Jochen Kieninger

Electrochemical Methods for the Micro- and Nanoscale

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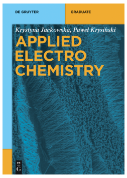

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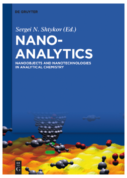

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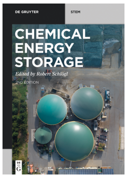

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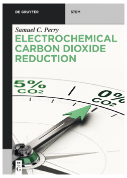

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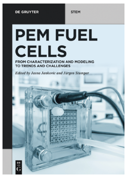

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Jochen Kieninger

Electrochemical Methods for the Micro- and Nanoscale

Theoretical Essentials, Instrumentation and Methods for Applications in MEMS and Nanotechnology

DE GRUYTER

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To my father
Emil Kieninger
(1937–2020)

Preface

Traveling is highly essential to broaden our horizons, discover new landscapes, and understand the perspective of the locals. Sometimes the journeys are adventurous or challenging; in most cases, they are pure pleasure and fun—if not in the situation itself at least in retrospective. Academic careers in interdisciplinary fields are similar to traveling to different cultures, striving for the best of all by understanding the different languages, thinking about the concepts, and listening to the different points of view. My own experience being a microsystems engineer with a background in physics and electronics, exposed to electrochemistry while developing sensors for biomedical applications is a typical course in this sense.

The outcome of my journey between the disciplines resulted in a class on electrochemical methods for master students in Microsystems Engineering. After teaching the topic a few semesters, the outline improved while students from different subjects such as Functional Materials, Embedded Systems Engineering, and Sustainable Systems Engineering attended the lecture and provided their feedback. The selection of topics proved to fit together perfectly. I realized that such a combination of a consistent electrochemical theory, coherent description of methods, insight into the instrumentation, and implications for the different applications in microelectromechanical systems (MEMS) and nanotechnology is unique. The positive feedback encouraged me to write a full textbook based on this class.

A vast and further growing field of application for electrochemical methods is the energy sector. Two primary drivers stick out: For systems smaller in size, it is the need for portable energy storage for mobile computers, smartphones, smartwatches, headphones, and any kind of wearables. Secondly, the increasing awareness of climate change and new strategies for “greener power” asks for efficient energy storage and energy conversion for both the power grid and automotive application. At the same time, elements like lithium commonly used for energy storage are not an optimal solution when thinking of widespread usage in large batteries, e. g., for electromobility. Here, other materials are needed to replace lithium and cobalt because of their limited resources, environmental concerns, and to avoid further exploitation of poorer nations. Beyond different materials for batteries also other storage forms of energy, e. g., as hydrogen gas, appears a promising alternative.

Nanotechnology allows us to fabricate materials for energy conversion and storage, electrochemical sensors, and to some extent, electrochemical actuators. Additionally, electrochemical methods are employed to make the nanosystem itself or for the characterization of the obtained materials. Studies with engineered nanostructures lead to an awareness of effects on the nanoscale, even when dealing with microscopic or macroscopic structures.

Electrochemistry seems far from natural processes when looking from the perspective of material science or energy systems. However, considering how information transfer happens while you read this preface, it is mainly about electrochem-

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istry. There are some optical effects to bring the information onto the retina of your eye (slightly different if you are reading the printed or electronic book), or maybe an acoustic pathway if you use a screenreader. But as soon as the information is within you, it is all about the interplay between (bio-)chemistry and electricity—the core domain of electrochemistry. With these thoughts in the back, it is clear why electrochemical methods are so powerful when considering applications in the biomedical field, in neurotechnology, and generally in the life sciences.

Many current MEMS devices incorporate an electrochemical principle with either sensor or actuator functionality. That is especially true for bioMEMS applied in life science. While most MEMS are designed using state-of-art microfabrication technologies, electrochemical features are often rudimentary developed, and hence lower overall system performance. Electrochemical analytical methods are widely used for sophisticated purposes in laboratories, often with ultramicroelectrodes exploiting microspecific features within macroscopic setups. However, there is little transfer of advanced electrochemical methods to lab-on-chip systems, although the performance of devices would increase by orders of magnitude with the same fabrication effort.

I hope you enjoy the journey described in this book as I did during writing—at least in retrospective—and be able to apply the knowledge to future micro- and nanosystems on which you are working. Besides, take your time to attend scientific conferences—they can be a good starting point for travel in its literal sense as well as to communicate the powerfulness of electrochemical methods in MEMS and nanotechnology.

Jochen Kieninger

About the book

The book has three parts. The first part contains electrochemical theory, discussion of the instrumentation, and information about the lab tools. Details are provided only to the level, which is needed to understand and apply the electrochemical methods. The second and major part explains classical and advanced techniques. All equations are adjusted to be consistent with the fundamentals. The last part discusses several fields of application and explains the therein used electrochemical methods with the specific terms of the area.

Undergraduate or master students can read the book linearly as a comprehensive textbook. They might discover in the third part of the book their future topic. For Ph. D. students, postdoctoral researchers as well as for researchers in the industry, the book will help by its clear structure to get fast answers from a specific section.

Throughout the chapters, you will find several tasks on different levels in a box with a pen in its pictogram. The given problems should help you to familiarize yourself with the topic, both by understanding the derivation of essential equations and by learning how calculations can be applied. On page 383, there is an overview of all tasks.

The difficulty level refers to students from a Master's program in Engineering:
■□□ Simple task, brings you in touch with the topic.
■■□ Medium level task, require more thinking or previous knowledge.
■■■ Difficult task, needs substantial time and effort to find the solution.

Depending on your background, you might feel the difficulty level differently and benefit from following the solutions. Nevertheless, I strongly recommend trying to solve the tasks on your own before checking the answers.

Please check www.electrochemical-methods.org. Here, you can find solutions for all tasks. Additionally, the webpage provides updates to the book and further information.

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Part I: **Fundamentals**

> “Nothing is too wonderful to be true, if it be consistent with the laws of nature.”
>
> Laboratory journal entry by Michael Faraday (1849)

1 Introduction

Electrochemistry can be understood as the part of chemistry in which electricity is involved. Classical textbooks often define electrochemistry from this perspective: "Electrochemistry is the branch of chemistry concerned with the interrelation of electrical and chemical effects" [1]. Consequently, in many faculties, the electrochemistry is accounted for physical chemistry. In contrast, it is mainly scientists with a background in microsystems engineering, nanoscience, material science, electrical engineering, or physics who are developing microelectromechanical systems (MEMS) and nanotechnology applications. Often the perspective is from the electrical effect, which extends from the electron-conducting phase (the electrical wire) to the ion-conducting phase (the electrolyte). In this context, we can understand electrochemistry as the interfacing discipline, which describes the transition between ion and electron conduction.

Looking back in history, researchers made the first observations of electrochemical phenomena during biological studies. However, the development of the discipline separated from biology until recent applications in electrophysiology, biosensors, or neuroscience. In the following section, we start a short and highly selective journey through history to follow the path from the biological interpretation to the modern understanding of electrochemical effects. A brief discussion of the current fields of applications follows illustrating the completely different environments in which electrochemical methods play a role. This chapter closes with an introduction to the electrochemical cell describing in more detail the arena in which the theory, methods, and applications discussed throughout this book play a role.

