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Optical Energy Storage by Bilayer Electrodes, Polymerized Coordination Compounds of Ruthenium or Iron

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Electrochemistry of bilayer electrodes has until now been investigated mainly in the dark. For the further development of the photoelectrochemistry of bilayer electrodes and its application to optical-energy storage, a polymer of *N*-[4-[2-(trimethoxysilyl)ethyl]benzyl]-*N*′-methyl-4,4′-bipyridinium dibromide ($BVSiBr_2$), a photoredox siloxane polymer, was employed as a photosensitive outer-layer, and bis(2,2′-bipyridine)bis(4-vinylpyridine)ruthenium(II) bis(hexafluorophosphate), $[Ru(bpy)_2(vpy)_2](PF_6)_2$, or tris(4-methyl-4′-viny-2,2′-bipyridine)iron(II) bis(hexafluorophosphate), $[Fe(vbpy)_3](PF_6)_2$ was electrochemically polymerized as the inner layer on the surface of an SnO_2 electrode. Direct and indirect photochemical reductions(trapping) of the outer layer siloxan polymer were attempted in the following ways: 1) the outer-layer, poly($BVSiBr_2$), was chemically trapped with a methylviologen radical, $MV^{+\cdot}$, produced photochemically in an illumination cell and transferred to the electrochemical cell, 2) the outer-layer was photochemically trapped by UV irradiation in the presence of photosensitive alcohols (*i*-PrOH and EtOH) and 3) by photochemical trapping with tris(2,2′-bipyridine)-ruthenium and triethanolamine. The lst and the 2nd methods yielded results expressed by cyclic voltammograms showing an accumulation of poly(BVSi$^{+\cdot}$), that is, a storage of optical energy in the outer-layer. The result of the 3rd method was negative.

One of the authors (Murray) has presented a theory and an experimental demonstration of a "two-layer electrode" which comprises two electroactive layers on a conducting electrode.[1—3] These are physically discrete and are formed of electroactive materials (usually not a semiconductor) with different redox potentials. The essence of a two-layer or "bilayer" scheme is that an electron transfer between the conductor electrode and the outer electroactive layer is forced catalytically by an electron-transfer mediation through redox states of the inner electroactive layer.

When photoreductive or photooxidative materials are used as the outer-layer components, photochemically excited energy is stored within a specific range of the electrode potential, depending upon the redox potentials of the inner-layer compounds. The reduced or oxidized excited state of the outer layer has been named the "trapped state," and this phenomenon has potential use for solar energy storage cells. This paper presents a few examples of this type of electrode.

Experimental

Chemicals and Equipments. The organosilane monomer *N*-[4-[2-(trimethoxysilyl)ethyl]benzyl]-*N*′-methyl-4,4′-bipyridinium dibromide ($BVSiBr_2$) (**1**) was prepared as described in the literature.[2] Onto a deck-glass, SnO_2 films, or inner films, a drop of a methanolic solution of $BVSiBr_2$ (*ca.* 8×10^{-3} mg in a 9 μL solution) was spread. A rapid methanol evaporation is recommended for producing a uniform film. For condensation polymerization, a hydrogen chloride vapor and warm moisted air were blown successibly on the monomer films, then stored in a vacuum oven for more than two hours. *N,N*′-dimethyl-4,4′-bipyridinium dichloride, methylviologen, ($MVCl_2$) hydrate, benzophenone and Et_4NClO_4 (TEAP) were reagent grade. The potentiostat and electrochemical cells were of conventional design and the SnO_2 electrodes were highly doped films on glass, as previously used.[2] Electrochemical potentials are with reference to a NaCl-saturated calomel electrode (SSCE). Before taking cyclic voltammograms, the electrolytic solution was flushed with N_2. An Hg lamp (Baush and Lomb 33-86-25-01) and a monochromator system were used for irradiations at 313 or 366 nm.

