Selected Fundamentals of Catalysis and Electrocatalysis in Energy Conversion Reactions – A Tutorial

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ABSTRACT

Electrochemical devices for energy conversion and storage applications have little in common with conventional electrochemistry. A significant advantage is the conversion of chemical into electrical energy and vice-versa, minimizing the amount of waste heat. Upscaling power density to values reaching up to 1 W cm^{-2} at current densities exceeding 1 A cm^{-2} goes along with downscaling transport distances of reaction partners inside and between electrodes. Substrates undergo structure- and element-specific interactions with electrode surfaces which are therefore not only interfaces for the exchange of electrons, rather they should be regarded as specific catalytic surfaces which together with the applied electrical bias potential determine the spectrum of available products. An understanding of these interactions is still in its infancy for many of the relevant systems, and therefore the developments are largely empirical and driven by intuition, supported by quantum-chemical calculations and spectroscopic methods. The manuscript is of tutorial nature and addresses the differences between electrocatalysis in energy conversion reactions and conventional electrochemistry, and it reveals what catalytic transformations at electrode surfaces have in common with traditional heterogeneous catalysis.

1. Introduction

Electrochemistry has traditionally been more a tool of materials characterization and process analysis than of synthesis. The vast majority of synthetic processes in chemistry is carried out using thermal activation in homogeneous phase or by heterogeneous catalysis, with electrochemical methods occupying a relatively small niche for selected processes. However, in the context of having to find a solution for securing sufficient energy to a growing world population with increasing demands while at the same time reducing the dependence on fossil fuels to curb the effects of climate change have led to a distinct revival of electrochemistry over the past several decades. The preferred and most flexible form of energy is electricity. However, storing electrical energy on the required massive scale is difficult but easier in the form of chemical bonds, *i.e.* as chemical fuels, preferentially liquids, which are also more easily transported over large distances using existing technology. The situation requires frequent interconversion between electrical and chemical energy on a large scale and with high roundtrip efficiency.

The developments in the energy sector have shifted the focus away from traditional analytical electrochemistry. However, while the new requirements are well kown among specialists, introductory textbooks have not kept up with the developments. It is the purpose of this tutorial text to make up for part of this deficit and introduce some of the key concepts.

## 2. Energy efficiency and the necessity of nanostructurization

Electrochemical reactions are those that can be separated into an oxidation and a reduction reaction and conducted in separate compartments (half-cells). The reactions occur at the surface of electrodes by exchange of electrons between reactant and the conducting electrode material. The electrons are forced to take their way through the electrical circuit where they can do electrical work or take up electrical energy. Simultaneously, ions cross over though the electrolyte between the two half cells to maintain charge neutrality. This requires that the separating element between the two compartments (a "salt bridge" or nowadays often a polymer membrane) must be able to conduct ions.

Figure 1a shows the traditional setup of an electrochemical cell that is found in most textbooks. It is appropriate for measurements in equilibrium or at low current densities. However, it is important to note that modern electrochemical devices for energy applications such as fuel cells or electrolyzers work at typical current densities of about 1

A cm^{-2}. In order to optimize energy efficiency one has to minimize resistive losses, described by Ohm's law:

$$\Delta U = R \cdot i \qquad (1)$$

where ΔU is the voltage drop, R is the resistance, and i the current. The power loss is the product of ΔU and i, so for the desired large values of i, ΔU must be minimal, which obviously requires R to be small. For any given area of parallel electrodes R is proportional to the distance between the electrodes, and this obviously has to be minimized. The key for the success of electrochemical power conversion devices lies in the setup shown in Figure 1b for a hydrogen fuel cell where anode and cathode are in direct contact with a polyelectrolyte membrane of a thickness of typically 50 μm or even less. For such a setup, the resistive voltage drop at a current density of 1 A cm^{-2} is ca. 20 mV, which still corresponds to an efficiency loss of as much as 25% of the available power [1]. Besides the distance between the electrodes, the resistance inside the electrodes and in the contacts as well as the choice of the electrolyte material are important.
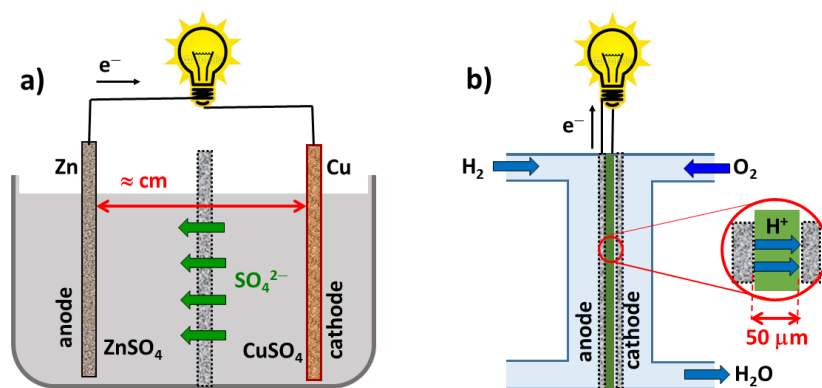
Figure 1. a) Daniell element in the traditional setup in which anode and cathode are separated by macroscopic distances, typically one to a few centimeters. b) Hydrogen fuel cell where anode and cathode are separated by a polymer-electrolyte membrane with a thickness of typically 50 μm. (color online)

