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116. Ruthenium Dioxide Electrodes as Suitable Anodes for Water Photolysis

by **Michael Neumann-Spallart, Kuppuswamy Kalyanasundaram, Carole Grätzel** and **Michael Grätzel**
Institut de Chimie Physique, Ecole Polytéchnique Fédérale, CH-1015 Lausanne, Suisse

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Summary

This paper presents a cell system in which a photoinduced redox reaction occurs in the cathodic compartment which is coupled to a RuO_2-anode. The light induced oxidation of the ruthenium complex $Ru(bipy)_3^{2+}$ by peroxodisulfate is used to illustrate that even under diffuse room light irradiation the photopotentials developed at the Pt-cathode are sufficient to afford water oxidation in the anode compartment. The oxygen produced at the RuO_2-electrode stands in a stochiometric relation to the current passed through the circuit. Implications for a cell system in which H_2 and O_2 are produced in separate compartments under illumination are discussed.

Introduction. - The photochemical production of hydrogen from water is of primary interest in the field of solar energy conversion. A viable approach to the solution of this problem is the combination of a photo-redox process

$$A + D \xrightarrow{h\nu} A^- + D^+ \quad (1)$$

where A stands for the electron acceptor and D for the photoactive donor with the catalytic step [1]:

$$A^- + H_2O \xrightarrow{cat.} \tfrac{1}{2} H_2 + OH^- + A \quad (2)$$

However, practical application of such a system can only be envisaged if the back conversion of the oxidized sensitizer D^+ to its original form under simultaneous oxidation of water can be achieved:

$$4D^+ + 2H_2O \longrightarrow O_2 + 4D + 4H^+ \quad (3)$$

Recently we discovered [2] that noble metal oxides can intervene as mediators in the oxygen generation process. RuO_2 in colloidal or macrodisperse suspension proved to be the most suitable choice of catalytic material [1c] [3]. Moreover, it was shown that by combining RuO_2 with colloidal Pt water can be cleaved under visible light illumination [4] of a solution containing $Ru(bipy)_3^{2+}$ as a sensitizer and

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methylviologen as an electron relay. Though of considerable academic interest, this system suffers from the fact that H_2 and O_2 are produced simultaneously as a gas mixture. Clearly, it is desirable to develop devices where the two gases are formed in separate compartments[1]. This concept was introduced in a preceding paper [1c] which described a halfcell containing RuO_2 as a redox catalyst and the $Fe(bipy)_3^{3+}/Fe(bipy)_3^{2+}$-couple as an electron relay for oxygen generation. An improved version of this device distinguished by its simplicity and long term stability is presented in this paper. It is sucessfully coupled with a second halfcell which through a light driven redox process supplies the electrical potential for O_2-evolution.

Experimental Part

Materials: $Ru(bipy)_3Cl_2$ was obtained from *Strem* and $K_2S_2O_8$ from *Merck (pro analysi).* Deionized water was distilled from alkaline $KMnO_4$ and subsequently twice from a quartz still. All other compounds were reagent grade and used as supplied.

Apparatus: Laser photolysis experiments were carried out with a JK-frequency doubled Nd-laser. The 530 nm pulse had a duration of approximately 20 ns. Details of the fast detection method have been published elsewhere [5].

Continuous photolysis experiments were carried out with a 450-W-Xenon lamp or a 150-W-slide projector. Suitable cut-off filters (450, 470 nm) were placed in front of the cell to remove UV. radiation. Oxygen was analyzed by the End-O-Mess oxygen-meter. The technique and experimental set-up have been described previously [1c] [6].

The design of the cell employed in the photoelectrochemical experiments is outlined in *Figure 1.* The system consists of three compartments (A, B, C), interconnected by porous discs, containing the SCE reference electrode, a platinium gauze electrode and the RuO_2-electrode[2]. It is prepared by depositing a thin layer of RuO_2 (2 µm) on 0.3 mm thick plates of Titanium of 8 cm^2 total surface area[3].

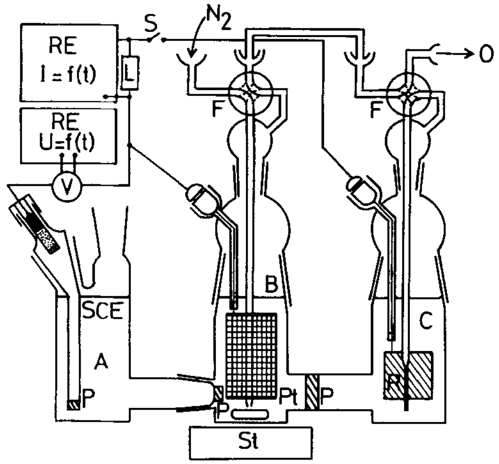

Fig. 1. *Electrochemical Cell.* L = 10 Ω resistor, S = switch, Pt = platinium gauze electrode (40 cm^2 geometrical area), P = porous glass disk, SCE = saturated calomel reference electrode, O = to trap (– 100°) and oxygen measuring device ('End-O-Mess'), St = stirrer, F = four way valve, V = digital voltmeter with recorder output, RE = recorder. RE = RuO_2 electrode.

