

Environmental Chemistry for a Sustainable World 74

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# Nanoelectrocatalysts for Energy and Water Treatment

 Springer

# Environmental Chemistry for a Sustainable World

Volume 74

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Kwena D. Modibane • Eric Lichtfouse  
Editors

# Nanoelectrocatalysts for Energy and Water Treatment

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# Preface

Getting clean water and sustainable energy is important for helping the economy grow and making sure we develop in a way that keeps things going for the long term. We know that giving people water and energy can have a big impact on the environment. Right now, we are dealing with some big challenges like using more energy and causing pollution in our water. With the world needing more and more energy and people getting worried about the environment, it is super important to have ways to change and store energy that is clean and will last.

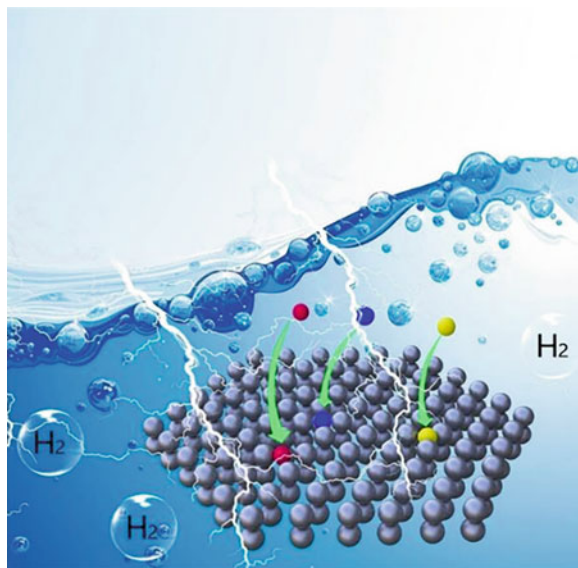
Amidst these challenges, materials play a key role. They can speed up chemical reactions without getting used up in the process. Specifically, electrocatalysis, which uses special properties of nanomaterials, is a big deal. It helps make electrocatalysts work better for energy and cleaning up wastewater (Fig. 1).

This book gives a big picture of the latest improvements in electrocatalysis. It discusses the chemistry and activity of nanomaterials in the context of energy and cleaning water. It covers a lot of different things, like the role of nanomaterials, new ideas in designing materials, and the properties of chemicals that are used. It also provides information about the challenges faced by advanced nanoelectrocatalysts and ways to overcome those challenges.

The chapters in the book are carefully chosen and cover a bunch of different things. They go from the basics and roles of electrocatalysis to how we can use nanomaterials to make hydrogen, deal with ethanol in fuel cells, and support fuel cells with carbon structures. Each chapter adds something to what we already know about how nanomaterials work for clean energy and water.

In Chap. 1, Lee and the team discuss the basics and roles of tiny electrocatalysis for clean energy and water. In Chap. 2, Elumalai and the team dig into the new things happening with tiny materials for making hydrogen more efficiently. Chapter 3, by Xaba and the team, looks at using nanoelectrocatalysts for ethanol in alkaline fuel cells. In Chap. 4, Prithi and the team explain how carbon structures help fuel cells as support materials. Chapter 5, by Matthews and the team, takes a good look at the problems and solutions for nanoelectrocatalysts in fuel cells, and in Chap. 6, Fuku

**Fig. 1** Electrocatalysts boost electrocatalytic reactions of hydrogen evolutions. Copyright, Wiley, 2022



and the team give details on making advanced Pd-based electrocatalysts for high-performance fuel cell systems.

Moreover, Chap. 7 by Monoma and the team shows how we are making progress with metal-organic framework composites for making hydrogen with electrocatalysis, and Chap. 8 by Nkele and the team focuses on making hydrogen using different emerging nanoelectrocatalysts. In Chap. 9, Fuku and the team explore the details of using bio-inspired metal-metal oxides as Pd support catalysts for turning CO<sub>2</sub> into electrofuels. Chapter 10, by Makelane and the team, introduces nanosensors made of special materials for finding organic pollutants in wastewater. Chapter 11, by Zikalala and the team, talks about new things happening with titania-carbon nanotube mixtures to make them work better for cleaning water with light. In Chap. 12, Rose and the team provide insights into a special kind of material made of silver, iron, and titanium dioxide that helps clean up industrial waste in water. Finally, in Chap. 13, Ndibewu and the team explain how we can use nanoelectrocatalysts to make getting rid of certain chemicals in wastewater easier.

We want to thank the authors who worked hard on this book and helped each other out during the writing and revising. A big shoutout to the Springer Nature team for supporting us from the start to getting the book ready. We hope this book is helpful for researchers, students, professors, and scientists in the field.

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# Chapter 1

## Fundamentals and Roles of Nanoelectrocatalysis for Sustainable Energy and Water



**Juhan Lee, Rafael Linzmeyer Zornitta, Katlego Makgopa,  
Jayaruwan Gunathilake Gamaethiralalage, Modibane Desmond Kwena,  
and Kumar Raju**

**Abstract** Electrocatalysis is a pivotal scientific discipline and a crucial part of industrial processes for the sustainable future for mankind. It is closely related to energy efficiency and the general processing rate of various electrochemical applications. Thus, a sound understanding of electrocatalysis provides versatile new functions and innovative solutions to numerous challenges we face in conventional and advanced technologies. Particularly, the challenges regarding the need for sustainable energy and water use arise with growing demands for more environmentally friendly, safer, and energy-efficient materials, which are less dependent on limited resources. In terms of resolving these challenging demands, the emergence

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Juhan Lee, Rafael Linzmeyer Zornitta and Katlego Makgopa contributed equally with all other contributors.

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of nanomaterials has brought a significant advance in technologies and enabled an in-depth and comprehensive understanding of electrocatalysis. In this book chapter, we explore various electrochemical applications of both conventional and advanced technologies by categorizing them into five functioning groups: harvest, removal, consumption, storage, and analytics. For these applications with a particular aspect of sustainable energy and water, we discuss the roles and fundamentals of electrocatalysis, including technical parts such as cell configuration and its core elements, as well as the theories of thermodynamics and kinetics. Furthermore, we discuss how nanomaterials development and research activities have contributed to the deep understanding of nanoelectrocatalysis by reviewing some of the recent progress of various technologies. Finally, we explore the roles and the trend of these advanced nanomaterials in electrocatalysis with a focus on the properties and the design of materials.

