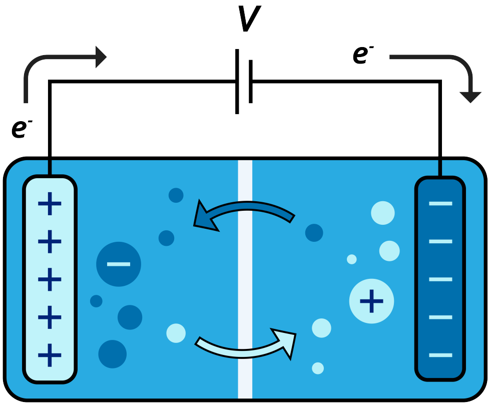
Introduction to Electrochemical Processes



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1

Introduction

Electrochemical processes are of importance in topics ranging from batteries to corrosion to water treatment. The key element is the electrochemical cell, as depicted in Fig. 1.1. In an electrochemical cell, there is an external circuit that transfers electronic charge (electronic current), electrodes where this electronic current translates to ionic current in the electrolyte (for instance, an aqueous solution, i.e., water containing ions), several 'bulk' phases of electrolyte, and additional layers that can be selective to the transport of one type of species over another, such as a membrane.[i]

Electrochemical processes are extremely useful and flexible. This is because they can do many things such as generate and store energy, provide clean water, and produce chemicals, and compared to other types of processes, there is an extra variable to tune the process. This is the electrical energy that we can use to directly influence reactions on electrodes. For instance, when reactants (such as H^+-ions) are at a low concentration, we can compensate for the resulting low reaction rates by decreasing the electrode potential in that electrode, and that will accelerate the reaction. This requires electrical energy but that can be a worthwhile investment.

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[i] In this book we use the terms 'species', 'solute', 'ion', 'component', and 'molecule', all as synonymous terms to refer to the species that are dissolved in the water, move through it, and often carry a charge, but can also be neutral.

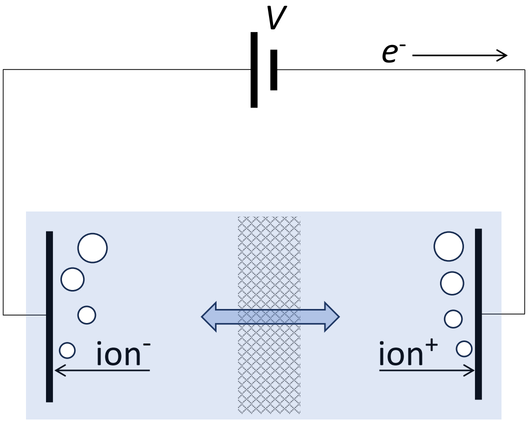
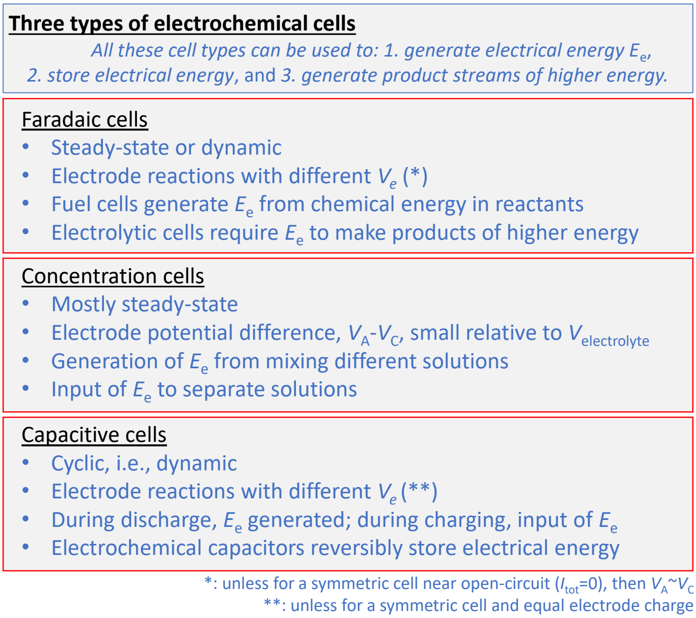


Fig. 1.1: An electrochemical cell consists of at least two electrodes, the anode and cathode. The current running through the external circuit, I, is equal to the current in the electrolyte phase. In the electrolyte, ions transport the current, and some react at the electrodes. Often there are multiple compartments as well as separators and membranes.

Electrode reactions can be very selective for the conversion of one species and not another, and suitable electrocatalysts or other methods (for instance, selective membranes placed in front of the electrode) can enhance this selectivity further.

An electrochemical cell would typically have two electrodes. But it is not necessarily two. An electrochemical process is also possible with one electrode (though not for very long), and you can also build electrochemical cells with more than two electrodes. As an example of electrochemical cells with more than two electrodes, you can consider the electrochemical cell of Fig. 1.1 and take the electrode depicted on the left, divide it in two separate electrodes and direct part of the electronic current to the one electrode, and part to the other. Et voilà, you have a three-electrode system. Other examples are the three-electrode measurement cell depicted in Fig. 7.1, where the main current runs between working and counter electrode, and a very small current goes to a third electrode, the reference electrode.



Three types of electrochemical cells

All these cell types can be used to: 1. generate electrical energy E_e, 2. store electrical energy, and *3. generate product streams of higher energy.*

Faradaic cells

- Steady-state or dynamic
- Electrode reactions with different V_e (*)
- Fuel cells generate E_e from chemical energy in reactants
- Electrolytic cells require E_e to make products of higher energy

Concentration cells

- Mostly steady-state
- Electrode potential difference, V_A-V_C, small relative to $V_\mathrm{electrolyte}$
- Generation of E_e from mixing different solutions
- Input of E_e to separate solutions

Capacitive cells

- Cyclic, i.e., dynamic
- Electrode reactions with different V_e (**)
- During discharge, E_e generated; during charging, input of E_e
- Electrochemical capacitors reversibly store electrical energy

*: unless for a symmetric cell near open-circuit (I_tot=0), then V_A~V_C
**: unless for a symmetric cell and equal electrode charge

Fig. 1.2: Electrochemical cells can be classified in three cell types, and each type can generate energy from resources, store (and release) electrical energy, and produce streams of higher energy.

Another three-electrode electrochemical cell is the process of corrosion of steel or any other metal, and the cathodic protection of these metal structures. A corrosion spot on a metal structure (for instance a transport pipe) is already two very nearby electrodes, one where the metal oxidizes and one where for instance oxygen in the water is reduced. These two electrodes can be right next to each other, on the same piece of metal, and the exact position, shape and size of each electrode can change in time. When we now use a third 'sacrificial' piece of metal (for instance, Zn), place it nearby and connect it to the metal structure, we end up with a three-electrode electrochemical cell. In this cell the electrode at the Zn/water interface (often in soil) pushes electrons into the other two electrodes, and reduces the electrode potential of these other two electrodes.

Thus electrochemical cells can have more than two electrodes, but often a good starting point is an analysis based on two.[ii] These two can be near one another on the same piece of metal, i.e., on the same electron-conducting material (for instance, a Faradaic region on the outside of a porous carbon particle, and capacitive ion storage inside), or can be well-separated as depicted in Fig. 1.1.

With two electrodes we can classify all electrochemical cells in three distinct cell types, as summarized in Fig. 1.2. All three cell types can do the same three things: extract energy from external (environmental) resources (chemical energy), store electrical energy (and later make it available again), and use electrical energy to produce chemicals, or otherwise increase the energy of product streams (for instance, bring a gas to higher pressure, separate a salt solution into fresh water and a concentrated salt solution).

[ii] In Ch. 2, we discuss in more detail two different definitions of the term electrode.

2

Fundamentals

Let us now discuss in more detail two-electrode electrochemical cells, such as depicted in Fig. 1.1. The cell consists of an electron-conducting ('metallic') external circuit, and an electrolyte phase, typically water with ions. These two phases must always be there. In between metal and electrolyte, there is the electrode, see Fig. 2.1. In addition there can be other elements, such as a gas that we bubble through. Solid salt phases can develop on the electrode (for instance, an oxide such as PbO_2, or an AgCl layer), or are in solution as insoluble salt particles, and there can be membranes that allow passage of ions. Such a membrane is also an electrolyte phase.

In an electrochemical cell, we have generally two phases, electrolyte (which are all phases with solvent and ions and other solutes; in this book we focus on the solvent water), and electron-conducting (i.e., metallic) phases such as the wiring and the electron-conducting parts of the electrodes. This complete electrochemical cell is electroneutral (EN), but not ach individual phase by itself. There can be a non-zero electronic charge in the metal, and then we also have a charge in the electrolyte phase, which is then due to ions, of the same magnitude but opposite sign as the charge in the metal. This charge is not be in the 'bulk' of metal or electrolyte, but is in the electrode, in separate metallic and electrolyte regions there, see Fig. 2.2.

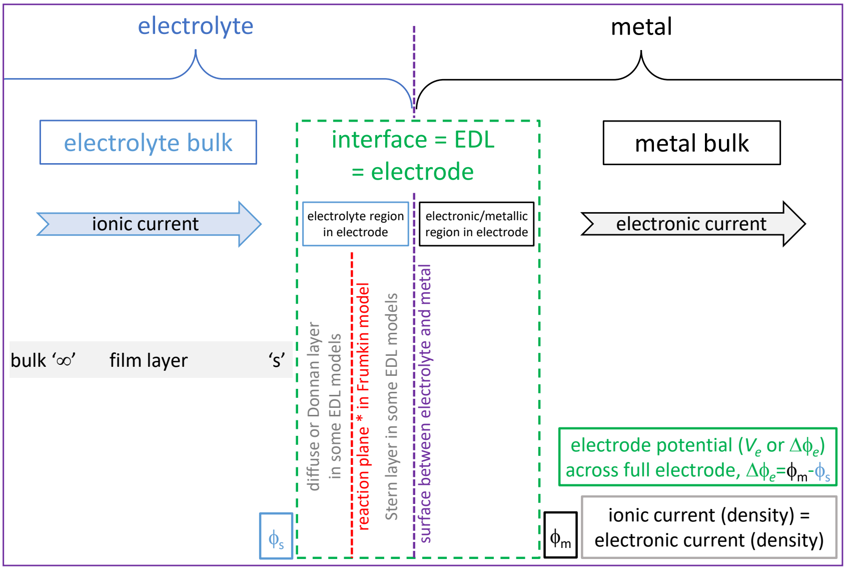


Fig. 2.1: The electrode is the interface located between a bulk electrolyte, and a bulk metal phase. It is a special type of electrical double layer (EDL). Inside the electrode is an electrolyte region and a metallic region, and between these two regions inside the EDL, is the electrolyte-metal surface. Just outside the EDL on the solution side, is the location called 's', separated by a film layer from the real bulk, '∞'. The ionic current entering an electrode at some point is always the same as the electronic current leaving. This is the case for a Faradaic process where the electrode structure does not change, and is also the case for a capacitive process where in time the charge that is stored in the separate EDL regions changes.

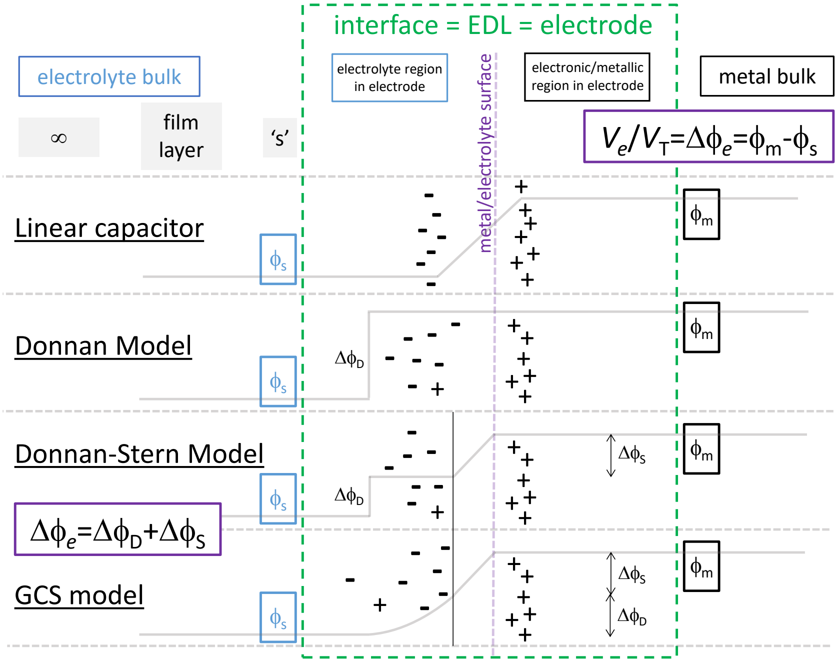


Fig. 2.2: Different models for the structure of the electrode. The electrode EDL structure is always based on a separation between ionic charge and electronic charge (or more regions of charge). All charges in the EDL add up to zero, i.e., as a whole the EDL is electroneutral (EN), i.e., it is uncharged. The electrode potential, V_e, or $\Delta\phi_e$, is the difference between the potential on the metal-side (just outside the EDL), ϕ_m, and that just outside the EDL on the solution side, ϕ_S. The electrode potential can have multiple contributions, for instance, because of a Donnan layer, $\Delta\phi_\mathrm{D}$, and a Stern layer, $\Delta\phi_\mathrm{S}$.

Bulk phases everywhere have a local charge density that is zero. Thus at any point in the aqueous phase, a summation over all ions of their concentration multiplied by their valency, is zero.[i] The same holds for any position in the metallic wires going into an electrochemical cell, i.e., they are EN at any position.[ii] The power source (also called: voltmeter, electrometer, or potentiostat), depicted at the top in Fig. 1.1, we can assume its net charge is zero as well.

So the only locations with a charge excess, are the electrodes. On the metallic side of the electrode, which is the region at the very surface of the metal, there is electronic charge, while there is ionic charge nearby in the water, in a region extending a few nanometers away from the surface, see Fig. 2.1. Both charges can be of either sign, for instance the electronic charge can be positive or negative.

This electronic charge on the metal-side in an electrode is compensated exactly by the ionic charge in the water, in the same electrode. This is a second EN-statement, next to the ‘overall’ EN statement presented above, that each electrode in itself, is overall electroneutral. It has regions with charge of one sign (on the metallic side) and region with charge of the other sign (on the side of the ions). This condition applies to all electrodes in an electrochemical cell.

An electrode can have more than two regions with charges. For instance, on the ionic side, we can have ‘free’ ions in the diffuse layer, and besides, there can be adsorbed ions, chemically bound to the metallic surface. Then the three types of charge are electronic charge, chemically bound charge, and free ion charge (or, diffuse charge). These three contributions together add up to zero.

This is a good point to discuss the word ‘electrode.’ This word can be confusing because there are two different meanings, first the theoretical meaning, and second a convention that has a technological origin. In many cases both meanings apply, i.e., they are valid at the same time, but sometimes a conflict arises. We will discuss the second meaning at the end of this chapter, and propose that when

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[i] And if this is inside a charged membrane (or other charged structure), also the membrane charge is included in the charge balance, as if the membrane is another type of ion with a certain concentration of charged groups per volume.

[ii] An exception would be consideration of ‘transmission line’ effects, of how electronic charge in metal wires interacts with countercharge just outside those wires. This leads to a distortion of electronic signals and can be analysed in RC-network models, by assigning (many) capacitors to represent this net charge of the wires.

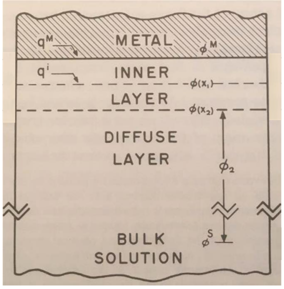

Fig. 2.3: A schematic from Mohilner (1966) illustrates that the EDL is the region between two bulk regions. In an electrochemical cell, one of these bulk phases is an electrolyte, and the other an electron-conducting phase, typically a metal.

there is a conflict, we call it electrode$^{\mathrm{TC}}$, with TC for 'technological convention', with the theoretical meaning of electrode not requiring this addition.

Theoretically, the word electrode refers to an interfacial structure, namely the interface between a bulk metallic phase and a bulk electrolyte phase. This interface is overall electroneutral, and includes the electrons on the metallic side of the electrode as well as adsorbed ions, and free ions in the diffuse layer on the ionic side, see Fig. 2.2. [Vetter (1967): 'An electrode can be, perhaps, best defined as consisting of several conducting phases in series, with one terminal phase being a metal and the other one an electrolyte.'] This charge-neutral interfacial structure also has another name, which is the electrical double layer (EDL). Thus, an electrode is a special type of EDL. An EDL is a structure that contains multiple regions that each have a different charge density, but overall is electroneutral, and is in between two 'bulk' phases, see Fig. 2.3.[iii,iv] Therefore across an EDL, just as across an electrode, a voltage difference develops, for electrodes called electrode potential, for which we will use the symbol V_e or $\Delta\phi_e$. This electrode potential is the difference in potential between the metallic side of the electrode and the electrolyte (just outside the electrode), see Fig. 2.2.

[iii] Also a third phase is possible, such a gas.

[iv] A bulk phase in this case can also be the film layer in front of the electrode, see §7.5.

An example of an electrode is when we place a non-charged copper wire in water containing Cu^{2+}-ions. Dependent on the concentration thereof, a certain number of Cu^{2+}-ions will deposit ('plate out'), or instead will dissolve from the metal piece. Let us assume the latter occurs. Thus, for each Cu^{2+}-ion which dissolves, two electrons are 'left behind', and these electrons go to the metallic side of the electrode (i.e., they will reside on the very top surface of the Cu-wire). Then on the electrolyte side of this electrode a slight positive charge develops. This we can call the countercharge, and this countercharge is due to an extra adsorption of cations and a slight desorption of anions. Thus a positive ionic charge develops. The negative charge in the metal, because of the left-behind electrons, and the positive charg in the electrolyte, when taken together add up to zero, i.e., the electrode as a whole is overall electroneutral. Note that the electrode is not the piece of copper by itself, and neither is it only the upper part of that piece of copper. Instead, the electrode is the full interfacial structure here, located at the outer surface of the copper, which in this example contains an excess of electrons, together with the ionic countercharge (=diffuse layer) right next to this surface.[v] These two regions of charge together are the electrode (and as a whole are EN), see Figs. 2.1-2.3.[vi]

The statements in this example are also correct when this reaction continues to run. Then we have Cu^{2+} continuously plating out from solution, with the electrode remaining at the top surface of this metal piece that slowly becomes more thick.

With two electrodes we can build an electrochemical cell. Of the entire system, we can define the *cell voltage*, V_{cell}. This is the measurable voltage difference between the two wires coming out of an electrochemical cell that has two electrodes, see Fig. 1.1. If there are no resistances in the wires, the cell voltage is the difference in voltage (i.e., potential) between the outsides of the metallic regions in the two electrodes, ϕ_{m}. In each electrode there is a certain electrode potential, V_e, which is the electrical potential in the bulk of the metal, ϕ_{m}, minus that in the electrolyte just outside the electrode, ϕ_{s}, see Fig. 2.2, i.e., it is a potential

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[v] We do not claim that a piece of copper in water is always negatively charged. That depends on the concentration of Cu^{2+}-ions and other ions in the water.

[vi] There can also be other regions of this EDL structure, such as adsorbed ions.

difference, $V_e/V_\mathrm{T} = \Delta\phi_e = \phi_\mathrm{m} - \phi_\mathrm{s}$.[vii] The different EDL models in Fig. 2.2 are discussed in detail in Ch. 5. A final potential difference in the cell is that across solution, i.e., the electrolyte phase, which in the geometry of Fig. 1.1, defining a difference as 'right' minus 'left', is V_sol. Thus we end up with the formal definition of the cell voltage

$$V_\mathrm{cell} = V_\text{in metal, A} - V_\text{in metal, C} = V_\mathrm{A} - V_\mathrm{sol} - V_\mathrm{C} \tag{2.1}$$

where we introduce index 'A' and 'C' for anode and cathode, which are names of the two electrodes located left and right. Thus, V_A and V_C are electrode potentials (in general, V_e), thus are a potential difference between the bulk metal and the electrolyte. It is customary to always draw the anode (A) left, and cathode (C) right, and Eq. (2.1) is based on that choice, in line with the drawing in Fig. 1.1. In this figure the current always flows left to right across the electrolyte (across the solution).

Of course Eq. (2.1) can have more contributions, for instance, the metallic side of the electrode is material X and it connects to a wire of material Y. Then there is an additional potential change there at the X/Y interface, which is called a (metal-metal) junction potential, or 'work function'. The electrolyte term, V_sol, has many contributions, including resistances in the bulk electrolyte, and if there is a membrane, then potential changes at the edges of the membrane and inside the membrane, etc...

Kirchhoff's law. Eq. (2.1) is often called *Kirchhoff's law*, describing that all voltage steps add up to zero, i.e., one can travel along any trajectory through the cell, starting at some position and when returning there, all voltage steps along that path add up to zero.

Alternatively, we don't use differences, but consider the (electrical, or electrostatic) potential, for which we use the symbol ϕ for dimensionless

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[vii] Note that V's are sometimes 'the' voltage at some point, and sometimes refer to voltage *differences*. The 'voltage at some point', a state variable that can gradually change through a phase, is generally not called a 'voltage', but called the (electrical, or electrostatic) potential, and then typically written without a subscript. This local potential, 'V', is often divided by the thermal voltage, V_T, to obtain the dimensionless potential, ϕ.

potential. These potentials can be multiplied by a factor V_T, the thermal voltage, to obtain a dimensional voltage, with unit V. Thus, $\phi = V/V_\mathrm{T}$. The thermal voltage is given by $V_\mathrm{T} = RT/F$, or equivalently, $V_\mathrm{T} = k_\mathrm{B}T/e$. At room temperature V_T is around 25.6 mV. Similar to Kirchhoff's law, we can now start at some position, at a certain potential ϕ, and then follow a path through the cell, moving through regions where the potential goes up, and other regions where it goes down, and then we ultimately return at the same point at the same potential. This of course seems completely obvious, because how could it be otherwise. In this regard, these potentials ϕ are no different than other state variables, such as temperature, which can also vary in a system, and following any kind of trajectory through a system, starting at a temperature T_0 at position x_0, after coming back at x_0, the temperature is of course again T_0.

Kirchhoff's law is nevertheless useful, because it helps to stress the point that this analysis applies to every possible trajectory that we can follow through an electrochemical cell, irrespective of how complicated it can get (including multiple electrodes, and complex geometries).

At this point, it is useful to describe the words 'open circuit' and 'short circuit'. In an open circuit, the flow of electrons through the wires is blocked. Thus, the current is zero. For a short period of time, there can still be a reaction in the electrodes, but after that the system goes to equilibrium, and electrode reaction rates go to zero. The cell voltage is now the open circuit (cell) voltage, $V_\mathrm{cell,OC}$.

The other operational mode is to short-circuit a cell, which means that the cell voltage is zero. We can achieve this condition by directly connecting the anode and cathode wires, i.e., by 'shorting' them.[viii]

Thus, through an electrochemical cell a current runs. Current is a number with symbol I and unit A (Ampère). If an electrode has surface area A, and all of the current I goes through that area, then the current density is I/A (unit A/m^2) (if

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[viii] A corrosion spot on a piece of metal can be described as a pair of short-circuited electrodes, because the metallic side is at one potential, which is because the electronic current that runs between those two very nearby electrodes, is very small.

the total current is distributes evenly). In a text about current densities, such as in Ch. 7, the symbol used is also *I*. Thus, the symbol *I* can be a total current with unit A, or a current density with unit A/m^2.

From the metal side of the cell this current *I* flows into (or out of) the electrode as electronic current. And on the electrolyte side it enters or leaves as ionic current, with the same numerical value, see Fig. 2.1. So the symbol *I* can be used both for the electronic current (density) on the metal side of the electrode, and for the ionic current (density) on the electrolyte side, because they have the same numerical value.

But 'are' they they the same? So even though the two currents, an electronic current in the metal, and an ionic current in the electrolyte, are the same in the sense that their numerical value is the same, they can be very different in a physical sense. In a purely capacitive process, they are indeed different. Electronic current arrives in the electrode and is stored on the metal-side, and ionic charge that was stored on the electrolyte-side now flows out of that region into the electrolyte. (This does not mean that ions leave the electrode. It can just as well be that ions go into the electrode, or it is '50/50' with the flow of ionic charge for 50% by ions of one type going in, and for 50% by ions of the other type leaving the electrode.)

For a purely Faradaic process, however, charged species will transfer between the two regions, for instance the electron. In this example, an electron entering the electrode is picked up by a molecule that arrives there, and this new molecule leaves the electrode again. In this case in some sense we can say that the electronic current 'becomes' ionic current, i.e., there is real transfer of a charged particle across the interface, in this case the electron. It can also be other charged particles that transfer across the electrode. For instance in metal plating it is ions that physically transfer across the electrode. This is why Faradaic electrodes are also called charge-transfer electrodes. (This terminology of a charge-transfer electrode refers to the transfer of physical particles such as ions or electrons across the electrode. This is important to note because in any electrode process electronic current arriving from one side is ‘transferred’ to ionic current on the other side. In a capacitive process this does not mean that physical particles are transferred across the electrode, but still there is ‘continuity’ of current from one side of the electrode to the other.) With this transfer of charged particles (electrons or ions) across the electrode (from bulk metal to bulk electrolyte, or vice-versa), the electrode itself does not change, and as far as the electrode is concerned, such a charge transfer (Faradaic process) can go on forever.

In all cases just discussed, capacitive and Faradaic, the electrode as a whole always remains electroneutral, and the two currents, one entering the electrode on one side, and the other exiting on the other side, are ‘numerically’ the same, and we can use the symbol I for both.

Thus, there are different types of charge carriers in an electrochemical cell. In a metallic phase (or semi-conductor), electrons carry the charge. And electrons are negatively charged, thus a positive current in a certain direction implies that it is electrons that are moving in the other direction. In electrolyte solutions, a current in some direction can be carried by cations moving in that same direction, or by anions moving in the opposite direction. But generally it is a combination of both, and all ions in solution participate to some degree in transporting the current across an electrolyte phase.

In an electrolyte phase, current density I is not the same everywhere. In the geometry of Fig. 1.1, I might have a certain value at the electrode, but the local current density in the electrolyte phase, a vector, $\mathbf{I}$, can have all kinds of directions and magnitudes. Typically, the current is highest along the shortest path between the electrodes, and it decreases the further we are away from this center region, but current also runs there. Thus the current that leaves an electrode first fans out, and then later converges again to the other electrode.

Nevertheless, for each cross-section across the electrolyte, the total current passing that cross-section, will be the same. If we draw any arbitrary surface S across the entire electrolyte phase, a surface through which all ionic current passes, then the integral over that surface of the local current density $\mathbf{I}$ multiplied by the normal vector, **n**, is equal to the total current, I, as described by

$$I = \int_S (\mathbf{I} \cdot \mathbf{n})\ \mathrm{d}S \tag{2.2}$$

which is valid for any plane that intersects the electrolyte phase completely (the intersection may include membranes, etc.) with one electrode now on one side, and the other on the other side. This is valid in steady state process, but also in a dynamic problem.

The only restriction to the above analysis is that it is valid for a cell with two electrodes such as in Fig. 1.1. A more general analysis is needed when we have more than two electrodes. Then we can envision, or draw, a closed surface fully enclosing a certain volume –let us call this volume a bubble– and the total current across the surface of this bubble (with contributions from electronic currents through the wires that pierce through this surface, and contributions from ionic currents in the electrolyte), i.e., all contributions combined, is zero, i.e., the enclosed volume stays electroneutral. This analysis requires that each electrode is either completely in or completely out of this bubble. This is because inside an electrode there is charge separation between different regions, so electrodes cannot be located 'half-way' at the bubble-surface. [ix]

Thus, in this approach, the current entering the bubble through wires is equal to the ionic currents leaving the same bubble through the surface of the bubble. This is valid for any bubble one can draw, including ones that include zero electrodes, or ones that contain any number of them. If we make the bubble very small, only encompassing a small region of bulk electrolyte (or metal bulk phase), then the result is that the divergence of the current density vector is zero, i.e., $\nabla \cdot \mathbf{I} = 0$. This is sometimes called Kirchhoff's second law.

[ix] Note that also in bulk electrolyte there can be regions with local charge separation, such as at the very edges of ion-exchange membranes, where also an EDL is formed ('Donnan layer'). These EDLs are a few nm in width across. The bubble cannot cut 'halfway' through these Donnan layers.

Anode and Cathode. We did not yet define the words ‘anode’ and ‘cathode’. These names are very easy. If we have a solution with only one type of anion and one type of cation, then the anode is the electrode to which anions move, or cations move away from (often a combination of the two). Or more generally, irrespective of electrolyte composition, the anode is the electrode where electrons leave from, to go into the external circuit. Or more officially, the anode is the electrode where the electronic current that arrives from the external circuit has a positive numerical value. The cathode is the other electrode, where cations move to, anions move away from. And now the electronic current arriving in it from the external circuit is negative, i.e., ‘real’ electrons arrive in the cathode. This definition is correct irrespective of whether we operate a cell as a fuel cell or electrolytic cell, or in any other case. For reversible electrochemical cells, which change the current direction every so often, see a discussion on p. 30.

When we draw an electrochmical cell, the anode is always left, and the cathode right, see the frontpage of this book.

Oxidation and reduction. If there are electrochemical reactions on the electrodes, and if it is only one, then on the anode, this reaction is an oxidation (for instance the OH^--ions that arrive react to oxygen gas and electrons). Electrons are then formed and they go into the metallic phase, the external circuit. Thus in this example, an anion reacts at the anode to become a neutral species and an electron is pushed into the metal.

