

Photoelectrocatalytic reactions of metal complexes at chemically modified electrodes

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Abstract. One of the outstanding properties of the ion-exchange membranes is their multiphase structure with microheterogeneous environment. Recently we have shown that ion-exchange membranes such as Nafion and clay can be effectively used in preparing chemically modified electrodes with adsorbed photoactive and electroactive molecules. A new photogalvanic cell was constructed by coating one electrode with Nafion- $[\text{Ru}(\text{bpy})_3]^{2+}$ and the other with clay- $[\text{Ru}(\text{bpy})_3]^{2+}$. This new photogalvanic cell showed an additive photogalvanic response on visible light irradiation. The quenching rate constants, k_q , for the reaction of excited state $[\text{Ru}(\text{bpy})_3]^{2+}$ adsorbed into the membrane with Fe^{3+} ion and cobalt(III) complexes were determined by photoelectrochemical methods. The photoelectrocatalytic reduction of oxygen to hydrogen peroxide at chemically modified electrodes was carried out by using $[\text{Ru}(\text{bpy})_3]^{2+}$ as sensitizer and macrocyclic cobalt(III) complexes as electron relay.

Keywords. Photoelectrochemical cell; chemically modified electrode; Nafion; clay; photoelectrocatalysis; solar energy conversion.

1. Introduction

Since global environment problems such as high levels of atmospheric carbon dioxide are reaching alarming proportions, solar energy conversion by artificial photosynthesis is becoming an increasingly important research subject. In photosynthesis, a series of redox reactions takes place by which an electron is transferred from one terminal to another through electron transfer between neighbouring redox centres (Biggins 1987). The reactions in photosynthesis are carried out in an immobilized state. Attempts to construct artificial photosynthetic apparatus have been made in terms of the use of microheterogeneous reaction environments such as micelle, bilayer etc. (Graetzel 1983; Kalyanasundaram 1987). However, the utilization of a macroheterogeneous membrane system (solid-solution interface) has not been exploited extensively (Kaneko and Woehrle 1988).

In photoelectrochemical cells, it has already been understood that homogeneous photoredox systems have only limited prospects of being applied to photodevices, because of the energy wasting fast back electron transfer reaction (figure 1). This problem can be overcome by using macroheterogeneous membrane systems (Kalyanasundaram 1987; Kaneko and Woehrle 1988; Graetzel 1989; Kaneko and Lin 1993). It has been shown that the immobilization of photochemical reaction components onto a chemically modified electrode is very effective in fabricating photoelectrochemical cells (Kaneko and Woehrle 1988; Lin and Kaneko 1993). In the fabrication of chemically modified electrodes (figure 2), the use of coating ion-exchange polymer or clay film is a promising approach (Gobi and Ramaraj 1994). Clays are interesting aluminosilicate layered

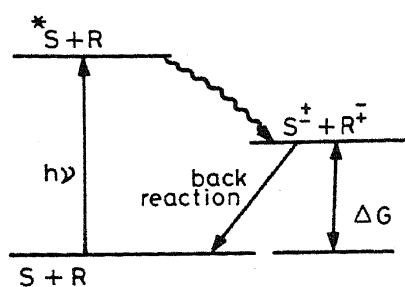


Figure 1. Photoredox system consisting of sensitizer (S) and electron relay (R): Energy wasting back electron transfer reaction in homogeneous medium.

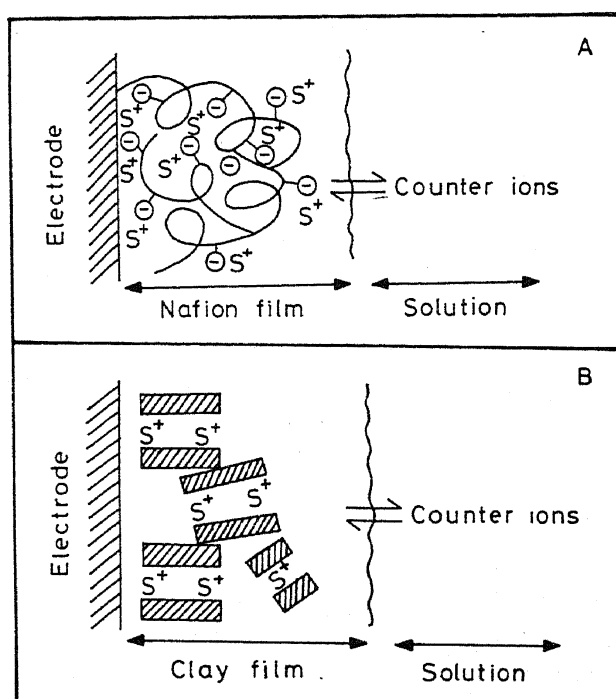


Figure 2. Electrode coated with Nafion (A) or layered clay (B). S^+ : ion-exchanged sensitizer molecule.