1.1 Short history of electrochemistry

It is surprising how late electrochemical effects were described as such – especially considering that many processes in nature, most prominently physiological mechanisms rely on electrochemical principles. With this in mind, it is quite ironic that Galvani attributed his observation of electrochemical phenomena as a biological effect, which later proved to be independent of biology.

1.1.1 Luigi Galvani – animal electricity

It was the 18th century when many scientists became enthusiastic about electrostatic effects. Luigi Galvani (1737–1798), graduated in medicine and philosophy, worked at the University of Bologna on "medical electricity." He was rubbing frog skin to provoke electrostatic effects. The legend says that while doing those experiments in 1780, his assistant touched the sciatic nerve of a frog leg lying around on the table with a

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metal scalpel, which might have picked up charges from previous experiments. Suddenly, the frog leg kicked as it still would be alive. Galvani attributed this action to what he called *animal electricity* and assumed the existence of an "animal electric fluid," which is flowing inside the nerves. This view was opposing the well-established balloonist theory dating back to the Greek physician Galen described in the second century. Galen believed that fluid flows in hollow nerves, causing muscle contraction. Replacing this model by animal electricity was a big step forward toward nowadays understanding of *bioelectricity*.

To remember the meaning of oxidation, imagine a lion called LEO who says GER. LEO reminds you of "Loss of Electrons is Oxidation," and GER stands for "Gain of Electrons is Reduction."

Galvani optimized his experiments as shown in Figure 1.1. He connected a copper wire to the nerve and a zinc wire to the lower part of the leg. The frog leg twitched whenever he brought the wires in contact. Today we can easily understand what happened in Galvani's experiment. Copper itself does not take part in the reaction but catalyzes the reduction of hydrogen ions to form molecular hydrogen while zinc gets oxidized and dissolves:

$$\text{Oxidation:}\quad \mathrm{Zn} \longrightarrow \mathrm{Zn}^{2+} + 2\,\mathrm{e}^- \qquad -0.76\,\mathrm{V} \tag{1.1}$$

$$\text{Reduction:}\quad 2\,\mathrm{H}^+ + 2\,\mathrm{e}^- \longrightarrow \mathrm{H}_2 \qquad 0\,\mathrm{V} \tag{1.2}$$

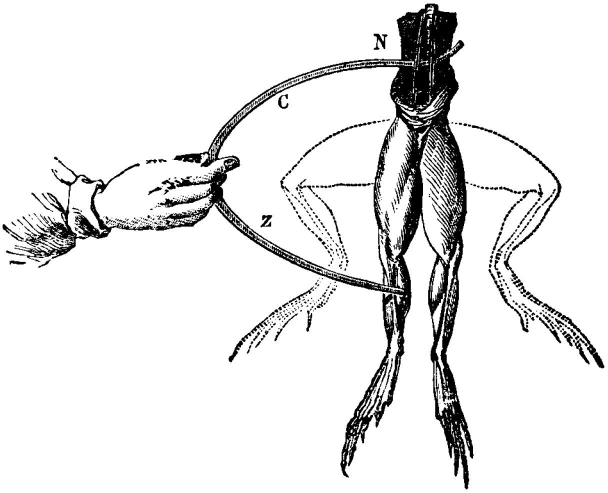

Figure 1.1: Galvani's famous experiment to demonstrate what he called animal electricity: A copper wire (C) connects to the sciatic nerve (N) and a zinc wire (Z) to the lower part of a frog leg. Upon contact of the two wires, the leg twitches [2].

The frog leg acts as both the electrolyte and the recipient for the electrical stimulation. The cell voltage can be up to 0.76 V, which is sufficient to cause twitching of the frog leg.

Galvani also did other experiments with frog legs. Inspired by Benjamin Franklin's work (1706–1790), he connected frog legs hanging outside his house with one wire to the roof and another cable to a deep well. When a thunderstorm approached, he observed twitching of the frog legs even before the actual lightning. Imagine how people looked at those activities at the end of the 18th century – it is not surprising that Galvani's work was later one of Mary Shelley's (1797–1851) inspirations writing her novel "Frankenstein."

1.1.2 Allesandro Volta – pile to disprove animal electricity

At the same time, Allesandro Volta (1745–1827) did research in experimental physics at the University of Pavia. Inspired by Galvani's findings on animal electricity, he repeated the frog leg experiments with the copper and zinc wires. However, he concluded that the observed effect is not an inherent property of the animal but can be generated chemically with two metals in a salt solution.

To proof his position, he constructed at the turn of the century a demonstrator, which we know today as the *Voltaic pile* (Figure 1.2).

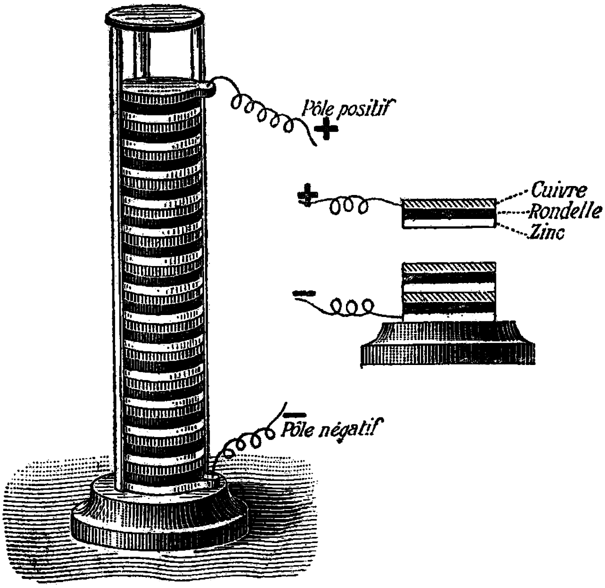

Figure 1.2: Voltaic pile with 14 stacked cells. Each cell consists of a copper electrode ("Cuivre"), a disk ("Rondelle") of cardboard soaked with salt water and a zinc electrode ("Zinc"). Image: Leçons de Physique (1904), courtesy of Éditions Vuibert.

During the experiments to find the optimal electrode materials, Volta realized that a pair of the same metals do not show any electricity, while copper and zinc showed the highest effect. He thereby discovered the electrochemical series. Initially, Volta used vessels in which he kept brine (a high concentration aqueous NaCl solution) with the metal pairs forming an electrochemical cell. Several connected elements in series results in a higher effect, measured in what we today call *electromotive force* (emf). In the Voltaic pile, cardboard soaked with brine was the electrolyte, and only stacking connected the individual cells. An inherent disadvantage of this early realization of a battery was the electrode blocking with hydrogen gas bubbles at the copper electrode.

1.1.3 John Daniell – early battery

In the following decades, many scientists attempted to improve the Voltaic pile with the goal of a constant power supply for more extended periods. In 1836, the British scientist, John Frederic Daniell (1790–1845), presented a two-fluid battery that was later called the *Daniell cell*.