The principle of minimizing energy losses by reducing the diffusion lengths of ions and thus the electrode distance applies to all electrochemical energy conversion devices that are expected to work at high power and thus high current densities, not only fuel cells and electrolyzers but also batteries and supercapacitors. Popular architectures consist of alternate electrode and separator thin foils that are folded to pouch cells or rolled to cylindrical devices. It should be adequate to update introductory textbooks in this respect.

Figure 1b illustrates another experimental progress towards high power cells. Conventionally, we are used to have the electrodes immersed into ion-conducting liquid (or also solid) electrolytes. These systems need to be stirred to decrease the depleted

diffusion layer around the electrode, even if the reactant is a dissolved gas. In contrast, today's polymer electrolyte fuel cells work with anode and cathode compartments filled with hydrogen and oxygen gas, and the electrolyte occupies only the thin separating layer between the electrodes with which it is in close contact. Transport of reactant gases to and of products from the electrode is much more efficient in the gas phase. The electrolyte is kept saturated with water by using humidified gases to ensure efficient ion transport, but care has to be taken to avoid flooding of the porous electrode structure (hydrophobized gas diffusion electrodes) to allow unhindered access of the gases.

From Ohm's law (eqn. 1) it is clear that the voltage loss and therefore also the power loss of an electrochemical cell is directly proportional to the current at which the cell is operated. Therefore, the efficiency of batteries decreases at high currents, *i.e.* when they are charged or discharged fast. It is simply a consequence of the Second Law of Thermodynamics that waste heat is dissipated under non-equilibrium conditions, but no current flows in equilibrium [1].

3. Electrical versus thermal reaction energy

The principal advantage of electrochemistry is that the free energy of reaction, ΔG°_R, becomes available in the form of valuable electrical energy instead of being wasted as heat of reaction (Figure 2, left). For example, the heat of reaction in an explosion of 1 mol H_2 with ½ mol O_2 to 1 mol of liquid water under standard conditions corresponds to ΔH°_R = −285.8 kJ mol^{-1}. Under reversible conditions, a sizable fraction of it, ΔG°_R = -237.14 kJ mol^{-1} or 83%, can be converted to electrical energy, represented by a reversible cell potential $\Delta U^\circ = -\Delta G^\circ_R/nF$ = 1.23 V. The reaction can thus be tamed by separating oxidation and reduction in two different compartments.

Perhaps even more interestingly, the reaction can be reversed by application of an external bias voltage $\Delta U \geq -\Delta G^\circ_R/nF$, n being the number of electrons transferred according to the reaction stoichiometry. This process, called electrolysis, is conducted in a setup as that shown in Figure 1b, but with more stringent requirements on the stability of the anode catalyst because of the high applied potential of water oxidation, $\Delta U \geq 1.5$ V. In this way, the highly endergonic water splitting reaction can be conducted at room temperature, yielding the hydrogen separated from the oxygen. Thermal catalysis would require temperatures in excess of 2000 °C, and the products would be obtained as an explosive mixture which in the absence of special measures would immediately react back to water. It is an essential advantage of electrocatalysis that it permits such endothermic reactions to be conducted under mild conditions (Figure 2, right) and that the products are obtained separated and not as mixtures.
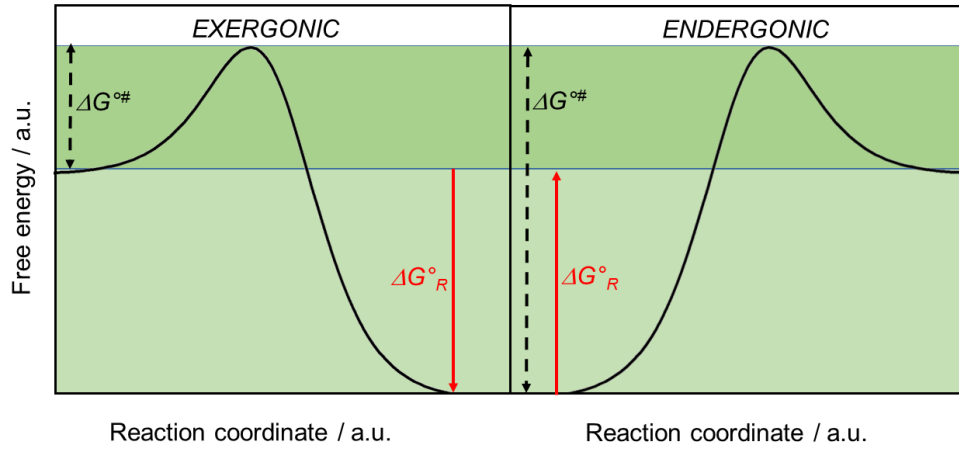
Figure 2. In an electrochemical process, the free energy of reaction, $\Delta G°_R = -nF\Delta U°$, is converted to valuable electrical energy in an exergonic process, while in an endergonic process, $\Delta U° \geq \Delta G°_R$ is supplied as electrical instead of thermal energy. (color online)