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[1] The presence of oxygen in the solution reduces the quantum yield for hydrogen production. Also the separation of the two gases is difficult and costly.

[2] The latter was generously provided to us by Prof. *Sergio Trasatti* from the laboratory of electrochemistry, the University of Milan, Italy. The preparation of this electrode is described in [7].

[3] The thickness of the RuO_2 layer was determined by gravimetry.

Connection to the Pt-electrode occurs through a 10 Ω load resistor. The potential between the SCE and Pt-electrodes was monitored on a strip chart recorder connected to the output of a digital voltmeter. Compartment A contained 1M Na_2SO_4, compartment B 10^{-2}M $K_2S_2O_8$, 1.5×10^{-4}M $Ru(bipy)_3^{2+}Cl_2$ and 1M Na_2SO_4, and compartment C 0.1M acetate buffer and 1M Na_2SO_4. Prior to illumination B and C were liberated from oxygen by passing highly purified nitrogen *(Carba)* through the solution. The final O_2-level was < 1 ppm as determined by the *End-O-Mess* instrument which is attached to C *via* a trap maintained at *ca.* $-100°$. After closing the two stopcocks (F) the solution in B was irradiated either with a 150-W slide projector lamp or normal fluorescent room light while monitoring light induced changes in the cell current and voltage. The gas evolved in the RuO_2 compartment was then transferred to the *End-O-Mess* by a stream of nitrogen and subjected to analysis.

Results and Discussion. - The aim of the present work was to show that a light induced redox reaction occurring in one compartment of the cell system can be coupled to oxygen production in the other halfcell. In particular it is attempted to verify that the back conversion of the oxidized sensitizer (D^+) into its original form can be achieved by transfering the positive charge through an external circuit to a RuO_2-electrode where water oxidation occurs. This paper will restrict itself to the discussion of a sacrificial photochemical system in which the acceptor A is used up irreversibly. Emphasis is being placed on the recycling of the sensitizer through an electrode reaction affording O_2-generation.

The photochemical system employed consists of an aqueous solution containing $Ru(bipy)_3^{2+}$ as a photoactive donor and peroxodisulfate as an acceptor. The thermal oxidation of $Ru(bipy)_3^{2+}$ by $S_2O_8^{2-}$ is kinetically inhibited and does not occur over a period of several hours. By contrast, if $Ru(bipy)_3^{2+}$ is excited by light the oxidation takes place very rapidly and with a quantum yield of 2:

$$2\,Ru(bipy)_3^{2+} + S_2O_8^{2-} \xrightarrow{h\nu} 2\,Ru(bipy)_3^{3+} + 2\,SO_4^{2-} \quad (4)$$

Boletta & Balzani [8] were the first to make use of this reaction in order to assess the quantum yield of the CT-exited state formation. In the following section the kinetic details of this process will be ascertained by using laser photolysis technique.

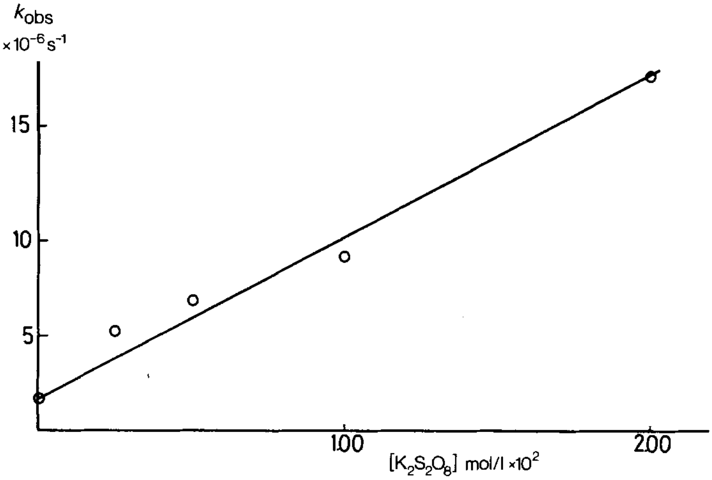

Fig. 2. *Oxidative quenching of* $Ru(bipy)_3^{2+}$ *emission at* $\lambda = 620$ *nm*