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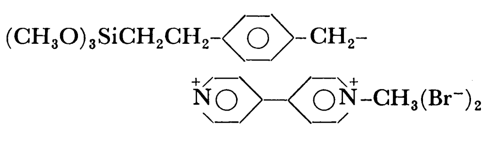

Electrochemical Polymerization of the Inner Films. The monomer complexes $[Ru(bpy)_2(vpy)_2]$ $(PF_6)_2$ (vpy=4-vinylpyridine) and $[Fe(vbpy)_3](PF_6)_2$(vbpy=4-methyl-4′-vinyl-2,2′-bipyridine) were prepared by a method from the literature by Mr. C. R. Leidner.[1] The electrochemical polymerization processes were carried out in a 2-mM** concentration of each complex in 0.1 M Et_4NClO_4/CH_3CN. The potentials applied to the electrode, SnO_2, in these solutions were cyclically swept between −0.8 and −1.8 volt *vs.* SSCE for about 20 min.[2] The coverages, Γ, of the insoluble polymers was determined electrochemically.

Results and Discussion

Photochemistry of BVSi^{2+} Monomer. For a preliminary check of the photochemistry of a BVSi^{2+} monomer solution, the following types of reductive solvents were used. The ratio of components CH_3OH, C_2H_5OH, *i*-C_3H_7OH, and CH_3CN in a mixed solvent A was 1:1:1:1 in volume, for solvent B 0.1:0:1:3; and for solvent C 0:1:0:4. Primes are used to designate solvents (A′ and B′) of which 4 mL were added to 5 mg of benzophenone. To purge the dissolved oxygen, nitrogen gas was bubbled into the solutions A, A′,

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** $1\ M=1\ mol\ dm^{-3}$.

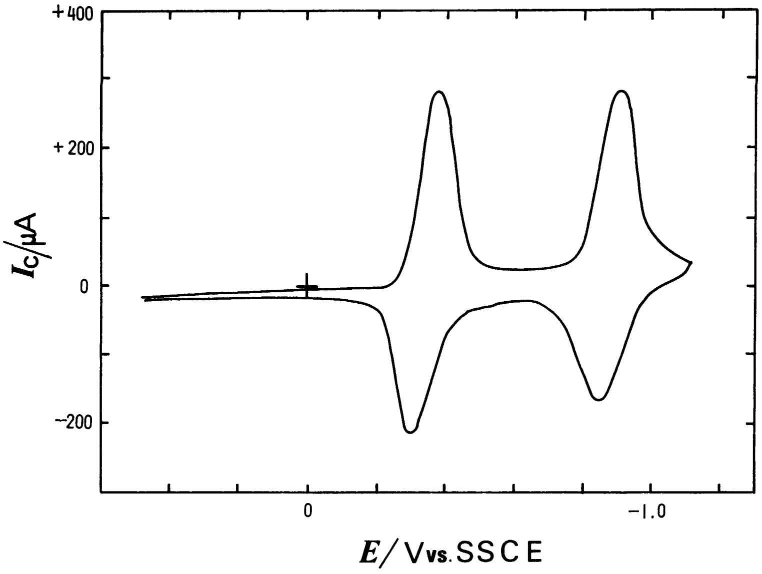

Fig. 1. Cyclic voltammetry of SnO_2/poly($BVSiBr_2$) layer electrode at 0.1 V/s in 0.1 M Et_4NClO_4/CH_3CN.

B and B′ of 2×10^{-4} M $BVSiBr_2$ for 20 min. The solutions were then irradiated at 313 and 366 nm. In solutions A and A′, a violet color emerged and increased in intensity for 50—60 min. It then slowly faded and after 3—4 h the solution became light yellow. In solutions B and B′ of $BVSiBr_2$ of the same concentration, the irradiation instantly made them intense violet; however the color tended to fade sooner than in the previous cases (solvents A and A′) with irradiation. To produce a more complete deoxygenation, a freeze-pump-thaw (FPT) method (4 or 5 cycles) was applied to solutions B′ and C. The $BVSiBr_2$ (2×10^{-4} M) in solution B′ exhibited a violet color even in the room light during the process of FPT. Then, the color faded away after one hour. Thereafter, no color appeared even upon irradiation with an intense light source.