**Keywords** Electrocatalysis · Electrocatalysts · Electrochemical thermodynamics · Electrochemical kinetics · Energy harvest · Energy storage · Nanomaterials · Sensors · Sustainable energy · Wastewater treatment

## 1.1 Introduction

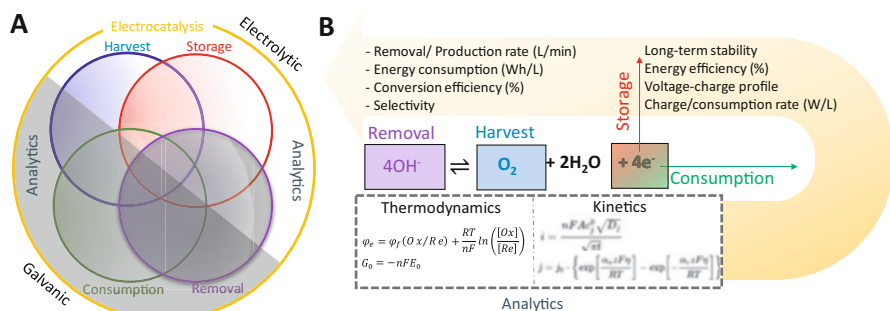
As a scientific discipline of studying physical and chemical processes involving the flow of electrons and ions and changes in chemical potential energy, electrochemistry has played a pivotal role in the development of science and technology. In modern life, we receive a range of benefits from electrochemistry and its applications even without noticing it. We use a variety of electronic devices by means of cell phones, tablets, televisions, and computers with the aid of electrochemical energy storage such as *batteries* and *electrochemical capacitors*. Electrochemistry is also essential in medicine for the purpose of clinical diagnosis, prognosis, and therapeutic action. The portable blood glucose meters became a blessing for patients with diabetes. Thus, the successful implementation of these meters on diabetic patients demonstrated that electrochemistry is capable of playing vital roles in fields other than just battery technologies, the *sensors*. These electrochemical sensors are essential not only for scientific or medical disciplines but also for forensics to detect explosive residues and the presence of illegal substances such as drugs.

In the kitchen or the storage rooms, we see that most of the utensils and food cans are coated with tin (Sn) by *electroplating*. Many other pure metals such as aluminum (Al), lithium (Li), and magnesium (Mg) are produced by extraction processes based on *electrolysis*. The latter is a crucial industrial process not only for the modern production of essential chemicals such as chlorine (Cl<sub>2</sub>), sodium chlorate (NaClO<sub>3</sub>), and sodium hydroxide (NaOH) but also for generating more green energy sources, such as hydrogen gas (H<sub>2</sub>), through water splitting. As we often hear from news media, hydrogen gas can be consumed in electrochemical cells known as *fuel cells* in

order to generate clean and alternative energy. The great advance experienced by the fuel cell technology occurred from the middle of the twentieth century, with an exponentially increasing interest due to the demand for more environmentally friendly technologies, the demand for energy-efficient systems, and the need for high energy density power for portable electronic applications.

Other approaches for sustainable energy applications are *photovoltaic* and *photoelectrochemical* cells, which rely on energy conversion from sunlight for generating electricity and conducting electrochemical reactions. These technologies have strengthened the role of electrochemistry in mitigating the energy crisis faced by the global community. Another essential role of the electrochemical process is found in the wastewater treatment used in industries. This process is capable of reducing the concentration of organic chemical compounds such as dyes, soaps, pharmaceutical compounds, among others. From the sustainability and environmental point of view, this kind of treatment is particularly attractive since no extra chemical is required for the water treatment.

As discussed with various examples, electrochemical applications are broad and diverse; in fact, they can be classified into five major categories (Fig. 1.1a) depending on the primary purpose of the process: removal (e.g., desalination, water purification), harvest ( $H_2$ ,  $O_2$ , metal extraction), consumption (alkaline batteries, fuel cells), storage (Li-ion batteries, double-layer capacitors), and analytics (e.g., ion-selective electrodes, glucose sensors, electronic tongue, electronic nose). The major goal of each process is achieved by applying core reactions; for example,



**Fig. 1.1** Electrocatalysis has played a pivotal role in various electrochemical applications which are categorized in five major sections (a) based on the primary purpose of the process (b): harvest, removal, storage, consumption, and analytics. (a) The applications can be operated either electrolytically (non-spontaneous), galvanically (spontaneously), or both. The shaded area represents the galvanic operation. The overlapping areas in the diagram depict the interdisciplinary or multifunctional processes in modern electrochemical applications. (b) By applying electrochemical reactions, some species can be removed or harvested. Since an electron transfer process is involved, these reactions can also enable storing or consuming electricity. Depending on the purpose of the applications, various performance parameters are considered, such as conversion efficiency and voltage-charge profile. Studying electrochemical thermodynamics and kinetics is essential for a comprehensive understanding of electrocatalysis as well as for analytical applications such as sensors

a conversion reaction from hydroxide ion (reactant) to oxygen gas and water (products) is represented (Fig. 1.1b). If this reaction occurs spontaneously, or galvanically (in fact, it is challenging to enable it spontaneously), four dissolved hydroxide ions are *removed* from the solution to *harvest* oxygen gas ( $O_2$ ) by yielding four electrons. The yield of electrons implies that such electrochemical processes can be utilized for generating electricity to fulfill the demand for energy *consumption*. In fact, the direction of a reaction can be changed when energy is invested (non-spontaneous or electrolytic) instead of gaining energy. This bidirectional feature of the reaction indicates that energy can be reversibly *stored* and consumed. In fact, it is thermodynamics that governs the direction of the spontaneity of the reactions, and kinetics governs the rate of the electrochemical reactions. A comprehensive understanding of these theories enables *analytical* measurements for desired properties of the materials or parameters of the systems.

The concept of reversible energy storage is one of the key requirements for the effective usage of energy. There are plenty of applications from conventional rechargeable batteries (lead-acid, Li-ion, and nickel-metal hydride batteries) and electrochemical capacitors (electrolytic and electric double-layer capacitors) to advanced energy storage systems like flow, solid-state, and metal-air batteries, flow capacitors, pseudocapacitors, and many other different forms of hybrid systems. Despite the different chemicals, materials, and cell designs, the electrochemical cell for energy storage applications shares the same essential performance requirements: high energy efficiency, long-term stability, fast charge/consumption rate, and voltage-charge profile. While the rest of them are self-explanatory, the voltage-charge profile is the central design element that determines the types of energy storage applications as well as electronic control units for effective and efficient control of the storage units. The voltage-charge profile is very similar to the shape of a water jar; it tells us how many electrons (water) we can store at various states of potentials (height). For capacitor applications, the voltage of the device is linearly correlated to the charge, and that is how the capacitive behavior is defined in physics. For battery applications, the profile has a distinctive plateau regime which is the potential range where chemical (redox) reaction occurs. The battery manufacturer reports this potential plateau as a nominal voltage that has to be matched with the input battery of electronic devices.

