An introduction to electrochemical energy conversion

From basic principles to where we stand

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Summary. — This paper is meant to provide a basic introduction to electrochemical energy conversion. It should be a low-barrier entry point for reading the relevant literature and understanding the basic phenomena, approaches and techniques. Starting with some basics of electrochemistry to establish the most important techniques, I will touch upon established electrochemical processes which are carried out today on industrial scale to finish with an outline of state-of-the art research on proton exchange membrane fuel cells and electrolysers for water splitting.

1. – Introduction

This text is intended to be an introduction for students who are interested in the basic principles of electrolysers and fuel cells (*i.e.*, the process of water splitting to generate oxygen and hydrogen and the reaction of hydrogen and oxygen to water) and provides some basic principles and ideas as well as further literature outlining the current state of the art in science and technology. While no text can be extensive in this respect, I hope to clarify the important concepts behind electrochemistry and help to understand how a certain device works and why it is built like this —and why scientists and engineers are still struggling with some of the fundamentals and some of the technical solutions.
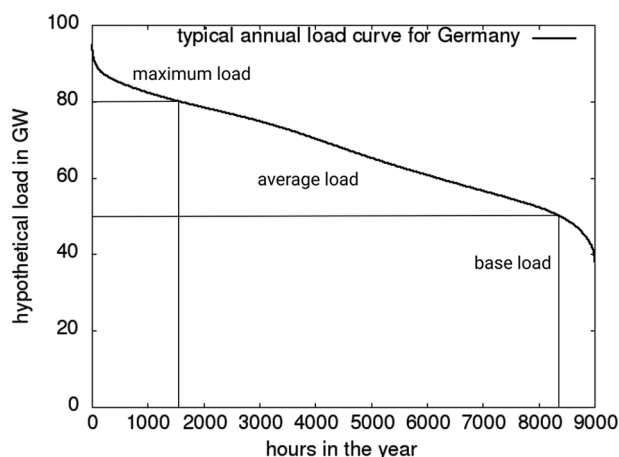
Fig. 1. – Typical annual load curve that displays how much load is required in a given grid (y-axis) for how many hours in a year (x-axis). Typical recent annual load curves for Germany can be found for example in [1]. Figure data based on [2].

2. – Motivation —the curse of intermittency and the need for energy storage

Standing at the shore of the Lago di Como, in deep discussion on topics related to climate change, energy and economy, scientific advances and engineering solutions it is time for dessert: The sweet and delicious Italian fruits or tempting treats like Canoli or Gelato. Sugar, the taste so irresistible for many of us, signaling our body that an appropriate supply of energy has been found. For nature, sugar, starch and fat have been the ultimate solution for a fundamental problem —how to make the energy that the sun supplies available in times when it is scarce. And scarce it often becomes, as intermittence is one of the most prominent features of the abundant renewable resources that the sun (and everything derived from it —wind, rain and biomass) bestows upon us. Hence, after mastering a way to harvest the solar energy, nature has come up with a way to convert and store intermittent resources.

A society that relies on renewable energies derived from the sun faces the exact same problem. Our current energy supply is based on technologies which are tailored to a 24/7 supply and industry is dependent on this infrastructure. And while almost every month there is a new press report about new records in the supply of power from wind or photovoltaics, many people wonder whether we can switch our whole electricity supply, even our whole energy supply to renewables. If you want the big picture, there is hardly any book that I can recommend as much as MacKay's "Sustainable Energy —Without The Hot Air" [3] (free pdf at `www.withouthotair.com`). Here, David MacKay makes a strong statement for devising plans "that add up" and demystifies statements like "every little helps".

While thinking about supply and demand on national scales, there is one thing that we should not disregard. This is illustrated by looking at what is called an annual load curve (see fig. 1). This graph illustrates how much (in this case electrical) power is needed
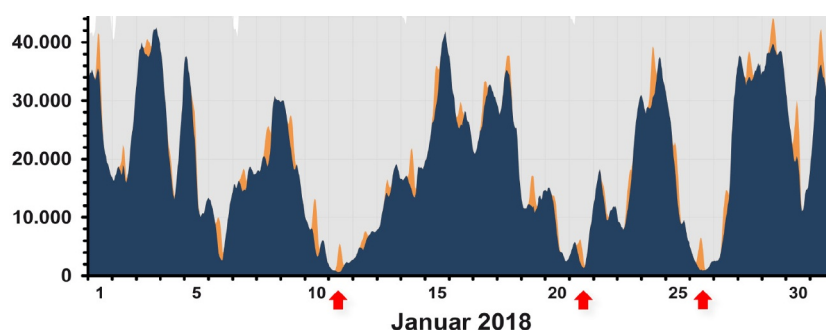
Fig. 2. – Wind (dark area/foreground) and PV (light area/background) electricity production in MW in Germany during January 2018. Note the high correlation of wind and PV power as well as the strong fluctuation and low minimal production in times of no wind/no sun. Figure adapted with friendly permission from [4,5].

for how many hours during a year. On the left side of the histogram we see that large quantities of electricity are only needed for a few hours at a time (hours of maximum load). However, looking at the right side of the graph (base load), we see that actually quite a lot of power is used 24/7 —most of this not being stand-by devices in our homes, but industry branches that require 24/7 operation.

Let us contrast this with a typical overview of the electricity production by wind or sun (see fig. 2). As we can see, there is strong fluctuation due to high and low wind times and due to day and night and also due to weather. While one at first glance might argue that this will average out over a country or even over a continent, we nowadays have very accurate data over the last decades, in fact for all of Europe [4]. An analysis of the data is disillusioning —best illustrated by how the *minimum* supply of electricity from wind and PV has developed during recent years (see data for Germany in fig. 3). Although the peak power has been increasing steeply and steadily, the minimum supply —as observed in times of little wind and sun— has almost been constant and very close to zero. Even if we could transfer electricity all over Europe, there would be no constant energy supply if we switch to 100% renewables. Accurate studies indeed suggest that even having ten or more times the peak power we would still require close to 100% backup capacity (note that in the following, I will be using an estimated 10% storage capacity which is quite optimistic in comparison). The only way to escape this dilemma is to store electricity in some way or another, just like nature stores solar energy in chemicals [6]. This needs to be done in large quantities and over longer timescales, as there is not only night and day but also summer and winter to cope with.

Do I need to mention that even our fossil fuels are nothing but sun energy stored in chemical compounds? Early life on earth was faced with abundant energy and abundant "building materials", but unfortunately in the form of a reduced earth curst and an oxidized atmosphere —estimates about pre-earth atmosphere imply that it mostly consited of water, nitrogen, carbon dioxide and practically no oxygen [7,8]. The heros of this
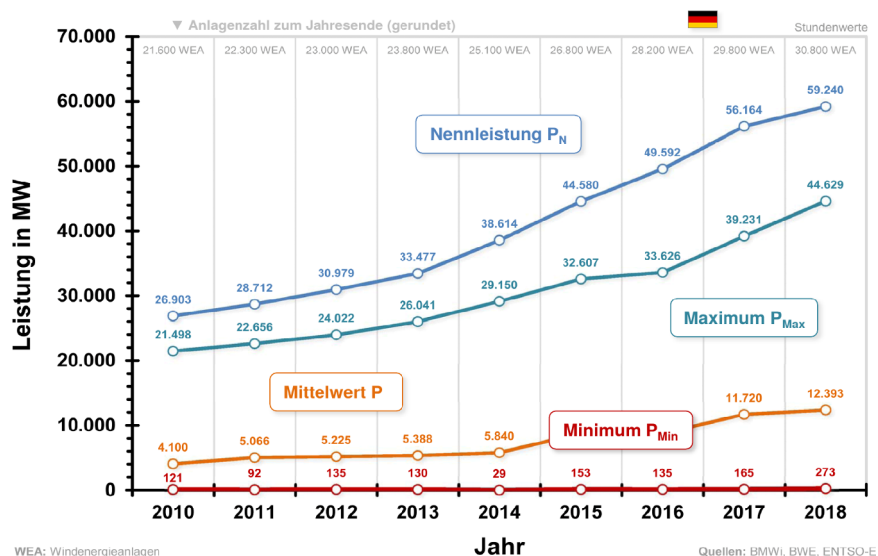
Fig. 3. – Development of wind energy in Germany since 2010. Power in MW plotted against the corresponding year. Top curve denotes nominal capacity ("Nennleistung"), second from top is maximum power generation ("Maxmimum"), "Mittelwert" is the average power generation and bottom curve denotes the minimum power gernation. Figure reprinted with friendly permission from [4, 5].

"pre-atmospheric earth" are cyanobacteria that succeeded in converting the atmosphere to oxygen-rich and carbon lean conditions. The carbon enriched in these organisms was not liberated into the atmosphere, but instead the organic material was buried and at high pressure and increased temperature converted into their final energy rich form, storing sunlight under ground for millenia. These treasures are the generous gifts of our predecessors we call "fossil fuels" and which our highly industrialized societies are built upon.

So how can we store energy in large quantities? Battery systems can be one of the solutions. The advantages are very low losses in storage and supply as well as quick response times and a growing industry that is constantly presenting refined systems. However, if we take a look at one highly developed system available —the battery of a modern electrical car— we see that we typically have a lithium-based system that weighs a few hundred kilos and has a capacity of around 100 kWh [9]. Let us say, we want to store 10% of Germany's electricity (520 TWh/y in 2017) [10]. For this purpose, we would actually need 5–10 of these batteries for each of the 80 million Germans (note that this includes every member of the family). This might even be feasible if we do not insist on storing a full year's supply —we would probably end up with a "one battery per person" scenario. But still, the lifetime of these batteries can be an issue (one suggestion is to use old "second-life batteries" from mobile applications as home storage [11]) and also the resources needed for battery production are not negligible [12, 13]. However, while batteries will play a vital role in modern societies as demonstrated by the 2019 nobel

prize in chemistry, we can guess that batteries alone are unlikely to be the sole solution for national dimensions.

