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Proton Exchange Membrane Fuel Cells Platinum-Free Oxygen Reduction and Performance Degradation by Start-Up/Shut-Down Events

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1. Introduction

Legal/Political Necessities for Zero-Emission-Vehicles (ZEVs)

For the first time ever, almost all existing countries have obliged themselves to lower greenhouse gas (GHG) emissions with the agreement reached by representatives of 195 countries at the platform of the *United Nations* in France 2015,¹ even if current political decisions may have volatile character and the U.S. recently even announced to withdraw their participation.² While this agreement does not contain explicit goals or thresholds for the emission of GHGs in each participating country, it obliges nations to define, pursue and document such. In 2014, $\approx 26\%$ and 23% of the GHG emissions in the U.S. and E.U., respectively originated from the transportation sector.^{3, 4} Thereby, transportation comprises the second largest GHG contributor by economic sectors in both regions (electric power industry is the largest contributor with 30% in the U.S. and 26% in the E.U., both in 2014).^{3, 4} Within transportation, a major fraction of GHG emissions is due to passenger cars (42% in the U.S. in 2014).³ In order to tackle the GHGs emanating passenger vehicles, eight federal U.S. states and one Canadian state together with four European countries founded the ZEV (zero-emission-vehicles) alliance. The *ZEV alliance* set its goal “to make all passenger vehicle sales in our jurisdictions ZEVs as fast as possible, and no later than 2050”.⁵ A goal due in 2050 may seem far in the future and indeed O’Neill and Oppenheimer have discussed the importance of appropriate timing in the reduction of GHG emissions with respect to the expected climate impact.⁶ However, there are also earlier political goals existing. A recent example can be found in the German federal council, which voted for a general prohibition of cars with internal combustion engines (ICEs) from 2030 on, although, admittedly, this vote is not legally binding.^{7, 8} In The Netherlands, the parliament gave an initial approval to ban new diesel or petrol cars from 2025,⁹ while Norway is likely to prohibit both, from the same year on.¹⁰

Current Status of ZEVs

A straight forward definition of the term zero-emission-vehicle (ZEV) was established by the *California Environmental Protection Agency*, i.e., referring to ZEVs only as vehicles without any possible local GHG emission during operation as it is the case for battery or fuel cell electric vehicles (BEVs or FCEVs).¹¹ However, the before mentioned *ZEV alliance* additionally include plug-in hybrid electric vehicles (PHEVs) into their definition of ZEVs.⁵

The *International Council on Clean Transportation* evaluated the current status of electric vehicles on the market according to a categorization into five groups of technology adopters, as can be seen in **Figure 1**.¹² Clearly, it is not necessary to elaborate all details of Rogers’ theory of the “*Diffusion of Innovation*” here.¹³ Briefly, it assumes a bell-shape for the probability that a new technology is adopted