On a cathode, the reaction is a reduction, for instance a cation, say Fe^{3+}, picks up an electron from the external circuit, and leaves as a Fe^{2+} ion. That an oxidation takes place on the anode, and a reduction on the cathode, is valid irrespective of what type of cell is used (irrespective of whether we have a fuel cell or electrolytic cell). Note that in these examples, an anion reacted on the anode, and a cation on the cathode, but it can just as well be that in both cases an anion reacts away, or a neutral species, or cations in both cases, or even that a cation reacts on the anode, and an anion on the cathode. Then the ion is charged even higher, for instance, when an anion reacts on a cathode and picks up an electron, it becomes an anion with a more negative charge.

In the examples just discussed, the ion that reacted away ended up with a higher valency when it was involved in an oxidation reaction (for instance, from negative to neutral), and ended up with a lower valency during a reduction (for instance, from more positive to less positive). However, even that is not necessary, because as we will point out later –see also B&F, Eq. (1.5.15) there– a reaction can be $\mathrm{O} + n\, e^{1-} + n\, \mathrm{H}^{+} \leftrightarrow \mathrm{R}$, i.e. a certain molecule O is reduced to a species R, but stays neutral, because it takes up electrons and protons.

What 'is' current? We did not yet discuss *what* carries the current, and what 'is' a current. The latter question is almost of a philosophical nature, and difficult to answer . . . Nevertheless, there are things we do know. We know that the concept of current exists, that we can measure it, and we can use it in theory. But what it 'is', is perhaps a question of a different order. Nevertheless, for a metallic phase all of this is rather straightforward: we simply have the electrons that carry the current and they move according to Ohm's law. But for an electrolyte phase, the situation is more complicated, with both anions and cations moving, often in opposite direction, with fluxes related in some way that at each point the local charge density ρ stays zero. Current can be carried by all ions but locally there is no accumulation of current, which means that at each position the divergence of the current density vector $\mathbf{I}$ is zero (except on electrodes). Interestingly, in a steady state process without mixing, even with many types of ions, often only one or two ions carry most of the current, with other types of ions not taking part. But if we start mixing, more of them participate. The degree to which each ion participates in the local current density relates to the topic of transport numbers, T_i, see B&D.

The technological convention of ‘electrode’. Until now we stressed that the word electrode refers to the complete interface between metal and electrolyte, and on the same ‘piece of metal’ there can be multiple electrodes, with different interfacial structures. This is the important conceptual, or theoretical, meaning of the word electrode. But there is also another meaning, one that is more technological. When confusion can arise, we will sometimes write electrode$^{\mathrm{TC}}$, where TC stands for ‘technological convention’. According to this convention, an electrode$^{\mathrm{TC}}$ is the piece of metal that we insert in water, or for instance a piece of porous carbon that we can connect with an external circuit and that will adsorb ions when it is electrified. So electrode$^{\mathrm{TC}}$ refers to the solid structure that can be handled and modified, and that we can connect to the electronic circuit. This meaning of electrode$^{\mathrm{TC}}$ often slips into a discussion that is actually about the electrode in its theoretical meaning, which we try to follow more closely in this book.

So electrode$^{\mathrm{TC}}$ is the ‘piece of metal’, or metal structure, on which there can be more than one ‘theoretical’ electrode. With corrosion, the steel structure is an electrode$^{\mathrm{TC}}$, but it has multiple ‘theoretical’ electrodes on its surface, where these –two, or more– electrodes form an electrochemical cell. Connecting with the Zn electrode$^{\mathrm{TC}}$, we obtain a three-electrode electrochemical cell, as discussed before.

3

Types of electrochemical cells

Electrochemical cells can be classified in three different *types*, see Fig. 1.2. Within each type, operation in three *modes* is possible. And all three types can have the same three *applications*. Eq. (2.1) plays an important role in analysing these cells and their operational modes.

In this chapter we focus on electrochemical cells where both electrodes are Faradaic, or both are capacitive, but in reality it can be much more complicated: we can also design a cell with one Faradaic electrode and one capacitive electrode, or we can have a porous electrode$^{\mathrm{TC}}$ that is Faradaic in one region, and capacitive in another, or for instance in time the same electrode$^{\mathrm{TC}}$ gradually changes from capacitive to Faradaic. In the next chapters we do not go into these complications but focus on a two-electrode electrochemical cell where both electrodes are either 100% Faradaic or 100% capacitive. See the box on p. 36 for more discussion on the combination of these types of electrodes.

3.1 Faradaic cells

The first type of electrochemical cell is the *Faradaic cell*, of which we show the current-voltage characteristic in Fig. 3.1. In a Faradaic cell we have two electrodes that both are Faradaic, i.e., there is transfer across the electrode of

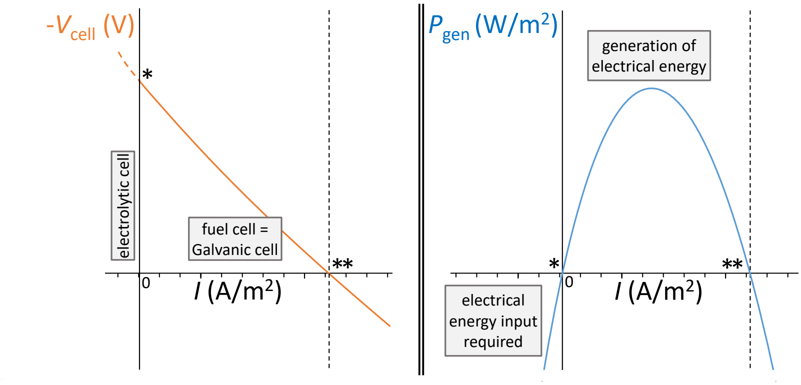

Fig. 3.1: Faradaic cells are characterized by a curve of cell voltage versus current. This polarization curve, or *i*–*V* curve, of the entire electrochemical cell identifies a fuel cell regime and an electrolytic cell regime. In the fuel cell regime, electrical power is produced by the cell, while in the electrolytic cell-regime, an input of electrical energy is required.

ions or electrons, see a box on p. 14. In a Faradaic electrode, one option is that incoming reactants pick up, or shed, an electron and then leave the electrode structure again, to go back to the same bulk phase as where they came from, or they go to another bulk phase. So an electron transferred across the electrode. The other option is that an ion transfers across the full electrode, exchanging between bulk electrolyte and a bulk metal phase. In both cases, in steady state operation the electrode structure remains unchanged.

We see in Fig. 3.1 that a Faradaic cell can be operated in any of three operational modes, namely the electrolytic cell-regime on the very left, the fuel cell regime (also called Galvanic cell) in the middle, and an impractical super-galvanic operational mode on the very right. We will not consider this last mode of operation. It is possible that the polarization curve runs through the origin, then operation is always as an electrolytic cell, i.e., energy must be supplied to the cell to make it run. The fuel cell and electrolytic cell are analysed in more detail in Fig. 3.2.

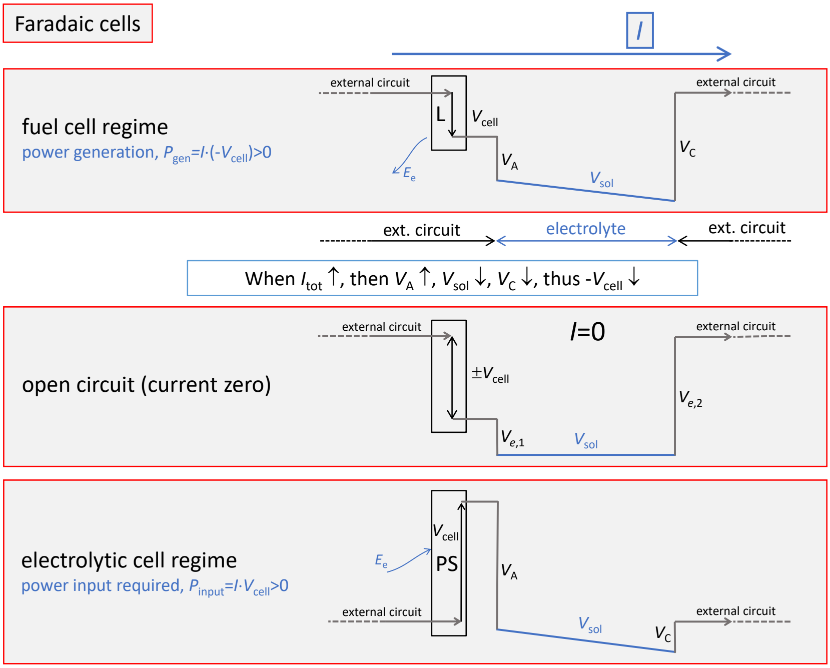

Fig. 3.2: Faradaic cells can operate as a fuel cell (also called: galvanic cell), and as an electrolytic cell. In the fuel cell mode, electrical energy, E_e, is generated in the load L that is placed in the external circuit. In the electrolytic cell mode, the cell is powered from an external source of energy. In all diagrams, current runs to the right, and the electrical potential in solution, i.e., in the electrolyte phase, decays in that direction to drive the ionic current.

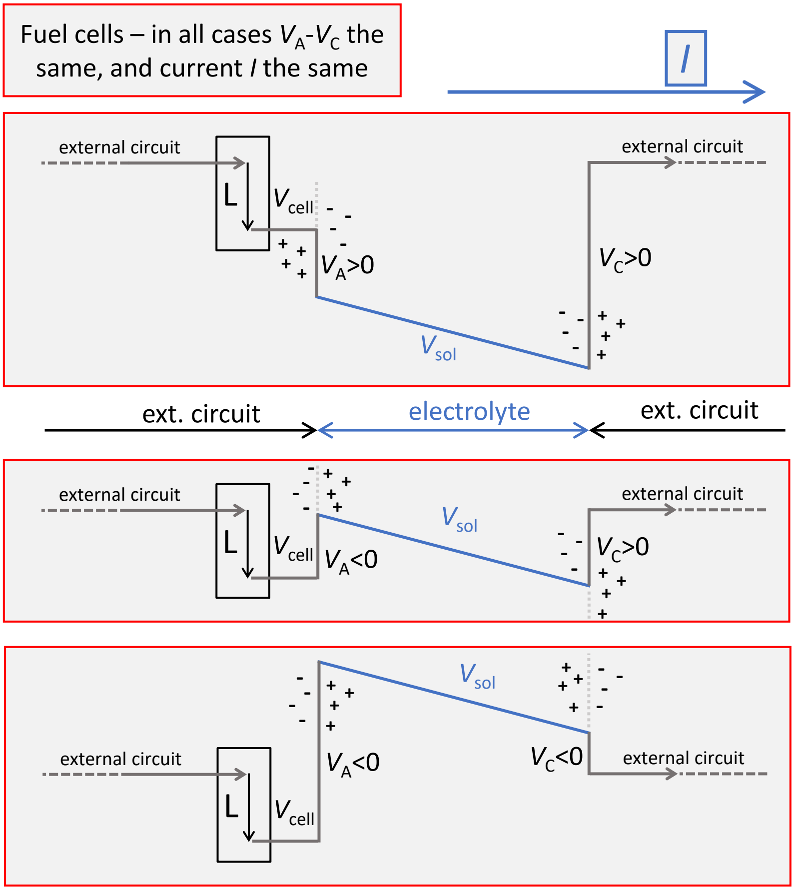

Fig. 3.3: Fuel cell operation requires that $V_A < V_C$, i.e., that $V_A - V_C$ is negative. This does not mean that V_A must be negative and V_C positive. Instead, as depicted here, also both these electrode potentials can be positive, and both can be negative. The electrode potential V_e relates to the charge in the EDL.

Here, in Fig. 3.2, we show profiles of the electrical potential across the electrochemical cell. We start with the electrolyte phase in the middle, go left to the anode, then to the power source, PS, or load, L, even further left, and via the wire from PS or L we go round to the other side, to the cathode on the very right. To extract electrical energy, E_e, in the load, the cell voltage V_{cell} must be negative.[i,ii]

In the fuel cell mode, the reacting components coming from any of the bulk phases (metal, electrolyte, gas) will reduce their chemical (Gibbs) energy when they react to product species. This reduction in their chemical energy can be used to generate electrical energy. In the electrolytic cell, it is the other way around. Chemical energy can also relate to concentrations: simply a difference in concentration between the solution near the anode and cathode of the same reactive ions, can generate a cell voltage, thus generate electrical energy, while the reverse process (to separate two solutions) requires input of E_e. If these effects relate to the electrodes, we categorize such cells as Faradaic cells, while we reserve the term ‘concentration cell’ for those cells where electrolyte effects are predominant, as will be discussed.

In the diagrams in Fig. 3.2 that relate to Faradaic cells, the current I is either zero or is directed to the right. In that same direction the potential in the electrolyte phase goes down to pull the ionic current through solution, in analogy with Ohm’s law, $I = -\kappa\, dV/dx$, where κ is an ionic conductivity. Electrode potentials can either go up or down, but interestingly, for a fuel cell the only requirement is $V_{\text{A}} - V_{\text{C}} < 0$, see Fig. 3.3.[iii]

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[i] This energy E_e is not to be confused with the field strength E, nor with the symbol E for electrode half-cell potentials that we use further on. It is neither the energy that we can store in a capacitive electrode, as we also discuss further on. Note that referring to an energy E_e here in Fig. 3.2 is not entirely correct, because a cell produces power (in W), and integrated over a time period, that leads to an energy E_e in J.

[ii] Note that in a *power source*, for which we use the abbreviation PS, the generated electrical power, P_{gen}, defined as a quantity that is generated by the electrochemical cell, would be negative. Thus only when the external device is a load, L, and current runs, then we have a positive power, P_{gen}, generated by the cell. This is for instance the case for the fuel cell regime in Fig. 3.1, while to the left, in the electrolytic cell regime, a power source, PS, is used, and we have a power input.

[iii] If the sign is opposite, and we still wish to describe this system in the conventional manner as a fuel cell, one just has to reverse (the labels of) anode and cathode. Thus, a fuel cell requires two electrodes with different V_e, and the electrode with the largest V_e is assigned as the cathode.

The fuel cell mode, or regime, is depicted at the top row of Fig. 3.2, as well as in all panels of Fig. 3.3. In a fuel cell we generate electrical energy, E_e. Thus in the electronic circuit, a load 'L' is placed and it will generate energy E_e because the electrons that flow through it (leftward) can go up in electrical potential. The electrons do this spontaneously, and thus drive the generation of E_e. Fuel cell operation can only be achieved for a limited range of currents and cell voltages. One way to assure that one operates at a suitable current, is to work (in practice, or in the imagination) with a 'load' as a passive element, for the present purposes of analysis similar to how a resistance is understood.[iv] The heat that is produced in this resistance is then equal to what potentially can be generated as electrical energy, E_e.[v] By using a resistance as a load, the resulting current is never too high.[vi] The load placed in the external circuit will slow down the flow of electrons, but never make it completely stop, thus power is always generated, see Fig. 3.1, right panel.

Interestingly, the maximum power is obtained at a current roughly half that of the short-circuit current (or, obtained for a cell voltage that is half the open-circuit voltage), and this is when the resistance in the load is about equal to the resistance of all other elements of the cell. If the load resistance is higher than this optimum value, the cell voltage is higher but the current decreases, and vice-versa for lower loads. At this condition of optimal load, note that the system operates at about 50% efficiency, i.e., for each two quantities of chemical energy that are being 'destroyed', only one becomes electrical energy; the other is lost as heat in the

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[iv] The load can for instance be a battery that is being recharged, but often the load is simply envisioned to act as a resistance. The heat produced in such a resistance (current × cell voltage) is then a measure of the electrical energy that can potentially be generated in a more suitable device (with a certain conversion efficiency). The load resistance will slow down the flow of electrons, but never reverse it, i.e., in this regard it is 'passive'. A realistic device such as a battery is more complex than a simple resistance because we aim to charge it slowly, and thus the cell voltage must not be too high at first, but then must slowly increase to charge the battery to completion. Thus, the recharge of a battery by our electrochemical cell is a time-dependent problem.

[v] Note that some heat is always produced in any energy conversion device, thus the generated E_e in a real load is always less than the total heat produced in the resistance that we use to simulate it.

[vi] To this load we can then assign any value of its internal resistance, from very low to very high. The maximum power produced by the load is when this internal resistance is approximately the same as the sum of all other resistances in the cell.

electrochemical cell (not in the load). This does not yet include energy losses (heat production) in the load. A more efficient operation requires the cell to work nearer to the open-circuit voltage, at a reduced power production rate (per unit time less energy is generated). For maximum efficiency we try to work very close to $V_{\mathrm{cell,OC}}$, thus at a low rate of power generation.[vii]

Energy Storage Devices (ESDs). Fig. 3.4 gives a overview of ESDs based on electrochemical cells. ESDs can be constructed based on each of the three types of electrochemical cells that are summarized in Fig. 1.2, with the fuel cell (FC) an ESD from the class of Faradaic cells, and the electrochemical capacitor (EC) an ESD from the class of capacitive cells.

The word *battery* does not have a strict definition. It mainly relates to cells of the Faradaic type, though not all devices in this class are called a battery (for instance, a hydrogen fuel cell is generally not called a battery), while also devices that are concentration cells are sometimes called a battery by manufacturers. An example of an electrochemical capacitor that is called a battery is the Li-ion battery. The term battery is sometimes associated with ESDs that have a finite, fixed, enclosure, as for consumer electronics, though also this definition is not strict (for instance, the redox flow battery is fed from external tanks). Or the term is used to impute that 'chemical effects' are at the basis of its operation, in contradiction to more 'electrostatic effects' that are then considered to be the driving forces in ECs. However, this latter association of the term battery with chemical effects is problematic, as we try to explain below.

According to a distinction where battery refers to chemical effects, and an EC to electrostatic effects (a distinction that we do *not* advocate), a battery then has a constant output voltage because it is based on a chemical reaction, with the output voltage in an EC variable because ECs are based on electrostatics and capacitance, and thus voltage is strongly dependent on

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[vii] In practice, operation near $V_{\mathrm{cell,OC}}$ can also be energetically inefficient, because of parasitic effects that come into play, such as leakage of salt between anode and cathode compartments, and thus we lose 'energy' because reactants mix up.

charge. A related distinction is then also drawn that ECs are fast because they use electrostatic effects, and batteries are slow because the ions are chemically bound.

These arguments to make a distinction between a battery and an EC, are not very convincing in our view. To begin with, a distinction based on the theoretical view of what happens exactly inside an electrode, is not very strong, because this depends on one's personal preferred theory, and this view can always change, and people don't have to agree. Because how to decide whether an effect is electrostatic or more chemical, or something else? There are many situations that are hard to classify: in the electrode, ions can bind to the surface, can associate with electrons, and we can't be sure what exactly occurs. As for the other criteria proposed to distinguish the two two types, we would argue that the rate of discharge seems not to be a very fundamental property to decide on whether a device is to be called a battery or not. And the stability of the output voltage is neither a strong criterion because many devices that are called a battery have a voltage that decays during use, including the Li-ion battery.

The Li-ion battery is an intriguing type of electrochemical capacitor, in which Li-ions are stored in the graphite anode during charging, and released during discharge, and the reverse for the cathode (made of a Li oxide or phosphate). Because of phase separation of Li-ions within the electrode, it has an output voltage that is rather stable, which makes it seem to behave in this regard to a Faradaic cell (but it is capacitive). Still, it is a capacitive cell.

Interestingly, a stable output voltage is not that essential when devices have an electronic management system (based on inductors and other electronic elements) that can deal with a decaying voltage during use. Such a system then provides a stable voltage output of any required level. For example, the voltage of a Li-ion battery can decrease by 20% during operation, but the output voltage stays at a required level.

Note that there also exists an electronic device called a (dielectric) capacitor. This electronic device consists of two metal wires (ends) separated

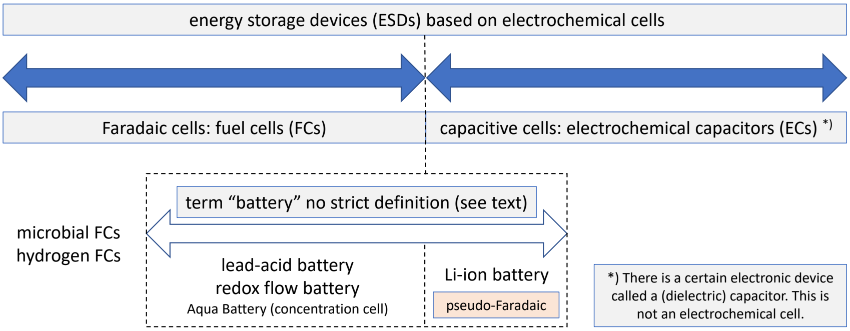

Fig. 3.4: Energy storage devices (ESDs) based on electrochemical cells are in one of two classes: fuel cells and electrochemical capacitors. The term battery has a loose definition.

by a dielectric (insulating) medium, and this device can store charge (i.e., negative charge in one metal, positive charge in the other; overall the device is electroneutral). This is not an electrode, and neither is it an electrochemical cell. This electronic device has a capacitance C (defined as (change in) stored charge in one metal end, over the (change in) voltage across the full device) that is almost independent of charge.

What Figs. 3.1 and 3.2 indicate, is that the same electrochemical cell (the same device) can in principle run in each of the three modes/regimes, and it is not the case that a certain device can only operate as a fuel cell, and another as an electrolytic cell. Fig. 3.1A presents for a Faradaic cell a curve of cell voltage versus current, i.e., the I-V curve, or polarization curve.[viii] With one and the

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[viii] Further on, we encounter polarization curves, for a concentration cell, and for a single electrode. Interestingly, they do not depend on whether a current is applied or a voltage. Both approaches are completely equivalent because I and V are uniquely related, and thus, whether we apply a certain current and measure voltage, or the other way around and apply a voltage and measure current, these two methods lead to the same set of I-V data. This is not the case for a time-dependent process. In that case, if we apply a certain current and measure the voltage, $V(t)$, that is different from an experiment where we apply a certain voltage and measure the current $I(t)$.

same device, we can work in three regimes: in the middle is operation as a fuel cell, to the left is the electrolytic cell, and to the right a non-practical regime where we push a fuel cell so hard that even though the reactions go in the ‘spontaneous’ direction, still energy must be invested.[ix]

Thus, the fuel cell regime in the middle of Fig. 3.1A is limited on two sides: on the left, the current direction reverses sign, and on the right V_{cell} switches sign. The first transition is at the open-circuit (cell) voltage, $V_{\text{cell,OC}}$, and we go from the fuel cell to the electrolytic cell mode. The other transition is at the short-circuit current, I_{SC}.

An important discussion is now whether the labels anode and cathode must be switched when the current direction is (repeatedly) reversed. This is a complicated and ambiguous topic for many reasons: do the words relate to a specific piece of metal, or to the operation at any moment in time. When confusion arises, it helps to give a fixed label to each metal piece (electrode$^{\text{TC}}$), whatever is the current direction. Indeed, in such a system with charge-discharge cycles, such as a lead-acid battery, the terms anode and cathode are based on how the cell functions during the key phase of operation. For a battery this key phase is discharge, i.e., when it is used, not during recharge. So in practice, after switching to the other mode of operation (from discharge to charge), the piece of metal, i.e., the electrode$^{\text{TC}}$, is called the same as before, so during charging, what is called cathode, has ionic current move away from it, which is opposite to the theoretical definition of the term cathode.

Note that for a perfectly symmetric system, with the same electrodes, we do not have three regimes, but only the electrolytic cell-regime that always needs an energy input to generate a current. This would be a curve that is point-symmetric around the origin in Fig. 3.1A. The input power P_{input} is zero for $I = 0$, and otherwise always positive.

The accompanying Fig. 3.1B describes the power that the cell generates, P_{gen}, which is the product of I and $-V_{\text{cell}}$. This power is positive in the fuel cell regime, and negative (we need to invest electrical energy) in the regimes both to the left and to the right. When the polarization curve is linear as in panel A of Fig. 3.1,

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[ix] This ‘super-galvanic’ regime seems not to have any practical use, but nevertheless its scientific study can be interesting and generate new insights.

then the power curve is parabolic, and the maximum power is obtained halfway, i.e., for a current that is half the short-circuit current, thus $I|_{P_{\text{gen,max}}} = ½\ I_{\text{SC}}$, with I_{SC} indicated by ** in Fig. 3.1. And we are at the same condition of maximum power when the cell voltage is half the open circuit voltage, thus when $V_{\text{cell}} = ½\ V_{\text{cell,OC}}$, with $V_{\text{cell,OC}}$ indicated by * in Fig. 3.1. Thus the maximum power in that case is obtained from

$$P_{\text{max,gen}} = {}^1\!/\!_4 \cdot I_{\text{SC}} \cdot |V_{\text{cell,OC}}| \,. \tag{3.1}$$

In the electrolytic cell there is no generation of electrical energy; if we calculate it, P_{gen} is negative; i.e., we must invest electrical energy in the non-spontaneous chemical reaction, see the third panel in Fig. 3.2. The products of the reaction have a higher chemical energy than the reactants, i.e., we store chemical energy.

Of course most device are optimized for a certain operation, thus we cannot simply reverse current in a fuel cell, and expect the system to switch graciously to electrolytic cell operation, or vice-versa. But reversible systems can deal with regular switching, such as concentration cells and capacitive cells. Also some Faradaic cells can operate ‘back and forth’, i.e., can be recharged (for instance the lead-acid battery).

When an electrochemical cell is operated in such a cyclic manner, i.e., with current in one direction for some time, and then with the current direction switched for another period of time, we can assign the terms ‘charge’ and ‘discharge’ to these two periods, where charging refers to the period with input of electrical energy (from an external source, into the cell), and discharge refers to period where electrical energy E_e is generated. Discharge is when an ESD is used to power another device. And charge, often called recharge, is when electrical energy is being stored in the cell. For such reversible systems we can calculate the round-trip efficiency, which is how much energy is generated from the cell (the ESD) in the discharge step, versus how much was put in during (re-)charge.

The open-circuit cell voltage. So how to find the open(-circuit) cell voltage, that separated the fuel cell regime from the electrolytic cell regime? Experimentally this is of course not very difficult, we just measure the voltage between the two wires from the electrochemical cell using a voltmeter (which internally has a very high resistance). Theoretically, because we are close to, or at, equilibrium, we can use the Nernst equation, to be discussed below, to calculate the electrode potential, V_e, for both electrodes, and subtract the two, which is then $V_{\text{cell,OC}}$. In this expression is a standard term, $V_{0,e}$. Though we do not know the two values of $V_{0,e}$, we do know the difference $V_{0,\text{A}}$–$V_{0,\text{C}}$ very accurately, because this difference is the same as the difference $E_{0,\text{A}}-E_{0,\text{C}}$ where the $E_{0,j}$'s are the standard half-cell potentials, which are tabulated versus the reference, being the standard hydrogen electrode (SHE). [Here it is assumed that one particular reaction takes place on the anode, and another well-defined reaction on the cathode. This is not generally the case.] The second element of calculating V_e relates to the concentrations of ions and other solutes (and gas phase species) near the electrode.

One complication in calculating $V_{\text{cell,OC}}$ is that often there is a membrane or filter in between anode and cathode compartments. Even if this layer is quite open, there can be an extra potential difference here, because of different diffusion coefficients of the various ions. In addition, when an ion-exchange membrane (a membrane very selective for cation transport versus anion transport, or vice-versa) is placed in between the two compartments of different composition, there is a potential across the membrane, and the measurement will also pick up this potential, and thus it must be added to the two electrode potentials when calculating the theoretical open circuit voltage.

3.2 Concentration cells

A second type of electrochemical cell also operates in steady state, but does not critically rely on electrode reactions. Instead, important is the electrical potential in the electrolyte phase. Examples are electrodialysis (ED) and reverse electrodialysis (RED) as the analogues of the electrolytic cell and fuel cell discussed previously. Indeed, also for concentration cells we can construct an I-V curve, or

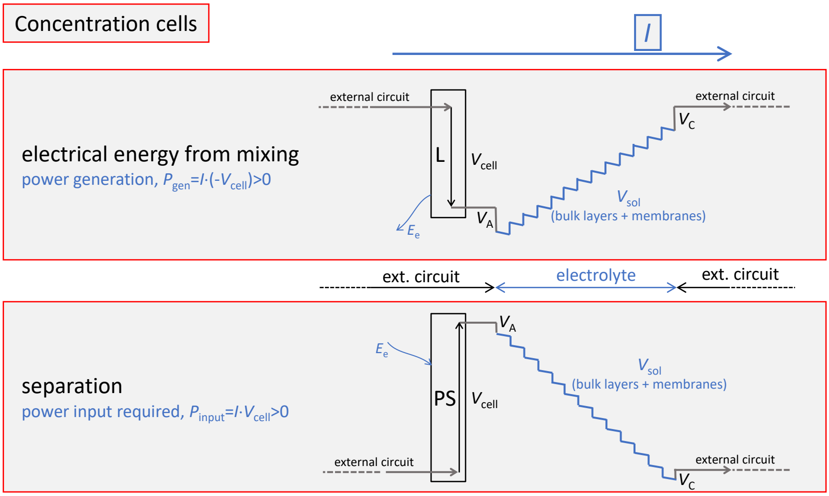

Fig. 3.5: Concentration cells can operate in a mode that generates electrical energy (for instance, from a salt concentration difference), and in a mode that requires energy input, for instance for water desalination.

polarization curve, similar to the curve for Faradaic cells, see Fig. 3.6, with three modes of operation similar to Faradaic cells.[x]

In ED, we use a large number of membranes to separate a salt solution of a certain salinity into two outflow streams, one with higher salt concentration, and one with a lower salt concentration, and this requires an energy input, while the net result is that the energy of the system has increased (in the form of a reduced ion entropy of the outflowing streams, compared to the inflow). ED is then the analogue of the electrolytic cell because a net electrical energy input is required. The opposite is a cell for RED (also called ‘osmotic power’, ‘nanopore power generation’, or ‘blue energy’), where electrical power is generated from mixing

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[x] Another type of cell depends on differences in concentration of electroactive ions, and how that affects the electrode potential. So in these cells the electrode reactions are of importance, and the voltage change across the electrolyte is as usual (B&F (2001), footnote on p. 65). We classify these cells as Faradaic cells.

two streams of different salt concentration (or different pH), again in a cell with many membranes. This cell is analogous to a fuel cell because we generate electrical energy from the decrease of energy of bulk solutions.

