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Challenges for (photo)electrocatalysis research

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Abstract

Semiconductor materials which allow electron transfer reactions via metal centered mechanisms have proven to be excellent electrocatalysts (e.g. substituted Chevrell-phases such as $Mo_4Ru_2Se_8$ for oxygen reduction, RuS_2 for oxygen evolution from water). They combine a high density of transition metal states (concentrated into small energy bands because of energy gaps) with the ability to induce coordination chemical interfacial mechanisms. A change of the electron number in the cluster, of the degree of substitution with foreign atoms, and of additional metal atoms introduced into channels besides the clusters allows far reaching conclusion on requirements for electrocatalysis during single and multi-electron transfer. A prominent additional property of catalysts of metal centered mechanisms is the ability to favor these compared to other electrochemical interfacial processes. This gives the catalysts a selective behavior with interesting possibilities for application (e.g. methanol fuel cell). At ambient temperature, technical catalysts do not match biological catalysts. The degree of order (decreasing entropy) which is reached during the process of electrocatalysis is recognized as an important quality factor. The most efficient way to build up temporary order is by dynamic self-organization in an open system. It requires the existence of autocatalytic processes. Mechanisms are discussed which may lead to an improvement of electrocatalysis via microscopic self-organization in (photo)electrochemistry and photosynthesis: the thermodynamic force of a reaction (e.g. photon energy, electrochemical potential) may induce a structural reorganization providing an optimized activation complex for charge separation (reaction center) or for multi-electron transfer during water oxidation (manganese complex of photosynthesis). © 1997 Elsevier Science B.V.

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1. Introduction

During the last decades research in electrocatalysis has experienced a significant progress mainly through the application of very modern research techniques and the use of improved electrode materials. In this connection, the strategy to combine electrochemical techniques with spectroscopic methods for interface studies has proven to be especially productive. In spite of these positive developments it has, nevertheless, to be concluded that the possibilities for innovative research have not yet been exhausted. This has already been demonstrated through the comparison with electrocatalytic systems from biological structures. Here it is realized that most complicated mechanisms of electron transfer are catalyzed near or at environmental temperature. In addition, it is remarkable that nature is accomplishing catalysis with abundant transition metals and does not need noble metals. A key advantage of natural systems is, however, that reactive and unstable molecular species can be handled in an appropriate way through molecular self-organization.

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Technical systems, on the other hand, have to be selected to show reasonable inherent stability. Nevertheless, the properties of present catalysts can be further developed to include improved characteristics. The aim of this contribution is to describe research initiatives which may prepare the development of new types of electrocatalysts.

2. Metal centered electron transfer

2.1. *d-State density and interfacial reactivity of semiconductor catalysts*

Our research group has worked for an extended period with the development of semiconducting transition metal compounds in which the energy bands are derived from transition metal d-states [1–3]. As explained in Fig. 1, illumination of such material types has the consequence that generated charge carriers react via metal centered interfacial mechanisms. Since in this way the metal centers are oxidized and reduced, respectively, they can adsorb or desorb ligands. We are dealing with light induced interfacial coordination chemical mechanisms. Illumination leads to a complex formation at the interface of the catalysts during which, in dependence of the chemistry of transition metals, electrolyte species react which otherwise are poorly reactive. In this way, the possibilities for catalysis are significantly extended. In principle, such reaction possibilities are also present around the metal centers in the electron transfer protein chains of biological membranes which are engaged in energy conversion processes of biological systems. Fig. 1 also shows that with a suitable choice of transition metal compounds