From our own experiences with diverse types of batteries, we know that not every battery can be applied for rechargeable energy storage applications. For instance, alkaline and lithium coin batteries are for disposable consumption use and not recommended for recharging. For this reason, these primary (non-rechargeable) batteries can be classified among energy consumption applications, as illustrated in Fig. 1.1a. According to this classification, electrochemical storage systems actually share the function with consumption applications. However, as we know from primary batteries, not all consumption applications share the area with storage applications. Simply, the reversibility of the core reactions is unfavorable for safety, cost, and technical reasons. For instance, it is theoretically possible to reverse the reaction in conventional fuel cells for producing oxygen and hydrogen gas. On the other hand, it is challenging to design this system due to engineering difficulties



(e.g., altering the direction of products and reactants) and complex electrochemical kinetics. As the latter limits the efficient usage of energy, it is more cost-effective to operate the conventional fuel cell systems only for consumption function. In this case, the hydrogen is produced separately by other processes like electrolysis, then stored and transported for use in fuel cell systems. However, tremendous research efforts are ongoing to develop reversible (or regenerative) fuel cells by resolving technologically challenging demands for commercialization (Gabbasa et al. 2014). For instance, developing bifunctional catalysts for both directions of the reaction is one of the major challenges to be overcome (Chen et al. 2018b).

Like in the case of producing hydrogen gas by electrolysis, we can obtain desired products by applying various electrochemical operations. As introduced earlier, pure aluminum can be extracted from molten bauxite (ore containing aluminum oxides) through the electrolysis process. Also, electrical energy can be generated by relying on electrochemical reactions triggered by sunlight; for instance, as a type of photoelectrochemical cell, dye-sensitized solar cells harvest energy from the sun. In many cases, these harvest applications do not rely on reversible electrochemical reactions but instead focus on how to convert from the reactants to the desired products in a more efficient and effective way (Roduner 2018a). Hence, high production rates and high energy efficiencies are desired. For discussing the latter aspects, various performance parameters exist depending on the type of the application. For instance, in the case of the electrolytic process, Faraday efficiency can address how effectively the electric current can contribute to the generation of desired products. For example, if 400 electrons were invested in producing 100 O<sub>2</sub> molecules, the Faraday efficiency would be 100%; hence, any loss of electrons by side reactions will reduce this efficiency.

Another practical way of discussing the efficiency of a harvest process is to report the unit production per unit energy input; for example, one could report that 50 kWh of energy was invested in harvesting 1 kg of hydrogen gas. For certain processes like photoelectrochemical processes, it is useful to discuss the efficiency of the conversion process in terms of output energy of the harvested chemical and the input of solar energy; the ratio of the latter is reported as conversion efficiency. For a comprehensive understanding of the production rate and energy efficiency of the harvest applications, the concept of overpotential is often discussed, which we will thoroughly review in Sect. 1.2.3.

On the contrary to harvest applications, the principal purpose of removal applications is to separate undesired species from the desired product. In the case of harvest applications, the desired products are one of the reaction products. For the removal applications, the desired removal species are not necessarily one of the reactants, as illustrated in Fig. 1.1a. For instance, the treatment of wastewater in pharmaceutical, textile, and other industries may be carried out electrochemically. One of the most common processes is the electrochemical advanced oxidation process (EAOP), which is based on the production of hydroxyl radicals that reacts with organic compounds in the waste solution. This process is strongly dependent on the type of electrode used for the electrodegradation process. For proper electrocatalytic electrodes, a complete conversion (or combustion) from organic

compounds to products is achieved, and only carbon dioxide and water are produced. Compared to other wastewater treatments, EAOP has the advantage of not employing chemicals during the treatment process; therefore, no extra waste is obtained after the treatment making the electrochemical treatment more environmentally friendly.

The efficiency of electrochemical technologies used for water treatment relies on different features. Most of the investigations are based on electrode materials and cell design. In the case of the EAOP process, the efficiency depends on the selective production of hydroxyl free radicals and the interaction of the radicals with the electrode surface. Another important factor vastly studied is the transport limitation of the organic species during the oxidation process. Some designs using porous carbon structures (e.g., reticulated vitreous carbon modified with  $\text{PbO}_2$ ) have been explored in order to improve the transport and efficiency of the electrodes. Since the electrooxidation process is a surface phenomenon, improvements related to the transport of compounds from the bulk of the solution to the electrode surface are of crucial importance. A broader discussion about the EAOP is provided in Sect. 1.3.6.

As we have seen before, harvesting and removal processes share a common ground, as they both require chemical selectivity in order to produce or remove desired products. This also paves the way into introducing another important concept in electrochemistry; analytics. While analytics itself is not unique to electrochemistry, it indeed plays a vital role. One of the oldest, most well-known, and robust electrochemical sensors is the glass pH electrode. In 1906, Max Cremer discovered the pH-sensitive glass membrane and developed the pH electrode in 1909. The first commercialized pH electrode was then introduced in the United States in 1936. Since then, ion-selective electrodes and electrochemical sensors, in general, have significantly progressed.

Ion-selective electrodes are by far the most used electrochemical sensor to this day (Bakker and Telting-Diaz 2002). As also being referred to as indicator electrodes, ion-selective electrodes respond to the activity (i.e., effective concentration) of the analyte for which it is sensitive. In order to measure this response, the ion-selective electrodes need to be coupled with a reference electrode. Then, the potential difference between the reference and the indicator can be measured using a potentiometer under zero-current conditions. This potential difference can then be correlated with the analyte activity using the Nernst equation, which is discussed later in this chapter (Sect. 1.2.2).

Apart from ion-selective electrodes, glucose sensors are also widely known and elegant electrochemical devices. Typical glucose sensors are amperometric (current measurement) sensors, where the reducing property of glucose is exploited. Glucose is oxidized via an enzyme-catalyzed reaction using glucose oxidase. The reduced form of the enzyme is oxidized in the presence of oxygen while producing  $\text{H}_2\text{O}_2$  as a by-product. This  $\text{H}_2\text{O}_2$  is finally broken down at the working electrode, which produces a current proportional to the glucose concentration. Essentially, the glucose sensor does not detect glucose directly, but it relies on the glucose oxidase enzyme for its selectivity towards glucose.

