Photo-induced Electricity Generated by Thin-layer Photogalvanic Cells Containing Thionine and Iron(II) Salt

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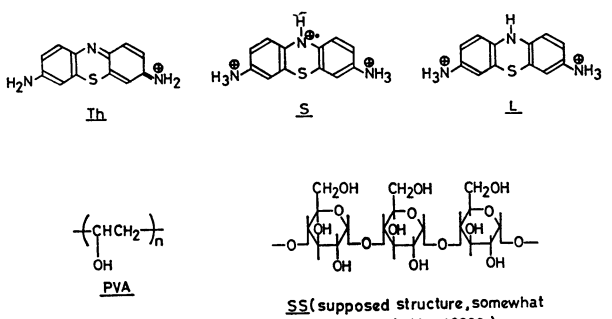
The photogalvanic effects of thionine and Fe(II) salt systems were studied by use of thin-layer photocells. Three systems of the cell components, *i.e.*, SnO_2/thionine–Fe(II) aq/Pt, SnO_2/thionine–Fe(II)-gelatinized reagent/Pt, and SnO_2/polymeric thionine membrane–Fe(II)/Pt, were compared. The photopotential ΔE and the photocurrent I were the largest in the third system. It was concluded that the excellent ability of the polymeric thionine system to generate the photo-induced electricity is due to the strong electrostatic repulsion between Fe^{3+} and the semi-species bound to the cationic polymers, since the repulsion diminished the short-circuit in a solution or the bulk-backward reaction with Fe^{3+}. The electron-recycling in a solution took place not only through the transportation of Fe^{3+} to the cathode, but also through the electron-exchange reaction between Fe^{2+} and Fe^{3+} *via* hydrogen bonds.

The mechanism of the photogalvanic effect in the photoredox reaction between thionine (thn) and Fe(II) has been studied by many investigators, especially in liquid-phase.[1-6] Few reports, however, describe photogalvanic cells composed of gel or membrane systems, although they are important from the viewpoint of application. We have prepared several types of photocell: (1) a double-Pt photocell containing thn–Fe(II) aq, (2) an SnO_2–Pt photocell of the same size as (1), and (3) a thin-layer type photocell containing thn–Fe(II) aq, thn–Fe(II)-gel (with a semi-permeable membrane), or polymeric thn–Fe(II). The following three points were examined:

(a) the electron-recycling mechanism in solution,
(b) the role of the SnO_2-electrode, and
(c) the factors which influence the photopotential ΔE and the photocurrent I.

Experimental

Reagents. Thionine (Tokyo Kasei Co., Ltd., reagent grade, Cl salt) was recrystallized from 50% aqueous ethanol solution before use. Its purity was confirmed by thin-layer chromatography after being eluted with a mixture of 2-propanol (5%) and chloroform. Analytical grade commercial reagents of acids, bases, and iron(II) sulfate containing 0.005% iron(III) were used without further purification. Soluble starch (Wakō Pure Chemical Co., Ltd., reagent grade for medical use) and poly(vinyl alcohol) (degree of polymerization=about 500) of commercial grade were purified by precipitating their hot aqueous solutions from excess methanol. Hydroquinone used as the reductant in the photoredox reaction was recrystallized twice. The formulas of the dyes and the polymers are given below. Thionine and its reduced species (Sthn=semi-thn, Lthn=leuco-thn) at pH 1—4[7,8] are as follows.



Preparation of Polymers. The ternary copolymer composed of hydroquinone, formaldehyde and piperazine residues was prepared by the Mannich-polyaddition-condensation-polymerization.[9] The thn-polymers were prepared by the reaction of poly(epichlorohydrin) (degree of polymerization=170, commercial reagent) with thn under the presence of triethylamine (HCl-remover). First, the prescribed amounts of the polymer and trimethylamine were reacted in an autoclave at 120 °C. The solvent, 50% aqueous *N,N*-dimethylformamide (DMF), was removed from the resulting solution. Solids were then dissolved in absolute methanol and reprecipitated with diethyl ether to yield copoly(epichlorohydrin-glycidyltrimethylammonium chloride) (QE). Next, QE and thn were reacted in absolute DMF at 60 °C in the dark. The solvent of the resulting solution was evaporated, and the product was washed with water until the filtrate showed no color of thn. The thn-polymers (BQEthns) thus obtained was to some extent cross-linked by thn nuclei, which are slightly soluble in methanol. When the reaction of QE and thn is carried out in the molar ratio, [thn]/[-CH_2Cl of QE] $\gg$10, the resulting BQEthn is entirely soluble in water, since the cross-linking by thn nuclei can be avoided.[10] The experimental conditions and results are summarized in Table 1. The structures of the polymers are given below.