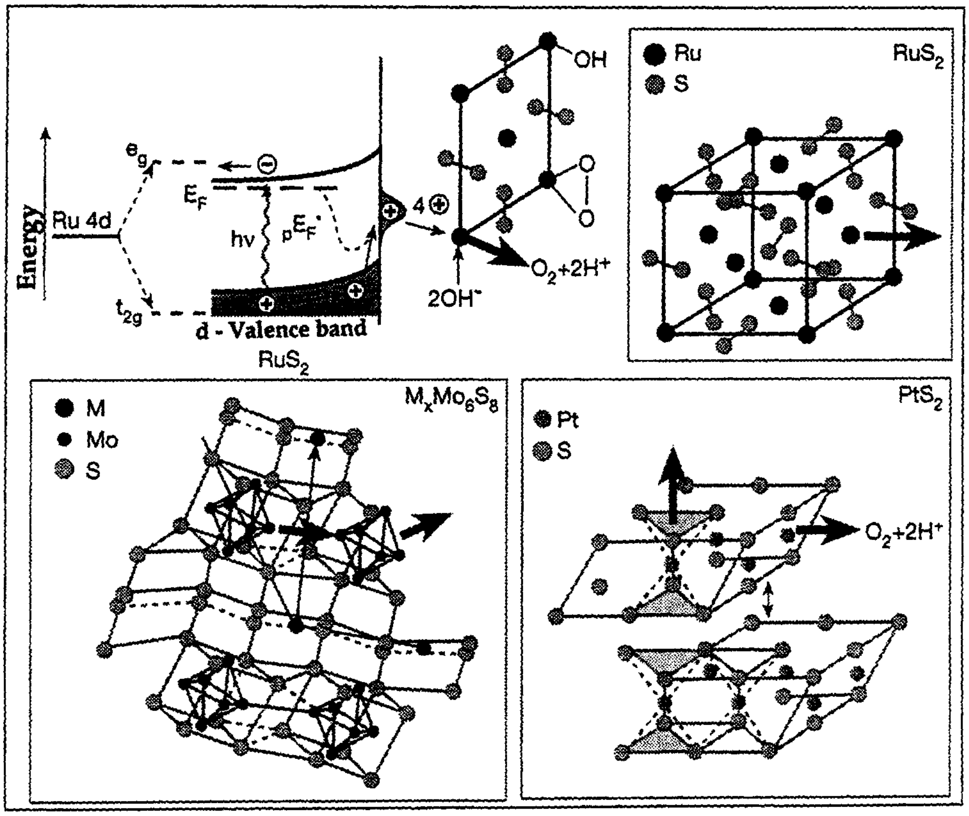


Fig. 1. Electronic scheme for the visualization of d-band semiconductors and the canalization of light-induced charge carriers into metal centered interfacial mechanisms. The processes are visualized with pyrite structured, layer structured and cluster containing materials.

with d-band character, the electron transfer reaction may either occur via individual interfacial atoms or via transition metal clusters which, because of their storage capacity for electron transfer, may be expected to facilitate multi-electron transfer. The experience is that this class of d-band materials provides a remarkable catalytic reactivity for multi-electron processes.

Corrosion reactions during which photo-generated minority carriers break chemical bonds in the interface are suppressed in d-band materials. The materials have, as already indicated, in addition the property to adsorb small molecular species such as for example OH^--ions which can form coordination complexes with the metals in the surface of the catalyst. How the light induced interfacial mechanism proceeds further depends essentially on the kind of metal centers involved. Iron atoms in iron disulfide form centers which cannot be oxidized so high as to react with water species until the liberation with oxygen. Rather, the adsorbed and oxidized water species are transferred to neighboring sulfide atoms so that ultimately the iron sulfide surface is oxidized to iron sulfate. When in the same crystal structure iron is replaced by ruthenium, the reaction mechanism is dramatically changed and oxygen evolution becomes possible.

2.2. *Photo induced oxygen evolution from water*

Ruthenium atoms in an illuminated ruthenium disulfide electrode, which is in contact with an aqueous solution, can – since ruthenium reaches a high oxidation state – oxidize water to gaseous oxygen. For light induced electrolysis of water, it is, thus, relevant that a semiconductor interface is chosen which can react with water during illumination so that a transition metal complex is formed which liberates oxygen during stepwise oxidation [4,5]. This is shown schematically in Fig. 2. The experience shows this process to be very efficient (quantum efficiencies of the order of 70% have been observed). In the case of ruthenium disulfide, the energy gap ($\Delta E_g = 1{,}3$ eV) is, however, too low to allow the conversion of solar energy without a supporting potential. Unfortunately, the ruthenium surface states which catalyze the water oxidation reaction are also too far displaced into the forbidden energy region to facilitate an energetically efficient energy conversion. Nevertheless, it is seen that the process of catalysis of light induced water splitting can even be generated with near infrared light, provided that the light induced positive charge carriers are channeled into a suitable metallic surface atom which

