247. Towards the Construction of a Complete Cyclic Water Decomposition System, Design and Operation of an Oxygen Producing Half Cell

by Kuppuswamy Kalyanasundaram, Olga Mićić, Edmondo Pramauro and Michael Grätzel

Institut de Chimie-Physique, Ecole Polytechnique Fédérale, CH-1005 Lausanne

(3.IX.79)

Summary

Oxygen is generated when aqueous solution of iron (III) tris (2,2'-bipyridyl), $Fe(bipy)_3^{3+}$, are brought in contact with catalytic amounts of powdered or colloidal RuO_2. The oxygen yield depends strongly on the pH, reaching a maximum between pH 7 and 8 where it corresponds to the stoichiometry of the reaction:

$$4\,Fe(bipy)_3^{3+} + 2\,H_2O \xrightarrow{\quad RuO_2 \quad} 4\,Fe(bipy)_3^{2+} + 4\,H^+ + O_2. \qquad (1)$$
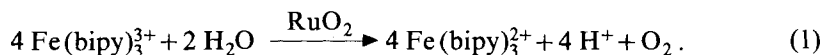
The rate of the reaction is so fast that it occurs practically upon dissolution of $Fe(bipy)_3^{3+}$ in the aqueous phase. In acidic media (pH 4), no O_2 evolution is observed. Instead, $Fe(bipy)_3^{3+}$ is converted to an intermediate which in the presence of RuO_2 yields O_2 upon neutralization.

The pH profile of the O_2 evolution occurring upon illumination of $Ru(bipy)_3^{2+}$ in the presence of the cobalt complex $[Co(NH_3)_5Cl]^{2+}$ was also investigated.

The surprisingly low energy losses (160 mV) in reaction (1) makes the construction of four quanta water splitting systems feasible.

Introduction. – The photolytic generation of hydrogen and oxygen from water by visible light is of fundamental importance in the field of solar energy conversion [1]. Earlier investigators have developed sacrificial systems which produce either hydrogen [2] or oxygen [3–5] from water under visible light illumination. Our efforts were initially directed towards exploring redox catalysts that could efficiently mediate the water reduction [6] and oxidation [7] step. Later, through combination of two types of catalyst, cyclic water cleavage was achieved [5]. The advantage of the system employed is its simplicity: Apart from the sensitizer and the two catalysts, the solution contains only one further component acting as an electron relay for H_2 production. However, there are also disadvantages resulting from the simultaneous production of the two gases. This promotes undesirable cross reactions reducing the quantum efficiency of the device. While the latter processes may be avoided through judicious design of molecular organizates it is nevertheless desirable to develop alternative systems in which H_2 and O_2 are evolved separately.

A device which should fulfil this purpose is depicted schematically in *Figure 1*. In the right half-cell, H_2 is generated through a light driven redox process under oxidation of a donor (D) to the cation (D^+). A reductant R, present in the left cell, provides electrons to reduce D^+ back to D. The coupling occurs electrochemically. In a subsequent thermal reaction mediated by a redox catalyst, R^+ is reconverted into R under simultaneous oxygen evolution. It should be noted that this scheme is different from the one proposed by *Bolton* [1d] in that four instead of eight quanta are consumed in the production of one O_2 molecule. Such a process can be achieved only if the catalytic oxygen evolution occurs with minimal loss of energy, *i.e.* close to the equilibrium potential of 0.82 at neutral pH. In the present paper, the performance of a half-cell is investigated which satisfies this requirement.

Experimental. – *Materials.* The two types of RuO_2 catalysts used in this study were $RuO_2 \cdot \times H_2O$, a powder supplied from *Alfa Inorganics*, and a RuO_2-sol, stabilized by a co-polymer of styrene and maleic anhydride, obtained from *Unilever Corp.*, Port Sunlight, G.B. The preparation of the colloidal solution was carried out by slowly mixing a neutral solution of RuO_4 in water (244 mg/50 ml) with an equivalent amount of aqueous solution (0.2%) of the co-polymer. The pH is adjusted to 8 and the solution stirred for 1 h. Under these conditions RuO_4 decomposes spontaneously to give RuO_2 which is prevented from aggregation by the protective colloid. The RuO_2 content is 2 mg/ml and the mean particle radius 300 Å, as determined by quasielastic light scattering technique.

The complex [Co(NH$_3$)$_5$Cl]Cl$_2$ was prepared according to a procedure described elsewhere [8]. The complexes Fe(bipy)$_3^{3+}$ and Fe(bipy)$_3^{2+}$ were synthesized as perchlorate salts according to literature procedures [9]. Ru(bipy)$_3^{2+}$ was purchased as the perchlorate salt from *Strem*, Inc., deionized water was distilled from alkaline permanganate and subsequently twice from a quartz still.