Fiigure 3a depicts how a reaction barrier is overcome by increasing the temperature in reactions conducted thermally by increasing temperature and contrasted in Figure 3b with the case of electrocatalysis without temperature increase. Higher temperatures might be disfavored because of the reduced stability of involved substrates or catalysts and because of the lower selectivity of reactions towards the desired products.

The rate of reaction is given by transition state theory as

$$k(\Delta U{=}0) = k_0 \exp\left(-\Delta G^{°\#}/ RT\right) \tag{2}$$

where the exponential term is a Boltzmann term that gives the fraction of reactants that have sufficient energy to overcome the free energy barrier of activation, $\Delta G^{°\#}$. In the presence of an applied potential ΔU, part of the necessary energy is supplied as electrical energy, $\alpha nF\Delta U$, which leads to a modified equation for the rate constant

$$k(\Delta U) = k_0 \exp\left((-\Delta G^{°\#}+\alpha nF\Delta U / RT\right). \tag{3}$$

The situation with the Boltzmann distribution shifted by $\alpha nF\Delta U$ is depicted in Figure 3b. The additional term represents the energy required to transfer $n = 1$ electrons from the electrode to the product. However, at the transition state, the reaction is not complete, and only a fraction α of the electron has been transferred. α often assumes values between 0.4 and 0.6. This demonstrates how the rate of product formation increases on increasing the applied potential ΔU.

The current or current density of an electrochemical reaction is proportional to the rate constant. Plotting the current against ΔU shows an exponential increase for values of ΔU well below the onset voltage, reflecting the fact that the higher energy reactants in the Boltzmann distribution are already above the activation barrier $\Delta G^{\#}$. The linear increase at higher potentials represents the growing reaction rate due to the increasing applied gradient. The onset potential obtained by linear extrapolation of the curve (red line in inset of Figure 3b) is the intercept at zero current. It is generally higher than expected based on the equilibrium standard free energy of reaction, ΔG°_R, because there are contributions to the activation energy from other sources, such as the energy of adsorption of the reactants on the catalyst surface (see Section 6 and Figure 5 below).
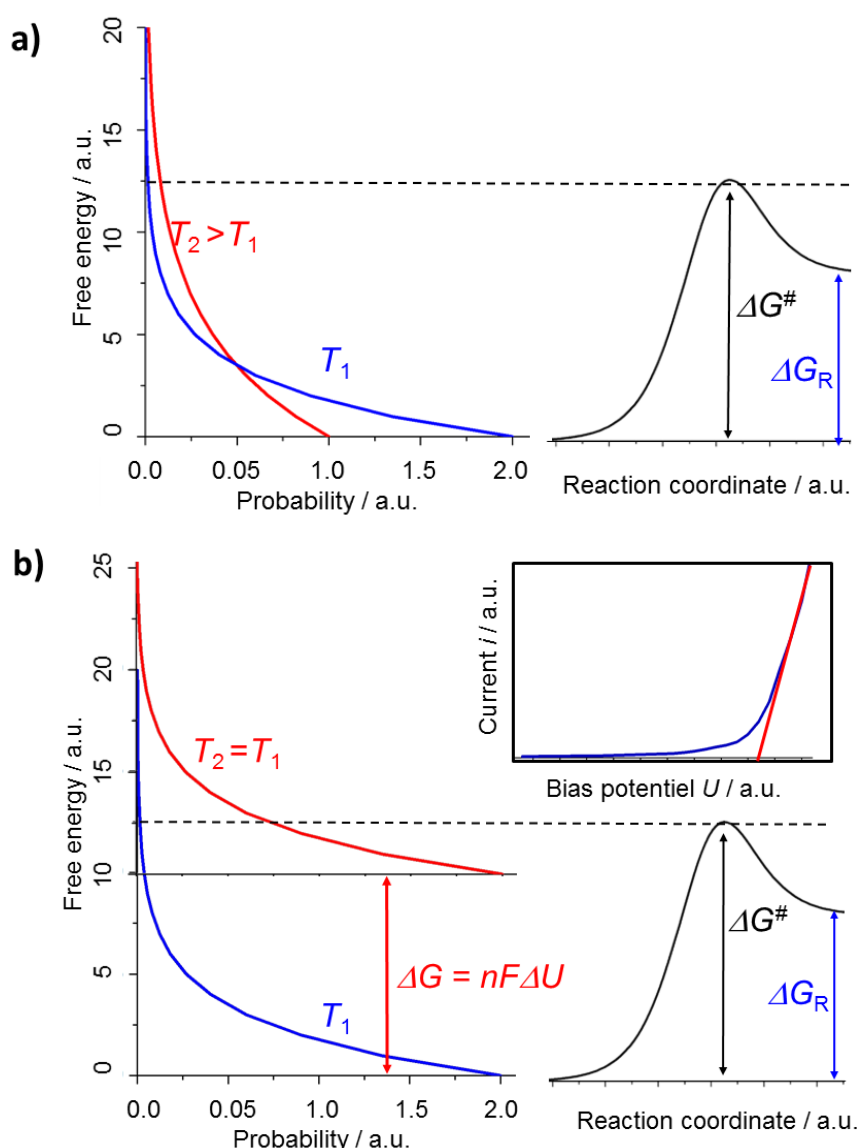