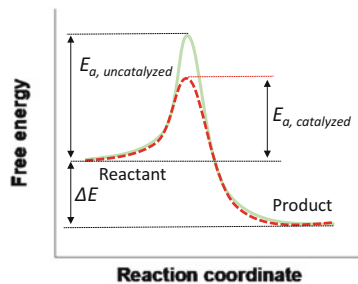
There are ample amount of examples of electrochemical sensors we can provide, such as the electronic nose, electronic tongue, and bio-sensors. However, it is worth probing this miniature world from a broader perspective. Miniaturization is indeed one of the biggest advantages electrochemical sensors have over other analytical methods. A highly favorable surface-area to volume ratio provides enough sensitivity, selectivity, and linear range for most applications. Combining these with widely available, powerful handheld smart devices opens up new possibilities for sensing devices that can be used not only by experts but also by the general public; we will discuss them in more detail in Sect. 1.3.7.

So far, various electrochemical applications have been introduced according to their key functions; and we discussed how these applications are mutually connected, for instance, harvest and removal, and storage and consumption. These mutual interactions can be represented by the overlapping areas in the diagram in Fig. 1.1a. As shortly discussed earlier, rechargeable batteries and advanced regenerative fuel cells share the aspects of storage and consumption applications. For these systems, not only chemical reversibility is of importance in terms of switching between galvanic and electrolytic processes in the cell but also electrochemical reversibility; particularly, from cyclability, energy efficiency, and kinetics.

Another example is reverse electrodialysis for producing electrical energy via concentration gradient, and at the same time, production of hydrogen gas (Nazemi et al. 2017). This is an intriguing case where harvest application was operated by the galvanic process, which also enabled consumption applications, as illustrated in the overlapping shaded area between harvest and consumption in Fig. 1.1a. Furthermore, there are many complicated systems in advanced technologies where more than two functions are integrated into one electrochemical system. For instance, ion-separation technologies based on reversible electrochemical reactions such as capacitive deionization and battery desalination is attractive emerging new technology due to their promising feature for efficient and effective water purification/desalination as well as recycling and production of particular chemicals (Srimuk et al. 2020). For instance, such systems can serve as rechargeable energy storage devices that could remove undesired species from feed solutions and harvest something simultaneously. Furthermore, knowing that electrochemical performance for such systems depends strongly on the feed solution concentration, they can potentially provide analytical function during the operation.

For the electrochemical applications in the same category, the performance requirements are similar, while differences arise depending on the details of the reactions and purposes. Despite the diversity of these requirements, the universal demands for electrochemical applications are to make the process more effective and more environmentally friendly, faster, and cheaper. In order to satisfy these universal demands, electrocatalysis has played a pivotal role broadly in almost every application. Due to the above statement, it is important to understand the fundamental role of a catalyst in chemical processes where an exchange of electrons is involved. Depending on the kinetics, some chemical reactions may occur very fast, while some can take a long time, thus requiring extra effort to reduce their completion time. Catalyst is a word often used in chemistry, especially in the discussion of chemical

**Fig. 1.2** The role of catalyst in reducing the activation energy barrier for a reaction



reactions. It is coined as one of the factors used to influence the rate of chemical reactions (Pagni 2002).

Catalyst is a substance that enables chemical reactions to proceed at a faster rate while not being consumed during the course of the reaction (Atkins et al. 2006). The mode of action for a catalyst is that it alters the reaction mechanism considerably, such that the energy barriers along the reaction coordinate are significantly lower (Fig. 1.2). This occurs by lowering the activation energy required by the reactants to reach the transition state, thus forming an activated complex and later transforming into the products. By lowering this energy barrier, the rate of the forward and reverse reaction is increased; thus, the reaction occurs at an enhanced rate. At an isothermal condition (constant temperature), the rate constant of the catalyzed reaction becomes greatly increased relative to the uncatalyzed reaction. The catalyzed reaction pathway adopts a lower  $E_a$ , but the *net* change in energy ( $\Delta E$ ) of the reaction is *not* affected by the presence of a catalyst (Atkins et al. 2006; Ertl 2009; Vang et al. 2007).

The reactions involving catalysts in their system are known as catalytic reactions, and the process of influencing these reactions by the use of catalysts is called “catalysis.” The science and technology of catalysis is of great significance as it affects our daily life. As much as catalysts can be simply classified into homogenous catalysts (i.e., those in the same phase with the reactants) and heterogeneous catalysts (i.e., those in different phases with the reactants), there are generally five broad classes of catalysis where catalysts are employed in current research activities (Roduner 2014). These classes include biocatalysis (which employs catalysts made-up of natural substances such as enzymes or biological cells), ultra-high vacuum (UHV) surface science catalysis (a catalyst is placed in the UHV where it is then exposed to small amounts of a compound of interest such as water, oxygen, and hydrogen at low temperatures), homogenous and heterogeneous catalysis, and electrocatalysts.

An electrocatalyst is a catalyst that participates in reactions involving the exchange of electrons/ electrons transfer (electrochemical reactions) between species. This specific form of catalysts functions at electrode surfaces, or they may also be the electrode surface themselves. Just as any type of catalyst, the electrocatalysts can exist in the form of a homogeneous (e.g., coordination complex or enzymes) or heterogeneous catalyst (metal surface or particles of nanomaterials). The

electrocatalyst boosts the electron transfer process between the reactants and the electrode often by facilitating intermediate chemical transformations on the reaction pathway.

In this book chapter, we will briefly review the most important and relevant fundamental principles of electrochemistry and discuss the roles of electrocatalysis for energy and water treatment by introducing both the traditional and advanced approaches with particular aspects when nanomaterials are involved in electrochemical applications. To start our journey, we will first need to understand the basis of the reactions in electrochemical cells. Hence, in Sect. 1.2, we will explore the construction of the electrochemical cells, including the roles of each component, theories regarding thermodynamics and kinetics, types of electrochemical reactions, and the advanced roles of membranes. Particularly, a comprehensive understanding of thermodynamics and kinetics is important as a fundamental foundation and essential building block of science and engineering for electrochemical applications. The thermodynamics and kinetics bridge the electrochemical observation to fundamental parameters, such as reaction rate constant, diffusion coefficient, and bandgap energy, as well as the quantitative information such as concentration and temperature. In this book chapter, we will have a particular emphasis on electrochemical kinetics, which will then be discussed extensively in terms of electrocatalysis. The fascinating roles of the latter (Sect. 1.3) will then be explored by introducing both conventional electrochemical applications with the theme “Energy” and “Water,” which have been inextricably linked to human activities. For these applications, the development of nanotechnologies played a crucial role in electrocatalysis; in that regard, we will review the conventional and advanced strategies of how nanotechnologies have contributed from an electrocatalysis point of view in Sect. 1.4.