What about other existing large-scale energy storage systems? Hydro power would certainly be a good option. In the US, one of the largest hydro power storage facilities is the Bath Country pumped storage station in Virginia. With a surface of one square kilometer it is able to generate a power of 3 GW that it can maintain for 11 hours [14], which amounts to 0.24 TWh. As a comparison: In Germany, the total hydro storage capacity is 7 GW in more than 30 sites and a total electricity production of 6 GWh in 2016 [15]. Our estimated 10% of Germany's electricity that we might need to store amounts to 50 TWh, so we are lacking a factor of around 1000 in Germany or would need 200 times a site as huge as the Bath Country pumped storage station (note that the Lago di Como has a surface of 146 square kilometers). I think it becomes obvious that we will have to come up with other strategies in order to arrive at numbers that actually add up —to say it in MacKays words.

Our technology today offers a broad variety of storage solutions. Flywheels, hydro-power, super capacitors, batteries, redox-flow-batteries, pressurized air, the methanol economy ... and the discussion about possible solutions is anything but settled. It seems the only thing certain is that future energy economies will be much more diverse and complex. Coming back to sugar and starch, evolution has found a solution to store energy in chemical bonds based on a process that uses abundant chemical compounds and a mechanism to exchange its internal energy currency into high energy molecules. If need be, it can convert those back and harvest the stored energy. In the following sections, I will focus on electrochemistry as a means to convert electricity to chemical energy. I will walk the reader through the basics towards understanding one of the many specific solutions: Water splitting and hydrogen as energy carrier [16]. Water is an abundant chemical compound and hydrogen can be used as fuel directly as it has a high energy density (high energy per kg of hydrogen, for high volume density high pressures are required) and it can be produced in large, centralized facilities [17], stored and transported. However, hydrogen can also be used for subsequent hydrogenation reactions to obtain methanol from CO_2 or to gernerate higher hydrocarbons, which can potenitally even be used as feedstock for chemical industry.
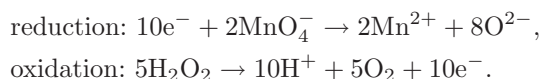
3. – Fundamental principles of electrochemistry

3`1. *Redox reactions*. – One of the basic concepts that we learn when we are interested in chemical reactions is that there is a broad variety of processes that are driven by the exchange of electrons between different species. These reactions are summarized as redox-reactions, as they include reduction —reactants gaining electrons and hence reducing their oxidation state —and the oxidation— reactants yielding electrons and increasing their oxidation state. A typical example would be the reaction of a colorful permanganate solution with hydrogen peroxide. This is an entertaining process which is accompanied by all the phenomena we love about chemistry —bubbling, steaming, color change etc. (add detergent and food color for additional effect) [18].
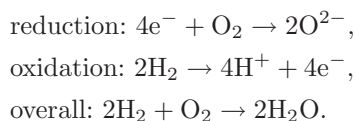
The basic reaction is

$$6H^+ + 2MnO_4^- + 5H_2O_2 \rightarrow 2Mn^{2+} + 5O_2 + 8H_2O.$$
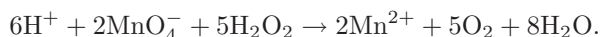
It is driven by the "urge" of manganese in the unfavorable oxidation state $+7$ to go to a lower oxidation state (in this case $+2$) by taking up electrons from the peroxide. In peroxide we find oxygen in the unfavorable oxidation state -1 to give up one electron to convert to elemental oxygen in the oxidation state 0. We can spell this out separately as

$$\text{reduction: } 10e^- + 2MnO_4^- \rightarrow 2Mn^{2+} + 8O^{2-},$$
$$\text{oxidation: } 5H_2O_2 \rightarrow 10H^+ + 5O_2 + 10e^-.$$

So on paper we have separated the reduction of manganese and the oxidation of oxygen into two *half-reactions* and denote the electrons which are exchanged. The fundamental driving force is the lower potential that the electrons experience in the products compared to the initial state. Let me give one more example —the chemical reaction we will mostly be concerned with: The reaction of hydrogen and oxygen (oxyhydrogen or *Knallgas*) to give water, which is also the fuel cell reaction, and —in reverse— the water splitting reaction:

$$\text{reduction: } 4e^- + O_2 \rightarrow 2O^{2-},$$
$$\text{oxidation: } 2H_2 \rightarrow 4H^+ + 4e^-,$$
$$\text{overall: } 2H_2 + O_2 \rightarrow 2H_2O.$$

The fundamental principle of electrochemistry is to realize that the corresponding *half-reactions* can actually, in practice, be split into separate compartments with the electron exchange proceeding through a conducting lead and the ion exchange through solution or an ion conductor. This leads us to a simple electrochemical cell setup, which is displayed in fig. 4. (For an extensive discussion on the thermodynamics, kinetcs and related phenomena I would refer the reader to [19].)

If the two half-reactions are combined, they give rise to a potential difference for the electrons. This can be observed as voltage and —if the resistance permits it— results in a current. Then the voltage corresponds to the electrochemical potential and the current is the number of electrons flowing in a given time interval and is proportional to the number of reactions occurring in the cell. The general terminology in electrochemistry is to denote the half-cell in which the reduction occurs as cathode and the half-cell in which the oxidation occurs as the anode (as a little help to remember: Picture a cat that is crimson red, as if it had fallen into a bucket of red paint —the **Red Cat** reminds you that the **Red**uction always occurs at the **Cat**hode).

The next step is to combine arbitrary half-cells and observe which reaction will occur. By measuring the potential for a series of cells with, for example, one identical half-cell, we can compare relative potentials. The convention is to set the half-cell potential of the reaction of hydrogen to protons to zero and to express all half-cell potentials with respect
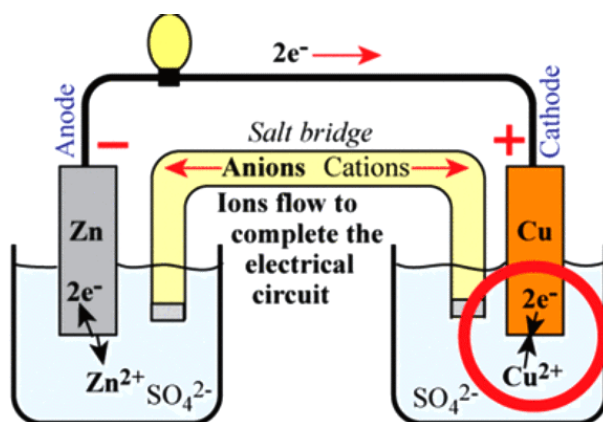
Fig. 4. – An electrochemical cell —a redox couple has been separated into two half-cell reactions, in this case the couple $Cu \rightleftharpoons Cu^{2+}$ and $Zn \rightleftharpoons Zn^{2+}$. Figure adapted with permission from [20].

to this arbitrary zero potential (this is also refered to as Standard Hydrogen Electrode (SHE)). This way, we obtain the electrochemical series (see table I).

Hence, if we combine two half-cells, for example one half-cell in which a piece of copper is immersed in a solution of copper sulfate ($CuSO_4$ with Cu^{2+} ions) and a half-cell with a piece of zinc immersed in a solution of zinc sulfate ($ZnSO_4$ with Zn^{2+} ions) as shown in fig. 4, we can expect a cell potential of 1.1 V (can you work this out from table I?). In the copper half-cell the metal with the lower redox potential is reduced —this electrode is the cathode on which copper is deposited from solution (half-cell potential of 0.34 V). On the zinc side, the anode, metallic zinc yields its electrons and dissolves (half-cell potential of -0.76 V). Note that the value of the half-cell potential in the electrochemical series gives us a direct indication of how easily or how difficult it is to oxidize or reduce a certain species. For metals, the electrochemical potential can actually be correlated to the Fermi level of the electrons in the metal, as has been discussed in detail by Trasatti [23, 24]. If we would replace the zinc by silver, the more noble silver would become the cathode and the silver ions would be deposited as metal while the copper dissolves at the anode and we would observe a cell voltage of 0.46 V.

Let us look at a few examples in the electrochemical series to get a feeling for redox potentials. The highly corrosive halides fluorine and chlorine, which in nature always occur as anions (remember, even a brick will "burn" if exposed to elemental fluorine!) [25] have half-cell potentials of 2.87 and 1.40 V. The metals aluminium and iron, which in nature always occur as cationic species in oxides, have half-cell potentials of -1.68 and -0.04 V. The noble metals platinum and iridium, on the other hand, have much lower half-cell potentials of 1.2 and 1.16 V.

Oxygen has a potential of 1.23 V for its reduction to water in acidic conditions, so that the reaction of hydrogen with oxygen *should* yield a potential of 1.23 V in an electrochemical cell. As a consequence, any electrochemical reaction in water must occur in

TABLE I. – *This table provides E_0 values for selected reduction reactions. Values have been taken from* [21, 22].

$Li^+(aq) + e^- \rightleftharpoons Li(s)$	-3.04
$K^+(aq) + e^- \rightleftharpoons K(s)$	-2.93
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	-2.71
$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$	-1.68
$O_2(aq) + 2e^- \rightleftharpoons O^{2-}(aq)$	-1.00
$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^- aq$	-0.83
$Zn^{2+}aq + 2e^- \rightleftharpoons Zn(s)$	-0.76
$Ni^{2+}aq + 2e^- \rightleftharpoons Ni(s)$	-0.26
$Ti^{2+} + 2e^- \rightleftharpoons Ti(s)$	-0.16
$Pb^{2+}aq + 2e^- \rightleftharpoons Pb(s)$	-0.13
$Fe^{3+}aq + 3e^- \rightleftharpoons Fe(s)$	-0.04
$2H^+aq + 2e^- \rightleftharpoons H_2(g)$	0.00
$Ir_2O_3 + 3H_2O + 6e^- \rightleftharpoons 2Ir(s) + 6OH^-$	0.10
$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^- aq$	0.22
$C(s) + 2H_2O \rightleftharpoons CO_2 + 4H^+ + 4e^-$	0.23
$Cu^{2+}aq + 2e^- \rightleftharpoons Cu(s)$	0.34
$CO(g) + 2H^+ + 2e^- \rightleftharpoons C(s) + H_2O$	0.52
$O_2(g) + 2H^+ + 2e^- \rightleftharpoons H_2O_2$	0.70
$Ag^+aq + e^- \rightleftharpoons Ag(s)$	0.80
$Br_2(l) + 2e^- \rightleftharpoons 2Br^- aq$	1.09
$Ir^{3+} + 3e^- \rightleftharpoons Ir(s)$	1.16
$Pt^{2+} + 2e^- \rightleftharpoons Pt(s)$	1.2
$O_2(g) + 4H^+aq + 4e^- \rightleftharpoons 2H_2O(l)$	1.23
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^- aq$	1.40
$MnO^{4-}aq + 8H^+aq + 2e^- \rightleftharpoons Mn^{2+}aq + 4H_2O(l)$	1.51
$Au^{3+} + 3e^- \rightleftharpoons Au(s)$	1.52
$F_2(g) + 2e^- \rightleftharpoons 2F^- aq$	2.87

a potential window between 0 and 1.23 V (note that this also depends on the electrode material, the pH etc.) as at lower potentials hydrogen is likely to be formed by reduction of protons at the cathode and oxygen evolution is likely to occur at the anode at higher potentials. We will come back to this "stability window of water" and the stability of a surface in electrochemistry in sect. **3**˙3.

