

Integration of Theory and Practice in Chemistry Teaching of Higher Education—Taking Electrochemistry as an Example

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The principles or laws involved in foundation teaching usually have prerequisite conditions or assumptions for their application. In order to help students quickly grasp the knowledge they need to learn and ensure the systematic nature of the teaching content, the completeness of the knowledge points, and the achievement of teaching tasks, the applicability of the principles or laws beyond the boundary conditions or assumptions is usually not extensively discussed. This often leads to deviations between theory and experiment in scientific research and practical applications, and is also a common cause of confusion in the process of connecting theory and practice. To address this weak link in the teaching of chemical principles or laws, we take several examples such as reversible processes in electrochemistry, Nernst equation, battery electrode polarization, *etc.*, to elaborate the connection between theory and practice as a supplement for teaching. We hope this could help students better understand what they have learned and to deal with problems by flexibly using the chemical laws and principles.

Keywords: foundation teaching, principles and applications, chemistry

Introduction

It is well known that scientific laws have limitations on their scopes of application. The setting of the prerequisite conditions for the derivation of chemical laws or the approximate treatment of the deduction process makes the application of the laws have certain limitations. The teaching of chemical laws involved in foundational education usually starts from the perspective of helping students master and apply basic principles. Beginners often overlook the boundary conditions of the laws. When they encounter specific and complex problems in scientific research and practical applications, they might have doubts about what they have learned, and even feel helpless in the face of problems, thus leading to a disconnection between theory and practice. For instance, the scope of application of the fundamental equation of thermodynamics, *i.e.*, whether it only applies to reversible processes, is a frequently discussed issue. In many textbooks, the derivation of the fundamental equation of thermodynamics is based on a closed system and reversible processes that only do volume work. This often gives the impression that the fundamental equation of thermodynamics only applies to reversible processes. For a homogeneous closed single-component system that only involves in volume work, we have the basic equation of Gibbs free energy thermodynamics as follows:

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$$dG = -SdT + Vdp$$

As long as the parameters that determine the system state, temperature T and pressure p are consistent with the external environment; the initial and final states of the process are determined. As a result, the changes in the state function G have a determined value. The above formula applies whether the process is reversible or not (T. Tong & J. Tong, 1989; Xing, 1991). Of course, for complex multi-component systems, such as irreversible processes involving phase transitions, the fundamental equation of thermodynamics only applies to reversible processes (Jiao, Chen, Liu, Zhang, Zhu, & Peng, 2020).

Taking electrochemistry as an example, we will herein illustrate the application conditions of relevant laws or formulas in basic physical chemistry education. Teaching with case studies, we will explain the limitations of the use of certain laws due to the prerequisite conditions set. Moreover, we will extend the application of chemical principles and laws to scientific research. Through in-depth discussions, students could flexibly apply what they have learned while understanding and mastering the connotation of basic chemical laws.

Problems and Discussions

Problem 1. Understanding of “Reversible Electrochemical Cell”

In chemical thermodynamics, a reversible change in thermodynamics is a process that can be reversed by an infinitesimal modification of a variable (Atkins & de Paula, 2006). In other words, the reversible process is characterized by an infinitely small change and is composed of a series of states that are very close to the equilibrium state (*i.e.*, quasi-static process); if following the reverse process, the system and environment can restore to their original states without any dissipative effects. It is well known that chemical energy can be converted into electrical energy *via* spontaneous reactions in principle; from this point of view, spontaneous processes cannot be reversible processes. However, electrochemistry often involves reversible cells and reversible reactions when discussing batteries and electrode reactions. According to the definition of reversibility in thermodynamics, reversible batteries are meaningless. Indeed, reversible processes are often used to deal with electrochemical processes or reactions, such as the use of the Nernst equation. This can be confusing for beginners. Then a problem arises—how to understand reversible processes in electrochemistry?

