Selected fundamentals of catalysis and electrocatalysis in energy conversion reactions—A tutorial

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A B S T R A C T

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.

Fig. 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

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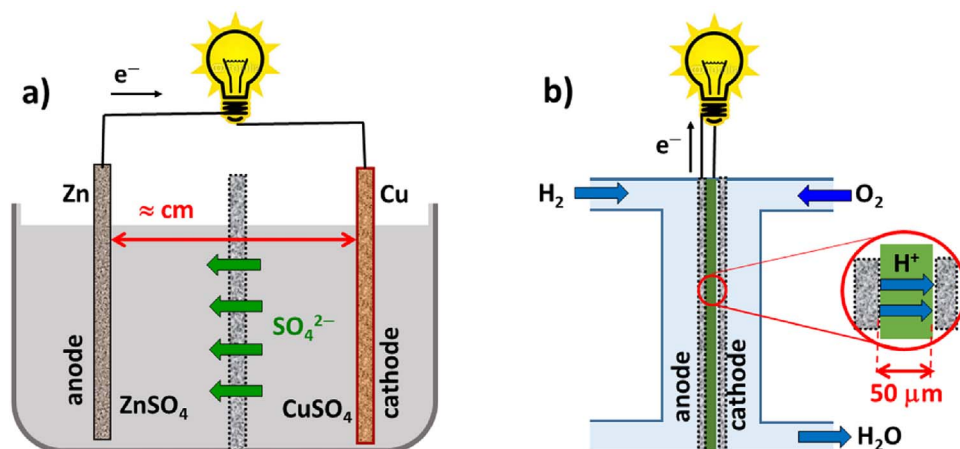
Fig. 1. a) Daniell element in the traditional setup in which anode and cathode are separated by macroscopic distances, typically one to a few centimeters. b) Hydrogen fuel cell where anode and cathode are separated by a polymer-electrolyte membrane with a thickness of typically 50 μm. (color online).

resistive losses, described by Ohm's law:

$$\Delta U = R \cdot i \tag{1}$$

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 Fig. 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.

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.

Fig. 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 (Eq. (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, $\Delta G°_R$, becomes available in the form of valuable electrical energy instead of being wasted as heat of reaction (Fig. 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 $\Delta H°_R = -285.8$ kJ mol^{-1}. Under reversible conditions, a sizable fraction of it, $\Delta G°_R = -237.14$ kJ mol^{-1} or 83%, can be converted to electrical energy, represented by a reversible cell potential $\Delta U° = -\Delta G°_R/nF = 1.23$ 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 $\Delta U \geq -\Delta G°_R/nF$, 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 Fig. 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 (Fig. 2, right) and that the products are obtained separated and not as mixtures.

Fiigure 3a depicts how a reaction barrier is overcome by increasing the temperature in reactions conducted thermally by increasing temperature and contrasted in Fig. 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

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

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

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

The situation with the Boltzmann distribution shifted by $\alpha nF\Delta U$ is depicted in Fig. 3b. The additional term represents the energy required to transfer $n = 1$ electrons from the electrode to the product. However,