materials and they are useful organizing media for photochemical reactions (Theng 1978; Newman 1987; Thomas 1988). Exchange of cations occurs between the silicate layers of the clay and the acidity and interlayer spacing depends mainly on the size of the exchanged cation (figure 3). The important aspects of the surface photochemistry of clay adsorbed sensitizer molecule are reduced mobilities of the immobilized molecules with respect to their mobility in solution, the stabilization of positively charged molecules and an increase in the selectivity of reactions (Thomas 1988; Gobi and Ramaraj 1994). In the fabrication of ion-exchange membrane, Nafion polymer is another promising material containing multiphase structure with microheterogeneous environment (figure 4) (Heisenberg and Yeager 1982; Ramaraj and Kaneko 1995). Even though the electrochemical properties of the ion-exchanged molecules could be influenced by the microheterogeneous environment imposed by the coating material,

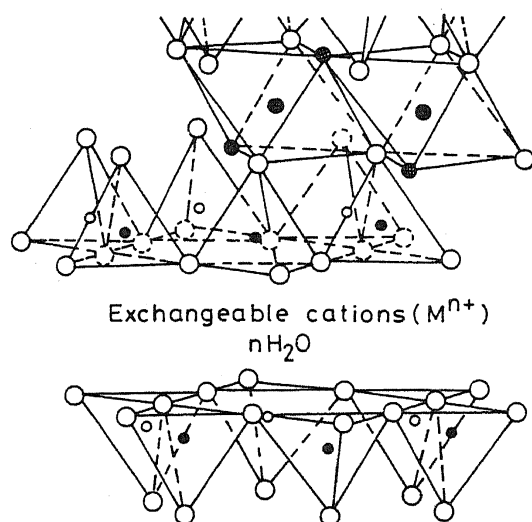


Figure 3. Structure of layered clay (montmorillonite): \circ oxygen atoms; \odot hydroxyl groups; \bullet silicon; \bullet aluminium, magnesium, iron sites.

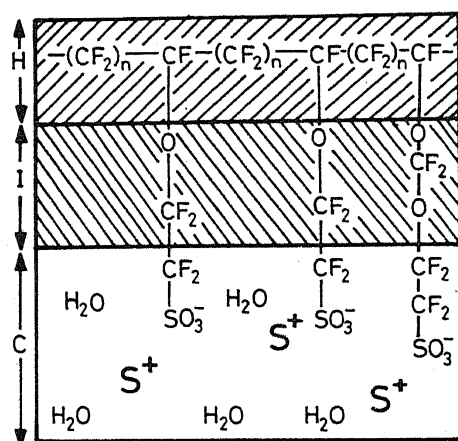


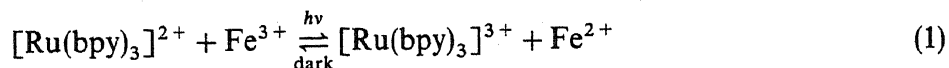
Figure 4. Schematic structure of Nafion film. H: hydrophobic fluorocarbon region; I: interfacial region; C: hydrophilic $-SO_3^-$ ionic cluster region.

no direct evidence has been reported concerning the photoelectrochemical properties of the ion-exchanged molecules (Gobi and Ramaraj 1994).

The photochemical processes occurring in a photoredox system will mainly depend on their immediate environment (Graetzel 1983; Kalyanasundaram 1987). When the photoredox molecules are bound to the chemically modified electrodes, the electron transfer quenching reaction can be accelerated (Gobi and Ramaraj 1994). The photoredox molecules, $[Ru(bpy)_3]^{2+}$, cobalt(III) complexes and Fe^{3+} ion, were used in the fabrication of photoelectrochemical cells with chemically modified electrodes (Gobi and Ramaraj 1992, 1993, 1994). The photoinduced electron transfer reaction mechanisms at the chemically modified electrodes and the exploitation of the stabilized high energy products in solar energy conversion were studied. This paper mainly summarises the work done in our laboratory on photoelectrochemical cells with ion-exchange membrane coated electrodes.

2. Photoinduced electron transfer reactions of $[\text{Ru}(\text{bpy})_3]^{2+}$ - Fe^{3+} photoredox system at Nafion and clay modified electrodes

The photogalvanic effect produced by the $[\text{Ru}(\text{bpy})_3]^{2+}$ - Fe^{3+} photoredox system was investigated in homogeneous medium,



and the energy conversion efficiency was found to be very low (Kalyanasundaram 1982). The photosensitizer, $[\text{Ru}(\text{bpy})_3]^{2+}$, was adsorbed into the Nafion or montmorillonite or bentonite clay (clay) matrix coated electrode and photoelectrochemical behaviour was studied in the presence of quencher Fe^{3+} ion (Gobi and Ramaraj 1993, 1994).