Figure 3. a) Thermal reaction: a high free energy of activation is overcome by increasing temperature from T_1 to T_2. The blue and red curves represent the corresponding Boltzmann distribution of the reaction partners. b) Electrochemical reaction: Instead of heating up the reaction system a variable amount ΔG is supplied

in the form of electrical energy $nF\Delta U$, and the Boltzmann distribution remains the same. Inset: schematic current voltage diagram. We omit the superscript ° on the free energy terms because the relation is valid equally for non-standard state conditions. (color online)

4. The effects of applying an electrical potential

Application of an electric potential to the electrodes influences the nature of the adsorbed species and the energy of their bond to the electrode surface. Also species in the immediate proximity of the surface, *i.e.* in the regime of the electrical double layer, are somewhat affected, but free reactants and products remain unperturbed. The interaction was demonstrated for example by Raman experiments of adsorbed CO on palladium (CO is a potential intermediate in electrochemical reduction of CO_2), revealing that the Pd−CO vibrational stretching frequency increased linearly, the shift reaching 15 cm^{-1} for an applied potential of −1 V and indicating that the bond to the metal becomes stronger. Simultaneously, the C=O stretch frequency decreased by 45 cm^{-1}, giving evidence that the CO bond strength decreases [2]. Effects are not only expected for ionic species but also for neutral dipolar and even for unpolar but polarizable adsorbates. For the potential of a diatomic Morse oscillator, the vibrational frequency of a molecule scales with the square of the bond dissociation energy. For adsorbed C=O, a relative frequency change of 45 cm^{-1} (2.3% of 1950 cm^{-1}) corresponds to an estimated change of the C=O bond energy of 12kJ mol^{-1} (1.1% of the bond energy of 1072 kJ mol^{-1}). This is significant, although perhaps not overwhelmingly high. For the Pd−CO bond, the change in the bond energy would amount to ca. 2% or 5.7 kJ mol^{-1} of its value in the absence of a bias potential (290 kJ mol^{-1} for Pd_2−CO [3]).

An alternative representation of the effect of an applied potential to an electrode on the free energy of reaction intermediates was developed in the group of Nørskov, based on the computational hydrogen electron (CHE) model [4]. The results of such a calculation for CO_2 electroreduction to formic acid ($\Delta G°_R$ = +43.0 kJ (0.44 eV) mol^{-1})

$$CO_{2,g} + 2H^+ + 2e^- \rightarrow (HCO_2)_{ads} + H^+ + e^- \rightarrow (HCOOH)_{ads} \rightarrow (HCOOH)_g \qquad (4)$$
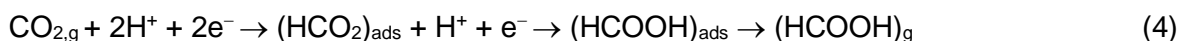
in the absence (black) and in presence (red) of an applied potential of −0.41 eV are shown in Figure 4. According to the model, on application of a potential ΔU the free energy $\Delta G°$ changes by $+e\Delta U$ (e is the positive elementary charge), corresponding to 1 eV or 96.5 kJ per mol for each electron-proton pair that is transferred to the reactant. The correction term accounts for the fact that it is easier to transfer an electron from the electrode to the adsorbate when a negative bias voltage is applied. In contrast to Figure 3b where E_a is the

overall apparent activation energy, Figure 4 gives the energies of the individual intermediates. Methods are developed also to calculate transition states where the calculations account for the partial charge (corresponding to α in eqn. 3) transferred along the reaction coordinate [5,6].