Initially, Daniell used a copper vessel filled with $CuSO_4$ solution. This setup replaced the reduction reaction causing hydrogen gas formation by copper plating:

$$\text{Reduction:} \quad Cu^{2+} + 2\,e^- \longrightarrow Cu \qquad 0.34\,V \tag{1.3}$$

To shield the zink electrode from the copper ions, Daniell mounted it into an ox-gullet filled with H_2SO_4 solution. The ox-gullet was brought into the center of the copper vessel and acted as a porous barrier allowing ionic conduction while hindering the mixing of the two electrolyte solutions. Later on, unglazed earthenware replaced the ox-gullet, and the copper electrode was in the middle, surrounded by an excess of $CuSO_4$. The zink electrode was outside the porous barrier, as illustrated in Figure 1.3.

The overall cell voltage without electrical load was up to 1.1 V, as can be seen from the difference in equilibrium potentials of equations (1.1) and (1.3). Further refinements comprised the replacement of sulfuric acid by a $ZnSO_4$ solution.

Recharging of the Daniell cell is not possible. Cu^{2+} ions can penetrate the porous barrier resulting in contamination of the electrolyte next to the zink electrode with copper ions. Upon application of a charging voltage, the copper ions would deposit onto the zink electrode destroying the battery's performance.

1.1.4 William Grove – early fuel cell

Sir William Robert Grove (1811–1896) was a fellow of the Royal Society, as was Daniell. The United Kingdom's national academy of sciences was a breeding ground for numerous scientific advances in Europe since the 17th century, and became after Italy,

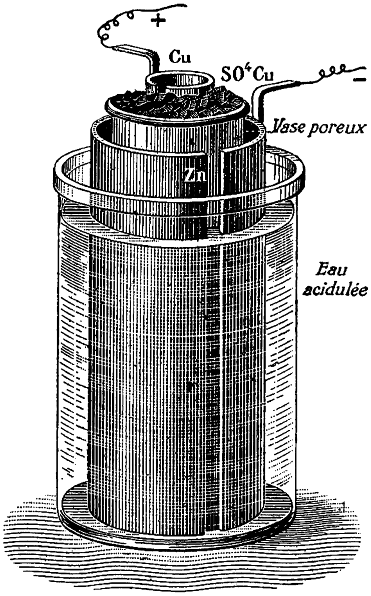

Figure 1.3: The Daniell cell was a significant improvement to the Voltaic pile. The copper electrode (Cu) surrounded by electrolyte with copper sulfate (“SO^4Cu”) was in the center. A porous vessel (“Vase poreux”) separated this electrolyte from the zink electrode in an acidic electrolyte (“Eau acidulée”). Image: Leçons de Physique (1904), courtesy of Éditions Vuibert.

the next hotspot for electrochemical developments. Grove improved the Daniell cell to obtain a higher cell voltage. He used platinum in aqueous nitric acid solution instead of the copper in a copper ion containing solution. However, the reduction reaction resulted in the release of the toxic gas nitrogen dioxide, which was one reason a slightly modified Daniell cell without platinum was later the preferred choice for the American telegraph system, by that time an important field of application for batteries.

In 1839, Grove came up with his gas-voltaic battery, what we nowadays call a *fuel cell.*[1] The gas voltaic battery contained two half-cells partially filled with gas as the fuel and an electrolyte. At the negative terminal, hydrogen gas was around the electrode. On the other side, oxygen was at the inert metal. The redox scheme providing electrical energy results in no waste products but water:

$$\text{Oxidation:}\quad H_2 \longrightarrow 2\,H^+ + 2\,e^- \tag{1.4}$$

$$\text{Reduction:}\quad O_2 + 4\,H^+ + 4\,e^- \longrightarrow 2\,H_2O \tag{1.5}$$

---

[1] Sir William Robert Grove is often named as the inventor of the fuel cell. However, already one year earlier, the German chemist, Christian Friedrich Schönbein (1799–1868), by then a professor in Switzerland, demonstrated the working principle of a fuel cell paving the way for the technical realization by Grove.

Practically, Grove stacked several of those cells together to achieve a higher cell voltage and even split again water in an electrolysis cell (Figure 1.4). He also stacked tens of such batteries to operate a carbon arc lamp.

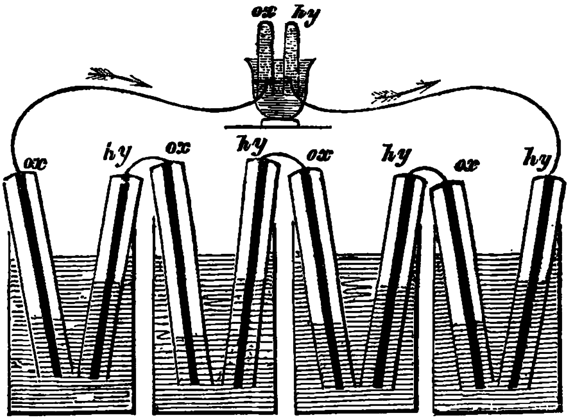

Figure 1.4: A series connection of four Grove's gas-voltaic batteries, which we would call today fuel cells. Each half-cell contains a platinum wire with acidic electrolyte in a partially gas-filled vessel. Each battery included a half-cell with oxygen ("ox") and hydrogen ("hy"). The smaller setup on top is an electrolysis cell proving the batteries' function [3]. Reprinted from Grove, On a Gaseous Voltaic Battery. Philosophical Mag Ser 3, 1842, 21 (140), 417–420, by permission of Taylor & Francis Ltd, http://www.tandfonline.com.

Today's fuel cells rely on the same principle. The reduction reaction uses oxygen either as a pure gas or from the air. Besides pure hydrogen gas, several hydrocarbons feed the oxidation reaction. A more detailed treatment on fuel cells can be found in Section 11.1.1.

1.1.5 Robert Bunsen – economic electrode material

Only two years later, Robert Wilhelm Eberhard Bunsen (1811–1899) came up with an improved setup nowadays referred to as Bunsen battery replacing the costly platinum with carbon, and thus paving the way for large scale applications. Many students today may recognize his name because of the Bunsen burner he invented. However, from an economic perspective, Bunsen's focus on cheaper electrode materials influences our daily lives much more.

The issue of high metal cost is a hot topic until today. In contrast to Bunsen's original approach, today's catalysts are not made of pure carbon but often are sophisticated functional materials with micro or nanosized features and, in many cases, decorated with metallic catalysts. Additionally, those materials may also offer more extended stability in harsh conditions or provide a high catalytic active surface area because of arrangement as a hierarchical micro-nanostructures (Section 9.2.2).

1.1.6 Michael Faraday – quantitative experiments

One of the most excellent experimentalists was Michael Faraday (1791–1867). Many significant technical and scientific breakthroughs go back to him, such as the invention of the dynamo, visualization of magnetic field lines, or the description of a magneto-optical effect, which we today call the Faraday effect.

Faraday was the first who made electrochemical experiments quantitative. In particular, he figured out that he needed a charge of 96 500 A s to deposit 108 g (what is 1 mol) of silver in a one-electron process. This number was an exact result compared to the modern formulation of what we today call *Faraday's law* in the more general writing

$$m = \frac{M}{zF} \cdot Q \tag{1.6}$$

with the constant $F = 96\,485\ \mathrm{A\,s\,mol^{-1}}$ attributed as *Faraday constant*, which is nowadays linked to fundamental constants rather than experiments. m is the mass, M the molar mass, z the valency, and Q the charge (Section 2.2.1).