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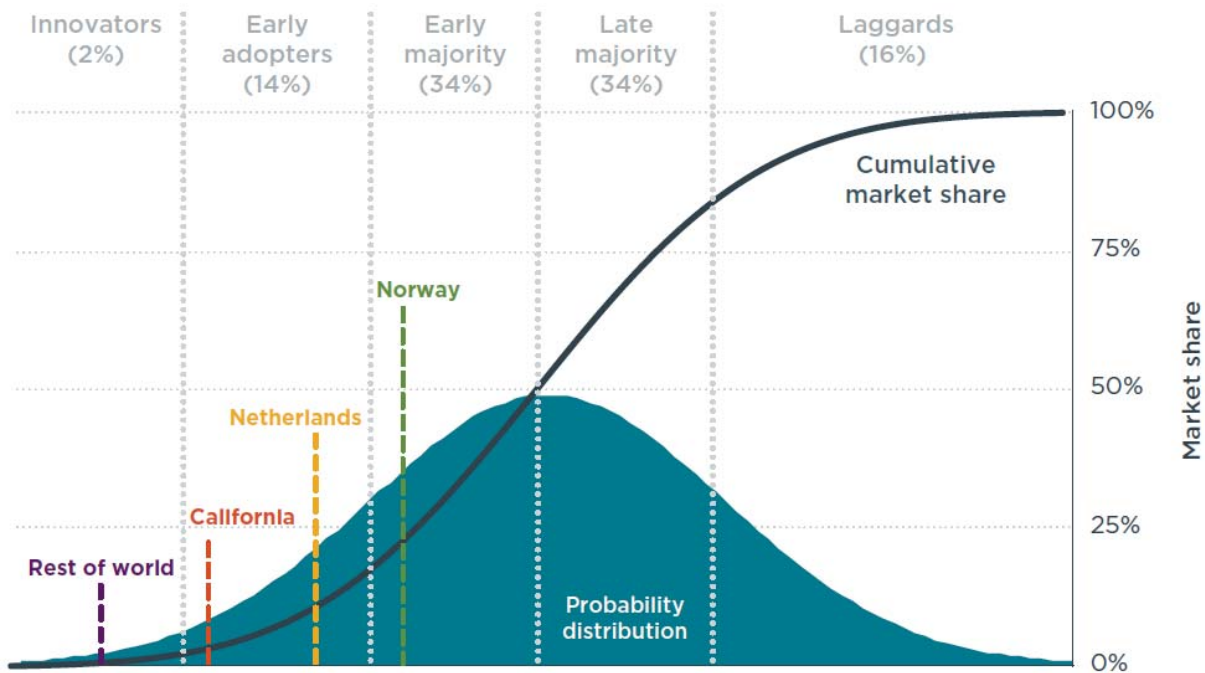


Figure 1. Electric vehicles and technology adoption in various markets as shown by Slowik and Lutsey.¹² Reproduced with permission of the *International Council on Clean Transportation*.

over time, and then converts the time axis into five categories, according to statistical metrics. From **Figure 1**, Norway is the only market which is approaching the tipping point, where electric vehicles are widely accepted, while all other countries are still settled in earlier stages of technology adoption. Norway's above mentioned tight goal of banning new ICE cars from 2025 in combination with its rich abundance of hydropower electricity is reflected by the comparably high market share of 22% electric vehicles.¹² Next highest, The Netherlands and California exhibit already significantly lower shares of electric vehicles on the automotive market, while other countries fall even more behind with an average share of <1%.¹² It should be noted that among ZEVs, current market shares of FCEVs sold seem rather negligible to date: in the period from 10/2015 – 10/2016, *Toyota Motor Co.*, one of the three car makers with commercialized FCEVs (status 12/2016)¹⁴⁻¹⁶ disclosed a share of $\approx 0.02\%$ for FCEVs of their overall car sales.¹⁷ The following paragraphs thus address benefits and hurdles the previously mentioned ZEV approaches have to overcome in order to increase *future* market shares.

BEVs and PHEVs. With the so far low shares of ZEVs within global car sales, it is necessary to overcome technological and financial hurdles: One critical restriction customers of BEVs experience is the generally low mileage, resulting from the limited energy density of battery systems, which is likely to restrict realistic driving ranges of mass-market vehicles to around 320 km or less, even taking into account projected technological progress.¹⁸ Gröger et al. have assessed available data in detail, finding that the before mentioned 320 km range will likely translate into battery-system cost and weight (net, i.e.,

excluding penalties from structural integration into vehicle) of $\approx 7.0 - 13$ k\$ and ≈ 220 kg per car, respectively.¹⁸ PHEVs, in contrast, can offer mileages on the order of conventional ICE cars, however, at the cost of gradually increasing their GHG emissions from essentially zero in purely electric drive mode towards levels of ICEs.¹⁹ As the purely electric drive mode of PHEVs is often restricted, e.g., to ≈ 35 km in case of the 2017 model *Toyota Prius Prime*,²⁰ or $\approx 37 - 40$ km for the 2015 *BMW 330e* sedan,²¹ truly zero emissions of PHEVs under daily-life applications are essentially not the case.