Note that as discussed above, the adsorbate is stabilized at the surface either by chemical bonds or by van der Waals interactions. Both are affected by the applied bias potential. This could lead to blocking of the surface by intermediates or products. A short reduction or inversion pulse of the applied potential (a "stripping cycle") may regenerate the system.
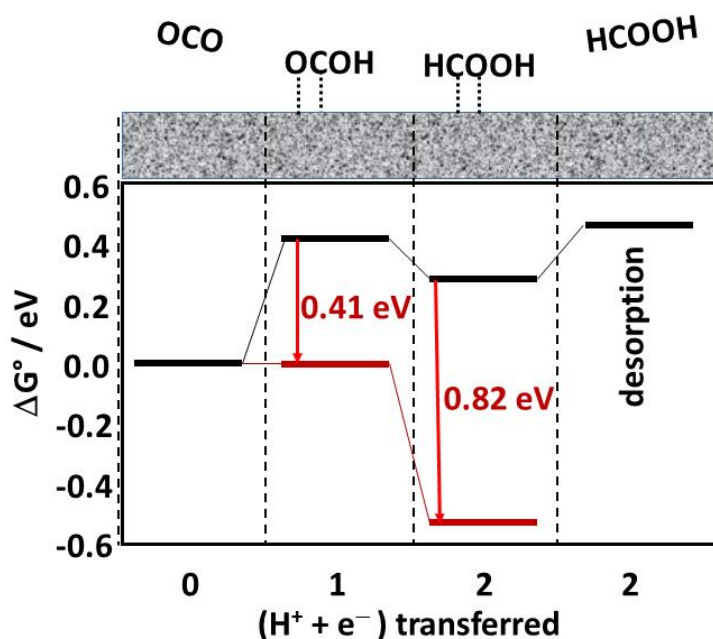
Figure 4. As an alternative to Figure 3, the energy levels of reaction intermediates and of the adsorbed product are shifted (red lines, lower trace) at an applied potential, chosen here to be -0.41 eV to bring the first intermediate, adsorbed OCOH, down to the level of the reactants. Data are for the electroreduction of CO_2 to formic acid, taken from Nørskov et al. [4]. (color online)

The product spectrum of CO_2 electroreduction changes with increasing bias potential, as determined quite early by Hori *et al.* [7] and more recently by Kuhl *et al.* [8]. Besides hydrogen, CO and formic acid form at low potential, while at higher potentials the product spectrum changes to methane and ethane, followed by n-propanol, allyl alcohol and ethanol and some other minor products. The varying product spectrum indicates that at higher potentials new reaction paths with higher activation energies towards new products become competitive. Furthermore, at higher bias potentials, products may remain bound to the surface sufficiently long to react to new products, including those involving C−C coupling.

Methanol, which is the major product in many thermally catalyzed experiments with CO_2 and H_2 on copper, forms at best in very small yields in electrocatalytic reactions. This demonstrates that the reaction mechanisms are different.

5. On the nature of the electrode

So far we have assumed that an electrode is simply a conductive material that exchanges electrons with a substrate that comes in sufficiently close proximity of its surface. This may be adequate for some of the traditional electrochemistry, but for what we are discussing here it is a gross oversimplification. We have already discussed that substrates attach to the electrode surface by forming van der Waals or chemical bonds. The substrate then needs to remain attached until the transformation is complete, and then it has to desorb. The electrode is thus much better described as a catalytic reaction partner that undergoes specific interactions with substrates. The products depend on the elemental chemical composition as well as on the microstructure of the electrode surface in a similar way as it is well known for conventional heterogeneous catalysts. We therefore often speak specifically of electrocatalysis instead of electrochemistry.

In a review of catalytic, photocatalytic and electrocatalytic conversion of CO_2 by Kodratenko *et al.* the main products were given as hydrocarbons on Cu, CO on Au, Ag and Zn, $HCOO^-$ on Pb, Hg, In, Sn, Cd, and Tl, and as H_2 on Ni, Fe, Pt, Ti and Ga [9]. Another detailed review focuses on CO_2 electroreduction and includes many more types of electrode materials, like metal alloys, oxides, complexes, enzymes and organic molecules, and it discusses further products [10]. Furthermore, a non-metallic electrocatalyst consisting of nitrogen-doped graphene quantum dots has been reported [11]. The variability of products and its dependence on the nature of the catalyst demonstrates impressively that specific interactions are present, but as today, little information is known about these.