Faraday was also a great science communicator. In his Christmas lecture series "On the Chemical History of a Candle," which he gave 1848/49 and repeated 1860/61, he explained physics, chemistry, and electrochemistry by considerations starting around a burning candle. According to reports, the lectures attracted not only juveniles, students, and scientists but also celebrities (Figure 1.5). So another thing to learn from history is that great scientists should be able to explain their topics simple to reach out and make their ideas persistent. In contrast, refusing honors like the offering of knighthood or becoming president of the Royal Society did not affect his legacy. Faraday was very religious and followed strict ethical standards. Being asked by the British government to support the production of chemical weapons, he denied it.

1.1.7 Walther Nernst – thermodynamics

Walther Hermann Nernst (1864–1941) was a German physicist and chemist, who worked most of his career at the University of Göttingen. During his habilitation in Leipzig, he linked the by then mainly experimentally driven electrochemistry with thermodynamics. He modeled the concentration by pressure assuming the electrolyte as an ideal gas, which allowed him to derive what we know as the Nernst equation (Section 2.2.3).

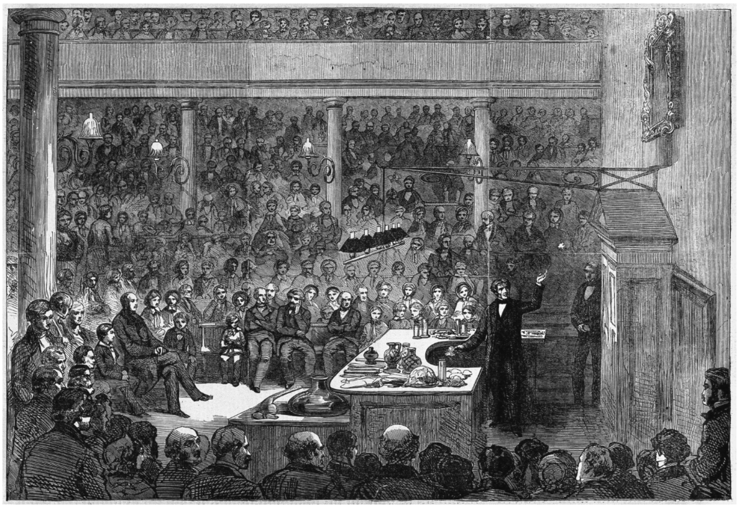

Figure 1.5: Michael Faraday in one of his Christmas lectures at the Royal Institution of Great Britain; also Prince Albert and his sons were in the audience. Wood engraving, 1856, after Alexander Blaikley. Image: Wellcome Collection (public domain).

While Nernst today is mainly recognized for the Nernst equation and maybe the Nernst diffusion layer, it was the Nernst heat theorem, now better known as the third law of thermodynamics for which he received the Nobel Price in 1920. Nernst was very serious about everything he did. While he made an outstanding contribution to thermodynamics and electrochemistry, Nernst worked with a similar passion for chemical weapons development throughout World War 1. During the Third Reich, he distanced himself from the Nazi regime and spoke for his Jewish colleagues what finally required him to retire in 1933.

For the decades after World War II, the shorter distance to the present makes it less easy to clearly identify the hallmarks. Significant contributions were possible because of advances in the instrumentation. More recently, improved computational capabilities led to novel approaches to model electrode reaction, such as density-functional theory (DFT) calculations, ab-initio molecular dynamics (MD), and cross-scale simulations. While the exact field of applications changed over the centuries, analysis of biological processes and energy storage respective conversion are the common threads. If you became interested, you can find a more detailed storyline of historical scientists shaping our nowadays understanding of electrochemistry from Shukla et al. [4].

1.2 Fields of applications

Electrochemical methods for the micro and nanoscale may seem to be a very narrow topic. However, looking at the many fields of application in which the methods play a crucial role, one might wonder why not all engineering curricula include a compulsory lecture on this topic. This section gives you an overview of a wide range of different areas. The intention here is to emphasize the broad range of applications rather than to provide a comprehensive list.

1.2.1 Biomedical sensors and point-of-care systems

Glucose monitoring is a big success story for widespread applications of biosensors. Since the 1970s, diabetes patients benefit from blood glucose measurements with finger pricking and later on complemented by continuous glucose monitoring (CGM) devices leading to better life quality and higher life expectancy. Section 10.1.5 discusses the various electrochemical methods playing together in a commercial glucose meter to detect glucose in a blood droplet.

Figure 1.6 shows a state-of-art CGM system. Diabetes patients can wear such systems for up to a week on the skin, e. g., on the belly or the arm. A tiny needle allows for continuous measurement of the tissue glucose concentration helping the patient control their glucose levels. In contrast to finger pricking alone, CGM provides continuous data, also during sleep. Additionally, the system can warn the patient when values exceed thresholds before the situation gets critical.

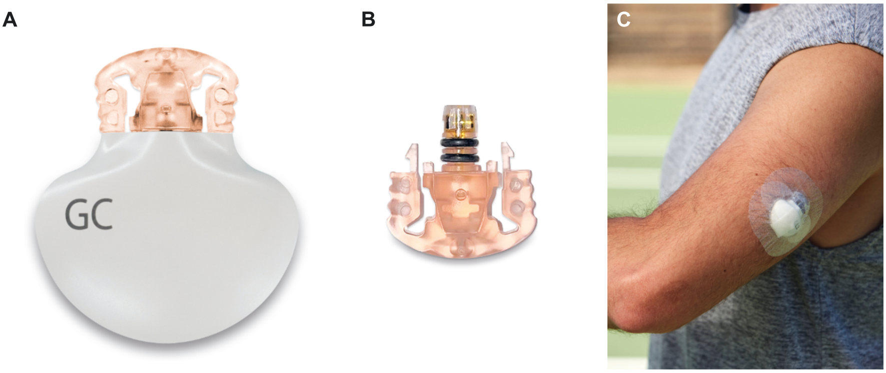

Figure 1.6: The Guardian Sensor 4 system allows continuous glucose monitoring (CGM) from interstitial fluid. The transmitter (A) incorporates a disposable sensor unit (B) with a tiny cannula, which the patient can place on the upper arm (C) or belly. Reproduced with permission from Medtronic GmbH, Germany.

While the focus for diabetes is on home use devices, parallel to this, clinical analyzers have matured, which include several biosensors together with ion-selective and oxygen sensors. Most of these sensors are relying on electrochemical measurement principles, while some use optical read-out based on absorption or fluorescence.

In addition to the blood glucose meter, many other point-of-care devices enable decentralized testing for specific substances or measurements at home, in emergencies, in doctor's offices, or directly at the bedside in hospitals. Enzymatic biosensors integrated with microfluidics allow multiparameter monitoring from tiny samples (Figure 1.7). Also, immunoassays are used in such point-of-care testing (POCT) systems, which utilize antibodies to detect the analyte selectively. Electrochemical methods allow the read-out and inherent signal amplification, as described in Section 10.1.7.

