PROCEEDINGS

△IS&T

SYMPOSIUM ON ELECTRONIC AND IONIC PROPERTIES OF SILVER HALIDES
Common Trends With Photocatalysis

part of the 44th Annual Conference

Editor: Boris Levy

Co Editors: Joseph Deaton   Ingo Leubner
                 Lawrence Slifkin   Annabel Muenter
                 Prashant Kamat   Tadaaki Tani

May 12-17, 1991
The Radisson Hotel
St. Paul, Minnesota

TOWARDS ARTIFICIAL PHOTOSYNTHESIS

Experiments with Silver Zeolites, Part 1

Robert Beer, Gion Calzaferri [*], Niklaus Gfeller, Jianwei Li, and Beate Waldeck
Institute of Inorganic and Physical Chemistry, University of Bern,
Freiestrasse 3, CH-3000 Bern 9, Switzerland

Summary

We explain the principle of a photochemical energy storage system, based on the oxidation of water by means of a silver zeolite system that is separated from the reductive part by a membrane. The process is split in three parts: the oxidation of water to oxygen, the reduction of water to hydrogen and the coupling of the two processes. Photoredox reactions are at our disposal for the oxidation of water and others for the reduction of water. Time has therefore come to try and realize the coupling between them which has to be accomplished by means of a membrane that allows the transport of electrons and protons from the oxidative to the reductive side and that prevents recombination reactions. To bring electrons from the reductive to the oxidative part, however, sufficient electron conductivity across the zeolite is needed. Experimental studies have led to the result that the resistance of even very thin silver zeolite pellets is by orders of magnitude too high. It is caused by the interface of the grain boundaries. We have therefore developed a technique for preparing zeolite layers as a dense monograin sheet onto an electrode which shows that the silver reduction and oxidation steps in the zeolite are quasi reversible. The technique described can be extended to different substrates such as Pt, graphite, glassy carbon, glass, quartz, tin dioxide and others. Having demonstrated that it seems likely for the transport processes of the zeolite part to be solved, we discuss two specific possibilities to couple the two half-reactions. The first is to combine on a membrane semiconductor particles able to accomplish water reduction with a silver zeolite. Excitation of the particles delivers the electrons necessary to reduce protons. The holes produced in this process are recombined with the electrons delivered by the reduced silver in the zeolite. Combination of the silver zeolite with an appropriate metal complex able to photo-reduce water or CO_2 is another possibility.

[*] Author to whom correspondence should be adressed.

1. Introduction

In artificial photosynthesis the goal is to mimic green plants and other photosynthetic organisms in their ability to use sunlight for making high-energy chemicals. This is a chemically difficult problem. The most desirable processes for chemical transformation and storage of solar energy are water splitting, carbon dioxide reduction and nitrogen reduction. Today none of these reactions can be carried out under solar irradiation with a significant quantum efficiency by means of an artificial molecular system. Nevertheless, a number of interesting approaches have appeared in the last few years and there is little doubt that chemists will succeed to design efficient molecular solar energy storage devices.[1] The principles of such an energy storing system are demonstrated in Figure 1.
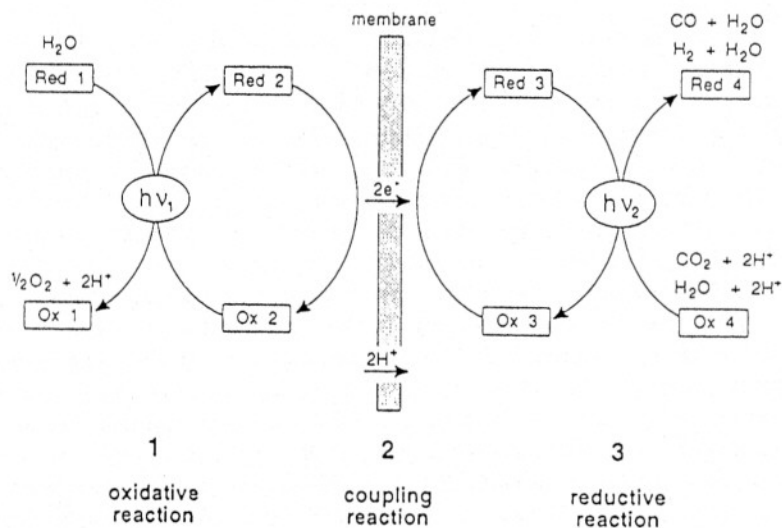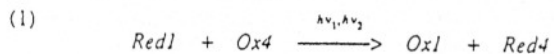

Figure 1:   Schematic device for the water splitting or carbon dioxide reduction. The net process is an endergonic oxidation-reduction reaction.