## 1.2 Understanding Reactions in Electrochemical Cells

To truly understand any electrochemical application, we first need to learn the basic configuration of an electrochemical cell (Sect. 1.2.1); later, the variety of cell architectures will be briefly introduced. At this stage, the cell reactions can be visualized with the aid of diagrams and chemical equations, and one could notice the primary purpose of a certain electrochemical cell. By understanding thermodynamics (Sect. 1.2.2), we could know the spontaneity of the cell reactions, the concept of standard electrode potentials, estimation of the cell operating voltage, and the correlation of the reaction potential to the concentration of reactants and products via Nernst Equation. Then, the concept and the role of electrocatalysis will be introduced in Sect. 1.2.3 by thoroughly reviewing the theory of electrochemical kinetics and mass transport. Particularly, the latter aspects will be explored by introducing the concept of overpotential, a current-dependent extra potential required other than that of thermodynamically determined value. However, the complexity arises in modern electrochemistry; in that regard, we will review the most critical types of electrochemical reactions (Sect. 1.2.4) by discussing the characteristic differences of each

type. Understanding the mechanisms of these reactions is a vital foundation to envisage the concept of irreversibility and the role of diffusion. In Sect. 1.2.5, the concept of diffusion will be extended to the membranes/salt bridge by introducing their roles in various modern electrochemical applications for energy and water-related technologies.

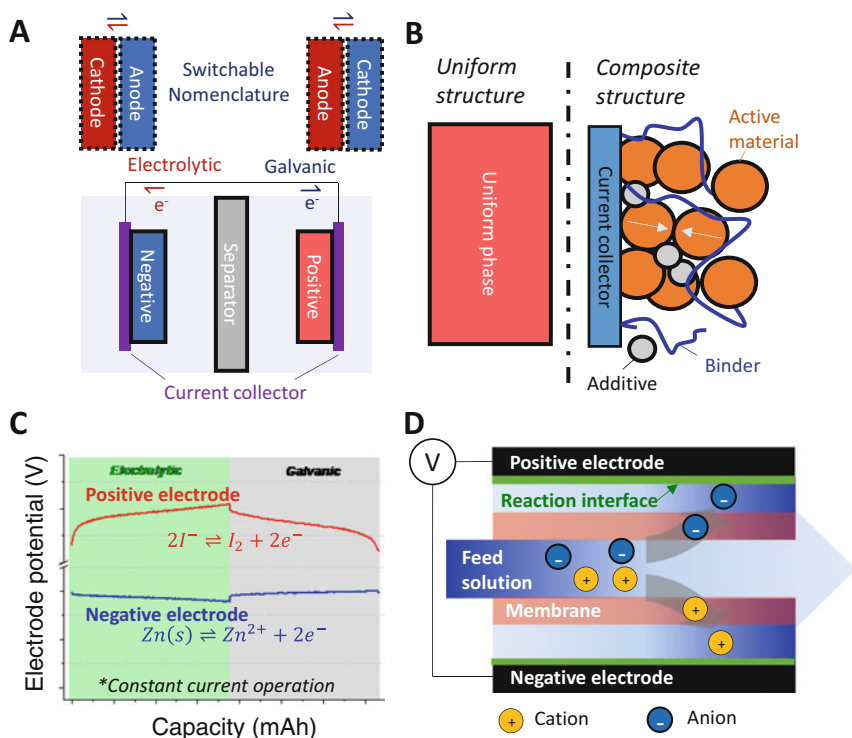
### 1.2.1 Cell Configuration

It is no exaggeration to say that cell design is an ensemble of technology and science and one of the most important considerations for planning a successful electrochemical application. Depending on the purpose of the application, the cell architecture varies broadly from the choice of materials, structures, and configurations. Therefore, studying cell architecture is one of the scientific disciplines for electrochemical applications, and countless patents have been filed in that regard. In the simplest form, an electrochemical cell consists of a pair of electrodes (anode and cathode), electrolyte, current collectors, and membrane/ separator (or salt bridge), as illustrated in Fig. 1.3a. The electrochemical reaction occurs at the interface between the electrode and the electrolyte during the cell operation, and therefore electrodes and electrolytes can be considered as the most active components in the cell.

#### 1.2.1.1 Electrolytes

An electrolyte is a substance that is dissolved as positively charged cations and negatively charged anions in solution; hence, it can be perceived as an ionic conductor. Depending on the tendency to be ionized in solution, electrolytes can be classified as strong (completely ionized) and weak (partially ionized). In general, strong electrolytes are better ionic conductors than weak electrolytes for the same molar concentration. Therefore, for the majority of electrochemical applications, primary electrolytes are chosen from strong electrolytes, whereas weak electrolytes are often applied as buffers to keep the constant pH value or other purposes. According to pH concentration, electrolyte solutions are further described as acidic ( $\text{pH} < 7$ ), neutral ( $\text{pH} = 7$ ), and alkaline ( $\text{pH} > 7$ ). The pH value of the electrolyte solutions plays a critical role in electrochemistry, and we will briefly discuss this in Sect. 1.2.2 again.

Depending on the types of the solvent (a substance that dissolves electrolyte and other substances) and their physical states, electrolyte solutions can be classified into aqueous, organic, molten salt, gel, and solid electrolytes. The solvent for aqueous electrolyte solutions is water, whereas various solvents can be applied to organic electrolyte solutions such as ethylene carbonate, dimethyl carbonate, propylene carbonate, and acetonitrile. Unlike these electrolyte solutions, some electrolytes can be in a liquid state without the presence of solvents (i.e., molten salts and gel electrolytes). Traditionally, high-temperature molten salts have played vital roles in