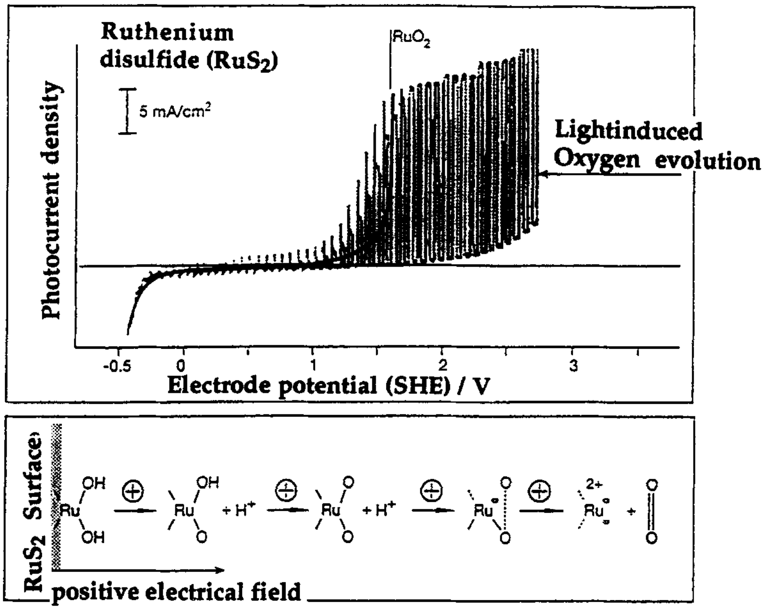


Fig. 2. Photocurrent voltage curve of a ruthenium disulfide electrode during oxygen evolution from water. The photocatalytic reaction is shown, which conducts to the liberation of oxygen.

can coordinate with water. Before, near approximately 1 V against the normal hydrogen electrode (NHE), the liberation of oxygen from water with light significantly increases, there is a flat shoulder which starts at approximately 0.5 V (NHE). Here already oxygen is liberated with a small quantum efficiency from water. This means that there are also catalytic surface states, which are situated close above the valence band of the semiconductor and therefore only cause small energy losses. The nature of these unusual catalytic surface states is not yet investigated. It can be hoped that via such model systems it can gradually be learned, how light can be used for energy efficient water splitting.

2.3. *Catalysis via transition metal clusters*

d-Band materials which transfer charges via clusters of transition metals have demonstrated an extraordinary catalytic efficiency. It was not yet possible to develop a reversible oxygen electrode (which can both, liberate oxygen from water and reduce oxygen to water) which would be of significant interest for electrochemical energy systems. The reason was that the developed cluster compounds which typically contain molybdenum were unstable for the anodic reaction (molybdate is formed), but the catalytic ability to reduce oxygen to water approaches that of the catalytic material platinum which has already found many technical applications. The efforts to learn how this catalysis via cluster materials can be optimized, by varying the element combination in a skilled way, have conduced to very interesting insights, even though for chemical reasons, only a limited number of atoms could be introduced into the desired compound.

Fig. 3 shows Tafel plots for the oxygen reduction current with cluster compounds composed of different elements. The following relevant properties could be derived from the experiments (in Fig. 3 indicated by symbols and arrows). The over potential losses for the reduction of oxygen to water drop the more, the higher the number of delocalized electrons within the clusters. Especially when individual molybdenum atoms in the molybdenum clusters are replaced by other atoms, catalysis is improved. It increases with a degree of substitution at least until two of the six atoms are replaced by ruthenium. When a pure molybdenum-octaeder is chosen in the cluster compound, its catalytic properties can be improved by introducing additional metals as close as possible in the channels between the clusters. In this way, the advantage of high electron density and of bi-metallic centers for multi-electron transfer catalysis become obvious. It appears to be possible that structural dynamics of these clusters is favorable during electrocatalysis. When four electrons are extracted from such a cluster, as occurs during oxygen reduction, its volume increases by 15%. In a certain respect, the cluster is able to breathe during the electron transfer reaction and may in this way exert an autocatalytic influence on electron transfer (compare later).

It is interesting that one-electron transfer processes such as involved in hydrogen evolution cannot be improved by clusters. The most catalytic individual atoms in the cluster determine the catalytic ability.