Apparatus. The experimental arrangement is shown in *Figure 2*. The solution is contained in a flask which is connected to a N_2 cylinder and through a trap to the *End-O-Mess* Oxygen Meter. The trap is necessary to freeze out water from the gas stream which interferes at high concentrations with the O_2 determination in the *End-O-Mess* meter. The quantitative analysis of the oxygen content of the gas by this instrument is based on the EMF of a Pt/ZrO$_2$/Pt(air) galvanic cell. The calibration of the system was performed by injecting varying amounts of oxygen in the solution and subsequent transfer by N_2 carrier gas to the O_2 meter.

In the photolysis experiments for light induced O_2 evolution, the powdered catalyst was initially contained in the side arm of the flask. Prior to irradiation, the whole system was carefully deaerated by flushing with N_2. The flask was then closed by means of the two stopcocks and illuminated by a 150 Watt slide projector lamp. At the same time the catalyst was added by turning the side arm in the upward direction. Alternatively, 2 ml stock solutions of colloidal RuO_2 (RuO_2 content 2 mg/ml) was
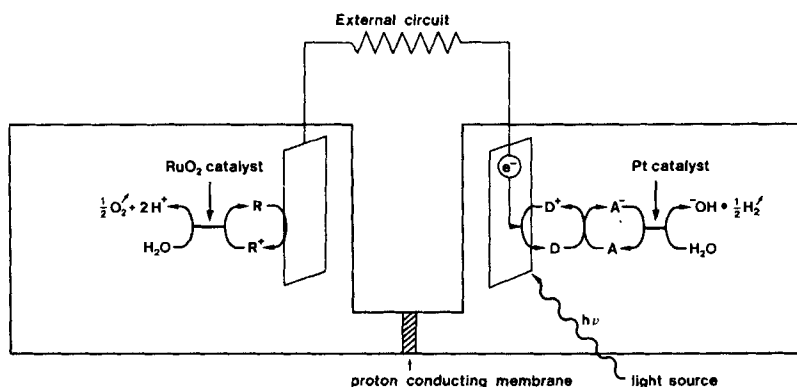

Fig. 1. *Cell device for cyclic water decomposition by visible light* (see text for explanation)

injected through the septum. The septum allowed also for removal of gas samples for gas chromatographic analysis.

In the thermal O_2 generation experiments, the solution contained initially only the buffer (0.1M) and the RuO_2 catalyst (30 mg/100 ml when in powdered form or 4 mg/100 ml when colloidal). Here, the solid $Fe(bipy)_3^{3+}$ was stored in the side arm of the flask. After deaeration, the $Fe(bipy)_3^{3+}$ (*ca.* 250 mg) was dissolved in solution stirred for a period of *ca.* 30 min. After this time or after termination of the photolysis, the gas evolved in the solution was flushed out and transferred to the O_2 meter by a stream of N_2, where the O_2 produced was analyzed quantitatively.

A test run was first made with an 8×10^{-3}M Ce^{4+} solution in 1N H_2SO_4 which, when brought into contact with *Alfa*-hydrated RuO_2 powder or a similar powder from *Merck*, gave oxygen in the dark under simultaneous reduction of Ce^{4+} to Ce^{3+}. This reaction is completed within 30 min and produces O_2 with an efficiency $> 80\%$. Nonhydrated RuO_2, though reducing Ce^{4+} to Ce^{3+}, failed to give oxygen and hence was not employed in the further experiments.

Results. – When $Fe(bipy)_3^{3+}$ is dissolved in aqueous solutions of neutral pH containing RuO_2 catalyst, oxygen is generated. This finding may be attributed to the oxidation of water by the iron complex according to the equation

$$4\,Fe(bipy)_3^{3+} + 2\,H_2O \xrightarrow{\quad RuO_2 \quad} 4\,Fe(bipy)_3^{2+} + O_2 + 4\,H^+. \qquad (1)$$
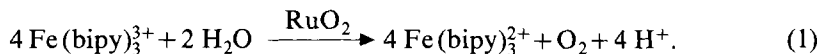
This process manifests itself by a decrease in the pH, a change in the absorption spectrum of the solution and the appearance of oxygen.