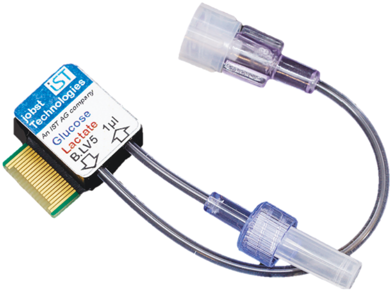

Figure 1.7: Enzymatic flow-through biosensor device: the cartridge contains sensors for glucose, lactate, glutamine, or glutamate. The low internal volume of 80 nl allows for samples' volumes below 1 µl. Reproduced with permission from Jobst Technologies GmbH, Germany.

Chemo and biosensors play an essential role in observing the metabolism in cells cultured artificially outside the organism [5], Section 10.1.8. The cells are either kept simply in culture or grown in chips comprising microfluidics to mimic even the function of organs (organ-on-chip). The goal of these approaches is to have a model with human cells in the lab, allowing drug tests to avoid animal experiments or even test several therapeutic strategies with a patient's cells to choose the most promising therapy for the individual patient. In the future, those approaches will be an essential part of personalized medicine.

1.2.2 Neuroscience, neurotechnology, and auditory nerve stimulation

Research in neuroscience requires information on the brain at many different levels. The realm spans from behavioral studies, investigation of the neural activity in particular functional units by magnetic resonance imaging, electrical signals recorded inside or outside the skull to detailed information about neurotransmitters on the molecular level. For the latter, carbon fibers, in combination with sophisticated electrochemical protocols act as electrochemical sensors. Fast scan cyclic voltammetry enables selective detection of dopamine with high temporal and spatial resolution (Sections 5.3.10 and 10.3.4). However, those approaches are limited to research in animals because of the vast invasiveness.

Neurotechnology enables recording the electrical signals and brain stimulation in humans by implants with noble metal electrodes on or in the neuronal tissue acting as a brain-computer-interface (BCI). Neurologists apply electrode arrays below the skull for intracranial electroencephalography or place stimulation electrodes into a specific brain region, even down to the cerebellum. This so-called deep brain stimulation (DBS) can help patients with Parkinson's diseases, epilepsy, Tourette syndrome, or severe cases of depression.

Figure 1.8 shows a commercial neurotechnological implant. It features electrodes to record signals, stimulation electrodes, and an electronics unit. The electronic units (1) connects from below the skin wirelessly to a control unit outside the patient, containing the power supply. The DBS electrodes (2) allow placement deep in the brain, e. g., in the thalamus or cerebellum. The array electrodes (3) deliver signals from their position on the cerebral cortex. Such electrodes are called electrocorticography (ECoG) array and can optionally stimulate. Depending on the application, the implants are dedicated for closed-loop operation, meaning the stimulation is autonomously applied based on the recorded signals. Commercial implants mainly rely on platinum or platinum-iridium alloys as the electrode material; many alternatives are discussed and evaluated in research (Section 10.3.3).

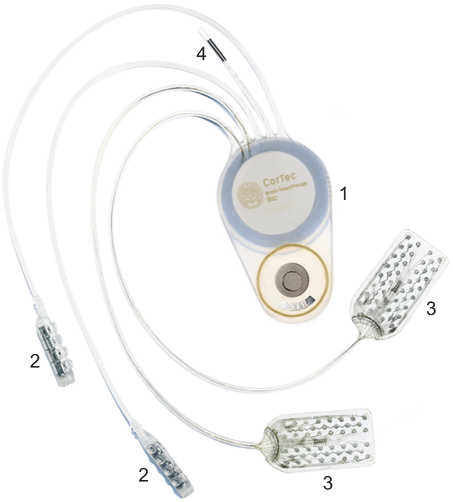

Figure 1.8: The Brain Interchange One system is a brain implant allowing the combination of various electrodes. The electronics unit (1) connects to DBS (2) and array electrodes (3). Reproduced with permission from CorTec GmbH, Germany.

The long-term stability of such electrodes is an essential prerequisite. Therefore, the corrosion behavior of such electrodes in the brain needs to be well understood and optimized. Here, electrochemical methods help better understand the processes at the tissue/electrode interface and allow for the investigation of possible corrosion mechanisms. Recent research points to the possibility of recruiting existing stimulation electrodes for electrochemical sensing, which even might allow for routine application in humans [6]. The next decade will show if such approaches are beneficial and safe enough to be applied with humans and eventually enter clinical routine. Section 10.3.5 discusses this topic in more details.

Another active implant is the cochlear implant (CI), allowing stimulation of the auditory nerve. After the cardiac stimulator, this is the second most frequently applied implant with electrical stimulation. For patients with severe hearing loss but intact auditory nerve, this implant stimulates the nerve with signals derived from an external microphone and converted by a speech processor.

Figure 1.9 shows a commercial CI with the electronic unit and the electrode array, which the surgeon inserts into the cochlea. The electrode array contains contacts for 12 channels, representing a specific frequency band in the hearing process. While patients mainly used a CI for orientation and speech understanding in the early days, current implants even enable listening to music.

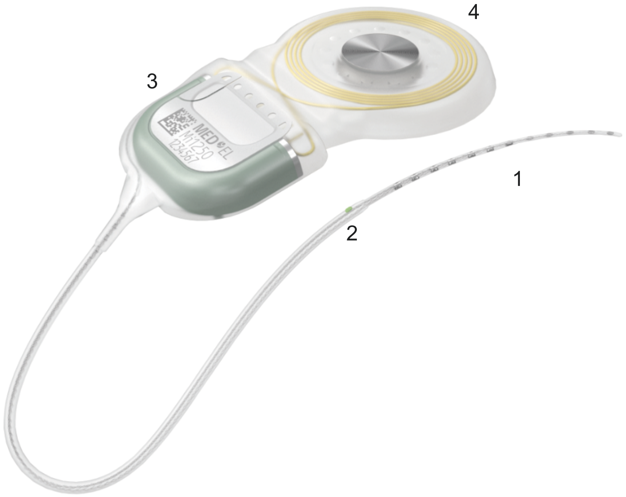

Figure 1.9: SYNCHRONY 2 Cochlear Implant with platinum electrodes for stimulation of the auditory nerve. The surgeon inserts the electrode array (1) with 19 platinum electrodes (7 pairs and 5 single electrodes at the tip) into the cochlea; the orientation marker (2) remains outside. The stimulator (3) with the coil (4) is located under the skin behind the ear. The coil of an audio processor attaches at the same position outside of the body. Reproduced with permission from MED-EL, Austria.

From an electrochemical perspective, the questions concerning the tissue-electrode interface are comparable to the situation with brain implants. Any discussion for brain implants on electrochemical methods helping understand the microenvironment, potential corrosions mechanism, and the electrochemical processes occurring in stimulation may similarly contribute to the field of auditory nerve stimulation and vice versa. Especially the long experience with CIs, including some patients wearing the electrodes over decades, may also help the brain implants, which have a younger clinical history and lower case numbers.

