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ENERGY CONVERSION IN SOLAR FUELS AND CHEMICALS

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KEYWORDS

Photoredox, Photoelectrolysis, Electrolysis, Microelectrodes, Water-splitting, CO₂-Reduction, Solar Energy.

ABSTRACT

The internal energy of matter rises when matter is supplied with energy. This can happen in several ways: The simplest possibility is to increase the temperature. This means sensible heat. A more involved possibility is connected with phase transitions. It is called latent heat. Complexity increases in case of heat of adsorption and heat of desorption. It increases even more in chemical transformations which means the formation of new compounds. All these principles can be used in solar energy conversion systems depending on the application envisaged. In thermochemical reaction pathways unspecific nuclear motions are excited while in photochemical reactions specific electronically excited states can be involved. It is very interesting to realize the close connection between photochemical and electrochemical redox reactions. In both cases electrons are moving from one electronic state to the other without involving nuclear motions according to the so called Franck-Condon principle. After discussing these general principles, reference is made to actual research on photoelectrolysis of water and carbon dioxide with microelectrodes and with molecular devices.

INTRODUCTION

Significant activity in solar energy research started immediately after the oil crisis in 1973 and it declined 10 years later, as soon as the oil prices started to decline. Considering energy and pollution problems we encounter every day, renewed interest in solar energy research in the near future is very probable.

Publications "SOLAR ENERGY"

Reviewed in CHEMICAL ABSTRACTS

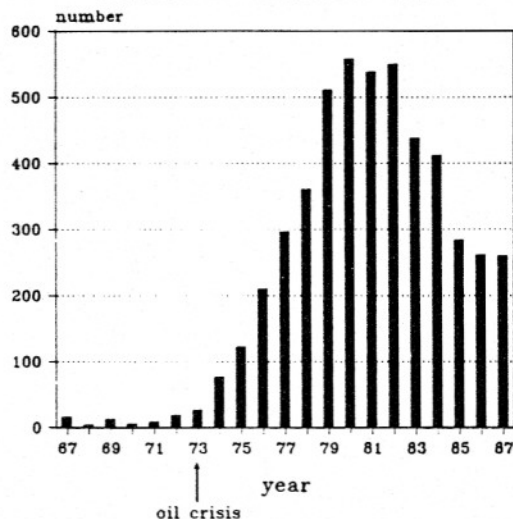


Figure 1

Number of publications containing the keyword "Solar Energy" reviewed in Chemical Abstracts.

Before discussing artificial systems, remember that we all live on the photosynthesis of green plants and that we shall always persist on this food and energy resource. It is therefore necessary to take care of it.

Photosynthesis of green Plants

World production of biomass:

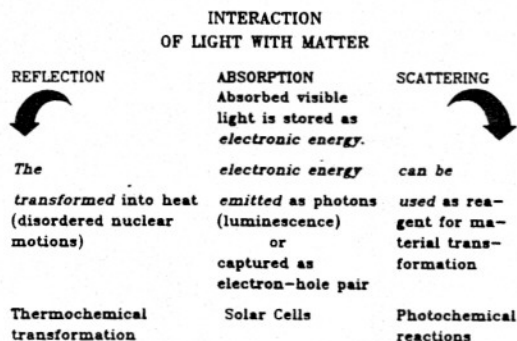
$1.7 \cdot 10^{11}$ tons/year

Photochemical primary processes in plants lead to storage of solar energy as sugar, starch, cellulose, fat, oil, protein and many other natural products.

The overall energy storage efficiency in plants reaches about 2% under ideal conditions. In our degree of latitude it is in the order of 0.1% (average over a year). Only about 12% of the land of the earth can be used for agriculture.

It is reasonable to search for artificial photochemical energy storage processes. Storage efficiencies of about 16% are expected to be possible.

The interaction of light with matter can be summarized as follows:



Reflected or scattered light is lost for our purpose. Only light which has been absorbed can be used. *Absorption of light* is therefore of fundamental importance. In the diagram above I refer to visible light. Absorbed light of longer wavelengths than about 1000 nm is not stored as electronic energy. It is directly transformed into energy of nuclear motions which means that it is transformed into heat in less than 1 ps. Approximately 60% of the incoming solar energy is of shorter wavelength than about 1000 nm. It can be used in photoelectrical, in photoelectrochemical and in photochemical devices [1].

Electronic energy can be transformed into heat, electron hole pairs and chemical bond energy. This corresponds to a common classification of useful energy [1,2]:

heat - electrical energy - chemical energy.