Important note on my nomenclature: In the following, I will denote the hydrogen evolution reaction as HER and oxygen evolution as OER (as parts of water splitting) and
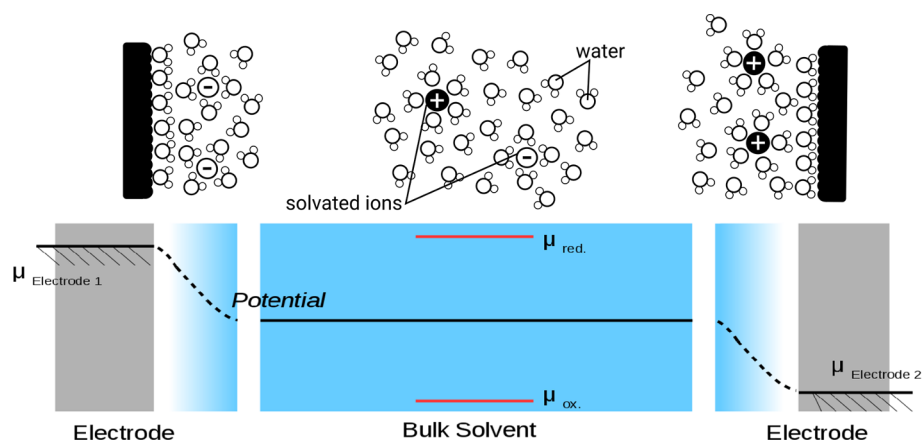
Fig. 5. – Schematic microscopic picture of solvent/ion distribution at the electrochemical interface and in the solvent (top). Potential distribution in the electrochemical cell (bottom).

the correspodning hydrogen oxidation reaction as HOR and oxygen reduction reaction as ORR (as parts of the fuel cell reaction).

3˙2. *Microscopic picture of electrochemical reactions*. – From the previous section we have learned that for an electrochemical cell we need some way of moving the electrons in and out of the system —the electrode. Furthermore, ions must move freely so that there is no electrochemistry without a solvent containing ions. If we are generating or consuming a gas like in water electrolysis or in the fuel cell, we reach a very high level of complexity quickly, as the three-phase boundary (solid-liquid-gas) becomes central to the process.

Figure 5 (bottom) illustrates the potential distribution in an electrochemical cell. Inside the electrodes, the electrons have the potential determined by the material properties and the applied potential. Deep in the solvent, the potential is determined by the redox potential of the solvent molecules (for a detailed description of the electrochemical interface I would refer the reader to [26].) Close to the interface, however, there is a steep transition from the potential in the electrode to the potential in the solvent, in which charged species and the dipoles of the solvent molecules arrange in order to minimize the overall energy of the interface, screening the surface charges (top of fig. 5). This region is refered to as *Helmhlotz layer* (or "double layer") and it is surprisingly thin (typically in the order of a nanometer) [27], as solvents like water and electrolyte solutions that contain high concentrations of ions can efficiently screen long-range Coulomb effects.

If an electrochemical reaction occurs in which a molecule is oxidized or reduced on the surface, we have to envision the microscopic process something like this: The molecule diffuses in solution, surrounded by solvent molecules with a solvation shell that is optimal for its current state. As it reaches the interface, the solvent structure changes due to the changing environment and the molecule starts to experience the potential of the
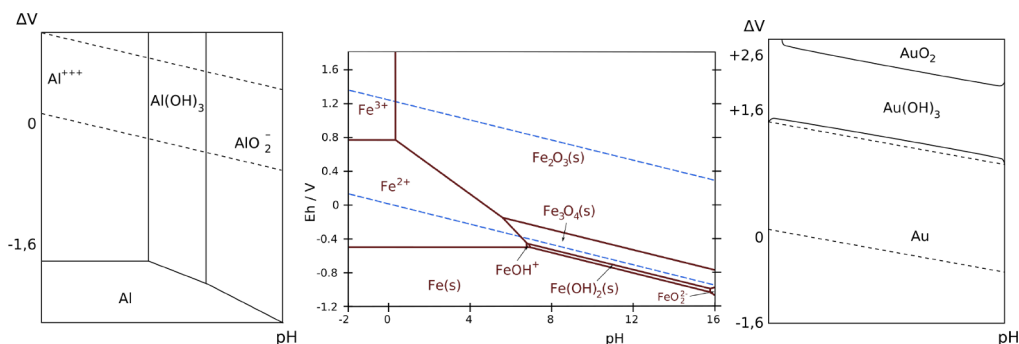
Fig. 6. – Pourbaix diagrams for aluminium, iron and gold. Dashed lines denote the stability window of water. (Source: Wikimedia `commons.wikimedia.org/wiki/File:Fe-pourbaix-diagram.svg`, `https://commons.wikimedia.org/wiki/File:D-pourbaix-Al.svg`, `commons.wikimedia.org/wiki/File:Pourbaix-Au.svg` under Creative Commons Attribution-Share Alike 3.0 Unported license.)

electrochemical interphase. In so-called *outer-sphere reactions*, an electron then tunnels from or to the molecule, changing its oxidation state. After the solvent has adjusted to the new state of the molecule, it diffuses from the vicinity of the surface. In an *inner sphere reaction*, the molecule actually diffuses to the surface, partly sheds its solvation shell and becomes an adsorbate. It then reacts, desorbs and is re-solvated before it diffuses away. This imaginative picture of the atomistic details illustrates how complex the process is, which factors contribute and how the interface and the solvent influence the states of the species involved. Note that many theories in electrochemistry are of phenomenological nature and focus on global variables and observables, but one should not forget that modern experiments and simulations allow us to gain deeper insights into the atomic length scales and the mechanistic details involved.

3˙3. *Electrochemical interface and electrode stability*. – Starting to study electrochemical reactions, one might be tempted to draw parallels to heterogeneous catalysis, in which a species is adsorbed, reacts and is desorbed. Here, the typical text book examples like reactions with hydrogen on platinum imply that the surface acting as catalyst is well defined and basically unaltered during the process [28]. While this can also be true in electrochemistry there are many cases when it will change its structure and even its composition during the electrochemical process.

Whether a surface itself is altered or stays inert during the electrochemical process can be rationalized by inspection of a Pourbaix diagram. The basic idea of a Pourbaix diagram is to plot the thermodynamically most stable state in a 2D landscape with one dimension being the pH in aqueous solution and the other dimension being the electrochemical potential [29]. This way, the Pourbaix diagram will tell us whether a metal will dissolve, deposit, passivate or stay unaltered under certain conditions. Figure 6 shows the Pourbaix diagrams for aluminium, iron, and gold.

We can see that aluminium, which is a base metal with very low oxidation potential, is oxidised in a large potential range. Nevertheless we can use aluminium in its metallic form, as it reacts with oxygen and is covered with a very stable and compact oxide layer (passivation). For iron the Pourbaix diagram already tells us that there are oxides (Fe_2O_3 and Fe_3O_4) and oxy-hydroxides ($Fe(OH)_2$) existing in a wide range of pH and potentials. In addition to this, the iron oxides are porous, brittle materials that will allow access to the bare metal and facilitate continous corrosion. Noble metals on the other hand, exhibit very large ranges of potential and pH in which the neat metal persists, and harsh oxidizing conditions are required (like elemental halides and strong acids in combination —*aqua iridia*) to force the metal into its ionic —and hence dissolvable— form.

3˙4. *Basic electrochemical experiments —cyclic voltammetry*. – One of the central experiments in electrochemistry that you will find over and over in the literature, no matter if it deals with engineering solutions, state-of-the-art analysis or materials science, is *cyclic voltammetry (CV)*. The basic idea of this technique is to test the current response of a half-cell reaction on a given electrode depending on the applied potential. This is preferentially carried out in a *rotating disc electrode* (RDE) setup, in which the electrode is actually spun in solution with typical speeds of 500–10 000 rpm. This has the advantage that the spinning quickly removes reaction products from the surface and provides defined mass transport conditions at the electrode, which ensures stable measurements and good reproducibility of the results [30, 31].

In order to outline what information can be obtained from a CV if the technique is applied to its full potential (and also because we will need this information in the following sections) let us focus on the CV of a crystalline platinum surface. The group of Feliu is world leading when it comes to clean and controlled electrochemical investigations on well-defined surfaces. I can only highly recommend to read some of the reviews and perspective papers published. There are several beautiful examples of which effects and which complications clean measurements of CVs will exhibit for example for platinum [32-35].

Figure 7 displays a cyclic voltammogram for a platinum polycrystalline surface, in which the sample is taken through a potential sweep from reducing to oxidizing potentials and back again. The current response is measured and obtained in the typical shape of a hysteresis curve. The processes behind the measured response are manifold as anything that leads to a flux of electrons contributes to the signal. This can be redox reactions in the vicinity of the surface but also processes like surface reconstruction, the formation of adsorbates up to the dissolution or deposition of entire surface layers.