The cyclic voltammograms were recorded for Nafion or clay adsorbed $[\text{Ru}(\text{bpy})_3]^{2+}$ electrode (represented as Pt/Nf/ Ru^{2+} and Pt/clay/ Ru^{2+}) dipped in 0.1 mM Fe^{3+} ion and 0.1 M HClO_4 and are shown in figure 5. For both $[\text{Ru}(\text{bpy})_3]^{2+/3+}$ and $\text{Fe}^{3+/2+}$ redox couples, $E_{1/2}$ values were shifted to more negative potentials at Pt/Nf/ Ru^{2+} electrodes than those at the Pt/clay/ Ru^{2+} electrode. Such shifts in $E_{1/2}$ values indicate a more favourable partition coefficient and stabilization of the more positively charged member of the redox pair in the Nafion film (Liu and Anson 1985; Porat *et al* 1991; Gomez and Kaifer 1992). This is expected from the stronger electrostatic interactions with the negatively charged sulphonic groups ($-\text{SO}_3^-$) of the Nafion film. The positive shift in redox potential at clay coated electrode shows that the less charged member of the redox couple is more stabilized and tightly bound to the clay coating (Leiber *et al* 1986; Naegeli *et al* 1986; Liu and Anson 1985). The plots of peak currents vs square root of scan rate for Pt/Nf/ Ru^{2+} and Pt/clay/ Ru^{2+} electrodes showed that the electron transfer process within the film is a diffusion controlled one.

A photoelectrochemical cell was constructed using Pt/Nf/ Ru^{2+} or Pt/clay/ Ru^{2+} electrode dipped in 1 mM Fe^{3+} ion and 0.1 M HClO_4 and irradiated with visible light. The Pt/Nf/ Ru^{2+} and Pt/clay/ Ru^{2+} electrodes showed different photoelectrochemical

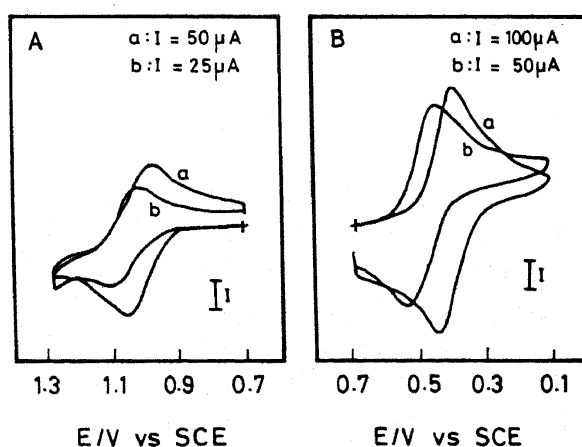
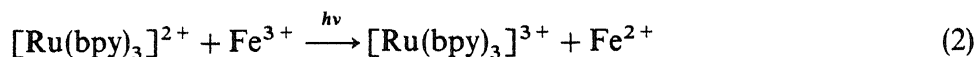


Figure 5. Cyclic voltammograms of $[\text{Ru}(\text{bpy})_3]^{2+}$ (A) and Fe^{3+} (B). Cyclic voltammograms at Pt/Nf/ Ru^{2+} (a) and Pt/clay/ Ru^{2+} (b) in 1 mM Fe^{3+} ion and 0.1 M HClO_4 . Scan rate 20 mV/s.

behaviour depending upon the coating material in the presence of Fe^{3+} ion as quencher (figure 6). The Pt/Nf/ Ru^{2+} electrode produced anodic photocurrent, while the Pt/clay/ Ru^{2+} electrode produced cathodic photocurrent. A new photogalvanic cell was constructed using Pt/Nf/ Ru^{2+} electrode as anode and Pt/clay/ Ru^{2+} electrode as cathode and Fe^{3+} ion as quencher (Gobi and Ramaraj 1994). When both the electrodes were irradiated, an additive photoresponse was observed (figure 6).

Upon irradiation, the adsorbed $[\text{Ru}(\text{bpy})_3]^{2+}$ absorbs light and undergoes electron transfer reaction with Fe^{3+} ion (2) (Kalyanasundaram 1982). The different



electrode reactions of the photoproduced $[\text{Ru}(\text{bpy})_3]^{3+}$ and Fe^{2+} ions could be determined by the microheterogeneous environment imposed by the coating materials. The photoproduced Fe^{2+} ion undergoes oxidation at Pt/Nf/ Ru^{2+} electrode and the $[\text{Ru}(\text{bpy})_3]^{3+}$ ion is reduced at Pt/clay/ Ru^{2+} electrode (figure 7). This electrodic reaction mechanism was confirmed by the measurement of photocurrent at different applied potentials using Pt/Nf/ Ru^{2+} and Pt/clay/ Ru^{2+} electrodes (Gobi and Ramaraj 1994).