Reversibility of electrochemical reactions. Changing the direction of the current in an electrochemical cell only changes the direction of the cell reaction, and no new reaction occurs. Such a cell is called chemically reversible. Similarly, the oxidation and reduction reactions of one electrode are inverse to each other, that electrode is called a reversible electrode. If changing the direction of the current not only results in different electrode reactions but also different net reaction processes, the cell is called chemically irreversible. It is relatively easy to understand that as long as the reaction proceeds according to a certain chemical reaction equation, and no side reactions outside the reaction equation occur, that is reversible process, regardless of whether it is in the forward or reverse direction. However, beginners are normally confused since thermodynamic reversibility is defined prior to electrochemical reversibility.

Difference between electrochemical reversibility and thermodynamic reversibility. Chemical cells cannot exhibit thermodynamically reversible behavior in practice. This is because all actual processes occur at a certain rate and with variables that are far from infinitely small. Therefore, the electrochemical processes cannot have thermodynamic reversibility. This raises the issue of “practical reversibility”. If a process still satisfies the thermodynamic formula within the required accuracy, it can be called a reversible process. In other words,

practical reversibility is not an absolute term, it largely depends on the observer's exact attitude and expectations towards the process (Bard & Faulkner, 2010).

In electrochemistry, if a system follows the Nernst equation or a formula derived from it, the electrode reaction is often referred to as thermodynamically or electrochemically reversible. For example, cyclic voltammetry (CV) is often used to determine whether the electrode process conforms to the Nernst equation based on the current density i and the electrode potential E (as shown in Figure 1a). For the Nernst wave of stable products, the peak current ratio of $i_{pa}/i_{pc} = 1$; or the closer the ratio is to 1, the closer the process is to be reversible. It is independent of the scanning rate, diffusion coefficient, and reversal potential E_λ as long as the value of $|E_\lambda - E_{pc}|$ is higher than $35/n$ in millivolt (mV). In addition, the difference of E_{pa} and E_{pc} approximately equals to $2.3RT/(nF)$, which is 59 mV for the process involving in only one electron transfer at 25 °C. For chemical cells, considering the existence of over-potential in practical applications, the peak current ratio of forward and reverse scans will deviate from the equilibrium state as shown in Figure 1b. Taking the oxidation and reduction of hydrogen on the electrode as an example, the forward reaction rate of proton generation and the reverse reaction rate of proton reduction depend on their respective activation energy and the initial and final states of reactants. The difference between the activation energies of the forward and reverse reactions is termed as G_{rxn} , which reflects the difference in electrode potentials of electrode chemical reactions. When the reaction reaches equilibrium under certain conditions, the net current density $j_0 = 0$ (shown in Figure 1b). For practically working chemical batteries, the polarization overpotential η reflects the actual deviation from the equilibrium, *i.e.*, the anode overpotential η_{anode} and cathode overpotential $\eta_{cathode}$ as well as the concentration of active substances deviate from the equilibrium state, *etc.*, as shown in Figure 1c.