The optical effects are illustrated in *Figure 3* where the lower curve with a maximum around 610 nm, ($\varepsilon = 380$M^{-1} cm^{-1}) was obtained from a 5×10^{-4}M solution of $Fe(bipy)_3^{3+}$ at pH = 0 [9] [10]. The quantity of 8.5×10^{-4}M $Fe(bipy)_3^{3+}$ when stirred for several minutes in a neutral, buffered solution containing RuO_2 powder as a redox catalyst yields the upper absorption curve shown in *Figure 3*. The features of this spectrum are identical with that of $Fe(bipy)_3^{2+}$ indicating that the latter is the reaction product [9] [10]. A quantitative analysis showed that the reduction is complete after 5 to 10 minutes of stirring. The rate of reaction is so fast that it occurs almost concomitantly with the dissolution of the solid $Fe(bipy)_3^{3+}$ complex in the aqueous medium. The yield of oxygen produced from the reduction of $Fe(bipy)_3^{3+}$
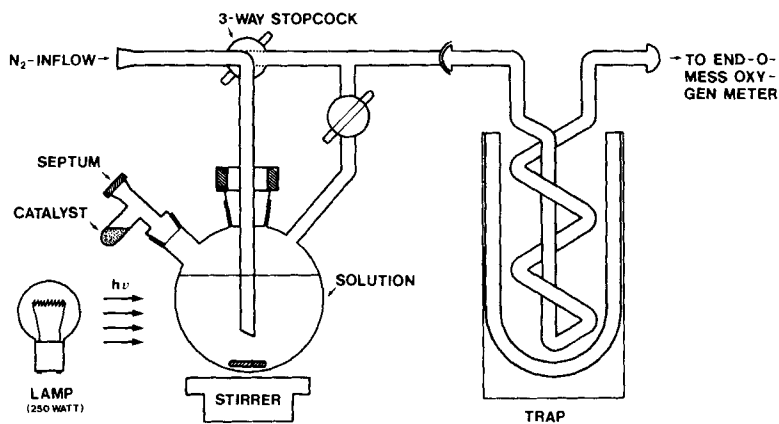

Fig. 2. *Scheme of the experimental arrangement used in the thermal and photo-induced oxygen evolution experiments*

is strongly dependent on the pH of the solution. Results are shown in *Figure 4*. In these experiments sufficient amount of buffer was added to the solution to avoid any changes in pH during the redox process. The yield is stoichiometric only within a relatively narrow pH region between 7 and 7.5 and decreases towards the acid and basic side. The decrease is particulary sharp towards smaller pH values. O_2 generation ceases to occur at $pH \leq 4$. It was noted however that acidic solutions of $Fe(bipy)_3^{3+}$ still underwent spectral changes when brought into contact with RuO_2. *Figure 5* shows the absorption spectrum of the product obtained at pH 4 after stirring with the catalyst. The absorption differs significantly from that of $Fe(bipy)_3^{2+}$ in that a strong peak appears in the wavelength region between 300 and 400 nm. Interestingly, if such a solution is neutralized to a pH of 7.5 and stirred with RuO_2 the spectrum converts to that of $Fe(bipy)_3^{2+}$ (*Fig. 5* upper curve). Simultaneously stoichiometric amounts of oxygen are produced.

Experiments were also carried out with a colloidal form of RuO_2 and the data obtained are included in *Figure 4*. This catalyst also efficiently mediates oxygen generation from water. In fact, the amount of colloidal RuO_2 employed in the experiments is about ten times smaller than in the case of the powder. Significantly, the maximum O_2 production is here observed at pH 9 where the yield reaches almost stoichiometric proportions.
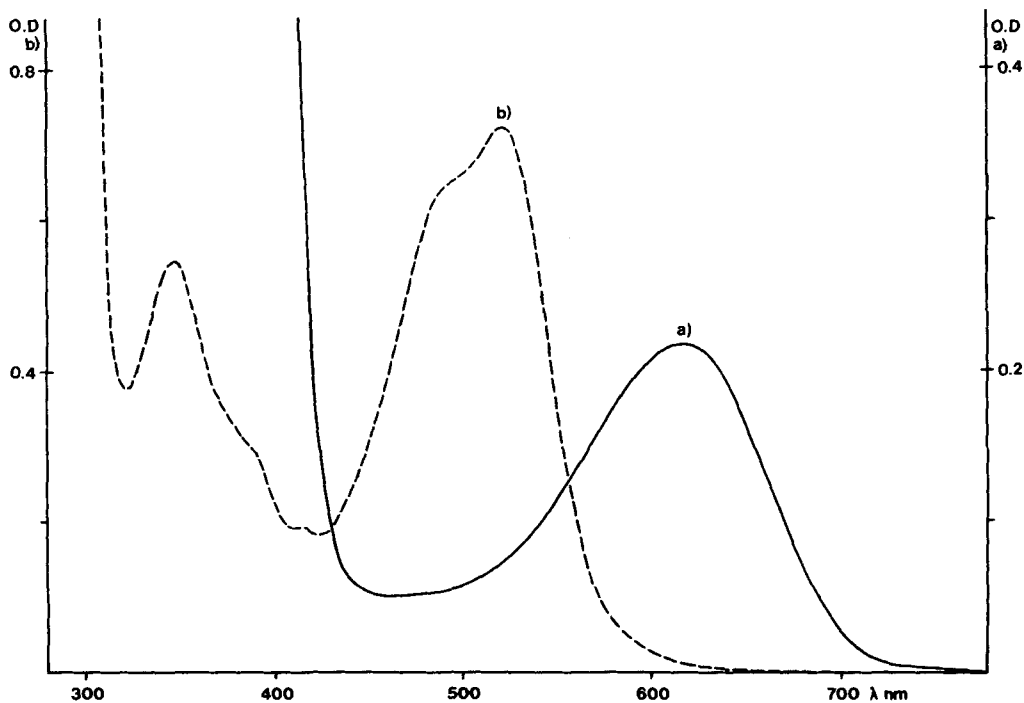