1.2.3 Microelectronics

Microelectronics and the semiconductor industry primarily benefit from electrochemical methods to electroplate copper as interconnects (Section 9.2.1). For a long, copper was the standard material for all interconnects, but further downscaling requires other materials less prone to migration than copper and, therefore, without the need of a barrier metal. Some fabs recently introduced cobalt for the tiniest structures in the 10 nm range close to the individual transistors. Another material candidate is ruthenium.

Besides, electrodeposition of various metals and alloys as well as electrochemical inline process control, such as for wet chemical etching, can be found in many fabs. While the large dimensions of the production lines require highly specific instrumentation devices and electrolyte handling, the underlying theory and concepts do not differ much from the other three fields described above.

1.2.4 Energy applications

Among the different fields of applications, it is the energy-related topic prospering most. In not much more than a decade, lithium-ion batteries became the essential electrochemical units, which are ubiquitous in our daily lives. We can find those rechargeable cells in a tiny hearing aid or earbuds, in smartwatches, in smartphones, in tablets, and in notebooks. Huger cells are part of cordless tools or store energy in electric vehicles. On an even larger scale, those batteries play an essential role in integrating renewable energies from solar and wind power into our power grid.

The Royal Swedish Academy of Science accounted for the importance of lithium-ion batteries by rewarding Stanley Whittingham, John Goodenough, and Akira Yoshino with the Nobel Prize in Chemistry 2019. In contrast to formerly developed batteries, the lithium-ion battery does not rely on electrochemical reactions of the electrode material but on lithium-ion movement between the electrodes in which the ions intercalate.

The human-made climate change and especially the latest public awareness of global warming directs many resources for research and business promotion to achieve a fossil fuel-free society, maybe even supported by negative carbon dioxide release. However, the drawback with any single-sides measures is the damage caused in other areas. For example, focusing on electrical mobility helps to avoid exhaust gas emissions from cars, but we also have to consider who, and under which circumstances, harvests lithium and especially cobalt. Researchers may provide solutions to avoid those metals in the long run, e. g., by using sodium instead or by relying on a completely different storage principle. Hydrogen gas, methane, *synthetic natural gas* (SNG), or synthetic fuels are possible alternatives to store energy with electrochemistry involved in the production and, in some cases, in the conversion back to electrical energy. Electrolysis allows the conversion of electrical power to gas, known as *power-to-gas* (P2G). Hydrogen forms directly from splitting water, processing to other fuels can even consume CO_2.

Among the complex relationships prescribing the climate on our planet, the common ground is that the atmospheric carbon oxide concentration increases rapidly (Figure 1.10), with a high likelihood leading to global warming. And, while there is controversy on the exact numbers, a substantial share of the CO_2 emission is human-made. I am sure that lowering or even reversing carbon dioxide emissions is essential for the future of the global population. I am also sure that electrochemical methods can play an important role here. On a detailed level, the exact direction is unclear. Many protagonists try to shape public awareness toward their own opinion either because of commercial interest or ideology, both in favor or against our environment. Any student, scientist, or engineer working in the energy field will face rational and emotional discussions. That is why I strongly recommend checking some basic facts continuously to find and adjust your own opinion and arguments. A starting point could be the web publication Our World in Data.[2]

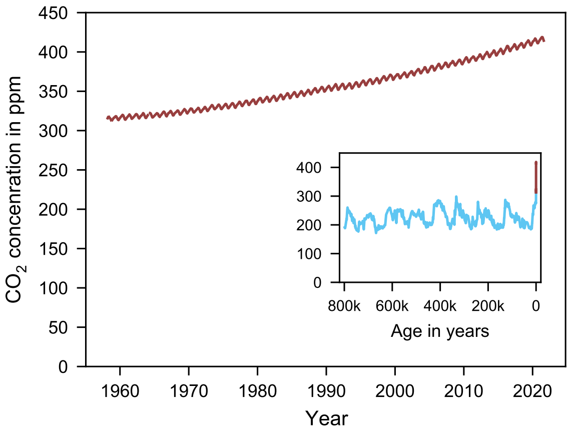

Figure 1.10: The atmospheric CO_2 concentration, measured since 1958 at the Mauna Loa Observatory, Hawaii, the so-called "Keeling Curve" [7]. Much more alarming is to see this curve in a larger context, in the inset combined with 800,000 years of ice-core data [8].

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[2] https://ourworldindata.org/co2-and-other-greenhouse-gas-emissions

1.3 Electrochemical cells

We now approach the arena of any electrochemical experiment. The arrangement of two electrodes in an electrolyte is called *electrochemical cell*. An electrolyte is an ion conductive phase, either liquid or solid. Formally, gases could also be considered as electrolytes, but ionized gas is normally considered to be part of the discipline of plasma physics rather than electrochemistry.

Most simple cases of an electrolyte are an aqueous solution of salt (such as potassium chloride) or an acid (such as sulfuric acid). In the electrolyte, current can flow due to ion conduction. In contrast, wires and circuitry through which currents can flow by electron conduction connect the electrodes. At the interface between electrode and electrolyte, redox processes take place, translating between ion and electron conduction.

!

The *anode* is the electrode at which the oxidation reaction occurs. The *cathode* is the electrode at which the reduction reaction takes place. While there are some mnemonic bridges to define the polarity of the anode for electronic parts, those hints can fail when considering electrochemical cells. To remember the terms anode and cathode correctly, one can think of **an ox** (imagine a male cattle ready to pull the plow) and a **red cat** (imagine a purring cat with red fur starring at you while you think about the cathode).

In general, two types of electrochemical cells can be distinguished (see Figure 1.11). In case a voltage is applied to the electrochemical cell (or a current source is connected), the arrangement is called *electrolytic cell*. At the positive terminal, the oxidation reaction occurs, and this electrode is accordingly called the *anode*. On the other side, at the negative terminal, the reduction reaction takes place, and it is therefore called the *cathode*. One example of the reactions in an electrolytic cell is the electrolysis of water, as indicated in Figure 1.11 (left). At the negative terminal, the reduction of protons produces hydrogen gas.

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The International Union of Pure and Applied Chemistry (IUPAC)[3] recommends drawing the anode always as the left half-cell of an electrochemical cell. The polarity flips left or right, depending on the cell being an electrolytic or galvanic cell.

The other type of electrochemical cell is the *galvanic cell* or *voltaic cell* referring to the works of Luigi Galvani and Allesandro Volta. In contrast to the electrolytic cell, the

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[3] The International Union of Pure and Applied Chemistry (IUPAC) is a worldwide organization that is part of the International Science Council, a nongovernmental organization uniting and representing scientists worldwide. One of the most considerable efforts of the IUPAC is the nomenclature of organic chemistry (published in the so-called “Blue Book”) and inorganic chemistry (“Red Book”). In this textbook, the electrochemical terminology mainly follows the guidelines for analytical chemistry, the so-called “Orange Book” [9].