**Fig. 1.3** Configurations and components of electrochemical cells and examples of electrochemical operations. (a) Basic cell configuration and electrode nomenclature. Even in the same electrochemical cell, the same electrode can be called either a cathode or anode, depending on the direction of the current. (b) Electrodes can have either a uniform structure or a composite structure. (c) Potential-capacity profiles for positive and negative electrodes. In this case, the electrode with the iodide redox couple always has a higher potential than that of the negative electrode with zinc redox couple. This negative electrode can be either mentioned as a cathode for electrolytic systems or an anode for galvanic systems. (d) A cell with a flow channel is separated by two membranes for some electrochemical applications such as electrodialysis, flow batteries, and capacitive deionization. The reactions at the interface between the electrodes and the electrolyte can drive the transportation of ions from the feed solution channel. Various types of membranes can be applied for enabling desired functions of the applications

various scientific disciplines and industrial processes, such as the discovery of metal elements and metal extraction processes. In modern science and technology, ionic liquids, which could be considered as low temperature (or room temperature) molten salts, have shown promising features for broad electrochemical applications, particularly for energy storage systems (Galiński et al. 2006). Nevertheless, the definition of the ionic liquid can still be perceived ambiguously (Wilkes 2002). When a flexible solid structure (e.g., polymers) is introduced to electrolytes, a gel-like feature can be obtained. Depending on the nature of the solid phase substance (macromolecular,

molecular, colloidal) and the liquid phase (organic, aqueous, polymer liquid, oil, ionic liquid), various subtypes are available for gel-like electrolytes with different characteristics (Marr and Marr 2016). In fact, electrolytes can be entirely in solid-state (West 1989), these provide ionic conductivity either by anions/ cations, or both, in various forms such as polymer, amorphous, and crystal structures (Wang et al. 2019).

The essential role of the electrolytes in an electrochemical cell is conducting ions; therefore, high ionic conductivity is preferred for the energy-efficient operation process. On the contrary, electronic conductivity is an undesirable property for the choice of electrolytes; otherwise, the cell will suffer from short-circuiting. In the latter case, electrons will flow from one electrode to the other electrode through the electronic conductivity of the electrolyte material instead of being consumed for desired electrochemical reactions. In that regard, when choosing an electrolyte material, the use of electronically conducting materials such as conducting polymers should be carefully applied (Lee et al. 2019). Depending on the type and the purpose of the applications, the characteristics and desired properties of electrolytes vary significantly.

For instance, in the case of removal applications, the electrolytes often contain species to be removed and generally flow into the electrochemical cell. Hence, the chemistry design of the electrolytes for such systems should be beneficial for the core removal reaction mechanisms and should be as sustainable as possible. Therefore, for water treatment processes, the choice of solvent is generally limited to aqueous electrolyte solutions, and any existing chemicals in the electrolyte should be abundant, reusable, non-toxic, and environmentally friendly. The design considerations for harvest applications are similar to that of removal applications. The choice of electrolyte materials is limited to those containing primary species for the production, for instance, molten salts in the metal extraction process. Also, they should be chosen to maximize the yield of the products with reasonable sustainability.

Unlike removal applications, many harvest applications are not tightly bound with environments and human health; therefore, for these cases, the focus of sustainability is rather economical and performance benefits for industrial processes. On the other hand, in sensing applications (e.g., ion-selective electrodes), the electrolyte must not interfere with the measurements. In such cases, electrolytes are chosen in a way that the cation and anion have almost equal mobilities, thus minimizing the magnitude of the junction potential. The most commonly used electrolytes are potassium chloride (KCl), lithium acetate (LiOAc), and ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ). Furthermore, these electrolytes are also used in high concentrations, typically around 3 M or 4 M. Therefore, it is also crucial that they do not leech into the sample solution since this could result in erroneous measurements, especially in lower analyte concentrations. In order to avoid this, the ideal electrolyte would contain no analyte ions.

For energy consumption and storage applications, electrolytes can be more flexibly chosen; as a result, vast numbers of different kinds of devices have been invented and investigated with almost all known categories of electrolytes. For



rechargeable energy storage applications, electrolytes with structural, electrochemical, and thermal stability are preferable for portable and reversible usage over hundreds of cycles. Except for some beneficial side reactions such as solid-electrolyte interface formation for Li-ion batteries, electrolytes for rechargeable energy storage systems should provide a sufficient potential range of stability window to cover the range of electrode reactions. For particular energy storage applications such as redox flow batteries or advanced energy storage systems with redox-electrolytes, electrolytes with redox-active species work as mediums for storing energy (Lee et al. 2019; Alotto et al. 2014). In such systems, charges can be stored in redox-active dissolved species in the electrolyte, unlike traditional energy storage systems where charge storage mechanism occurs at the electrode surface or bulk in the electrode material.

### 1.2.1.2 Electrodes

Quite the opposite to electrolytes, electrode materials should be electronic conductors, which can also be ionic conductors; high electronic conductivity assures energy-efficient transport of electrons in the electrode materials for desired electrochemical reactions. The majority of the electrode materials are based on metallic conductors (fuel cell, electrolysis) and semiconductors (solar-cell, energy storage devices), while superconductors have also been explored as electrodes mostly for fundamental researches (McDevitt et al. 1993; Abe et al. 2010; Rosamilia et al. 2019). Typically, electrode materials are present in a stationary solid-state; however, liquid and slurry/suspension-type electrode materials have also been active in research (Lee et al. 2016c; Ventosa et al. 2015; Porada et al. 2014).

The electrodes in a solid-state can be either a uniform phase like an enormous chunk of graphite rod for industrial electrolysis process or a composite material with multiple phases (Fig. 1.3b). In the latter case, the electrode components can be further classified into binders, active materials, and additives. In general, the major roles of binder agents are (i) to ensure the cohesion between the particles, (ii) to provide strong adhesion to current collectors, and (iii) to enable facile fabrications (Bresser et al. 2018). Depending on the application, binders could also be used to improve hydrophilicity or hydrophobicity of the electrode (Park and Choi 2010). Active materials are those involved actively in core electrochemical reactions, and additive agents are introduced to support the lacking properties of the active materials; for instance, carbon black is a common additive for enhancing the electronic conductivity of the electrode.

### 1.2.1.3 Current Collectors

The major role of the current collectors is to complement the poor electronic conductivities of electrode materials such as electrodes with semiconductor features; therefore, high electronic conductivity is a desired property. Additionally, they

should be electrochemically stable without undergoing detrimental phase transitions nor chemomechanical degradation. For instance, copper and aluminum are often applied for energy storage devices with organic solvent: copper for low electrochemical potential range (below 2.5 V vs. Li/Li<sup>+</sup>) and aluminum for high potential range (above 2.5 V vs. Li/Li<sup>+</sup>). For instance, cathode materials in commercially available lithium-ion batteries generally use thin aluminum foils or carbon-coated aluminum foils as current collector materials.