3. Selectivity of electron transfer

3.1. *Site specific electron transfer*

In classical electron transfer theory the probability for electron transfer is dependent on the density of electronic states in the semiconductor which are globally provided as a function of energy. A site specific interaction is not considered to be important. Experience with d-band semiconductors indicates an unrecognized effect insofar as certain kinds of redox systems transfer electrons to the illuminated semiconductor with significantly higher probability as compared to others. It is found that electron donors which can coordinate with metal centers in the surface (which are oxidized during illumination) are significantly more efficient as electron donors (e.g. I^-) compared with those which cannot chemically interact with such surface atoms (e.g. Fe^{2+}) (see Fig. 4). Studies with inhibitors of organic and inorganic nature which are adsorbed in small quantities on iron disulfide surfaces show that electron transfer from I^- and Fe^{2+}, respectively, can selectively be inhibited. This means that these redox species transfer electrons to different sites in the surface. While the I^--species reacts by direct chemical interaction with an iron atom in the interface, Fe^{2+} donates its electrons probably

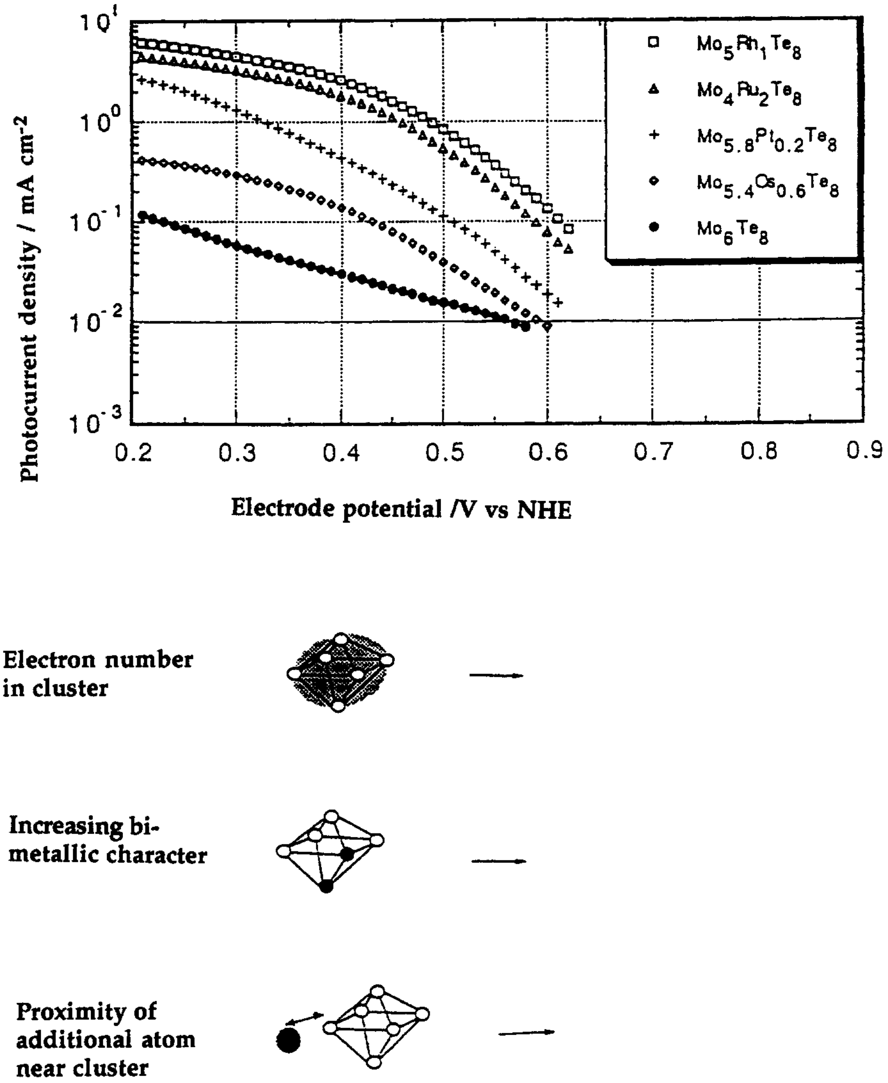
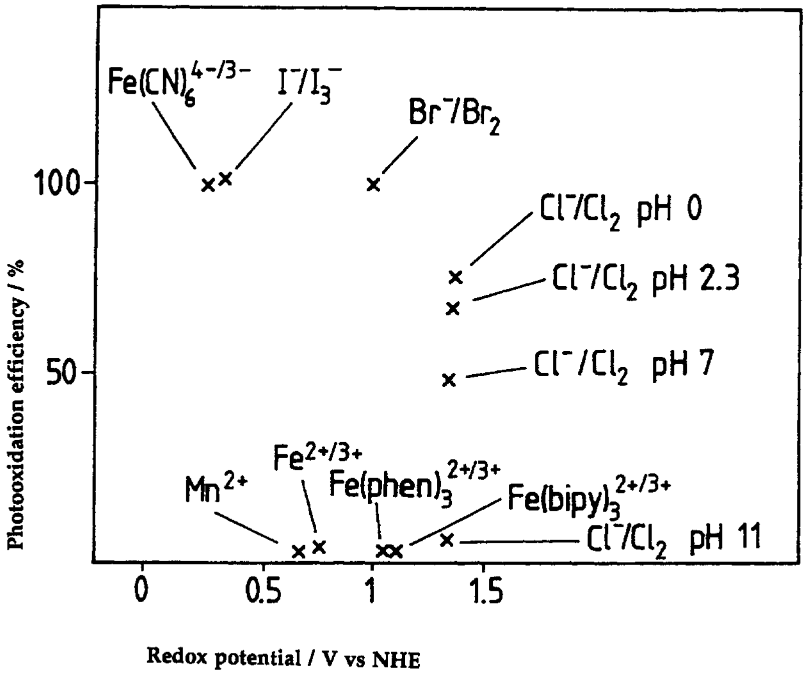