Another challenge battery cars face is the time requirement for charging. At the 3.6 kW charging power of a typical household electrical outlet (in the E.U.), charging 42 kWh (projection in accordance to 320 km range¹⁸) into an EV battery requires >11 h. If one – irrespective of physical and chemical restrictions of batteries under fast charging conditions – were willing to charge the same battery in a time frame that is similar to the refueling time of an ICE car (assume 5 min), it would require an overwhelming charging power of >500 kW. For comparison, the 2015 average name-plate output of a wind turbine in the U.S. is $\approx 2,000$ kW, i.e., only four times larger – if it were to run at full power constantly.²² Plans exist to set up a charging network, consisting of about 400 stations capable of up to 350 kW charging power along long-distance travel routes in Europe.²³ Current *superchargers* installed by *Tesla Motors Inc.* are capable of up to 120 kW charging power.²⁴ However, such publically dispersed charging stations are rare (≈ 750 *Tesla* superchargers worldwide in Dec. 2016²⁵), thus a majority of electric vehicle customers will require charging at their homes. While it may not be necessary to charge an electric vehicle battery at maximum rate while being at home, either the above mentioned time frame of ≈ 11 h needs to be accepted, or additional charging power needs to be installed. If electric vehicles were to set the market majority, the latter option would likely be limited by the electrical power available at private homes. For example, in Germany, DIN 18015-1 regulates the standard installed power in private houses comprising of 1 to 100 apartments, ranging from ≈ 15 to ≈ 100 kW in total.²⁶ Projecting the costs associated with the expansion of essentially all private electric infrastructure is beyond the scope of this work, however it can be assumed monetarily unattractive.

Taking into account previously ignored physical and chemical restrictions, it needs to be noted that materials nowadays typically used in lithium-ion batteries, as, e.g., based on LiFePO_4 as cathode material, have demonstrated, in principle, to be (dis-)chargeable at high rates (i.e., corresponding to the exchange of one full equivalent of their maximum energy content in fractions of an hour), as was reviewed, for example, by Kucinskis et al.²⁷ and Zhang.²⁸ However, fast charging is known to lead to unwanted reactions as, e.g., Li plating²⁹ and is ultimately reducing lifetime.^{30, 31}

Along with the difficulties of range restriction and long “refueling” time compared to ICE cars discussed in the above paragraphs, the associated necessity for the customers to change their behavior when switching from ICE cars to BEVs may be most critical, as was recently summarized by M. N. Eisler:³²

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“The question is not whether the battery electric vehicle can be made to adapt to society but whether society is willing to adapt to it.”

FCEVs

In contrast to users having to adapt their behavior to meet the requirements of BEVs, FCEVs powered with hydrogen can offer usage patterns similar to ICE cars. SAE norm J2601 states a standard fueling time target of ≈ 3 minutes,³³ and previously demonstrated fueling times from 20 - 95% state-of-charge (at a total capacity of 5 kg hydrogen) are close to this target, i.e., at ≈ 3.3 minutes.³⁴ As a rule-of-thumb, a hydrogen consumption of ≈ 1 kg/100 km provides a good estimate.¹⁹ Thus, driving ranges similar to ICE cars are realistic, and *Toyota* demonstrated a single fueled travel from Osaka to Tokyo (≈ 560 km) already in 2008.³⁵

PEMFC Limitations

In the style of 1928 U.S. presidential candidate Herbert Hoover promising two cars in every garage, in 2005 Mathias et al.³⁶ went a step further asking *“Two Fuel Cell Cars In Every Garage?”* Their article summarizes major hindrances and challenges proton exchange membrane (PEM) fuel cells have to overcome for a successful penetration of the automotive market. One major hurdle is cost, with the U.S. Department of Energy (DoE) defining a target of \$40/kW by 2020 and an ultimate target of \$30/kW for the complete automotive fuel cell power system. At a 2015 cost projection of \$53/kW, neither of these targets is met to date (see **Figure 2**). Durability is the second target which is not yet met or close to being met currently. This Ph.D. thesis devotes a chapter to each of the mentioned PEMFC shortcomings, dealing with potential catalyst materials for the reduction or substitution of Pt, which finally aims at lowering costs; and dealing with issues regarding durability related to repeated start-up/shut-down of PEMFCs. Both issues will be explained further in the following.