Fig. 3. a) *Absorption spectrum of a* 5×10^{-4}M *Fe(bipy)*$_3^{3+}$ *solution* (pH = 0) $(\varepsilon_{610} = 380$M^{-1} cm$^{-1})$ (1 cm cell); b) *Absorption spectrum of the product obtained after mixing* 8.5×10^{-4}M *Fe(bipy)*$_3^{3+}$ *with aqueous solution of a buffer* (pH 7) *containing 30 mg RuO$_2$ powder* $(\varepsilon_{522} = 8650$M^{-1} cm$^{-1})$ (0.1 cm cell).
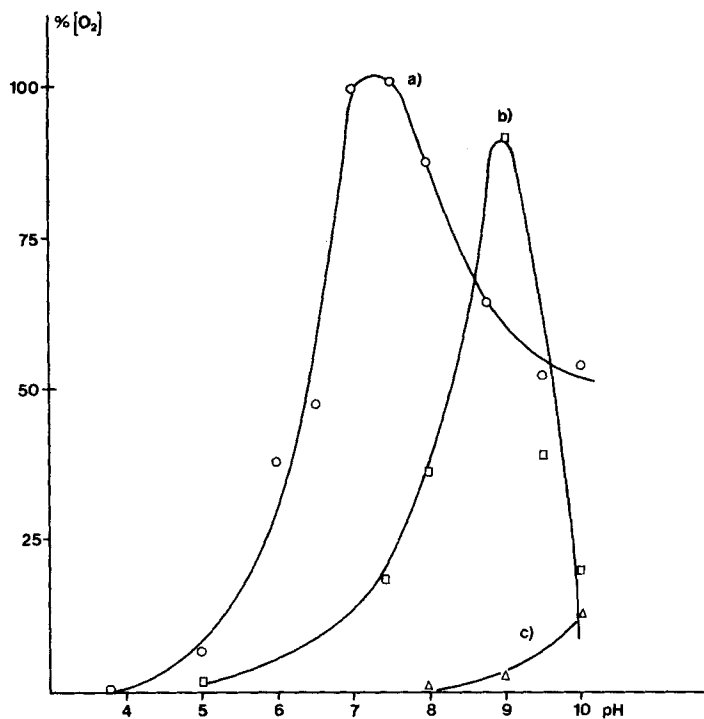
Fig. 4. *Oxygen yields as a function of pH from Fe(bipy)$_3^{3+}$.* a) RuO$_2$ powder (30 mg/100 ml solution); b) Colloidal RuO$_2$ (4 mg/100 ml solution); c) Catalyst free solution.

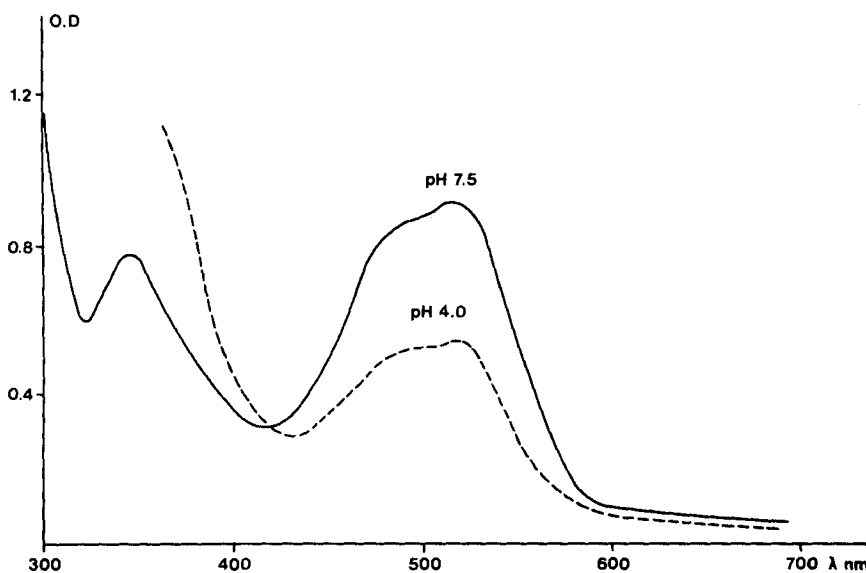Fig. 5. *Absorption spectrum of the product obtained after mixing 10^{-3}M Fe(bipy)$_3$(ClO$_4$)$_3$ with aqueous solution of a buffer containing 30 mg RuO$_2$ in 100 ml.* a) pH = 7.5; b) pH = 4.0.