Fig. 3. Tafel plot of the oxygen reduction in 1 N H_2SO_4-solution for differently substituted octaeder-clusters in Chevrell phases. It is visualized how a higher electron density in the clusters, a higher proportion of binary metal character in the cluster, or additional metal atoms in the crystal channels near the clusters can produce lower over-potential (positively displaced reduction curves) and thus a more favorable catalysis.

via a sulfur site as electron transfer bridge into the semiconductor valence band. For an exact characterization of electron transfer, the effort appears to be necessary to consider the specific interaction sites in the interface. This makes the situation of electron transfer more complicated, however, also opens interesting new possibilities for catalysis. The fact that metal centered electron transfer reactions can proceed very efficiently allows it to control them preferentially so that side reactions may be suppressed. This indeed succeeded with a cluster compound for oxygen reduction which proceeds via a direct four-electron reaction with only a few percent of hydrogen per oxide formation. In this case, the oxygen can very efficiently interact with the Ru_xMo_y-surface center. A parallel reduction or oxidation of methanol would be much



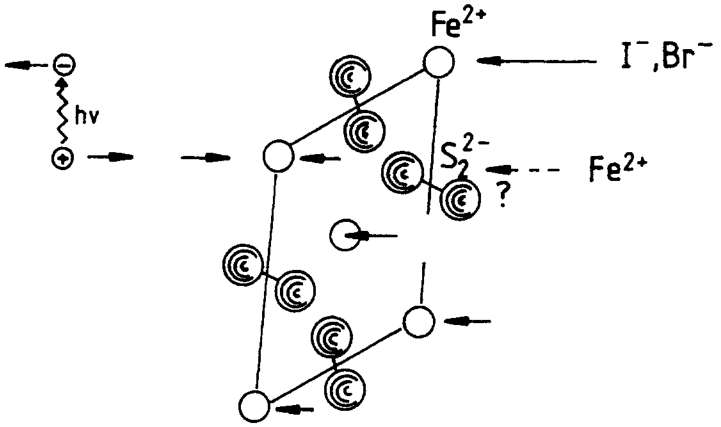


Fig. 4. Light-induced oxidation efficiency of different electron donors on iron disulfide surfaces measured with a rotating ring disc electrode. The suggested reaction pathways for electron transfer from I^- and Fe^{2+} are indicated.

less probable which has been experimentally confirmed. Addition of methanol does not lead to a depolarization of this oxygen electrode. Catalysts of this kind are therefore selective. When used as oxygen reduction catalyst in a methanol fuel cell, the separator membrane, which should prevent methanol from penetrating to the oxygen electrode, may be omitted without deteriorating the electrochemical properties of the system. The electrochemical catalytical behavior of such a layer, in the absence and in the presence of methanol during oxygen reduction is shown in Fig. 5. With reaction selective catalysts, new strategies for improved economy and innovative technology in fuel cells become possible [7].