Apparatus. The over-all photobleaching rate constant k and the degree of photobleaching Δ% (=([Sthn]+[Lthn]) $\times 100/[thn]_0$) were measured with a stopped-flow rapid-scanning spectrophotometer (Union Giken Co., Ltd., RA-1300) modified into a cross-illumination system,[11] with a 100 W

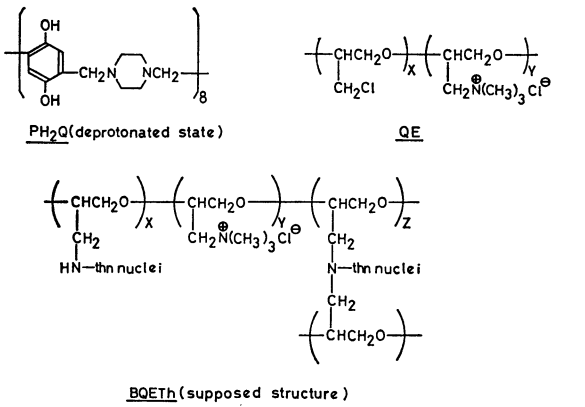


TABLE 1. PREPARATION AND CHARACTERISTICS OF POLYMERS

Polymer	Starting material g (mol)	Solvent (ml)	Time (h)	Products Y (%)	C% / N%	Cl (%)	Note
PH_2Q	H_2Q 11.0 (0.1) CH_2O 6.0 (0.2), Pip-2HCl 14.5 (0.1)	50% aqueous methanol (100)	12	98	5.143	24.2	2HCl salt
QE(1)	PEP 9.3 (0.1) TMA 30 (0.5)	50% aqueous DMF (60)	48	95	14.816	33.68	x=21%
QE(2)	PEP 9.3 (0.1) TMA 30 (0.5)	50% aqueous DMF (60)	60	95	12.462	32.77	x=26%
BQETh(1)	QE(1) 0.5 Th 5.0 (abt. 0.02)	absolute DMF (50)	48	94	4.763	18.91	x=19%, y=79%, z=2%
BQETh(2)	QE(2) 0.5 Th 7.5 (abt. 0.03)	absolute DMF (50)	48	97	4.703	18.10	x=23%, y=74%, z=3%

Pip-2HCl; piperazine·2HCl, TMA; trimethylamine. z% was estimated from the correlation of C%/N% with Cl%.

tungsten illumination light source and a 50 W measureing light source. The intensity of the latter was weakened to 0.03% of the former by use of neutral filters. It was confirmed that the illumination with the latter has little influence on the photoredox reaction. The photopotential ΔE and the photocurrent I of the thn-reductant systems were measured with the photocells illustrated in Figs. 1 (a)—(f), in which the SnO_2 electrode prepared by the usual chemical-vapor-depositing method (about 100 Ω/cm, transparent Nesa glass) was used, with a vibrating reed electrometer (Takeda Riken Co., Ltd., Model TR-84 BS).

Measurements. The prescribed amounts of thn and reductant solutions were bubbled with pure N_2 for 1 h before use, which was completely deoxygenated with use of the alkaline pyrogallol aq, sodium dithionite aq. and chromium-(II) perchlorate aq-zinc amalgam towers. The two reactant solutions were then taken into the syringes of the cross-illumination apparatus separately under N_2 and were rapidly mixed into a 2 mm-flow cell (dead time=450 μs). The rapid spectral changes with time due to the photobleaching of thn were measured. k was determined from the initial section of time-decay curve according to the pseudo-first order plots, and Δ from the final absorption intensity at a certain photo-equilibrium state. The values of ΔE and I were obtained by use of the photocells under pure N_2 atmosphere in a dry-box, their stationary values being recorded. Unless otherwise stated, the illumination light intensity was adjusted to 10 mW/cm² (>350 nm). The specific viscosity represented by η_{sp} was measured with an Ubbelohde viscometer at 25.0±0.04 °C.

