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Introduction

The Earth, a dynamic and interconnected system, relies fundamentally on the Sun as its primary energy source. All naturally occurring raw energy on our planet, whether directly or indirectly, stems from the radiant power of the Sun. From the growth of plants through photosynthesis to the formation of fossil fuels over millions of years, the Sun's energy plays a pivotal role in shaping the Earth's energy landscape. Wind patterns and water movements, too, are consequences of the Sun's heating of the Earth's surface. Over the course of evolution, humans have acquired the knowledge to harness and convert these raw natural energies into forms, such as electricity and heat, useful for sustaining daily life. This journey of transformation has resulted in various interchangeable forms of energy, which have become the foundation of our modern existence. In Figure 1.1, we show the six forms of energy that humans have learned to interchangeably transform, underscoring their essential role in supporting and shaping our daily lives.

However, the law of energy conservation requires that energy cannot be created nor destroyed. This means that even though energy changes its form, the total quantity of energy always stays the same. For example, many of the energy converters widely used today involve the transformation of chemical energy through thermal energy into electrical energy. The efficiency of such systems is limited by the fundamental laws of thermodynamics. As of today, the conversion efficiency from naturally occurred fossil fuels to useful electricity is ~35% on average. Such a low efficiency implies a faster depletion of fossil fuels and more emissions of greenhouse gas (CO_2) into the atmosphere. In this aspect, those direct energy-conversion devices, such as fuel cells and electrolyzers that bypass the intermediate step of chemical-to-thermal conversion, are advantageous. Unbound by the thermodynamic law, these direct energy converters can achieve high efficiency, thus less fuel consumption and carbon emissions in producing the same amount of electricity. Electrochemical cells are a representative class of such high-efficiency direct energy converters. They are currently deemed one of the best technologies to address all aspects of energy-related challenges such as emissions/pollutions, efficiency, intermittency, cost, and supply chains.

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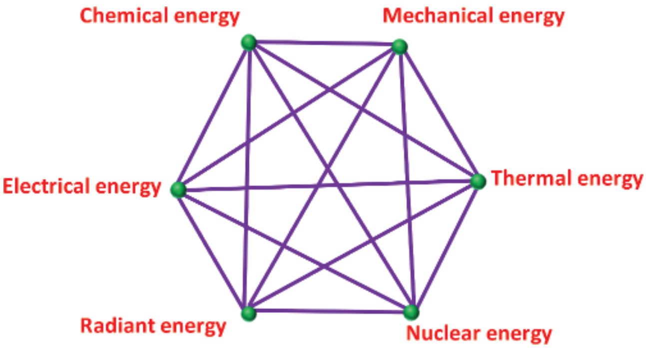


Figure 1.1 Six forms of energy and their interchangeable transformations.

1.1 Brief History of Electrochemical Cells

The history of electrochemical cells began with Italian physicist Alessandro Volta. In 1800, he demonstrated a so-called “voltaic pile”, see Figure 1.2 [1], in which Cu and Zn discs were separated by cardboard or felt spacers soaked in salt water (the electrolyte). This is believed to be the first prototype of the modern battery producing electrical current from chemical reactions. Following Volta’s pioneering work, British scientist Humphry Davy was the first to link the production of electricity with the occurring chemical reactions (precisely Gibbs free energy change of the reactions). His student Michael Faraday took a step further predicting how much product can be produced by passing a certain amount of electric current though a chemical compound, a process that he called “electrolysis” and later known as Faraday’s law.