$BVSi^{2+}$ (8×10^{-3} M) in solvent B′ exhibited intense violet upon Hg-lamp irradiation. By shaking the sealed Pyrex tube, the violet color quickly faded. This procedure was repeated more than ten times. The time needed for one cycle became longer and longer; finally, the blue-violet color faded away without further recovery. Upon Hg-lamp irradiation, 8×10^{-3} M $BVSi^{2+}$ in solvent C exhibited a blue color which was much weaker in intensity than in the previous case. Shaking the tube did not cause a weakening of the color and continuous irradiation caused the color to intensify to a certain degree. Fading was very slow and a recovery of the color was possible with UV irradiation.

Such nonpermanent colorations of a $BVSiBr_2$ monomer in several solvents indicate:

1) a photochemical generation of the $BVSi^{\dagger}$ radical;

2) a more or less slow reoxidation of $BVSi^{\dagger}$ to $BVSi^{2+}$ by some oxidants which probably exsist as impurities, even in the purified solutions by freeze-pump-thaw (FPT) method; and that

3) the mechanisms of the coloration are different, depending upon the solvent and/or the photoactive reductants.

Poly($BVSiBr_2$) Film on SnO_2 or Glass. The coverage of the polymer on the substrate can be first calculated from the concentration and the spread volume of the stock solution. This is shown to be 7—8×10^{-9} mol/cm^2 upon assuming uniform films. Secondly the electrochemically determined coverage was calculated from the cathodic peaks on the cyclic voltammogram ($BVSi^{2+/1+/0}$) in CH_3CN (0.1 M TEAP), and the values obtained are 2.36, 3.9, 2.16, and 2.93×10^{-9} mol/cm^2 (average value $2.8\pm0.7\times10^{-9}$ mol/cm^2), as shown in Fig. 1. The difference in the coverages estimated by the above two methods (2.8/8=0.35) can be attributed to a nonuniformity of the film thickness and/or a partial polymerization which might have resulted in the dissolution of a monomer or oligomer of $BVSiBr_2$. The nonuniformity resulted in an underestimation of the coverage in the electrochemical determination.

Preliminary qualitative tests regarding solvents for the photochemical reduction of a poly ($BVSiBr_2$) film on a substrate were as follows. Solvent A dissolves films slowly under UV irradiation, and both the solution and the films became violet. This lasted for a while. In solvent B′, the irradiation caused changes in the colors of the films on both glass and SnO_2 to black or violet. These lasted for more than one month in vessels isolated from oxygen. The stability of the color of a polymer film which differs from the case of the monomer can be attributed to the insensitivity of polymeric solids towards oxidants in comparison with that of a monomer.

TABLE 1. COMPARISON OF AMOUNTS OF THE OUTER-LAYER POLY ($BVSi^{2+}$) AND THE EFFECTIVE AMOUNTS OF ($BVSi^{\dot{+}}$) COMPONENTS ON THE INNER-LAYER $[Ru(bpy)_2(vpy)_2](PF_6)_2$ OR $[Fe(vbpy)_3](PF_6)_2$ IN THREE WAYS

Inner layer	$[Ru(bpy)_2(vpy)_2](PF_6)_2$ 5×10^{-8} mol cm^{-2}	$[Fe(vbpy)_3](PF_6)_2$ 8×10^{-9} mol cm^{-2}
$BVSi^{2+}$/mol cm^{-2} estimated		
From volume of soln.[a]	5×10^{-7}	1.5×10^{-8}
From untrap-curve after Electrochem-trapping[b]	6.2×10^{-8}	1.2×10^{-8}
From untrap-curve after Being trapped by $MV^{+\cdot}$[b]	7.6×10^{-8}	1.0×10^{-8}

Scan rate: 20 mV/s. a) $BVSi^{2+}$ stock solution: 23 mg of the dibromide in 25 ml of ethanol. b) Effective value of poly($BVSi^{\dot{+}}$) calculated by Eq. 1.