(1)
$$Red1 \;+\; Ox4 \;\xrightarrow{h\nu_1, h\nu_2}\; Ox1 \;+\; Red4$$

We split the process in three parts: the oxidation of water to oxygen in reaction 1, the reduction of water to hydrogen in reaction 3 and the coupling of 1 and 3. The energy is added to the system by photons $h\nu_1$ and $h\nu_2$ which excite Ox2 and Red3 respectively. Reaction **2** has to fulfil the condition that the two electrons from Red2 are quantitatively transferred to Ox3. At the same time protons must move from 1 to 3 to satisfy electroneutrality. A membrane is needed to separate the oxidative and reductive reaction spatially.[2] It has to prevent energy and material consumption caused by side reactions between redox systems [(Red1,Ox1),(Red2,Ox2)] and redox systems [(Red3,Ox3),(Red4,Ox4)].

2. Oxidative part

The bottle-neck in chemical approaches to artificial photosynthesis on a molecular level has always been the photo-oxygen production from water. A number of photochemical experiments have shown that on illumination of silver zeolites in aqueous dispersion the Ag^+ ions are reduced and molecular oxygen is evolved.

(2)
$$[(Ag^+)_n, mH_2O]Z \;\xrightarrow{h\nu}\; \left[Ag_n^{(n-r)+}, rH^+, \left(m - \frac{r}{2}\right)H_2O\right]Z + \frac{r}{4}O_2$$
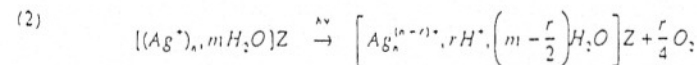
Z represents the negatively charged zeolite lattice. Reaction (2) is followed by partial transfer of the zeolitic protons to the solution, which results in a decrease of pH according to:

(3)
$$\left[Ag_n^{(n-r)+}, rH^+, \left(m-\frac{r}{2}\right)H_2O\right]Z + r'H_2O \;\rightleftharpoons\; \left[Ag_n^{(n-r)+}, (r-r')H^+, \left(m-\frac{r}{2}\right)H_2O\right]Z + r'H_3O^+$$

Investigation of the spectral sensitivity of reaction (2) has lead to the surprising result that a self-sensitization takes place: the further the reaction proceeds, the more the sensitivity shifts from initially near UV to visible wavelengths out into the red range. The experimental techniques used and the results obtained have been described in detail.[3]

As demonstrated by the self-sensitization, new chromophores with bathochromically shifted absorption are produced in the process of the photoreaction. They are themselves able to drive the photoreaction if they are excited. Quantumchemical calculations of the Extended Hückel type of silver ions in zeolitic environment have provided the background to understand the nature of the electronic transition.[4] It was found that the lowest energy transition is a ligand to metal charge transfer (LMCT), exciting an oxygen lone-pair electron to the silver species coordinated by the zeolite. Our interpretation is supported by the finding that the calculated first ionization potential of about 10.7 eV for the spherosiloxane $H_8Si_8O_{12}$ - which can be regarded as a model for the 4-4 SBU in zeolite A - is in good agreement with the experimental photoelectron spectrum.[5] To get a feeling for the consequences of this relatively high lying oxygen lone pair we have to compare it with the first ionization energy of the water molecule, observed at 12.6 eV and attributed to the energy of the p-type lone pair of the water molecule.[6] The calculations on the silver zeolites predict bathochromic shifts if interaction among silver species within the zeolite is taken into account. The self-sensitization phenomenon can therefore be rationalized by the photoinduced formation of partially reduced silver clusters which absorb at longer wavelengths and then transfer their energy to reactive sites. To explain the oxygen release we imagine that the lifetime of the holes generated in the oxygen lone pairs is sufficiently long so that they can accumulate and the reaction with the water takes place. We expect that further insight can be obtained by studying the Dember effect in a manner as described by Levy and coworkers,[7] by applying photoelectrochemical measurement techniques and theoretical methods.[8]

Silver zeolites are also capable of photo-producing Cl_2 if dispersed in a 0.2 M aqueous KCl solution of low pH. Self-sensitization occurs[x,x] similar to the water oxidation. The electronic transition involved seems to be well described as charge transfer from the chlorine anion to the positively charged silver ion or silver cluster-ion.