Some of the current collectors may not be thermodynamically or electrochemically stable in a particular cell system; in this case, the passivation mechanism plays a crucial role. For instance, aluminum current collectors are considered to be vulnerable to corruptions in lithium-ion battery cells (Zhang et al. 2005; Myung et al. 2009). However, passivation layers (e.g., Al<sub>2</sub>O<sub>3</sub> and AlF<sub>3</sub>) can be formed depending on the detailed chemistry of the cell systems, for instance, the types of the electrolyte and the contents of impurities and additives. Due to high electronic conductivity, current collectors could be perceived as a part of the electrode materials in a wide perspective.

#### 1.2.1.4 Separators

For successful (at least for the desired time scale) reactions at the electrodes in electrochemical cells, the electrode compartments should be connected with mediums that are ionically conductive. Since the latter can be achieved by the flow of ions in electrolyte solutions when two electrodes are immersed in the same electrolyte solution, the desired reactions can take place without a need for an additional cell component. For instance, when two plates of Pt electrodes are applied to an aqueous electrolyte solution, and a sufficient electrochemical potential is applied in the circuit between these electrodes, hydrogen and oxygen gas can continuously evolve as long as the solution is not running out nor any undesired degradation process occurs. However, in some applications, a separation of electrolytes is required to each electrode compartment, which can be achieved by introducing a salt bridge or an ion-exchange membrane. In this case, the purpose of introducing this component is to prevent the mixing of two different electrolytes between electrode compartments. These substances are generally known as separators, and depending on the types of the materials and separation mechanisms, various classes of materials have been applied.

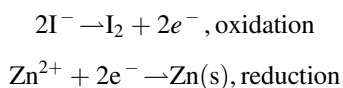
From the mechanism point of view, the electrolytes can be separated based on the size of the molecules (physical filter), charge exclusion mechanism (Donnan effect), or diffusivity (selective ionic conductor). A widely applied example of physically minimizing the transport of ions between two different electrolytes is an agar (a jelly-like substance) salt bridge, which prevents a rigorous mixing process (Shao and Feldman 2007). For instance, the electrolyte in reference electrodes can be separated from the electrolyte of an experimental setup by a junction filled with agar or porous glass materials. In general, this junction is filled with saturated electrolytes with similar diffusivity to minimize liquid junction potential, which arises due to different

diffusivity through the junction (Revil 1999). While these junctions are examples where a slow diffusion process and similar diffusivity are required, completely different requirements are necessary for some applications. For instance, the desired properties of the junction (a thin membrane in this case) between two electrolytes in redox flow batteries are fast diffusion of ions with high permselectivity, a selective ion transport of a particular type of ions against the other types of ions. These ion-exchange membranes together with advanced selective ion conductors based on various selective diffusion mechanisms are expected to play a pivotal role not only for conventional applications but also for innovative advanced applications; we will review this aspect again in Sect. 1.2.5.

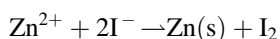
Regardless of electrolyte separation, two electrodes are required to be as close as possible to each other without causing a short-circuit for some high current applications. The short-circuit can be prevented when a thin non-electronic conductor separator is introduced, which will enable the ionic connection between the electrodes. These separators also enable pressure between the electrodes and current collectors (if involved); hence contact resistance can be mitigated, and a densely packed structure can be achieved. These kinds of separators are essential for compact portable energy storage systems such as battery pouch cells (Siegel et al. 2013).

### 1.2.1.5 Electrode Nomenclature

As illustrated in Fig. 1.3a, an electrochemical cell requires at least a pair of electrodes, and in most cases, different reactions occur at each electrode. For instance, when two metal electrodes are immersed in a cell containing  $\text{ZnI}_2$  aqueous electrolyte, the following reactions may occur at each electrode for an electrolytic process (Fig. 1.3c):



Hence, the overall reaction can be summarized as:



The electrodes are often called cathodes and anodes depending on electrochemical applications. Both fundamentally and conventionally (Fig. 1.3a), cathodes are defined as the electrodes where reduction reaction occurs, and vice versa for anodes. Since electrochemistry has greatly developed after the introduction of voltaic (or galvanic) cells in history, the direction of the reaction in the cell was spontaneous. Hence, the cathodes and anodes could be defined during discharging (galvanic) process without confusion. Later, since the emergence of rechargeable (secondary) batteries in history, the previous definition could have been confusing as the conventional definition by where oxidation and reduction occur depending on

whether the cell undergoes spontaneous (discharge) or non-spontaneous (charging) reactions. However, a reasonable convention was made by following the nomenclature from the primary batteries that cathodes and anodes are defined during the discharging process.

In the case of conventional electrolysis (non-spontaneous), the fundamental way of defining electrodes is the same as that of primary batteries, but the reaction spontaneity is different; as illustrated in Fig. 1.3a, the flow of electrons is different during cell operation. Hence, defining electrodes for electrolysis applications is completely the opposite to that for the battery applications; in fact, the fundamental way of defining electrodes has not changed. For this reason, the use of cathodes and anodes notation can be confusing, particularly for researchers from different fields. This can become even worse when there is no agreement about the notation rules in emerging new scientific societies. In fact, there is another way of defining electrodes based on their polarity. In most applications, one electrode has a higher electrical potential than the other electrode. For instance, in the case of a rechargeable battery (Fig. 1.3c), the electrical potential of a cathode is always higher than that of the anode, leading to its notation *positive electrode*, and *negative electrode* for the anode. By this definition, we could prevent the confusion arising by discussing the same phenomenon for different applications.

The nomenclature with positive/negative electrodes can be applied in most of the applications; however, there are some exceptions where a complex operation is applied particularly in interdisciplinary research areas such as capacitive deionization (CDI) and battery desalination we discussed earlier in Fig. 1.1. The deionization process in a CDI cell occurs when a potential bias is applied between a pair of electrodes. Therefore, one electrode is polarized positively, and the other is polarized negatively. For electric double-layer (EDL) based electrodes, the ions present in the solution are attracted to and stored on the surface of the electrodes, causing the desalination of the solution. After electrode saturation, the regeneration may be carried out by simply short-circuiting the electrodes or by reversing their polarity.

As observed, by defining the CDI process in this way, we use the terms positive and negative electrodes to describe the electrodes after polarization during the charging step. Still, this electrode nomenclature can also be misleading since the CDI operation runs in cycles, and the polarity of the electrodes may be reversed many times. For instance, carbon electrodes modified with functional surface groups should be discharged by applying a small inverse potential (compared to the charging potential). Since this type of approach can enhance the total capacity of the electrode to remove ions, the CDI systems based on it are known as enhanced CDI, or e-CDI (Biesheuvel et al. 2015).