High Platinum Demand. In their article, Mathias et al. identify membrane and electrocatalyst as major cost drivers, where they consider the cost for membrane material $> \$15/\text{kW}$ for the low production rates in 2005, while projecting values of approximately $\$1.5/\text{kW}$ for a production rate equivalent to approximately one million fuel cell cars per year,³⁶ which would render a large-scale commercialization of FCEVs viable from a membrane cost point-of-view. Electrocatalysts as second major cost driver target values $< \$5/\text{kW}$ (obtained from the 2020 DoE target of $0.125 \text{ g}_{\text{Pt}}/\text{kW}$,³⁷ multiplied with an estimated cost of $\$35/\text{g}_{\text{Pt}}$ in the catalyst³⁶). At a gross power of 100 kW, this would correspond to $\approx \$450/\text{car}$ for the $12.5 \text{ g}_{\text{Pt}}$ in the catalyst, while current FCEV manufacturers use Pt rather on the order of $30 \text{ g}/\text{car}$,^{38, 39} corresponding to $\approx \$1,050/\text{car}$. It is not only because of this cost gap that automotive suppliers target $\approx 12 \text{ g}_{\text{Pt}}/\text{car}$ by 2020,³⁸ but also with view on platinum availability. In 2010, already 34% of the platinum world production of 181 t were used in the automotive industry,⁴⁰ and in 2015 this number had even

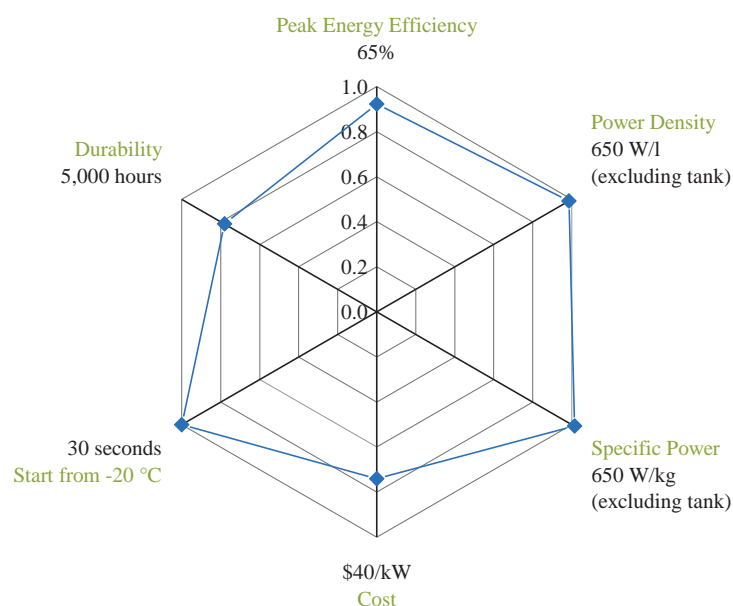


Figure 2. Fuel cell power system 2020 targets versus 2015 status (blue) for light-duty vehicle applications (the status is indicated as a fraction of the targets). Cost status is for a modeled system when manufactured at a volume of 500,000 units/year. Reprinted from the U.S. Department of Energy Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan (updated 2016).³⁷

increased to $\approx 42\%$,⁴¹ notably with an overwhelming share of ICE vehicles, which use significantly less platinum per vehicle than current FCEVs. It can be easily deduced that a significantly increased demand for Pt in the automotive sector would induce drastic Pt shortages on the world market. Even if nowadays (projection for 2016) 26% of the platinum produced comes from recycling,⁴¹ from the PEMFC point-of-view material based solutions are desirable to lower the absolute demand for platinum.