Chemical Trapping with Photochemically Produced $MV^{\dot{+}}$ Representative examples of a bilayer electrode for chemical trapping are as follows: 5×10^{-7} mol of $BVSi^{2+}/5\times10^{-8}$ mol of poly($[Ru(bpy)_2(vpy)_2](PF_6)_2$)/$SnO_2$ and 1.5×10^{-8} mol of $BVSi^{2+}/8\times10^{-9}$ mol of poly($[Fe(vbpy)_3](PF_6)_2$)/SnO_2. The amounts of $BVSi^{2+}$ were estimated from the spread volumes and the concentrations of the stock solutions, whereas those of inner complex films were evaluated from cyclic voltammograms. As shown in Table 1, the iron-polymer film was adjusted to be thinner than the ruthenium-polymer film, since the structure of poly($[Fe(vbpy)_3](PF_6)_2$) is tighter and stabler than that of poly($[Ru(bpy)_2(vpy)_2](PF_6)_2$). When the inner film is not tight enough to separate the outer film from the electrode, a leak causes cathodic current peaks of the $BVSi^{2+}$ at the usual potentials of $BVSi^{2+/1+}$and $BVS^{1+/0}$, that is, at −0.34 and −0.865 V *vs.* SSCE, respectively. For this reason, Ru-complex films were made to be about ten times as thick as Fe-complex films (in moles). In order to obtain precise amounts of trapped poly ($BVSi^{+\cdot}$) in the process of untrapping, the outer films, poly ($BVSi^{2+}$), were made to be more than twice that of the inner films (in moles).

Poly($BVSi^{2+}$) in outer films was reduced using photochemically reduced methylviologen ($MV^{\dot{+}}$) as follows; 4×10^{-3} M of a $MVCl_2$ hydrate stock solution in a mixed solvent (1 mL, C_2H_5OH+9 mL, CH_3CN) was irradiated with an Hg lamp in a glass vial under nitrogen bubbling and an addition of 10 mg of benzophenone. One mL of the intense-blue solution produced photochemically within 5 min was transfered through Teflon tubing using the pressure of the nitrogen gas to the electrochemical cell where the bilayers on SnO_2 were set in 10 mL CH_3CN(TEAP). After holding it in the ($MV^{2+}/MV^{\dot{+}}$) solution at an open circuit for 10 to 15 min, cyclic voltammograms of the Ru-complex bilayers were recorded between +0.5 and +2.0 V, and between +0.5 and +1.8 V for the Fe-complex bilayer.

As shown in Figs. 2A and 2B, the first anodic peaks are much larger than the cathodic peaks and the successive anodic peaks in the second and the third cycles. These differences are mainly attributed to the theoretically expected untrapping currents of the poly ($BVSi^{\dot{+}}$). In these potential ranges, the oxidation of poly ($BVSi^{\dot{+}}$, $BVSi^0$) in the outer films and Ru^{2+} in the inner films takes place, but poly ($BVSi^{2+}$) is not reduced (owing to the rule of the bilayer). The integrated values of anodic and cathodic currents during the 2nd and 3rd cycles are expected to be equal if the untrapping of poly ($BVSi^{\dot{+}}$) is completed during the first anodic scan. However, it is apparent from Fig. 2A that even in the 2nd and 3rd cycles the equalities do not hold. As the voltammogram was taken in a solution which still contained $MV^{\dot{+}}$, the untrapped $BVSi^{2+}$-unit would be trapped to form $BVSi^{\dot{+}}$-unit again in the whole period of time. This causes the above-mentioned inequality between the integrated cathodic and anodic currents. This tendency is emphasized when the inner film is resistive for the transport of the charge which originates from the outer film, as is shown in the case of a Ru-complex inner film.

In order to avoid this ambiguity, based on a continuing trapping by $MV^{\dot{+}}$ in the calculation of the untrapping charge ($BVSi^{\dot{+}}\rightarrow BVSi^{2+}$), the trapped bilayer electrodes were quickly washed with aceton and were untrapped in a methylviologen-free acetonitrile (TEAP) solution. For the bilayer with a Ru-complex, the results were calculated using

$$\int I_a \mathrm{d}t - \int I_c \mathrm{d}t = \int I_a(BVSi^{\dot{+}})\mathrm{d}t. \qquad (1)$$

These are shown in the 3rd row of Table 1. The expected equality on the 2nd and 3rd reverse processes was satisfactorily effected.