The experiments were carried out with deaerated aqueous solutions containing Ru(bipy)$_3^{2+}$ (10^{-4} M), acetate buffer (pH 4.7, 0.1 M) and varying concentrations of $S_2O_8^{2-}$. The decay of the Ru(bipy)$_3^{2+}$-emission at 620 nm was measured by time resolved spectroscopy. *Figure 2* shows a *Stern-Vollmer* plot of these data. From the straight line drawn through the experimental points one obtains a specific quenching rate of $k_s = 8 \times 10^8 \text{M}^{-1}\text{s}^{-1}$ at an ionic strength of *ca.* 0.1 M indicating that this process is essentially diffusion controlled. The products resulting from the quenching reaction can be identified from *Figure 3.* A spectrum with a maximum at 680 nm which is characteristic [9] of Ru(bipy)$_2^{3+}$ can be observed 4 µs after laser excitation. The kinetic details are given in the inserted oscillograms which show the time course of the events at 680 nm. In the absence of $S_2O_8^{2-}$ one observes the formation of a transient absorption after laser excitation which decays with the same time constant as the emission at 620 nm. This is attributed to the CT-excited state of Ru(bipy)$_3^{2+}$. Curve b was taken in the presence of 5×10^{-3} M $S_2O_8^{2-}$. Its features are characteristic for a two step formation of Ru(bipy)$_3^{3+}$, one resulting from the electron transfer quenching:

$$\text{Ru(bipy)}_3^{2+*} + S_2O_8^{2-} \longrightarrow \text{Ru(bipy)}_3^{3+} + SO_4^{2-} + SO_4^{-} \qquad (5)$$

and the other from the subsequent reduction of SO_4^--radicals:

$$SO_4^- + \text{Ru(bipy)}_3^{2+} \longrightarrow \text{Ru(bipy)}_3^{3+} + SO_4^{2-} \qquad (6)$$

The overall reaction (equ. 4) corresponds to light induced oxidation of Ru(bipy)$_3^{2+}$ with a quantum yield of two, as shown by *Bolletta & Balzani* [8]. The Ru(bipy)$_3^{3+}$ produced is relatively stable at pH 4.7 (0.1 M acetate buffer). Thus, continuous illumination leads to complete conversion of the (2+)- into (3+)-state. This is

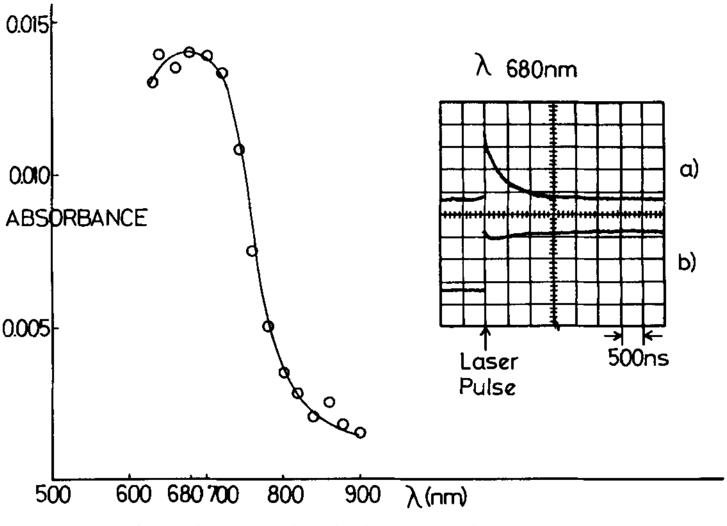

Fig. 3. *2 transient spectrum obtained 400 ns after the laser pulse from a solution containing Ru(bipy)$_3^{2+}$.* Insert: oscillograms showing the temporal behaviour of the absorption at λ = 680 nm, a) Ru(bipy)$_3^{2+}$ (10^{-4} M), b) in the presence of $K_2S_2O_8$ (5×10^{-3} M).