It is also possible to apply cell voltages starting from negative to positive (or vice versa), therefore, extending the operational voltage window of the CDI cell by employing ion-exchange membranes (Sect. 1.3.2). In this case, the positive and negative electrodes are interchanged repeatedly (Biesheuvel and Van Der Wal 2010). In these cases, it makes no sense to use the terms positive and negative electrodes. The same applies to anodically and cathodically polarized electrodes, which are common terms used to describe the positive and negative electrodes in

CDI, respectively. A common example is the use of inverted CDI (i-CDI), in which the electrode polarized cathodically removes anions, and the electrode polarized anodically removes cations (Biesheuvel et al. 2015). The i-CDI may be achieved by completely modifying the potential of zero charge of the used electrodes or by placing an anion exchange membrane over the cathode and a cation exchange membrane over the anode. In this context, the use of the terminology positive and negative (or anodic and cathodic) should be carefully chosen and well described for specific situations, such as reported only for charging or for discharging steps during the desalination process.

So far, we have introduced the simplest possible cell architecture for electrochemical applications. Depending on the desired purpose of the cell, additional functions can be applied by introducing flow channels, varying channel structure, applying functional membranes with various arrangements, modifying electrode structure, and incorporating reference electrodes. As we have described for CDI applications (Fig. 1.3d), the flow channel structure brings versatile functions for electrochemical applications. One of the key roles of the flow channels is to provide continuous operations. For fuel cell applications, the channel structure provides a continuous supply of feedstock ( $\text{H}_2$  and  $\text{O}_2$ ) and the removal of products (water), which is enabled by bipolar plates (Hermann et al. 2005). For some applications, a multi-channel structure is applied to enhance the overall process efficiency, like in the case of electro dialysis (Al-Amshawee et al. 2020). The aspect of membranes and flow channel design will be discussed again in more detail in Sect. 1.2.5. Also, a reference electrode is a pivotal component for analytics as well as monitoring and controlling of electrochemical processes; their mechanism and applications will be shortly introduced in the next section.

### 1.2.2 Thermodynamics: A Driving Force for the Reactions

In the previous section, we have learned a basic and advanced cell design of electrochemical cells while discussing the detailed roles of each cell component. Hence, we now have an understanding of how the desired functions (harvest, removal, storage, consumption, analytics) are achieved via core electrochemical reactions in a cell with a particular architecture. But, we still have to explore the origin of spontaneity and the driving force of electrochemical reactions. We have reviewed that some of the reactions take place spontaneously (primary batteries and fuel cells), and some of them (electrolysis, electroplating) are not. In thermodynamics, the Gibbs free energy is the property that governs the reaction spontaneity. For electrochemical systems, the Gibbs free energy is the maximum non-expansion work which can be done by a reaction at constant temperature and pressure, particularly when a certain amount of electrons traveled via a potential difference ( $\Delta\phi$ ).

$$\Delta G = -nF\Delta\phi \quad (1.1)$$

where  $\Delta G$  is in kJ/mol,  $n$  is the number of electrons transferred in the reaction,  $F$  is Faraday's constant ( $9.6485 \times 10^4$  C/mol, a product of Avogadro's constant and the elementary charge) representing the charge per mole of electrons.

For instance, in the case of an galvanic cell consisting of  $\text{Zn(s)}|\text{Zn}^{2+}||\text{Cu}^{2+}|\text{Cu(s)}$  with a cell potential of 1.10 V, the reaction Gibbs free energy to convert  $\text{Zn(s)}$  and  $\text{Cu}^{2+}$  to  $\text{Zn}^{2+}$  and  $\text{Cu(s)}$ , respectively, is  $-2 \times 9.6485 \times 10^4 \text{ C/mol} \times 1.10 \text{ V} = -212 \text{ kJ}$ . The negative value indicates that the reaction is spontaneous (galvanic); it also implies that we need to apply energy to reverse this reaction (electrolytic). In the case of standard conditions (all gases are at 1 or 1.01 bar, 1 M concentration for all participating solutes, at 298.15 K, and metals in pure states), the above equation is expressed with the standard reaction Gibbs free energy and the standard potential. In the previous case with  $\text{Zn(s)}|\text{Zn}^{2+}||\text{Cu}^{2+}|\text{Cu(s)}$  under the standard condition, the standard cell potential is known to be 1.10 V. When the negative electrode compartment is replaced with Pt for  $\text{H}_2(\text{g})/\text{H}^+(\text{aq})$  redox reaction, the standard cell potential becomes 0.34 V. By setting this particular  $\text{H}_2(\text{g})/\text{H}^+(\text{aq})$  potential value to zero at any temperature, we now can express that the standard electrode potential ( $\phi^0$ ) for  $\text{Cu}^{2+}/\text{Cu}$  is 0.34 V vs. SHE (standard hydrogen electrode). In this manner, the standard electrode potentials values of many redox couples have been known and reported.

Since the standard electrode potential for  $\text{Zn}^{2+}/\text{Zn}$  is  $-0.76 \text{ V}$  vs. SHE, we now know that Zn becomes a negative electrode when coupled with a copper (Cu) electrode, and Zn (s) will be spontaneously oxidized to  $\text{Zn}^{2+}$  while  $\text{Cu}^{2+}$  will be reduced to Cu (s). Hence, we can easily predict the voltage of a cell when the standard electrode potentials are known for the half-reactions at both electrodes, and which electrode will be reduced and oxidized. In that regard, we could also expect that a redox couple with more positive standard electrode potential has a higher tendency to oxidize the redox couple at the other half-cell while also being reduced. In this case, the oxidized form of this couple is an oxidizing agent, and the oxidizing strength depends on the potential difference between the redox couples of each half-cell.

From the primary batteries, most of us have experienced that the cell voltage is weakening by the end of its lifetime, and this is caused by the consumption of the reactants while more products are generated. By relying on the Nernst equation, we can calculate the potential of the cell when the concentration ratio between the reactants and products is known.

It is also important to look at how we derive this famed Nernst equation. If you recall the fundamentals of thermodynamics, you may remember that when  $\Delta G < 0$ , the reaction is thermodynamically favorable, when  $\Delta G > 0$ , the reaction is thermodynamically unfavorable, and when  $\Delta G = 0$ , the reaction is in dynamic equilibrium. When a spontaneous reaction proceeds towards its equilibrium, the  $\Delta G$  approaches 0 with time. Consequently, the reactants are being consumed, whereas the product