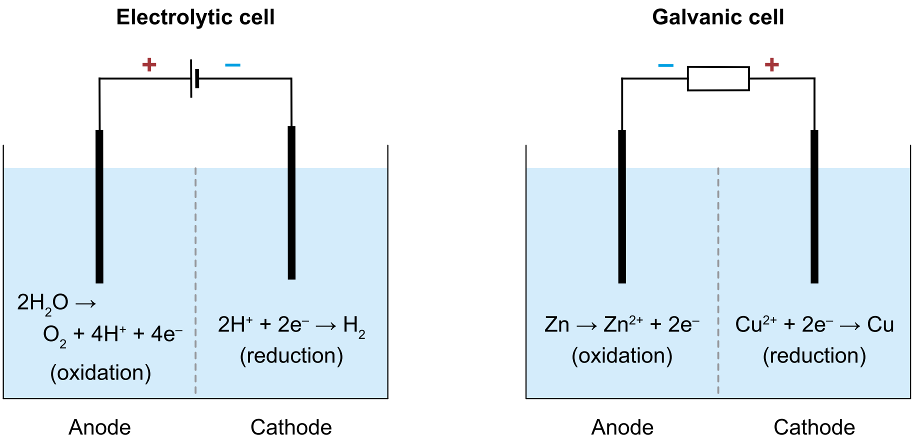
Electrolytic cell
+
−
$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$
(oxidation)
$2H^+ + 2e^- \rightarrow H_2$
(reduction)
Anode
Cathode
Galvanic cell
−
+
$Zn \rightarrow Zn^{2+} + 2e^-$
(oxidation)
$Cu^{2+} + 2e^- \rightarrow Cu$
(reduction)
Anode
Cathode

Figure 1.11: Electrochemical cells: the electrical circuit powers the electrolytic cell, the galvanic cell delivers charge to the electrical consumer. Please note the different polarities of the anode/cathode depending on the type of cell.

electrical circuit acts as a consumer, and the electrochemical cell delivers charge. In the most simple case, a resistor connects the two electrodes. The anode, the electrode at which the oxidation occurs, is more negative than the electrode at which the reduction occurs. Thus the positive terminal of a galvanic cell is the cathode. A typical example of this type of cell is a battery getting discharged. The right cell in Figure 1.11 illustrates the situation in a Daniell cell (Section 1.1.3).

Both types of electrochemical cells deal with electrochemical processes at non-equilibrium. Energy either is brought into the electrochemical system from the electrical circuits (electrolytic cell), or an electrical circuit consumes the charge stored in the electrochemical cell (galvanic cell). The reactions in electrolytic cells do not occur spontaneously, while in a galvanic cell, the reactions run spontaneously once the electrical circuit is closed.

1.3.1 Primary and secondary cells

A nonrechargeable battery[4] is called a *primary cell* and is always a galvanic cell. A rechargeable battery is called a *secondary cell* and is an example of an electrochemical cell, which can be both electrolytic and galvanic cell. The well-known lead-acid battery, which is still prevalent in cars with combustion motors, is an example of what a secondary cell is. It is an electrochemical cell with two lead electrodes in an aqueous sulfuric acid solution as the electrolyte. The lead electrode at the positive terminal is coated with a paste containing lead oxide (PbO_2). During supplying (galvanic cell), the negative terminal is the anode, and the reactions are

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[4] Strictly spoken, a *battery* is the technical realization of one or several connected primary or secondary cells in an appropriate package.

$$Pb + SO_4^{2-} \longrightarrow PbSO_4 + 2\,e^- \qquad (-) \tag{1.7}$$

$$PbO_2 + 4\,H^+ + SO_4^{2-} + 2\,e^- \longrightarrow 2\,H_2O + PbSO_4 \qquad (+) \tag{1.8}$$

In a discharged battery, both electrodes are covered with $PbSO_4$. During discharge, the SO_4^{2-} is removed from the electrolyte solution lowering the concentration of the sulfuric acid. As the density of an aqueous sulfuric solution strongly depends on its concentration, a hydrometer allows checking the charge status of a lead-acid battery.

While recharging the battery (electrolytic cell), the positive terminal is the anode, and the reactions are reversed:

$$PbSO_4 + 2\,e^- \longrightarrow Pb + SO_4^{2-} \qquad (-) \tag{1.9}$$

$$2\,H_2O + PbSO_4 \longrightarrow PbO_2 + 4\,H^+ + SO_4^{2-} + 2\,e^- \qquad (+) \tag{1.10}$$

The nominal cell voltage of the lead-acid battery cell is 2.05 V. Therefore, a car battery contains six cells connected in series. Nowadays, commercial batteries contain grid electrodes instead of lead plates to increase the effective surface area but still feature sufficient current conduction. Repetitive discharge/charging cycles might cause dendrites' growth, eventually resulting in a short-circuit of the affected cell. Therefore, separators are introduced in between the two electrodes allowing ion conduction but avoiding direct contact of the two electrodes. Figure 1.12 shows a commercial lead-acid battery used in cars.

1.3.2 Half-cell

An electrochemical cell can be seen as two separate *half-cells* consisting of one electrode in an electrolyte each (Figure 1.13A). The theoretical treatment of an electrochemical cell usually considers two independent half-cells. With macroscopic electrodes in a large electrolyte vessel, this concept can be widely applied. For microscopic setups, the two involved electrodes often cannot be treated independently because of unwanted or desired cross-talk in-between (Section 10.1.7).

In case cross-talk between the two electrodes in an electrochemical cell should be avoided or different electrolytes for the two half-cells are required, an ion-permeable membrane can separate the half-cells (e. g., the separator in Figure 1.12) or a *salt-bridge* (Figure 1.13B). A salt-bridge connects the two half-cells by the same or a different ion-conducting medium. Practically glass or polymeric tubes are used, either with a tiny diameter or filled with a jellified salt solution to avoid flow between the two half-cell electrolytes. Depending on the salt solutions considerable diffusion potentials (Section 4.2.5) can develop.

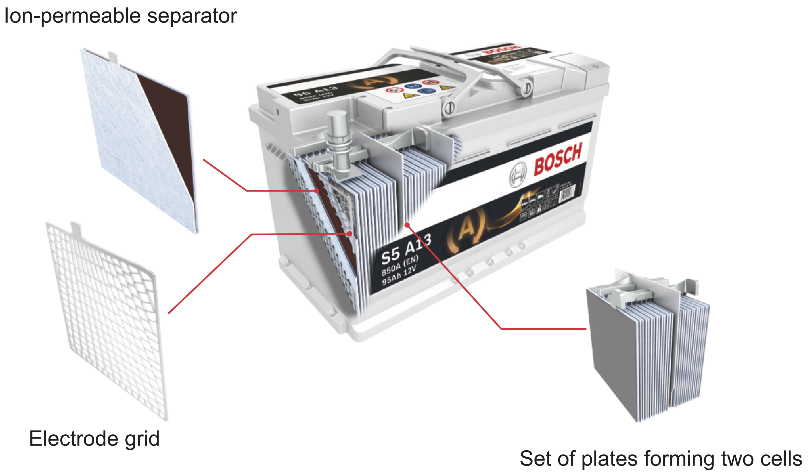
Ion-permeable separator
Electrode grid
Set of plates forming two cells

Figure 1.12: Commercial lead-acid battery for cars. Each of the six cells consists of several electrode plates connected in parallel. The grid electrodes' design allows for optimal current distribution; a lead alloy increases their corrosion resistance. Ion-permeable separators avoid direct contact between neighboring electrodes. Adapted with permission from Bosch.