shown in *Figure 4* where the spectrum of a 10^{-3}M $Ru(bipy)_3^{2+}$ solution is recorded prior and after 20 s photolysis with the Xe-lamp in the presence of 10^{-2}M $S_2O_8^{2-}$. The 452 nm band of $Ru(bipy)_3^{2+}$ is bleached with the concommitant formation of the $Ru(bipy)_3^{3+}$ absorption. Apparently such a short light exposure suffices to render the oxidation process practically complete. In fact, if no precautions are taken to avoid excitation of $Ru(bipy)_3^{3+}$, the latter will undergo further photoreactions - presumably photooxidation to higher valency states. The recovery of $Ru(bipy)_3^{2+}$ in the dark takes place over a period of 1 to 2 hours in agreement with the results obtained by *Creutz & Sutin* [10]. This process is however not quantitative. Spectral observations demonstrate that $Ru(bipy)_3^{2+}$ does not regain completely its initial value a broadening of the peak appearing towards the red. Also, the thermal reduction of $Ru(bipy)_3^{3+}$ to $Ru(bipy)_3^{2+}$ fails to result in any significant oxygen evolution at pH 4.7 as shown by *End-O-Mess* analysis.

The picture changes drastically when experiments are carried out with solutions to which RuO_2-powder[4]) (30 mg/60 ml) was added as a redox catalyst. In this case no bleaching of the $Ru(bipy)_3^{2+}$ absorption is observed. This indicates that $Ru(bipy)_3^{3+}$ produced *via* photooxidation by $S_2O_8^{2-}$ is rapidly converted back to the (2+)-state. We found that this reaction proceeds under generation of oxygen, *i.e.* according to:

$$4\,Ru(bipy)_3^{3+} + 2\,H_2O \xrightarrow{\text{cat.}} O_2 + 4\,H^+ + 4\,Ru(bipy)_3^{2+} \qquad (7)$$

The quantitative O_2-analysis was performed by illuminating the reaction mixture with the slide projector lamp for *ca.* 1 minute and subsequent stirring with the redox catalyst in the dark for several minutes. The gas evolved during the dark

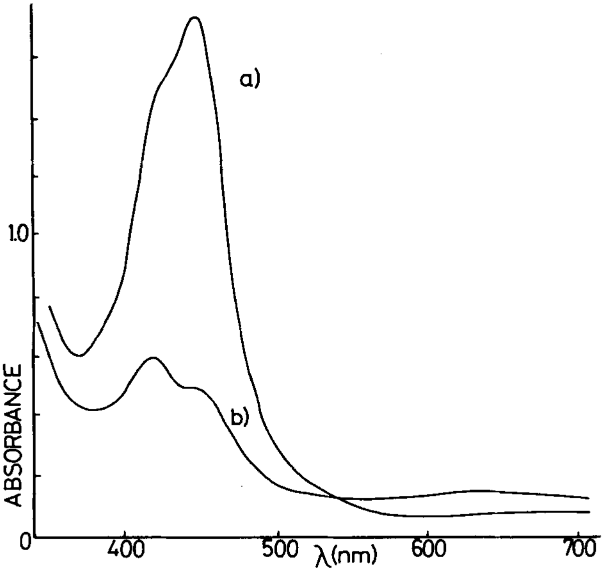

Fig. 4. *$Ru(bipy)_3^{3+}$ formation from $Ru(bipy)_3^{2+}$ upon photolysis in presence of $K_2S_2O_8$, 1.5×10^{-4}M $Ru(bipy)_3^{2+}$, 1×10^{-2}M $K_2S_2O_8$, pH = 4.7* (acetate buffer); a) *Before photolysis*, $\lambda = 452$ nm, $\varepsilon = 14500$ l/(M. cm), $Ru(bipy)_3^{2+}$; b) *Immediately after 20 s photolysis* with 450 W Xenon lamp, cut-off filter $\lambda = 450$ nm, $\lambda = 420$ nm ($\varepsilon = 3600$) (M^{-1} cm^{-1}), $Ru(bipy)_3^{3+}$.

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[4]) The material used was RuO_2-hydrated powder from *Alpha Inorganics*.

phase is transferred by a stream of nitrogen to the *End-O-Mess* analyzer. This cycle was repeated several times, oxygen being produced each time. These observations confirm earlier results [3] showing that reaction 7 is catalyzed by RuO_2.

In the following we shall attempt to perform the $Ru(bipy)_3^{3+}$ reduction and water oxidation processes separately in the two compartments of the cell system shown in *Figure 1*. Instead of using RuO_2-powder as a redox catalyst this material serves now as an electrode which is inserted into the pH 4.7 buffer solution of compartment C, while the reaction mixture of $Ru(bipy)_3^{2+}$ (10^{-4} M) and $K_2S_2O_8$ (10^{-2} M) is kept in compartment B. The latter is equipped with a platinum gauze electrode where the potential U against SCE is around 0.5 V in the dark (the value of U was found to be rather insensitive to the presence of oxygen). Short circuiting of the two electrodes in the dark results in negligibly small currents ($I < 1$ µA). Both cell current and potential are drastically affected upon exposure of the system to light. Thus, when the 150-W projector lamp is used to illuminate the solution the photopotential rises within a few seconds to *ca.* 1.0 V (SCE) with a concommitant increase of the cell current to 300-400 µA. In fact, the sensitivity of the system to light exposure is so high that a simple fluorescent room lamp suffices to produce the same alterations in the cell current and voltage. This is illustrated in *Figure 5* which shows the behaviour of U and I under room light illumination.