(4)
$$[Ag^+]_n Z[mCl^-]_{ads} \;\xrightarrow{h\nu}\; [Ag]_n^{(n-r)+} Z[(m-r)Cl^-]_{ads} + \frac{r}{2}Cl_2$$
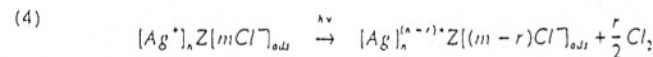
The pronounced pH dependence of this reaction is illustrated in Figure 2. The results can be summarized as follows. Below pH 4 aqueous Ag^+ zeolite dispersions produce Cl_2 in a photochemical reaction in the presence of Cl^-. On changing from acidic to alkaline conditions a shift from chlorine to oxygen production is observed.

The experimental arrangement was as described in:[3b] 550 mg $Ag_{9.7}Na_{2.3}[(AlO_2)_{12}(SiO_2)_{12}]$ was dispersed in 100 ml 0.2 M aqueous KCl and irradiated at 370 nm with a light flux of 5 mW/cm². For each pH intervall the time dependent signal is shown in Figure 2. Oxygen was measured by means of a Clark sensor[3a] and chlorine by means of a Clark-like Cl_2 sensor.[3c] The large driving force of the recombination reaction $Ag + 1/2\ Cl_2 \rightarrow AgCl$ with a standard redoxpotential of $E^0 = 1.14$ V must be considered to appreciate the photoproduction of chlorine with visible light.
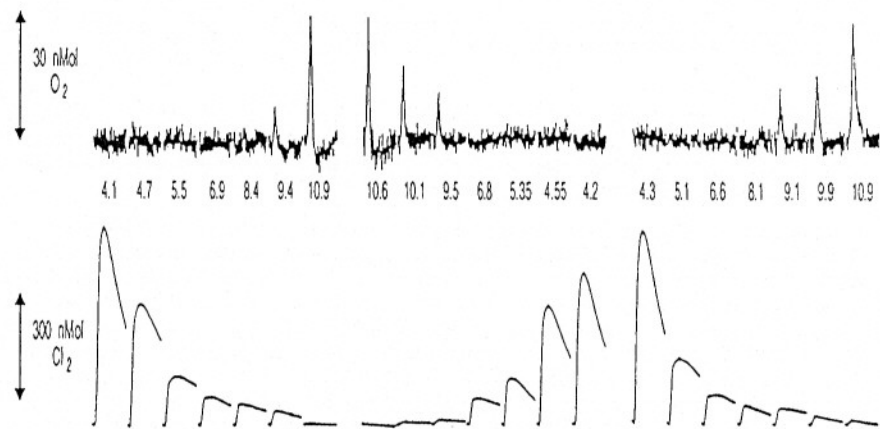

Figure 2: pH dependence of photo-chlorine evolution in an aqueous dispersion of an Ag^+ zeolite A irradiated at 370 nm (light flux 5 mW/cm²).

Based on these observations we have constructed a photogalvanic cell $\{Ag/AgCl||Cl^-/Cl_2\}$ with an experimental open circuit potential of 1.07 V.[3c] Experimental and theoretical studies have shown that the photocurrents observed where limited by transport processes which means that the current-voltage characteristics could be significantly improved. Similar experiments have been carried out in presence of Br^- and of I^-. The observed corresponding open circuit photopotentials are 0.7 V and 0.55 V.

Having two reactions at our disposal for the oxidative part 1 in Figure 1, we consider some thermodynamic arguments on the energy stored in reactions (2) and (4) respectively. The energy stored in reaction (4) can be estimated without many assumptions to be in the order of up to $-E^0 \approx -1.14$ V. The situation is less obvious for the photo oxygen production (2). The pH dependent standard reduction potential of reaction (5) in pure water at room temperature is equal to $E^0 = 1.23V - 0.059V \cdot pH$.

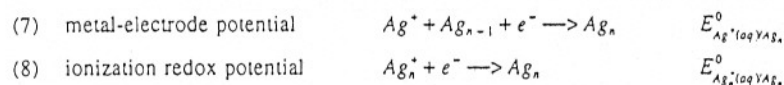(5) $\qquad 1/2\ O_2 + 2\ H^+ + 2e^- \longrightarrow H_2O$
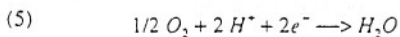
Estimation of the redox potential of the photochemically produced silver species in the zeolite according to (2) is more involved. The potential difference ΔE between oxygen reduction (5) and silver oxidation in the case of bulk silver ($E^0(Ag^+/Ag_{bulk}) = 0.8$ V) is well known to be negative for pH values lower than 7.2.