Compared to the Faradaic cells, what is different in these concentration cells, is that the electrode potentials, V_e, can be the same or similar on both electrodes, we just do not care much, as they are low relative to the total cell voltage, see Fig. 3.5, and V_{cell} is now determined not by the electrodes, but by what happens inside the electrolyte phase. Especially RED is interesting, where even though the ionic current flows left to right through the electrolyte phase, and thus in each layer outside the membranes the potential decreases, the same as for the Faradaic cell designs, see Fig. 3.2, nevertheless, as in a 'water mill', in each membrane (when well-designed) the potential is lifted up, such that ultimately $V_{\text{sol}} > 0$. This is then opposite to the general case which is that V_{sol} is negative ('going down') (see also p. 67 in Vetter, 1967).

Thus, also for these cells, a polarization curve and a power curve can be constructed, see Fig. 3.6, the same as in Fig. 3.1 for the Faradaic cells. The open-circuit potential, $V_{\text{cell,OC}}$, which is the cut-off between ED and RED, depends on the salt concentrations in the two streams and the number of membranes, M: $|V_{\text{cell,OC}}| = M \cdot V_{\text{T}} \cdot \ln c_{\text{high}}/c_{\text{low}}$.[xi]

3.3 Capacitive cells

In capacitive cells, when a current is applied, the different regions in the electrodes change in time. It is not possible to operate the process in steady state, because more and more electrons are stored, as well as more and more ions (or less and less, dependent on current direction, ion type, etc.). Important capacitive cells are electrochemical capacitors used to store electrical energy, where electronic and ionic charge is stored inside the electrode, i.e., inside the EDL structures located at the metal-electrolyte interface, with the Li-ion battery a prime example.

This battery is not based on a Faradaic process. In a Faradaic process one component, originating from outside the electrode, is converted inside the electrode

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[xi] For an ideal 1:1 salt and perfectly selective membranes. Membranes are alternatingly anion-selective and cation-selective. The number of membrane pairs in a stack is given by $N = M/2$.

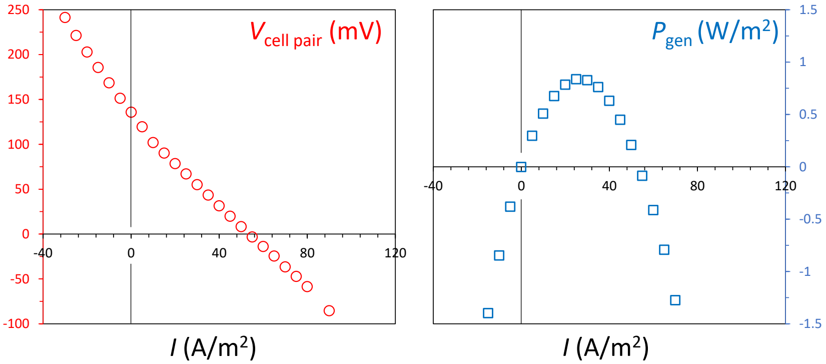

Fig. 3.6: An I-V curve, or polarization curve, for a concentration cell running in each of the three possible modes, with RED operation in the middle, and ED on the left. The cell consists of $N = 5$ pairs of ion-exchange membranes (IEMs), each of 20 cm^2 area, with 160 μm wide channels. The channels are fed alternatingly with 17 mM and 500 mM NaCl solution, with a flow rate per channel of 12 mL/min (empty channel residence time $\tau = 1.6$ s). A redox solution flows along the two electrodes in channels separated by IEMs from the desalination channels. Neosepta AEX and CMX IEMs are used. The voltage reported is that across a pair of membranes and adjoining channels, and power P_{gen} is per m^2 total membrane (the area of both membranes in a cell pair is counted). Voltage is measured with reference electrodes across the N membrane pairs; thus, excluding end-electrodes.

and leaves again, as is the case for the lead-acid battery, and also for reversible hydrogen fuel cells; these are Faradaic systems. But charging of a Li-ion battery is simply transporting Li-ions from one electrode to the other, thereby changing the Li-concentration and chemical potential inside the two electrodes, and thus also changing the electronically stored charge.

Capacitive and Faradaic electrodes in an electrochemical cell. An interesting question is whether the two electrodes in an electrochemical cell such as in Fig. 1.1 need to be of the same type, i.e., do both need to be capacitive, or both Faradaic? The answer is: no. Each can be of either type, and each can also be a mixture of boths. There is no constraint at all here. Indeed, in reality any practical electrode will have some Faradaic reactions occurring even though they may be small. And after a change in conditions, also in a Faradaic electrode, we have a dynamic situation for some time, and then capacitive effects briefly play a role. Thus, always all electrodes to some extent are subject to both processes. Nevertheless, in a very good electrochemical capacitor, the Faradaic effect will be small. And vice-versa, if an electrode operates in steady state (i.e., no changes in time), it means there is only Faradaic operation because capacitive effects are then absent.

So there are many options. The only constraint to the complete cell operation is that during steady state operation, the capacitive current is zero. And if this is so, then the Faradaic process has the same rate in both electrodes. Thus, if we are in the steady state, and there is some non-zero current, although each of the electrodes certainly has a certain EDL structure with separated regions of opposite charge, these regions are not being charged further over time. Thus, the capacitive current is then zero, $I_c = 0$, and all of the electronic current arriving in an electrode is used for the Faradaic process, and that is the case in both electrodes.

4

Faradaic and capacitive electrode processes

We can now shift our attention to the level of a single electrode and discuss the clear distinction between Faradaic and capacitive electrode processes.

In general, we know that in an electrode, even without any process going on, i.e., when the current is zero, that an electrode has regions of positive and negative charge, and thus there is an electrode potential, V_e, see Fig. 2.2. Now we run a current through the electrode, and then the electrode charge and potential will change, i.e., the structure of the EDL (i.e., of the electrode) changes. We also know that the electronic current arriving on the metallic side, is equal –numerically– to the ionic current that leaves the electrode and goes into the electrolyte phase (gases typically do not carry current). There are two fundamentally different processes about what now exactly happens in the electrode:

1. *Faradaic electrode process*: There is transfer of charged particles (electrons or ions) across the electrode, thus from the metallic side to the electrolyte side (or vice-versa); or

2. *A capacitive, or non-Faradaic, electrode process*: There isn't such a transfer of electrons or ions. Electrons arrive, and ions arrive. But none 'transfers across the electrode' to the other side.

Option 1 implies that there is an oxidation or reduction reaction at the electrode *with the reactants entering the electrode and products leaving the electrode*. Examples can involve water reacting to H_3O^+ and O_2, or Fe^{2+} reacting to Fe^{3+}. In both cases also electrons transfer across the electrode between electrolyte and metal. All of these species (H_2O, H_3O^+, O_2, Fe^{2+}, Fe^{3+}) enter, and leave, the electrode, with electronic charge transferring from the electrolyte phase to the metal. The other option is that it is not the electron that transfers across the electrode, but the ion. This is the case for plating and for corrosion. In a plating reaction, a metal ion, for instance Cu^{2+}, transfers from the bulk electrolyte phase across the electrode, and becomes incorporated into the metal bulk phase. Corrosion, for instance of an iron structure, is the reverse of this, now a metallic atom, say Fe, transfers across the electrode and becomes an ion (often immediately incorporated in a 'solid salt', i.e., an iron-oxide phase). Thus we have in all these cases charged particles (ions or electrons) that transfer across the electrode from one bulk phase to another.

Another example is the reaction $2H^+ + 2e^- \longrightarrow H_2$, where an H^+-ion arrives at the electrode, picks up an electron, and leaves as gaseous H_2. All these examples are Faradaic electrode processes. As long as reactants are supplied, and products removed, a Faradaic process can run forever, and the electrode potential stays the same. The electrode doesn't store any ions or electrons: everything that enters, also leaves again. There is a certain EDL structure, with a certain number of electrons and ions, but while the process is ongoing, these numbers do not change, unless we change conditions in solution, or change the current. Faradaic electrodes are also called charge-transfer electrodes, and this terminology refers to the transfer of physical particles across the electrode, see a box on p. 14.

In option 2 there is no such transfer of charged particles across the electrode. Ions can enter the electrode and do interesting things there, such as adsorb to the metal surface, and associate with electrons. It can completely give off an electron or react with one, and this we can call an electrode reaction. But for a capacitive process, the products of this electrode reaction do not leave the electrode. Instead, they stay and accumulate inside the electrode.

The reverse situation is that there are no ions entering, but only ions leaving. This is the case in a charge-discharge cycle of an electrochemical capacitor. Then, during one phase ions go in, and in another it is the same ions that leave again. Integrated over a cycle, the ions are unchanged, they are not converted, and also the electrode is unchanged. In this type of electrode process, when a current is applied, the electronic charge in the electrode changes in time (and likewise the charge on the ionic side), i.e., we store both types of charge, and therefore the electrode potential continues to change over time.

Thus, there is a clear difference in how a Faradaic electrode and a capacitive electrode respond to applying a (constant) current: either the electrode potential is stable, or it continuously changes.

Interestingly, to make the distinction, we do not need to know what exactly happens in the electrode on the atomic scale, which is a very good thing because we may never know these details for certain. We can make models, but these theories about the atomistic details of how ions are stored, there are many of them, and there may be ongoing scientific discussions, and what is someone's preferred theory, that can always change again. Instead, to make the distinction between Faradaic and capacitive electrode processes, we only have to consider the observable, macroscopic, behaviour of the electrode, because that suffices to clearly make the distinction between the two processes. As we discussed before, this difference only depends on the question whether or not *both* reactants *and* products of an electrode reaction are able to freely go in and out of the electrode. For the ions and other (neutral) reactive species to have this freedom or not, that determines whether after a current is applied, the concentration of ions and thus the charge in the electrolyte regions of an electrode is constant, or instead continues to change, and thus whether the electrode potential is constant or changes in time. Thus, to determine whether a process is Faradaic or capacitive, we can analyse how an electrode responds to an applied current. And thus we can make the distinction Faradaic versus capacitive based on experimental observations, without having to assume anything about what we believe exactly happens inside the electrode.

We do know that in a capacitive process, more and more electrons and ions are stored in time (if we continue to apply current), this will lead to the cell voltage continue to change, until it is so high (or, so low) that a Faradaic process develops.[i]

Thus, we can summarize much of the above in the simple equation (Vetter, 1967)

$$I = I_c + I_F \tag{4.1}$$

which states that part of the current (density), I, arriving through the external circuit into an electrode, will result in a capacitive current, I_c, and the other part will be Faradaic current, I_F.[ii] The general concept of Eq. (4.1) can be found in various classical textbooks, describing that all capacitive current relates to absorption of charged species inside the electrode, and all Faradaic current relates to processes that can run in steady state, i.e., 'forever', with the electrode not changing in time, because reactants and products do not accumulate in the electrode. Three quotes from classical sources are provided in Fig. 4.1.

Sometimes the two processes occur simultaneously, but often one is more important than the other. Which of the two is the most important we can find out, for instance, by applying a step change in voltage. If the the current quickly goes up (it 'spikes'), but then goes down to zero, we have a capacitive process and $I = I_c$. If the current goes to a new constant level, we have a Faradaic electrode process, and thus $I = I_F$.

For an electrode where both capacitive and Faradaic processes take place, we can set up a charge balance for the electronic charge in an electrode

$$\frac{d\sigma_e}{dt} = I_c = I - I_F \tag{4.2}$$

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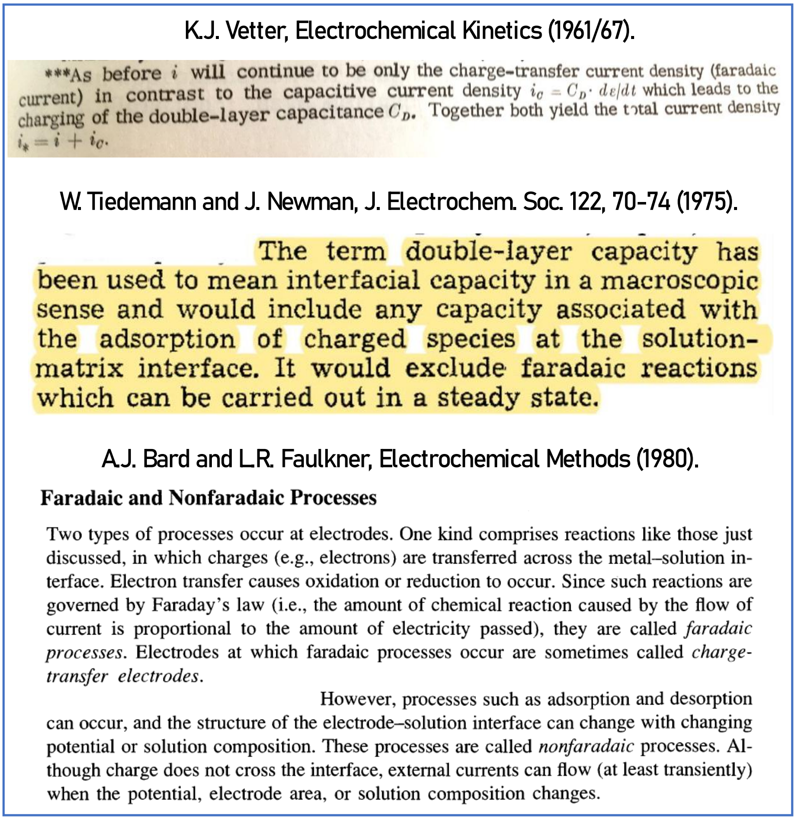
[i] An exception is when ions in the material phase-separate, as happens for Li-ion batteries in an organic solvent, where a Li-ion concentrated and a Li-ion dilute phase develop. In that case we do store more and more electrons and ions, but as long as both phases coexist, and we (dis-)charge the battery very slowly, the potential is stable. So even though the electrode is capacitive, and the number of electrons stored increases, it is because of phase separation that it is possible for the electrode potential to stay constant.

[ii] Here we define the positive direction as going from metal into the electrolyte as is drawn for the anode in Fig. 1.1. We then have a plus-sign in Eq. (4.1) for the Faradaic current, which implies that the Faradaic reaction is defined as positive in the oxidation direction.



K.J. Vetter, Electrochemical Kinetics (1961/67).

***As before i will continue to be only the charge-transfer current density (faradaic current) in contrast to the capacitive current density $i_C = C_D \cdot d\varepsilon/dt$ which leads to the charging of the double-layer capacitance C_D. Together both yield the total current density $i_* = i + i_C$.

W. Tiedemann and J. Newman, J. Electrochem. Soc. 122, 70-74 (1975).

The term double-layer capacity has been used to mean interfacial capacity in a macroscopic sense and would include any capacity associated with the adsorption of charged species at the solution-matrix interface. It would exclude faradaic reactions which can be carried out in a steady state.

A.J. Bard and L.R. Faulkner, Electrochemical Methods (1980).

Faradaic and Nonfaradaic Processes

Two types of processes occur at electrodes. One kind comprises reactions like those just discussed, in which charges (e.g., electrons) are transferred across the metal–solution interface. Electron transfer causes oxidation or reduction to occur. Since such reactions are governed by Faraday's law (i.e., the amount of chemical reaction caused by the flow of current is proportional to the amount of electricity passed), they are called *faradaic processes*. Electrodes at which faradaic processes occur are sometimes called *charge-transfer electrodes*.

However, processes such as adsorption and desorption can occur, and the structure of the electrode–solution interface can change with changing potential or solution composition. These processes are called *nonfaradaic* processes. Although charge does not cross the interface, external currents can flow (at least transiently) when the potential, electrode area, or solution composition changes.

Fig. 4.1: Three passages from classical sources on the distinction between capacitive and Faradaic processes.

where σ_e is the charge density (in C/m^2 or in C/m^3) on the metal-side of the electrode.[iii] According to Eq. (4.2), the electronic charge depends on the current flowing in from the external circuit, I, minus the current used by the Faradaic reaction, I_F. The Faradaic current is often envisioned as a leakage current, representing that some of the current that arrives is not stored, but leaks away, while the other part is stored, and that is the capacitive part.

When the electrode behaves as a simple capacitor, then the charge σ_e is proportional to the electrode potential, V_e, by

$$\sigma_e = C\,V_e \tag{4.3}$$

where C is the capacitance of the electrode, a number with unit F/m^2 or F/m^3, where F is 'Farad', which is F = C/V. If there is no Faradaic reaction, thus $I_F = 0$, and if we now do an experiment at fixed current density (this is the current 'going into the electrode', I), then σ_e increases linearly in time, and thus the electrode potential V_e will do the same. This is not so interesting.

But if we also have a Faradaic reaction, and the rate thereof depends on σ_e (or, equivalently, see Eq. (4.3), we can say it depends on V_e), then the calculation becomes more interesting. In general, an oxidation reaction goes faster when V_e is higher (more positive), which is because electrons are negative, and thus the higher the electrode potential, the more they prefer to leave the ions and go into the metal phase. Thus, a simple expression for I_F can be

$$I_F = +\,kV_e \tag{4.4}$$

where k is a kinetic rate constant with unit A/V/m^2. If we insert Eqs. (4.3) and (4.4) in Eq. (4.2), we arrive at

$$\frac{dV_e}{dt} = \frac{I - kV_e}{C} \tag{4.5}$$

[iii] In the text that follows, many properties are either per unit area, and thus '/m^2' is part of the unit, or per unit volume, and then the unit has a part that is '/m^3'. The area-definition is for an electrode that has a well-defined surface area, while the volume-based definition is relevant for porous electrodes. This applies to the charge density σ_e, capacitance C, power P, energy, E, and for the currents, I, I_C, and I_F. In practice, many of these properties are defined per mass of electrode, not volume or area.

which we can integrate from $V_e = 0$ at $t = 0$ for a constant I to arrive at the result that the electrode potential first rapidly increases and then levels off to a constant value when I_F equals the applied current I. Thus, the final value of V_e is given by $V_e = I/k$, and a higher current I leads to a higher V_e in the steady state. The capacitive part is absent in steady state; that part only decides on how long it takes to reach steady state.

If we have many data of the electrode potential V_e versus current I in steady state, we can construct a polarization curve which is a plot of current I against electrode potential V_e (or vice-versa), and such a curve provides a fingerprint of the behaviour of the electrode (the Faradaic reaction rate as function of potential), independent of capacitive effects.

Three-electrode setup. The best method to obtain an *i*-*V* curve of a single electrode, is a setup, or experiment, with three-electrodes. In this setup, the electrode under study is the working electrode (WE), while the counter electrode (CE) provides the current, and we have a reference electrode (RE) placed near the WE. The voltage between WE and RE is measured, and this is generally called the electrode potential, *E*, reported jointly with the type of RE that was used (for instance, Ag/AgCl), or the number is converted to an *E* relative to a standard, such as the standard hydrogen electrode, SHE (as if that standard electrode was used). As we will discuss in Ch. 7, see p. **??**, the potential *E* differs from the electrode potential V_e by a constant factor.

To have this constant factor, this fixed difference between E and V_e, we must avoid a significant voltage difference between WE and RE across the solution between them. This is accomplished by the use of a very low current between WE and RE (a high ‘impedance’ of the RE), a high salt concentration in solution (for instance, 1 M) and placing the RE very near the WE.

Still, the possibly large current between WE and **CE** results in voltage changes in solution, which can lead to a voltage difference in the solution between WE and **RE** (see also B&F, p. 24). And there will be a film layer in front of the WE, and the effect thereof will be current-dependent. In any case, if everything works out, $V_e = E + c_1$ and c_1 is a constant factor.

Interestingly, across the RE the voltage change is a fixed value because it is a Faradaic electrode that can be made to operate very near equilibrium, and thus for the RE the Nernst equation, that we will discuss later, applies.

RC network analysis and electrochemical impedance spectroscopy (EIS). Presented above was a simple example of an RC network calculation, where RC refers to a 'resistance-capacitor' scheme, or network. In this example there was no real resistance, though in this calculation the Faradaic reaction had the same mathematical structure as a resistance placed in parallel to a capacitor. We analysed the case of a constant current, but experiments more often are based on a certain imposed (cell) voltage (signal). In RC network models often more elements are used, placed in series and in parallel, thereby constructing an entire network of elements in the calculation. And in the related experiments, the voltage signals or currents are not set to constant values, but vary periodically around a mean value.

There are generally two possibilities for the type of experiment and analysis using RC circuits. The first is a repeatedly varying 'saw tooth' profile in cell voltage, and this experiment is called 'cyclic voltammetry' (CV). The resulting CV diagrams show many features, such as peaks and troughs, and specialists are able to extract useful information from these diagrams. The second type of experiment is to apply a sinusoidally changing electrode voltage or current, of a certain frequency and amplitude (around a mean), repeated at many frequencies spanning many orders of magnitude, and this is called Electrochemical Impedance Spectroscopy (EIS). Theoretical analysis is easier when one is familiar with complex number analysis, focusing on the real and imaginary parts of the 'complex impedance.' A very interesting read on this topic is pp. 125–141 in P.J. Nahin, An imaginary tale: The story of $\sqrt{-1}$ (1998), where the famous Rayleigh's puzzle is also discussed.

Two reasons for the popularity of EIS analysis and experiments are that:

1. The experiments can be done precisely with special electronic equipment.

Diagrams called Nyquist- and Bode-plots are then automatically generated and they provide much information about the behaviour of electrodes.
2. If one is familiar with complex numbers, the theory is relatively straightforward when the various equations in the theory are linear. This is often the case when the amplitude of the voltage signal is low (for instance, an oscillation with an an amplitude of 10 mV). With special software, accurate RC network fits are obtained from a measured complex impedance.

Electrochemical methods based on titration of charge. For capacitive processes, there are two methods not related to the RC circuit methods discussed above, which generate equilibrium data that help us to characterize an electrode. First is the galvanostatic intermittent titration technique (GITT). In this method, for a short duration a current is applied to an electrode, then the current is switched off to let the electrode 'relax', and after this hold-period the voltage is recorded. This process is repeated many times, with ongoing increments of charge.[iv] A series of data points is obtained in this way for the electrode voltage as function of accumulated charge. In another type of titration method the voltage is stepped up in increments, and the total current that flows after each step-change is recorded and integrated over time, to calculate a charge, to again construct a dataset of charge versus voltage.

This second method can be called 'voltage-step titration', recording the change in charge after each step in voltage. Ideally, without a Faradaic leakage current, the two titration techniques just discussed lead to the same equilibrium data of electrode charge against voltage. These data can then be recalculated to the capacitance C of the electrode as function of electrode charge and/or as function of voltage, see Fig. 5.1 for an example.

This finalizes our general discussion of capacitive and Faradaic electrodes. Next, we continue with a discussion of first capacitive electrodes, in Ch. 5, and then Faradaic electrodes in Ch. 6. There we also discuss redox potentials and Pourbaix diagrams. In Ch. 7, we continue with Faradaic processes, and from

§7.7 onward, capacitive capacitive effects are included in our analysis of dynamic (time-dependent) experiments.

5

Capacitive electrode processes

5.1 Introduction

Electrodes are a special type of electrical double layer (EDL). We can also phrase it that electrodes have an EDL structure. Physically, this means that within an interfacial region of a few nanometer thickness they contain multiple regions of opposite charge sign, and across this EDL an electrode potential develops, see Fig. 2.2. Overall the EDL is electroneutral. An important EDL property is the capacitance, C. It is the change in electrode charge σ_e with a change in electrode potential V_e,

$$C = d\sigma_e / dV_e \tag{5.1}$$

and generally, capacitance C depends on charge σ_e and electrode potential V_e. Note that charge, σ_e, and voltage, V_e, are uniquely related, i.e., there is one unique (equilibrium) σ_e-V_e curve for a certain electrode in a certain solution.

If we know how capacitance depends on electrode potential, or on electrode charge, we can integrate Eq. (5.1), which then leads to the two options

$$\Delta\sigma_e = \int_1^2 C\left(V_e\right) \mathrm{d}V_e \quad , \quad \Delta V_e = \int_1^2 C^{-1}\left(\sigma_e\right) \mathrm{d}\sigma_e \tag{5.2}$$

where (...) indicate that C is a known function of the electrode potential, V_e, or of electrode charge, σ_e. Eq. (5.2) shows how a higher capacitance implies that we can store more charge for a certain voltage change. Vice-versa, a high capacitance has the effect that a certain increase in charge only changes the electrode potential slightly. A very good electrochemical capacitor can store much charge, and when charge is released the voltage only slightly decreases, thus the capacitance must be high.

Interestingly, for all capacitive electrodes there is a maximum electrode potential beyond which Faradaic reactions start to play a role. This maximum potential depends on the electrolyte composition, and on which ions and other (dissolved) molecules are present. In an application to store energy, the electrode will not be charged to potentials beyond this maximum. So one of the aims in the development of ESDs is to increase this maximum voltage as much as possible, which leads to more charge storage. And the energy that can be stored increases more than linearly with the maximum voltage, as will be shown next.

The energy in the charging of an electrode can be calculated as follows. We describe here the minimum energy required to charge a capacitive electrode, and this is the energy stored. In reality we need to input more energy than we store, because of energy losses during the charging process, as we discussed on p. 27. At each moment in the charging process, the power input, P_{ch} –that which will be usefully stored– is current density I times electrode potential V_e (unit W/m^2), and the energy E (unit J/m^2) that will be stored in the electrode, is the integral of P_{ch} over time,[i]

$$E = \int_t P_{\mathrm{ch}} \mathrm{d}t = \int_t I\, V_e \mathrm{d}t\,. \tag{5.3}$$

We can combine Eq. (5.3) with Eq. (4.2) (for $I_F = 0$) and arrive at the energy required to go from one value of electrode charge to another (1 to 2),

$$E_{1\rightarrow 2} = \int_1^2 V_e \mathrm{d}\sigma_e \tag{5.4}$$

which can be integrated if we know how the electrode voltage depends on electrode charge. Many EDL models are available to this end, which we will discuss further

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[i] This energy E is the energy that is stored in the capacitive electrode, and is not the electrical energy E_e that is continuously produced or required in a fuel cell or concentration cell, such as depicted in Fig. 3.2 and Fig. 3.5.

on, but let us first assume a direct proportionality, as also assumed in Eq. (4.3), thus $\sigma_e = C\, V_e$. Inserting this in Eq. (5.4) leads to

$$E_{1\rightarrow 2} = \int_1^2 C^{-1}\sigma_e \mathrm{d}\sigma_e = \frac{1}{2\,C}\left(\sigma_{e,2}^2 - \sigma_{e,1}^2\right) \tag{5.5}$$

and if $\sigma_{e,1}$ is zero, and we implement Eq. (4.3) once again, we arrive at (we leave out numbers 1 and 2)

$$E = ½\, C\, V_e^2 \tag{5.6}$$

stating that the stored energy in a capacitive electrode increases quadratically with electrode potential, V_e. This result depends on capacitance C being constant along the charging curve, and that the electrode was initially uncharged. The analysis only described the ‘thermodynamic’ or ‘minimum’ energy to charge the capacitive electrode, which then results in the stored energy. It did not describe how much energy we had to invest to charge it to this degree, because the analysis did not include any of the losses because of resistances to transport of ions and electrons. During charging, these losses can be 5–50% of the final stored energy. And during discharge (when the stored energy is released, i.e., used), again 5-50% is lost in resistances. Therefore the round-trip energy efficiency can be anywhere in the range 25–90%.

Energy losses during charging of an electrochemical capacitor, EC. In the text above, an analysis was made of a single capacitive electrode. In a electrochemical cell there is also another electrode. That can be Faradaic, but let us assume it is also capacitive, thus we have an electrochemical capacitor (EC), a special type of ESD. Let us also assume they are the same. We again start at an uncharged cell, $\sigma_{e,1} = 0$, and we go to the final charge ‘2’, leaving out subscript 2 from this point onward. If we stay close to equilibrium, the cell voltage is $V_{\mathrm{cell}} = V_{\mathrm{A}} - V_{\mathrm{C}}$. Thus $V_{\mathrm{cell}} = 2|V_{\mathrm{A}}| = 2|V_{\mathrm{C}}|$ because we assumed the two electrodes behave in the same way: when one is charged with x C, the other is charged with -x C, and we started with both being uncharged, and their capacitances are the same. Thus the energy stored in this ESD is twice that of each capacitive electrode, and thus we end up with $E = {}^1\!/\!_4\, C\, V_{\text{cell}}^2$, where C was defined by Eq. (5.1). If we charge at a current I, and have a resistance R, in series to the two capacitors, a resistance for instance due to ionic current in the electrolyte, the energy loss over the charging period is $E_{\text{loss}} = \sigma_e\, I\, R$. This equation implies that the lower is I, the less energy loss we have in the charging process. For instance, when we reduce I by a factor of two, the energy loss goes down by two. Note as well that because the charging time doubles at the twice-lower current, the heat production *rate* due to energy losses, P_{loss}, goes down by a factor 4. This helps to keep temperature excursions in the EC low, which may be good to extend the life of the ESD. All of this shows that it is advantageous to charge slowly. During discharge, the same resistances play a role. But now the main resistance is the device that is powered, so currents are generally lower.

In the design of ESDs we aim for a high electrolyte conductivity (low resistance) by working at a high salt concentration of several M. And we design the device in such a way that the distance for current to travel across the electrolyte is small, because that reduces the resistance R. We need a minimum distance to avoid the risk of a electronic current crossing across the electrolyte layer. The current *density* must be low for a low energy loss, and thus the cell has a very high area across which the current flows. For these reasons the electrode will be thin and wide, i.e., it is constructed as a thin porous film. For ECs where EDL formation (charging) requires ions from the layer between the electrodes, then the layer cannot be too thin as it would limit the supply of these ions.