This CV is not carried out to 0 V but is reversed just before, so we do not observe the steep decrease of cathodic current that corresponds to hydrogen evolution starting at 0 V (see table I). Moving towards higher potential (0.1–0.4 V) a region is reached which often contains distinctive features. These depend on the composition of the electrolyte (which ions are in the solvent and how easily they adsorb) and the structure (termination, defects, steps etc.) of the surface. This is the region in which hydrogen ions/atoms that had been adsorbed on the surface are desorbed. The phenomenon of hydrogen
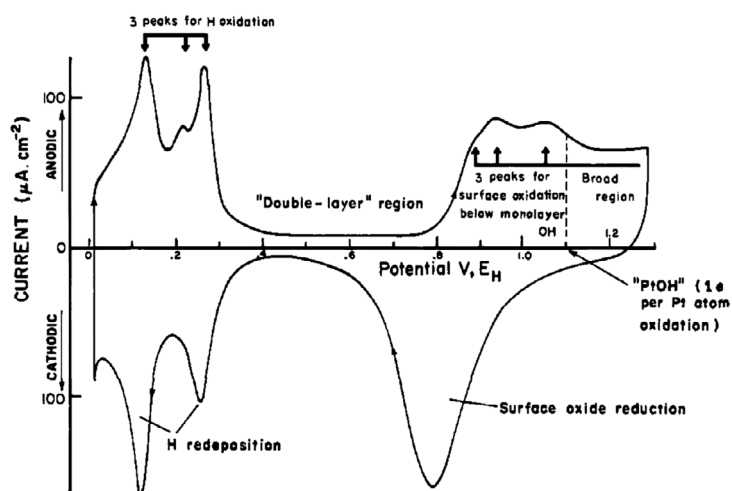
Fig. 7. – Cyclic votrammogram: Potentiodynamic current-potential profile for a polycrystalline platinum electrode in pure aqueous sulfuric acid. Figure adapted with permission from [36].

species existing at the surface without actually reacting below these potentials is called hydrogen under potential deposition (HUPD). The potential at which the HUPD peaks appear even allows to gain some information about adsorption strength and adsorption sites [37] (actually, it turns out the situation is more complex, as usual [38]). Note that in oder to observe these details, the platinum surface first has to be cleaned from strongly adsorbing impurities —for a fuel cell catalyst this means that strongly adsorbing impurities (like CO and many other carbon-based impurities) can block catalytic cites and hence "Poison" the catalyst.

Next, there is a region in which only a small current is observed (0.4–0.8 V) which is attributed to capacitive effects of ions and the dipoles of solvent molecules in the double layer. Going to potentials above 0.8 V, further current peaks indicate the emergence of oxygen species (denoted here as "surface oxidation below monolayer"). While oxygen evolution only starts beyond 1.5 V on platinum, already starting from around 0.8 V oxygenated species adsorb on the surface, forming a layer of hydroxides, physisorbed oxygen and eventually oxides. This is accompanied by the corresponding oxidative currents which again show some distinctive peaks depending on which sites on the surface are involved or whether other ions in the solution influence the process.

The first thing to remember when learning about surfaces in electrocatalysis (we also touched upon this when talking about the Pourbaix diagrams) is that depending on the pH, the material and electrolyte, the surface will be a different one for different potentials (see fig. 18 for the Pourbaix diagram for platinum). For platinum, working at potentials below 0.3 V we are likely to be dealing with metallic platinum on which hydrogen atoms and molecules are adsorbed. Going to 0.5 V, there should be only negligible amounts of atomic hydrogen on the surface and above 0.8 V the surface becomes increasingly
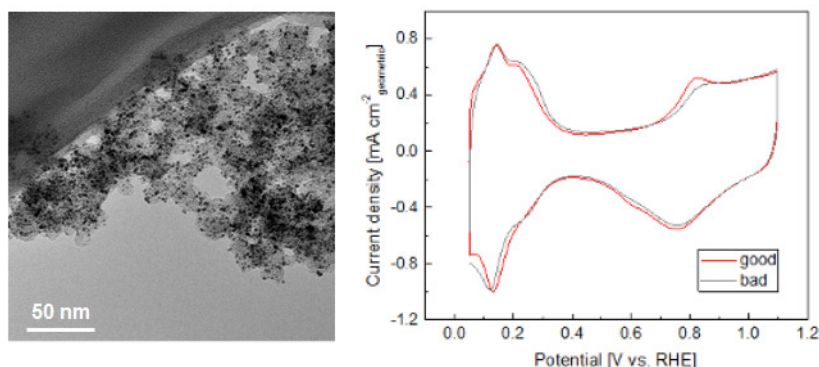
Fig. 8. – Left: Transmission Electron Microscopy (TEM) images of platinum nanoparticles on "Vulcan" carbon. Right: Representative examples for voltammograms for this catalyst ("good" and "bad" refer to well-cleaned and insufficiently cleaned samples, which is reflected in the sharpness of the distinct features). Images adapted from [39].

modified by oxygenated or even oxide species. Hence, if we want to learn something about a catalyst for the oxygen reduction reaction, studies on *ex situ* systems will tell us little about the surface under reaction conditions. Because of this, one should also think about the a catalyst material that has been prepared in the lab as *nominal* catalyst that only converts to its —often unknown— catalytic state in reaction conditions, in the electrochemical cell at operating potential.

If we now imagine that there are several processes that constantly change the catalyst surface like concentration gradients, local changes in pH and potential or fluctuations in current and potential, it can easily be understood why people from catalysis use terms like dynamic, working or even *living* catlyst.

Now let us compare fig. 7 with fig. 8, which has been obtained from a "real" catalyst by the Arenz group, who have worked intensively on studying platinum nanoparticles in electrocatalysis [40-42]. Nanoparticles are favored as catalysts in fuel cells due to their high catalytic activity and high surface to volume ratio, allowing for very low amounts of the expensive material (we shall come back to this later). The differences are quite obivous and reflect the differences in the catalyst structure. While the platinum surface only contains a limited number of adsorption sites, the nanoparticles are much more inhomogenous and the adsorption strength even depends on the size of a nanoparticle. As the CV provides information integrated over all features the signals here are much broader.

As we will be looking more closely at water splitting later, let us assemble a hypothetical design, using platinum forhydrogen evolution on the cathode and one of the best catalysts available for oxygen evolution, which is "iridium/iridium oxide" for the anode. Two typical CVs of the corresponding materials are shown in fig. 9. The top panel shows the CV for a platinum-based material on the right and the left panel shows a polarization curve if the potential is driven into the hydrogen evolution regime at low potentials. The bottom panel shows the CVs of different iridium-based materials on the
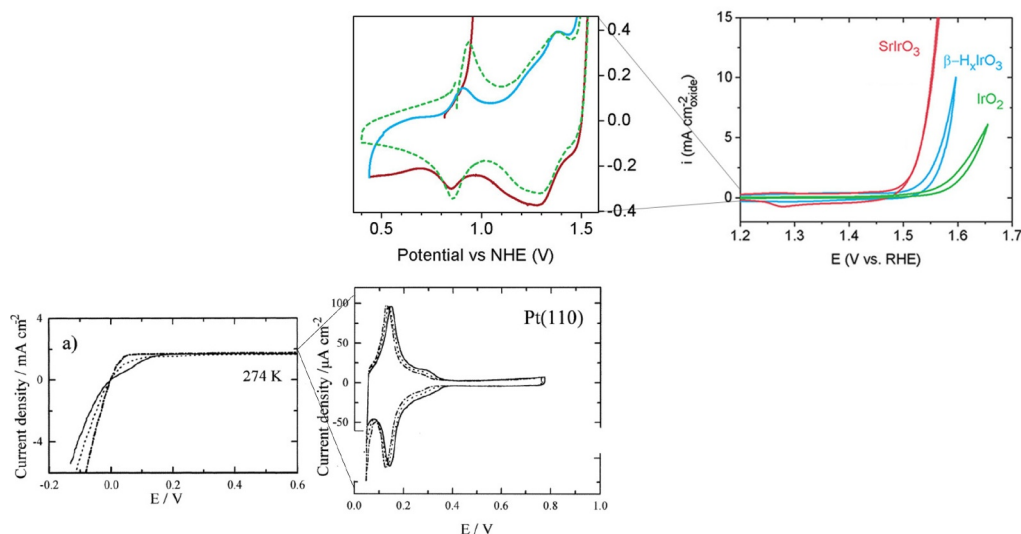
Fig. 9. – Top: CV and potential curve for OER on three different iridium-based catalysts. In the center, the corresponding CV is shown, on the right side the polarisation curve for OER is plotted. Figure adapted with permission from [43]. Bottom: Analogous CV (center) and potential curve for HER (left) on platinum. Figure adapted with permission from [44].