3. Photoelectrochemical investigation of $[\text{Ru}(\text{bpy})_3]^{2+}$ -macrocyclic cobalt(III) complex photoredox systems at Nafion and clay modified electrodes

Photoelectrochemical cells were constructed using Pt/Nf/ Ru^{2+} and Pt/clay/ Ru^{2+} electrodes and macrocyclic cobalt(III) complexes ($[\text{Co}(\text{cyclam})(\text{H}_2\text{O})_2]^{3+}$; cyclam = 1, 4, 8, 11-tetraazacyclotetradecane; $[\text{Co}(\text{teta})(\text{H}_2\text{O})_2]^{3+}$; tetra = 5, 5, 7, 12, 12, 14-hexamethyl-1, 4, 8, 11-tetraazacyclotetradecane) as quenchers (Gobi and Ramaraj 1994),

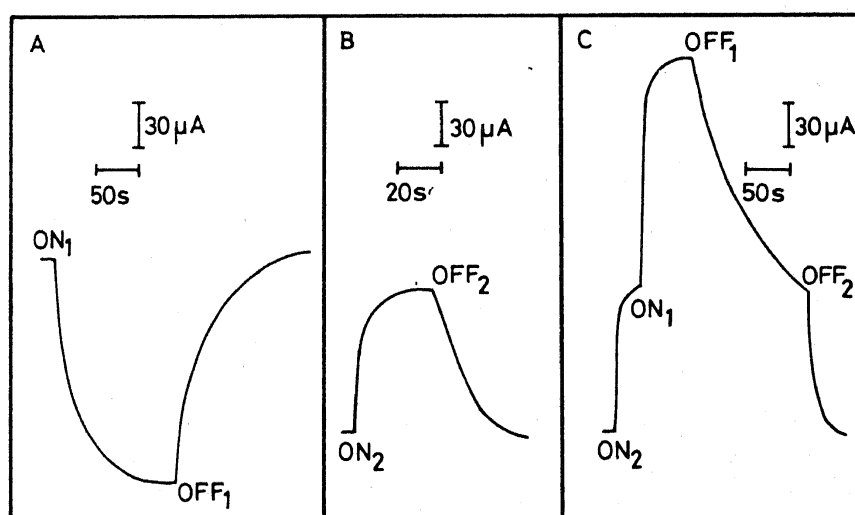
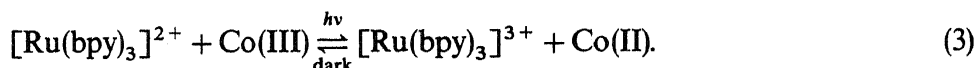


Figure 6. Steady state photocurrent (I_{ph}) observed at Pt/Nf/ Ru^{2+} (A) Pt/clay/ Ru^{2+} (B) and Pt/Nf/ Ru^{2+} / Fe^{3+} /Pt/clay/ Ru^{2+} (C) dipped in 0.025 M Fe^{2+} ion and 0.1 M HClO_4 . ON₁ and OFF₁: light 'on' and 'off' conditions for Pt/Nf/ Ru^{2+} electrode. ON₂ and OFF₂: light 'on' and 'off' condition for Pt/clay/ Ru^{2+} electrode.

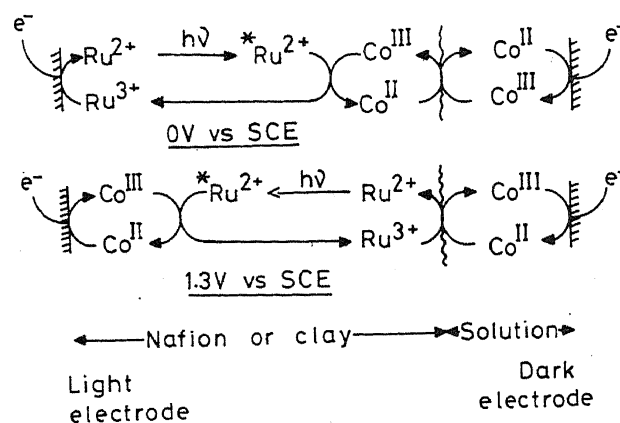


Figure 7. Schematic picture of electrode reactions observed at Pt/Nf/Ru²⁺ and Pt/clay/Ru²⁺ electrodes dipped in Fe³⁺ and HClO₄ solution.

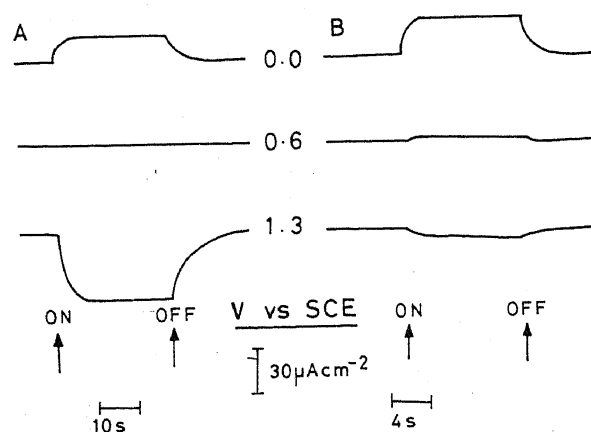


Figure 8. Photocurrent vs time plots for the electrodes ((A): Pt/Nf/Ru²⁺ and (B): Pt/clay/Ru²⁺) dipped in 0.15 mM [Co(cyclam)(H₂O)₂]³⁺ and 0.1 M HClO₄ at different applied potentials. ON and OFF: light 'on' and 'off' conditions.