This analysis of energy storage relates to ECs, such as an electrode made of the intercalation material that we discuss below, as well as for the Li-ion battery, where Li-ions are stored inside the electrodes. The lead-acid battery is different. Here energy storage does not relate to the capacitance of the electrode, but this is a battery based on Faradaic processes where all solid Pb-phases, such as PbO_2, are in the vicinity of the electrode.

An example of a capacitive electrode which does not have a constant capacitance is described in Fig. 5.1. It is an intercalation material, a material that forms a cubic crystalline structure consisting of the atoms Fe, Ni, C, and N. Electronic charge resides in the crystal matrix, and cations can diffuse from outside the material into the pores, or holes, within this crystal. The capacitance for this material is described by an EDL theory called the extended Frumkin isotherm (EFI). The capacitance of this material, expressed in F/g, according to the EFI, is given by

$$C = \frac{F^2 c^*_{\max}}{RT} \left(\frac{1}{\vartheta} + \frac{1}{1-\vartheta} + g' \right)^{-1} \tag{5.7}$$

where $c^*_{\max}$ is the maximum cation concentration in the material in mol/g, and where g' is an energy of repulsion between ions in the material (a negative value implies attraction). Furthermore, ϑ is the intercalation degree, a number between 0 and 1 which describes to what percentage the material is filled with cations, with $\vartheta = 0$ referring to completely empty and $\vartheta = 1$ to completely full.[ii] Zero ϑ also corresponds to zero charge.[iii] The charge per gram of material is given by $\Sigma = c^*_{\max}\,\vartheta$, which is the stored charge relative to the material in the most ‘uncharged’ limit (when $\vartheta = 0$).[iv] If the interaction parameter g' is zero, the expression for capacitance simplifies to $C \propto \vartheta\,(1-\vartheta)$ and this expression shows how capacitance goes to zero when $\vartheta \rightarrow 0$ and is at a maximum when $\vartheta = ½$, as also shown in Fig. 5.1. This is also the case when $g' \neq 0$.

This material only adsorbs cations, because the crystal –which is the electron-conducting side of the electrode, with the ions inside the pores representing the

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[ii] A technical point is that even when $\vartheta = 0$, we believe there are still mobile cations left, but they cannot be removed (they can be exchanged for other cations, though), because it is impossible to charge the matrix of this material more positive. The concentration $c^*_{\max}$ refers to the maximum concentration of ions that can be removed, or added.

[iii] Implicit in much of the text above, is that the total charge of an electrode is zero. Thus when we refer to ‘the’ charge, it is that in one of the regions of the electrode. And electrochemical methods do not really measure the charge (in any of these regions) as such, but measure the *change in charge* relative to a prior situation.

[iv] Interestingly, for $g' < -4$, the EFI predicts that ions in the material phase-separate for a certain range of ϑ-values, and capacitance will be infinite in that range. We can use a Maxwell construction to find the electrode potential V_e when two phases exist simultaneously, a potential which is then independent of charge if we (dis-)charge slowly enough.

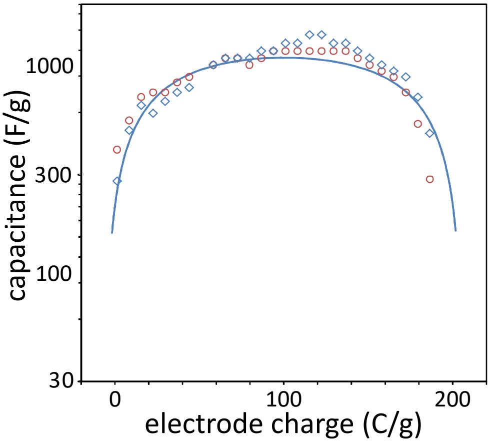

Fig. 5.1: The capacitance of a porous capacitive material (nickel hexacyanoferrate) measured in a three-electrode setup with 1 M Na_2SO_4 in water as obtained by the galvanostatic intermittent titration technique (GITT), as function of the charge of the electrode.

ionic side– is always negatively charged, even after we extracted all electrons to the maximum. Thus anions from solution do not want to enter this material at all.

An interesting question is the difference in absorption between different cations in such a material, dependent for instance on ion size and ion valency. This brings us to the point that EDL models (thus also models of the electrode) must also describe how many of each type of ion absorb for a certain electrode charge. In the material just discussed, anions do not absorb, but in general, both anions and cations absorb in an electrode. The exact amount is important, for instance when these electrodes are used to desalinate water, and must be described by the EDL model. We briefly discuss two such models.

5.2 Donnan EDL model for porous electrodes

The first model that includes both anions and cations absorbing in an electrode is the Donnan model. This is a model generally used for porous electrodes^{TC} such as carbon that have significant absorption both of cations and anions. To find the concentration of anions and cations in the electrode (i.e., in the water-filled pores inside the electrode$^{\mathrm{TC}}$ material), we use the Boltzmann equation, which we derive from chemical equilibrium of a species i that exchanges between two phases, in this case between bulk electrolyte, ∞, and inside the electrode, 'in'. The balance of chemical potential is[v, vi, vii]

$$\mu_{0,i} + \ln c_{\infty,i}/c_{\mathrm{ref}} + z_i\phi_\infty = \mu_{0,i} + \ln c_{\mathrm{in},i}/c_{\mathrm{ref}} + z_i\phi_{\mathrm{in}} \tag{5.8}$$

which we can rewrite to

$$c_{\mathrm{in},i} = c_{\infty,i} \cdot \exp\left(-z_i \Delta\phi_{\mathrm{D}}\right) \tag{5.9}$$

where ∞ refers to outside the electrode, in bulk electrolyte, and $\Delta\phi_{\mathrm{D}}$ is the (dimensionless) Donnan potential, $\Delta\phi_{\mathrm{D}} = \phi_{\mathrm{in}} - \phi_\infty$. In the simplest Donnan model, $\Delta\phi_{\mathrm{D}} = \Delta\phi_e = V_e/V_{\mathrm{T}}$, i.e., this theoretical Donnan potential is set equal to the electrode potential, see Fig. 2.2. The concentrations in the electrode, c_{in}, have unit mol/m^3, i.e., mM, because they are defined per unit volume of pores that are inside the electrode.

Based on the Boltzmann equation, Eq. (5.9), we can calculate the charge in the electrode, i.e., in the ion-filled pores in the electrode, as

$$\sigma_e = -\sigma_{\mathrm{ionic}} = -\left(c_+ - c_-\right) = 2c_\infty F \sinh \Delta\phi_{\mathrm{D}} \tag{5.10}$$

where we assumed that we only have monovalent cations and anions, i.e., a symmetric 1:1 salt, with a salt concentration in the electrolyte bulk of c_∞. We

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[v] All chemical potentials in J/mol are divided by *RT*, resulting in chemical potentials, μ_i, used here that are dimensionless.

[vi] Throughout this book, the term 'chemical potential' is used for the sum of all possible contributions to the potential of a species. We do not use a terminology where this term only relates to concentration effects, and that when charge is included, it is extended to *electro*-chemical potential. That would lead to a cascade of terminology when affinity and excess volume effects are also included, or gravity (for colloids), or the insertion pressure, or the effect of polarization force etc. Thus, we always use chemical potential for the summation over all these contributions, described by the symbol μ_i.

[vii] The EFI of Eq. (5.7) is also based on such a balance of chemical potential, extended with competition for empty sites (Langmuir), and including ion-ion attraction inside the material (Frumkin). For a full account, see B&D.

implemented that the ionic charge and electronic charge add up to zero: $\sigma_{\text{ionic}} + \sigma_e = 0$. Though the electronic charge is not really located inside the pores, but rather inside the solid (electron-conducting) structure around these pores, we nevertheless define the electronic charge density per unit pore volume. So when we know the electrode charge σ_e and bulk salt concentration c_∞, we can use Eq. (5.10) to calculate the Donnan potential, $\Delta\phi_{\text{D}}$, and then use Eq. (5.9) to calculate for each ion the concentration in the pores within the electrode. We can also add up these two concentrations, to obtain the total concentration of all ions in the pores, which will always be larger than the total ion concentration in bulk solution, which for a 1:1 salt is $2\,c_\infty$.

The capacitance in the Donnan model is given by

$$C_{\text{D}} = V_{\text{T}}^{-1}\,\frac{d\sigma_e}{d\Delta\phi_{\text{D}}} = \frac{2c_\infty F}{V_{\text{T}}}\cosh\Delta\phi_{\text{D}} = V_{\text{T}}^{-1}\sqrt{\sigma_e^2 + (2c_\infty F)^2} \tag{5.11}$$

and thus around zero charge, $\sigma_e \sim 0$, the capacitance is at a minimum, at $C_{\text{D}}|_{\text{min}} = 2c_\infty F^2/RT$. This minimum capacitance increases with salt concentration. Thus for a given Donnan potential, we can store more charge at the same voltage when c_∞ increases.

The energy of charging a Donnan layer (starting at $\sigma_e = 0$) follows from Eq. (5.4),

$$\begin{aligned} E = \int_0^{\sigma_e} V_{\text{T}}\Delta\phi_{\text{D}}\mathrm{d}\sigma_e &= V_{\text{T}}\Delta\phi_{\text{D}}\sigma_e - V_{\text{T}}\int_0^{\Delta\phi_{\text{D}}} \sigma_e \mathrm{d}\Delta\phi_{\text{D}} = \\ &= 2RTc_\infty \cdot (\Delta\phi_{\text{D}}\sinh\Delta\phi_{\text{D}} - \cosh\Delta\phi_{\text{D}} + 1) \end{aligned} \tag{5.12}$$

which at low $\Delta\phi_{\text{D}}$ simplifies to the classical Eq. (5.6) when we identify the capacitance C in Eq. (5.6) as $C_{\text{D}}|_{\text{min}}$ given above.

An important extension is to include next to the Donnan layer an additional capacitance C_{S}. This layer is called the Stern layer. It behaves as a ‘ simple capacitor’, located between the ionic charge on the one side, and electronic charge on the other side. Note that there are no ions or charge ‘inside’ this layer. The voltage across the Stern layer is the Stern potential, V_{S}, and is proportional to the electrode charge, $\sigma_e = C_{\text{S}}V_{\text{S}}$. Here σ_e is in C/m^3 and C_{S} in F/m^3 (the m^3 refer to pore volume in the electrode). Instead of a dimensional voltage, V, a non-dimensional Stern potential can be used, given by $\Delta\phi_\mathrm{S} = V_\mathrm{S}/V_\mathrm{T}$. The Donnan potential and Stern potential add up to the electrode potential

$$\Delta\phi_e = V_e/V_\mathrm{T} = \Delta\phi_\mathrm{D} + \Delta\phi_\mathrm{S} \tag{5.13}$$

and this is the modified Donnan (mD) model that can be used to describe the adsorption of ions and electronic charge in certain types of porous electrodes.

If we differentiate each term in Eq. (5.13) with respect to σ_e, we arrive at

$$\frac{dV_e}{d\sigma_e} = \frac{dV_\mathrm{D}}{d\sigma_e} + \frac{dV_\mathrm{S}}{d\sigma_e} \tag{5.14}$$

and when we define the overall, Donnan, and Stern, capacitances as

$$C_e = \frac{d\sigma_e}{dV_e} \quad , \quad C_\mathrm{D} = \frac{d\sigma_e}{dV_\mathrm{D}} \quad , \quad C_\mathrm{S} = \frac{d\sigma_e}{dV_\mathrm{S}} \tag{5.15}$$

we arrive at

$$\frac{1}{C_e} = \frac{1}{C_\mathrm{D}} + \frac{1}{C_\mathrm{S}} \tag{5.16}$$

i.e., the capacitance of the complete EDL (electrode) is obtained from the addition of the inverse of the two capacitances that are in series. The expressions for C_D and C_S can be inserted in here to obtain the total electrode capacitance, C_e, as function of electrode charge. In this case, we still have an increase of C_e when we move from zero charge to either negative or positive charge (the curve is again completely symmetric around $\sigma_e = 0$), but now C_e levels off at a high charge because the capacitance of the total electrode is now dominated by the constant Stern capacitance, i.e., in the limit of a high charge, we have $C_e \longrightarrow C_\mathrm{S}$.

The mD model can be further extended to include specific adsorption of ions or ion size effects. Also extensions are possible where ions are part of acid-base reactions which depend on local pH, and that local pH, via Eqs. (5.9) and (5.10), depends again on σ_e. Clearly, there are many ways to extend the mD model. As an example, an interesting effect is that of ion volume. When we include ion volume, then at high electrode charge, the capacitance –that was levelling off based on the Stern effect– now decreases again at an even higher charge, which is in line with classical data for the capacitance of mercury electrodes.

The minimum energy E required to reversibly charge an electrode (i.e., if there are no losses; resulting in the energy that is stored), that energy can also be calculated based on the mD model (and by any other EDL model). Interestingly, we can simply add up the energy to charge the Stern layer and the Donnan layer, because from Eq. (5.13) we can derive that $E_{1\rightarrow 2} = \int_1^2 V_e \mathrm{d}\sigma_e = V_\mathrm{T}\left(\int_1^2 \Delta\phi_\mathrm{D}\mathrm{d}\sigma_e + \int_1^2 \Delta\phi_\mathrm{S}\mathrm{d}\sigma_e\right)$. Thus, each individual contribution, $\Delta\phi_j$, can be integrated separately over the electrode charge, σ_e, to obtain the energy of the EDL.

5.3 Gouy-Chapman-Stern EDL model for planar electrodes

Often for electrodes that are more or less planar, a more complicated EDL model is used. In contrast to the mD model, this model only has a simple solution for a 1:1 salt (or other z:z symmetric salt). This is the Gouy-Chapman-Stern (GCS) model. Compared to the mD model, what is the same is that we again have the linear Stern capacitance next to a layer that contains ions, but now we do not simply use Eq. (5.9) for the region that contains ions (the pore volume in the Donnan approach), but based on the Poisson-Boltzmann theory, a different result is obtained. Effectively the Donnan pore volume is replaced by the 'diffuse layer', see last row in Fig. 2.2, and see the very similar Fig. 2.3 which is from the book by Mohilner (1966).

The Donnan and diffuse layer concepts are in many regards the same: they contain ions that are free to exchange between the electrode and bulk, and the concentration of counterions is increased and of coions decreased, relative to bulk, and this diffuse layer again stores ionic charge, σ_ionic. The only difference is that in the diffuse layer in the GCS model for planar electrodes, that ions have a continuously varying concentration from very high (or very low) near the metal (near the electrode$^\mathrm{TC}$), gradually changing to bulk values some nanometers away, while in the Donnan model we simply have one value of ion concentration (different for anions and cations) in the pores that are inside the electrode, which is different 'stepwise' from the value outside the electrode. Mathematically, the

GCS model is in many regards the same as the Donnan model, with the potentials $\Delta\phi_\mathrm{D}$ (we use the subscript D now for diffuse layer, which before was for Donnan layer) and $\Delta\phi_\mathrm{S}$ adding up to the electrode potential, $\Delta\phi_e$.

The description of the Stern layer is only slightly changed, to

$$\sigma_e = C_\mathrm{S} \Delta\phi_\mathrm{S} V_\mathrm{T} \tag{5.17}$$

with σ_e in C/m^2 and C_S in F/m^2. The different units for σ_e and C_S compared to the Donnan model, show that the GCS model is 'area-based' while the Donnan model is 'volume-based'. Now, in the GCS-model, for a 1:1 salt, the expression for σ_e becomes the classical Gouy-Chapman equation (sometimes called Grahame equation), given by

$$\sigma_e = \sqrt{8\varepsilon R T c_\infty} \cdot \sinh\left(\Delta\phi_\mathrm{D}/2\right) = 4\, F\, \lambda_\mathrm{D}\, c_\infty\, \sinh\left(\Delta\phi_\mathrm{D}/2\right) \tag{5.18}$$

where $\Delta\phi_\mathrm{D}$ is the diffuse layer potential, where $\varepsilon = \varepsilon_\mathrm{r} \cdot \varepsilon_0$, with for water, $\varepsilon_\mathrm{r} \sim 78$, while ε_0 is that of vacuum ($\varepsilon_0 = 8.854 \cdot 10^{-12}$ C/V/m). The Debye length, λ_D, is given by $\lambda_\mathrm{D} = \kappa^{-1}$ where κ is the inverse Debye length, which for a 1:1 salt is given by $\kappa = \sqrt{2F^2 c_\infty / \epsilon R T}$. Also in the GCS-model we have $\sigma_e + \sigma_\mathrm{ionic} = 0$. As Eq. (5.18) shows, we can store progressively more charge (at the same diffuse layer potential) with increasing c_∞, but now the dependence is to the power ½, not proportional to c_∞, as it was in the Donnan model. Note that in this GCS model, just as in the mD model, there are no ions adsorbed in the plane that separates the 'D' and 'S' layers –which is the Stern *plane*– and neither are ions adsorbed inside the Stern layer.

Also for the GCS model many extensions are possible, to account for multiple types of ions, ions with volume, protonation reactions, and many other effects.

For a 1:1 salt, the capacitance of the diffuse layer in the GCS model (unit F/m^2) is given by

$$C_\mathrm{D} = V_\mathrm{T}^{-1} \frac{d\sigma_e}{d\Delta\phi_\mathrm{D}} = F\sqrt{2\varepsilon c_\infty / RT} \cdot \cosh\left(\Delta\phi_\mathrm{D}/2\right) \,. \tag{5.19}$$

The Boltzmann isotherm. For future reference, it is useful to rewrite the Boltzmann equation, Eq. (5.9), to

$$V_{\mathrm{D}} = V_0 - \frac{RT}{z_i F} \ln \frac{c_{\mathrm{in},i}}{c_{\infty,i}} \tag{5.20}$$

where we included an extra voltage, V_0, that shows up if in Eq. (5.9) there would be an extra partition coefficient, Φ_i, because of an extra term $\mu_{\mathrm{exc},i}$ or $\mu_{\mathrm{aff},i}$ in Eq. (5.8).

This equation, which is the Boltzmann equation, is an example of an isotherm: it describes the relationship between the concentration of an ion in two phases at equilibrium, i.e., it describes the distribution of a species between two phases that allow for the ion to equilibrate between them. In our example these phases are on the one hand bulk solution, and on the other hand the electrode. Many types of isotherms exist for charged surfaces, extending Eq. (5.20) by including effects such as a limited availability of adsorption sites (Langmuir), and an energetic interaction between adsorbed species (Frumkin). The key point is that they describe the concentration of the same species, distributing between two phases, in this case between bulk and electrode.

Though these isotherms are always of relevance, for all electrode processes, they are predominantly associated with the study of capacitive electrode processes, because then we need to know the change of EDL properties (such as ion adsorption) as function of charge and electrode potential. In the next section on Faradaic electrodes, we will encounter a different equation, the Nernst equation, which looks deceptively similar to Eq. (5.9), but could not be more different. Instead of relating the distribution of the same ion, between a bulk phase and an electrode, as the isotherm of Eq. (5.9) does, the Nernst equation relates the concentrations of *different species*, that are all in the same or in different *bulk phases*.

The Boltzmann equation, and the resulting isotherm, follows from equating the chemical potential *of the same ion* that is in different phases, and one of these phases is the electrode. The same as for the Boltzmann equation, also the Nernst equation follows from a chemical potential balance, but now it is one where the chemical potential of a reactant in some bulk phase, together with that of the electrons in a metal, is set equal to that of the product species, again located in a bulk phase. These expressions are very different.

6

Faradaic electrode processes

6.1 Introduction

In all Faradaic electrode processes, such as the lead-acid battery, the Ag/AgCl reference electrode, fuel cells, or for that matter any electrode reaction that is in the well-known lists of standard half-cell potentials, in all these processes, none excepted, there is a reactant and a product of the reaction, and the reactant arrives from a bulk phase, and the product will return to a bulk phase.[i] None of the species stays in the electrode. Thus, as long as the bulk phase contains reactants, a Faradaic process can go on forever.

When discussing Faradaic processes, we must discuss the *direction* and the *rate*. The direction of a Faradaic electrode process is determined by the chemical potentials of the species just outside the electrode in the various bulk phases, and the direction also depends on the potential of the electron. Let us first discuss the electron. The more negative the electric potential in the metal (where the electron comes from) relative to the electrolyte bulk phase, the more an electron has a propensity to leave the electrode (this is because an electron is negative,

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[i] The bulk phases can be electrolyte, metal (as in plating), a solid salt (for instance, an AgCl-layer formed on the electrode), or a gas phase (for instance, H_2 or O_2). The electrolyte can be water, but also an ion-exchange membrane, or a solid state ion-conducting material.

and negative species prefer to go to where the electric potential is higher), and thus a *reduction reaction* becomes more favourable when the metal potential is further decreased (relative to the potential in solution). In a reduction, a species O picks up an electron and is reduced to a species R. Thus, the more negative V_e (the electrode potential, which is the potential in the metal minus that in the electrolyte), the more a reaction shifts in the direction of reduction.

The direction of the reaction is also determined by the chemical potentials of the molecules and ions involved in the reaction. If for instance one is a neutral molecule from a gas phase, such as O_2 or H_2, we can change the gas pressure. A higher pressure will make the chemical potential of these molecules go up, and then a species coming from the gas phase will more quickly react away.[ii]

Terminology of reacting ions on electrodes. The terminology used to describe the species that react on electrodes, is not so easy. It is also complicated because one may be more familiar with reactions in solution where *two* reactions, a reduction and an oxidation, take place simultaneously. In the latter case, one reactant is called the electron donor, the other electron acceptor, i.e., the terminology is used for two different reactants, with the two or more products not explicitly labelled. The same words are also used for an electrode process, but now based on a single reaction.

Thus for a reaction on a certain electrode, we use the same words, but now they refer to the ions on either side of a reaction equation. And we do that irrespective of the direction in which the reaction goes, and we can also use them when the reaction rate is zero.

The symbol ‘O’ is used for the oxidized species, the species in the oxidized state, the oxidant, the electron acceptor. Symbol ‘R’ is used for the reduced species, the species in the reduced state, the reductant, the electron donor.

Thus, in a reduction, a species O is reduced to become species R, by

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[ii] This would also be the case when a gaseous molecule, such as O_2, does not directly adsorb, but when it first dissolves in water, and then reacts as a dissolved species, because this concentration in the water will be proportional to the pressure of O_2-gas. Instead, when H_2 and O_2 gases develop at at an electrode, these molecules may form a gas phase directly.

picking up electrons, i.e., the species O is an electron acceptor. In the reaction it will pick up electrons. And when that reaction is reversed, or simply looked at in the reverse direction, we have an oxidation, where now a species R is oxidized to become species O, and electrons are released from the molecule, i.e., are donated to the external circuit.

The terminology ‘oxidant’ and ‘reductant’ refers to what a species reacting away, can do *to another species*. For instance, if oxygen is reduced, it allows *another species* to be oxidized (this can be in solution, at the same electrode, or at a very different electrode), and thus oxygen is an oxidant.

It is customary to write a reaction in the direction of reduction, $O^{z_O} + n\,e^- \rightarrow R^{z_R}$, irrespective of whether the reaction actually went in this direction, or in the opposite direction. Here n refers to the number of electrons involved. Thus, this right-directed arrow → does not imply that the reaction went in that direction.

We introduced here the charge (valency) of the ions involved, and in this reaction, we logically must have $z_\mathrm{O} = z_\mathrm{R} + n$. But this simple change of valency is not a general rule. It is not valid when for instance the proton, H^+, is also involved. For instance, we can have an oxidation where the oxidant O accepts (absorbs) two electrons as well as two protons, to become the reduced species R. But the valency of that molecule is unchanged, because also two protons are formed. Thus, we can write for this reaction: $\mathrm{O} + n\,e^{1-} + n\,\mathrm{H}^+ \rightarrow \mathrm{R}$, see B&F, p. 36.

6.2 The Nernst equation

For the solutes dissolved in the electrolyte, the ion entropy, i.e., a term related to concentration, is an important contribution to the chemical potential. For molecules such as OH^- and H^+, pH is a measure of their concentration. Assuming ideal thermodynamics and neglecting non-idealities related to ion activity coefficients, then the chemical potential of an ion is independent of the concentration of other species, and simply given by $\mu_i = \mu_{0,i} + \ln\left(c_i/c_\mathrm{ref}\right) + z_i\phi$, the same as was used in the derivation of the Boltzmann equation, Eq. (5.9), with the reference concentration for instance chosen as $c_\text{ref} = 1$ M.

Let us take a simple reaction, $O^{z_O} + n\,e^- \longrightarrow R^{z_R}$. An example is a reaction with Fe^{3+} as oxidant, and Fe^{2+} as reductant, with $z_O = 3$, $z_R = 2$, and $n = 1$.

Equality of chemical potential of reactants on the one hand, and products on the other is given by $\mu_O + n \cdot \mu_e = \mu_R$, where μ_e refers to the electron in the metal.[iii,iv,v] In the chemical potential, ions have a concentration-term and an electrostatic term, while electrons only have the latter; in addition all species have a standard '0' term as well. For the reaction $O + n\,e^- \longrightarrow R$ we then obtain the balance of chemical potentials

$$\mu_{0,O} + \ln c_O + z_O\phi + n \cdot \left(\mu_{0,e} + z_e\phi_\text{in metal}\right) = \mu_{0,R} + \ln c_R + z_R\phi \qquad (6.1)$$

where concentrations c and potentials ϕ without an index are those in solution (electrolyte) just outside the electrode. The electron valency is $z_e = -1$.

Now, the potential in the metal phase, minus that in solution, is the electrode potential, $\Delta\phi_e = V_e/V_T$. Making use of $z_O = z_R + n$, we arrive at

$$\ln c_O - n \cdot \left(\Delta\phi_e - \Delta\mu_0^*\right) = \ln c_R \qquad (6.2)$$

where $\Delta\mu_0^* = \left(\mu_{0,O} - \mu_{0,R}\right)/n + \mu_{0,e}$. We multiply all sides by $V_T = RT/F$ and end up with the *Nernst equation*

$$V_e = V_0 - \frac{RT}{n\,F} \ln \frac{c_R}{c_O} \qquad (6.3)$$

where $V_0 = V_T\,\Delta\mu_0^*$ is a reference potential for that particular reaction on that electrode material. It is different by a constant factor from the standard half-cell potentials, that are often written as E_0.[vi]

[iii] Further on we discuss where exactly concentrations are evaluated, either in the bulk of the solution, ∞, or right between electrode and the film layer, at position 's', see Fig. 2.1.

[iv] If more than one reductant or oxidant molecule is involved in the reaction, the respective term μ_O or μ_R is multiplied so many times.

[v] All terms with concentrations in the expression for μ_i, should officially be c_i/c_ref but we can leave out a term c_ref when it cancels out further on in a calculation. And, if we express concentration in the right unit, such as M, we are fine as well. Remember that the unit M is shorthand for mol/L, not mol/m^3, and the latter is the same as mM.

[vi] This factor depends on the type of metal of the electrode.

You may note the similarity between Eq. (6.3) and the Boltzmann isotherm, Eq. (5.20), but you will by now also appreciate that this is only a superficial resemblance, without there being an actual correspondence between the two expressions. The two equations have a complete different background, and a very different meaning of the symbols that are involved: in the Boltzmann isotherm, V_{D} is the potential in one region of the electrode relative to bulk electrolyte, while the concentrations involved are of the same ion, and there is a z_i that is the charge of the ion; instead, in the Nernst equation, V_e is the electrode potential (the difference in potential between metal and electrolyte, across the full electrode), irrespective of the choice of EDL model, while the concentrations are those of two different ions, and the prefactor n is the number of electrons involved in the electrode reaction. The term V_0 in the Boltzmann isotherm relates to an affinity difference of the ion to distribute between the two phases, while V_0 in the Nernst equation ultimately relates to the Gibbs energy of the reaction between different ions. Clearly, the two equations are very different.

Interestingly, the Boltzmann isotherm plays a significant role in capacitive processes, and the Nernst equation in Faradaic processes. So they are used in very different contexts.

Eq. (6.3) is a valid formulation for an electrode reaction in the simple case of the two ions coming from, and going back to, solution. But what about other situations? For instance, metal plating where the reduced species is part of the metal bulk. Then a term $\ln c_{\mathrm{R}}$ is not in the derivation and then does not show up in Eq. (6.3). How gas pressures are included is discussed further on.

Let us analyse the Nernst equation for the example of metal plating. In plating, if we increase the concentration of the cation in solution, c_{O}, that will make it easier for them to plate out, so at equilibrium, the counterforce, which is an electrical effect, should push back, to make the converting to a metal more disadvantageous for the cations. That means the electrode potential should go up (cations do not prefer locations of higher potential). When we check Eq. (6.3), it indeed predicts that at equilibrium a higher c_{O} leads to a higher V_e.

6.3 The Nernst equation in water

The previous example related to metal plating. Next we discuss the reduction of protons, H^+, to H_2-gas.[vii] For gases, the partial pressure in unit atm or bar (these are very close) is used in the Nernst equation for electrode equilibrium. Note also that *two* H^+-ions are required and two electrons for the formation of one H_2-gas molecule. Therefore, the Nernst equation is given by

$$V_{e,\mathrm{H^+/H_2}} = V_{0,\mathrm{H^+/H_2}} - \frac{RT}{2F} \ln \frac{p_{\mathrm{H_2}}}{[\mathrm{H^+}]^2} \tag{6.4}$$

where we introduce in an ad-hoc fashion how a component that participates 'twice' in such a reaction has a 'power two' in the ln-argument; this can be formally derived when we start again at Eq. (6.1) and multiply the contribution of that component by a factor two.