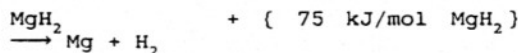
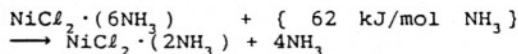
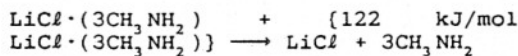
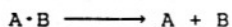
Electrolysis of water by means of electricity produced in solar cells is feasible nowadays. It depends mainly on economic considerations whether this option will be used on a large scale. Let us therefore focus on thermochemical and photochemical options and start to discuss the influence of heat on matter.

The internal energy of matter rises when matter is supplied with energy. This can happen in several ways:

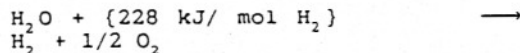
- The simplest possibility is to increase the temperature. This means sensible heat.
- A more involved possibility is connected with phase transitions such as melting of ice. It is called latent heat.
- Complexity increases in case of heat of adsorption and heat of desorption.
- It increases even more in chemical transformations which means the formation of new compounds.

All these principles can be used in solar energy conversion systems depending on the applications envisaged. The main advantage of phase transitions with respect to sensible heat is that higher energy storage densities at medium storage temperatures can be obtained. A nice demonstration example working at 52 °C is a mixture of 92% sodium acetate + 8% sodium formate [3]. Higher energy densities can be obtained by using heat of adsorption and heat of desorption as e.g. in zeolite-water + heat = zeolite + water [4]. The highest energy storage densities are obtained in chemical transformations. There are different possibilities available:

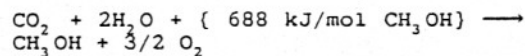
Cleavage of addition compounds (ΔH^0):



Dissociation of a compound ($\Delta G^0, \text{gas}$):



More complex reactions ($\Delta G^0, \text{gas}$):



Cleavage of addition compounds is possible at relatively low temperatures, 200 - 300 °C, while dissociation of water or carbon dioxide reduction occur above approximately 3000 °K. Cyclic thermochemical reactions have been developed to lower this temperature to about 1100 °K. As an example, a metal or a metal oxide is heated with water to produce $MO + H_2$. In a second step, MO is decomposed into $M + 1/2 O_2$ [5]. One should realize that in photochemical and in electrochemical devices it is possible to run these reactions at room temperature. It is therefore interesting to ask for the basic difference between thermochemical and photochemical reaction pathways.

COMPARISON:

THERMOCHEMISTRY/PHOTOCHEMISTRY

In thermochemical reaction pathways unspecific nuclear motions are excited according to Boltzmann's energy distribution law while in photochemical - and often also in electrochemical - pathways specific electronically excited states can be involved.

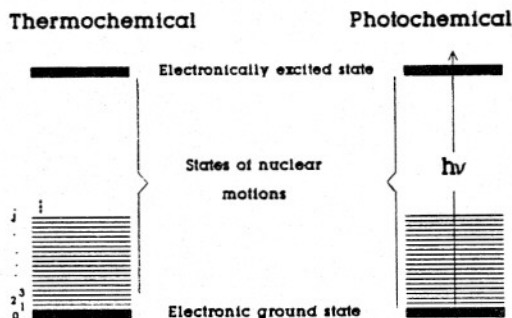


Figure 2

Comparison of thermal and electronic excitation of matter.

States of nuclear motions are randomly excited according to Boltzmann's energy distribution law by heating matter. Absorption of photons in the near IR, in the visible and in the UV part of the solar spectrum leads to electronically excited states, far away from thermal equilibrium.

After absorption of light the energy of the photon is first stored for some nanoseconds or microseconds as kinetic energy of the electrons. Following the absorption, there are three types of relaxation processes which can occur:

- The electronic energy is transformed into heat,
- or it is emitted as photons;
- the third possibility is that it is captured in an intermediate relatively long living state from which a chemical reaction can occur, such as the primary steps in the natural photosynthesis of plants.

These three types of relaxation processes are shown in Figure 3. The maximum thermodynamic efficiency of a photoreaction is 71%. This limit is, however, unrealistic. If we imagine a single threshold device it is about 29%, the same as for solar cells. In a real system we have some further losses which make it realistic to expect that solar energy storage devices of about 16% storage efficiency should become possible [6,7].

