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Thermo-Photochemistry

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1. Direct Solar Photoconversion to Fuels and for Chemical Processes

Direct solar photoconversion refers to the absorption of sunlight by photoactive substances thereby inducing the direct formation of useful fuels (such as H_2, CH_4, alcohol) or chemical products (such as NH_3, vitamin D, fine chemicals, etc.). Also included among the chemical processes are the environmental benefits derived from photodestruction of toxins and pollutants (such as chlorinated hydrocarbons, dioxins, etc.). The photoactive substances can be in the form of solids (e.g. semiconductors), molecules, or biological materials; these systems can be respectively classified as photoelectrochemical, photochemical, and photobiological. Chemical reactions with positive free energy changes (uphill energy storing reactions) as well as those with negative free energy changes (downhill reactions) are included; the term photocatalysis will be applied to both types of reactions where the rate of reaction is increased in the presence of light. Also included in the term photoconversion are systems in which the photoactive substances are present in a macroscopic, two-dimensional form (e.g. an electrode) or as dispersed particles (colloids or particle suspensions in fluids).

There are many advantages of the direct photoconversion approach. First, novel chemical pathways can be achieved at illuminated semiconductor surfaces in contact with chemical reagents that cannot be achieved at metal electrodes, even at the same electrode potential; this has been demonstrated especially for organic oxidation reactions. Second, the direct photoconversion system is a one-step process with higher theoretical conversion efficiency compared to multi-step processes (such as photovoltaics plus dark electrochemistry or biomass conversion). Third, novel hybrid system can be constructed (e.g., bio/semiconductor or photo/thermal) as discussed below. Forth, novel, more simple, and potentially better reactor designs are possible with direct photoconversion systems. And fifth, novel effects (such as hot carrier conversion processes) can only be achieved through direct photoconversion.

In the current structure of most renewable energy programs in IEA Member countries, direct solar photoconversion is not included as a separate, identifiable program, unlike photovoltaics, wind, ocean, biomass, solar thermal, and geothermal. We believe it is necessary to establish direct photoconversion as an important, separate component of a viable R&D program for renewable energy.

1.1. Heterogeneous Systems and Effects of Temperature and Photon Flux

Similar to suspensions of semiconductor powders in liquids one could conceive of semiconductor powders suspended in a gas, especially for high-temperature direct absorption. In this context the question arose whether semiconductors would work at all at temperatures as high as 1000 °C because the efficiency of charge separation decreases with temperature. High band gap semiconductors may deteriorate less with increasing temperature. In any case, the need for high-temperature semiconductors is acknowledged.

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For direct absorption, both homogenous and heterogenous systems are possible. For the homogenous gas-phase reactions it might be difficult to reach high enough absorptivity, though high temperature might help to increase the absorptivity of some gases. Heterogenous systems, such as e.g. powders suspended in fluids, offer advantages as direct absorbers, both because of higher optical absorption by multiple scattering and shorter absorption length and because the absorption takes place precisely at the site of the reaction, the solid/gas interface. Thus the reaction site is the hottest part of the system.

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Considerable interest is focussed on possible synergisms between high temperature and high photon flux. Conventional photochemistry is carried out at room temperature, whereas conventional thermochemistry does not exploit the photons which constitute energy quanta in the range up to 3 eV. While reactions in which the products carry little or no entropy are expected to deteriorate with increasing temperature, there might be reactions, e.g. producing gases from solids, in which the entropy of the products is less than that of the educts. Such reactions might be endothermic in the sense that they consume heat in addition to the radiant energy and/or might increase in efficiency with increasing temperature. The search for and the identification of such reactions appears a rewarding field. A better theoretical understanding of such processes is also required.

The question of optimum temperature for direct conversion is difficult. Besides, the temperature might not be an easily controlled parameter in conjunction with photon fluxes in the range of several MW/m^2. The range of temperature prevailing under these conditions is probably above 1000 K, which is roughly a factor 4 higher than the ambient temperature and at the same time a factor 4 lower than the temperature of the sun.

1.2. Solid Ionic Conductors in Solar Energy Conversion Systems

Solid ionic conductors are a class of materials in which charge transport is effected by mobile ions rather than by the electronic mechanisms found in metallic or semiconducting materials. They are also referred to as solid electrolytes. They may be organic, like the fluorinated polymer nafion™, which is a hydrogen ion («proton») conductor, or inorganic. Also the mobile species may be anionic, such as the doubly charged oxygen ion in zirconium dioxide, or cationic as in the nafion case or in B-alumina. In general for the inorganic solid ionic conductors, which are ceramic materials, sufficient ionic mobility is achieved only at elevated temperatures, typically 300 °C for B-alumina and 850 °C for stabilized zirconium dioxide.