In the light of the results obtained with the $Fe(bipy)_3^{3+}$ system it seemed interesting to examine the pH profile for the O_2 evolution from the analogous ruthenium complex $Ru(bipy)_3^{3+}$ [4] [5] [7] which follows the equation

$$4\,Ru(bipy)_3^{3+} + 2\,H_2O \rightarrow 4\,Ru(bipy)_3^{2+} + 4\,H^+ + O_2. \qquad (2)$$
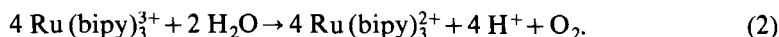
In these experiments $Ru(bipy)_3^{3+}$ was produced in a photo-induced oxidation [4] [5] of the bivalent complex by $Co(III)(NH_3)_5Cl^{2+}$

$$Ru(bipy)_3^{2+} + Co(NH_3)_5Cl^{2+} \xrightarrow{h\nu} Ru(bipy)_3^{3+} + Co^{2+} + 5\,NH_3 + Cl^-. \qquad (3)$$
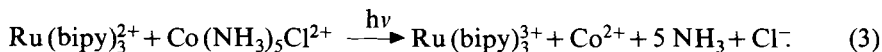
This photo redox reaction is irreversible since the reduced cobalt complex is rapidly destroyed through ligand loss and formation of Co^{2+} aquoions [11].

Experimental results are shown in *Figure 6*. The conversion efficiency refers here to the initial concentration of $Co(NH_3)_5Cl^{2+}$. It corresponds to the amount of oxygen produced after 3 hours of irradiation divided by one fourth of the quantity of $Co(NH_3)_5Cl^{2+}$ employed. The oxygen generation is cyclic with respect to the ruthenium complex [4] [5]. When RuO_2 powder is employed as a catalyst, we find a maximum corresponding to 30% stoichiometric conversion at pH 4.8. The efficiency decreases sharply towards higher pH values, and more gradually towards lower pH values. Interestingly, the colloidal RuO_2, though present at much lower concentration than the powder, generates O_2 more efficiently around pH 3, matching the performance of the RuO_2 powder at the other pH values.
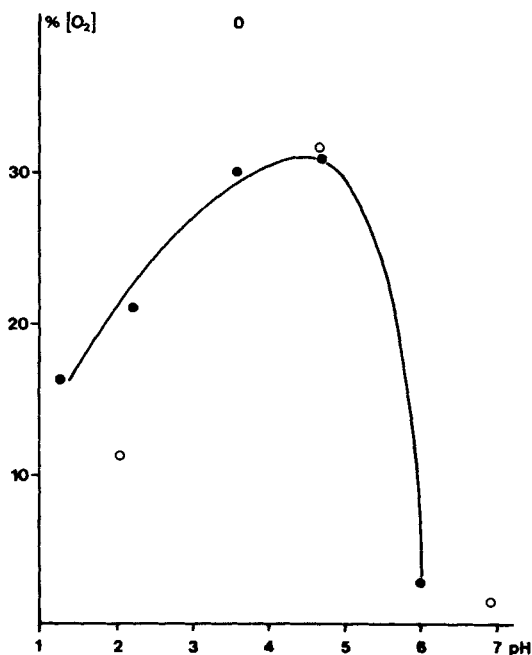

Fig. 6. *Oxygen yields from the photolysis of 10^{-4}M $Ru(bipy)_3^{2+}$ in the presence of 10^{-2}M $[Co(NH_3)_5Cl]Cl_2$ as a function of pH.* ●: 30 mg/100 ml RuO_2 powder, O: 4 mg/100 ml RuO_2 colloidal (3 hours photolysis with a 150 W projector lamp).

Discussion. – The reduction of ML_3^{3+} salts, where M stands for Fe, Ru, Os and L for phenanthroline or bipyridyl and their derivatives occurs homogeneously in alkaline solutions [12]. For $Fe(bipy)_3^{3+}$, detailed mechanistic investigations have been carried out by *Nord & Weinberg* [13] [14] and *Shafirovich et al.* [15]. It is agreed that the primary step involves addition of OH^- to the complex. The yield of O_2 depends strongly on the pH, maximum amounts corresponding to 75% stoichiometric conversion being obtained at pH 13.