(6) $\qquad \Delta E = E^0_{Ag^+/Ag_{bulk}} - E^0_{(\frac{1}{2}O_2, 2H^+/H_2O)} = -0.43V + 0.059V \cdot pH$

The electrochemical potential of silver clusters in aqueous environment is a pronounced function of cluster size as we know from the work of Henglein,[9] Mostafavi et. al.,[10] and Yonezawa et.al.[11] Since coordination of Ag^+ in zeolite occurs partly by framework oxygen and partly by water molecules, the solvation energy may be somewhat different from that in pure water. In the absence of better information we assume that this difference can be neglected and that the solvation free enthalpy in the zeolite can be approximated by the free enthalpy of hydration ΔG_h.

Henglein stresses the occurrence of two different potentials for the silver system:

(7) metal-electrode potential $\qquad Ag^+ + Ag_{n-1} + e^- \longrightarrow Ag_n \qquad E^0_{Ag^+/aq\gamma Ag_n}$

(8) ionization redox potential $\qquad Ag_n^+ + e^- \longrightarrow Ag_n \qquad E^0_{Ag_n^+/aq\gamma Ag_n}$

The limit of the metal-electrode potential for bulk silver is equal to 0.8 V. We will show that the corresponding ionization redox potential is equal to 0.0 V.

The metal-electrode reduction potential of silver clusters can be calculated from the thermodynamic cycle 1 explained below. Energies are expressed in eV. In this and the following cycles we neglect the free enthalpy of hydration of silver atoms and neutral silver clusters which is expected to be in the order of 0.1 eV or less[9] and we always refer to room temperature.

Cycle 1   metal-electrode potential

Ag_n	$\rightarrow$	$Ag_{n-1} + Ag(g)$	$-\Delta G_b(n)$
$Ag(g)$	$\rightarrow$	$Ag^+(g) + e^-(g)$	Ip_{Ag}
$Ag^+(g)$	$\rightarrow$	$Ag^+(aq)$	$\Delta G_h(Ag^+)$
$e^-(g)$	$\rightarrow$	e^-_{NHE}	ε

$Ag_n \qquad \rightarrow \qquad Ag_{n-1} + Ag^+(aq) + e^-_{NHE} \qquad \Delta G_{Ag^+/Ag^+/aq}$

$\Delta G_{Ag^+/aq\gamma Ag_n} = -[Ip_{Ag} + \Delta G_h(Ag^+) + \varepsilon - \Delta G_b(n)]$

(9) $\qquad \boxed{E^0_{Ag^+/aq\gamma Ag_n} = Ip_{Ag} + \Delta G_h(Ag^+) + \varepsilon - \Delta G_b(n) = -1.8\ eV - \Delta G_b(n)}$

The electrochemical potential $E^0_{Ag^+(aq)/Ag_n}$ depends on the ionization energy of silver atoms in the gas phase Ip_{Ag}, the energy ε involved in bringing an electron from the vacuum (infinity) to the level of the standard hydrogen electrode, the free enthalpy of hydration $\Delta G_h(Ag^+)$ of the silver cation and on the binding free enthalpy $\Delta G_b(n)$ of a silver atom to the silver cluster Ag_{n-1}. Ip_{Ag}, ε and $\Delta G_h(Ag^+)$ are known. The binding free enthalpy $\Delta G_b(n)$ of a silver atom to a cluster Ag_{n-1} has been measured for n = 1,2,3.[12] Plieth calculates the binding free enthalpy for larger clusters from the free enthalpy change associated with the change in surface area in the transference of one mole bulk metal to the dispersed form.[13]

$$(10) \qquad Ag_{N_L} \longrightarrow \frac{N_L}{n} Ag_n$$

As a first approximation he considers the small particles as spheres of radius r. The surface area and the volume of the particles are determined by the particle number n and the molar volume V_M of silver. If γ represents the surface tension of silver particles the change of free enthalpy with surface area A is given as:

$$(11) \qquad dG = \gamma \cdot dA \qquad\qquad A = 4\pi r^2 \qquad\qquad \tfrac{4}{3}\pi r^3 = n\frac{V_M}{N_L}$$

$$dG = \frac{8\pi\gamma}{3}\left(\frac{3V_M}{4\pi N_L}\right)^{2/3} n^{-1/3} dn \qquad\qquad dA = \frac{8\pi}{3}\left(\frac{3V_M}{4\pi N_L}\right)^{2/3} n^{-1/3} dn$$