Transformation
of electronic excitation energy in

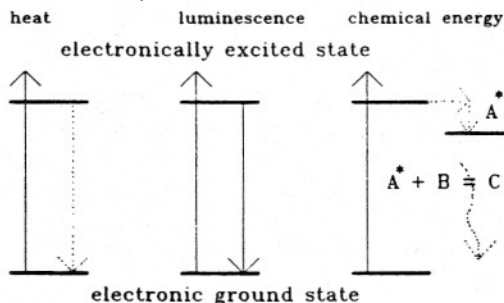
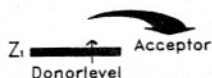


Figure 3

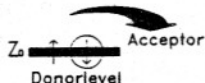
Relaxation processes of electronically excited states showing that excitation energy can result in heat, in luminescence or in chemical energy.

It is very interesting to realize the close connection between photochemical and electrochemical redox reactions. As shown in the figure below electrons are moving from one electronic state to the other in both cases, without involving nuclear motions. This is the so called Franck-Condon principle which plays an important role in the theory of photochemical and of electrochemical reactions.

Photochemical Redoxreactions



Electrochemical Redoxreactions



Z_0 : electronic ground state

Z_1 : first electronic excited state

Figure 4

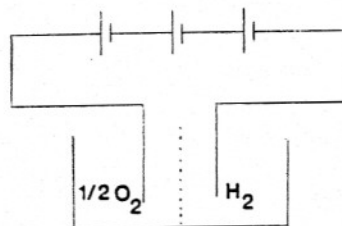
Comparison of photochemical and electrochemical redox reactions.

PHOTOELECTROLYSIS OF WATER WITH MICROELECTRODES

Imagine conventional photoelectrolysis of water with three or four macroscopic photocells in series as shown in figure 5. This solar energy conversion system would certainly work with several percent storage efficiency. In order to reduce system costs, it would be interesting to miniaturize the electrodes so that no macroscopic wiring would be necessary. A system with three or four microelectrodes in series and an ion permeable membrane is shown schematically in the lower part of this figure. It would certainly be a challenging engineering problem to realize such a device.

Photoelectrolysis of Water with Microelectrodes

Conventional: Makroelectrodes



Unconventional: Microelectrodes

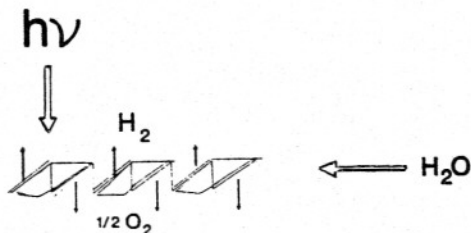


Figure 5

Photoelectrolysis of water with conventional macroelectrodes and a futuristic device with microelectrodes which needs no macroscopic wiring.

An even more exciting possibility is to reduce the size of the electrodes down to molecular scale which means to use them as photocatalysts. Different attempts have been made in this direction with partial success [8-11]. The bottleneck in these experiments has always been the oxygen production from water. We have successfully worked on this reaction [1,12] so that it has become interesting to try and realize water-splitting or CO_2 reduction. Our research approach is explained in Figure 6. For the reductive part we rely on systems developed by other research groups [8-11] while the oxidative part is designed according to a system developed in our laboratory [12]. The problem to be solved is to connect the oxidative part which delivers the two electrons and the two protons to the reductive part. To understand the system, it is important to realize that the redox potential of small metal clusters is very different from the redox potential of the bulk metal [7,13,14]. Another important point is that the photooxidative and the photoreductive reactions must not take place simultaneously since the modified zeolite can act as an electron storage device.

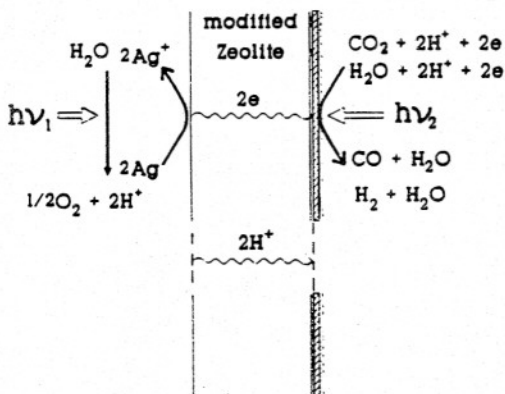


Figure 6

Complete photoredox system for water-splitting and carbon dioxide reduction. Electrons are moving through a modified zeolite while protons are transported through ion permeable membranes.

The attractive aspect of this approach is that the reductive, the oxidative and the electron conducting parts can be studied separately. To develop our understanding of the oxidative and of the electron conducting parts, we have made photochemical, spectroscopic and theoretical studies [1,12,15,16].

Acknowledgements

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