Results and Discussion

Electron-recycling Mechanism. The photocells, one composed of double-Pt electrodes (a), and another of SnO_2–Pt electrodes (b) are shown in Figs. 1(a) and (b), respectively. The two photocells have similar size and surface area of electrodes (2.0 cm²) and also the same distance, 3.5 cm between the two electrodes. In the case of (b), visible light was cast onto both or one of the cell chambers, the light intensity being 10 mW/cm² on the surface of each electrode. The thin-layer photocells composed of a thn-Fe(II) aqueous solution, a gelatinized thn-Fe(II) aqueous system and a membrane-gel system are shown in Figs. 1(c)—(f). The surface area of SnO_2 and Pt electrodes is 3.0 cm² and the distance between the electrodes 2 mm. The visible light of the same intensity as in (a) and (b) was cast through the transparent SnO_2 electrode.

The electron-recycling mechanism proposed for the photogalvanic cells composed of thn-Fe(II) is as follows.[1-6]

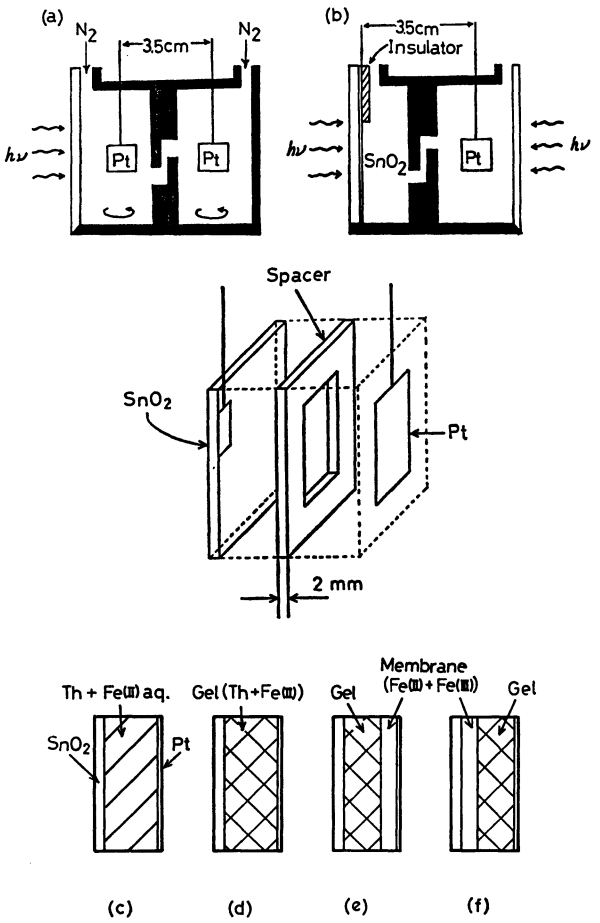
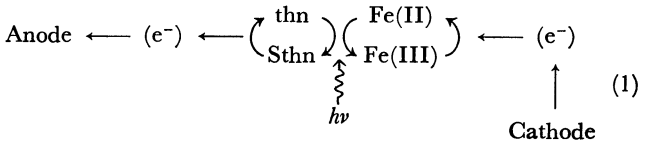


Fig. 1. Photogalvanic cells.
(a); d (distance between two electrodes) =3.5 cm, A (surface area of an electrode) =2.0 cm², (b); d=3.5 cm, A=2.0 cm², (c)—(f); d=2.0 mm adjusted by a spacer, A=3.0 cm². Visible light (>350 nm, 10 mW/cm²) was used, if no captions are given. Visible light can be illuminated onto both the cell-chambers of the photocell (b).



(1)

Only a few investigations have been carried out on the electron-recycling mechanism inside the cell despite its importance. It is doubtful that Fe(III) formed in an illuminated chamber is transported to the cathode *via* infinite pathway in a molecular scale due to diffusion, since the cathodic active species of Fe(III) would disappear by the possible bulk-backward reaction with Sthn or Lthn in the course of transportation. Therefore, another sufficiently fast mechanism should exist in order to cause the electron-recycling in solution.