Both anodic and cathodic photocurrents were observed with Pt/Nf/Ru²⁺ and Pt/clay/Ru²⁺ electrodes at different applied potentials (figure 8). The photoresponse was switched between cathodic and anodic by controlling the applied potentials. The origin of the anodic and cathodic photocurrents was discussed in terms of an oxidative quenching of the excited state [Ru(bpy)₃]²⁺ complex by cobalt(III) complex (3) followed by electrochemical reduction or oxidation of the photoproducts [Ru(bpy)₃]³⁺ and cobalt(II) complexes (figure 9).

4. Determination of excited state electron transfer quenching rate constant (k_q) at chemically modified electrodes

The photoresponse observed using Pt/Nf/Ru²⁺ or Pt/clay/Ru²⁺ electrode with Fe³⁺ or cobalt(III) complex as quenchers showed that the photoproduct [Ru(bpy)₃]³⁺ and Fe²⁺ ion or Co(II) complex were participating in the electron transfer reactions at the modified electrode (Gobi and Ramaraj 1994). During photolysis, the membrane adsorbed [Ru(bpy)₃]²⁺ absorbed light and the resulting excited state [Ru(bpy)₃]²⁺

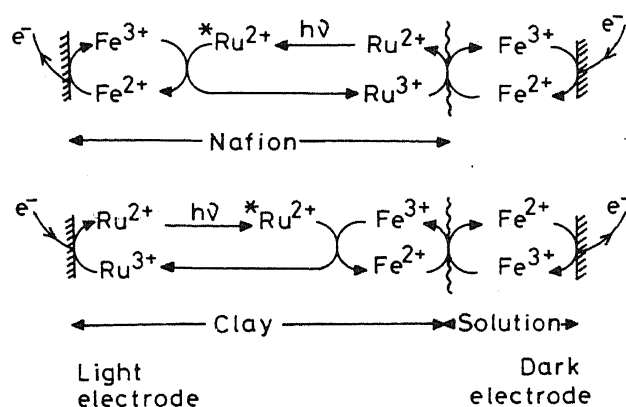
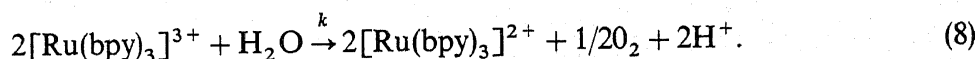
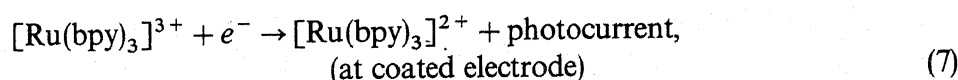
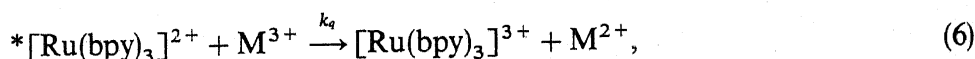
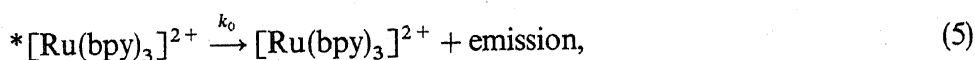


Figure 9. Light induced electrode reactions at Pt/Nf/Ru²⁺ or Pt/clay/Ru²⁺ electrode at 0 V and 1.3 V (SCE). Co^{III}: macrocyclic cobalt(III) complexes referred in the text.

(* $[\text{Ru}(\text{bpy})_3]^{2+}$), underwent oxidative electron transfer reaction with Fe^{3+} ion or Co(III) complex and produced $[\text{Ru}(\text{bpy})_3]^{3+}$ and Fe^{2+} ion or Co(II) complex. The electrode reactions of the photoproduct $[\text{Ru}(\text{bpy})_3]^{3+}$ and Fe^{2+} ion or Co(II) complex produced cathodic or anodic photocurrents (figure 10).

