. In a solution, natural convection is the predominant mass transfer mode, and it ensures the uniform concentrations of all species. However, the velocity of the fluid decreases sharply upon approaching a solid surface. Thus, within a very thin layer near the electrode surface, convection can be neglected. Diffusion and migration are predominant in the near surface reaction of electrodes (called the Nernst boundary layer). If the excess of an inert electrolyte is added to a solution and its concentration is much higher than that of the electroactive species, the electric field and migration rate in the solution can be greatly reduced. Thus, diffusion will be the only predominant mass transfer mode within the thin layer near the electrode surface (called diffusion layer).