In fuel cells, electrolyzers and other electrocatalytic converters there is an external supply of reactants, and the products are removed. In contrast, batteries are sealed, and only electrical current and waste heat are exchanged with the environment. In modern devices like rechargeable lithium ion batteries the electrodes have no catalytic function, rather they are storage devices. The anode normally consists of graphite, and various oxides containing redox-active transition metal ions (e.g. Co^{3+}/Co^{4+} or Fe^{2+}/Fe^{3+}) are used for the cathode. Both materials are in contact with a metallic current collector and separated by an electrolyte and an insulating diaphragm that can transmit the Li^+ ions. On charging, the Li ions intercalate into the graphite up to a stoichiometry of neutral LiC_6, taking up an electron that is released from Co^{3+}. On discharging, this process is reversed, *i.e.* Li^+

moves back out of graphite and intercalates in the oxide where it possesses a different chemical potential, while Co^{4+} is restored to Co^{3+}. This forward-backward dynamics is sometimes called a "rocking chair" mechanism.
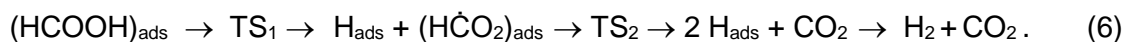
6. On the nature of transient intermediates

The dehydrogenation of gaseous formic acid

$$HCOOH \; \rightarrow \; TS \; \rightarrow \; H_2 + CO_2 \qquad \Delta G°_R = -43.0 \; kJ \; mol^{-1} \; E° = +0.11 \; V \tag{5}$$
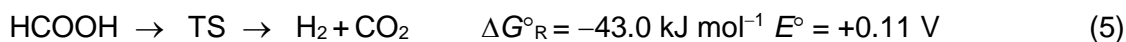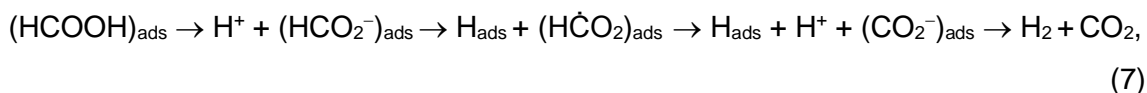
is thermodynamically spontaneous and can in principle occur in a one-step process. However, it is highly activated because it involves a strained four-ring transition state TS [12]. Introducing a water molecule as a catalyst opens a new reaction path by expanding the transition state to a six-ring and lowers the activation energy significantly.

On the surface of a heterogeneous catalyst one can imagine that the two hydrogen atoms dissociate off one after the other and recombine in a further step on the catalyst surface:

$$(HCOOH)_{ads} \; \rightarrow \; TS_1 \rightarrow \; H_{ads} + (H\dot{C}O_2)_{ads} \rightarrow TS_2 \rightarrow 2 \; H_{ads} + CO_2 \rightarrow \; H_2 + CO_2 \,. \tag{6}$$

The same reaction can be conducted electrochemically. In this case, the hydrogen atoms are detached at the anode not as atoms but as electrons and protons, either in a concerted or a non-concerted way,

$$(HCOOH)_{ads} \rightarrow H^+ + (HCO_2^-)_{ads} \rightarrow H_{ads} + (H\dot{C}O_2)_{ads} \rightarrow H_{ads} + H^+ + (CO_2^-)_{ads} \rightarrow H_2 + CO_2,$$
$$\tag{7}$$

and they take different ways to the cathode where they are reassembled first to surface-adsorbed H atoms and then to H_2.

It is obvious from the above example that electrocatalytic and thermally catalyzed reactions may involve different ionic and free radical intermediates and transition states even if the reactions were conducted on the same catalytic surface. Furthermore, we may ask whether there is a consequence of charge separation when the electron is conducted through the electrical circuit while the proton diffuses through the electrolyte. This issue will be discussed here for the example of the hydrogen dissolution prototype reaction:

$$\tfrac{1}{2} \, H_2 \; \rightarrow \; H^* \; \rightarrow \; H^+ + e^- \tag{8}$$
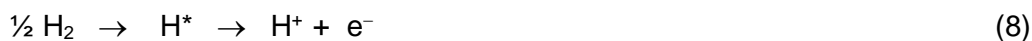
that is shown in Figure 5. Reactant and product state are by definition degenerate under standard state conditions.