The remarkable effect introduced by the RuO_2 catalyst is that it reduces the pH requirement for O_2 evolution by 6 units and renders the process quantitative. Energetically, this corresponds to a lowering of the threshold energy for the reaction by 354 mV or 8 kcal/mol. In fact, from the standard potentials of the two couples involved in the redox reaction, $E^\circ(O_2/H_2O) = 820$ mV and E° $(Fe(bipy)_3^{3+})$-$(Fe(bipy)_3^{2+}) = 980$ mV [14], the driving force of the oxygen generation reaction at pH 7 is only 160 mV/electron transferred or 3.6 kcal/equiv. in energy loss through irreversibility. It is the low overvoltage characteristic for water oxidation on RuO_2 [16] that minimizes the energetic losses.

The mode of intervention of RuO_2 in the oxygen generation process may be best understood in terms of electrochemical concepts. The two coupled redox reactions occurring on the RuO_2 particle are depicted schematically in *Figure 7*. The particle serves as a microelectrode for which the theory of local elements [17] may be applied. The cathodic branch indicates the reduction of $Fe(bipy)_3^{3+}$ (or $Ru(bipy)_3^{3+}$) while the anodic branch corresponds to water oxidation. Two heterogeneous electron transfer reactions across the RuO_2/water interface are involved in the overall reaction described by equ. (1) or (2). A decrease in the particle potential results in an increase of the rate of the cathodic electron transfer process, while
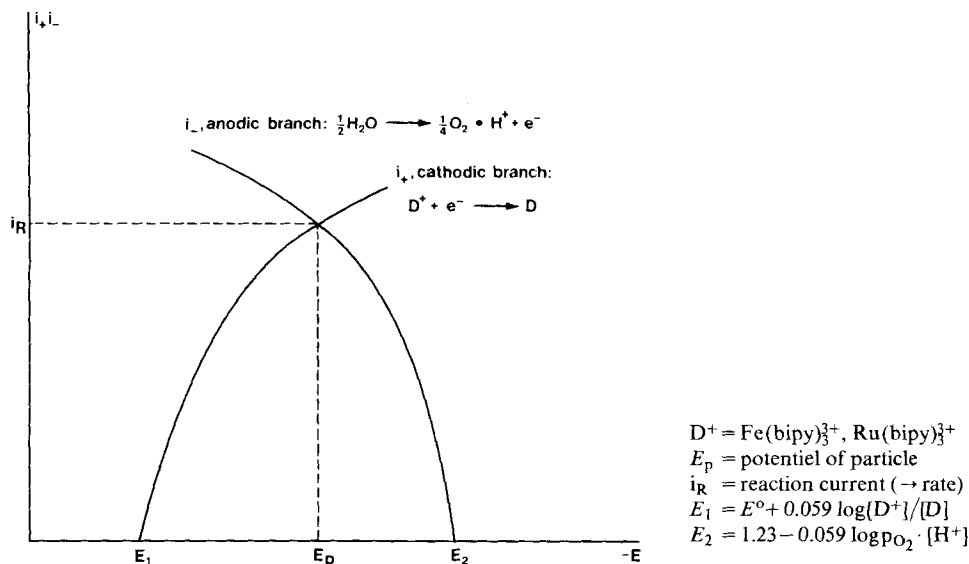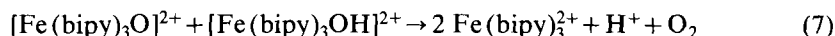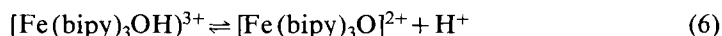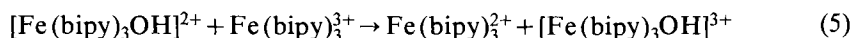

Fig. 7. *Current-voltage diagram for coupled redox-processes occurring on the RuO_2 particle*

that of the anodic reaction is retarded. Under steady state conditions, the RuO_2 will assume a potential E_p which is given by the intersection of the two current-voltage curves. At this potential a current i_R will flow which defines the overall re-action rate. It appears that in the case of $Fe(bipy)_3^{2+}$ the driving force of 160 mV suffices to make reaction (1) occur rapidly and quantitatively. The lack of oxygen formation noted in acidic solution is expected for electrokinetic and thermodynamic reasons: The potential E_2 approaches E_1 or passes even to its anodic side, retarding or precluding O_2 evolution reaction (1).