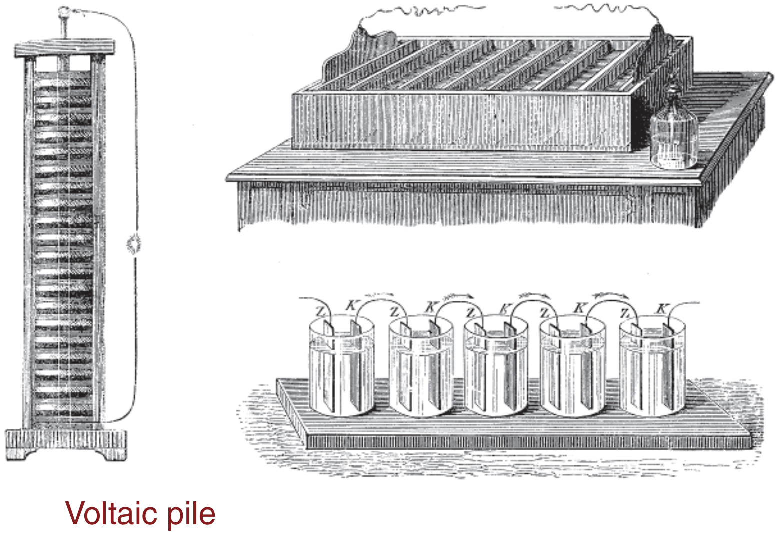


Figure 1.2 Volta’s voltaic pile [1]. Source: acrogame/Adobe Stock.

The above two important works laid the foundation for today's electrochemical cells to produce power and chemicals.

Modern electrochemistry has now become a branch of chemistry studying the interplay of electrical and chemical energy. Governed by Faraday's law, a large portion of this field deals with the study of changes in chemical energy (or Gibbs free energy) caused by the passage of an electrical current or vice versa, the production of electrical current by chemical reactions [2]. These basic laws of electrochemistry have been successfully applied to a wide range of fields from fundamental phenomena (e.g. electrophoresis and corrosion) and to technologies (batteries, sensors, fuel cells, water electrolyzers, smelters, and metal platers), making significant impacts on every part of our life and economy.

1.2 Configuration of Electrochemical Cells

In electrochemical cells, chemical and electrical energy can be reversibly transformed into each other. An electrochemical cell consists of three basic components: **electrolyte, cathode**, and **anode**. Electrolyte is an ionic conductor and electron insulator. Cathode is the electrode where reduction reactions (accepting electrons from external circuit) occur, while anode is the opposite electrode to cathode, where oxidation reactions (releasing electrons to external circuit) take place. Therefore, both cathode and anode are typically electron conductors and catalytically active to the respective reduction and oxidation reactions. As such, they are often labeled as electrocatalysts by electrochemists to differentiate from conventional catalysts in chemical catalysis that do not involve electron transfer from/to external circuit. At the device level (e.g. batteries, electrolyzers, and fuel cells), current collector is also considered as an integral component of the cell. The performance (e.g. power, or chemical production rate) of an electrochemical cell is generally determined by the ohmic resistance of electrolyte and current collector, and polarization resistances (activation and concentration) of the two electrodes.

The modern electrochemical cells primarily comprise fuel cells, electrolyzers, and batteries, but are often extended to include pseudocapacitors (supercapacitors) and photoelectrochemical cells that involve electron transfer. Fuel cells are a type of concentration or galvanic cell operated in an **open system** for the purpose of producing electrical power. For a continuous power generation, the underlying chemical reactions must be spontaneous, which is characterized by a negative Gibbs free energy change and a positive electromotive force (EMF) or Nernst potential (E_n). Conversely, electrolyzer is a type of electrolytic cell operated in an open system for the purpose of producing chemicals. Since the underlying chemical reactions are non-spontaneous, which is characterized by positive Gibbs free energy change and negative E_n, electrical current is needed to drive the reaction. If the produced chemicals can be stored externally for later use, electrolyzers are also viewed as an energy storage device. The capacity of fuel cells and electrolyzers is scaled by the **surface area** (**not by mass**) because they are open systems.

In contrast to fuel cells and electrolyzers, batteries operate as a **closed (or semi-closed) system** with alternating power ($E_n > 0$) and chemical production ($E_n < 0$) modes. The chemical energy is shuttled between the two electrodes with electrons as the charge regulator through the external circuit. Therefore, the capacity of a battery is influenced by the mass of active electrodes and typically scaled by **weight** and/or **volume**.