This equation for the reaction $2\mathrm{H}^+ + 2e^- \longrightarrow \mathrm{H}_2$ can be rewritten to show the dependence of electrode potential on pH, via $\mathrm{pH} = -{}^{10}\log[\mathrm{H}^+]$, resulting in

$$V_{e,\mathrm{H^+/H_2}} = V_{0,\mathrm{H^+/H_2}} - V_\mathrm{T} \cdot \left(\ln \sqrt{p_{\mathrm{H_2}}} + \ln 10 \cdot \mathrm{pH}\right) \tag{6.5}$$

where the term $V_\mathrm{T} \cdot \ln 10$ is $\sim$ 59 mV at room temperature. Thus, this equation predicts that when pH goes up by one point, at equilibrium the electrode potential goes down by 59 mV. Let us see if that makes sense: if pH goes up, the H^+ concentration decreases. This would make the reduction reaction (towards H_2) more difficult. To still be at equilibrium, we can help the reaction in the reduction direction by enticing the electrons to react with H^+ (more than before), and to that end the electrode potential must go down, which indeed is the prediction of Eq. (6.5). This is because decreasing the electrode potential, V_e, implies that the electrolyte will be at a higher potential relative to the metal (more than before), and thus electrons look more favourably to the prospect of leaving the metal and going into solution. Thus at equilibrium, (i.e., at zero current), a higher pH results in a lower V_e.

This is equilibrium, but what does this mean in practice, in a cell with two electrodes? If we produce H_2-gas, then this reaction takes place at the cathode

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[vii] See an earlier footnote explaining that we use the term 'proton' as shorthand for what officially is the hydronium ion, H_3O^+.

(the cations H^+ move to this electrode, thus it is the cathode). If we do this at a certain current, and we now increase pH by one point, and if nothing else changes, the electrode potential decreases, see Eq. (6.5), to make it more favourable for an electron to come out of the metal. That means the cell voltage goes up (because $V_{\text{cell}} = V_{\text{A}} - V_{\text{C}} - V_{\text{sol}}$). Because $V_{\text{cell}} \cdot I$ is the electrical energy we need to invest (with I running to the right as in Fig. 3.2), this increase in pH leads to the energy going up. Thus, making H_2-gas from high pH water is more energy-consuming than from low-pH water (considering only the cathode-side). That of course seems obvious all along: if you reduce the concentration of a reactant, and you want the reaction rate to stay the same, you have to pay for that somehow. Alternatively, if this cell runs at a certain V_{cell}, an increase in pH will reduce the rate of this process (i.e., will reduced the current),[viii] and the current may even switch sign. This is because at constant V_{cell} the increase in V_{C} must be compensated by a lower voltage difference across resistances in the cell, and to do that the current must go down, and may even reverse sign. Thus, an analysis based on the equilibrium electrode potential can help in evaluating operation of an electrochemical cell.

The interesting and useful thing about Eq. (6.5) formulated as function of pH, is that it helps to appreciate that the reaction of H^+ with an electron to H_2 is in the end the same as –and cannot be distinguished from– a reaction of water, H_2O, with the same electrons to again H_2, and now forming OH^-. Writing out this second reaction, converting a concentration of OH^- to pH, and translating a term $V_{0,H_2O/OH^-/H_2}$ to $V_{0,H^+/H_2}$ by implementing a factor that relates to the water dissociation constant, K_{w}, we ultimately end up with the same result. Thus, Eq. (6.5) is valid at any pH, irrespective of whether the reaction is written as H^+ reacting to H_2, or of water reacting to H_2 and OH^-. The resulting expression for the electrode potential, V_e, versus pH, comes out the same.

This really is very good news. The same equation for V_e, Eq. (6.5), is therefore valid at any pH, from very low to very high. There is no need to decide or assume which ion from the water it is that takes part in the reaction. And we certainly do not have to use this equation twice, for a reaction involving H^+, and

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[viii] The current goes down even though within the cathode we still assume equilibrium, i.e., the reaction kinetics in itself is not slowed down.

one involving OH^-. All of this relates to the very fast reaction between H^+ and OH^- that takes place throughout the aqueous phase, and the fact that therefore the chemical potentials of these two ions are tightly coupled. Thus, an electrode reaction involving water can be based on one arbitrarily chosen ion, and literature has converged on a choice for the H^+-ion. Of course at high pH, it will be the hydroxyl ion that is predominantly present in the system and will in fact be the ion involved in a reaction, but still the electrode reaction can be evaluated by focusing on the H^+-ion. The same situation applies to all reactions involving H^+/OH^-, including the reduction of O_2.

6.4 An electrochemical cell with the redox reaction acetate to bicarbonate

An example is the reaction of organic molecules such as glucose or acetate, towards CO_2 and the related dissolved ions, H_2CO_3, $HCO_3{}^-$, and $CO_3{}^{2-}$, in the absence of oxygen. In literature there is often the discussion how many H^+ are involved and which species react. Is it carbonic acid, or bicarbonate, or carbonate? And the same question for the acetate ions. Extending on §6.3, we will explain that these questions may not be that difficult to solve.

Let us consider the oxidation reaction, from acetate to carbonate. Acetate has two forms: the acetate ion, and the neutral acetic acid molecule. The latter is the protonated form of the former (both we call ions below). For the bicarbonate ions, we have three types of ions, from neutral to -2 charged. Based on elemental balances (stoichiometry) we know that the reaction of one ion from the acetate group, leads to the formation of two ions in the bicarbonate group (irrespective of which ion type reacts or is formed), while 8 electrons are released (go into the external circuit).

Out of all the ions in each group, we use the neutral form as the basis of analysis in the Nernst equation. Thus we focus on HAc and H_2CO_3. Then the reaction, which involves 8 electrons, must also involve 8 H^+-ions. This is because the other species we consider are neutral, and the overall reaction balance must have equal charge on each side. Again, in reality it may be that hydroxyl ions are the main species involved in transport and reaction, and not the protons, and the transport modelling will tell us if this is the case, but in writing out the reaction stoichiometry, and in the Nernst equation, we base the analysis on the H^+-ion.

Based on the knowledge that 8 electrons are involved for one acetate molecule reacting away, while two carbonate ions are formed, we know the production rate of acetate and of carbonate (each as a group) when we know the current that goes to this reaction. This last statement relates to the fact that in reality part of the electrical current that arrives in an electrode is also used for other reactions, for instance, water reacting to O_2-gas, electrons, and H^+. In that case the current efficiency is lower than 1, because not all of the electronic current is used for the intended reaction.

The Nernst equation for this reaction, based on one acetic acid molecule, HAc, reacting to two carbonic acid molecules and 8 electrons, is

$$V_e = V_0 - \frac{RT}{8F} \cdot \ln \frac{[\mathrm{HAc}]}{[\mathrm{H_2CO_3}]^2[\mathrm{H^+}]^8} \tag{6.6}$$

and thus

$$V_e = V_0 - V_\mathrm{T} \cdot \left(\frac{1}{8} \ln \frac{[\mathrm{HAc}]}{[\mathrm{H_2CO_3}]^2} + \ln 10 \cdot \mathrm{pH} \right) . \tag{6.7}$$

If we now operate a fuel cell, the aim is to have V_cell as negative as possible, and thus, based on Eq. (2.1), we know that V_A must then be as negative as possible. With the oxidation of acetate to bicarbonate on the anode, this means that V_e in Eq. (6.7) must be as low (negative) as possible, and thus a high pH is advantageous.

To summarize, in Eqs. (6.6) and (6.7) above, it works well to use the concentrations of the two neutral species HAc and H_2CO_3, even when ionic forms of these groups are more prevalent. Of course we can always implement an acid-base equilibrium, for instance between HAc on the one hand, and Ac^- and H^+ on the other (related by an acid-base equilibrium constant K), and then a term $+V_\mathrm{T}/8 \cdot \ln K$ is added to V_0, while also a term $1/8 \cdot \ln[\mathrm{H^+}]$ is added to $\ln 10 \cdot \mathrm{pH}$, which then results in a rather inelegant expression with the involvement of 7 protons. But the final result will numerically come out just the same.

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Thus, to describe equilibrium, the problem is more simple than perhaps anticipated. We do not have to evaluate equations such as Eq. (6.7) in a different way at different values of pH, and neither do we have to decide which species exactly is the one participating. As long as we can assume that in solution all acid-base reactions (reactions involving the H^+-ion) are sufficiently fast, the Nernst equation such as Eq. (6.7) suffices, set up with one species from the group of reactant ions, and one species from the group of products.

But how to describe the rate of such a (biochemical) reaction, with species of different protonation degrees, involving protons as well? A full description is based on electrocatalytic processes at a surface, or the biochemical networks inside cells, see De Lichtervelde *et al.* (2019). But in the absence of such a detailed model, a good starting point is to build a more simple kinetic model that is thermodynamically consistent, and can deal with ions with different protonation states (like the three types of bicarbonate just discussed).

A model that can do that, is as follows. For each half-reaction we calculate the equilibrium electrode potential, and 'between' the half-reactions we add a resistance. Across this resistance, when the reaction proceeds, and current flows from the one to the other half-reaction, a voltage difference develops, in analogy with Ohm's law. The equilibrium electrode potential can be based on an arbitrarily chosen species from each group of ions, and a choice for the neutral species is often the easiest. In §6.5, we will make such a calculation for simultaneous sulphate reduction and iron oxidation, i.e., corrosion.

6.5 Corrosion of iron by of sulphate reduction

In this section we develop the model just mentioned in the context of corrosion of iron. Corrosion is an electrochemical process where currents are very small, but the process leads to the deterioration and subsequent breakdown of metallic structures. Methods to reduce and eliminate corrosion are therefore important. The study of corrosion can lead to understanding how to reduce corrosion currents by reducing driving forces or creating resistances to the flow of current. In a corrosion process, there is a very large driving force for current to flow. This is because most metals (pure and alloys) are thermodynamically highly unstable in most natural environments, and for instance with oxygen as oxidant, there is a large driving force for metals to oxidize. Thus corrosion protection has the aim to keep the metals in the thermodynamically unstable state arrived at after smelting and metalworking of metal ores (such as metal oxides).

Thus, the study of corrosion as an electrochemical process is about reducing currents from very low to zero. It is therefore very different from processes discussed in prior chapters that are about enhancing rates, energy storage, etc. Corrosion is furthermore different for two more reasons. First, the anode and cathode are not 'designed' pieces of metal, made into a specific shape and connected to a power source or load with wires. Instead, they form spontaneously, somewhere on a metal surfce, and over time they change their shape and are covered with oxidic material. The two electrodes are also close: the oxidation of metal somewhere (anode) is accompanied for instance by oxygen reduction (cathode) in a region very nearby. Secondly, corrosion is a spontaneous process, similar to a fuel cell, but no energy is extracted. There is no load L placed in the electrical circuit to generate energy. The two or more electrodes are short-circuited on the metallic side. Because of the low currents, also on the ionic side the electrodes are often at the same electrolyte potential, and all resistances to reaction are 'in' the two electrodes, or in just one of them. The main rate limitation can also be the diffusion of oxygen to the bare metal. Thus, both on the metal-side and on the electrolyte-side, the electrodes are short-circuited. Thus,the two electrode potentials, V_j, are the same. Each of these V_j's includes a thermodynamic part and a kinetic part (relating to reactions or ion transport within the electrode). The thermodynamic part of the electrode potential (Nernst) and the kinetic part, they together lead to a certain electrode potential in an electrode, and because the current is the same in both electrodes, a specific value of current develops in the cell such that both electrodes end up with the same V_j. This V_j is now a function of the two equilibrium potentials and the two kinetic factors describing both electrodes. The resulting, single, value for V_j is the corrosion potential, and because it is due to the interplay of multiple electrodes, it is also called a 'mixed' potential.

Thus, in reality, resistances in a corrosion process are in the electrodes. However, in the simple model that we explain next, we assume the main resistance to current is in solution in between the electrodes. This is done because it makes the model easier to set up, while mathematically, it leads to the same result as when the resistance was assumed to be in one of the electrodes. In §6.6, we consider a theory for cathodic protection with not one, but three resistances, each associated with a different electrode.

We make a calculation for the corrosion of iron due to sulfur-reducing bacteria (in an environment without oxygen, i.e., anaerobic). The species being reduced is the sulphate ion (HSO_4^-, SO_4^{2-}) and it becomes a sulfide ion, HS^-, which can be protonated and then it evaporates as H_2S. The SO_4^{2-}-ions accept electrons in this reaction, and thus the reduction to HS^- takes place at the cathode. The electrons are donated by the oxidation of solid iron, Fe^0, which leads to the formation of Fe^{2+}-ions and Fe^{3+}-ions, and this happens at the anode. When Fe^{2+} oxidizes to Fe^{3+}, also an electron is donated, without involvement of Fe^0. We include in the calculation the formation of $Fe(OH)_3$ as a separate phase (solid or amorphous product). At a later stage one can also include formation of other minerals or ion pairs such as FeS, $FeCO_3$, as well as gaseous H_2S.

The sulphate ion can have various protonation degrees, and the reaction also involves protons. This may suggest a high complexity to the reaction problem, but that is actually not the case, as discussed in §6.5. We simply need to implement that irrespective of the protonation degrees of reactants and products, 8 electrons are accepted when a sulphate ion reacts to a sulfide ion.

Writing the reaction as that between bisulphate and bisulfide, we have at equilibrium the Nernst equation at the cathode

$$V_{\mathrm{C,eq}} = V_0|_{\mathrm{s}} - \frac{RT}{8F} \cdot \ln \frac{[\mathrm{HS}^-]}{[\mathrm{HSO_4}^-]\,[\mathrm{H}^+]^8} \tag{6.8}$$

where $V_0|_{\mathrm{s}}$ is the reference potential for this reaction which relates to E_0 according to $V_0|_i = E_0|_i + V^*_{\mathrm{ref,eq}}$. For the reaction described by Eq. (6.8), $E_0|_{\mathrm{s}} = +236$ mV. We do not need to know the reference value $V^*_{\mathrm{ref,eq}}$, which does not influence the final calculation. So we proceed as if $V_0|_{\mathrm{s}}$ is a known constant, and the same is the case for other $V_0|_i$'s.

On the anode we have the reaction of Fe to Fe^{2+} (reaction I) and to Fe^{3+} (reaction II), for which the equilibrium electrode potentials are given by

$$\begin{aligned} V_{\mathrm{A,eq}} &= V_0|_{\mathrm{I}} + 1/2 \cdot V_{\mathrm{T}} \cdot \ln[\mathrm{Fe}^{2+}] \\ V_{\mathrm{A,eq}} &= V_0|_{\mathrm{II}} + 1/3 \cdot V_{\mathrm{T}} \cdot \ln[\mathrm{Fe}^{3+}] \end{aligned} \tag{6.9}$$

where the two $V_0|_i$'s relate to the respective $E_0|_i$-values in the same way as described above (related by a constant difference $V^*_{\text{ref,eq}}$). The resulting equilibrium electrode potential, $V_{\text{A,eq}}$, is one value, because both reactions take place on the same electrode. The two E_0-values are $E_0|_{\text{I}} = -445$ mV and $E_0|_{\text{II}} = -40$ mV. Thus, at equilibrium, these two Nernst equations also determine the ratio in the concentration of Fe^{2+} over Fe^{3+} according to

$$E_0|_{\text{II}} - E_0|_{\text{I}} = \frac{V_{\text{T}}}{6} \ln \frac{[\text{Fe}^{2+}]^3}{[\text{Fe}^{3+}]^2} \tag{6.10}$$

which we can derive by subtracting one from the other the two equations of Eq. (6.9). Here in Eq. (6.10) we must use the two concentrations in the concentration scale of M. This equilibrium applies when there still is solid iron, Fe^0, available as reactant. It predicts that as long as Fe^0 is available (and Fe(OH)_3 or Fe_2O_3 are not yet formed), that the Fe^0 that dissolves is overwhelmingly in the form of Fe^{2+}. When all Fe^0 is gone, then only Eq. (6.9) applies, and another electrode is able to drive up E_{A}, for instance by oxygen reduction, and all Fe^{2+} will be oxidized to Fe^{3+}. But this only happens after all Fe^0 is gone.

We now set up a model that is not at equilibrium, and thus the current and the corrosion rate are not zero. Because large part of the calculation do consider (chemical) equilibrium, we call this a dynamic equilibrium model. In the electrochemical cell, similar to the geometry of Fig. 3.2, we therefore include a resistance to current at some point in the circuit. We can include it in one of the electrodes, as a reaction overpotential η (a concept we will discuss in Ch. 7), but it is easier to describe both electrodes as being at equilibrium, as already discussed above, and assume that the resistance is located in solution, and thus $V_{\text{sol}} = -R_{\text{sol}}\, I$. The exact origin or location of this resistance, whether in solution or in one of the electrodes, does not matter to the resulting model. We make use of Eq. (2.1) to relate the different voltages in the cell. The cell voltage in Eq. (2.1) is set to zero, i.e., $V_{\text{cell}} = 0$, because the two metal sides are short-circuited. As mentioned, each electrode is considered to be at equilibrium, thus we replace each electrode potential V_j by the equilibrium value, i.e., $V_j \rightarrow V_{j,\text{eq}}$, and thus we can use Eq. (6.8) and the two Eqs. (6.9). This set of equations, together with Eq. (2.1) and the equation above for V_{sol}, suffices to calculate the current I and the two electrode potentials, V_A and V_C, as function of all concentrations, in combination with ion mass balances that describe the composition of the solution over time.

We can also combine these equations into a set of two algebraic equations, one of which is

$$I \cdot R_\mathrm{sol} = V_\mathrm{C,eq} - V_\mathrm{A,eq} = \Delta E_0 + V_\mathrm{T} \left(\frac{1}{8} \ln \frac{[\mathrm{HSO_4}^-]}{[\mathrm{HS}^-]} - \frac{1}{2} \ln [\mathrm{Fe}^{2+}] - \ln 10 \cdot \mathrm{pH} \right) \tag{6.11}$$

where $\Delta E_0 = E_0|_\mathrm{s} - E_0|_\mathrm{I}$. Alternatively, we have the same equation but not as function of Fe^{2+}, but as function of Fe^{3+}. The second algebraic equation is the equilibrium between Fe^{2+} and Fe^{3+} given by Eq. (6.10).

What these equations predict is for instance that with a higher concentration of sulphate, the reaction will go quicker, and the same when we remove HS^- from solution, or when we remove the Fe^{2+}- or Fe^{3+}-ions from solution. In addition, we have an influence of pH: sulphate reduction will go faster at low pH. Note that in all of these cases the ‘goes faster’ is not because reaction rates are enhanced kinetically as such (all of them are modelled to be at equilibrium, i.e., infinitely fast), but only because the driving force goes up ($V_\mathrm{C,eq} - V_\mathrm{A,eq}$), which thereby increases the current because of the relation we proposed between current and voltage across solution. The increasing driving force is solely because the concentrations of reactants go up or those of products go down.

We solve these two equations together with overall electroneutrality (charge neutrality) of the solution, the water autodissociation equilibrium, the protonation equilibrium of HS^- to $\mathrm{H_2S}$, and the equilibrium for the complexation of Fe^{3+} with OH^- to soluble $\mathrm{Fe(OH)}^{2+}$ and $\mathrm{Fe(OH)_2}^+$, and to the solid phase $\mathrm{Fe(OH)_3}$. In an extension of this code, also formation of the solid FeS can be included, and evaporation of $\mathrm{H_2S}$. We can combine these equations with mass balances for a closed system (batch reactor) for all conserved groups (such as the S-atom, and the Fe-atom), and can study what happens when sulphate ions reduce to sulfide, while iron oxidizes. The conversion rate relates to the current I because for each ion from the group $\mathrm{HSO_4}^-/\mathrm{SO_4}^{2-}$ converted to sulfide ($\mathrm{HS}^-/\mathrm{H_2S}$), 8 electrons are accepted, which are donated by the reactions on the anode. There, the flow of electrons is equal to the summation of several formation rates times a multiplier, namely the formation rate of Fe^{2+} times two, and the formation rates of Fe^{3+},

$Fe(OH)^{2+}$, $Fe(OH)_2{}^+$, and $Fe(OH)_3$, all times three. The calculation will self-consistently predict the formation rate of each individual ion or complex. There is no need for a separate balance for protons; instead, the calculation predicts how pH changes during the process, and this pH is directly coupled to all protonation equilibria in the system, and thus the rate of corrosion.

Results of this calculation are presented in Fig. 6.1, where we start with a 10 mM solution of H_2SO_4 solution at pH 3.0 (thus $[Na^+]$=18.1 mM, pK_{SO4} 1.99) and availability of solid iron, Fe^0. This is all we need to define the starting condition. We include in the calculation not only Fe^{2+}- and Fe^{3+}-ions, but also the complexes of Fe^{3+}, which are $Fe(OH)^{2+}$ and $Fe(OH)_2{}^+$. These complexes have a much higher concentration than the Fe^{3+} ion itself, but they do not change the outcome of the calculation, because all these dissolved Fe^{3+}-based ions have a very low concentration compared to the Fe^{2+} ions. Much more significant is the formation of $Fe(OH)_3$ as a solid product, described by $K = [Fe^{3+}]/[H^+]^3$ with concentrations in M, for which $K \sim 9100$ M^{-2}. We make a calculation analysing the composition of the solution and the electrode potentials, at various levels of sulphate conversion, which relates to how much charge was transferred from anode to cathode. So the x-axes in Fig. 6.1 are similar to a time axis, but when current goes down over time, which it will as panel B shows, the same increment in charge transfer takes more and more time. The current is a function of the difference between E_C and E_A, similar to an Ohmic resistance for ion transport. In panel E there is a moment indicated by ⊗ where the two electrode potentials become the same, and current will go to zero, i.e., equilibrium is then reached. But before reaching that point, the time increments will grow to infinity, i.e., we never reach this point, which is not directly obvious in this representation.

We notice that with increasing charge transfer (increasing conversion of sulphate), pH first slowly and then more rapidly increases to values around pH 10 and higher. The rapid increase in pH corresponds to a steep decrease of the current and of the cathode potential. Thus corrosion is slower at high pH, which is because the sulphate to sulfide electrode potential, V_C, rapidly decreases, while the anode potential is not influenced. Without the possibility for the formation of $Fe(OH)_3$, pH increases to around pH 12, and at some point the two electrode potentials become the same (⊗ in panel E) and the process stops. However, the outcome is

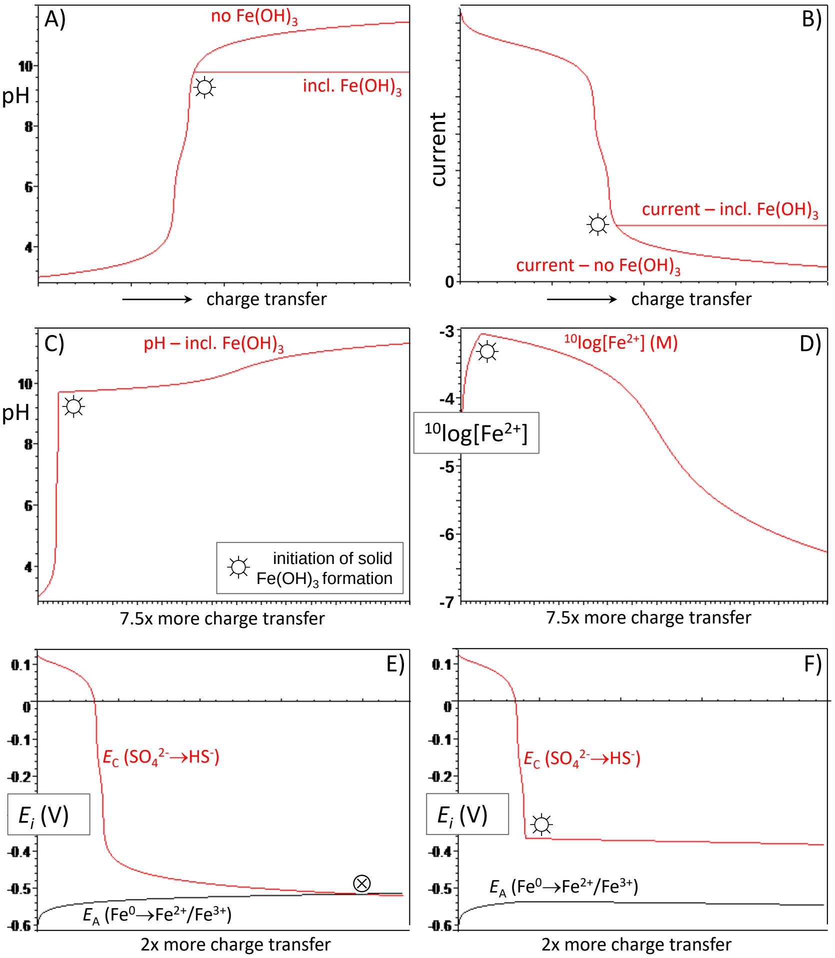

Fig. 6.1: Calculation results of the dynamic equilibrium model for the reduction of sulphate to sulfide, and simultaneous iron oxidation. In all panels the x-axis is the total charge transfer. Panels E and F describe 2× more charge transfer than A and B, and panels C and D 7.5× more. Panels A and B show results for pH and current with and without the possibility of solid $Fe(OH)_3$ formation. If this solid product forms, this takes place from the point indicated by ☼. After that, all variables still change, such as depicted for pH in panel C and for $[Fe^{2+}]$ in panel D. Panels E and F show the electrode potentials E_i of anode and cathode, in panel E without formation of solid $Fe(OH)_3$, and in panel F, with. In that case, sulphate reduction and iron oxidation continue until almost all sulphate is reduced.

very different if formation of $Fe(OH)_3$ is included: as panel A shows, after the moment that $Fe(OH)_3$ starts to form, indicated by ☼, pH levels off at pH ~ 10, and the decrease in current and in E_C (see panel F) is halted. However, this levelling off is only temporarily, and after some time pH again increases (panel C). But in this case, until all sulphate is gone, the electrode reactions continue because the two electrode potentials remain significantly apart, resulting in a driving force for current (panel F).

The explanation of each aspect of these calculations may not be very obvious in many cases. But the point is to bring across the message that the dynamic equilibrium model as was explained above, and which is based on only a few equations, is able to make all of these predictions, which can be compared with experimental observations. Of course, a more complete model for (bio-)corrosion also includes other species such as the carbonate system which buffers pH, and other types of iron complexes and solid and gaseous substances. Also details of the metabolism of the microorganisms that are involved must be included.

6.6 Cathodic protection of a metal against corrosion

As discussed in §6.5, a metal structure can corrode, converting metal into soluble cations at an anode, with simultaneously a cathodic reaction, for instance the reduction of sulphate to sulfide. In this section, we consider the reduction of oxygen as the cathode reaction. To protect a metal structure, such as for instance steel, an alloy with main component Fe, a well-known method is cathodic protection, where a sacrificial metal, such as Zn, is wired to the piece of metal to be protected. We now have a three-electrode electrochemical cell. We assume the three electrodes are short-circuited; thus, on the metal side, the potential is the same in all electrodes in this problem, and we set that value to zero. And all three electrodes have a different electrode potential V_j. So how to calculate the directions and magnitudes of the currents? At what condition is the anode protected? We present a simple calculation that provides a first approach to solve this problem.

Thus, on the solution side, the potential near each electrode is $-V_j$, and this is different for each electrode. These potentials, V_j, are a constant factor different from the electrode potential in the E-scale. Thus we can switch to the E-scale, and then the potential in solution near the electrode is $E_{\mathrm{sol},j} = -E_j$, see Fig. 6.2.

Differences in the three $E_{\mathrm{sol},j}$ lead to currents flowing between the three electrodes. These currents depend on the geometry of the electrolyte phase between the electrodes, how far apart they are, and what is the surface area of the electrodes. Thus we can make a 2D or 3D calculation based on Laplace's law, $\nabla^2\phi = 0$, where ϕ is the electrical potential in solution, that we solve in the space between all three (or more) electrodes, and then we calculate the currents from/towards each electrode. Such a calculation assumes a constant conductivity throughout the entire phase between the electrodes. In a more detailed calculation, other processes are included as well, such as a limitation in the supply of reactants, for instance in the diffusion of oxygen to the cathode, or barriers to the flow of ions near the anode.

In a simplified calculation, we assign a resistance to each electrode, which could either relate to a kinetic limitation in the electrode reaction, or to a transport process just outside the electrode. And across the bulk solution phase, we assume there are no changes in potential. In this simplified calculation, we must consider the three currents shown in Fig. 6.2B, each directed from an electrode into bulk solution. They add up to zero: $I_\mathrm{A} + I_\mathrm{C} + I_\mathrm{S} = 0$ (for panel A, $I_\mathrm{S} = 0$). Each of these currents is given by $E_{\mathrm{sol},j} - E_\infty = I_j \cdot R_j$, where E_∞ is the potential in bulk solution.