Ideally, the adsorption free energy of H* bound to the electrode surface is zero. This property was calculated for H* on Pt and found to amount to ca. 90 meV for a fractional surface coverage $\theta = \frac{1}{4}$ [13]. Since the proton-electron recombination is likely non-activated this number corresponds also to the activation overpotential of the reaction. Platinum is among the metals with the highest exchange current densities i_0 (for an electrode in equilibrium with the electrolyte, *i.e.* at zero overpotential, there is no net current through the interface since the forward current is balanced by the backward current – the two are of equal magnitude and called exchange current density). There can thus not be any significant contribution of charge separation to the activation energy of this process, which is reasonable because when an electron enters one end of the circuit another electron leaves simultaneously at the other end. The same is true for protons entering and leaving the electrolyte, and there is charge neutrality in both media under equilibrium.
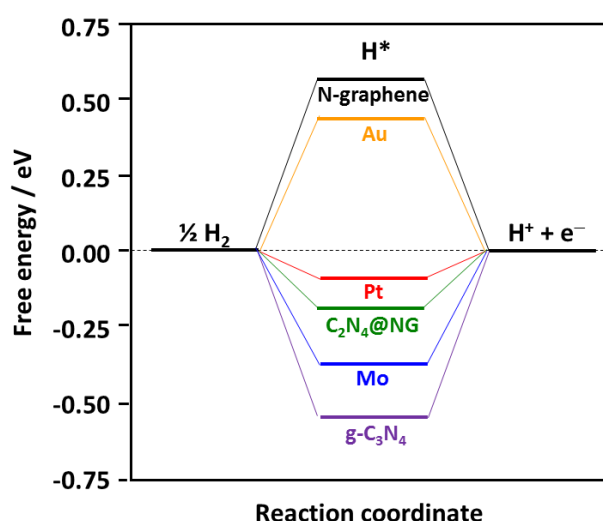
Figure 5. Free energy diagram of the hydrogen dissolution reaction under standard state conditions of 1 bar H_2 pressure and pH 0 at 298 K. H* represents the adsorbed state of the atomic hydrogen intermediate on the various catalytic surfaces gold, platinum, molybdenum, nitrogen doped graphene (N-graphene, NG), graphitic carbon nitride (g-C_3N_4) and the resulting hybrid structure C_2N_4@NG. Drawn based on data from [13,14]. (color online)

Experimentally, it is only the magnitude of $\Delta G°$ of adsorption of H* that is observed, because both, negative and positive values translate into activation energies, either on adsorption or on desorption. Gold for example has a positive value, which means that

there is no spontaneous formation of H*. Interestingly, also metal-free electrode materials based on graphene or analogous structures were recently shown to have good catalytic activity for hydrogen dissolution or evolution. In particular, a hybrid structure between nitrogen-doped graphene and graphitic carbon nitride was found to be nearly equivalent to Pt [14].

7. An instructive example: Electro-reforming of methanol

Thermodynamically, an aqueous solution of methanol is unstable towards decay to CO_2 and water:

$$CH_3OH + H_2O \rightarrow 3\,H_2 + CO_2 \qquad \Delta G° = -15\text{ kJ mol}^{-1}, E° = 0.026 \text{ V.} \qquad (9)$$

However, nobody has ever seen hydrogen and carbon dioxide gas bubbling out of a bottle of aqueous methanol on the shelf – the activation barrier of this reaction is far too high for it to occur at any significant rate. Much effort was therefore put into the development of new molecular catalysts to accelerate this reaction and make methanol a useful chemical storage agent of hydrogen [15,16], but so far the conversion rate is still too low to make the system commercially attractive near room temperature.