Integrating from N_L to n results in the following expression:

$$(12) \qquad \Delta G(n) = c \cdot [n^{2/3} - N_L^{2/3}] \qquad \text{with} \quad c = \frac{\gamma}{N_L^{2}}(36\pi N_L V_M^2)^{1/3} = 3.1762 \quad eV$$

The binding free enthalpy $\Delta G_b(n)$ can be associated to $\Delta G(n)$ and to the free enthalpy of sublimation $\Delta G_s = 2.6 \quad eV$ as follows:

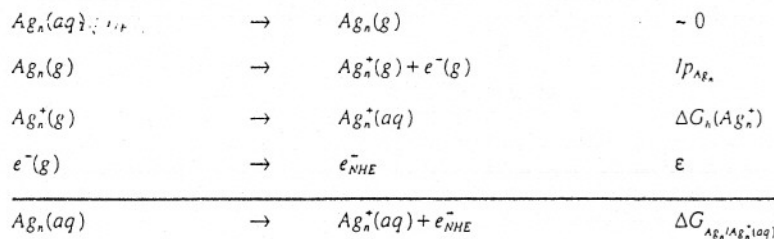$$(13) \qquad -\Delta G_b(n) = \Delta G(n-1) - \Delta G(n) + \Delta G_s$$
$$-\Delta G_b(n) = 2.6 eV + c \cdot [(n-1)^{2/3} - n^{2/3}]$$

Inserting this result into (9) and substituting for Ip_{Ag} and ε their numerical values of 7.6 eV and -4.5 eV respectively, we obtain the astonishingly simple equation (14) for the metal-electrode potential of silver clusters. Comparison of the experimentally available values for n = 1,2,3 with the calculated values in Table 1 shows, that even for these small particles for which the theory is not expected to be applicable the correct order of magnitude is obtained. Of course the oscillations caused by the specific electronic structure of the particles is not reproduced by (14). We conclude that reliable values can be obtained for clusters of more than about 10 atoms.

$$(14) \qquad E^0_{Ag^+(aq)/Ag_n} = 0.8 \, eV + c \cdot [(n-1)^{2/3} - n^{2/3}]$$

A similar expression can be derived for the ionization redox potential by means of cycle 2.

Cycle 2 ionization redox potential

$Ag_n(aq)$	$\rightarrow$	$Ag_n(g)$	~ 0
$Ag_n(g)$	$\rightarrow$	$Ag_n^+(g) + e^-(g)$	Ip_{Ag_n}
$Ag_n^+(g)$	$\rightarrow$	$Ag_n^+(aq)$	$\Delta G_h(Ag_n^+)$
$e^-(g)$	$\rightarrow$	e^-_{NHE}	ε

$$Ag_n(aq) \rightarrow Ag_n^+(aq) + e^-_{NHE} \qquad \Delta G_{Ag_n^+(Ag_n^+(aq)}$$

$$\Delta G_{Ag_n^+(aq)/Ag_n} = -\left[0 + Ip_{Ag_n} + \Delta G_h(Ag_n^+) + \varepsilon\right]$$

$$(15) \qquad \boxed{E^0_{Ag_n^+(aq)/Ag_n} = Ip_{Ag_n} + \Delta G_h(Ag_n^+) + \varepsilon}$$

The ionization redox potential depends on the ionization energy of the Ag_n cluster and on the free enthalpy of hydration of the cluster ion. Experimental values for Ip_{Ag_n}, n = 1,2,3,4 have been published and the free enthalpy of hydration $\Delta G_h(Ag_n^+)$ can be calculated from the Born equation.[11] The first three redox potentials in Table 1 differ slightly from those reported by Henglein[9] because in our calculation the small entropy contributions are taken into account.

Table 1: Redoxpotential of silver clusters as calculated from equations (9), (14) and (15)

n	$Ip_{Ag_n}^{a)}$	$\Delta G_h(Ag_n^+)^{b)}$	$E^0_{Ag_n^+(aq)/Ag_n}$	$\Delta G_b(n)$	$E^0_{Ag^+(aq)/Ag_n}$
1	7.6	-4.9	-1.8	0.0$^{c)}$	-1.8 (-2.4)$^{d)}$
2	7.3	-3.9	-1.1	-1.27$^{c)}$	-0.5 (-1.06)
3	6.2	-3.4	-1.7	-0.6$^{c)}$	-1.2 (-0.76)
4	6.3	-3.1	-1.3		(-0.6)
.					.
10					(-0.2)
.					.
100					(0.34)
.					.
∞	4.5	0.0	0.0	-2.6	+0.8

a)[14], b)[11], c)[12], d) values in parentheses have been calculated from eq. (14).