Let us assume each electrode is at equilibrium, and at standard conditions, thus we can use $E_\mathrm{C} = 1.23$ V (for oxygen reduction), $E_\mathrm{A} = -0.445$ V for Fe(s) to Fe^{2+}, and $E_\mathrm{S} = -0.77$ V for Zn-oxidation. We can now calculate how resistances must relate to one another, to make cathodic protection work. Thus we calculate the condition that a current of $I_\mathrm{A} < 0$ is predicted. In that case, at the anode, where a metal oxidizes, the current is reversed and cations may even reduce to the metallic form. Based on the equations just presented, we can derive that the criterion for this reversal is when

$$R_\mathrm{S} < R_\mathrm{C} \cdot \frac{E_\mathrm{A} - E_\mathrm{S}}{E_\mathrm{C} - E_\mathrm{A}} \tag{6.12}$$

and thus, to protect a metal structure from oxidation, we see from Eq. (6.12) that first of all, we need a sacrificial electrode with $E_\mathrm{S} < E_\mathrm{A}$. Furthermore, we notice that the resistance of the anode, R_A, is irrelevant, but the other two resistances,

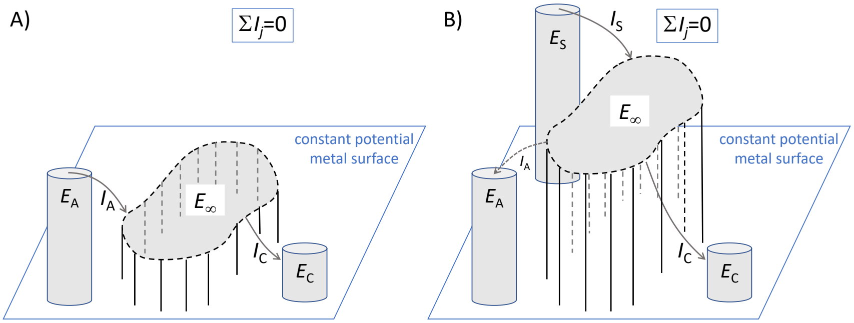

Fig. 6.2: On a metal surface, a particular spot can oxidize, i.e., corrode (anode A, electrode potential E_A) because of a reaction on a cathode, C, see panel A. But because of a sacrificial electrode S, that has a more negative electrode potential, E_S, see panel B, the oxidation of A can be halted. Comparing panels A and B, the current to the anode, I_A, is reversed, and corrosion is halted. The height of each bar refers to *minus* the potential E of that electrode.

R_C and R_S, they play an important role. The resistance of the sacrificial electrode cannot be too high, relative to the resistance in the cathode. For the stated values of E_j, the resistance R_S must be less than approximately one-fifth of R_C. Then, irrespective of the anode resistance, electrons will not be drawn from the anode, and thus it is protected against oxidation. The required low resistance of the sacrificial electrode is promoted by a large area in direct contact with water, while the resistance in the cathode for oxygen reduction must be high, thus this reaction is ideally limited to only one or a few weak spots on the metal (for instance, where a protection by paint is damaged). So a sacrificial electrode can function, even when it is quite far away from the location to be protected, as long as the resistance in the cathode(s) is high enough.

In summary, we provided a calculation that shows how cathodic protection of a metal (from oxidation) can be understood in a simple model that includes electrode potentials (of the three electrodes that play a role) and two electrode resistances. It is not enough when the sacrificial electrode has a lower electrode potential than the anode, but potential losses because of electrode reactions and ion transport must be part of the analysis.

It might now seem that in solution there is a potential, E_∞, that depends on the electrodes and their resistances. But the solution potential is a value determined by other factors, and it is actually the potential in the metal that depends on these factors. The metal potential relative to that in solution, is the corrosion potential, E_{corr}, and it is calculated by

$$E_{\text{corr}} = \frac{\sum_j E_j/R_j}{\sum_j 1\ /R_j}\,. \tag{6.13}$$

Of interest in Eq. (6.13) is that an electrode x of which the resistance increases, for instance by placing it further away from the other electrodes (but still in short-circuit contact with them via the metal phase), or by making it smaller in area, that this electrode x will contribute less to E_{corr}. So the potential across the resistance associated with x, which determines its current, is increasingly determined by the *other* electrodes, especially those that are close to one another. If one electrode has a much smaller resistance than all other electrodes, that one determines the corrosion potential. Corrosion potential is the same as the redox potential that will be discussed in §6.7.

Thus we illustrate in Fig. 6.2A the situation that the solution potential (relative to that in the metal) is in between that of the anode and cathode, similar to what will occur in any spontaneous electrochemical cell that is short-circuited. And thus both the oxidation on the anode and reduction on the cathode occur in the usual fashion, with I_{A} then a positive number (oxidation is defined as positive; positive charge is pushed into the solution phase) and I_{C} is a negative number (reduction currents are defined as negative). In panel B, a sacrificial electrode protects the anode (and cathode) because the oxidation now occurs in the sacrificial electrode S. For the cathode, we have a reduction current just as before, and for the anode the current now also has the direction of a reduction. As a consequence, Fe-ions near the electrode might even become metallic again.

In practice, instead of using a piece of metal that spontaneously acts as a third electrode, and which is sacrificed, it is also possible to use a power source and any kind of electrode structure where for instance oxygen is formed from water. This situation is similar to Fig. 6.2 but now E_{S} of the sacrificial electrode is replaced by that of oxygen evolution, plus the cell voltage generated by the power source.

6.7 The redox potential of a solution, and Pourbaix diagrams

In this last section, we return to §6.5, and the oxidation of Fe^0 to either Fe^{2+} or Fe^{3+}. It is interesting to recombine the two equations of Eq. (6.9) to

$$E_{A,eq} = E_0|_{III} - V_T \ln\left([Fe^{2+}]/[Fe^{3+}]\right) \tag{6.14}$$

where $E_0|_{III} = 3 \cdot E_0|_{II} - 2 \cdot E_0|_I = +770$ mV, which exactly corresponds to the E_0-value for the reduction of Fe^{3+} to Fe^{2+}. So that reaction is 'enclosed' in the two reaction equilibria of Eq. (6.9). When there is no Fe^0 left, then Eqs. (6.9) and (6.10) no longer apply, but Eq. (6.14), the Nernst equilibrium between Fe^{2+} and Fe^{3+}, still holds. So now a certain ratio between the concentrations of Fe^{2+} and Fe^{3+} in solution, will result in an anode potential, $E_{A,eq}$, and if this is the most important redox couple in the system, this will be the 'redox potential' of the solution, E_H.

The redox potential of a solution is set by the redox couple that has the most balanced ratio between oxidized and reduced forms. Instead, a redox couple where one of the involved ions (either the one in the reduced form, or in oxidized form) is present at a minute fraction of the other, does not set the redox potential.

In environmental systems, the redox potential can be set by many possible redox couples, and can involve for instance oxygen, manganese, carbonate, acetate, nitrate, sulphate, and sulfide. As just mentioned, one of these reactions sets the redox potential, which is the reaction that has the largest buffer capacity, i.e., the reactant and product of this reaction (the redox couple) are both present in reasonably large amounts. If instead a redox couple is present in almost fully oxidized or fully reduced form, then the ratio between oxidant and reductant in this couple very quickly changes when a few electrons are donated or accepted from another couple. So this reaction does not set E_H, it rather follows it. It is the couple with the largest redox buffer capacity that sets E_H.[ix] One may now

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[ix] A numerical calculation of a solution with several redox couples of different concentrations and E_0's will show this to be the case.

wonder, what is it that E_H represent. What it describes is a solution's tendency to donate electrons to other dissolved species, or to accept them. The higher is E_H, the stronger is the tendency of the various molecules in solution, to accept, i.e., to strip, electrons from (new) molecules. So it describes the oxidizing power, with a solution of a high E_H having a high oxidizing power. On the other end of the scale (very low E_H), the solution has a high tendency to donate electrons: a newly arriving molecule will likely be reduced, if that is chemically possible.

The E_H-sensor, which is an electrochemical cell with a Pt-electrode in direct contact with the solution, connected to a reference electrode, does not give a response to all redox couples (see an example below). But because there are other redox couples which 'follow' the E_H set by the most buffered couple, as explained above, the E_H-sensor still functions in measuring E_H. The redox couples that it gives a good response to, are for instance Fe^{2+}/Fe^{3+} and Mn(IV)/Mn(II). Oxygen reduction is not measured by an E_H-sensor, though the measured redox potential does give a good indication of the concentration of oxygen in the water, and this might relate to the reversible formation of $Pt(OH)_2$ on the electrode surface (Stumm and Morgan, p. 361). The redox potential E_H is often rewritten to a $\mathrm{p}\epsilon$, or pe, by dividing E_H by $\ln 10 \cdot V_\mathrm{T} \sim 59$ mV (no additional minus sign).

In environmental systems, some examples of redox couples are as follows. With sufficient dissolved oxygen, thus for regular aerobic respiration, where carbohydrates are converted to CO_2 and water, the redox potential is around +820 mV. When oxygen levels drop, and if available, then Fe^{3+} takes over as electron acceptor and then E_H is around +750 mV. At even more reducing conditions (when there is no Fe^{3+} left), Mn(IV) becomes the main electron acceptor (oxidant), and then Co(III), U(VI), NO_3^- (at +400 mV), then SO_4^{2-} (as in the example of §6.5) at E_H -220 mV, then the reduction of CO_2 to methane at -250 mV, the reduction of S^0 at -270 mV, and ultimately the reduction of CO_2 to acetate at -300 mV. Thus, the measurement of E_H provides information on what are the molecules in a sample that have the largest redox buffer capacity.

Related to the redox potential are plots of E_H, or pe, versus pH, called Pourbaix diagrams. They contain much useful information about what species can form dependent on E_H and pH. However, they might also be confusing because they do not clearly convey how a process with various reactions works, and how they can be described for instance in the way we did in §6.5.

In the familiar Pourbaix diagram for iron, Fe, we have at low pH a sequence with increasing E_H of solid Fe, Fe^{2+}, Fe^{3+}, and then a line for oxygen. What does all of this mean? The diagram shows what state of the iron is most prevalent, dependent on E_H and pH. For ambient O_2 concentrations (aerated conditions), the redox state is described by a line that starts at E_H = 1.23 V at pH 0, decaying with a slope of 59 mV/pH. This line sets the E_H of a solution saturated with oxygen gas at a pressure of 1 bar, i.e., for $p_{O_2} = 1$ bar.

At equilibrium, E_H is equal to the two electrode potentials; thus, we can use E_H for $E_\mathrm{A,eq}$ in Eq. (6.14), and obtain the result that for instance at pH 2, the concentration of Fe^{3+} is about 10^6 times larger than of Fe^{2+}. When the oxygen pressure goes down, then E_H goes down as well, and more and more of the Fe^{3+} is reduced to Fe^{2+}. At some point, when the oxygen partial pressure is at a very low value, almost all of the iron is in the Fe^{2+}-form. And then comes a point that solid Fe is formed. Or in reverse, starting at low E_H, if solid Fe is being oxidized, the ions that are formed are predominantly Fe^{2+}. As long as some solid iron is still present, the concentrations of Fe^{2+} and Fe^{3+} are related by Eq. (6.10), and this equation predicts that an overwhelming part of all dissolved iron is in the Fe^{2+}-form. With increasing E_H (for instance because oxygen is continuously added), at some point all solid iron is gone, and more and more of the Fe^{2+} converts to Fe^{3+}. Thus, with increasing E_H, the ratio of Fe^{2+} to Fe^{3+} goes from very large, to very small. The point where we switch over from predominantly Fe^{2+} to predominantly Fe^{3+} is given by Eq. (6.14) inserting here a ratio of Fe^{2+} over Fe^{3+} equal to unity, thus we switch when $E_\mathrm{H} = E_0|_\mathrm{III}$ = +770 mV.

A second element in Pourbaix diagrams is the formation of the various oxidation products, which are soluble ions, such as $Fe(OH)_2{}^+$, and insoluble solid products, such as $Fe(OH)_3$. These oxides can have associated water molecules, for instance written as $Fe(OH)_3$, or when they are less hydrated, it can be FeOOH or Fe_2O_3. When no electrons are involved, the related boundaries in Pourbaix diagrams are vertical. For instance, for the formation of $Fe(OH)_3$ from Fe^{3+} and OH^-, this vertical line is typically drawn at a pH~4.

Thus, Pourbaix diagrams by themselves may not be of direct help to find out which ions and solid phases are formed. Instead, we have to formulate all mass balances and equilibrium relationships, and solve them, for instance in a way similar to the calculation of §6.5. Equilibrium between different half-reactions is then solved by setting the electrode potentials equal to one another, such as for the two reactions in Eq. (6.9). We can have kinetic limitations when the reactions occur on different electrodes. In that case a cell calculation can be set up with resistances in or near the electrodes and/or in solution, resulting in the dynamic equilibrium model introduced in §6.5.

These kinetic limitations are also possible in solution, without an explicit electrode process. For instance, when a solid iron oxide is formed based on the Fe^{2+}-ion at low E_H, such as $Fe(OH)_2$, and if now E_H increases, then it takes a long time before $Fe(OH)_2$ transforms to the thermodynamically more stable solid oxide Fe_3O_4 (in which there is a mixture of Fe^{2+} and Fe^{3+}), and at even higher E_H to Fe_2O_3. As a first approach, the dynamic equilibrium model can again be used to describe these processes.

7

Electrode Kinetics

7.1 Introduction

In Ch. 6, we focused on the equilibrium electrode potential, $V_{e,\mathrm{eq}}$, using the Nernst equation. In the present chapter, we go beyond the Nernst equation to model the rate of an electrode reaction, i.e., we study Electrode Kinetics. We start with the Frumkin equation which includes EDL effects, which we then simplify to the Butler-Volmer equation. We also include the film layer in front of the electrode and describe dynamic operation including capacitive effects.

In this chapter it becomes important where in solution we evaluate ion concentrations. We distinguish between a concentration at the surface, with index s, i.e., right next to the electrode, and concentrations in bulk electrolyte, ∞, see Fig. 2.1. In between these two positions is a film layer. From now on, concentrations in the Nernst equation are those at the surface, s, not in bulk (unless there is no current, then they are the same). The concept of the film layer will be discussed in §7.5. The film layer influences concentrations at the surface and thus reaction rates, and when we have multiple competing electrode reactions, transport across the film layer influences the relative rate of each process, i.e., selectivity.

Electrocatalysis. In this chapter we combine expressions for the rate of electron transfer with the modelling of mass transport in front of the electrode. However, these two processes are just two elements in a much longer series of transport steps. More generally, ions must first diffuse through the water to the electrode, adsorb at the electrode, perhaps dissociate, or combine with other molecules, diffuse over the surface to reach a particular site, participate in an electron-transfer reaction there, and after that the product of the reaction diffuses away, first over the surface, and after desorption diffuse away from the electrode. These detailed processes are studied in the field called electrochemical catalysis, or electrocatalysis.

In this chapter we do not discuss the processes on the electrode surface in as much detail as in electrocatalysis. Instead, we describe transport of ions and other solutes through the film in front of the electrode, and combine with an electrode reaction described by the Butler-Volmer equation. In §7.8–7.10, we use the Frumkin equation which describes how the structure of the EDL influences the electrode process.

7.2 The Frumkin equation for the rate of an electrode reaction

To describe the rate of an electrode reaction, the Frumkin equation is one of the most general starting points. A key feature is that it highlights how the EDL structure influences the electrode reaction rate, which is an important effect. Nevertheless, we urge caution because in the Frumkin equation ions from solution or other bulk phases (after moving through a film layer), directly participate in an electrode reaction, neglecting other transport steps across the electrode surface that can also be rate-limiting, as discussed in the box above.

According to the Frumkin equation, the Faradaic reaction rate, in the direction of oxidation, is given by

$$J_F = k_{\mathrm{O}} c_{\mathrm{R}}^{*} e^{+\alpha_{\mathrm{O}} n \Delta\phi_{\mathrm{S}}} - k_{\mathrm{R}} c_{\mathrm{O}}^{*} e^{-\alpha_{\mathrm{R}} n \Delta\phi_{\mathrm{S}}} \tag{7.1}$$

where concentrations c^*_O and c^*_R are at the *reaction plane* * inside the electrode, see Fig. 2.1. The Faradaic rate, J_F, is in mol/m^2/s and can be multiplied by nF to a current density I_F in A/m^2. The number of electrons that take part in the reaction of one molecule R to O (or vice-versa), is n. We assume here that one molecule R reacts to one molecule O. The coefficients α_j are numbers between 0 and 1, and sum up to unity: $\alpha_\mathrm{O} + \alpha_\mathrm{R} = 1$, and generally $\alpha_\mathrm{O} = \alpha_\mathrm{R} = ½$ is used.

The Frumkin reaction rate includes the influence of a jump for the electron across an inner layer, from the metal to a location in the EDL, where it meets with a reactant ion for a reduction, or the electron goes in the other direction for an oxidation. Within the modified Donnan model and the GCS-model, this inner layer across which the electron jumps is the Stern layer, with an associated potential change $\Delta\phi_\mathrm{S}$, see Fig. 2.2. Thus, $\Delta\phi_\mathrm{S}$ is the step an electron makes when it leaves an ion at the reaction plane and enters the metal phase. The ions at this reaction plane, which in these EDL models is the Stern *plane* –for which we use the notation * in Eq. (7.1)– have a concentration given by the Boltzmann equation

$$c^*_i = c_{\mathrm{s},i} e^{-z_i \Delta\phi_\mathrm{D}} \tag{7.2}$$

where index * refers to the Stern plane, and index s to a position just outside the EDL structure, i.e., just outside the electrode, see Fig. 2.1.

For $J_F = 0$, or when both kinetic constants are very high, combination of Eqs. (7.1) and (7.2) results in the Nernst equation, Eq. (6.3), making use of $\Delta\phi_e = \Delta\phi_\mathrm{D} + \Delta\phi_\mathrm{S}$, see Eq. (5.13). Ion concentrations in the Nernst equation are those just outside the electrode, at position s. The two k-values lead to the standard state potential of that reaction, V_0. This also means that the two k-values are not independent, but if one is known or estimated, the other follows automatically if V_0 is already known.

Eq. (7.1) describes how the EDL structure plays a role in the reaction rate. Thus it includes the role of other ions than the ones reacting, because they can modify $\Delta\phi_\mathrm{D}$, the Donnan or diffuse layer potential. These effects are well known to influence the reaction rate, especially with mixtures of ions of different valencies.

The other interesting aspect of Eq. (7.1) is that it highlights the relevance of the electronic charge density, σ_e. This is first of all because $\Delta\phi_\mathrm{S}$ in Eq. (7.1) is proportional to σ_e, according to Eq. (5.17). Secondly, σ_e determines $\Delta\phi_\mathrm{D}$, for instance according to the Gouy-Chapman equation, Eq. (5.18). In this way it is possible to write Eq. (7.1) completely in terms of charge σ_e and ion concentrations just outside the EDL. Thus, the full problem can be formulated as function of charge σ_e, instead of the electrode potential, V_e. But a certain EDL model must then be assumed, suh as the GCS model.

7.3 The Butler-Volmer equation

A significant simplification is made when it is assumed that $\Delta\phi_\mathrm{S} \gg \Delta\phi_\mathrm{D}$, and then the concentrations in Eq. (7.1) become those just outside the electrode ($* \longrightarrow$ s), which results in the Butler-Volmer (BV) equation

$$J_F = k_\mathrm{O} c_\mathrm{s,R} e^{+\alpha_\mathrm{O} n \Delta\phi_e} - k_\mathrm{R} c_\mathrm{s,O} e^{-\alpha_\mathrm{R} n \Delta\phi_e} \tag{7.3}$$

with $\Delta\phi_e$ the electrode potential, $\Delta\phi_e = V_e/V_\mathrm{T}$, the same as V_e in Ch. 6, but from now on, V_e will also be used for an electrode reaction that is not at equilibrium.

Eq. (7.3) is a general representation of the BV equation and it can be extended in various ways, for instance to include species with a fixed potential (such as metal atoms in a metal bulk phase) by removing the related concentration from Eq. (7.3). Or that one of the ions in the reaction cannot leave the electrode, resulting in a modification of Eq. (7.3) by including an occupancy-related term ϑ that increases as the reaction proceeds.[i]

However, traditionally Eq. (7.3) is not used in the form above but it is further modified. The first step is to again derive the Nernst equation for equilibrium, which based on Eq. (7.3) becomes

$$\Delta\phi_{e,\mathrm{eq}} = \phi_0 - \frac{1}{n} \cdot \ln \frac{c_\mathrm{s,R}}{c_\mathrm{s,O}} \tag{7.4}$$

where we introduce ϕ_0 which is $\phi_0 = n^{-1} \ln\left(k_\mathrm{R}/k_\mathrm{O}\right)$. Note that this $\Delta\phi_{e,\mathrm{eq}}$ is the electrode potential at equilibrium *with the concentration of ions next to the electrode*, at position s, see Fig. 2.1.

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[i] The electrode process is then no longer Faradaic, but capacitive.

We combine Eqs. (7.3) and (7.4), introduce the (dimensionless) reaction overpotential, $\eta = \Delta\phi_e - \Delta\phi_{e,\mathrm{eq}}$, and then derive

$$J_F = J_{\mathrm{exch}} \cdot \left(e^{+\alpha_{\mathrm{O}} \cdot n \cdot \eta} - e^{-\alpha_{\mathrm{R}} \cdot n \cdot \eta}\right) \tag{7.5}$$

where J_{exch} is the exchange current density, given by $J_{\mathrm{exch}} = k_{\mathrm{exch}}\, c_{\mathrm{s,R}}^{\alpha_{\mathrm{R}}} c_{\mathrm{s,O}}^{\alpha_{\mathrm{O}}}$, with $k_{\mathrm{exch}} = k_{\mathrm{O}}^{\alpha_{\mathrm{R}}} k_{\mathrm{R}}^{\alpha_{\mathrm{O}}}$. If we assume $\alpha_{\mathrm{O}} = \alpha_{\mathrm{R}} = ½$, then Eq. (7.5) can be written as

$$J_F = 2 \cdot J_{\mathrm{exch}} \cdot \sinh\left(½ \cdot n \cdot \eta\right) . \tag{7.6}$$

Because the reaction is not infinitely fast, the BV-equation predicts an electrode potential that is higher or lower than the equilibrium potential by a value η. For an oxidation (electrons go from ions in solution into the metal), η is positive, and η is negative for a reduction.[ii]

At a low reaction overpotential, i.e., when we are near equilibrium, the BV equation simplifies to

$$J_F = J_{\mathrm{exch}} \cdot n \cdot \eta\, . \tag{7.7}$$

If now J_{exch} is taken as a constant, Eq. (7.7) results in a linear relationship between overpotential and current, with the inverse of J_{exch} representing a resistance. That makes Eq. (7.7) similar to the linear resistance model of §6.5, that was implemented on the left of Eq. (6.11). But a difference is that now the linear resistance depends on concentrations of O and R via the expression for J_{exch}.

A useful formulation of the BV-equation is to rewrite Eq. (7.3) to (B&F, p. 102)

$$J_F = J_{\mathrm{exch}}^{\infty} \left\{ \frac{c_{\mathrm{s,R}}}{c_{\infty,\mathrm{R}}}\, e^{+\alpha_{\mathrm{O}}\, n\, \eta^{\infty}} - \frac{c_{\mathrm{s,O}}}{c_{\infty,\mathrm{O}}}\, e^{-\alpha_{\mathrm{R}}\, n\, \eta^{\infty}} \right\} \tag{7.8}$$

where $\eta^{\infty} = \Delta\phi_e - \Delta\phi_{e,\mathrm{eq}}^{\infty}$, in which $\Delta\phi_{e,\mathrm{eq}}^{\infty} = \phi_0 - n^{-1} \ln\left(c_{\infty,\mathrm{R}}/c_{\infty,\mathrm{O}}\right)$, thus $\Delta\phi_{e,\mathrm{eq}}^{\infty}$ is similar to Eq. (7.4), but now based on bulk concentrations, $c_{\infty,i}$. In Eq. (7.8), we introduce the exchange current density *based on bulk concentrations*, $J_{\mathrm{exch}}^{\infty} = \left(k_{\mathrm{O}} c_{\infty,\mathrm{R}}\right)^{\alpha_{\mathrm{R}}} \cdot \left(k_{\mathrm{R}} c_{\infty,\mathrm{O}}\right)^{\alpha_{\mathrm{O}}}$. Eq. (7.8) is useful when there is a fixed bulk concentration, because then $J_{\mathrm{exch}}^{\infty}$ and $\Delta\phi_{e,\mathrm{eq}}^{\infty}$ are constants.

[ii] This is different in some engineering textbooks, for instance, on fuel cell design. There η's are used as quantities that are always positive. This is certainly intuitively appealing, but can also be problematic when the model is used outside its intended range of use.

All dimensionless potentials ϕ can be multiplied by V_T to a potential V, and if we then assume $\alpha_\mathrm{O}=\alpha_\mathrm{R}=½$ and set $n=1$, and neglect a difference between $c_{\mathrm{s},i}$ and $c_{\infty,i}$ (i.e., neglect the film layer), Eq. (7.8) simplifies to

$$J_F = 2J_\mathrm{exch}^\infty \sinh\left(\tfrac{1}{2}\eta^\infty\right) = 2J_\mathrm{exch}^\infty \sinh\left(\tfrac{1}{2}\left(V_e - V_{e,\mathrm{eq}}^\infty\right)/V_\mathrm{T}\right) \tag{7.9}$$

which we will use in §7.7.

7.4 How does electrode potential V_e relate to voltage E?

In §3.1 and §6.5 it was already discussed that the electrode potential, V_e, relates to a measurable property, E. This relation between V_e and E is illustrated in Fig. 7.1. This term, E, is often called the electrode potential, relating to the type of reference electrode. However, the electrode potential is V_e. Instead, E is a measurable voltage (difference), not very different from the concept of a cell voltage, V_cell; it is a voltage difference between the metal lead of a working electrode (WE), and the metal lead of a reference electrode (RE), through which only a tiny current flows. Thus we will call E a voltage, or a voltage difference.

Fig. 7.1 explains the layout of a typical electrochemical experiment. The working and counter electrodes (WE and CE) are similar to the anode and cathode in earlier figures, such as Fig. 3.2, while the external device (which before was a load L or power source PS) is replaced by a device called potentiostat. In all other respects, it is the same as before. The terms WE and CE reflect that the WE is the electrode we aim to study in detail, while the CE is just there to 'provide the current.'

In this scheme a third electrode is added, which is a reference electrode, abbreviated as RE. It is placed near the WE. Hardly any current goes through the RE. The voltage between WE and RE, V_u, must be small, and to achieve that the RE is placed close to the WE. This is important because the current between WE and CE leads to voltage changes across solution. The use of background salt can help to reduce V_u, but is not always possible, because the experiment then has less correspondence to the process that we aim to study.

Following a trajectory from WE to RE, first through the electronic circuit, and

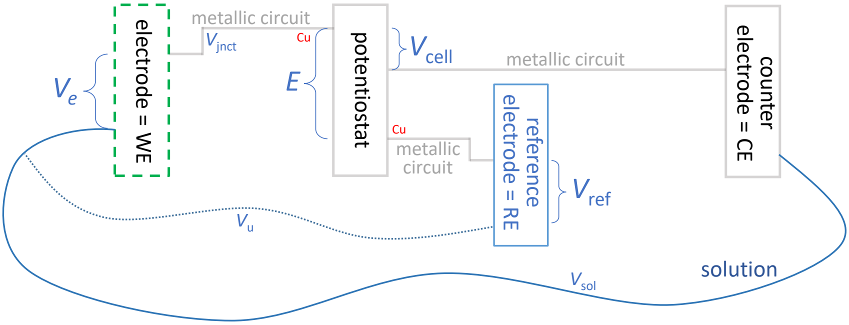

Fig. 7.1: The measured voltage E is directly related to the electrode potential V_e by a constant factor. To change E, the potentiostat adjusts the current in the WE-CE circuit, which modifies V_e, and this changes E. It has no direct control over E, but processes inside the WE determine E.

then back through solution, we can add up all voltages, and obtain

$$V_e = E + V^*_{\text{ref,eq}} + V_{\text{u}} \quad , \quad V^*_{\text{ref,eq}} = V_{\text{ref}} \pm \Sigma_j V_{\text{jnct},j} \tag{7.10}$$

where V_{ref} is the electrode potential of the reference electrode. The term V_{jnct} is a metal-metal junction potential, or work function, which is a constant voltage difference across the various metal-metal connections in the circuit, see Fig. 7.1, and values of these work functions are tabulated. Such a junction can be located between WE and potentiostat, and between potentiostat and RE. For instance, it develops when a connecting wire is Cu and the metal in the RE is made of Pt or Ag.

The conclusion of Eq. (7.10) is as follows: as long as V_{u} can be neglected, or is always the same value, then the voltage E, equals V_e, only with a constant offset. Thus we can measure changes in E, and know precisely by how much the electrode potential V_e was changed. We do not know the exact value of V_e, but we do know by how much we are changing it.

It is sometimes assumed that the potentiostat has control over E, i.e., can change it, and in this way change the potential on the metal side of the WE. With conditions in solution assumed to stay the same, the voltage across the WE is therefore changed and thus the reaction rate changed as well.

However, the potentiostat does not have direct control over E. Instead, a potentiostat can only push more or less current into the cell circuit of the CE and WE. Then, processes in or near the WE will be more or less out of equilibrium, and thus V_e will change. And now, because of the change in V_e, E will change as well. This is because all other voltage steps in the loop from WE to RE and back, see Fig. 7.1, are constant, not influenced by a change in current, and thus according to Eq. (7.10), a certain change in V_e will result in the same change in E. And this change in E is measured.

In practice, the potentiostat has a control system that rapidly adjusts the current to reach a certain setpoint for E. Thus it might seem as if we are changing E directly, but we only did that in the most indirect way, by a process which involves the entire circuit, with a current running from the CE through the electrolyte, to the WE, to changes in V_e of the WE, and then finally E was changed.

With now the voltage E explained and its relation to V_e, in §7.5 we present equations for the relationship between current and E in steady state. This is called the polarization curve, or *i*-*V* curve, of an electrode. (In §3.1 a polarization curve for an entire electrochemical cell was discussed.) We analyse these cases using the BV-equation, in combination with a film layer in front of the electrode. After this steady-state analysis, we discuss the dynamics of electrode response.

7.5 Steady state current as function of voltage E

In the present section we describe the relation between the electrode current (in a WE) and the voltage E. As discussed, in reality, a potentiostat does not really apply a certain E, but it adjusts the current between WE and CE such that the measured E quickly reaches a certain setpoint. But in steady state, all of this does not matter, because we only care about the relationship between current and E.