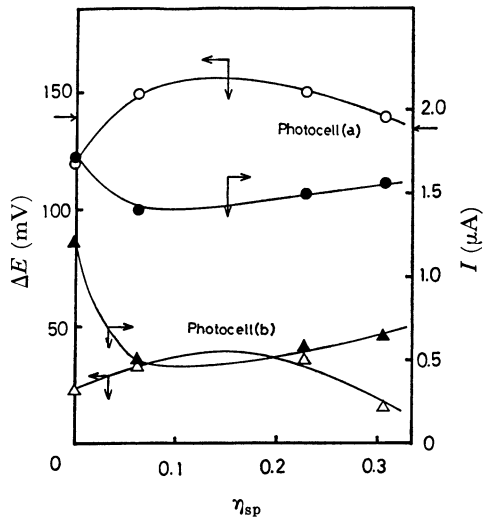


Fig. 2. Effect of added SS on ΔE and I of thn–Fe(II) systems. $[thn]_0=7.17\times10^{-5}$ mol/l, $[Fe(II)SO_4]_0=10^{-2}$ mol/l, $[Fe(III)]_0=5.0\times10^{-7}$ mol/l, pH 2.0-HCl, under N_2, without stirring.
(○,●); photocell (a), (△,▲); photocell (b). The arrows indicate ΔE and I without SS and with the most appropriate stirring of the solution, in photocell (a). η_{sp} indicates the specific viscosity of SS-added solution.

The effect of added SS (soluble starch) on ΔE and I in the thn–Fe(II) aq system is shown in Fig. 2, in which the abscissa indicate the specific viscosity of the solution (η_{sp}). Both ΔE and I measured without stirring of the solution remain almost unchanged with the increase of specific viscosity, which should decrease the transportation of Fe(III) from the illuminated cell-chamber to the cathode. They show the almost constant values of 150 mV and 1.5 μA, respectively, under the given conditions, whereas the effect of added PVA (poly(vinyl alcohol)) (Fig. 3) shows a bell-shaped curve. With increase in PVA concentration, ΔE and I become constant. The anomalous behavior in the PVA system cannot be understood from only the consideration that the electron-recycling in solution proceeds through the Fe(III) transportation.

It is well-kown that there is a very rapid electron-exchange reaction of 10^{-9}—10^{-12} s between Fe(II) and Fe(III) *via* hydrogen bonds in an aqueous solution;[12]

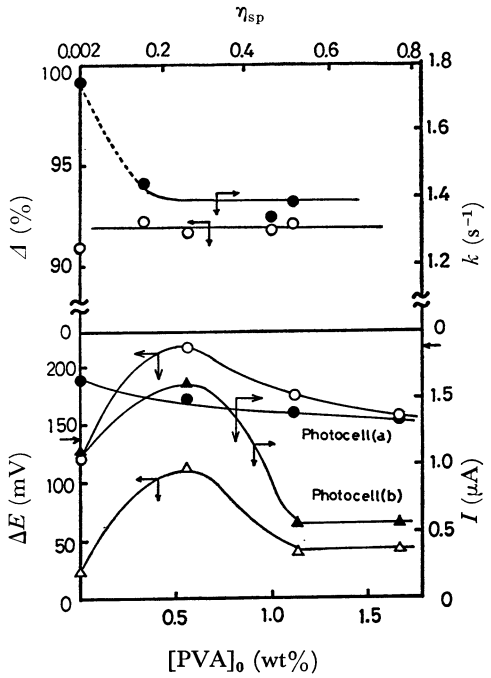
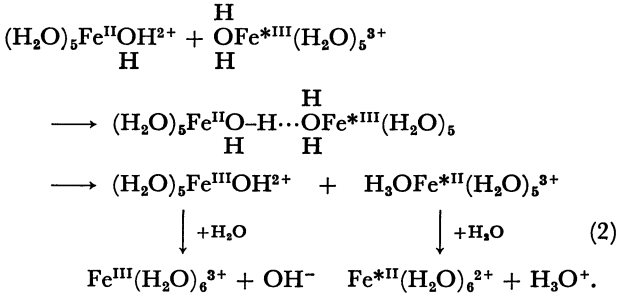
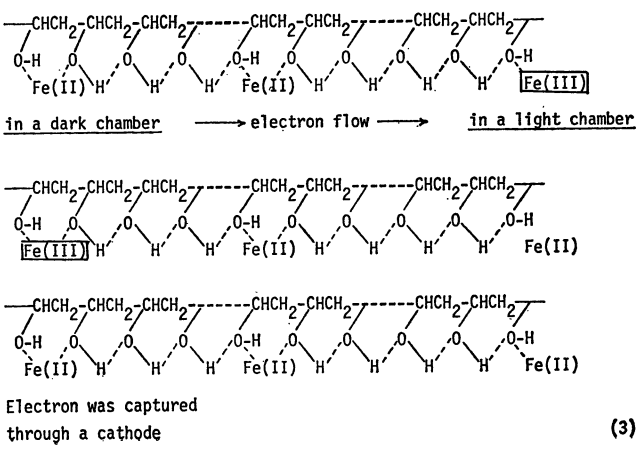


Fig. 3. Effect of added PVA on Δ, k, ΔE and I of thn–Fe(II) systems. The conditions are the same as in Fig. 2.