One of the approaches to reduce the amount of Pt that is needed to derive sufficient electrocatalytic activity (mainly necessary for the oxygen reduction reaction;⁴² ORR), is the utilization of more abundant co-metals,⁴³⁻⁴⁸ or other noble metals,⁴⁷ e.g., Pd alloyed with Pt.^{47, 49-51} A second approach is the investigation of completely noble-metal free electrocatalyst materials, like metal-nitrogen-carbon based compounds as, e.g., Fe-N-C⁵²⁻⁵⁴ and Co-N-C,⁵⁵ which have already demonstrated high activity for the oxygen reduction reaction, or partially oxidized valve metals,⁵⁶⁻⁷⁰ which were shown to have promising corrosion resistance in an acidic environment.

Numerous studies have been published in the above described field. This work contributes two sections, one is section 3.1, investigating the electrocatalytic activity of palladium nanoparticles supported on carbon black towards the oxygen reduction reaction. While Pd has mainly been used as a co-material of Pt in previous studies (see above), its intrinsic electrocatalytic properties for the ORR are little investigated (details can be found in section 3.1, p. 57 ff). The other one is section 3.2 (p. 69 ff.), where an



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approach towards noble-metal free ORR electrocatalysts is evaluated, focusing on the so far little understood ORR on valve metal oxides, in the form of zirconium based (sub-)oxidic nanoparticles supported on high surface area carbon.

PEMFC Durability. Mathias et al. identify another hurdle for the widespread commercialization of FCEVs being the durability of PEMFC components.³⁶ While there are several comprehensive reviews available dealing with general lifetime challenges of automotive PEMFCs, as e.g., from Wu et al.,⁷¹ Borup et al.,⁷² and Dubau et al.,⁷³ as well as with a specific focus on catalyst layer degradation as given by Wagner et al.⁷⁴ and Zhang et al.,⁷⁵ this present work is focusing on the catalyst layer. Thus, in section 2.1.4, a brief overview of main challenges in catalyst layer durability is given.

2. Theoretical Concepts and Experimental Methods

This chapter briefly describes theoretical concepts and experimental methods which are not detailed in the chapters of published work (3 and 4), but are essential for the conducted work.

2.1. Background on PEMFC Electrochemistry

Electrochemical reactions in general describe the “*interrelation of electrical and chemical effects*”.⁷⁶ In an electrochemical reaction, an (or several, v) oxidized active species Ox is (are) reduced to reduced species Red by uptake of one or several (z) electrons from the – typically solid – electrode surface, or vice versa:



A characteristic descriptor for the thermodynamic equilibrium of an electrochemical reaction is the standard reduction potential of the respective reaction, which is referenced to the standard hydrogen electrode (see below).

2.1.1. Relevant Electrochemical Reactions and Thermodynamics

All electrochemical standard reduction potentials are referenced to the standard hydrogen electrode (SHE), describing the potential (V_{SHE}) which is established when the following reaction is in equilibrium at a hydrogen partial pressure of 1 bar and at a proton activity of one:



Owing to its high catalytic activity for this reaction, Pt is usually used experimentally. Equation (2) describes the hydrogen evolution reaction (HER) when proceeding from left to right, and the hydrogen oxidation reaction (HOR) from right to left. The HOR is considered as the fundamental reaction occurring on the anode electrode of a PEM fuel cell in this work. By definition, the HOR/HER (Equation (2)) has a standard reduction potential of 0 V_{SHE} .

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The second reaction of interest for PEMFC electrochemistry is the oxygen reduction reaction (ORR; left to right) and oxygen evolution reaction (OER; right to left), which exhibits a standard reduction potential of $1.23 \text{ V}_{\text{SHE}}$.⁷⁶



A third reaction of relevance to commonly used PEMFC materials is the highly irreversible carbon oxidation reaction (COR) at a standard reduction potential of $0.21 \text{ V}_{\text{SHE}}$.⁷⁷