1.3 Half-Reactions in Electrochemical Cells

The overall reaction of an electrochemical cell is represented by a chemical reaction. This chemical reaction is made up of two independent half-electrode reactions that describe the real chemical changes at the two electrodes. Each half-reaction describes electro-active species involved in electron transfer at the corresponding electrode and defines a fixed potential E (E^0 under standard condition); refer to Appendix B for these values. The open circuit voltage OCV of a full cell is, therefore, the difference of the electrode potentials of the two half-electrode reactions,

$$\mathrm{OCV} = E^0(+) - E^0(-) \tag{1.1}$$

For the half-reaction of interest, the electrode at which it occurs is called the working electrode (WE). To accurately characterize its behaviors, a three-electrode cell configuration is needed, where a reference electrode (RE) and counter electrode (CE) are included, see Figure 1.3.

Example 1.1
Calculate the OCV of the cell: (−) $Cu(s)|Cu^{2+}(aq)$ ||salt bridge|| $Ag^+(aq)|Ag(s)$ (+).

Solution
From Appendix B, $E^0(Cu/Cu^{2+}) = 0.520\,V$, $E^0(Ag/Ag^+) = 0.7996\,V$,
$OCV = 0.7996 - 0.520 = 0.2796\,V$.

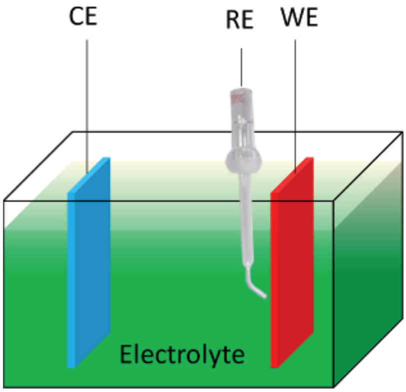
The functionality of RE is to provide a constant potential to which the potential of WE is referred. Therefore, RE is an electrode made up of phases of a constant composition, which enables it, by Gibbs's phase rule, to exhibit a fixed potential at a given temperature and pressure, even under the passage of small currents. Thus, they are also termed "nonpolarizable electrode." The primary reference, chosen by convention, is the normal hydrogen electrode (NHE), *aka*. the standard hydrogen electrode (SHE), $Pt|H_2\ (a = 1)|H^+\ (a = 1)$, represented by the half-reaction of

$$2H^+ + 2e^- = H_2 \tag{1.2}$$

Its thermodynamic potential has been assigned zero at all temperatures. However, SHE is not convenient to use. In practice, the saturated calomel electrode (SCE), $Hg/Hg_2Cl_2/KCl$ (saturated in water), is commonly used as a RE, which has a standard potential of 0.242 V versus SHE and the half-reaction of

$$Hg_2Cl_2 + 2e^- = 2Hg(l) + 2Cl^- \tag{1.3}$$

Figure 1.3 A typical three-electrode setup for standard electrochemical characterization.



Another commonly used RE is the silver–silver chloride electrode, Ag/AgCl/KCl (saturated in water), with a potential of 0.197 V versus SHE, in which the electrode reaction is

$$\mathrm{AgCl} + \mathrm{e}^- = \mathrm{Ag} + \mathrm{Cl}^- \tag{1.4}$$

Note that the Ag/AgCl RE should be avoided for use in alkaline electrolytes due to the reaction of Ag with OH^-, forming Ag_2O that blocks the electrode tip. A table of commonly used reference electrode potentials can be found in Appendix A.

Each half-reaction has a fixed potential (E^0) under standard condition ($a = 1$, $P = 1$ atm, $T = 25\,°$C). The modern electrochemistry defines the standard potential of the half-reaction accepting electrons from the external circuit as the tabulated values; for easy reference, they are listed in Appendix B. By this definition, when the potential of an electrode is moved from its open-circuit value toward more positive potentials, the active species with the most positive E^0 will be reduced first and is deemed as the **oxidant**. Therefore, strong oxidizing agents are found in anions and/or neutral species with high positive E^0. Vice versa for the potential of an electrode is moved from its open-circuit value toward more negative potentials, in which the active species with the most negative E^0 will be oxidized first and deemed as the **reductant**. Thus, strong reducing agents are found in cations and/or neutral species with high negative E^0. In discussing electrochemical cells, the electrode at which reductions occur is called the cathode, and the electrode at which oxidations occur is the anode. A current in which electrons cross the interface from the electrode to electrolyte is a cathodic current, while electrons flow from electrolyte into the electrode is an anodic current. Therefore, in electrolytic cells, the cathode is deemed negative (−) with respect to the anode; but in galvanic cells, the cathode is viewed positive (+) with respect to the anode.