The excited state electron transfer quenching rate constant (k_q) for the photoredox system in homogeneous solution can be easily determined by using Stern-Volmer equation (Rohatgi-Mukherjee 1986). However, the direct determination of k_q for photoredox systems at chemically modified electrode is not known. The k_q for the quenching of $*[\text{Ru}(\text{bpy})_3]^{2+}$ can be calculated photoelectrochemically using the photoresponse obtained at Pt/Nf/Ru²⁺ and Pt/clay/Ru²⁺ electrodes under different quencher concentrations (Gobi and Ramaraj 1994). The various electron transfer reactions occurring at the modified electrodes are:



The photocurrent (I_{ph}) produced at different quencher concentrations (M^{3+}) is given by (9) (Nishida *et al* 1989),

$$\frac{1}{I_{\text{ph}}} = \frac{k^{1/2}}{2FA\alpha I_0 C_0 D^{1/2}} \left[1 + \frac{k_0}{k_q [Q]} \right], \quad (9)$$

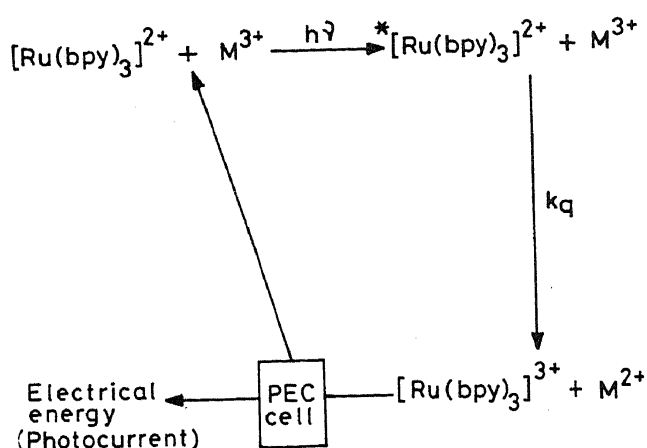


Figure 10. The photoredox system $[\text{Ru}(\text{bpy})_3]^{2+} - \text{Fe}^{3+}$ or Co^{III} complex and generation of photocurrent. k_q : excited state electron transfer quenching rate constant. PEC: photoelectrochemical cell.

where

- I_{ph} = photocurrent induced at the modified electrode,
- k = pseudo-first order rate constant for the reduction of $[\text{Ru}(\text{bpy})_3]^{3+}$ by H_2O molecule,
- F = Faraday constant,
- A = surface area of the modified electrode,
- α = absorption coefficient of $[\text{Ru}(\text{bpy})_3]^{2+}$,
- I_0 = intensity of the incident light on the modified electrode,
- C_0 = initial concentrations of $[\text{Ru}(\text{bpy})_3]^{2+}$ at the modified electrode,
- Q = quencher concentration (Fe^{3+} , $\text{Co}(\text{III})$ complexes),
- k_0 = phosphorescence decay constant for the adsorbed $[\text{Ru}(\text{bpy})_3]^{2+}$,
- k_q = photoinduced electron transfer quenching rate constant for $[\text{Ru}(\text{bpy})_3]^{2+}$ and Fe^{3+} or $\text{Co}(\text{III})$ complex system.

A plot of $[I_{\text{ph}}]^{-1}$ vs $[Q]^{-1}$ should be linear with slope $k_0 k^{1/2} / 2FA\alpha I_0 C_0 k_q D^{1/2}$ and intercept $k^{1/2} / 2FA\alpha I_0 C_0 D^{1/2}$. The photoproduct $[\text{Ru}(\text{bpy})_3]^{3+}$ complex was also reduced by water molecules and the reduction was found to be efficient in the adsorbed state (Memming and Schroppel 1979). The quenching rate constants at Pt/Nf/Ru^{2+} and Pt/clay/Ru^{2+} electrodes were determined for the electron transfer reaction between $[\text{Ru}(\text{bpy})_3]^{2+}$ and Fe^{3+} ion or $\text{Co}(\text{III})$ complex using the equation,

$$\frac{1}{I_{\text{ph}}} = (\text{intercept}) \left[1 + \frac{k_0}{k_q [Q]} \right], \quad (10)$$

considering the fact that the diffusion-controlled electron transfer process occurs in homogeneous solution as well as in Pt/Nf/Ru^{2+} and Pt/clay/Ru^{2+} electrodes (Gobi and Ramaraj 1994).

For Pt/Nf/Ru^{2+} and Pt/clay/Ru^{2+} electrodes, the photocurrents were measured at different concentrations of Fe^{3+} ion or $\text{Co}(\text{III})$ complexes. The plot of $[I_{\text{ph}}]^{-1}$ vs $[Q]^{-1}$ showed a straight line as shown in figure 11. The k_q values calculated are given in table 1. The reported values k_0 of the excited state life time of $[\text{Ru}(\text{bpy})_3]^{2+}$ ion-exchanged into Nafion and clay colloid were used for the determination of k_q values with the assumption