In order to account for actual activities a_i of species i , which are generally $\neq 1$, it is necessary to correct the standard reduction potential $E_{\text{Ox|Red}}^{\text{rev},0}$ of any electrochemical reaction, i.e., Equation (1) by the Nernst-Equation:

$$E_{\text{Ox|Red}}^{\text{rev}} = E_{\text{Ox|Red}}^{\text{rev},0} + \frac{R \cdot T}{z \cdot F} \ln \left(\frac{a_{\text{Ox}}^v}{a_{\text{Red}}^v} \right) \quad (5)$$

Here, R ($8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$) is the universal gas constant, T is temperature in K and F ($96,485 \text{ C} \cdot \text{mol}^{-1}$) is the Faraday constant and other parameters as described above. The reduction potentials of HER/HOR, ORR/OER and COR exhibit the same variation with proton activity, i.e., $R \cdot T/F \cdot \ln(a_{\text{H}^+})$. The resulting potential vs. pH relationship of the HER/HOR (red dashed line in **Figure 3**) is commonly referred

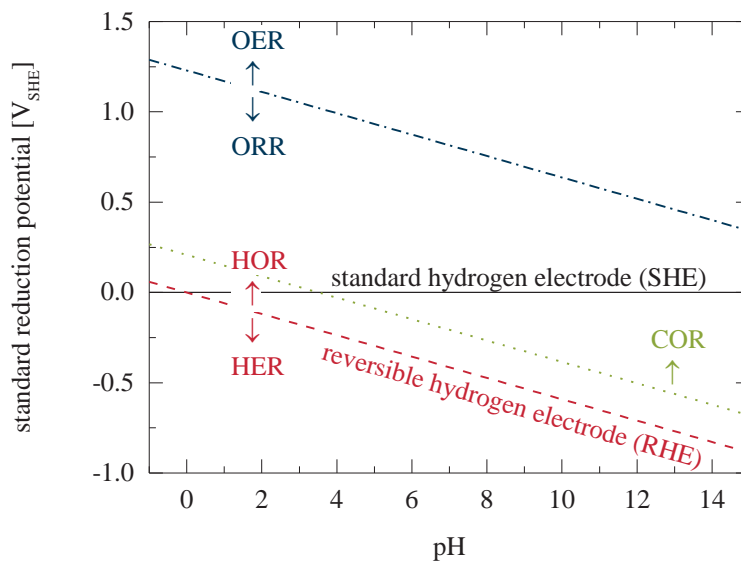


Figure 3. Pourbaix diagram of (liquid) water, comprising of HER/HOR (red dashed line) and ORR/OER (blue dash-dotted line) and including COR (green dotted line) at $25 \text{ }^\circ\text{C}$, 101 kPa gas partial pressures.

to as reversible hydrogen electrode scale (RHE, since it reflects the standard reduction potential of the HOR/HER at any proton activity (i.e., pH)). Thus, it can be seen from **Figure 3** that the reversible potentials of the previously described reactions (ORR/OER and COR) exhibit pH dependent values when referenced to the standard hydrogen electrode SHE, but exhibit constant values against the RHE scale. Generally, fuel cell relevant reactions can take place at various pH values (a commonly assumed value for PEMFCs is pH =0 while typical values for acidic aqueous experiments mimicking the PEMFC environment are around pH =1; see section 2.2.3). As a result, the RHE scale is used in this work for referencing the potential of any PEMFC relevant reactions (indicated by an index attached to the unit of potential: V_{RHE}).

In electrochemical devices, galvanic or electrolytic cells, typically two electrochemical reactions are combined, each occurring at one electrode, to yield an overall redox reaction as the sum of both, balanced by the exchanged number of electrons. The exemplary galvanic cell in **Figure 4** combines Equations (2) and (3) to yield an overall reaction



where oxygen is being reduced to water and oxidizes the hydrogen. Obviously, this reaction is identical to the overall reaction occurring in a PEMFC during operation. Notably, in this case (see **Figure 4**), the electrons pass the external electrical circuit from the electrode with lower potential (where HOR occurs) towards the electrode with higher potential (ORR), passing an external electrical load. In case the electrical load is another electrochemical device, e.g., a battery, the internal current of this battery is reversed