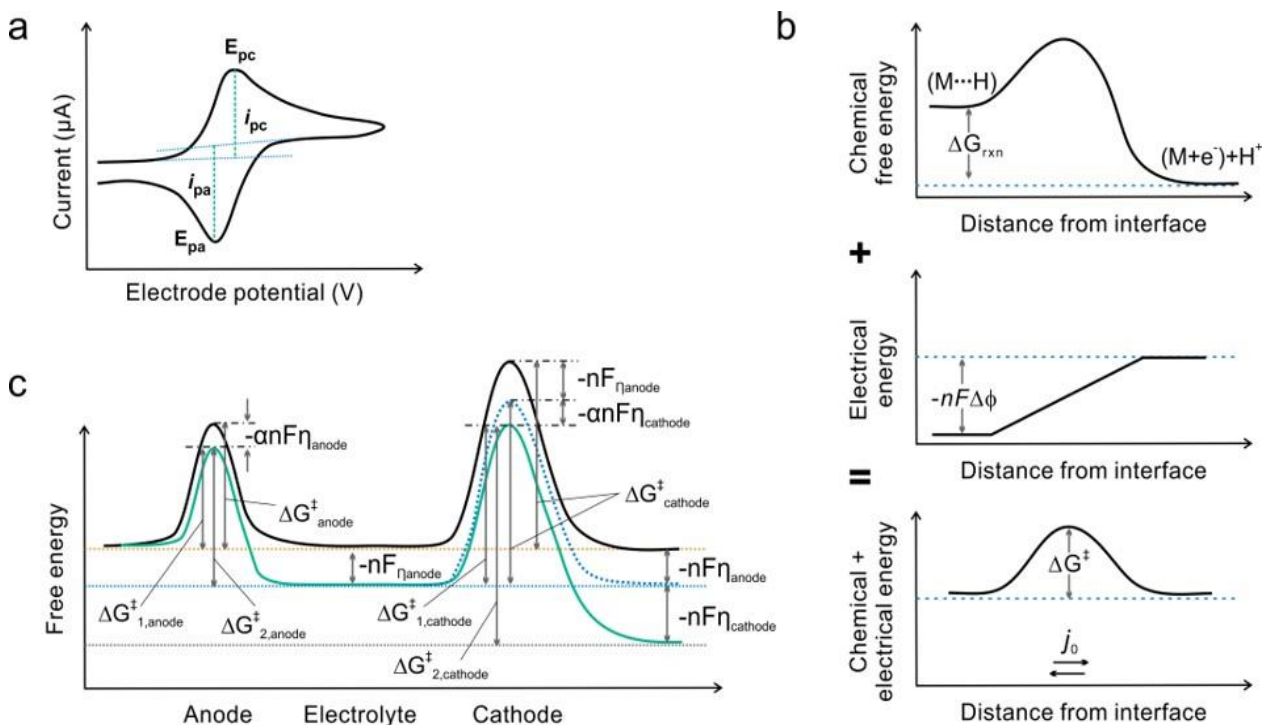


Figure 1. Schematic diagram of cyclic voltammetry (a, upper left); chemical energy and electrode potential in the equilibrium state of a cell (b, upper right); deviation from the equilibrium state due to electrode polarization in a cell (c, lower figure).

In summary, the reversible process in electrochemistry can occur both forward and reverse without any side reactions. In practice, when the variables involved in electrochemical processes are negligible, it can be treated approximately as a reversible process. For galvanic cells and electrolytic cells, the charge transfer (current density) involved in the kinetic process is not a small variable, so the deviation from the equilibrium state cannot be approximately reversible, and the existence of overpotential and polarization are the results of this deviation.

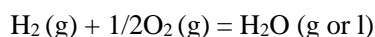
Problem 2. Limitations of Nernst Equation Caused by Approximate Treatment of Substance Activity

For an electrochemical reaction, $aA + bB = cC + dD$, the expression of Nernst equation is:

$$E = E^\theta - \frac{RT}{nF} \ln \frac{a_C^c a_D^d}{a_A^a a_B^b} \quad (1)$$

Limitations of treating solvent water activity as one. For reactions in aqueous solutions, the solvent water activity is usually assumed to be one, and this approximation has little effect on dilute electrolyte solutions and the resulting derivation can be ignored. However, for systems with high electrolyte concentration and low water content, this assumption can lead to significant deviations, especially for systems involving water in the reaction. In electrochemical processes, adjusting the activity of water can be used to suppress side reactions such as hydrolysis, thereby promoting the reaction in a favorable direction. For example, in the newly developed water-based zinc battery, the battery side reaction of producing ZnO and $Zn(OH)_4^{2-}$ occurs in the presence of water. Reducing the water content is an effective way to suppress such side reactions. Specifically, when $VOPO_4 \cdot xH_2O$ is used as the cathode material of the zinc battery, it will decompose and dissociate in water, leading to a decrease in the battery voltage and capacity. However, adding low-cost and highly soluble $ZnCl_2$ and H_3PO_4 to the water electrolyte can effectively reduce the activity of water, thereby suppressing the decomposition and dissociation of $VOPO_4 \cdot xH_2O$ (Shi, Song, Qin, Li, Guo, Liu et al., 2019).