The drop in O_2 yield, observed when the pH is increased above 8, may be explained by OH^- adduct formation [12–15] [18]:

$$Fe(bipy)_3^{3+} + OH^- \rightarrow [Fe(bipy)_3OH]^{2+}. \tag{4}$$
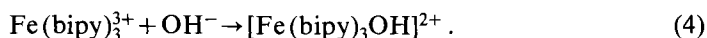
Although the OH^- adduct may subsequently give O_2, i.e. via the sequence of homo-geneous reactions [13] [14] [18]

$$[Fe(bipy)_3OH]^{2+} + Fe(bipy)_3^{3+} \rightarrow Fe(bipy)_3^{2+} + [Fe(bipy)_3OH]^{3+} \tag{5}$$

$$[Fe(bipy)_3OH)^{3+} \rightleftharpoons [Fe(bipy)_3O]^{2+} + H^+ \tag{6}$$

$$[Fe(bipy)_3O]^{2+} + [Fe(bipy)_3OH]^{2+} \rightarrow 2\,Fe(bipy)_3^{2+} + H^+ + O_2 \tag{7}$$

the efficiency of this process is low reaching a maximum of 75% only at pH 13 [15]. It appears that the colloidal RuO_2 can intervene in these reactions more effi-ciently than the powder, since an O_2 yield of 90% is obtained at pH 9. On the other hand, relatively low yields are observed with this catalyst in neutral solution. More experiments are required to elucidate further this interesting effect.

It was pointed out above that in acidic solution, i.e. pH 4, the redox catalyst is ineffective in mediating O_2 generation. Instead, $Fe(bipy)_3^{3+}$ can undergo hydrolysis (equ. 4) and subsequent electron transfer (equ. 5). The dashed curve in *Figure 5* may in fact represent the absorption spectrum of the intermediate $[Fe(bipy)_3OH]^{3+}$. The latter could play an important role in as much as it produces oxygen in the presence of RuO_2 if the conditions are thermodynamically favorable, i.e. at pH 7. Once it is deprotonated, homogeneous pathways, equ. 7, may be favoured.

It is instructive to compare the results obtained with the $Fe(bipy)_3^{3+}$ system to the photolysis data in *Figure 6*, where O_2 was evolved from the $Ru(bipy)_3^{3+}$ com-plex according to equ. 2. We note first that this reaction occurs also in catalyst free solution, the yield attaining a maximum (about 80%) at pH 9 [18]. At this pH, the driving force for reaction (2) calculated from $E^\circ(Ru(bipy)_3^{3+/2+} = 1.26$ V [19], is *ca.* 560 mV. Interestingly, almost the same chemical potential, i.e. 520 mV is re-quired to drive reaction (1) under optimum conditions (*i.e.* pH 13).

The effect of the catalyst is to decrease the energy requirement of these two reactions, hence shifting the optimum pH to smaller values. In both cases, the pH shift is 5–6 units corresponding to a decrease of the 'overvoltage' loss of 300–360

mV. With colloidal RuO_2 the maximum conversion efficiency in the $Ru(bipy)_3^{2+}$ system is found at pH 3, corresponding to a driving force of only 200 mV, in very close analogy to the $Fe(bipy)_3^{3+}$ system.

Such low energetic losses make the design of a complete water splitting system, that would require only four visible photons per molecule of oxygen produced, feasible.

$Fe(bipy)_3^{2+}$ is a viable candidate to be used as a reductant in the O_2 producing half-cell depicted in *Figure 1*, on the left side. In the other half-cell, water is reduced to hydrogen and an electron donor D oxidized to D^+. The D/D^+ potential has to be slightly higher than 1.0 V to provide a driving force for the cell current through which $Fe(bipy)_3^{2+}$ is oxidized to $Fe(bipy)_3^{3+}$ and D^+ reduced to D. Redox-sensitizers such as $Ru(bipy)_3^{2+}$ and hydrophobic derivatives with higher E° values [20] or metalloporphyrins and phthalocyanines would be suitable candidates for D. The latter should preferably be associated with the electrode to avoid mass transport problems and render the D^+ reduction fast.

The threshold photon energy required for the operation of such a cell is composed of the following terms

$$E_{thr} = 1.23 + E_{irr}(H_2) + E_{irr}(O_2) + \Delta E_{el} .$$

Counting 200 mV each for the irreversible energy losses in the hydrogen and oxygen generation step and 300 mV for ΔE_{el} which drives the cell current one obtains $E_{thr} \simeq 2$ V corresponding to a wavelength of 620 nm. Such an energy converter could operate with an efficiency of 20% or more [1b] on solar light.

REFERENCES

[1] a) *M. Calvin*, Photochemistry and Photobiol. *23*, 425 (1976); b)*G. Porter & M. D. Archer*, Interdisc. Sci. Rev. *1*, 119 (1976); c)*J. R. Bolton*, 'Solar Power and Fuels', ed. Academic Press N.Y. 1977; d)*J. R. Bolton*, Science *202*, 705 (1978).