Regarding the numerical values in Table 1 we conclude that it is reasonable to assume that the silver species produced in the photoredox reaction (2) are stronger reductants than bulk silver. Our information of the photochemically produced silver species regarding their size, geometry,

electronic structure, and the influence of the zeolite environment on their redox potentials and redox kinetics is still poor. It is highly desirable to design experiments that give us directly access to these properties in the appropriate environment.

3. Reductive part

The reductive half reaction 3 in Figure 1 has been studied by many groups under a variety of conditions. Two main fields can be distinguished. One is based on semiconductor particles and the other on transition metal complexes. Both of them having their advantages and disadvantages, it is too early to judge which approach will be more successful.

Let us first comment on the semiconductor particles approach comprehensively reviewed by Memming.[15] An example is the system based on CdS particles also used by Reber et al.[16] To catalyse the photochemical H_2 evolution they coated parts of the semiconductor surface with Pt. The system works very efficiently, especially if the CdS is doped with Ag_2S. CdS as well as most of the other semiconductors is not stable due to photocorrosion on the surface caused by the photogenerated holes. It has been demonstrated to be stable, however, if the holes produced are filled with electrons. This is usually done by working under so called sacrificial donor conditions using eg. tertiary amines. In the case of CdS it was shown that the donor S^{2-} enhances both, the stability of the semiconductor particles and the H_2 evolution.

An especially elegant experiment has been carried out by Meissner, Memming and Kastening who investigated a membrane consisting of small particles of single-crystalline CdS embedded in a polyurethane polymer film.[17] With this set-up they were able to split the two half reactions in two cell compartments containing different electrolytes and could therefore investigate both sides of the particles separately. Adding a catalyst onto one side of the CdS surface and adding S^{2-} to the solution on the other, they found H_2 production not only when using Pt as a catalyst but also with RuO_2, usually known to catalyse oxidation processes. They concluded that almost every catalyst is able to evolve H_2, but it might not be possible to find conditions where O_2 and H_2 can be evolved together from the same semiconductor particle, even when using specific catalysts. Many other systems for H_2-evolution are discussed in the literature.[18]

Regarding the approach via transition metal complexes we mention the investigations carried out by Lehn et al.[19] For a complex consisting of a $Ru(bpy)_3^{2+} \cdot Co^{2+}$ combination simultaneous evolution of $CO + H_2$ was reported, when irradiated in $(HOCH_2CH_2)_3N$ and dimethylformamide containing CO_2. Under the same conditions the photocatalyst {$Re(bpy)(CO)_3X$, $X=Cl,Br$} produced CO selectively. The rhenium complex did show much better performance than the {$Ru(bpy)_3^{2+} \cdot Co^{2+}$} system, not only due to its selectivity, but also due to its much higher efficiency.

Interesting complexes are obtained with p-phenyl-terpyridine (ptpy) as a ligand.[20] In a recent study of $M(II,d^6)$-4'-ptpy complexes it was shown that it is reasonable to describe the excited MLCT state as $[(L)M(III)(L^{--})]$ because the perpendicular conformation of the two ligands causes all π orbitals to be twofold degenerate and therefore a small distortion is sufficient to stabilize the localized situation.[21] We have also observed that the $[Re(ptpy)(CO)_3Cl]$ complex reduces CO_2 under appropriate conditions in a similar way as described by Lehn for the $[Re(bpy)(CO)_3Cl]$.

4. Coupling oxidation/reduction

Having photoredox reactions at our disposal for the oxidation reaction 1 in Figure 1 and for the reduction reaction 3, time has come to try and realize the coupling 2 of them. We have already argued that 2 has to be realized by means of a membrane that is able to transport electrons and protons and to prevent recombination reactions. Carbon monoxide as well as hydrogen (Red4) are capable of reducing Ag^+ zeolites. Studying the reactivity of carbon monoxide with Ag^+ ions in some detail we have found[22] that at room temperature silver oxide and silver carbonate react much faster than Ag^+-A zeolites, the kinetics of the latter reaction showing a pronounced dependence on the water content and a significant dependence on the exchange conditions; no reaction takes place in the absence of water. Immersion of the stable dry Ag^+-CO zeolite complex in an alkaline aqueous environment, however, results in immediate reduction of Ag^+. These studies do support our opinion that the whole system can only work with a membrane that prevents material exchange between the two parts, but enables the transfer of electrons and protons.