For electrochemical reactions involving gases, the deviation caused by assuming the activity of water to be one may be more complicated compared to reactions in solution. Take the reaction of one medium and low temperature fuel cell as an example:



The generated water might be in liquid (l) or gas (g) phase, and the change in Gibbs free energy $\Delta_{r,m}G^\theta$ of the reaction is thus different, depending on the fuel cell operation temperature. This leads to differences in the electrical energy obtained from the chemical reaction, and therefore affects the magnitude of E^θ . According to the Nernst equation, the theoretical electromotive force of the designed cell is:

$$E = E^\theta - \frac{RT}{nF} \ln \frac{a_{H_2O}}{a_{H_2} a_{O_2}^{1/2}} \quad (2)$$

If the activity of water is assumed to be one, then the electromotive force of the cell is only related to the gas partial pressures involved in the reaction, that is:

$$E = E^\theta - \frac{RT}{nF} \ln \frac{1}{a_{H_2} a_{O_2}^{1/2}} \quad (3)$$

In practical operation, water management in fuel cells is a critical issue that cannot be ignored. For ion-conducting electrolytes, the water content and relative humidity (RH) can affect the ion conduction mechanism as well as the electrolyte conductivity (Wang, Liang, Tang, Grosjean, Shahnas, Lahann et al., 2018). For fuel

cells, liquid water penetrating into the gas diffusion layer can affect gas transport and electrode reactions, and can even cause electrode flooding, thereby affecting the activity of the catalyst. If the operating temperature of the fuel cell exceeds 100 °C, the presence of water vapor will affect the gas partial pressure on the electrode, thus affecting the electromotive force of the cell. In addition, when the fuel cell works with acidic electrolyte, water is generated on the positive electrode side as a product (positive electrode reaction: $2\text{H}^+ + 1/2\text{O}_2 + 2\text{e} = \text{H}_2\text{O}$, negative electrode reaction: $\text{H}_2 - 2\text{e} = 2\text{H}^+$), while in alkaline medium, water is generated on the negative electrode side (negative electrode reaction: $\text{H}_2 - 2\text{e} + 2\text{OH}^- = 2\text{H}_2\text{O}$, positive electrode reaction: $1/2\text{O}_2 + 2\text{e} + \text{H}_2\text{O} = 2\text{OH}^-$), simultaneously acting as a reactant participates in the positive electrode reaction. As results, factors related to water content such as humidity and water mass transfer processes all have an impact on the performance of the cell. Therefore, water management is a crucial technical issue that cannot be ignored in fuel cells, and it plays a vital role in the operation and energy efficiency of the cell.

Limitations of treating solid substance activity as one. In electrode reactions, it is often encountered that a substance (element) is reduced and deposited on the solid electrode surface. When using the Nernst equation for calculation, the activity of the solid substance involved in the reaction is generally treated as one. In actual electrodeposition processes, the initial activity of the substance is much smaller than its reversible state activity. If the activity of the substance is treated as one, the theoretically calculated equilibrium potential and the actual deposition potential will deviate greatly. For example, under potential deposition (UPD) refers to the phenomenon that the potential of a substance (such as a metal) undergoing monolayer electrodeposition deviates significantly from the thermodynamic reversible potential (Jiang, 1988; Enrique, Lisa, & He ćtor, 2001). For metals, the potential of UPD is usually more positive than the reversible potential. It is generally believed that this is because the interaction between the deposited atoms is weaker than that between the substrate and the deposited atom. In fact, the activity (a_m) of the deposited metal is related to the coverage degree (θ) and activity coefficient on the electrode surface before covering the heterogeneous electrode surface completely (Matsuda, Yoshida, & Umeda, 2022). In the calculation of reversible potential, assuming the activity of the deposited substance as one will inevitably lead to inconsistency between the theoretically calculated potential and the actual deposition potential. Of course, the reasons for UPD are complex, involving many factors such as the deposition substrate, ion adsorption on the electrode surface, and temperature. The related researches are still continued (Guo, Tan, Li, Hu, & Zhang, 2013). It is worthwhile mentioning that the deposited elements are not limited to metal elements, but also include non-metal elements, nanoparticles, and other substances, and their interface properties and principles are also involved (Uenishi & Ibe, 2023; Dai, Zhang, Zhang, Cui, Ye, Hong et al., 2023).