By scanning from −1.5 to +2.0 V *vs.* SSCE at 20 mVs^{-1} in CH_3CN (TEAP), the outer layer can be trapped (reduced) and untrapped electrochemically; by this method, an effective amount of the electrochemically reducible $BVSi^{2+}$ through the inner film (Ru-complex) under the experimental conditions was estimated and is shown in the 2nd row of the table. The values in the 2nd and 3rd rows are nearly equal, whereas that in the lst row (estimated from the volume of the solution) is very much different. This can presumably be attributed to an incomplete untrapping process due to the thickness of the inner film, which

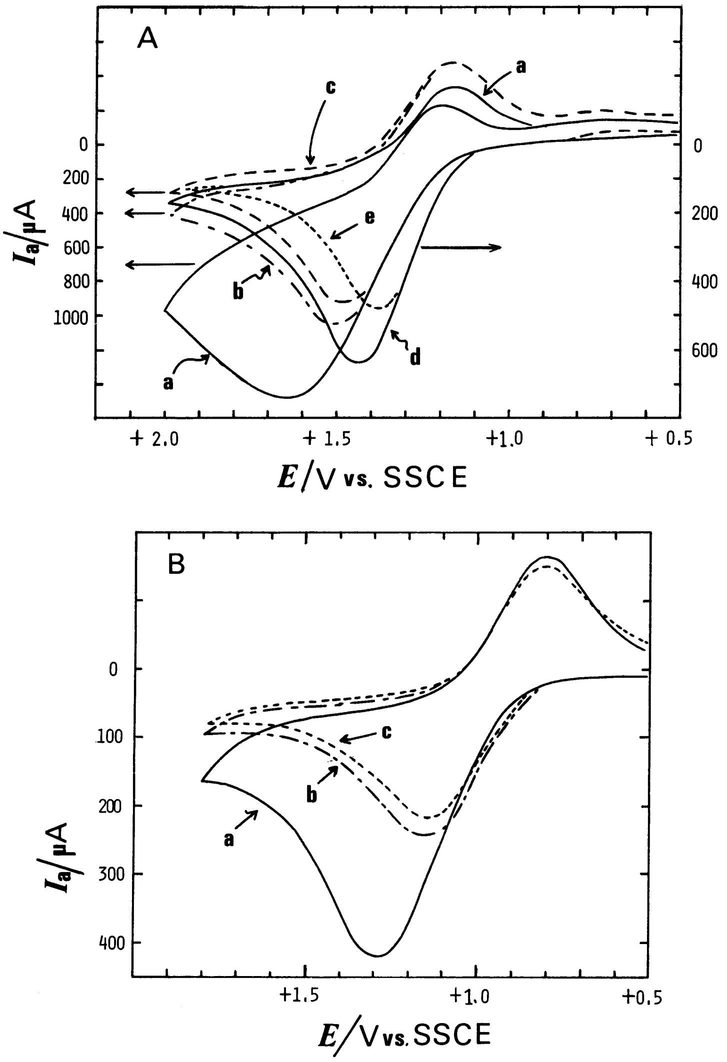

Fig. 2. Untrapping of outer-layer poly(BVSi$^{+\cdot}$) trapped by $\mathrm{MV}^{+\cdot}$ in CH_3CN (0.1 M Et_4NClO_4). A) $[Ru(bpy)_2(vpy)_2](PF_6)_2$ inner layer, curve a: 1st scan at 100 mV/s after an exposure for 15 min to $\mathrm{MV}^{+\cdot}$, b: 2nd scan at 100 mV/s immediately after the 1st scan, c: 4th scan at 100 mV/s immediately after the 3rd scan, d: 1st scan at 20 mV/s after an exposure for 13 min to $\mathrm{MV}^{+\cdot}$, e: 2nd scan at 20 mV/s immediately after the 1st scan. B) $[Fe(vbpy)_3](PF_6)_2$ inner layer. curve a: 1st scan at 100 mV/s an exposure for 14 min to $\mathrm{MV}^{+\cdot}$, b: 2nd scan at 100 mV/s immediately after the 1st scan, c: 3rd scan at 100 mV/s immediately after the 2nd scan.