1.4 Faradaic and Non-Faradaic Reactions

It is important to recognize that there are two types of processes possibly occurring at electrodes of an electrochemical cell. One is reactions in which electrons are transferred across the electrode/electrolyte interface, causing oxidation or reduction to occur. Since half-reaction follows Faraday's law, it is often called **faradaic process**. Good examples of Faradaic cells are fuel cells and batteries. Another kind is processes such as adsorption and desorption of active species on the surface of electrodes. These processes change the electrode's surface structure, potential or electrolyte composition, but do not transfer electrons across the electrolyte/electrode interface. Therefore, they are referred to **as non-faradaic processes**. Good examples of non-Faradaic cells are electrochemical double-layer capacitors and pseudocapacitors [3].

An electrode at which no electron transfer can occur across the electrode/electrolyte interface, regardless of the potential applied, is called an **ideally polarizable electrode (IPE)**. While no real electrode can behave as an IPE over the whole potential range available in electrolytes, some electrode–solution systems can approach ideal polarizability over limited potential ranges. An immediate example is Hg/KCl electrode/electrolyte interface.

The IPE features a horizontal line on polarization i-E curve. Since electrons cannot cross the IPE interface when a potential (V) is applied, the behavior of the electrode/electrolyte interface is similar to that of a capacitor. As is commonly known, when V is applied across a capacitor with capacitance C, charge (Q) will accumulate on its metal plates until Q satisfies $Q = C * V$. The separation of charged species and oriented dipoles at the electrode/electrolyte interface is called the **electrical double layer (EDL)**, which will be discussed in Chapter 6. Therefore, the electrode/electrolyte interfacial impedance of an electrochemical cell is often modeled by a double-layer capacitance of the non-Faradaic process, C_{dl}, in parallel to charge transfer resistance of the faradaic process, in the equivalent circuit modeling of electrochemical impedance spectroscopy; the latter will be discussed in detail in Chapter 7.

1.5 Nernst Equation

The faradaic half-reactions can be generalized into

$$O + ne^- \underset{k_\mathrm{b}}{\overset{k_\mathrm{f}}{\rightleftarrows}} R \tag{1.5}$$

If the kinetics of electron transfer of (1.5) are fast and $k_\mathrm{f} = k_\mathrm{b}$, the activities of O (a_O) and R (a_R) at the electrode surface can be assumed to be at equilibrium, the corresponding potential E_n of (1.5) can be expressed by

$$\begin{gathered} E_\mathrm{n} = E^0 + \frac{RT}{nF}\ln\frac{a_\mathrm{O}}{a_\mathrm{R}} = E^{0'} + \frac{RT}{nF}\ln\frac{C_\mathrm{O}}{C_\mathrm{R}} \\ E^{0'} = E^0 + \frac{RT}{nF}\ln\frac{\gamma_\mathrm{O}}{\gamma_\mathrm{R}} \end{gathered} \tag{1.6}$$

Eq. (1.6) is often referred to as **Nernst equation**. It provides a linkage between electrode potential E and the concentrations of active species in the electrode process. E_n is also known as Nernst potential. It is often measured as OCV of a cell. If a system follows the Nernst equation or an equation derived from it, the electrode reaction is often said to be thermodynamically or electrochemically reversible.

Example 1.2
Consider a concentration cell Cu(s)|$CuSO_4$(aq)a_1 ||salt bridge||$CuSO_4$(aq)a_2|Cu(s). Calculate E_n of the cell at 25 °C if $a_1 = 0.75$ and $a_2 = 0.25$.