left and the right panel shows the polarization curve if the potential is driven into the oxygen evolution regime at high potentials. Note that in the different plots the current response in the CV is usually one to two orders of magnitude smaller than for the polarization curves during which much larger currents are observed as oxygen and hydrogen are being evolved. Interestingly, the broad scan CV for the HER seems to rise steeply immediately after reaching the onset potential around 0 V. This is the desired optimal current profile for a nearly reversible reaction and an optimal catalyst. As soon as the potential is sufficiently high for the one electron transfer to a proton, hydrogen atoms form hydrogen molecules and desorb. Applying higher reducing potentials will then just yield more hydrogen and higher currents as a consequence. For the anode and the OER, the picture is quite different. From thermodynamics we would expect the OER at potentials around 1.2 to 1.3 V (note that the kinetics of this reaction, *i.e.* the reaction rates, can be described by the Butler-Volmer equation [19]). For all catalysts we observe a CV with several features between 0.5 and 1.5 V, so we can guess that the material or the surface undergoes several changes or several other processes occur. Only after 1.5 to 1.6 V a significant increase of the current is observed due to oxygen evolution. So here, in contrast to the HER, we do observe a significant *overpotential* of 0.4 V. Hence we can conclude that the OER half-reaction is sluggish in comparison to the HER and there appear to be some processes in the oxygen reduction and evolution that seem to require larger barriers and/or high energy intermediates. Note that the OER actually requires four electrons to make one O_2 molecule in contrast to only two for H_2. Looking at the
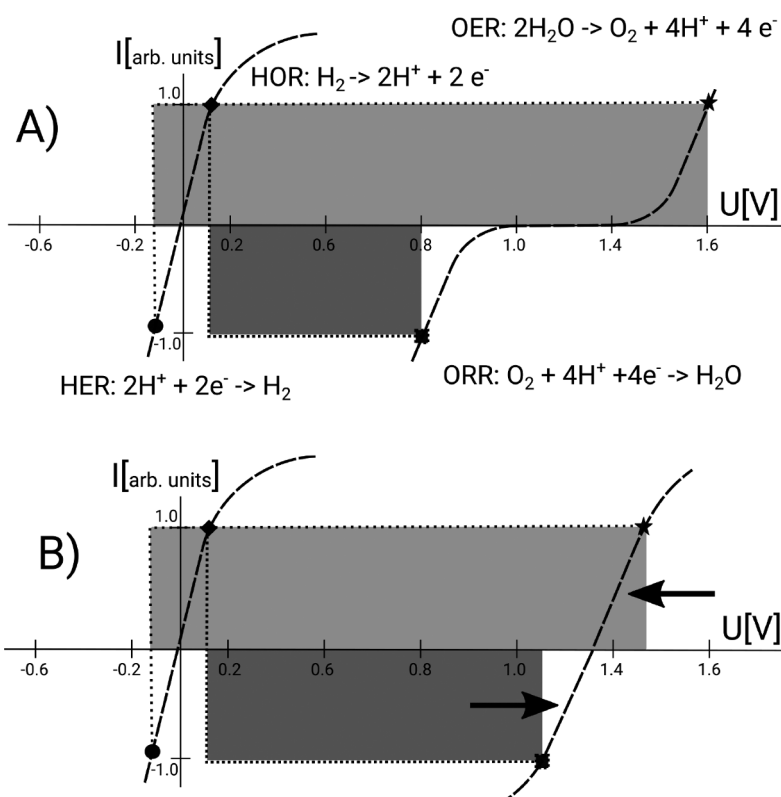
Fig. 10. – Hypothetical electrochemical cell in which we contrast the efficiency of water splitting (HER and OER, light grey boxes) with a fuel cell process (HOR and ORR, dark grey boxes). The top scheme (A) illustrates the real situation with a high overpotential for OER and ORR, to bottom scheme (B) illustrates what would change (indicated by the black arrows) if the oxygen reactions would be close to reversible (original scheme courtesty of Anna Mechler).

reverse reaction —the fuel cell process— a similar picture can be observed (note that I have not included the corresponding figure here). The oxidation of hydrogen to protons immediately proceeds above potentials of 0 V while the oxygen reduction reaction to form water only starts around 0.9–1.0 V rather than the expected 1.23 V.

Now we can put the two half-cells and the four half-reactions (hydrogen evolution (HER), hydrogen oxidation (HOR), oxygen evolution (OER) and oxygen reduction (ORR)) together into one hypothetical polarization curve scheme: fig. 10 illustrates which effects are essential for designing an efficient chemical energy conversion process based on water electrolysis and the fuel cell reaction. Let us see what happens if we put a one unit of current on our arbitrary y-axis into an electrolyser or obtain the same current from a fuel cell reaction: For an electrolyser, the corresponding reactions are the OER on the cathode (top right, denoted by star) and the HER on the anode (bottom left, denoted by circle). Overall, the targeted current is reached at a cell voltage of roughly

1.7 V, which we can attribute to the half-cell reactions occurring at -0.1 V from HER and 1.6 V for OER. The energy required is proportional to the surface as $E = I \cdot U$ as indicated by the light grey box (top of fig. 10(A)). For the fuel cell reaction we have hydrogen oxidation (top left, denoted by diamond) and oxygen reduction (bottom right, denoted by square) yielding our current of 1 at a voltage of 0.7 V (adding the 0.1 V of HOR and 0.8 V for ORR). Note that the energy we obtain from this reaction (dark grey box) amounts to a lot less than what was required to split water. The efficiency can be estimated as $0.7/1.6 \simeq 0.44$. This estimated efficiency of 44% is a little pessimistic compared to state-of-the-art systems, but even if the scheme is quite simplified we can still use it to understand that the decisive factor for the conversion process is mostly the kinetics of the oxygen reduction and evolution. If we had reversible oxygen reactions, the curve for OER/ORR would look like fig. 10(B). Here, the difference between the energy required for generating a given amount of hydrogen and oxygen and for running them through a fuel cell would be much less. While we cannot cheat the basic thermodynamics, it would still be possible to increase the efficiency of the process greatly.

Note that in practice the obtained efficiency is indeed even lower as many other things influence the overall process. Among these are diffusion limits and mass transport, conductivity losses for electrons and ions, Ohmic losses in the devices and many more.

There is, of course a limit on the maximum efficiency, as a driving force is needed to go beyond adiabatic processes. Note that for fuel cells, one actually quite often finds the statement that the fuel cell process is not bound by the limits of Carnot efficiency as it does not include an combustion process of some kind. While it indeed does not include steps in which thermal energy is converted into mechanical energy, there is no way around thermodynamics. I would just like to point out one reference which contains a comprehensive discussion why the thermodynamic limits of an electrochemical process are similar to any other process in which chemical energy, thermal energy, mechanical energy or electrical energy are converted into each other [45]. The basic idea for a comparison of the fuel cell process is that the electrical energy is obtained from the reaction enthalpy of the chemical reaction in the cell. Similarly, for a Carnot process, the thermal energy of the hot well can be generated by the combustion corresponding to a chemical reaction. A corresponding temperature can, for example be estimated using the adiabatic flame temperature of the process. This leads to the desired connection which allows both processes to be compared, and, unsurprisingly, the maximum efficiencies are identical. Hence, if put on common ground electrochemical energy conversion is not different from other energy conversion processes.

Why are the oxygen reactions so sluggish? Obtaining information about the working catalyst is an extremely challenging task (we shall also discuss this later), but so far there are several approaches to rationalize this problem. I have already mentioned that for the ORR and OER, four electrons have to be transfered, and several intermediates will be present on the surface. If only one of them is energetically unfavorable this will result in a bottleneck for the whole reaction network. An inspiring approach to develop new ideas is to draw parallels between electrocatalysis and biocatalysis. Nature has evolved tremendously efficient enzymes to drive either process and achieves high efficiencies by

specifically adapting the reaction center and its surronding for every single step and intermediate. A discussion on similarities and differences between electrocatlysis and biocatalysis can be found in [46].
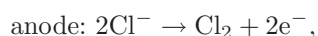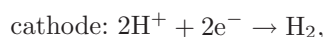
4. – Two examples for electrochemical processes that are large parts of our economies

Before turning to the topic of large-scale electrochemical energy storage systems and discussing the state of the art in materials science, interface design and electrocatalyst development, I would like to roughly outline two examples of the application of electrochemical processes in industry. How large can electrochemical processes be scaled up and which technologies are typically applied?

Let us take a look at the products of chemical industry and look for large-scale applications of electrochemistry. What chemicals are produced world wide and what are the largest annual productions volumes? One of the all time champions of chemicals is probably sulfuric acid with a production of more than 250 million tons worldwide. Ethylene and propylene are also large-scale products with productions of more than 120 million tons worldwide and 70 million tons worldwide. Not to forget ammonia, with its importance for fertilizers (170 million tons per year) [47].

In most lists of large-scale industrial chemicals we will also find our first candidate —chlorine. It is produced in quantities of more than 50 million tons per year worldwide [47] and it is an essential ingredient for chemical industry. It is, for example, used in producing PVC, polyurethane or silicones and for the synthesis of fine chemicals and pharmaceuticals.

From the electrochemical series we find that chloride to chlorine has a half-cell potential of $-1.4\,\text{V}$, so chlorine is a very potent oxidizing agent. Hence, it is difficult to come by an even better chemical oxidation agent to convert chloride into chlorine. While chloride ions are abundant and available cheaply in rock salt or in brine, the most efficient way of reducing it to chlorine is by means of electrochemistry. The overall reaction to yield chlorine is

$$\text{cathode: } 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2,$$
$$\text{anode: } 2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-,$$
$$\text{overall with Na}^+ \text{ as cation: } 2\text{NaCl} + 2\text{H}_2\text{O} \rightarrow \text{Cl}_2 + \text{H}_2 + \text{NaOH}.$$

Typically, brine solution (sodium chloride) is electrolysed and side products are sodium hydroxide and hydrogen. (Sodium hydroxide can also be found in our list of large-scale products, actually because it is a side product of chlorine synthesis. While being used in paper and textile industry, supply is actually greater than demand.) The separation of cathode and anode reactions is of special importance in this process and is achieved using an appropriate diaphragm (this process is also termed "diaphragm process" in contrast to the "mercury amalgam" process) which nowadays is a cation exchange membrane (see fig. 11). In practice the process is actually done at 4–5 V at 400 kA.
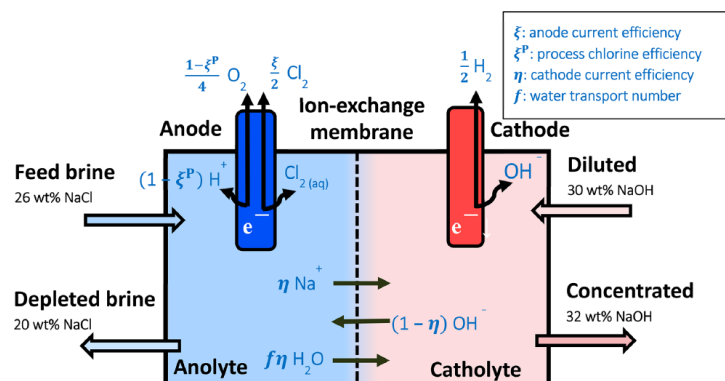
Fig. 11. – Schematic overview of a membrane-based clorine alkaline electrolyser. Figure adapted with permission from [48].

A second glance at the reaction and our electrochemical potential series should get us thinking: As the potential for chlorine evolution is larger than that for oxygen evolution, our electrolysis cell should be producing oxygen and hydrogen, instead of chlorine and hydrogen. However, as we have seen above, the overpotential of an electrochemical reaction can play a decisive role. In this case, it raises the potential for the oxygen evolution to over 1.4 V such that indeed chlorine is produced, not oxygen (note that also high concentrations of NaCl are used).