causes the large electrical resistance. It also corresponds to the fact that the untrapped-charge value calculated with Eq. 1 for a fast scan rate (100 mVs^{-1}), is smaller than that for the above case (20 mVs^{-1}).

Contrary, in the case of an iron-complex inner film, the three values in the table were in fair agreement each other. This is probably because of a complete untrapping of outer film species due to the smooth transport of the charge through the inner/outer-film interface and the bulk of the inner film. Also the smoothness is consistent with the independence of the untrapped charge value using Eq. 1 for the scan rates. However, there is still a small discrepancy between the values in the 1st and those in the 3rd row. This is attributable to the nonuniformity of the thickness of the outer film, which might result in an incomplete untrapping in the thicker parts.

In all these speculations uncertainties regarding an evaluation of the electrode area and graphical integrations of cyclic voltammograms were inevitable. Upon considering this, any detailed discussion concerning these minor discrepancies are unnecessary.

Attempts of Photochemical Trapping of $[Ru(bpy)_2(vpy)_2](PF_6)_2$/Poly($BVSiBr_2$) by Direct Irradiation in The Presence of Alcohols or $[Ru(bpy)_3]$. In an electrolytic cell with a quartz window the bilayer elec-

TABLE 2. UNTRAPPING OF PHOTOCHEMICALLY TRAPPED POLY(BVSi‡)/[Ru(bpy)$_2$(vpy)$_2$](PF$_6$)$_2$ BY ALCOHOLS UNDER UV IRRADIATION (366 nm)

Reductant added to 25 mL CH$_3$CN(TEAP)			amount/10^{-9} mol of oxidation between +0.5 and +1.8 V				$\gamma=\frac{Q_a^{(1)}-Q_a^{(2\text{ or }3)}}{Q_a^{(2\text{ or }3)}}$ %	
			Q_a		Q_c			
			trial A	trial B	trial A	trial B	trial A	trial B
1%	EtOH	1st[b]	11.5	11.6	9.3	10.0	25	33
		2nd	9.2	8.7	9.0	9.0		
[1%	EtOH]	1st	14.7	13.5	12.8	12.6	40	39
4%	*i*-PrOH]	3rd	10.5	9.7				
[1%	EtOH]	1st	8.4		6.08		29	
4%	*i*-PrOH	3rd	6.5		6.45			
	Bz$_2$C=O[a]]							
[1%	EtOH][c]	1st	7.1		5.0			
4%	*i*-PrOH						20	
	Bz$_2$C=O[a]]	3rd	5.9		5.0			

a) Benzophenone. b) Sequence of cycling between +0.5 and +1.8 V *vs.* SSCE. c) In dark.