Problem 3. Electrode Structure and Electrochemical Processes

The electrodes cited in textbooks, whether they are active electrodes (such as zinc, silver, copper, *etc.*) or inert electrodes (such as platinum), are mostly metal materials (such as metal sheets) that conduct electrons. In experimental teaching, such as the measurement of electromotive force of Daniel cell, the involved electrodes are copper/zinc metal electrodes. This often creates a misunderstanding for beginners that the electrodes in the battery are plate or rod-shaped electronic conductors. In practice, when assembling the electrodes of a battery, it is necessary to consider the transport of the species involved in the electrode reaction. For processes involving catalysis, it needs to consider the specific surface area of the catalyst to obtain higher energy conversion efficiency. In addition, the density and price of electrode materials should also be considered in order to achieve high specific capacity and low cost of the assembled batteries. Therefore, the structure of the used electrodes is

much more complex than can be satisfied by a single metal plate. Understanding the electrode structure in electrochemical cells benefits students to understand processes such as electrochemical reactions and energy conversion.

If electrochemical reactions involve fluids, porous conductive materials, *e.g.*, carbon fiber/cloth, are usually used as electrode materials, and their pores are an indispensable structural component for gas (or liquid) transport. In addition, although electrochemical reactions theoretically occur at the interface between the electrode and the electrolyte, the occurrence of a reaction is far from enough for a smooth geometric interface; it still needs a certain “thickness”. There are mass transfer processes of electrons and ions to ensure the continuous progress of the reaction. Therefore, the electrode structure not only includes electronic conductors, but also contains a certain amount of ion conductors (as shown in Figure 2) (Li, Aili, Hjuler, & Jensen, 2016). Understanding the electrode structure in electrochemical reactions is beneficial to understand the process of electrochemical reactions and energy conversion.

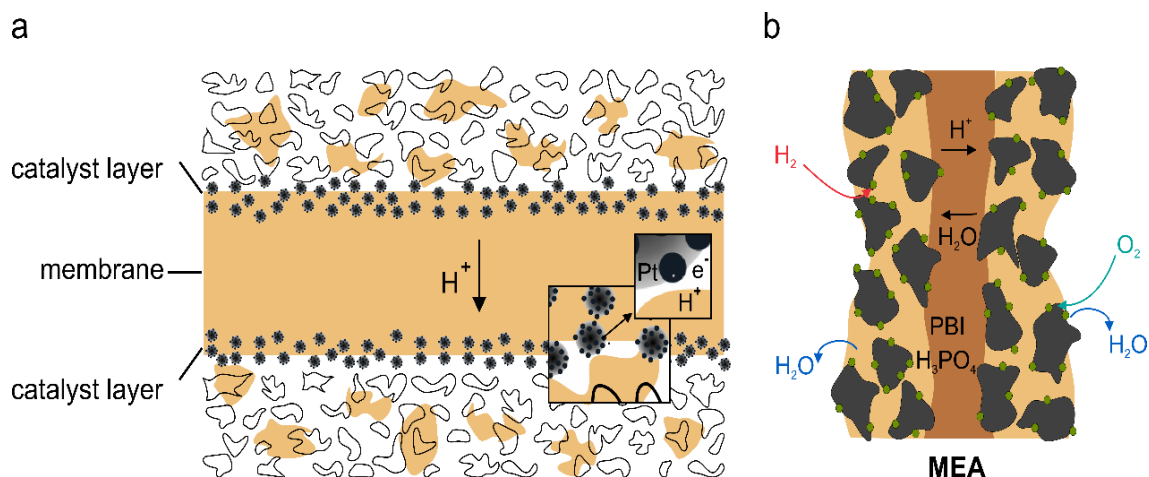


Figure 2. Assembly structure of battery electrodes, electrolytes (left), and schematic diagram of mass transfer in multiphase electrode structure (right).