By now we are not concerned about proton transport, a problem that might become important in a later stage. To bring electrons from 1 to 3 sufficient electron conductivity across the zeolite is necessary. Experimental studies have led to the result that the resistance of even very thin silver zeolite pellets is by orders of magnitudes too high to guarantee sufficient electron conductivity. The cause of the far too high resistance lies in the interphase of the grain boundaries. We have therefore developed a simple and fast technique for preparing monograin zeolite layers by covalently linking 1 μm sized zeolite A, 0.2 μm sized zeolite Y, and also zeolite L particles in a photochemical modification as a dense sheet onto an electrode which shows the silver reduction and oxidation steps in the zeolite to be quasi reversible.[23] Our technique can be extended to many different substrates. Up to now we have applied it to Pt, graphite, glassy carbon, glass, quartz and to tin dioxide.

Let us state that in the cyclic voltammograms observed with a dense monograin layer of silver zeolite A on a Pt electrode a shift of the cathodic and the anodic peak potentials with respect to silver bulk is observed.[23a] This indicates the formation of Ag_n^{m+} species as discussed in section 2. However further experiments are needed to support this interpretation.

We have seen that the problem of the transport processes on the zeolite part very likely can be solved. Let us therefore try to become more specific regarding the coupling of the oxidative and the reductive parts. Two appealing possibilities to combine the two half-reactions are explained in Figure 3.

The first one is to combine a semiconductor particle with a silver zeolite. Excitation of the semiconductor delivers the electrons to reduce protons. The holes produced in this process, recombine with the electrons delivered by the reduced silver zeolite. A problem demanding careful consideration is the junction between zeolite and semiconductor. Combination of the silver zeolite with an appropriate metal complex able to photo-reduce water or CO_2 is another possibility. It leads to an interesting coupling scheme between LMCT and MLCT states.[24]
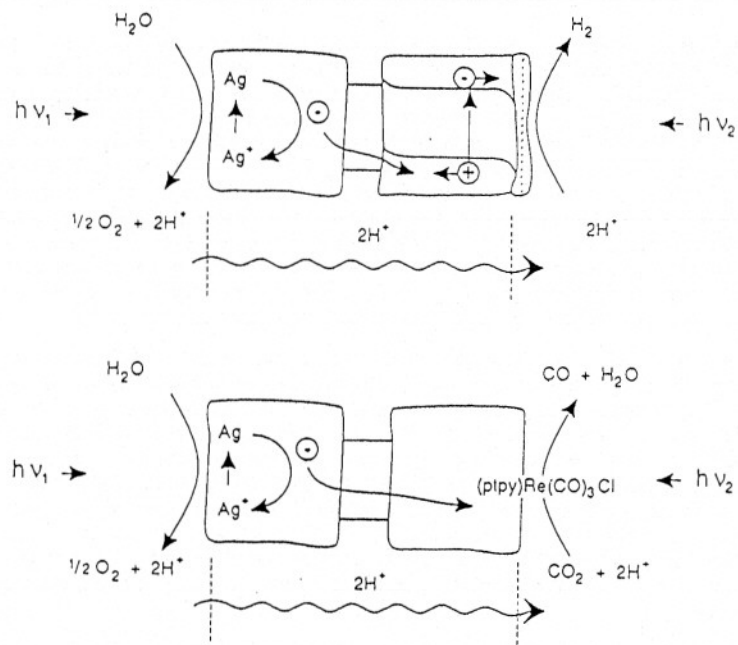
Figure 3: Possibilities of coupling the two half-reactions 1 and 3 in Figure 1 separated by a membrane. In both cases the silver zeolite photoredox system is used to drive the water oxidation. The water reduction is either achieved by semiconductor particles, top, or by an inorganic metal complex such as (ptpy)Re(I)(CO)$_3$Cl,[25] [Ru(II)(bpy)$_3$]$^{2+}$ and others.

Acknowledgement

References

[1] (a) T.J. Meyer, *Acc. Chem. Res.*, 1989, 22, 163; (b) E. Pelizzetti, M. Schiavello (eds.), *Photochemical Conversion and Storage of Solar Energy*, Kluwer Academic Publishers, Dordrecht, 1991.

[2] G. Calzaferri, 'Solar Energy 88', Proceedings 3rd International Summer School, Kaprun/Austria, August 3-13, 1988, G. Faninger (ed), *IFF, Klagenfurt*, 1989, 119.