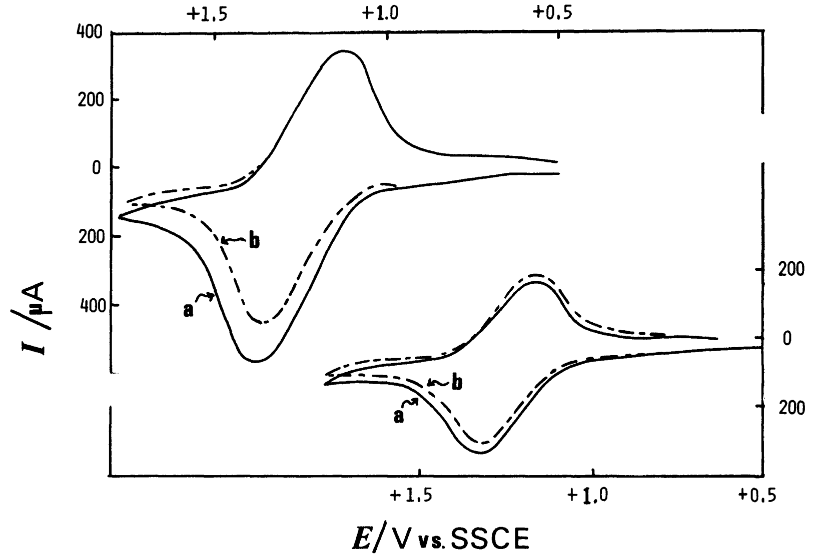

Fig. 3. Untrapping of poly(BVSiBr$_2$)/[Ru(bpy)$_2$(vpy)$_2$](PF$_6$)$_2$/SnO$_2$ after UV irradiation in 1% EtOH, 4% *i*-PrOH, and 95%CH$_3$ CN. Left: curve a: 1st scan after irradiation at 366 nm through quartz window for 25 min, b: 3rd scan immediately after twice successive scans; Right: curve a: 1st scan after 25 min N$_2$ flush in dark, b: 3rd scan.

trode was dipped in a 1% ethanol solution in CH$_3$CN (TEAP). The solution was then irradiated with 366 nm light from a xenon lamp with an UV cut filter (<350 nm) for 15 to 25 min. A cyclic voltammogram between +0.5 and +1.5 V *vs.* a AgCl/Ag electrode on the bilayer electrode suggested a gradual photodecomposition of the layers. Thus, the trapping and untrapping can be evaluated by

$$\gamma = (Q_a^{(1)} - Q_a^{(3)})/Q_a^{(3)}, \tag{2}$$

where graphically integrated electrical charge values, $Q_a^{(1)}$ and $Q_a^{(3)}$, stand for electrochemically oxidized amounts of poly (BVSi‡) in the 1st cycle and the 3rd cycle, respectively. $Q_c^{(i)}$ (the *i*-th cathodically reduced amount) and $Q_a^{(i)}$ in several trials involving different solvents where 2-propanol (4%) and benzophenone (45 mg in 20 mL of solution) were successively added, are tabulated in Table 2 as well as γ values for each. As can be seen from the Table 2 and Fig. 3, ethanol and 2-propanol are effective in photochemical reductions; but, a further addition of benzophenone caused a simultaneous reduction of Q_a, Q_c, and γ. Irradiation with 366 nm light in the presence of benzophenone caused the photoactive substances in the bilayers to be decomposed, resulting in the disappearance of the cathodic and the anodic peaks.

Expecting a trapping of poly(BVSi^{2+}) in the outer film, the Ru-complex bilayer was immersed in a CH$_3$CN (TEAP) solution which contained a sensitizer 8×10^{-6} M [Ru(bpy)$_3$]$^{2+}$, and a sacrificial reductant, 4×10^{-5} M triethanolamine. It was then irradiated at 450 nm (200 Watt xenon lamp, monochromatized, with UV cut filter). No remarkable effect was observed except a gradual decrease in the redox currents in the cyclic voltammogram.

Conclusion

Three types of photoenergy conversion to chemical energy and its storage have been attempted using bilayer electrodes which were composed of a poly ($BVSi^{2+}$) outer layer and an Fe- or Ru-complex inner layer:

1. The outer layers were trapped by $MV^{\overset{+}{\cdot}}$ (reductant) derived photochemically from MV^{2+},
2. The outer layers were photochemically trapped in the presence of ethanol and 2-propanol, and
3. Photochemically excited $[Ru(bpy)_3]^{2+}$ with a sacrificial reductant, *i.e.*, triethanolamine, was not reductive to the outer layer.

The results show that the stable radical, $MV^{\overset{+}{\cdot}}$, and the alcohols which are permeable through the poly($BVSi^{2+}$) film, are effective for the outer film. However, the excited species of $[Ru(bpy)_3]^{2+}$, with a lifetime of about 10^{-6} s, is not effective in such a heterogeneous redox reaction.

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