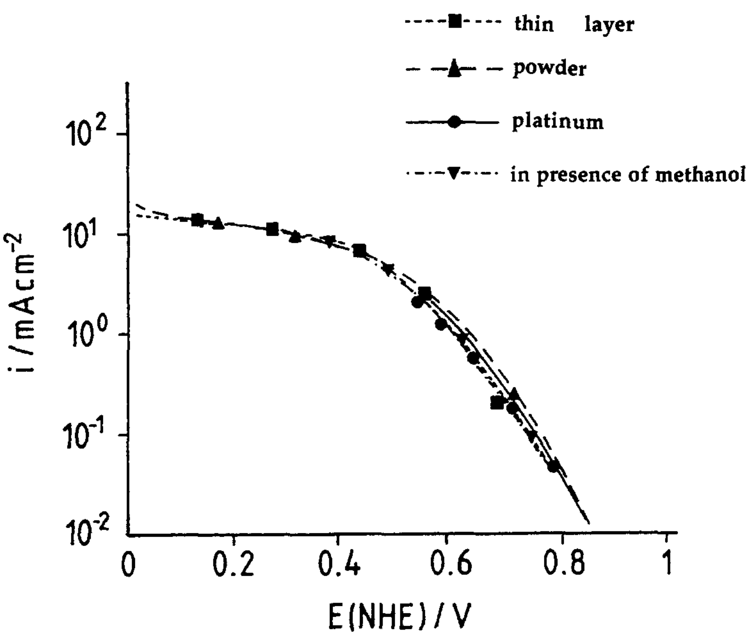


Fig. 5. Tafel plot of the oxygen reduction current of a $Mo_xRu_yO_zSe_N$ thin layer in 1 N H_2SO_4-solution. The catalytic behavior of a platinum layer in contact with the same electrolyte is compared and the lack of a methanol influence on $Mo_xRu_ySe_z$ demonstrated.

4. Synergetic mechanisms in electrocatalysis

4.1. Oscillating hydrogen evolution

Traditionally, the concepts of electrochemistry have been derived from near equilibrium thermodynamic theory. One example is hydrogen evolution which may be interpreted as a prototype of a quasi reversible reaction. As recently shown, hydrogen may also be liberated during an oscillating non-linear reaction, that means far from equilibrium during a synergetic process [8] (Fig. 6). In this model experiment, a copper indium diselenide electrode was used, which was placed in contact with a hydrogen peroxide containing solution. The photo potentials oscillated in dependence of the light intensity and oscillations occurred synchronously with the liberation of hydrogen. This non-linear photoelectrochemical system works because of autocatalytic steps which lead to oscillating, chaotic or multi-state mechanisms. Far from equilibrium, new phenomena occur which exhibit a very special entropy behavior. Under certain conditions, entropy may be exported. This means that order can locally be generated. This is a significant property of oscillating and structure formation mechanisms. Up to now it has been barely investigated to what extent such properties of non-linear systems for the increase of order, which have so successfully supported the development of life, may be used for improved electrocatalysis.

The overview in Fig. 7 summarizes investigations, which have been performed during recent time in order to clarify this question [9–11]. In the presence of autocatalytic electrochemical or photoelectrochemical mechanisms, it may be possible to export entropy (or disorder) from interfaces. This means, that in spite of current flow, order could in principle be maintained or interfaces could continuously be regenerated. How such processes could be handled artificially is not yet clear in detail. However, it is obvious that biological mechanisms can be stabilized by self-organization as long as they are contained in biological structures the environment of which provides the necessary autocatalytic chemical reaction pathways. If they are extracted, they are quite rapidly subject to irreversible changes.