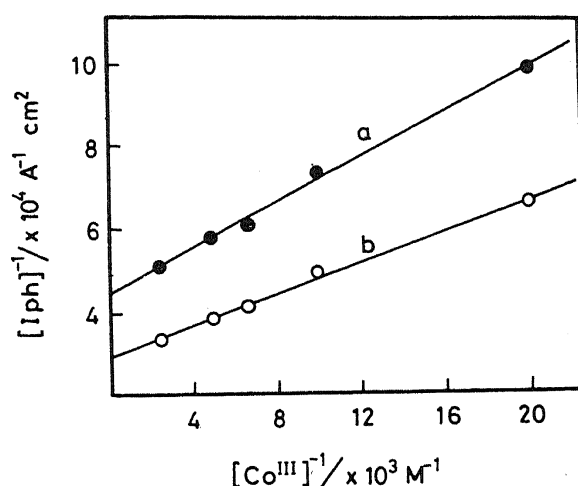


Figure 11. $[I_{ph}]^{-1}$ vs $[Co^{III}]^{-1}$ plots for Pt/Nf/Ru²⁺ (a) and Pt/clay/Ru²⁺ (b) electrodes under applied potential 0 V (SCE). Co^{III}: [Co(cyclam)(H₂O)₂]³⁺.

Table 1. Excited state electron transfer quenching rate constants determined at Nafion and montmorillonite clay modified electrodes with macrocyclic cobalt(III) complexes and Fe³⁺ ion. HClO₄ = 0.1 M (Gobi and Ramaraj 1994).

Quencher	Pt/Nf/Ru ²⁺ $k_q (\times 10^{10})(M^{-1} s^{-1})$	Pt/clay/Ru ²⁺ $k_q (\times 10^{10})(M^{-1} s^{-1})$
[Co(cyclam)(H ₂ O) ₂] ³⁺	2.6	4.0
[Co(teta)(H ₂ O) ₂] ³⁺	2.1	1.6
[Co(teta)(H ₂ O)(NO ₂) ₂] ²⁺	9.6	4.7
Fe ³⁺	1.9	0.14

that the above systems would be similar to the reported one. A k_0 value of $1.6 \times 10^6 s^{-1}$ for [Ru(bpy)₃]²⁺ in Nafion membrane (Lin *et al* 1993) and $2.4 \times 10^6 s^{-1}$ for [Ru(bpy)₃]²⁺ in clay (DellaGuardia and Thomas 1983) were used to calculate the k_q values. The k_q values were also determined for [Ru(bpy)₃]²⁺-Fe³⁺ or Co(III) complex photoredox system in homogeneous solution and it was in the order of $10^9 M^{-1} s^{-1}$. The k_q values calculated for [Ru(bpy)₃]²⁺ at Pt/Nf/Ru²⁺ and Pt/clay/Ru²⁺ electrodes (table 1) are 10–100 times higher than the corresponding values in homogeneous solution. It is reasonable to assume that the electron transfer quenching rate constant in a heterogeneous phase would be higher. The positively charged metal complexes exchanged into Nafion or clay films enhanced the charge separation and stabilization of the photoproducts at the modified electrodes.

5. Catalytic reduction of dioxygen to hydrogen peroxide at chemically modified electrodes

The current interest in chemically modified electrodes originated with the hope that catalytically active molecules incorporated in the ion-exchange membrane could be used for electro- or photoelectrocatalysis (Murray 1984; Kaneko and Woehle 1988). In recent years, a number of reports on the chemically modified electrodes have appeared and significant progress has been made in analysing the various factors that may limit

the current in electrocatalytic systems. However, not many catalytic systems are known for catalytic reduction of dioxygen to hydrogen peroxide at chemically modified electrodes. Particularly photoelectrocatalytic reduction of dioxygen is not yet attempted using chemically modified electrodes. By attempting photoelectrochemical method, we can utilize light energy to drive the multielectron process of dioxygen reduction to hydrogen peroxide.

The homogeneous catalysis of electroreduction of dioxygen (O_2) using macrocyclic cobalt(III) complexes and metalloporphyrins has been already reported (Geiger and Anson 1981; Anson *et al* 1985). Recently, chemically modified electrodes have been used for O_2 reduction by adsorbing cobalt porphyrins into the films (Buttry and Anson 1984; Anson *et al* 1985). We have recently reported the photoelectrocatalytic reduction of O_2 to H_2O_2 using $[Ru(bpy)_3]^{2+}$ - Co(III) photoredox system at Pt/Nf and Pt/clay electrodes (Gobi and Ramaraj 1992).