[2] a) *B. V. Koryakin, T. S. Dzhabiev & A. E. Shilov*, Dokl. Akad. Nauk. SSSR *238*, 620 (1977); b)*J. M. Lehn & J. P. Sauvage*, Nouveau J. Chim. *1*, 449 (1977); c) *K. Kalyanasundaram, J. Kiwi & M. Grätzel*, Helv. *61*, 2720 (1978); d)*A. Moradpour, E. Amouyal, P. Keller & H. Kagan*, Nouveau J. Chim. *2*, 547 (1978); e) *B. O. Durham, W. J. Dressick & Th. J. Meyer*, J. chem. Soc. Chem. Commun. *1979*, 381; f) *P. J. De Laive, B. P. Sullivan, T. J. Meyer & D. G. Whitten*, J. Amer. chem. Soc. *101*, 4007 (1979); g) *A. I. Krasna*, Photochemistry and Photobiol. *29*, 267 (1979); h) *T. Kawai, K. Tanimura & T. Sakada*, Chem. Letters *1979*, 137; i) *M. Kirsch, J. M. Lehn & J. P. Sauvage*, Helv. *62*, 1345 (1979).

[3] a) *S. Leutwyler & E. Schumacher*, Chimia *31*, 475 (1977); b) *P. A. Jacobs, J. B. Uytterhoeven & H. K. Beyer*, J. chem. Soc. Chem. Commun. *1977*, 128; c) *S. M. Kuzurcki & E. M. Eyring*, J. Amer. chem. Soc. *100*, 6790 (1978).

[4] *J. M. Lehn, J. P. Sauvage & R. Ziessel*, Nouveau J. Chim. *3*, 423 (1979).

[5] *K. Kalyanasundaram & M. Grätzel*, Angew. Chemie, Int. Ed. *18*, 701 (1979).

[6] a) *J. Kiwi & M. Grätzel*, Angew. Chemie *91*, 659 (1979); b) *J. Kiwi & M. Grätzel*, Nature, in press; c) *J. Kiwi & M. Grätzel*, J. Amer. chem. Soc., in press.

[7] a) *J. Kiwi & M. Grätzel*, Angew. Chemie Int. Ed. *17*, 860 (1978); b) *J. Kiwi & M. Grätzel*, Chimia *33*, 289 (1979); c) *M. Grätzel*, in 'Dahlem Conferences 1978 on Light-Induced Charge Separation', H. Gerischer, J.J. Katz, eds. Verlag Chemia, 1979, p.299; d) *J. Kiwi & M. Grätzel*, Angew.Chemie, Int. Ed. *18*, 624 (1974).

[8] *W. L. Jolly*, 'The Synthesis and Characterisation of Inorganic Compounds', Prentice-Hall, Englewood Cliffs, N.J., 1970, p.461.

[9] *J. Baxendale & N. K. Bridge*, J. Phys. Chem. *59*, 783 (1955).

[10] *A. W. Adamson, W. L. Waltz, E. Zinato, D. W. Watts, P. D. Fleischaner & R. D. Lindholm*, Chem. Rev. *68*, 541 (1968).

[11] a) *H. D. Gafney & A. W. Adamson*, J. Amer. Chem. Soc. *94*, 8238 (1972); b) *G. Navon & N. Sutin*, Inorg. Chem. *13*, 2159 (1974); c) *J. N. Demas & A. W. Adamson*, J. Amer. Chem. Soc. *95*, 5159 (1973).

[12] a) *F. Blau*, Monatsh., *19*, 647 (1898); b) *W. W. Brandt, F. P. Dwyer & E. C. Gyarfas*, Chem. Rev. *54*, 959 (1955); c) *M. Anbar & J. Pecht*, Trans. Faraday Soc. *4*, 744 (1968).

[13] *G. Nord & O. Wernberg*, J. Chem. Soc. Dalton *1972*, 866.

[14] *G. Nord & O. Wernberg*, J. Chem. Soc. Dalton *1975*, 845.

[15] *V. Y. Shafirovich, A. P. Moravskii, T. S. Dzhabiev & A. E. Shilov*, Kinetika i. Kataliz *18*, 509 (1977).

[16] *M. H. Miles, E. A. Klaus, B. P. Gunn, J. R. Locker & W. E. Serafin*, Electrochim. Acta *23*, 521 (1978).

[17] *C. Wagner & W. Traud*, Z. Elektrochem. *44*, 391 (1978).

[18] *C. Creutz & N. Sutin*, Proc. Nat. Acad. Sci. USA *72*, 2858 (1975).

[19] *D. A. Buckingham & F. Sargeson*, in 'Chelating Agents and Metal Chelates', F.P. Dwyer & D.P. Mellor, eds. Academic Press, N.Y., p.299.

[20] *P. J. Delaive, J. T. Lee, H. Abruna, H. W. Sprintschnik, T. J. Meyer & D. G. Whitten*, Adv. Chem. Ser. *168*, 28 (1978).