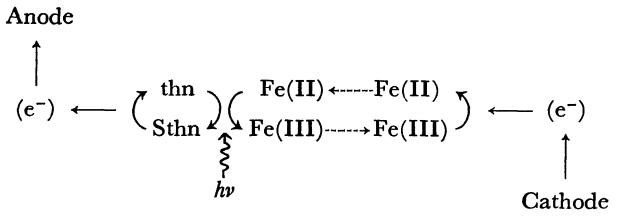
(2)

If this mechanism is valid, the reason for the increase of ΔE and I despite the fact that the values of k and Δ are constant when PVA was added in a small amount can be explained, since PVA forms the intramacromolecular hydrogen bonds which would enhance the electron-exchange reaction between Fe(II) and Fe(III) more easily:



(3)

The value of ΔE and I given in Figs. 2 and 3 were obtained without stirring the solution. Values obtained under appropriate stirring are indicated by arrows at each axis in photocell (a), without addition of SS or PVA. The very small difference between these values and those indicated by circles suggests that stirring of the solution has no remarkable influence on ΔE and I. In other words, the transportation of Fe(III) from the illuminated cell-chamber to the cathode is not the main pathway for the electron-recycling in solution. Thus, the electron-recycling mechanism of the thn-Fe(II) photoredox systems in the aqueous media was considered to be as follows.



Electron-exchange *via* hydrogen bonds and/or ion-transport (4)

The side hydroxyl groups of SS are less effective than those of PVA, probably because they cannot form the polymeric hydrogen bonds intramacromolecularily due to their rigid chain-backbone.

Characteristics of SnO_2 Electrode. The circles and triangles in Figs. 2 and 3 are the values measured with photocells (a) and (b), respectively, where both cell chambers of photocell (b) were illuminated. The values of ΔE and I obtained by use of photocell (b) without stirring are much smaller than those obtained by use of photocell (a). The direction of electron-flow is Pt(L) →Pt(D) in photocell (a), and Pt(L)→SnO_2(L) in photocell (b), where L and D indicate illuminated and dark, respectively. If we consider that SnO_2 is an n-type semiconductor, the direction of electron-flow is irregular in the latter case. SnO_2 seems to select Fe(III) as the electrode-active species, although Sthn also exists (Table 2). Three illumination methods were examined for photocell (b), *i.e.*, visible light cast onto the Pt-camber, onto the SnO_2-chamber and onto both the chambers. As for I and the direction of electron-flow, the systems of Pt(L)–Pt(D) and Pt(L)–SnO_2(D) gave almost the same result. The I values was very small for the SnO_2(L)–Pt(D) in which the direction of electron-flow SnO_2(L)→Pt(D). The I values of SnO_2–Pt(L) system with stirring was the largest, the direction being Pt(L)→SnO_2(L). From the consideration that (1) the effect of stirring is remarkable, (2) the value of I is the largest when the solution is stirred, and (3) the direction is Pt(L)→SnO_2(L) in the SnO_2(L)–Pt(L) system in contrast to the n-type characteristics of SnO_2, there might be some other electrode-reaction differing from the mechanism generally proposed for the case of Pt(L)–Pt(D) systems as given by Eq. 1 or 4.