On the basis of model calculations, it could be shown that a kind of self-organized electron transfer

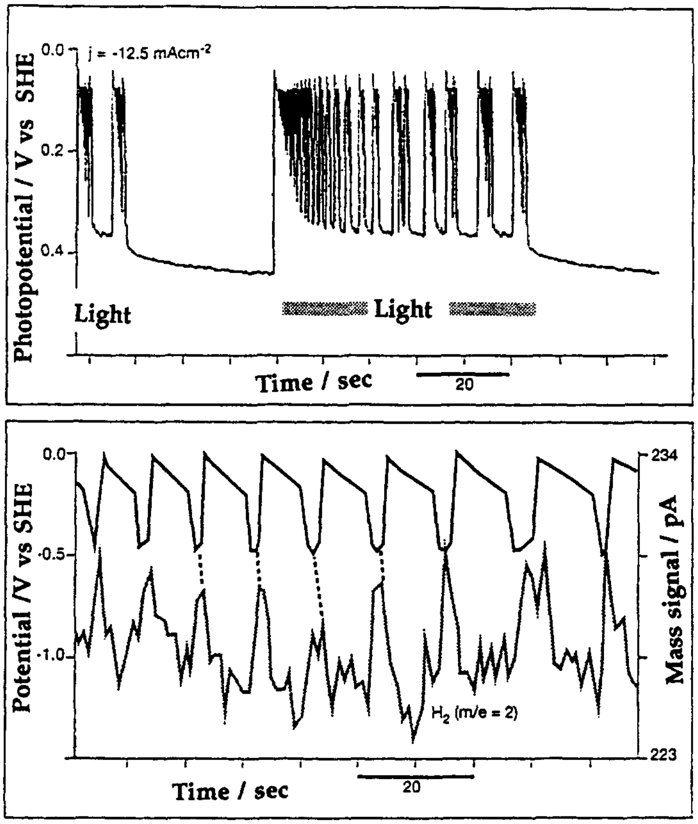


Fig. 6. Light-induced galvanostatic potential oscillations of copper indium diselenide electrodes in contact with hydrogen peroxide containing electrolyte solution. The mass spectroscopically (DEMS=differential electrochemical mass spectroscopy) determined oscillations of hydrogen liberation are demonstrated.

is possible, which is significantly more efficient than the classical case of electron transfer (Marcus), which has been discussed up to now [11]. Traditionally the electron transfer within the scope of the model of Kramer has been discussed as an escape of an electron from a potential well. For this process, an internal friction is considered which is related to the interaction between electron and molecular environment. Friction losses are typically passive which means that energy is being converted into heat. But physics also knows an active friction during which a friction force can convert from negative to positive action (e.g. a violin bow and string which interact in such a way as to initiate a stable limit cycle oscillation). Considering an active molecular friction, that means an active structural dynamic cooperation of the macromolecule or its environment, the rate constant for an electron transfer reaction can be increased by several orders of magnitude. In molecular terms, such a process can be understood in the following way: part of the energy which is provided for the electron transfer (chemical energy or light energy) may be transferred as phonon or confirmational energy in such a way that the electron transfer is supported via an active friction. In the case of a protein, the molecular structures discussed to be passively intervening in distant donor–acceptor coupling [15] have to assume an energetically active role. The additionally activated energy (used for the feed back or autocatalysis loop) is a decisive factor for the improvement of the activation complex for electron transfer. Purely mechanistically it has to be demanded that the macromolecular structure or the medium around must play an active role and not a passive one during the electron transfer. The self-organized electron transfer, that means electron transfer during which energy is provided via an autocata-