In the model, the Butler-Volmer equation is combined with equations for transport of reactant ions from bulk, through the film layer, to the electrode, and vice-versa for the ions produced in the electrode. The film layer has various names, such as stagnant (diffusion) layer, (diffusion) boundary layer, concentration polarization layer (CP layer), and Nernst layer. We use the term film layer.

In B&D, four models for the film layer are described, where the first model includes diffusion and migration in the direction x to the surface across a layer of a certain thickness; the second model includes dispersion due to eddies, mixing, or turbulence, in the same x direction; the third combines the first model with flow, or 'refreshment,' along the surface, i.e., a flow in a direction y, with the refreshment rate independent of x; while in the fourth model the refreshment rate increases with x.

Interestingly, when molecules only diffuse, without the electromigration contribution due to the electrical field, all these models lead to the steady state flux of a species to be proportional to the concentration difference between bulk and surface

$$J_i = k_\mathrm{L} \left(c_{\infty,i} - c_{\mathrm{s},i}\right) \tag{7.11}$$

where concentration $c_{\mathrm{s},i}$ is the surface concentration that can be used in the Nernst equation for the electrode reaction. At steady state, Eq. (7.11) can always be used for neutral species, while for ions it can be used when we have much background salt (addition of extra salt ions that do not react at the electrode). Then the electric field is masked and ions do not flow by electromigration, but only because of a concentration gradient. In that case, their charge does not influence their rate of transport. [iii]

Thus, we can analyse the steady state by combination of the film model for reactant R and product O (without electromigration, as for a large excess of background salt), Eq. (7.11), in combination with the BV-equation, for instance Eq. (7.5). Thus we have three coupled equations, for J_F, $c_{\mathrm{s,O}}$, and $c_{\mathrm{s,R}}$, in combination with $J_F = J_\mathrm{R} = -J_\mathrm{O}$. Flux J_F is defined positive for a reaction in the oxidation direction, and thus it has the same sign as J_R, the flux toward the electrode of the species in the reduced state. The product of the electrode

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[iii] There are situations that Eq. (7.11) applies even when electrical fields do play a role in ion transport. This is the case for an electrolyte with only two types of ions, i.e., a binary salt (valencies and diffusion coefficients, z_i and D_i, of the two ions can be different from one another). But at the film-electrode boundary, J_i and k_L relate in a specific way to the concentration gradient there, see B&D. Thus, it is possible to set up a model with two charged species, and many neutral species, with transport through the film layer for each of the species described by Eq. (7.11).

reaction, O, has a flux with opposite sign. The fluxes J are in mol/m^2/s, and can be multiplied by nF to obtain a current density, I, in A/m^2.

For steady state, this current I can be expressed as function of E by combining Eqs. (7.4), (7.5), and (7.10), resulting in

$$J_F = J_{\text{exch}} \cdot \left\{ \exp\left(\alpha_{\text{O}} \left(\frac{nE'}{V_{\text{T}}} + \ln \frac{c_{\text{s,R}}}{c_{\text{s,O}}} \right) \right) - \exp\left(-\alpha_{\text{R}} \left(\frac{nE'}{V_{\text{T}}} + \ln \frac{c_{\text{s,R}}}{c_{\text{s,O}}} \right) \right) \right\} \tag{7.12}$$

where we assume $V_{\text{u}} = 0$ (note that $V_0 = E_0 + V^*_{\text{ref,eq}}$), and where $E' = E - E_0$, i.e., E' is the measured E minus the standard state potential of the redox reaction.

Eq. (7.12) is the most general result, and we combine it with Eq. (7.11) for all species that participate in the reaction, and that set of equations can be solved. These equations predicts a limiting current at high E' of $J_{\text{lim,a}} = k_{\text{L}} c_{\infty,\text{R}}$ when the concentration of the reactant R decreases to zero at the electrode. At very negative E' the limiting current is $J_{\text{lim,c}} = -k_{\text{L}} c_{\infty,\text{O}}$.[iv]

Results of such a calculation are shown in Fig. 7.2 for the reduction of Ce^{4+} to Ce^{3+} ($n = 1$), for three cases with the same concentration of Ce^{4+}, but different concentrations of Ce^{3+} (increasing in direction of arrow). Data are from K.J. Vetter, *Z. Physik. Chemie* **196**, 360–377 (1950). Just as Vetter, we find that the best fit is obtained for $\alpha_{\text{R}} = 0.25$. We furthermore use $k_{\text{L}} = 32$ μm/s, $k_{\text{exch}} = 3$ μm/s, and $E_0 = 1.45$ V. With these parameter settings, we can fit all three datasets over the entire range adequately. Interestingly, this good fit of several datasets by the same theory with the same parameter settings, is more the exception than the rule. For instance, Vetter also reports data for an electrode process with Mn-ions, and while a single dataset can always be fitted by the theory above, this is not possible for a series of related I–V-curves with different concentrations of reactants and products. Also the oxidation of Ce^{3+} to Ce^{4+} does not allow a good fit by the above theory, because of formation of oxygen bubbles. This situation shows that much information is obtained from a series of related polarization curves, where only bulk concentrations of reactants and products are changed.

If we only consider operation in one direction, for instance oxidation, and

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[iv] Indices ‘a’ and ’c’ relate to anodic and cathodic, see B&F, p. 30. B&F use J_F in the reduction direction and thus their limiting currents have the ±-signs opposite to here, see their p. 109.

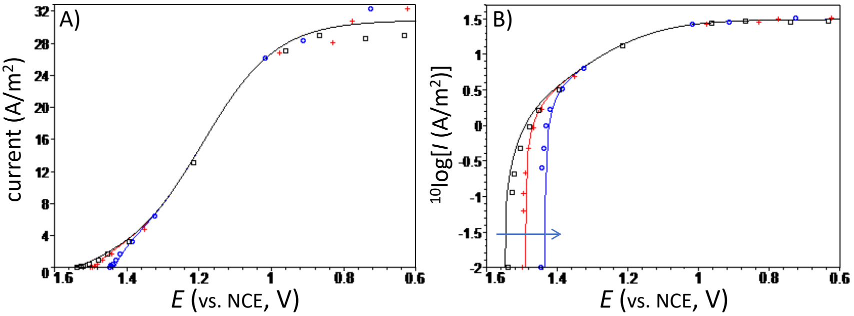

Fig. 7.2: Polarization curve for the reduction of Ce^{4+} to Ce^{3+} in 1 M H_2SO_4 for $[Ce^{4+}] =$ 10 mM and $[Ce^{3+}] = 0.1$, 1, or 10 mM (direction of arrow). Data from Vetter (1950) and theory based on Eqs. (7.11) and (7.12).

assume all resistance is in the electrode reaction (i.e., the redox reaction is slow compared to mass transfer), then E' is high, while mass transfer to the electrode can be neglected (concentrations at the surface are equal to those in bulk). Then in Eq. (7.12) we only have to consider the first exp-term, set concentrations $c_{s,j}$ to a constant value, and then we arrive at

$$E' = a + (\alpha_O n)^{-1} \cdot V_T \cdot \ln(10) \cdot {}^{10}\log(J_F) \tag{7.13}$$

which is called the Tafel equation, which predicts that in a plot of ^{10}log(current) versus electrode potential, such as Fig. 7.2B, (part of) the data are on a straight line with slope $V_T \ln 10/n\alpha_O$. In this context, Fig. 7.2B is then called a Tafel plot. Because of the many assumptions required in its derivation, the Tafel equation has a limited range of applicability. Indeed, we notice in Fig. 7.2B that there is no such region where the data are on a straight line.

We return to Eq. (7.12) and assume $\alpha_O = \alpha_R = ½$. Then we can derive

$$J_F = \left(1 + 2\,\frac{k_\text{exch}}{k_\text{L}} \cdot \cosh\left\{\frac{1}{2}\frac{E'}{V_T}\right\}\right)^{-1} \cdot 2 \cdot J^{\infty}_\text{exch} \cdot \sinh\left\{\frac{1}{2}\left(\frac{E'}{V_T} + \ln\frac{c_{\infty,R}}{c_{\infty,O}}\right)\right\} \tag{7.14}$$

which does not include concentrations at the surface, but only in bulk.

The above expressions formulate current J_F as function of a voltage E'. To translate J_F to a current I, J_F must be multiplied by n and by F to arrive at a current in A/m^2. Let us reiterate that the above derivation assumes V_u to be zero. If we do not want to make that assumption, we return to the equations in §7.3, and we can then implement a relationship where for instance V_u is proportional to current.

The equations for the polarization curve can be simplified when we return to Eq. (7.8) and based on the film model implement that $c_{\text{s,R}}/c_{\infty,\text{R}} = 1 - J_F/J_{\text{lim,a}}$ and $c_{\text{s,O}}/c_{\infty,\text{O}} = 1 - J_F/J_{\text{lim,c}}$, resulting in an implicit relationship between J_F and η^∞ given by

$$\frac{J_F}{J_{\text{exch}}^\infty} = \left(1 - \frac{J_F}{J_{\text{lim,a}}}\right) e^{+\alpha_\text{O}\eta^\infty} - \left(1 - \frac{J_F}{J_{\text{lim,c}}}\right) e^{-\alpha_\text{R}\eta^\infty} \tag{7.15}$$

which is Eq. (3.5.32) in B&F (p. 109). We can multiply η^∞ by V_T to arrive at a ΔE, which is the step change in voltage E, relative to the situation of zero current, i.e., $\Delta E = V_\text{T}\eta^\infty$. If we implement $\alpha_\text{O} = \alpha_\text{R} = ½$, and make the conversion $\Delta E = E' + \frac{1}{n} \cdot \ln\left(c_{\infty,\text{R}}/c_{\infty,\text{O}}\right)$, Eq. (7.15) can be rewritten to Eq. (7.14).

7.6 Electrode response to a change in E – I

In the present section we discuss how in time the electrode responds after a step-change in E, i.e., we we describe the dynamic behaviour, until we reach steady state. For this calculation, equations for the electrode reaction rate are still valid, but the film model with a linear dependence of flux on the overall concentration difference, that is no longer correct. Instead, ion transport must now be modelled dynamically (i.e., as function of time; transiently). And how this is done depends on the choice of the film layer model. (In §7.5 four types of film layer models were summarized, that describe in different ways dispersion or convection along the surface.) Just as in the steady state, with enough background salt we can neglect the electromigration effect, and the basic equation is the mass balance for transport of neutral species which is Fick's second law extended with dispersion or convection. In the present section we use the classical boundary film model which only includes diffusion.[v]

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[v] Also in the dynamic case, with a maximum of two charged ions (and any number of neutral solutes), thus also in the absence of background salt, the full diffusion-plus-migration transport problem can be solved by Fick's second law, as if there is only diffusion, see §7.9 and B&D.

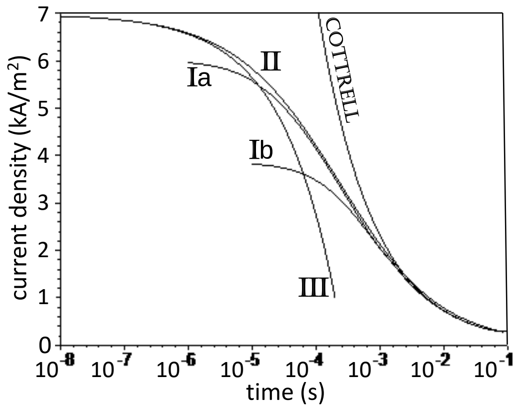

Fig. 7.3: After a voltage step-change ΔE, the current directed to an electrode in front of which is a film layer, starts at a high value, decreases, and levels off to the steady state current. Curves Ia and Ib are based on a full discretization of the film layer into a large number of gridpoints (Ia, $n = 100$) and a smaller number (Ib, $n = 20$), while curves II and III are analytical results by Vetter. The Cottrell equation is shown as well.

Using this model we can analyse the change from the initial current (directly after the step change) to the final current, which are both positive finite values, All of this is quite different from the Cottrell equation often used in literature, which predicts that the current starts at infinity and goes to zero. The Cottrell equation considers the limit where $J^{\infty}_{\mathrm{exch}} \rightarrow \infty$, i.e., the electrode reaction is infinitely fast and follows the Nernst equation. Therefore, the initial current is infinite, and because there are no other resistances or capacitances, ion concentrations instantaneously reach the steady state values.[vi]

The Cottrell equation is based on an analysis where the electrode is always at kinetic equilibrium, i.e., the Nernst equation applies at any moment in time. The sudden change in E now leads to a sudden change in the *equilibrium* electrode potential, i.e., $V_{e,\mathrm{eq}}$, and thus instantaneously we must have a step change in

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[vi] Though a classical approach in literature, these assumptions are unrealistic. The Cottrell approach is also puzzling for the reason that, if the electrode reaction is so fast, then why study it in the first place.

the ion concentrations just outside the electrode (at position s) to new values, and afterwards these values remain unchanged. However, these are unrealistic assumptions. Furthermore, diffusion of ions to the electrode is modelled assuming there is a stagnant layer of infinite thickness, and thus the fluxes of ions will ultimately decrease to zero. The resulting Cottrell equation for a reaction in the direction of oxidation is (Vetter, Eq. (2.207); B&F, Eq. (5.4.160))

$$I/F = J_F = \sqrt{D/(\pi t)} \cdot c_{\infty,\mathrm{R}} \cdot \left(1+\theta^{-1}\right)^{-1} \tag{7.16}$$

where we assume equal D for the oxidant and reductant, and a one-electron reaction. The factor $\theta = c_{\mathrm{s,O}}/c_{\mathrm{s,R}}$ is the ratio of ion concentrations at the surface after the step change ΔE (after that step change, these concentrations are unvarying in time in the Cottrell approach). This factor is given by $\theta = c_{\infty,\mathrm{O}}/c_{\infty,\mathrm{R}} \cdot \exp\left(\Delta E/V_{\mathrm{T}}\right)$ where $\Delta E = V_{e,\mathrm{eq}} - V_{e,\mathrm{eq}}^{\infty}$.[vii] Eq. (7.16) can be used irrespective of the bulk concentrations of the O and R species, but does assume that prior to the step change of ΔE, there is equilibrium of the system (absence of concentration gradients).

We make two improvements to the Cottrell-based analysis. We replace the Nernst equation by the BV-equation, i.e., the electrode reaction of itself now has a finite rate, and we model diffusion across a film layer of a certain realistic thickness, not assuming there is diffusion into stagnant semi-infinite layer.

In this new approach we start at a very high current, but this current is not infinite. Ion concentrations right next to the electrode start at the value before the step-change and then start to change (the *change* is at first infinitely fast, then slower), but they do not immediately go to the final values as in the Cottrell approach. The final steady state current is finite, which is also different from the Cottrell analysis where current decreases to zero.

Full numerical calculation results are presented in Fig. 7.3 based on Eq. (7.6) for the BV equation (thus assuming $\alpha_{\mathrm{O}} = \alpha_{\mathrm{R}} = ½$), in combination with Fick's

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[vii] Let us note again that the direct relation between ΔE and concentrations at the electrode surface not only assumes the Nernst equation (infinitely fast reaction kinetics) but also the absence of a voltage difference outside the electrode, for instance in the film layer. In the absence of background salt, however, there are these extra voltage changes, and then the direct linear relationship between E and V_e is lost.

second law, $\partial c_i/\partial t = D_i \cdot \partial^2 c_i/\partial x^2$, solved for reductant and oxidant across a film of thickness $\delta = 20\ \mu$m. The current J_F relates to the gradient in concentration at the surface according to $J_F = \pm D_i \cdot dc_i/dx|^{\mathrm{s}}$. The ±-sign depends on the species and the coordinate direction. With the coordinate x pointing from the electrode into solution, then for the R-species, and with J_F defined in the oxidation direction, the + sign is used. Bulk concentrations of O and R are 30 mM and we apply a step change in voltage of $\Delta E = 0.4$ V (before the step change the current is zero). Diffusion coefficients of both ions are $D_i = 2 \cdot 10^{-9}$ m^2/s, and k_{exch}=1.0 μm/s. Results are presented in Fig. 7.3 as function of the number of gridpoints used to discretize the transport film, either $n = 20$ or $n = 100$. The two numerical calculations overlap after 1 ms, but before that moment, the calculation at $n = 100$ is closer to a semi-analytical approach that is valid for early times. That approach we discuss next.

For diffusion into an unstirred semi-infinite space (not a fixed film layer thickness), Vetter gives the full solution of this problem in his Eq. (2.429). This equation is valid for unequal ion diffusion coefficients, and unequal bulk concentrations of the O and R species. We evaluate that equation, which is line II in Fig. 7.3. It only fails at longer times because it predicts the current to decrease to zero. Vetter also provides an analytical solution for early times as his Eq. (2.431). His formula is valid for all values of $c_{\infty,\mathrm{O}}$ and $c_{\infty,\mathrm{R}}$, and for unequal diffusion coefficients of the O and R species. Written for the case that $c_{\infty,\mathrm{O}} = c_{\infty,\mathrm{R}}$ and equal diffusion coefficients of the O and R species, this equation becomes

$$\frac{J_F}{J_{F,0}} = 1 - 4 \cdot k_{\mathrm{exch}} \cdot \cosh\left(\frac{1}{2}\frac{\Delta E}{V_{\mathrm{T}}}\right) \cdot \sqrt{\frac{t}{\pi D}} \tag{7.17}$$

which is an analytical expression for the current versus time after a step change ΔE. This solution is shown as line III in Fig. 7.3 and correctly predicts the initial behaviour after the step change in E, but after some time falls off too quickly. We can compare Eq. (7.17) with the Cottrell-equation, also provided in Fig. 7.3, and it may be clear that the initial behaviour is better predicted by Eq. (7.17), while the Cottrell equation is better at later times. Interestingly, compared to the Cottrell equation, the dependence on time and diffusion coefficient is exactly reversed in Eq. (7.17), where the change in current (from the initial value) positively depends on the square-root of time, and negatively depends on D, whereas the Cottrell equation has these dependencies exactly reversed.

7.7 Electrode response to a change in *E* – II

The system response as discussed in §7.6 will be different in reality. The control system of the potentiostat responds to a change in the setpoint for E, by adjusting the current directed to the counter electrode. These adjustment processes are not instantaneous, but take time (Vetter, p. 366). Therefore, and because of the effect of charge storage, a temporary overshoot of current is possible, and it can even happen that the current starts to oscillate around the final, steady state, value, as we show below. Modern potentiostats avoid these problems because of advanced control software and high quality components. Nevertheless, the calculation illustrates the intricacies of control strategies for electrochemical systems.

We analyse here the simplest possible control strategy, where the system adjusts the current, I, directly based on the offset in E. The offset is the difference between the setpoint, E_{set}, and the measured voltage E, and thus we assume the potentiostat to work according to

$$\frac{dI}{dt} = \alpha \left(E_{\mathrm{set}} - E \right) \tag{7.18}$$

where we introduce the response factor, α.

In the calculation, besides the electrode reaction, which mathematically behaves as a non-linear resistance, we include a small capacity placed in parallel. Thus the total circuit current I is a summation of a Faradaic and a capacitive current, $I = I_F + I_c$, see Eq. (4.1). The capacity can be in wires or other electronic elements but can also be the electrode itself. This last option we analyse in §7.8. For the Faradaic current we use Eq. (7.9). The capacitive current I_c charges a linear capacity according to $C \cdot dV_e/dt = I_c$ (editor's note on p. 363, p. 366, footnote p. 373, Vetter).

To solve this model, we must relate the electrode potential V_e to the measured voltage E. Before the change in setpoint, the system is in equilibrium, thus $V_e = V_{e,\mathrm{eq}}^{\infty}$. These two V_e's relate to E according to $V_e = E + V_{\mathrm{ref,eq}}^{*}$ ($V_{\mathrm{u}} = 0$), and with ΔE the change in E relative to the equilibrium situation, it is the

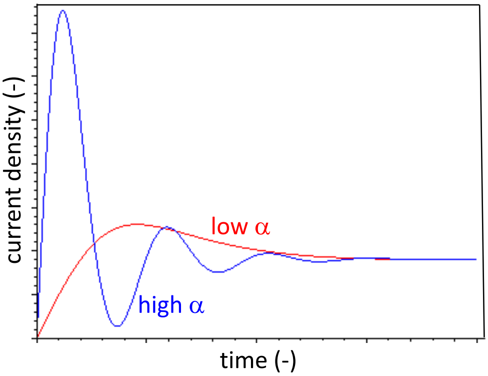

Fig. 7.4: After a change in the setpoint for the voltage E, the potentiostat will adjust the current to reduce the offset in E, With a capacity in the circuit, then dependent on the control strategy and the response factor α, the generated current can shoot over the target and start to oscillate.

case that $\Delta E = V_e - V_{e,\mathrm{eq}}$, and thus the Faradaic reaction rate becomes $J_F = 2\,J^{\infty}_{\mathrm{exch}}\sinh\left(½\,\Delta E/V_{\mathrm{T}}\right)$. The potential E before the change in setpoint is some value E^*, and thus after the change in setpoint, $E = E^* + \Delta E$. We define $\Delta E_{\mathrm{set}} = E_{\mathrm{set}} - E^*$. Thus the right side of Eq. (7.18) now becomes $\alpha\,(\Delta E_{\mathrm{set}} - \Delta E)$.

We can now make a calculation where we start at $\Delta E = 0$ and we choose a value for ΔE_{set}. Results of this calculation are shown in Fig. 7.4 for a low and high value of the response factor α. Fig. 7.4 shows that over the time period considered, the current can shoot beyond the target, and even start to oscillate (B&F, p. 572). Mass transfer limitations because of the film layer were not yet considered, as if we are before 1 μs in the calculation of Fig. 7.3. The effect of the film layer will be discussed in §7.9.

7.8 Comparing the Frumkin and Butler-Volmer models

In §7.7, the BV-equation was used and an extra capacity was placed in parallel to the electrode. Within the Frumkin model for electrode kinetics, Eq. (7.1), however, these elements are an integral part of the EDL model that is used, for instance the GCS model. Jointly, these elements predict the electrode charge and how it changes in time, all of which is not predicted by the BV-equation.

In a model based on the Frumkin equation, the charge of the electrode, σ_e, relates to current according to

$$\frac{d\sigma_e}{dt} = I - I_F \tag{7.19}$$

and this charge determines the Stern potential, $\Delta\phi_\mathrm{S}$, according to Eq. (5.17), and the diffuse layer potential, $\Delta\phi_\mathrm{D}$, according to Eq. (5.18). Now that we use the Frumkin equation, Eq. (7.1), instead of the BV-equation, a capacity effect is automatically included.

Results of a calculation for the same control loop strategy as in §7.7 are presented in Fig. 7.5 and we make the same assumptions, especially that concentrations just outside the electrode do not change in time. We assume the reactant R is neutral, and the product O of the oxidation reaction is a cation. We set $\phi_0 = \ln(k_\mathrm{R}/k_\mathrm{O})$ to zero. We use the GCS model with $c_\infty = 30$ mM and $C_\mathrm{S} = 1.0$ F/m^2. We start at an uncharged electrode and at time zero step up the setpoint for E to $\Delta E_\mathrm{set} = 0.1$ V. When we reach the steady state, the Donnan potential is $\sim$75 mV, and the Stern potential $\sim$25 mV. The capacitance of the EDL is much smaller than in §7.7, and thus the system responds much more quickly, about 10× faster. The response factor α is now set to a much larger value than before, but the overshoot is still much less. At time zero, when current starts to flow, all of the current is used to charge the EDL, with the Faradaic reaction still zero. Thus, for this short period, the electrode process is purely capacitive. This situation changes after that short period, and when the steady state is reached, capacitive charging has gone to zero, and all current is used for the Faradaic reaction.

This example calculation hopefully showed that it is not that difficult to make a calculation for an electrode with a certain EDL structure, for an electrode process that is a mixture of capacitive and Faradaic currents, with the ratio between these two processes rapidly changing in time.

In the calculation just presented, based on the Frumkin-equation, concentrations just outside the electrode were assumed to be constant. In §7.9, we discuss in more detail the effect of changes in ion concentrations next to the surface because of a film layer.

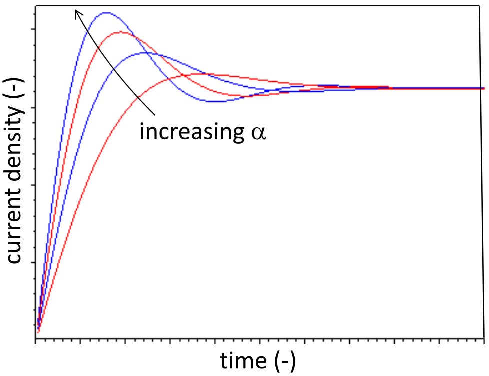

Fig. 7.5: For an electrode process described by the Frumkin equation, charge storage in the electrode is an integral part of the calculation. For the same control strategy as in Fig. 7.4, we show here results for the Frumkin model in combination with the GCS-model. The time scale is about 10× less than in Fig. 7.4, while α is larger than in Fig. 7.4.

7.9 The effect of film layer mass transport on the electrode response

In §7.8, the Frumkin equation was used in an example calculation where the electrode charge increased in a short period from 0 to 35 mC/m^2. But it was assumed that ion concentrations just outside the electrode did not change. In reality, these concentrations will change, and this will affect the electrode. First of all, this is because (in this example) the neutral reactant must diffuse to the surface, while the cation that is formed must be removed, by diffusion and electromigration, and thus concentrations will change through the film layer in front of the electrode. The second effect is that the increase in electrode charge requires a counterbalancing ionic charge in the diffuse part of the EDL. In our example calculation, the electronic charge is positive, and thus anions must flow into the EDL to compensate that charge. We first discuss the effect of a mass transfer limitation because of the film layer, and discuss ion storage in the EDL in §7.10.

In our example calculation, we have the neutral reactant R, the product O which is a cation, and there is an inert anion to compensate the charge of the cation at any position in the film layer (as well as in the bulk, away from the electrode). The anion and cation have the same bulk concentration, c_∞. When cations are produced in the electrode, their concentration increases, and thus the anion concentration must also increase there, by flowing from outside the film layer toward the electrode. This leads to an increase in the salt concentration that is used in the GCS model. Thus, in the present section, we do not assume there is a large concentration of background salt.

We use the same dynamic film model as on p. **??**, with the same diffusion coefficient, D, for all three molecules in this problem. Thus, Fick's second law is solved for the neutral reactant, and for the two ions (which have the same concentration another because of local electroneutrality). At the electrode, neglecting ion storage in the EDL, the Faradaic current, I_F, is directly related to the molar fluxes of the reactant, R, arriving through the film layer, and of the oxidant, O, flowing away, according to

$$I_F/F = J_\mathrm{R} = -J_\mathrm{O} \tag{7.20}$$

where we define the ionic fluxes in the direction from bulk to electrode (coordinate x pointing from bulk to electrode surface), and I_F is defined in the direction of oxidation. For the neutral species R, at the surface the flux is given by $J_\mathrm{R} = -D\, dc_\mathrm{R}/dx$, and its concentration will decrease towards the electrode. The cation, which is the oxidant, with index O above, leaving is produced at the electrode, while the anion has a zero flux at the electrode (the electrode blocks the anions). In this case, the relation between molar flux of cations and the concentration gradient at the surface (electrode) has an additional factor 2 compared to a neutral molecule, thus: $J_+ = -2\,D\, dc_\mathrm{R}/dx$. This factor 2 is because cations not only leave the electrode because of a concentration gradient, but are also aided by the electrical field there. This same electrical field (gradient in electrical potential) will also pull anions toward the electrode, building up in concentration, to ensure we have local electroneutrality at each position in the film. Thus, both anion and cation have a concentration that goes up toward the electrode. Because of this factor 2, for the cation, concentrations in the film change a factor 2 less than for the neutral reactant. Results for current after a change in the setpoint for E, are presented in Fig. 7.6 and show stronger oscillations than in previous calculations where the film layer was neglected (Fig. 7.5). Thus the film has an effect on the structure of the diffuse layer, and thereby an effect on the rate of the electrode reaction.

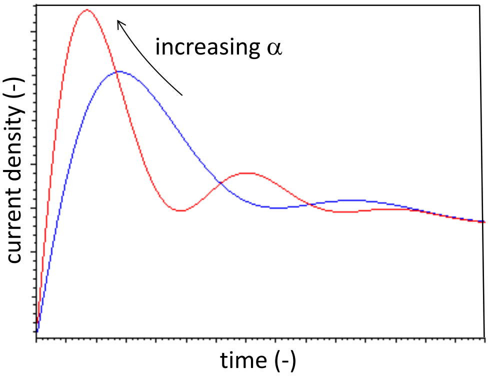

Fig. 7.6: For the same control strategy as in Figs. 7.4 and 7.5, we show here results for the Frumkin-model in combination with the GCS-model for the structure of the EDL, including the effect of mass transport in a film layer in front of the electrode.

7.10 The effect of ion storage in the EDL on electrode response

Until now, accumulation of ions in the EDL was neglected in the calculation. However, this effect can be important. This is because the EDL needs ionic countercharge to balance the electronic charge that develops. In our example a positive electronic charge develops, and thus anions are required in the diffuse part of the EDL. The cations that are formed in the electrode reaction cannot compensate the electronic charge, but they must move out of the diffuse layer. For a steady state problem, this EDL effect is irrelevant and the calculation of §7.9 suffices. However, for a dynamic problem, after a step change in potential or current, as well as for cyclic operation at high frequency, ion storage in the EDL will make a difference.

Because we now consider accumulation of ions in the EDL, Eq. (7.20) is no longer valid for the oxidation product, i.e., the cations. It remains valid for the neutral reactant molecule. Eqs. (7.18) and (7.19) also remain valid. The following modifications must now be made to account for ion accumulation.