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Solid ionic conductors are already established in some branches of energy technology. Energy storage in the sodium sulfur battery is through $Na^{\oplus}$ transport in a B-alumina solid electrolyte. High-temperature electrolysis of water, as in the German «Hot-Elly» project, relies on $O^{2\ominus}$ transport in a zirconia membrane. The same material is also applicable in methane fuel cells, and is used as a combustion gas analytic sensor in automotive and industrial application. Recent publications report innovative chemical reactions at solid electrolyte/gas interfaces, such as methane activation (*Steele*, Imperial College, London, UK), and selective oxidation of xylene to phthalic anhydride for example, can be proposed.

To date, however, all solid ionic devices have employed conventional thermal fuel and electrical inputs, with little attention to the solar option. It is suggested that materials research be directed to systems with direct photoactivation of ionic mobility, for example through the phonon spectrum of the solid. In materials with mixed electronic and ionic conductivity, the electric fields generated by photovoltaic structures such as Schottky junctions could result in ionic charge transport and therefore in electrochemical effects such as electrolysis or selective oxidation at the solid/gas interface. In short, mobile charge carrier concentration gradients, however induced, are equivalent to chemical activity gradients, and could be exploited.

A closely related concept to ionic conduction is intercalation in which a guest species is incorporated into a host solid lattice, at defect sites, interstitially, or at structural voids. The incorporation of ions from solution following photoinduced charge transfer at semiconductor-liquid electrolyte interfaces has been demonstrated (*Tributsch*, Hahn-Meitner-Institut, Berlin; *McEvoy*, EPF Lausanne). A solar rechargeable battery similar to the conventional lithium intercalation cell is one possible development.

It is evident that the concept of photoelectrochemistry, hitherto accepted as light-induced processes at the semiconductor/electrolyte interface, must be generalized to include mass and charge transport within solids by photoinduced ion mobility and intercalation processes.

1.3. Non-Thermalized (Hot) Carrier Photoconversion

High conversion efficiency is a critically important requirement for most solar energy conversion systems. This is because of the dilute nature of solar energy and the fact that the required large, «up-front» capital investment for solar energy conversion systems decreases approximately linearly with conversion efficiency.

With a single band gap (or energy threshold) type of absorber, the maximum attainable thermodynamic conversion efficiency is 32%. For semiconductor photoconvertors, a major energy loss factor in this analysis is the thermalization of the original energy of the photogenerated charge carriers (electrons and holes) to the energy levels of the band edges of the semiconductor. That is, it is assumed in the above thermodynamic analysis that all photogenerated electrons and holes loose their excess energy above the band gap as heat to the lattice before they are converted into other forms of chemical or electrical energy. If one would be able to utilize the photogenerated charge carriers from solar photoexcitation for energy conversion before they thermalize and equilibrate with the lattice, then the maximum attainable thermodynamic efficiency increases to 68%. Under such conditions, the electron temperature (assuming that the hot electrons are in equilibrium with each other and that all the excess photon energy goes into electrons and not holes) is about 3000 K, while the lattice temperature is 298 K. This analysis gives the same conversion efficiency attainable by a sequential series of different band-gap absorbers exactly matched to the solar spectral distribution.

The achievement of hot carrier photoconversion processes is very difficult because the charge carrier thermalization times are very fast, typically 2–10 ps for bulk semiconductors. This means that the charge-transfer times have to be even faster to successfully compete with thermalization. Ways must be found to decrease thermalization times in semiconductors or increase electron-transfer times from the semiconductor into the chemically reacting phase.

It has recently been found that thermalization times in semiconductors can be significantly increased through quantization effects in semiconductor superlattices and quantum wells; thermalization times from 50 to 300 ps have been reported. Also, evidence of hot electron transfer from illuminated semiconductors has been reported by several groups. Additional research on hot carrier photoconversion should be done to evaluate the prospects for ultimately achieving very high conversion efficiencies.

1.4. Bio/Semiconductor Hybrid Systems

It is proposed that studies be conducted on hybrid systems containing an optimum combination of biological and semiconductor components, in which the best aspects of each component are utilized. Thus, semiconductors are excellent for harvesting solar radiation and generating charge separation; biochemical enzymes are excellent for driving very specific chem-

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ical reactions at high kinetic rates. This concept has already been demonstrated for p-type InP semiconductor electrodes coupled through an electron mediator (methylviologen) to formate dehydrogenase to drive the photoreduction of CO_2 to formic acid. This photo-process is difficult to achieve with semiconductors alone. Other semiconductor and enzyme combinations should be investigated to discover new efficient systems for the photoproduction of fuels and chemicals.

1.5. Use of Temperature Gradients

In every kind of absorber the light flux coming from one side only will lead to a temperature gradient between front (illuminated) and back (dark) side. This results in a gradient also in the chemical potential of species on the two sides and a flux of molecules from the hotter to the cooler side. A simple example is solar distillation, as used on a large scale already e.g. in direct solar driven desalination plants. Here the energetically uphill reaction from salt water to pure water is driven by the temperature gradient.

It should be investigated whether and how a temperature gradient could be used in a solar reactor to support a desired light-driven reaction as e.g.

- a photoelectrochemical intercalation process as a possible combination of both photoconversion and storage of solar energy, or
- the separation and/or storage of photochemically or photoelectrochemically produced chemicals or energy carriers as for example hydrogen to store in a hydride.