To beginners, it is easy to understand that electrode potential is related to electrode material and temperature, but difficult to comprehend the electrode potential is also affected by the surface state of the electrode. Knowing the possible structure of the electrode is helpful to this understanding. For example, Table 1 shows the over-potential of hydrogen and oxygen on platinum electrodes. Both hydrogen and oxygen exhibit significant differences in over-potential on platinum black and platinum electrodes. The over-potential of the gas on platinum black electrodes is significantly lower than that on smooth platinum electrodes. Compared with smooth platinum electrodes, platinum black-coated platinum electrodes can provide a higher platinum specific surface area, and increase the density of adsorbed gas on the platinum surface for higher catalytic activity, thus reducing the activation over-potential and facilitating catalytic oxidation/reduction of gases (Matsuda, Yoshida, & Umeda, 2022; Kunimatsu, Senzaki, Samjesk é Tsushima, & Osawa, 2007). In addition, the greater the current density, the greater the over-potential of the electrode, and the difference in activation over-potential between these two electrodes becomes more obvious. Although the factors that cause over-potential are complex and there is no mature and perfect theory to explain it, realizing the differences in electrode structure can be helpful in understanding related experimental results.

Table 1

Over-Potential η of H_2 and O_2 on Platinum Electrodes (Fu & Hou, 2022) (298.15K)

Electrode Current density/ $A \cdot m^{-2}$	η (smooth Pt)		η' (Pt black)	
	H_2	O_2	H_2	O_2
10	0	0.72	0	0.4
100	0.16	0.85	0.03	0.52
1,000	0.29	1.28	0.041	0.64
10,000	0.68	1.49	0.048	0.77
50,000	-	-	0.051	-

Problem 4: Application of the Difference in Temperature Dependence Between Electronic and Ionic Conductors

In electrochemistry, there are two types of conductors. The first type of conductors is electronic conductors, which are used for the transport of electrons. The electrode materials are generally electronic conductors. The second type of conductors is ionic conductors, which are normally used as electrolytes for the transport of ions from one electrode to another within the electrochemical cell. Redox electrochemical reactions usually occur at the electrode interface, and the activation effect of the catalyst loaded on the electrode is closely related to the specific surface area and utilization rate of the catalyst. As mentioned in the previous section, in order to effectively transport the electrons and ions generated by the reaction, the electrode structure is multiphase that includes both electronic conductors and ion conductors. However, only ion conduction is possible for the electrolyte. Otherwise internal short circuits may occur and lead to the failure of the electrochemical cell (Zhang, Sahraei, Wang, 2016; Seo, Goh, Park, & Kim, 2018).

For batteries such as lithium-ion batteries or zinc batteries, the formation of metal dendrites may cause internal short circuits in the battery. This type of short circuit is not caused by the penetration of the membrane by electronic conductors, but by a momentary electron flow generated by interfacial reactions, which is called a “soft short circuit” (SS) as shown in Figure 3 (left). SS refers to the small localized electrical connection between two electrodes that allows the co-existence of direct electron transfer and interfacial reaction. It is common in all metal batteries, particularly at high current densities and capacities, but is hardly identified for systematic cell tests (Xu, Ge, Shen, & Yang, 2022; Li, Chen, Wang, Pei, & Zhi, 2022). However, based on the opposite changes in the conductivity of electronic conductors and ion conductors with temperature, it is possible to determine whether a soft short circuit has occurred through experimental testing.