First of all, the external (imposed, measurable, electronic) current, I, is equal to the current carried by anions and cations outside the EDL (at any point in the film layer), thus

$$I + F \sum_i z_i J_i = 0 \tag{7.21}$$

where the summation runs over anions and cations, and we can evaluate these fluxes anywhere, for instance at the film layer/EDL interface, which is position 's'. Furthermore, we can use the Frumkin equation, Eq. (7.1), with the concentration of the neutral reactant, c_R^*, the same at the reaction plane as at position 's', which is outside the EDL. For the cation, we use Eq. (7.2) to relate concentrations at these two positions. We must now also track the excess adsorption, Γ_i, of one of the ions in the EDL. We can do that for the inert ion, and then that balance is

$$\frac{d\Gamma_-}{dt} = J_- \tag{7.22}$$

where J_i is the flux of ion i from film layer into the EDL. We solve this balance for the anion, jointly with overall electroneutrality of the EDL, which is

$$\sigma_e + F \cdot (\Gamma_+ - \Gamma_-) = 0\,. \tag{7.23}$$

Furthermore, the GCS model is used for the charge, σ_e, according to Eq. (5.18), as well as to relate the excess ion adsorption (unit mol/m^2) to $\Delta\phi_\mathrm{D}$, which for an anion in a 1:1 salt solution is given by

$$\Gamma_- = F^{-1} \cdot \sqrt{2\varepsilon RT c_\infty} \cdot \left(\exp\left(\Delta\phi_\mathrm{D}/2\right) - 1\right) \tag{7.24}$$

where the salt concentration, c_∞, is evaluated at the film layer/EDL interface, position 's' (the same for c_∞ in Eq. (5.18) for σ_e).

The final equation is a boundary equation for the diffusion rate of anions and cations. Based on §7.4 in B&D we know that for equal diffusion coefficients of anion and cation, the salt concentration gradient is given by

$$J_+ + J_- = -2\,D\,\left.\frac{dc}{dx}\right|^{\mathrm{s}} \tag{7.25}$$

where index s refers to evaluation at the film layer/EDL interface.

Results of this calculation are presented in Fig. 7.7. At time zero, we change the setpoint for E by 0.4 V (from equilibrium before), and we track how all currents develop in time. In this calculation the concentration at the surface only changes by 1 or 2 mM, so the film layer does not matter too much (we use the same values for film layer thickness and diffusion coefficient as in §7.6). We furthermore use $k_{\mathrm{exch}} = k_{\mathrm{O}} = k_{\mathrm{R}} = 0.01$ A/m^2/(mol/m^3), and Stern capacity $C_{\mathrm{S}} = 0.3$ F/m^2.

What Fig. 7.7 shows, is that current I increases steadily at first, and in that period anions are being stored in the EDL, while cations are expelled. The Faradaic reaction hasn't yet started, i.e., I_F is still very low. After a short time, cation expulsion slows down, and even later anion adsorption declines strongly while the Faradaic reaction takes off and cation flow out of the electrode increases again. The increase in cation flux is because the Faradaic reaction starts to produce more and more cations, and they must flow out of the EDL in which the number of anions and cations has reached constant values. Because of the high value of α chosen to define the control system, the current goes beyond the steady state value and then decreases again. In that period of decrease, anions again flow out of the EDL. When after some time steady state is reached, all currents will be the same, except for the anion flux, which is then zero.

So this last calculation, as presented in Fig. 7.7, predicts the rates of cation and anion adsorption in the EDL, that add up to the applied current, I. This information on the flow of individual ions was not generated in the calculation of §7.9, see Fig. 7.6, but there an assumption had to be made which ions contributed to the current I. In §7.9, the assumption was that only cations were involved. In the present section, these contributions of the two ions are not predefined, but are calculated by the model, and in the early stages after a change in setpoint, these contributions change rapidly.

Thus, the present calculation shows that EDL effects, including accumulation of cations and anions, can be included in a dynamic model for an electrode reaction. In reality of course the processes in an electrode are even more complicated, for instance involving diffusion of adsorbed species across the surface to sites where the reaction takes place, so the present calculation only covers part of all electrode processes. But it does show that if we wish to do so, EDL effects can be rigorously implemented, and in this way we can study how in a few ms, an electrode can transform from 100% capacitive behaviour, such as in the first 0.2 ms in Fig. 7.7, to almost completely Faradaic after 2 ms.

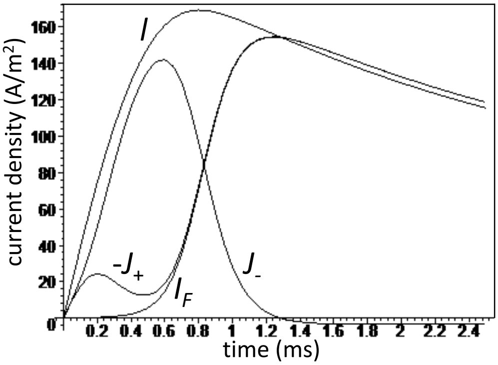

Fig. 7.7: Electrode response in a calculation that includes ion accumulation in the EDL. From time zero onward, there is a flux of anions into the EDL, J_-, while cations are expelled (flux out of the EDL is J_+). The electrode changes from completely capacitive behaviour at early times to almost completely Faradaic at later times. The difference with the situation in Fig. 7.6 is that now both ions can flow in and out of the electrode, and the ratio between their fluxes changes in time and is calculated by the model. (In this figure, fluxes J_i have been multiplied by F resulting in a flux with unit A/m^2.

8

Electrode reactions including surface transport

In this last chapter we evaluate a model for Faradaic processes where we combine transport limitations in the film layer (i.e., in solution), with transport across the surface of an electrode, before molecules participate in a redox reaction. We will assume these transport process are all the rate limiting steps, and the actual transfer of an electron is infinitely fast, so there is no electrochemical rate limitation or reaction overpotential.

We evaluate the case that reaction is simply ‘stochastic’: each adsorbed molecule simply has a certain change per unit time to react. The second calculation is that molecules must diffuse over the surface to reach sites for electron transfer. We develop an elegant mathematical approach for this situation.

9

Summary

In this textbook we gave an overview of the three types of electrochemical cells, which are Faradaic cells, capacitive cells, and concentration cells. We explained that all these three types can be used to harvest and story energy, to provide energy, and to convert chemicals or separate solutions. We explained that electrochemical cells can also have a single electrode, or more than two, and that it is possible to combine electrodes, for instance a Faradaic electrode can be combined with a capacitive electrode. We also explained how in any practical electrode, both capacitive and Faradaic effects can occur. It is explained how the electrode is a special type of electrical double layer (EDL), and is the structure of the interface between an electrolyte solution, and a metal.

For capacitive electrodes, we discussed various EDL theories, such as the Donnan model and the GCS model. We showed how to calculate the power and energy that can be stored.

We discussed the corrosion of iron, based on iron oxidation and the reduction of sulphate to sulfide. After that we discussed in detail cathodic protection of a metal structure using a third, sacrificial electrode. To solve these problems, a dynamic equilibrium model was introduced based on the Nernst equation for each half reaction and a linear overpotential-current relationship. Finally, we discussed the redox potential and Pourbaix diagrams.

In Ch. 7, the Nernst equation was extended to the Frumkin equation which describes in detail electrode reactions including a model for the EDL. The simplification of this equation is the Butler-Volmer (BV) equation which can be combined with expressions for transport of ions across a film layer that is in front of the electrode. We analyse in detail the functioning of a three-electrode setup based on the BV-equation and analyse dynamic behaviour after a change in setpoint. A final detailed dynamic calculation combines an EDL model and the Frumkin equation and the film layer.

In Ch. 8, a modified framework is presented for electrode reactions where the final electron-transfer reaction is assumed to be infinitely fast, i.e., locally at equilibrium. But transfer of molecules across the surface, and accumulation for dynamic problems, is assumed to play a role.

All of the above topics are first described conceptually, and after that analysed mathematically. The equations from Ch. 7 are compared with equivalent results in textbooks by Vetter (1961) and Bard and Faulkner (1980). We provide a glossary of relevant terminology, an overview of certain technical conventions, and provide a list of key literature references.

10

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11

Glossary

⊙ **Binary salt solution** - An electrolyte solution with only one type of cation and one type of anion. The valencies of the two ions and their diffusion coefficients can be different. Thus, a solution of NaCl is a binary salt, as well as a solution of $CaCl_2$.
⊙ **Bulk (phase)** - The volumetric phase next to an interface in which concentrations and potentials change slower in time than the rate of change in the interfacial region. Often to describe the bulk phase, the symbol '∞' is used, referring to 'of infinite extent'. The bulk phase generally has a concentration that does not vary with position, or at least varies much less than in the interface. Local electroneutrality holds in the bulk phase.
⊙ **Capacitance of an EDL, of an electrode** - The slope of the curve of electrode charge versus electrode potential, measured at equilibrium. Capacitance is a function of electrode potential and charge, it is not just a single number.
⊙ **Capacitive electrode process** - An electrode process in which the electrode structure (gradually) changes when a current is applied, and thus, the electrode potential also changes in time.
⊙ **Capacity of an EDL, of an electrode** - The measurable property of a capacitive electrode as the change in charge of the electrode when the electrode potential is changed from one to the other value (potential window), often divided by volume

or mass of the electrode. If reference is made to ‘the’ capacity, this refers to the maximum, or limiting, value, i.e., an even larger potential window will not change the measured capacity.

⊙ **Cell voltage** - The measurable voltage between two electrodes.

⊙ **Charge** - An amount, often with unit C(oulomb). By dividing with Faraday’s number, F (F = 96485 C/mol), the number with unit C is converted to a number with unit mol. Charge can be positive and negative, and charge can flow. The flow of charge is called a current. Part of an ionic solution (electrolyte) can contain charge, *ionic charge*, and likewise in a metal there can be charge. This latter charge would then be called *electronic charge*. Important is to note that a positive electronic charge in some region, means there is a deficit of electrons there. And the statement ‘the electronic charge goes up,’ means electrons leave this region. See also entries *EDL charge* and *Electrode charge*.

⊙ **Charge tranfer electrode** - An electrode where electrons or ions (i.e., charged particles) are transferred across the full electrode in an ongoing electrode reaction, i.e., an electrode in a Faradaic electrode process.

⊙ **Charging step / Discharge step** - In a cyclic electrochemical process, then over a full cycle there is a period where the cell is charged, and a period where it is discharged. These periods can be called ‘steps’. Some condition is changed when we go from one step to the other, such as a change in current direction, or a change in the setpoint of the cell voltage.

⊙ **Chemical equilibrium** - Equilibrium related to transport or reactions of species (such as ions). For instance referring to an EDL structure where it can be assumed that the structure of the EDL (as defined by concentration and potential profiles) does not directly depend on transport processes. An EDL is an equilibrium structure because it directly adapts to a change in an external parameter. Also when there is transport of ions or current across an interface, the equilibrium EDL model can still be used. Chemical equilibrium also relates to chemical reactions between species, with concentrations related by an equilibrium expression, involving a constant, K. Also here, there can still be a non-zero reaction rate. Only in *the equilibrium state* are these reaction rates zero.

⊙ **Coion (also written as co-ion)** - The ion of the same charge sign as the charge of the surface, membrane, or other porous medium. Often at a lower concentration compared to outside the EDL or porous medium.

⊙ **Conductivity** - The conductivity, or conductance, of an ionic solution has unit σ or κ, and can also be called electrical conductivity. The unit is S/m (with S for Siemens) or $(\Omega.\mathrm{m})^{-1}$, where $\mathrm{S} = 1/\Omega = \mathrm{A}/\mathrm{V}$. Often Ω is called (and written as) 'Ohm'. The volumetric resistance ρ of an electrolyte solution is $\rho = 1/\sigma$ with unit Ω.m.

⊙ **Conductor, or metal** - A conducting phase, or conductor, conducts electrons not ions. It will be the wires connecting electrodes to a power source or other type of electrometer. There is no background charge. || The terms 'Ion conductor', and 'ion conductivity' relate to the electrolyte phase.

⊙ **Coulombic efficiency** - For a cyclic process of charge and discharge, the ratio of 'returned charge' (the charge (unit Coulomb) transferred between the electrodes during the discharge step), over 'charge input' (the charge transferred between the electrodes during the charging step). A dimensionless number, less than unity.

⊙ **Counterion** - The ion of a charge sign opposite to the (fixed) charge of a surface or porous material. Often therefore at an enhanced concentration compared to outside the EDL or porous medium.

⊙ **Dielectric** - A dielectric (material) is a material, or a layer, that does not *contain* any type of charged species, neither electrons nor ions. In the context of the dielectric capacitor, it is also implied that it does not *conduct* any type of charge. The Stern layer, a theoretical element of EDL modelling, is also a dielectric layer, i.e., it does not contain charge, but charge can jump across the Stern layer. A synonymous term is *insulator* or insulating layer.

⊙ **Diffuse double layer** - An erroneous term, conflating diffuse layer and EDL. What is meant is: diffuse layer.

⊙ **Diffuse layer** - A theoretical element of an EDL model, relating to the ions and potential profiles in an electrolyte, due to a balance of electrostatic and entropic forces. The thickness of the diffuse layer relates to the Debye length, which decreases with increasing salt concentration, as well as with increasing valency of the ions.

⊙ **Diffuse layer potential, Donnan potential** - Both these potentials have the symbol $\Delta\phi_\mathrm{D}$. In a Gouy-Chapman-(Stern) model, this is the potential across the diffuse layer, thus the potential at the Stern plane relative to outside the EDL. In a Donnan model, for instance for ion-containing micropores, $\Delta\phi_\mathrm{D}$ is the potential inside the pore, relative to outside the pore.

⊙ **Dynamic** - A dynamic process is not at steady state, thus some or all process elements change in time. Note that for many processes it is often the case that certain elements are in chemical equilibrium (for instance the EDL structure), other elements are in steady state (transport across a film layer), and yet other elements are dynamic (accumulation of salts in reservoirs). Which modelling approach to choose, and how to combine these elements, are key aspects of electrochemical process modelling and design.

⊙ **EDL, or electrical double layer** - The EDL is the structure at the interface between bulk phases (i.e., it *is* the interface), in situations where at least some charged species such as ions are involved. Across the EDL there is a voltage difference, and within the EDL are regions of opposite charge. On the two sides outside the EDL there are two electroneutral bulk phases. These phases either contain charge carriers (ions in an electrolyte, or electrons in a conductor) or do not (insulator). The field strength, E, in the EDL (very dependent on position in the EDL) is much higher than in bulk, where is very low, or zero. The EDL as a whole is electroneutral. EDL is also the name for the set of equations describing the EDL structure, i.e., the relationships between charge, potential, and ion adsorption.

⊙ **EDL charge** - If an EDL is overall electroneutral, how can it be we generally use the term ‘EDL charge’ and related concepts such as the capacitance of an EDL? The answer is that these terms, like EDL charge, refer to one of the regions of the EDL. For instance, it refers to the region that can be associated with the (electron-)conducting phase (inside the EDL), thus related to the electronic charge stored in the EDL. See also entries *Charge* and *Electrode charge*.

⊙ **Electrode** - A special type of EDL, namely formed at the interface of a (semi-)conductor and electrolyte. The EDL is an interface (see entry on *Interface*) and includes the several regions of opposite charge formed in this region where conductor and electrolyte are in contact. On one side of the electrode is the electroneutral bulk metallic phase, and on the other side the electroneutral bulk electrolyte. The processes at, or in, an electrode can be capacitive or Faradaic, or both types of processes occur simultaneously. A Faradaic process involves transfer of ions or electrons across this interface. This is the formal, theoretical, definition of an electrode.

⊙ **Electrode$^{\mathbf{TC}}$** - The technological convention (TC) of the word electrode refers to the physical structure, to 'the piece of metal'. In this definition of the word electrode, in an oxidation reaction an electron 'goes into the electrode.' However, in the theoretical meaning of the word electrode, in an oxidation reaction, an electron is liberated from ions already in the electrode, and the electron then *leaves* the electrode to go into the electronic circuit (metal wires).

⊙ **Electrode charge** - The charge in an electrode, by which is meant the charge in one or more of the regions of the electrode. It does not refer to the electrode charge as a whole, because the electrode as a whole is always electroneutral, and thus the total charge is zero. Often the term refers to a difference in charge between two situations (such as moments in time, as in 'the charge was increased by 5 C'), and generally refers to the charge on the metallic (electron-conducting) side. See also entries *Charge* and *EDL charge*.

⊙ **Electrode potential** - The potential across the electrode. Note, the electrode is the EDL structure at the interface of (multiple) phases, at least one of which conducts electronic charge and at least one of which conducts ions. The electrode potential is a function of the electrode (EDL) charge.

⊙ **Electrode reaction** - The reduction or oxidation reaction at an electrode, which involves electrons, and species coming from nearby non-metallic bulk phases, of which one phase at least is an electrolyte phase. Often the electrode reaction involves reactant species adsorbed to the surface and the reaction product is also an adsorbed species, which subsequently desorbs. An example is the oxidation of an adsorbed H-atom, to a proton, H^+, with an electron going into the metal phase. Reactions at an electrode (for instance, between adsorbed species) that do not consume or produce electrons, are not called an electrode reaction.

⊙ **Electrolyte** - A phase that contains ions, ions that move around because of diffusional and electrostatic forces. In a liquid electrolyte there can also be convection. Many porous materials contain an electrolyte. For instance, inside the pores of intercalation materials, porous carbons, ion-exchange membranes, or other gel-like structures made of charged polymer, there is a solvent (often, water) and mobile ions dissolved in the solvent. In a solid electrolyte, or solid salt, for instance AgCl, ions can move relative to the other ions, but there is no solvent.

⊙ **Electrometer** - The name for all devices that can impose and record currents and voltages applied to an electrochemical cell. Electrometer refers to a voltmeter, power source, battery, load, potentiostat, as wll as galvanostat.

⊙ **Electron acceptor** - A species that (is able to) take(s) up an electron, in the process being reduced. For simple ions, its charge then becomes more negative (but there are exceptions when also one or more protons are simultaneously taken up). Before the reaction, it is in the oxidized state, afterwards it is in the reduced state. This could be at an electrode, but this terminology also refers to reactions in solution. Then, while species A is the electron acceptor, another species D donates the electron. While species A is reduced, species D is oxidized. Thus, species A is the oxidant (the reaction leads to another species being oxidized).

⊙ **Electron donor** - A species that (is able to) give(s) off an electron, in the process being oxidized; its charge becomes more positive. Before the reaction, it is in the reduced state, afterwards it is in the oxidized state. This could be at an electrode, but this terminology also refers to reactions in solution. Thus, while species D is the electron donor, another species A accepts the electron. While species D is oxidized, species A is reduced. Thus, species D is the reductant (the reaction leads to another species being reduced).

⊙ **Electroneutrality** - The condition that at a certain position, or inside an entire phase, a solution, electrolyte, has an equal numbers of positive charges as negative charges. These numbers are based on a summation over all ions, of their valency and concentration. Thus all these ionic charges add up to zero. When also a charged ‘matrix’ structure, such as an ion-exchange membrane, is present, the charge of that structure is also included in the electroneutrality balance (a balance which adds up to zero). Also called charge neutrality.

⊙ **Electronic circuit, or external circuit** - The connection from one electrode to the other via metallic wires. Often there is a potentiostat (electrometer) in the circuit, or another device that functions as a load, or as a battery.

⊙ **The equilibrium state** - A situation where there are no net flows, no fluxes, no net reactions. Of each reaction, the reaction rate is zero.

⊙ **Faradaic electrode process** - An electrode process with current flowing, and that in principle can go on forever, because the composition of the electrode does not change in time. Ions and electrons enter the electrode (the EDL) from one bulk phase adjacent to the electrode, and also leave the EDL again to the same, or to another, bulk phase (after having reacted to other molecules). Ions or electrons transfer across the EDL in a Faradaic process.

⊙ **Field Strength** - The (electrical) field strength, **E**, is a vector, and describes the negative of the gradient of the electrostatic potential, $\mathbf{E} = -\nabla V$. When only one spacial coordinate needs to be considered, x, we have $E = -dV/dx$. In this book we general use the dimensionless potential $\phi = V/V_\mathrm{T}$, where V_T is the thermal voltage' given by $V_\mathrm{T} = RT/F$, and thus $E = -V_\mathrm{T}\, d\phi/dx$.

⊙ **Interface** - The region formed when two different phases or materials are brought in contact. The interface is not an ideal mathematical infinitely thin 2D layer, i.e., it is not a *surface*. Instead, it has a thickness. Others have then proposed the term ‘interphase’ but we use the more common term ‘interface.’

⊙ **Ionic current (density)** - The current carried by ions. Current (density) can have unit A, A/m^2 or mol/m^2/s.

⊙ **Migration or Electromigration** - The movement of an ion or other charged solute inside an electrolyte phase or charged porous structure because of a local non-zero electrical field. One of various driving forces that can act on an ion.

⊙ **Molar flux** - The molar flow rate of a species divided by the perpendicular surface area through which the flow goes, thus with unit mol/s divided by m^2, resulting in the unit mol/(m^2.s). In transport studies careful attention is required to distinguish *interstitial* and *superficial* flow rates, fluxes, and velocities.

⊙ **Oxidant, oxidizing species** - see entry *electron acceptor*.

⊙ **Porous electrode** - A porous electrode is a multi-phase system containing electroneutral regions with water and ions (electrolyte), containing an electron-conducting (and -containing) ‘matrix’ phase, and a structure for mechanical strength. The interface of electrolyte and conductor, i.e., the EDL, is often formed inside sub-nm sized micropores, which are electrolyte-filled pores in direct contact with the electron-conducting matrix.

⊙ **Redox reaction** - A reaction in a solution where an electron is transferred from one molecule to another. In general these molecules are charged, and then change their charge. Electron-transfer of course is more general, for instance when in a gas phase methane and oxygen react to water and CO_2, but then this term is not used. It is also not used for a reaction on an electrode; that is then called electrode reaction, or reduction or oxidation (whichever applies).

⊙ **Reductant** - see entry *electron donor*.

⊙ **Round trip efficiency** - An efficiency number between 0 and 1, describing how much energy (unit J) is provided by an energy storage device during use (discharge), relative to the energy used to recharge the device.

⊙ **Semi-conductor** - Similar to a metal, a semi-conductor also has electrons as charge carriers, but in addition the material has fixed charges ('p-doping' or 'n-doping'). The conductivity is much lower than in a metal.

⊙ **Space-charge region** - The same as diffuse layer, often used to describe the diffuse layer inside a semiconductor material.

⊙ **Stern layer** - A theoretical element of an EDL model. The Stern layer is a constant-capacitance element between the diffuse layer and the charged surface. It does not contain charge itself. Its thickness can be assumed to relate to the (hydrated) radii of counterions, because that represents the closest-approach distance of the centers of the counterions to the surface. A typical value is $C = 0.1 - 0.2$ F/m^2. Also called Helmholtz layer.

⊙ **Stern plane (Outer Helmholtz plane)** - Also a theoretical element of an EDL model, being the surface, the dividing plane, between the Stern layer and the diffuse layer. It is not a plane that contains counterions (though it is often depicted like that in textbooks), but instead it is simply the closest approach distance for the centers of ions to the charged surface. (In advanced EDL models, beyond GCS theory, adsorption of ions in this plane can be included.)

⊙ **Surface** - Mathematical two-dimensional plane without a thickness.

⊙ **Steady state** - The condition that in a certain region, or everywhere in a process, there are no observable (macroscopic) changes *in time*. In a theory, this means that in that region, all accumulation terms d/dt in mass and heat balances are zero. There still may be non-zero flows and reactions in that region.

⊙ **Valency** - The valency of an ion, or an ion's charge, is a discrete signed number, such as +1, +2, or -1 or -2, etc. It does not have a unit. And it is 'signed', that is, it is a positive number for a cation, and a negative number for an anion. A solute can also have a valency of 0 (e.g. carbonic acid).

⊙ **1:1 salt solution** - A salt solution with both the anion and cation monovalent, such as KCl and NaCl. See also *binary salt.*

Technical conventions

The following terminology can sometimes be ambivalent. Our approach is as follows.

1. Two parameters x and y are *linearly* related when they relate according to $y = a \cdot x + b$, with a and b constants. Variables x and y are also *proportional* to one another when $b = 0$. Thus a proportional relationship is a special type of linearity, i.e., a proportional relation is also linear, but a linear relationship is not necessarily showing proportionality between x and y. When x and y relate according to $y = x + b$, i.e., $a = 1$, this is a specific type of linearity, for which we have no specific term. We can write 'are the same except for a constant offset b.'

2. Often we define an axis, a positional coordinate, which we generally give the symbol x. By default this coordinate axis runs 'left to right' in the descriptions that we use, i.e., it 'points to the right'. If we then state that a flux, or velocity, or current (density), is positive, has a positive value, or 'points to the right', all of these statements mean the same thing.

3. If we then define a difference in a parameter, Y, often written as ΔY, this is generally the value of the parameter on a position (more to the) right, minus its value at a position (more to the) left, i.e., a ΔY is always defined 'right minus left' in the axis convention just defined. Donnan and diffuse layer potentials in an EDL model, $\Delta\phi_{\mathrm{D}}$, are always defined as inside the EDL/Donnan layer, minus outside the EDL, or, at the Stern plane, minus outside the EDL. A Stern layer

potential is likewise the potential at the 0-plane (or in the metallic phase), minus the potential at the Stern plane. Electrode potentials, V_e, are the potential inside the metallic phase minus that in the electrolyte (both outside the EDL).

4. The words ‘electric’ and ‘electrical’ can refer to the electron-conducting phase (e.g., metal), as well as to electrolyte. i.e., they have a broad meaning also encompassing the electrolyte. Thus ‘electric(-al) current’ can also refer to the ionic current in solution.

5. However, the word ‘electronic’ does refer to the electron-conducting, metallic, phase. Thus electronic charge or electronic current is charge or current in the ‘wires’ or other external circuit elements. Note that ‘electronic charge’ or ‘electronic current’ is not defined as that of the electrons, i.e., the negative charge carriers. Instead, all currents, ionic and electronic, describe the flow of charge. Thus with a coordinate axis x pointing ‘to the right’ (see point 2 above), a positive current means that there is a net transport of positive charge carriers to the right, or negative charge carriers to the left. This goes both for ionic current, as well as for electronic current. Thus when we write that there is a certain electronic current of $I = 5$ A flowing through a wire to an anode, we can envision this is as a flow of $I/F \sim 50$ μmol/s of electrons flowing in the opposite direction, out of this anode through the wire.

6. We use both the terms current and current density to refer to a current in A/m^2. Sometimes a current (density) is also in mol/(m^2.s) (with symbol J_{ch} or J_F then often used), and multiplying by Faraday’s constant converts this to a current in A/m^2. Sometimes current has the unit of A for the overall (integrated) current into an electrode (transported through a connecting wire). In all these cases the symbol I can be used.

7. We use the word adsorption and absorption without implying the formal distinction between adsorption at an interface and absorption inside a volumetric medium. This distinction is not always easy, and therefore we use both words interchangeably.

8. When we use the word ‘potential’ this most often refers to an electrical potential, i.e., a voltage, often in dimensionless units, with symbol ϕ.

9. Charge is often in C or C/m^2 or C/m^3, sometimes in mol/m^2, or mol/m^3. Faraday's constant makes the conversion between the C-based and mol-based charge.

10. Concentrations are written as c or as [...], and both notations have the same meaning. For volumetric concentrations the official unit is mol/m^3 which is the same as mM. We also use M, but please remember this is mol/L. Concentrations can also be in (μ)mol/m^2 for a concentration per surface area.

11. We use the words 'unit' and 'dimension' interchangeably, i.e., they have the same meaning.

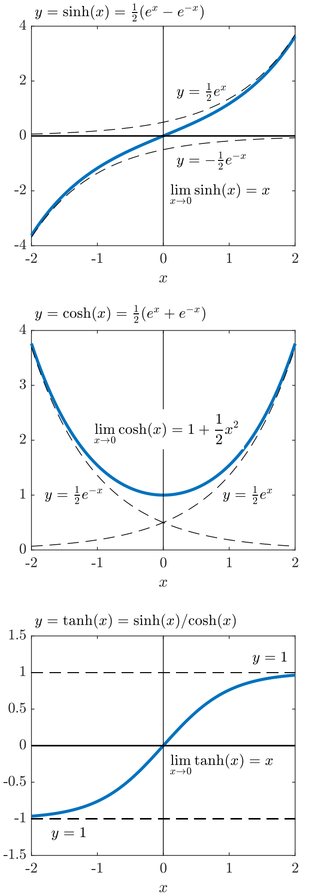
12. When we include acid-base reactions, involving (de-)protonation of ions, ions can be neutralized. For instance the bicarbonate ion can be protonated to a neutral carbonic acid molecule. In problems involving such neutralized species, we take the liberty to call all species ions, not just when the charge is positive or negative, but also when the charge of an ion is zero.

13. In water the concentration and fluxes of H_3O^+- and OH^--ions are often of relevance. Instead of writing H_3O^+ for the hydronium ion, we often use the shorthand of writing proton, or H^+-ion.

14. The words increase, decrease, lower, higher, up, and down are ambivalent for properties that can be both negative and positive. For all these words two meanings are possible, either referring to I. the numerical value moving left or right on the number scale, for instance that a change from +1 to -2 is a decrease, but II. it can also refer to a change in the magnitude of a numerical value. In that second meaning a change from -2 to -1 is a decrease. We try to avoid ambiguities and for instance in the latter case use the terminology 'becomes less negative'. The words larger, smaller, more, and less, they do not have this ambiguity; they refer to the magnitude of a property going up or down.

Hyperbolic functions

In the theory of electrochemical processes, the hyperbolic functions are frequently used. Therefore we summarize in the figures below their most important characteristics, including limits for $x \longrightarrow 0$ and $x \longrightarrow -\infty, \infty$.



The three hyperbolic functions $\sinh(x)$, $\cosh(x)$, and $\tanh(x)$, often used in the theory of electrochemical processes.

For comments, corrections, and questions, you can email the authors at
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