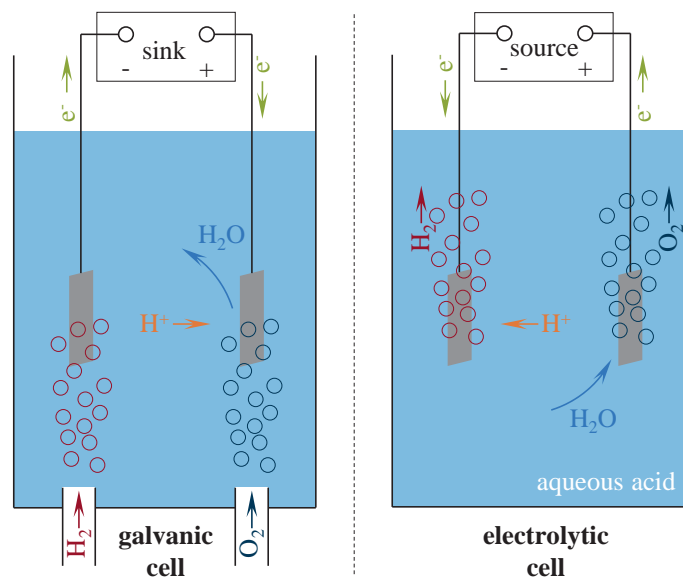


Figure 4. Sketch of an exemplary simple galvanic and electrolytic cell with two platinum electrodes in an aqueous acid.

2. Theoretical Concepts and Experimental Methods

compared to its nominal direction, thus the battery is charged. In contrast (see right side of **Figure 4**), in an electrolytic cell, electrical energy supplied by an external source is consumed and converted into chemical energy, in form of produced hydrogen and oxygen. While by strict convention, one calls the electrode where reduction occurs cathode and the electrode where oxidation occurs anode, sometimes one can find static definitions of the terms *anode* and *cathode* in the electrochemistry literature, especially when dealing with rechargeable batteries. Here, it is typical to use the denomination according to the discharge of the battery, i.e., the negative electrode would be the anode, and the positive electrode the cathode. Also in this work, we use a static definition of anode and cathode, according to the *nominal* PEMFC reactions, in order to avoid possible confusion in chapter 4.

For a general understanding of PEMFCs, constructing redox reactions comprising of components from Equations (4), (2) and (3) can often be helpful means, e.g., in understanding dysfunctions like fuel starvation or start-up/shut-down events. The correlation between the reversible potential E^0 of an electrochemical cell and the Gibbs free energy of the corresponding (redox) reaction ΔG_R^0 is given by:⁷⁶

$$E^0 = -\frac{\Delta G_R^0}{n \cdot F} \quad (7)$$

Here, n is the number of exchanged electrons. While details will not be elaborated here, one can derive correlations like the temperature dependence of reversible cell potentials in electrochemical devices from Equation (7).

2.1.2. Reaction Kinetics and Electrocatalysis

The pure thermodynamic picture of electrochemical reactions described in the previous section is not capable of reflecting the correlation between current drawn/supplied by the external circuit and the actual cell potential at this current. In the purely thermodynamic picture, an infinitesimal deviation from the reversible potential already would allow for an infinite reaction rate (equivalent to current) in the corresponding direction. In reality, a current drawn/supplied to an electrochemical system is always associated with an additional voltage penalty η_k (kinetic overpotential) that needs to be subtracted/added from/to the reversible potential in order to yield the actual kinetic cell voltage as a function of current. For anodic reactions, $\eta_k \geq 0$, while for cathodic reactions, $\eta_k \leq 0$. Electrochemical kinetics are often described by the Butler-Volmer equation, which sums over anodic and cathodic contributions.⁷⁸

$$i = i_0 \cdot \left[\exp\left(\frac{\alpha_a \cdot F}{R \cdot T} \eta_k\right) - \exp\left(-\frac{\alpha_c \cdot F}{R \cdot T} \eta_k\right) \right] \quad (8)$$