[3] (a) G. Calzaferri, B. Sulzberger, *J. Photochem.*, 1982, 19, 321; (b) G. Calzaferri, S. Hug, Th. Hugentobler, B. Sulzberger, *ibid.*, 1984, 26, 109; (c) G. Calzaferri, W. Spahni, *ibid.*, 1986, 32, 151; (d) G. Calzaferri, W. Spahni, *Chimia*, 1986, 40, 435 and 1987, 41, 200; (e) R. Beer, G. Calzaferri, W. Spahni, *ibid.*, 1988, 42, 134.

[4] G. Calzaferri, L. Forss, *Helv. Chim. Acta*, 1986, 69, 873, and, 1987, 70, 465.

[5] G. Calzaferri, R. Hoffmann, *J. Chem. Soc. Dalton*, 1991, 917.

[6] D. W. Turner, C. Baker, A.D. Baker, C.R. Brundle, *Molecular Photoelectron Spectroscopy*, Wiley-Interscience, London, 1970.

[7] B. Levy, *Photogr. Sci. and Engr.*, 1971, 15, 279; B. Levy, *Photochemical Conversion and Storage of Solar Energy*, E. Pelizzetti, M. Schiavello (eds.), Kluwer Academic Publishers, Dordrecht, 1991, p. 337.

[8] R. Hoffmann, *Solids and Surfaces*, VCH Weinheim, 1988.

[9] A. Henglein, *Ber. Bunsenges. Phys. Chem.*, 1990, 94, 600.

[10] A. Mostafavi, J.L. Marignier, L. Amblard, J. Belloni, *Rad. Phys. Chem.*, 1989, 34, 605; A. Mostafavi, J.L. Marignier, L. Amblard, J. Belloni, *Z. Phys. D*, 1989, 12, 31.

[11] Y. Yonezawa, K. Kawai, M. Okai, K. Nakagawa, H. Hada, *J. Imag. Sci.*, 1986, 30, 114.

[12] K. Hilpert, K.A. Gingerich, *Ber. Bunsenges. Phys. Chem.*, 1980, 84, 739.

[13] W.J. Plieth, *J. Phys. Chem*, 1982, 86, 3166.

[14] K. Franzreb, A. Wucher, H. Oechsner, *Z. Phys. D*, 1990, 17, 51.

[15] R. Memming, *Topics in Current Chemistry*, 1988, 143, 79.
R. Memming, *Photochemical Conversion and Storage of Solar Energy*, E. Pelizzetti, M. Schiavello (eds.), Kluwer Academic Publishers, Dordrecht, 1991, p. 193.

[16] N. Bühler, K. Meier, J.-F. Reber, *J. Phys. Chem.*, 1984, 88, 3261;
J.-F. Reber, M. Rusek, ibid, 1986, 90, 824.

[17] D. Meissner, R. Memming, B. Kastening, *Chem. Phys. Letters*, 1983, 96, 34.

[18] A. Harriman, M.A. West, *Photogeneration of Hydrogen*, Academic Press, London, 1982; A. Moradpour, E. Amouyal, P. Keller, H. Kagan, *Nouv. J. Chim.*, 1978, 2, 547; C.A. Craig, L.O. Spreer, J.W. Otvos, M. Calvin, *J. Phys. Chem.*, 1990, 94, 7957.

[19] J. Hawecker, J.-M. Lehn, R. Ziessel, *J. Chem. Soc., Chem. Commun.*, 1983, 536.

[20] W. Spahni, G. Calzaferri, *Helv. Chim. Acta*, 1984, 67, 450.

[21] E. Amouyal, M. Bahout, G. Calzaferri, *J. Phys. Chem.*, 1991, 95, 7644.

[22] G. Calzaferri, W. Suter, B. Waldeck, *J. Chem. Soc., Chem. Commun.*, 1990, 485.

[23] (a) G. Calzaferri, K. Hädener, J. Li, *J. Chem. Soc., Chem. Commun.*, 1991, 653;
(b) M.D. Baker, J. Zhang, *J. Phys. Chem.*, 1990, 94, 8703.

[24] R. Beer, G.Calzaferri, J. Li, B. Waldeck, *Coord. Chem. Rev.*, 111 (1991) 193.

[25] Gion Calzaferri†, Konrad Hädener and Jianwei Li *J. Photochem. Photobiol. A: Chem.*, 64 (1992) 259-262