Note that we again discover the oxygen evolution to be sluggish compared to other reactions, in this case it actually facilitates chlorine evolution. Another thing to note is a technical issue: As chlorine gas is produced at the anode, is can easily be envisioned that the reaction conditions are extremely corrosive at potentials of several volts with an electrode that is immersed in chlorine gas and brine. Hence, very resistant materials are used as electrodes, in this case often titanium or even platinum or platinum alloyed with other nobel metals like ruthenium.

The next electrolysis product we turn to has a few similarities —it is also produced in the order of 60 million tons per year worldwide —this is rather a coincidence —and it also requires large potentials, which is no coincidence at all, but rather the reason why it is beneficial to do it via electrolysis. However, what we are aiming at in this case is rather a reduction, a reduction that requires 1.66 V and converts alumina to aluminium. This metal, although used in such a broad variety of applications —from tin foil to aerospace applications— is one of the least noble metals we know. It is metastable, however, it passivates with a remarkably stable oxide layer. The industrial process we will look at is called the Hall-Héroult process (see fig. 12) in which a molten mix of alumina (Al_2O_3) and cryolite (Na_3AlF_6) —which is used to lower the melting point of the mix— are electrolysed at temperatures around $1000\,°C$. Just like for the chlorine electrolysis, typical voltages are around 4–5 V at currents around 200 kA. The overall
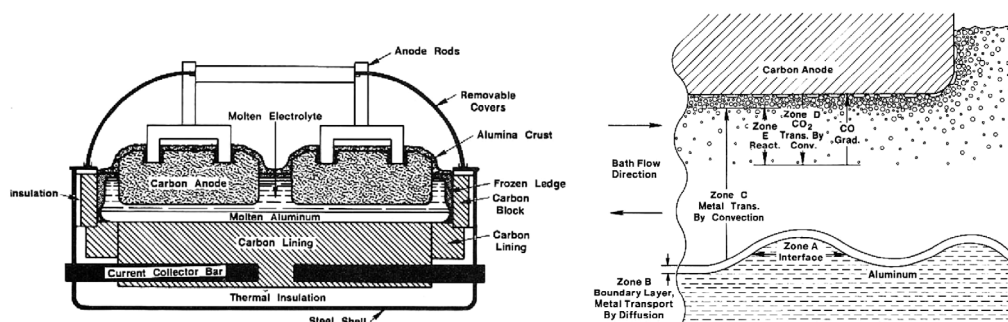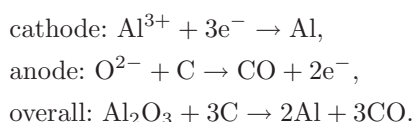
Fig. 12. – Typical cell setup for the Hall-Héroult process (left) and closeup schematics of the interface regions. Figure adapted with permission from [49].

process consists of

$$\text{cathode: } Al^{3+} + 3e^- \rightarrow Al,$$
$$\text{anode: } O^{2-} + C \rightarrow CO + 2e^-,$$
$$\text{overall: } Al_2O_3 + 3C \rightarrow 2Al + 3CO.$$

Note that typically more CO_2 is formed at the anode than CO (so a parallel process is: $2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2$). Why do we produce CO and CO_2? The electrons needed to reduce Al^{3+} come from the oxygen, and in principle the anode half-cell reaction should be oxygen evolution. However, as oxygen readily oxidizes carbon, this extra reaction is used to reduce the cell voltage for the overall process. Hence, in practice rather than evolving oxygen on the anode, a sacrificial anode is used that is made of carbon that is converted to CO and CO_2 in the process.

In Germany, the annual production for chlorine between 2010 and 2015 was around 5 million tons and with an estimated energy consumption of 3000 kWh/t this amounts to 15 TWh of electricity per year. Aluminium production in Germany has been above 500 000 t per year and with an estimated energy consumption of 15 MWh/t so we end up with 5–10 TWh. Both together add to around 20 TWh (please keep this number in mind for the next section!) which are comparable to around 4% of the German annual electricity consumption and in agreement with what these industries usually state for themselves [50, 51]. This shows that as far as electrolytic processes are concerned, industry provides several examples for fascinating and highly evolved processes that are being carried out today and in very large scales.

5. – Hydrogen, oxygen and water —fuell cells and electrolysers

In the introduction I have already elaborated on how water splitting and hydrogen as energy carrier is one possible solution to store energy and overcome the problems associated with the intermittency of renewable energies. However, we also have to ask

the question whether it is feasible to use hydrogen production in industrial scale to convert and store electrical energy from renewables on a national scale. I have been using Germany as an example (well, yes, I'm German ...) here, but I would encourage you to research the numbers and do the math for your country. I more or less randomly chose the optimistic 10% of Germany's electricity that we should be able to store, which amounts to something like 50 TWh.

Now we actually come to the main reason why I have been discussing chlorine and aluminium electrolysis in the previous section. Looking at the bare numbers for already existing industry branches that rely on electrochemical processes, it seems feasible to suggest water electrolysis as a solution to the large-scale storage problem. We are already using close to 5% of the electricity in Germany to do electrolysis, so building up a water electrolysis and hydrogen infrastructure for 10% is challenging but does not seem so unlikely anymore.

What do we need? Two components: a water electrolyser and a fuel cell. While the latter has been and is developed to higher and higher efficiency and performance, water electrolysis technology is surprisingly old, but still has a long way to go and much more potential to be explored, depending on how you look at it. This is actually not as contradictive as it seems at first sight: Fuel cells offer the opportunity to reduce the emissions of mobility and offer profits as high-tech products while electrolyzers yielding hydrogen are not an attractive technology as long as hydrogen is also available cheaply from abundant fossil resources.

5˙1. *Hydrogen and oxygen to water —Proton Exchange Membrane (PEM) fuel cells.* – If we look at the simple conceptual electrochemical cell setup in fig. 4 one might get the impression that an electrolyser and a fuel cell setup should look something like this. The truth, of course, is far from it and we shall go through it component by component for the fuel cell and then move on to the electrolyser to talk about conceptual differences.

Note that in the following, I will zoom in more and more on very specific systems, technologies and problems as covering the vast field of fuel cells and electrolysers is literally impossible in one excerpt. For an overview over fuel cell technology, there are several reviews that I list in refs. [52-54]. But before turning to the PEM-FC that I will discuss in the following, let me emphasize that, by doing this, I am actually skipping a highly relevant system, that has many advantages in practical applications —the solid oxide fuel cell (SOFC) and the solid oxide electrolyzer cell (SOEC) [55,56]. I will not go into detail here, but recommend that you educate yourself on this system and compare to the low-temperature solutions I will discuss in the following.

The basic half-cell reactions for the fuel cell reaction have already been discussed in sect. **3**˙1 and we have also already outlined that the process should yield a cell voltage of 1.23 V but the overpotential of the oxygen reduction reaction and Ohmic losses, diffusion processes etc. lower this to an actual 0.7–0.9 V.

So what can we do need for an optimal operation? First of all, optimal diffusion and transport of reactants and electrons. For this purpose, we want to bring anode and cathode as closely together as possible while strictly avoiding gas crossover in order
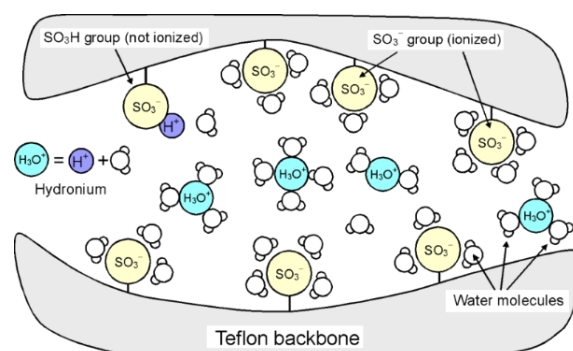
Fig. 13. – Schematic illustration of a proton conducting membrane like Nafion. A fluorinated carbon backbone offers high chemical stability while sulfonate groups that can easily be protonated and deprotonated ensure high ion conductivity. Figure from [57] under Creative Commons Attribution License.

to counter unwanted reactions. Whatever separates anode and cathode should hence prevent hydrogen and oxygen from permeating and at the same time allowing protons to be shuttled towards the cathode. For this purpose, Nafion (see fig. 13) is the go-to solution nowadays. Chemically, mechanically and thermally very stable, a very good proton conductor and insulating against short circuiting the cell it has proven to be a versatile material that has found extensive application as membranes in electrochemistry. In order to achieve short distances between the two sides of the membrane, the key design of a fuel cell (and an electrolyser) is the membrane-electrode-assembly (MEA). This already implies the setup: Membrane and electrodes are actually one piece, and reactants, products as well as the current are delivered on the backside of the corresponding side of the MEA (see fig. 14). This leads us to a typical cell construction —with the membrane in its center, the catalyst formulations —a catalytic material together with a support material and something called binder, that allows to prepare a catalyst ink that sticks are coated onto the membrane. This is then mounted between two plates which act as electrical contact and contain a flow field. The flow field is an array of channels designed in such a way that the reactant gasses are optimally supplied and products are optimally removed from the interface.