Electro-reforming of methanol may become a valuable alternative to homogeneous or heterogeneous hydrogen production. It is a process that slowly gains publicity [17,18]. The setup, shown in Figure 6, is essentially just an anaerobic version of the direct-methanol fuel cell. In the absence of oxygen at the cathode the reaction stops at the production of hydrogen and does not proceed to water. Note that no reactant is supplied at the cathode. Indeed, the reaction could proceed at the anode alone. In such a case, the hydrogen would be obtained at the anode side in a mixture with CO_2. So what is the point of doing it electrochemically? Application of a positive voltage at the cathode polarizes the adsorbed methanol molecule and supports the extraction of electrons and thus the oxidation. This enhances the reaction rate beyond that of the catalyst alone. Furthermore, electron and proton are forced to migrate to the cathode where they recombine to hydrogen. The rate of hydrogen production can be tuned and adapted to the actual need by the size of the bias potential. Also, by setting the potential back to zero the electrochemical enhancement stops instantly. Electro-reforming of methanol aboard a car may provide an attractive option for the flexible production of hydrogen on demand for operation with a hydrogen fuel cell since it is much easier to transport a liquid methanol-water mixture a tank than hydrogen [17].
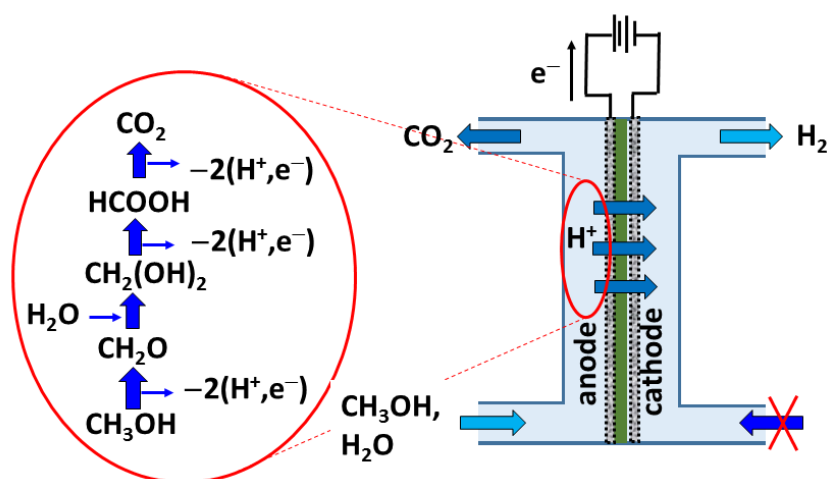
Figure 6. Electro-reforming of methanol yields hydrogen in a device that is essentially a direct-methanol fuel cell in the absence of oxygen at the cathode. Note that the reactants enter only the anode but not the cathode compartment. (color online)

8. Heterogeneous and electrocatalysis: advantages and disadvantages

Among the multitude of chemical reactions, only those that can be divided into an oxidation and a reduction can be conducted electrochemically. The reactants must be able to undergo a spontaneous or a forced electron exchange with suitable electrodes. This is a severe constraint for electrochemical reactions. There are, however, also clear advantages:

- Electrocatalysis of exergonic processes allows converting chemical energy into electricity, a form of energy that is much preferred over heat.
- Conversely, the necessary energy of endergonic processes can be supplied in the form of electrical energy, which allows strongly endergonic processes to be conducted near room temperature. This for example permits the direct electroreduction of CO_2 with water, two of the most stable molecules, while in thermal catalysis one would resort to H_2 (that may first have to be produced in an energy-intensive process from water or from other molecules) in place of H_2O.
- The rates of electrochemical reactions can be controlled by adjusting the current in the electrical circuit.
- It is not absolutely necessary but often convenient that the anode and cathode compartments are separated by an ion-conducting membrane. This avoids convective mixing of reactants and permits the oxidized and the reduced products to be obtained separately.

The reduction of CO_2 to methanol and water consists of three steps if we count formic acid and formaldehyde as intermediates. Each step consumes one mol of H_2 per mol of CO_2. Depending on the mechanism we have in addition single H reduction steps and

water elimination. In any case, no matter whether it is conducted by heterogeneous or by electrocatalysis, it is a multy-step process. It is quite a challenge to carry this out in a one-pot process since all the steps have to proceed under the same conditions, *i.e.* at the same pressure, temperature, possibly pH, on the same catalyst surface, at the same potential in electrocatalysis, and it must occur at the same rate.

The development of catalytic and electrocatalytic reactions is done largely empirically as a black-box processes, based on experience and intuition, but spectroscopic methods can detect intermediates, and quantum-chemical calculations can suggest realistic mechanisms and guidance to proceed to a detailed understanding. While electrocatalysis has the additional parameter of the applied potential, the analytical methods of electrochemistry also provide additional insight.

9. Conclusions

Electrochemical processes in the context of energy conversion and storage reactions have little in common with traditional electrochemistry which is primarily an analytical method. The high power densities require new device architectures in which ion transport distances are reduced to the micro- and nanometer range in order to minimize resistive energy losses. Round-trip energy efficiency becomes a central issue for cyclic processes.

To achieve high power densities it is of advantage to supply reactants and remove products via the gas phase in order to optimize transport efficiency. Electrodes should be separated by a thin electrolyte membrane in good electrical contact.

In contrast to thermal heterogeneous catalysis, electrocatalytic processes convert excess free energy to electrical power instead of heat. Conversely, strongly endergonic processes can be conducted near room temperature by supplying the necessary energy in the form of electricity.

Electrodes are not simply conductive surfaces that exchange electrons with species in close proximity. They undergo specific interactions with adsorbed substrates and take the role of catalysts with considerable selectivity. Details of this are not yet well understood and are subject of active research. In this respect, density functional calculations and spectroscopic methods are of valuable help.

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Graphical abstract