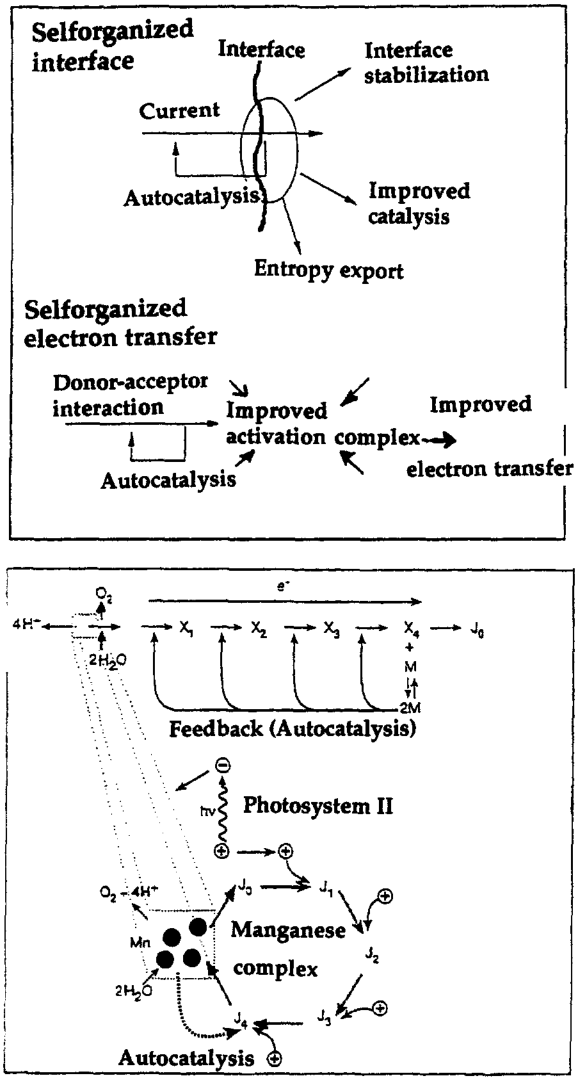


Fig. 7. Overview over electrochemically interesting problems for which progress can be expected via entropy export through autocatalytic mechanisms (dynamic self-organization). A synergetic multi-electron transfer is indicated as it could proceed during the last step of photosynthetic water oxidation.

lytic loop at the right moment for an ordered (self-organized) transition complex, may have found application in biological molecular structures. Precondition is a molecular complex, which is able to conduct small amounts of energy via molecular electronic structures as required for autocatalytic processes.

On the basis of model calculations it was possible to demonstrate that self-organized electron transfer can also occur in a collective way which means that several electron transfer processes are coupled in such a way that one process exerts a feedback on the next. When a suitable degree of feedback is provided, it can be demonstrated, that electrons become dependent on each other (one electron 'slaves' the others), that means one step necessarily causes the next step without the appearance of an intermediate state. In contrast to classical electrochemistry, which only knows single electron transfer processes which of course can rapidly follow one after another, the non-linear theory can prove that collective electron transfer is possible. This possibility is energetically of significant interest since important mechanisms of energy conversion involve multi-electron transfer processes which proceed at a more favorable potential compared to successive individual electron steps with well-defined intermediates.

One of the scientifically most fascinating catalytic processes is the light induced water splitting in photosynthesis. Technical attempts to develop catalysts for water splitting concentrate on highly catalytic transition metals and unusually stable compounds which resist a very positive oxidation potential. Such criteria seem to contradict the manganese complex of photosynthesis: First, it is very labile, then it contains the element manganese as a metal center which up to now has found no application as a technical catalyst. In addition, theoretical calculations exist which exclude that any known and imaginable stable manganese complex would be able to oxidize water [13]. All these contradictions can reasonably be explained when concluding that nature catalyzes water splitting during the last step in the cycle of the manganese complex via a synergetic mechanism. This means that entropy is exported via autocatalytic steps or in other words, order is built up. This generates a temporary activation state of high catalytic activity which is able to catalyze the multi-electron transfer from water. A relatively simple model allows to simulate such a process and to deduce oscillating properties. It is important to note that photosynthetic membranes actually oscillate which is reflected in both, the oxygen evolution and in other processes in the photosynthetic electron transfer chain [16]. It is up to now not clarified by what mechanisms these oscillations are generated. The model of synergetic water splitting predicts the ability to oscillate as an unseparable part of photosynthetic water splitting and imagines the proceeding molecular process for example in such a way that two protons react with the manganese complex in the first step in order to liberate six protons. This would be an autocatalytic process which finally leads to the net liberation of four protons as known from the water splitting process.

If, as we propose, photosynthetic energy conversion really takes advantage of dynamic self-organization, if the reaction center [14] as well as the water splitting complex [12] optimize and perfectionate their structure while energy is flowing through, they may become model systems towards a new frontier in dynamical molecular processes supporting catalysis.

5. Outlook

Compared with the performance of biological examples of (photo)catalysis, (photo)electrocatalytical research has still a long way to go. In order to explore novel possibilities for the increase of catalytic activity and for the development of new classes of catalytic materials, it is reasonable to experimentally and theoretically explore unconventional routes. Three initiatives from our research group, metal-centered electron transfer, selectivity during electron transfer and synergetic mechanisms of catalysis have been discussed. It may be a combination of such, and other not yet well-explored mechanisms which have facilitated the evolution of high activity of biological catalysts.

For further reading

Ref. [6]

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