The design of membrane, flow field and bipolar plates are crucial for minimizing the losses and optimizing the efficiency of the fuel cell. However, if we want to dig deeper into what limits the performance and practicability, we have to go down to the atomistic level. Here, there are three main aspects that have to be controlled for optimal operation. The first thing is the three-phase boundary. Converting gas into liquid water on a solid catalyst is one of the most challenging setups for catalyst optimization. First of all, the interface between the different media has to be maximized (porosity is the key here). Then, the catalyst has to be accessible to the reactants and products must be removed efficiently. Furthermore, we need a good catalyst that lets the fundamental reaction proceed with minimal reaction barriers and avoids unfavorable intermediates
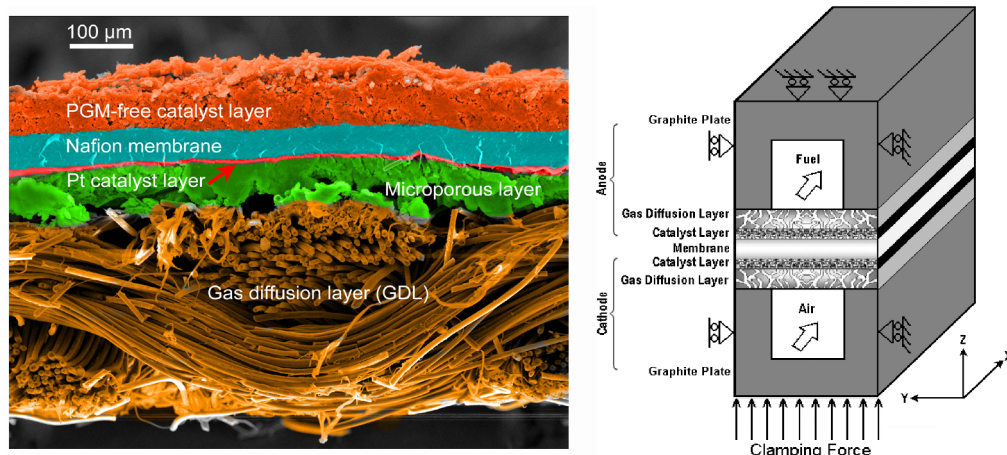
Fig. 14. – Left: Scanning Electron Microscopy (SEM) micrograph of a PEMFC MEA (see also [57]). Source: Wikimedia (`commons.wikimedia.org/wiki/File:SEM_micrograph_of_an_MEA_cross_section.jpg`) by Xi Yin under Creative Commons Attribution-Share Alike 4.0 International license. Right: Schematic view of the corresponding cell. With permission from [58]. Note that in practice, several extended cells of this type will be stacked to obtain the actual fuel cell.

or side reactions. Finally, the noble metal catalyst is also very pricy, so we should aim at low catalyst loadings and a material that has high surface to volume ratio, as the surface is the active part, while the volume of the material is not in contact with the reactants. The material choice that has been evolving over the last decades are pure or alloyed platinum nanoparticles supported on graphitic carbon which is a cheap, robust, and conductive material with high surface area. Note that on the anode, materials experience the oxidizing half-cell potential around 0 V while at the cathode the oxygen reduction reaction is associated with a reducing potential of around 0.8 V. If we consult the Pourbaix diagram of platinum (see fig. 18) and check the potential range between 0 and 1 V in acidic conditions we see that metallic platinum is mostly stable in this region.

But why platinum as catalyst? If we want to understand what makes a good catalyst for the ORR, we first need to acknowledge the complexity of this reaction. In order to convert an oxygen molecule to two water molecules on a catalyst, the oxygen atom has to interact with the catalyst, the oxygen-oxygen bond has to be cleaved and along the way four electrons and four protons are required (see fig. 15 left). Afterwards, the product has to be removed from the catalyst. If one only considers the possibility of transferring protons and electrons together the decisive question is at which step is the oxygen-oxygen bond cleaved. An early bond cleavage might generate oxygen atoms or hydroxides (OH or OH^-) while a late bond cleavage might first generate peroxide (H_2O_2) before going to water [59].

Which path is taken depends on the catalyst material, the surface structure, the pH and even the electrolyte composition [60]. While this illustrates the complexity of the reaction system, there are some very helpful concepts that have been developed to
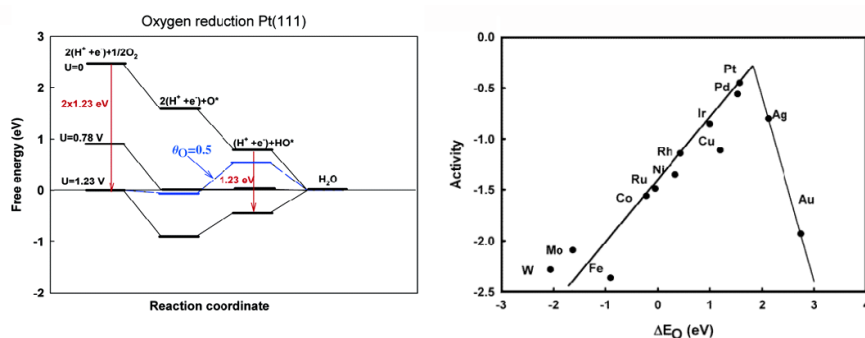
Fig. 15. – Nørskov an coworkers discuss the origin of the overpotential for the ORR in detail. Left: computed reaction path depending on the applied potential. Right: volcano plot for the ORR, for which the oxygen adsorption strength is plotted agains the activity of a catlyst material. Figure reproduced with permission from [61].

rationalize the different influences. The first one is Sabatier's principle. It outlines the importance of adsorption of reactants and desorption of products: If the reactants bind too weakly to the catalyst, few molecules will be adsorbed and reaction rates will be low. If they bind too strong, they will block the catalyst and reaction rates will also be slow, so there is an optimum adsorption energy [61, 62]. Furthermore, there have been many studies showing that if reactants and products are somehow structurally related, it is often true that the adsorptions strengths are also related. Hence, if the reactants bind very strongly to the catalyst, so will the products, effectively impeding removal of products from the catalyst, blocking reaction sites and ultimately decreasing reaction rates.

As a consequence, if one plots the activity of a given catalyst against the adsorption energy of reactants and products (this even works for intermediates) one obtains a typical "volcano plot" with an incident increase and then a decrease after passing through an optimal adsorption strength (see fig. 15).

The scaling relations derived from this principle are a whole subject by themself and thoughts about their generality and how to use them to optimize catalyst systems has helped to develop several new Ansätze for catalyst systems [63, 64]. For hydrogen and oxygen, this optimal adsorption strength lies very close to the value observed on platinum, which is the reason why it is used as catalyst. Several attempts have been made to further optimize this system by synthesis of alloys with cobalt or nickel or by developing core-shell structured nanoparticles to further increase activity, surface-to-volume ratio and to replace the inactive platinum atoms in the bulk of the nanoparticles by less scarce materials [65, 66].

Another focus of research to optimize fuel cell catalyst is understanding the processes that limit their lifetime. The basic question is what decreases the number of catalytic sites in the material over time. For platinum nanoparticles, several mechanisms have been identified and even quantified under controlled conditions: Sintering of particles, Ostwald ripening (the process of smaller particles shrinking and larger particles growing
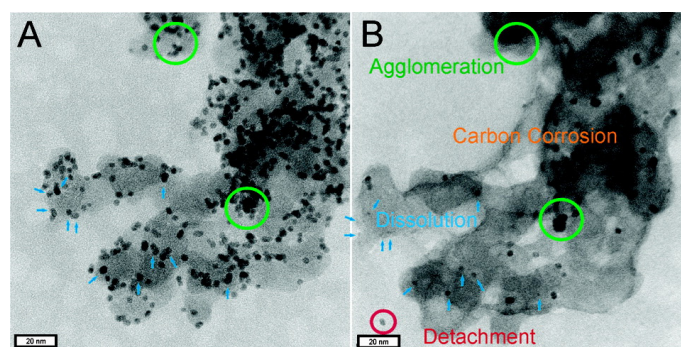
Fig. 16. – In their study, Meier *et al.* managed to find idential locations of a platinum nanoparticle for TEM imaging before and after successive electrochemical tests. This way, they were able to study and quantify catalyst degradation mechanisms for these materials. Figure reproduced with permission from [67].

due to dissolution and redeposition of atoms in solution), particle detachment and carbon degradation (see fig. 16) [67,68]. Here, also simulations have been able to contribute to the state of understanding we have now by studying of how and where nanoparticles interact with the carbon support [69-71].

You can imagine that for a computational chemist working on atomistic modeling of catalysts this is an exciting field with the potential to develop novel materials by rational design based on fundamental understanding of the reaction mechanism.

The good news is: Recently, there has indeed been a breakthrough that will allow for significantly lower catalyst loadings, improving the systems performance and durability. However, it was *not* about optimizing things at the atomistic level. I have already stressed the complexity of dealing with three-phase boundaries above and the breakthrough made is connected to exactly this. If you have a catalyst in a porous material that converts reactant gasses to a liquid, maintaining consistent operation conditions is crucial —if water floods the support pores or the catalyst is not exposed to the gas-phase, poor performance due to insufficient transport is the result (see fig. 17). So, after all, it is not surprising that the real breakthrough was achieved by rationalizing how the surface morphology of the support and the pore size distribution can be optimized, ultimately leading to materials with greatly improved performance [72,73].

5˙2. *Water to hydrogen and oxygen —electrolysers*. – For a typical PEM electrolyser, the cell setup consists of a membrane, which forms a unit with the catalysts coated on it and is sandwiched between flow field and bipolar plates [74]. So overall, the design is very similar to a fuel cell with specific changes, as water is the reactant and the products are gasses. But conceptually, this is where the similarities end. The basic outline of the operation conditions should suffice to highlight the differences: At the cathode, reducing potentials are used to convert protons, taking up electrons, to hydrogen. At the anode, these electrons are obtained by oxidizing the oxygen atoms in water to dioxygen. The
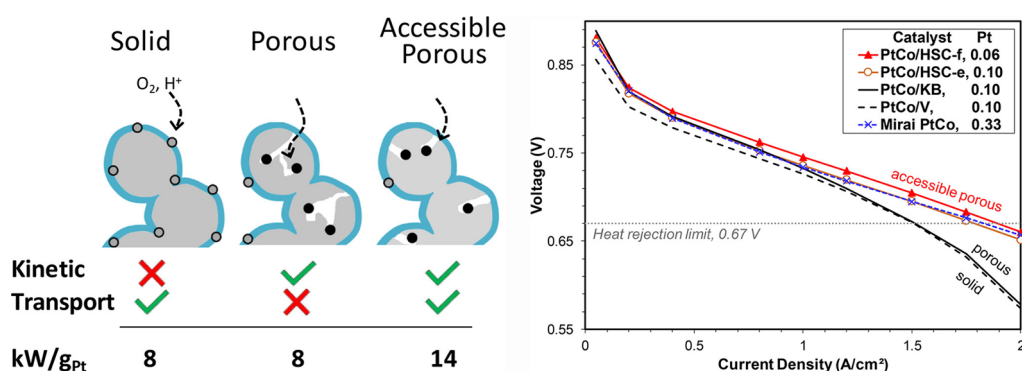
Fig. 17. – Yarlagadda *et al.* report on how different types for pore structures in carbon materials influence catalyst activity. Black cycles denote active, grey cycles denote less active nanoparticles, blue denotes adsorption of ionomer on the support material. The panel on the right shows how increased activity is obtained when accessible pores are available. Figure reproduced with permission from [72].

half-cell potential of this reaction should be 1.23 V, but as we have seen already it is actually closer to two volts in practice. So, while in the fuel cell, our catalyst for the oxygen reduction is subject to "mild" potentials, here we are dealing with oxidizing potentials between 1.5 and 2.0 V. One glance at our electrochemical potential series (table I) shows that this is in-between the oxidizing power of chlorine and fluorine! Maybe you have seen a video of how much this is —elemental fluorine (half-cell voltage of 2.87 V) will react so violently with anything that it will ignite a brick if it is subjected to fluorine. Anyone who has ever used a chorine (or hypochlorite) based bleaching agent or detergent will know how aggressive even that 1.36 V oxidizing power of chlorine is.