The Pt/Nf/ Ru^{2+} and Pt/clay/ Ru^{2+} electrodes in combination with $[Co(cyclam)(H_2O)_2]^{3+}$ or $[Co(teta)(H_2O)_2]^{3+}$ complex were used as photoelectrocatalysts for O_2 reduction. The electrochemical properties of Co(III) complexes at Pt/Nf and Pt/clay electrodes were very similar to that recorded in homogeneous solution. When O_2 was introduced into the cell containing Pt/Nf/ Ru^{2+} /Co(III) or Pt/clay/ Ru^{2+} /Co(III) electrode, a large increase in the cathodic peak current was observed with a new reduction wave at the negative potential region. The electroreduced Co(II) complex reacts with O_2 to produce $Co^{III} - O_2^-$ adduct and the adduct undergoes reduction around 0.1 V (SCE) to produce hydrogen peroxide at pH 1. The amount of H_2O_2 produced in dark by controlled potential electrolysis at -0.1 V(SCE) using Pt/Nf/ Ru^{2+} and Pt/clay/ Ru^{2+} electrodes were determined. The H_2O_2 yield was nearly

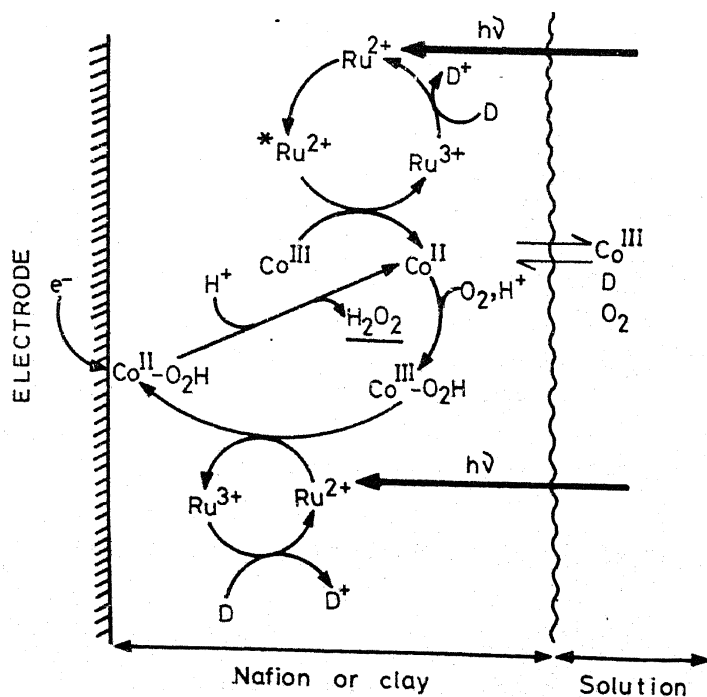


Figure 12. Photoelectrocatalytic reduction of dioxygen at Pt/Nf/ Ru^{2+} or Pt/clay/ Ru^{2+} electrode. Co^{III} : macrocyclic cobalt (III) complexes. Ru^{2+} : $[Ru(bpy)_3]^{2+}$ and D: H_2O or ethylenediaminetetraacetic acid.

100% according to the charge passed through the modified electrodes when Co(III) complex was used as electrocatalyst for O_2 reduction. When the Pt/Nf/ Ru^{2+} or Pt/clay/ Ru^{2+} electrode was irradiated with visible light the H_2O_2 yield was increased to nearly 200% of the charge passed through the modified electrode (Gobi and Ramaraj 1992). Such an increase in H_2O_2 yield was not observed in the dark. This observation showed that the photoinduced electron transfer reaction occurred between the adsorbed $[Ru(bpy)_3]^{2+}$ and Co(III) complex (3) (figure 12). The photoproduct $[Ru(bpy)_3]^{3+}$ was reduced by electron donor such as triethanolamine (TEA) or H_2O (Memming and Schroppel 1979). The photoproduct macrocyclic Co(II) complex reacted with O_2 to form $Co^{III} - O_2H$ at pH 1 (Geiger and Anson 1981; Gobi and Ramaraj 1992; Niederhoffer *et al* 1984). The further electroreduction or photoelectroreduction of $Co^{III} - O_2H$ complex yielded H_2O_2 . The excited state electron transfer quenching rate constants for Pt/Nf/ Ru^{2+} /Co(III) and Pt/clay/ Ru^{2+} /Co(III) were determined using photoelectrochemical method and it was in the order of $10^{10} M^{-1} s^{-1}$ (Gobi and Ramaraj 1994).

6. Conclusion

We have demonstrated that the immobilization of $[Ru(bpy)_3]^{2+}$ and Fe^{3+} ion or Co(III) complex in solution (solid-solution interface) brings about efficient photoinduced electron transfer processes in Nafion and clay matrices which can be used for photoelectrochemical cells or multielectron transfer photocatalytic processes. The excited state electron transfer quenching rate constants were determined for the immobilized photoredox systems using the photoresponse observed at the chemically modified electrodes. The observed photoelectrochemical behaviours at Nafion and clay modified electrodes show the important role played by the macroheterogeneous organized assembly systems in the electrode reactions. The photoelectrochemical systems summarised in this paper demonstrate the importance of the immobilization of photoredox molecules in a membrane system. This would help in understanding the one-electron process occurring at the membrane-bound reaction centre in photosynthesis.

Acknowledgement

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