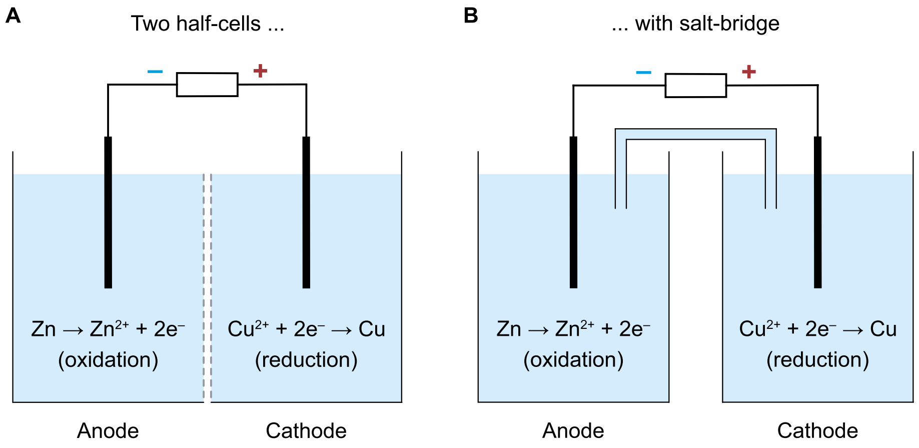
A
Two half-cells ...
B
... with salt-bridge
–
+
–
+
Zn → Zn²⁺ + 2e⁻
(oxidation)
Cu²⁺ + 2e⁻ → Cu
(reduction)
Zn → Zn²⁺ + 2e⁻
(oxidation)
Cu²⁺ + 2e⁻ → Cu
(reduction)
Anode
Cathode
Anode
Cathode

Figure 1.13: An electrochemical cell (here a galvanic cell) can be considered as two half-cells (A). Also, in practical realization, an electrochemical cell can be arranged by two half-cells connected with a salt-bridge allowing ion conduction (B).

1.3.3 Electrochemical cell in equilibrium

In equilibrium, without external current flow, an electrochemical cell can exhibit a potential difference between its electrodes called *open circuit potential* (OCP) or more correctly *open circuit voltage* (OCV).[5] In the example depicted in Figure 1.14 two half-cells connected by a salt-bridge form the electrochemical cell. The electrical circuit is closed by a voltmeter (with ideally infinite internal resistance). Therefore, no current flow is possible, and the measured cell voltage E_{cell} is the difference between the OCPs of the two half-cells. In each half-cell, a reversible redox reaction takes place with no net current (the current of the backward reaction balances the current of the forward reaction). Because at each electrode, there is the oxidation and the reduction taking place, the terms anode and cathode are not meaningful.

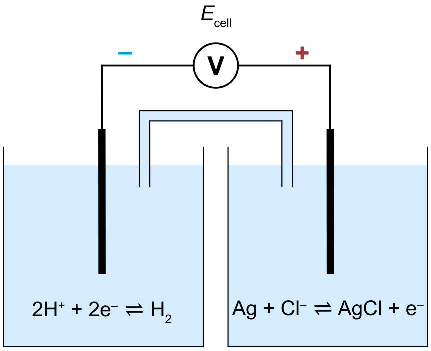
E_{cell}
−
V
+
$2H^+ + 2e^- \rightleftharpoons H_2$
$Ag + Cl^- \rightleftharpoons AgCl + e^-$

Figure 1.14: An electrochemical cell in equilibrium. The cell voltage E_{cell} is the difference between the open circuit potentials (OCPs) of the two half-cells. The left half-cell could be the standard hydrogen electrode (SHE) used to define the zero-point of the electrochemical potential scale.

In the example of Figure 1.14, the left half-cell is the hydrogen electrode. With platinum as electrode material, an electrode with unity activity of protons (pH 0) and a gas supply for hydrogen gas (normal pressure $p_{\mathrm{N}} = 101.325\,\mathrm{kPa}$) bubbling around the electrode the setup is called *standard hydrogen electrode* (SHE), and its potential is defined as 0 V (Section 4.2.1).

The right half-cell comprises an Ag/AgCl electrode. That is a silver electrode coated with silver salt in an electrolyte with Cl^- ions (Section 4.2.2). In this example, it is helpful to have the hydrogen gas in the electrolyte of the left half-cell only. Therefore, the two half-cells are connected by a salt-bridge, an aqueous, conducting phase, which hinders significant ion exchange between the two half-cells. Especially with reference electrodes, a bridge electrolyte separated by diaphragms is common (Section 4.2.5). In a microchip, a thin capillary filled with the salt solution has the same role.

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[5] In electrical engineering, the term *potential* is the level of a single terminal, while the term *voltage* is used for the difference between two potentials. In electrochemistry, the terms are sometimes not strictly separated, e. g., in some textbooks or research papers the term *open circuit potential* (OCP) is used for the measured cell voltage in equilibrium, although the term *open circuit voltage* (OCV) would be more appropriate.

2 Electrochemical theory

Textbooks can present electrochemical theory in at least two ways. The more formal way is to start with the equilibrium and progressing toward the general nonequilibrium case. The focus is on rigorous derivation from thermodynamics. The second possibility is to consider electrochemical processes in general and introducing the equilibrium as a special case. I believe this route is more in line with the practical approach to electrochemistry, therefore, this chapter goes that way.

The goal here is to learn all the essentials to understand and successfully apply electrochemical methods. Accordingly, the chapter aims at a condensed rather than all in-detailed presentation. Deeper understanding and more details can be obtained from various other textbooks [1, 10–12]. For more information on specific aspects, the text sometimes refers to the original works.

Traditionally, electroanalysis took care for reduction processes only. Therefore, it is common to present the theory by examining the reduction process. Although in many fields of application oxidation processes prevail, this chapter presents either both or follows the classical approach of explaining the reduction case and describing the change required to apply the theory to the oxidation case to avoid confusion of the reader when working with different textbooks.

The traditional focus on the reduction process causes another confusion: an electrical current generated by a reduction has a negative sign in terms of the convention in physics, electrical engineering, or electronics. For long, scientists, especially in the context of polarography, displayed the reduction currents with positive numbers as these processes were the ones of interest. Nowadays, we face an inconsistent situation: some publications, particularly older ones or from the United States, prefer current-potential diagrams with positive currents for the reduction (“reduction up”). Simultaneously, the majority of the application-driven literature follows the more rational way (“oxidation up”). See also the infobox in Section 5.3.

2.1 Conventions

The different disciplines contributing to the electrochemical theory in combination with the practical methods cause a mix up of notation and labeling of the variables. Therefore, this chapter starts with an introduction to the conventions used in this book. Besides Chapter 7 on electrochemical impedance spectroscopy and some briefly mentioned methods, it was possible to label all quantities uniquely.

Potential vs. energy

The electrical potential E in Volts (V) is referred to the potential of the standard hydrogen electrode (Section 4.2.1) if nothing else is specified. Depending on the context,

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