Also T-gradient forced concentration differences could be useful in getting a desired electrical potential difference as e.g. a pH difference between front and back surfaces of a photochemical diode. Further interest in ion concentration differences may result from the use of ionic conductors as photoelectrodes.

Direct photodriven mass transport may be possible either in ionic conductors («photoionic pumping») or in new, not yet investigated, porous conducting or semiconducting materials like special zeolites or polymers with open structures enabling mass transport (pumping) driven by electrical and/or chemical potential gradients through the material. Also photo-driven actively transporting membranes might be possible using materials with light-induced conformation changes (as known from biological systems) either for mass separation processes such as water purification, or for producing electrical or chemical potential differences.

1.6. Photodetoxification

Very high oxidation and reduction potentials are achieved on light absorbing materials such as semiconductors or dyes after electron excitation. These potentials can be used easily for oxidative or reductive destruction of nearly all organic molecules. In addition reductive deposition of metals from metal ions can occur. Both types of reactions can also occur at the same time. As has been shown experimentally already by several groups worldwide, these reactions can be used for conversion of pollutants in aqueous solutions down to very low concentrations (even to below the detection limits of ppb or ppt). Two kinds of reaction systems are possible:

- *Removal of pollutants from solutions:* Here the polluted solution passes in contact with photoactive particles in suspension or immobilized on porous membranes, or over a surface of an illuminated light-absorbing material (e.g. a semiconductor), where the organic material normally is oxidized after absorption and metals are deposited.
- *Reactions in the gas phase:* In principle the same reactions are also possible at the solid/gas interface in a gas or vapour stream passing through an illuminated powder or filter. Homogeneous gas-phase photodissociation of pollutants has also been investigated.

The possibility of photodetoxification as described above has been proven experimentally and prototypes of «solar filters» have been developed. Further research is necessary, however, to find out among others what the specificity of the reactions is for a desired reaction type:

- what kind of reactions can be driven;
- what are the reaction products for a given specific waste solution;
- how the specific reaction pathway may be tuned into a wanted direction;
- what materials can be used as light-absorbing materials besides TiO_2, up to now the most widely used substance (with other semiconductors, dyes, etc.);
- whether and how additional catalysts as e.g. noble metals can be useful.

Photodetoxification is in principle a very simple and highly efficient method, of interest already for special applications such as the cleaning of recycled water in spacecraft from low-level residual pollutants, as well as for the removal of traces of very highly toxic substances as e.g. dioxins. Therefore the price of these systems does not need to meet the goal set by fossil fuels. Special applications provide several niches for application. As an environmental protection measure it secures in addition political support.

However, the integration of photodetoxification into a direct R&D effort is necessary to open up this very promising pathway for insertion of solar driven processes into our economy.

2. Nonlinear Photochemistry at High Solar Intensities

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The technology of solar energy concentrators is developing rapidly. At the moment it is possible to reach sufficiently high photon densities that will undoubtedly open up new photochemical channels involving nonlinear absorption processes and leading to new products or destroying more efficiently undesirable reactants. Furthermore, it will allow the use of a large portion of the solar energy spectrum in such nonlinear absorption processes.

Fig. III 3 illustrates these ideas. Suppose the photochemistry threshold is at $h\nu_1$, as determined by the free energy of the reaction. Thus photons of frequencies ν_1 or higher in the solar spectrum have to be absorbed to cause the photochemical process at low solar intensities. The photochemistry discussed here could be molecular dissociation, molecular ionization, photoelectron ejection as present in a semiconductor, or simply bimolecular photochemistry between a molecule excited to level 1 upon collision with another molecule.

If ν_1 is not absorbed by the system or is of such high value to have very low inten-

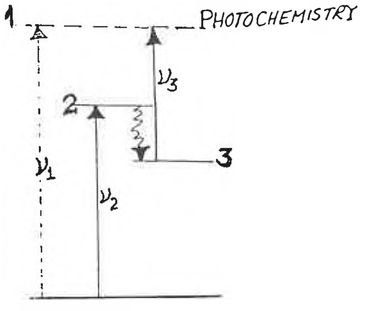

Fig. III 3. Nonlinear photochemistry could lead to new reactions or enhance existing ones by absorbing more than one photon from the different regions of the solar spectrum at high solar intensities.

sity in the solar spectrum at the earth surface, no photochemistry will be observed at low solar intensities. However, at high solar intensities, molecules reaching level 2, upon relaxation to the metastable level 3, might have strong absorption to levels at or higher than level 1. This can thus lead to observed photochemistry.

Even for molecules where photons at frequency ν_1 have high intensity and for which absorption to both states 1 and 2 is strong could benefit from the nonlinear absorption process. This is accomplished by absorbing photons of frequencies ν_1 and ν_2 followed by relaxation to level 3 and then absorbing photons of frequency ν_3 to reach levels near level 1 which could lead to an enhanced efficiency of the photochemistry. Furthermore, this will allow for the usage of a larger fraction of the solar spectrum in inducing the photochemical reaction.

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