Solution
From Eq. (1.6) and $E^0 = 0\,V$, $n = 2$, $E_n = 8.314$ (J/K/mol) × (273 + 25) (K)/2/96,500 (As/mol) × ln(0.75/0.25) = 0.014 V.

1.6 Overpotential and Reaction Rate

When an electrical (faradaic) current is passed through the cell, the electrode equilibrium is disturbed (polarized) and the original electrode potential will change. The departure of the electrode potential from the equilibrium value upon passage of current is termed **polarization**. The extent of polarization is measured by the overpotential, η,

$$\eta = E_{app} - E_{eq} \tag{1.7}$$

Note that $E_{eq} = E^0$ if the cell is under the standard condition.

Since an electrode process is a heterogeneous reaction occurring only at the electrode/electrolyte interface, its rate ($\dot{m}$) is connected to the current i in the following form:

$$\boxed{\dot{m}\left(\frac{\text{mol}}{\text{s}\cdot\text{cm}^2}\right) = \frac{i}{nFA}} \tag{1.8}$$

Eq. (1.8) is also known as **Faraday's law**. When a steady-state current is reached, the rates of all in-series reaction steps in the electrode process are the same. The magnitude of this rate is often limited by one or more slowest reactions (called *rate-determining steps or RDS*).

Example 1.3
A galvanic cell consisting of standard concentrations: (−) Cu(s)|Cu^{2+}(aq) ||salt bridge|| Ag^+(aq)|Ag(s) (+) is connected to a small light bulb at 0.12 A for 40 minutes. How many grams of copper are dissolved from the anode?

Solution
The total charge passing through the light bulb is 0.12 A × 40 (min) × 60 (s/min) = 288 (As), which is equivalent to 288 (As)/2/96,500 (As/mol) = 1.49×10^{-3} mol. With the atomic weight of Cu, 63.546 g/mol, the total amount of Cu dissolved from the anode is 1.49×10^{-3} (mol) × Cu 63.546 (g/mol) = 0.0948 (g).

1.7 Several Important Features of Electrochemical Cells

Due to its direct reversible electrons-to-molecules conversion, electrochemical cells generally have fast response time, high power/energy density, high conversion efficiency, and low/zero emissions. Specifically for open electrochemical cell systems such as fuel cells and electrolyzers, this is reflected by the high power density or chemical production rate at high conversion efficiency compared to internal combustion engines or chemical reactors. For closed electrochemical cell systems such as batteries and capacitors, this is not only reflected by the high energy density and efficiency, but also in design flexibility of power and energy to meet specific needs. Above all, because of monolithic design, electrochemical cells are usually compact in geometry and can be easily made into modular and scalable systems for volume- or weight-limited applications such as transportation and distributed generations. However, the commercial viability of an electrochemical cell system is almost exclusively determined by service life (years or degradation rate) and cost ($/kW, $/kWh/cycle). In large-scale stationary energy storage systems, these two criteria have become the major considerations for capital investments and commercial development.

References

1 Decker, F. (2005). Volta and the ‘pile’. In: *Electrochemistry Encyclopedia*. Case Western Reserve University.

2 Faraday, M. (1834). On electrical decomposition. *Philos. Trans. R. Soc.* 124: 77–122. https://doi.org/10.1098/rstl.1834.0008.S2CID 116224057.

3 Bard, A.J. and Faulkner, L.R. (2001). *Electrochemical Methods: Fundamentals and Applications*. New York, USA: John Wiley & Sons, Inc.

Problems

1.1 For a Cu-Zn galvanic cell, use the standard electrode potentials listed in Appendix B to calculate E_n of the cell.

1.2 The electrolysis of molten $MgCl_2$ is used to obtain Mg metal. Calculate how many amps are needed to produce 35.6 g of Mg in 2.50 hours?

1.3 How many minutes does it take to produce 10.0 liter of oxygen gas under standard condition by electrolyzing neutral water with a current of 1.3 A? How much H_2 is produced at the same time?