Within a few minutes the current rises to 325 µA where it is sustained throughout the irradiation period of one hour. It declines sharply after the light has been turned off. Similar features are displayed by the potential curve, U assuming a value of *ca.* 1 V under illumination and decaying after dark conditions have been reinstalled. The photo-current observed at the Pt-electrode is attributed to the reduction of $Ru(bipy)_3^{3+}$ produced in the photo-redox reaction (4):

$$e^-(Pt) + Ru(bipy)_3^{3+} \longrightarrow Ru(bipy)_3^{2+} \tag{8}$$

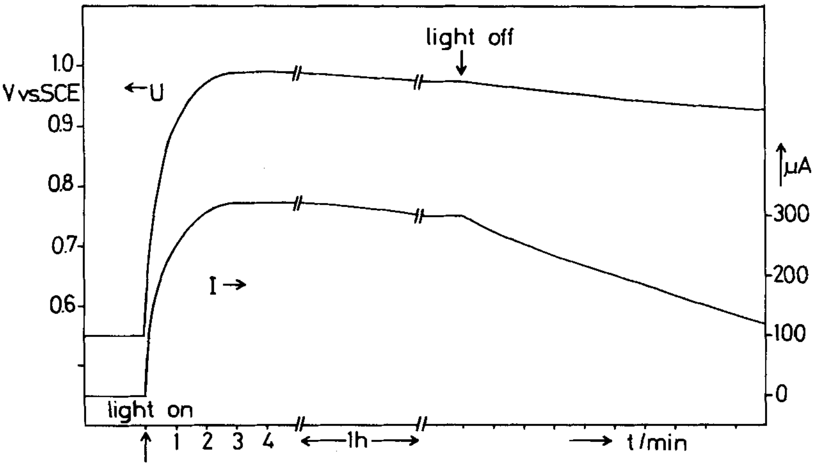

Fig. 5. *Current and potential evolution during a photoelectrochemical experiment*

This process can be followed readily by spectroscopic observations following light exposure. The decrease of the current is associated with a conversion of $Ru(bipy)_3^{3+}$ into the $Ru(bipy)_3^{2+}$ absorption spectrum. Under continuous illumination $Ru(bipy)_3^{2+}$ is recycled to the (3+)-state through the photo-driven redox process (equ. 4). This condition is maintained as long as $S_2O_8^{2-}$ acceptor is available which explains the sustained photocurrent and potential. The complementary reaction in the RuO_2-anode compartment was found to correspond to O_2-generation from water. In fact, coulometric analysis showed that this process is stochiometric, four electrons being passed through the circuit for every oxygen molecule produced.

$$2\,H_2O \longrightarrow O_2 + 4\,H^+ + 4\,e^-\,(RuO_2) \qquad (9)$$

The oxygen production rate was 0.07 ml/h. RuO_2 is distinguished by its low overvoltage for O_2-evolution from water, which in acidic condition is not matched by any other electrode material [11]. Overvoltages of *ca.* 150 to 250 mV suffice to operate the O_2 producing halfcell at current density of 10^{-4} to 10^{-2} A/cm^2. Higher current densities are hardly required in cell systems which attempt to use sunlight for water splitting as the power density of solar radiation is low (average *ca.* 20 mW/cm^2).

Conclusions. - From the present study the important fact emerges that RuO_2 anodes operating in the dark complement in a suitable fashion halfcells in which light energy conversion is achieved through photoredox processes. The latter reaction has to produce an electroactive substance like $Ru(bipy)_3^{3+}$ which tunes the cathode to a potential sufficiently high to afford water oxidation on the other side. The O_2-evolution halfcell presented earlier [1c] contained apart from the electrode, a redox catalyst and an electron relay. The present data show that this can be simply replaced by a RuO_2 coated titanium sheet immersed in a buffer solution. Such a device avoids problems arising from the diffusion of the electron relay to the surface, undesirable chemical side reactions and deterioration of the catalyst. In fact, during several months of operation we have not observed any decrease in the performance of RuO_2-electrode employed. This may be due to the fact that mild pH and temperature conditions prevail in these experiments.

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