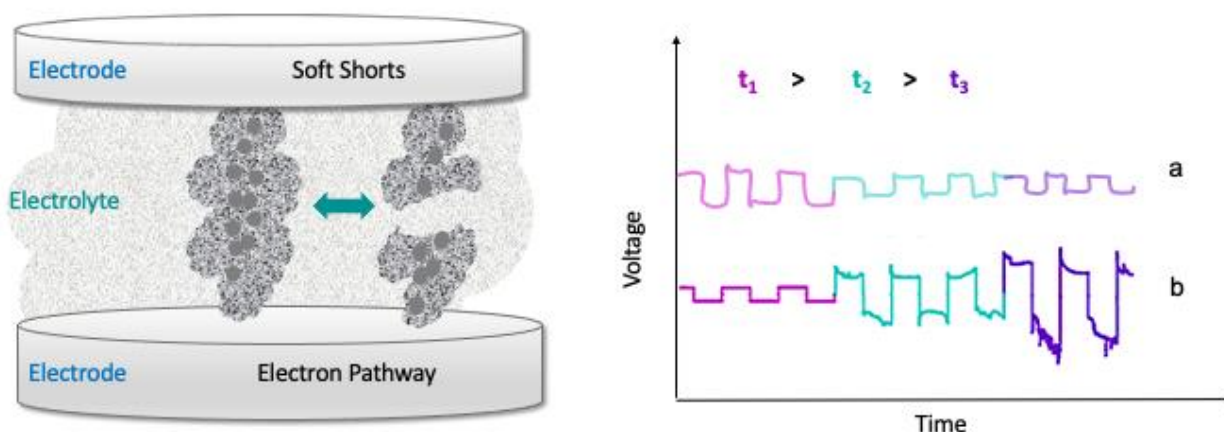


Figure 3. Schematic occurrence of soft short circuit in a battery (left), and related experimental phenomena (right, variation of voltage drop as the decrease in temperature with (curve a) and without (curve b) soft short circuit.

When a soft short circuit occurs in a battery, the Ohmic drop by ion transport of the electrolyte will be replaced by internal electron transfer. As the working temperature of the battery decreases, the resistance of electron conduction will decrease, as shown in Figure 3 (right curve a). When the temperature does not decrease much, there may be no significant change in electron conduction resistance, and the battery voltage may remain unchanged as the temperature decreases. When there is no soft short circuit, the resistance mainly comes from the ion conductor, and the migration rate of ions decreases significantly as the temperature decreases, resulting in an increase in the ohmic voltage drop of the battery (Figure 3, right curve b). Therefore, by measuring the variation of the battery voltage with temperature, it is convenient to determine whether a soft short circuit has occurred in the battery.

Summary

The principles covered in basic chemistry courses have broad and important applications in scientific research, production, and other processes. In scientific research, the basic principles of chemistry can be used to understand and explore related process mechanisms, and to design and create new methods and knowledge. In production practices, the application of chemical principles can lead to technological innovation and the creation of new products. In the process of constructing a basic knowledge system for beginners, it is essential to deeply understand the connotation, assumptions, boundary conditions, and to extend related issues of chemical principles to integrate and flexibly apply their knowledge. This article analyzes and discusses some aspects of electrochemistry as an example, aiming to closely link theoretical knowledge with practical applications and to stimulate readers' interest in the subject. We hope this article could "serve as a stepping stone" for attracting readers.

Author Contributions:

WANG Zejun: Conceptualization, Writing-Original Draft, Writing-editing and Visualization;

CHEN Shuai: Methodology, Investigation, and Validation;

HE Ronghuan: Supervision, Conceptualization, Writing-review & editing.

All authors read and approved the final manuscript.