A glance at the Pourbaix diagrams for noble metals (see fig. 18) reveals what this means in terms of materials science: Platinum will be platinum oxide and iridium alike. In fact, pretty much all noble metals will oxidized beyond 1.5 V. Hence, the catalyst for the OER must be different from a catalyst for ORR because, as we have seen before, platinum, for example, will be platinum at ORR potentials, but will be platinum oxide at the elevated OER potentials. The benchmark catalyst for high-performance acidic PEM electrolysis of water is currently iridium, or actually iridium oxide [77]. One of the reasons for this is also the fact that it is a *conducting* oxide, which certainly helps in bringing electrons from the surface to the electric leads (note that the corresponding platinum oxide is an insulator). IrO_2 is one of the few materials that are actually *stable* in these harsh conditions. Overall, for OER finding a stable material is almost equally important to finding an active material, as one cannot afford to apply rare noble metal catalysts if the material degrades in a matter of hours. Hence, what might seem a very exotic research topic has obtained increasing attention in recent years: *Noble metal corrosion.* Knowing how and under which circumstances metals like platinum and iridium corrode, degrade and dissolve is highly relevant for electroctatlytic processes that require high potentials (see fig. 19) [78, 79].
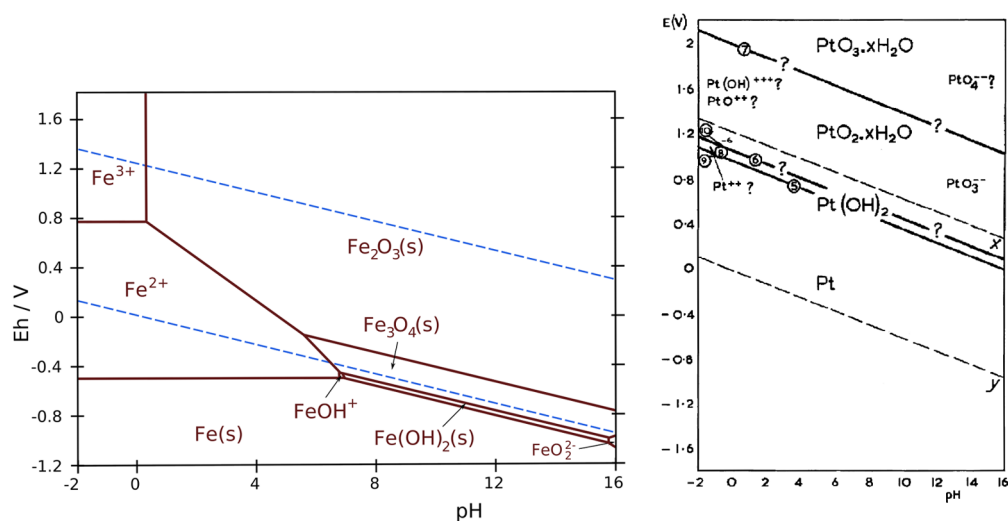
Fig. 18. – Left: Pourbaix diagram from iridium (in HCl), dashed lines denote stability window of water. Right: Pourbaix diagram for platinum. Reproduced from [75] under Creative Commons Attribution 4.0 International License. Reproduced from [76] under Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International License.

Note that while many papers that can be found in the literature focus solely on activity, in a recent study, we have presented a test protocol to monitor activity but with an equal focus on the durability of a material. First results suggest that current catalysts
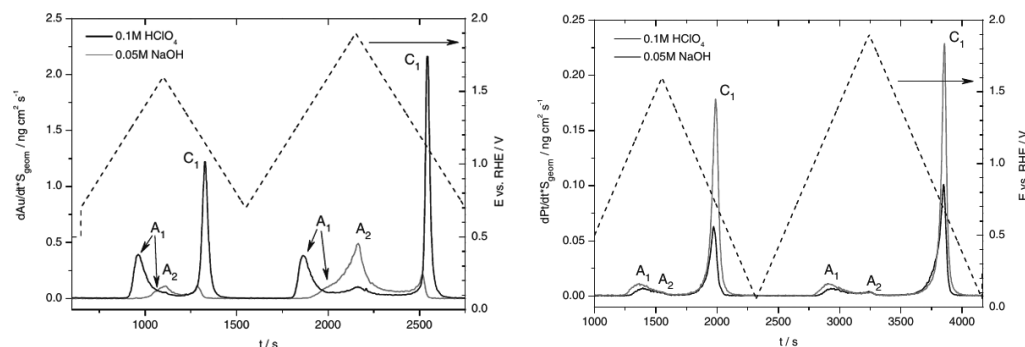

Fig. 19. – By coupling a mass spectrometer to an electrochemical flow cell, the group of Mayrhofer was able to study noble metal corrosion in detail. The dashed lines indicate the applied potential while the solid signals quantify dissolved noble metal ions [80]. The investigation of gold corrosion (left) and platinum corrosion (right) show that for both cases no continous corrosion occurs, but noticable amounts of noble metal are dissolved while *reducing* the oxide formed at higher potentials. Figure reproduced from [81] under Creative Commons licence (Attribution-NonCommercial-NoDerivatives 4.0 International CC BY-NC-ND 4.0).

span a broad range including highly active materials that degrade very quickly but also materials that are very stable but only mediocre catalyst for the OER [82].

One might think that in the end improving PEM electrolysers is a mere engineering problem —just like developing materials for high temperature combustion chambers or fusion reactors. However, there is another complication— if we want to understand and optimize materials, we need in depth studies of the material. However, the material we need to investigate only exists at high potentials, as noble metals will revert to their elemental state without the applied potential. Hence, it seems inevitable to do *in situ/in operando* (on the "working" catalyst) studies in order to learn anything about the actual system under operating conditions. For an electrocatalytic system, this means using a surface sensitive method on an inhomogeneous material (note that supports and catalysts tend to be black powders or coatings in practice) in an electrolyte which is, at the same time, the reactant in an electrochemical cell. This immediately eliminates ultra high vacuum and low temperature measurements which are often applied in surface science. In situ/in operando techniques that are selective and sensitive enough, like modern x-ray absorption spectroscopy, have only just reached the maturity to be applied to these complex problems. This is the reason why we have only started to obtain a more detailed understanding of the relevant processes and properties in recent years.

To give you a rough idea, one of these methods is outlined in fig. 20. Using x-ray photoelectron spectroscopy, which is sensitive to the electronic structure around a nucleus, one has the chance of observing changes in the material during the reaction. While approaches like this will help us to understand more and more details of the complex underlying processes, innovative methods like this take a huge effort to set up thorough studies to interpret the results [84].

6. – Summary and concluding remarks

Hopefully, this proceeding has been helpful in understanding why electrochemistry is a key component for energy conversion in a sustainable energy scenario.

We have seen how electrochemistry takes chemical reactions and disassembles them into half-cell reactions so that chemical energy can be converted directly into electrical energy or vice versa. The driving force behind this is the potential of the electrons and can be systematized in the electrochemical series. We have learned about some basic electrochemical experiments and that the electrochemical potential not only drives reactions but also induces changes in the materials. Hopefully, I have been successful in outlining the basic influences on electrochemical reactions like electrolyte, surface composition and morphology, what an overpotential is and how it can be reduced. We have glimpsed at two large-scale industrial processes that utilize electrochemical setups and discussed national scales (using Germany as an example) for the production of chemicals but also for the conversoin of energy. The latter is done via electrolysers and fuel cells if we chose to focus on water splitting and hydrogen as energy carrier and we have looked at conversion losses, where they come from and how they can be minimized.
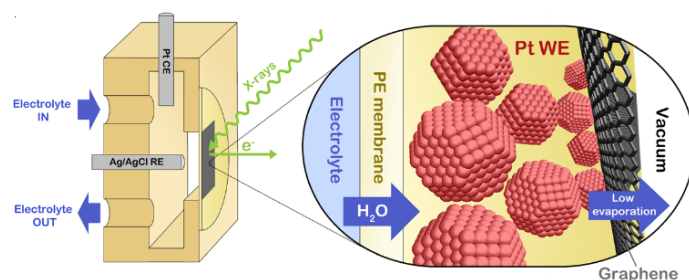
Fig. 20. – Experimental setup for an electrochemical cell for operando x-ray photoelectron spectroscopy. The group of Schlög *et al.* have recently published several spectacular exeriments that allow to monitor the change development of the bulk and the surface during an electrocatalytic reaction by combining electrocatalytic experiments and synchrotron radiation. Figure from [83] under the terms of this ACS AuthorChoice/Editors Choice via Creative Commons CC-BY agreement.

My resume would be to state that storing energy on national scales can be achieved using this route and while fuel cell technology is very close to being available in large scales for mobility and stationary applications, water electrolysis still poses some challenges. However, even as most plants are in the pilot stage currently, large companies are surpassing the MW scale and have already stared planning bigger facilities yet. And although we might face several challenges in the future, I firmly believe that the joint efforts of research facilities and industry, of chemists, physicists and engineers, of synthesis, analysis, materials science, modelling and device engineering will enable us to understand limitations and innovate better solutions.

While I hope to have given an overview from basics into the challenges for state-of-the-art systems, most of all I hope to have encouraged the inclined reader to dig in a little deeper and follow up on reading the literature provided in my overview —there is much exciting science and technology to discover!

* * *

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