References

- Atkins, P., & de Paula, J. (2006). In *Atkins' physical chemistry* (p. 39). 7th Ed. Beijing: Higher Education Press.
- Bard, A. J., & Faulkner, L. R. (2010). In *Electrochemical methods fundamentals and applications* (pp. 32-33). Translated by Y. Shao, G. Zhu, X. Dong, B. Zhang, 2nd Ed. Beijing: Chemical Industry Press.
- Dai, Y., Zhang, C., Zhang, W., Cui, L., Ye, C., Hong, X. et al. (2023). Reversible Zn metal anodes enabled by trace amounts of underpotential deposition initiators. *Angewandte Chemie International Edition*, 135, e202301192.
- Enrique, H., Lisa, J. B., & Hector, D. (2001). Underpotential deposition at single crystal surfaces of Au, Pt, Ag and other materials. *Chemical Reviews*, 101, 1897-1930.
- Fu, X., & Hou, W. (2022). In *Physical chemistry* (p. 133). 6th Ed., Second Volume. Beijing: Higher Education Press.
- Guo, L., Tan, J., Li, W., Hu, G., & Zhang, S. (2013). Underpotential deposition. *Progress in Chemistry*, 25, 1842-1857.
- Jiang, L. (1988). Underpotential deposition. *Chemistry*, 18, 9-13.
- Jiao, Y., Chen, S., Liu, W., Zhang, J., Zhu, M., & Peng, B. (2020). How to understand the applicable conditions of the basic thermodynamic equation of $dG = -SdT + Vdp$. *Chinese Journal of Chemical Education*, 41, 102-106.
- Kunimatsu, K., Senzaki, T., Samjeské, G., Tsushima, M., & Osawa, M. (2007). Hydrogen adsorption and hydrogen evolution reaction on a polycrystalline Pt electrode studied by surface-enhanced infrared absorption spectroscopy. *Electrochimica Acta*, 52, 5715-5724.

- Li, Q., Aili, D., Hjuler, H. A., & Jensen, J. O. (2016). In *High temperature polymer electrolyte membrane fuel cells, approaches, status, and perspectives* (pp. 298, 408). Switzerland: Springer.
- Li, Q., Chen, A., Wang, D., Pei, Z., & Zhi, C. (2022). "Soft shorts" hidden in zinc metal anode research. *Joule*, 6, 269-279.
- Matsuda, S., Yoshida, Y., & Umeda, M. (2022). Electroreduction of CO₂ to CH₄ without overpotential using Pt-black catalysts: Enhancement of faradaic efficiency. *International Journal of Energy Research*, 46, 9919-9925.
- Seo, M., Goh, T., Park, M., & Kim, S. W. (2018). Detection method for soft internal short circuit in lithium-ion battery pack by extracting open circuit voltage of faulted cell. *Energies*, 11, 1669.
- Shi, H., Song, Y., Qin, Z., Li, C., Guo, D., Liu, X. et al. (2019). Inhibiting VOPO₄·xH₂O decomposition and dissolution in rechargeable aqueous zinc batteries to promote voltage and capacity stabilities. *Angewandte Chemie International Edition*, 58, 16057-16061.
- Tong, T., & Tong, J. (1989). Discussion on the applicability of basic equations of thermodynamics. *College Physics*, 9, 16-17.
- Uenishi, T., & Ibe, M. (2023). Effect of electrochemical surface area on carbon dioxide electrolysis using anionic electrolyte membrane electrode assembly. *Fuel*, 346, 128309.
- Wang, Z., Liang, C., Tang, H., Grosjean, S., Shahnas, A., Lahann, J. et al. (2018). Water-stable nanoporous polymer films with excellent proton conductivity. *Macromolecular Rapid Communications*, 39, 1700676.
- Xing, T. (1991). Re-discussion on "applicability" of basic equations of thermodynamics. *College Physics*, 5, 19-20.
- Xu, Y., Ge, X., Shen, W., & Yang, R. (2022). A soft short-circuit diagnosis method for lithium-ion battery packs in electric vehicles. *IEEE Transactions on Power Electronics*, 37, 8572-8581.
- Zhang, X., Sahraei, E., & Wang, K. (2016). Li - ion battery separators, mechanical integrity and failure mechanisms leading to soft and hard internal shorts. *Scientific Reports*, 6, 32578.