Clark and Eckert reported that the direction of electron-flow is SnO_2(L)→Pt(L).[14] This cannot explain the results we obtained by use of a thin-layer photocell (Figs. 1(c)—(f)). The distance between the SnO_2 and Pt electrodes is 0.1 mm in Clark and Eckert's cell, but in ours 2.0 mm. The effect of UV light, which might cause distortion of the energy band of SnO_2 as illustrated in Fig. 4(a), is summarized in Table 3. The results indicate that the additional UV-illumination brought about the anodic polarization of SnO_2 to decrease the electron-flow, Pt(L)→SnO_2(L). Hence it is considered that the SnO_2 illuminated by visible light

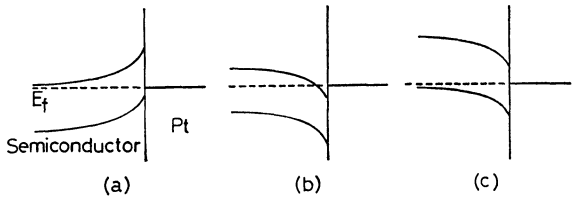


Fig. 4. Polarized state of semiconductors.
(a): Anodic polarization, (b): ohmic contact, (c): cathodic polarization.

TABLE 2. CORRELATION OF PHOTOCELLS (a) AND (b)

Photocell	Electrode	Illumd-electrode	ΔE (mV)	I (μA)	Stirring	Direction of e⁻
(a)	Pt(L)–Pt(D)	Pt(L)	120	1.6	o	Pt(L)→Pt(D)
		Pt(L)	100	1.5_2	x	Pt(L)→Pt(D)
(b)	Pt–SnO_2	Pt	190	1.5_0	x	Pt(L)→SnO_2(D)
		SnO_2	35	0.53	x	SnO_2(L)→Pt(D)
		Pt and SnO_2	80	2.7_5	o	Pt(L)→SnO_2(L)
		Pt and SnO_2	40	1.0	x	Pt(L)→SnO_2(L)

$[thn]_0=4.3\times10^{-5}$ mol/l, $[Fe(II)SO_4]_0=4.3\times10^{-3}$mol/l, $[Fe(III)]_0=2.15\times10^{-7}$ mol/l, pH 2.0-HCl aq, under N_2.

TABLE 3. EFFECT OF UV-LIGHT ON ΔE AND I IN THE PHOTOCELL (c)

Light source (mW/cm²)	ΔE (mV)	I (μA)	Direction of e⁻	Remark
Vis(0.267)	30	0.78	Pt(L)→SnO_2(L)	a)
Vis(0.267)+UV(0.01)	20	0.70	Pt(L)→SnO_2(L)	a)
UV(0.01)	1.5	0.02	Pt(L)→SnO_2(L)	a)
UV(0.01)	10	—	SnO_2(L)→Pt(L)	b)

a) $[thn]_0=1.0\times10^{-4}$ mol/l, $[Fe(II)SO_4]_0=5.0\times10^{-2}$ mol/l, $[Fe(III)]_0=2.5\times10^{-6}$ mol/l, pH 2.0-HCl aq, under N_2. b) pH 9.0-NaOH aq.

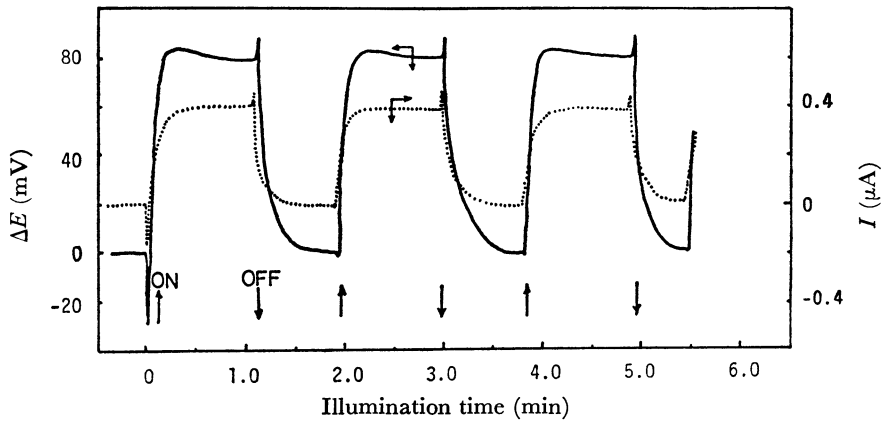


Fig. 5. On-off behavior of ΔE and I in photocell (c).
$[thn]_0=1.0\times10^{-4}$ mol/l, $[Fe(II)SO_4]_0=5.0\times10^{-2}$ mol/l, $[Fe(III)]_0=2.5\times10^{-6}$ mol/l, pH 2.0-HCl aq, under N_2. (+) values indicate the electron-flow Pt(L)→SnO_2(L).

has a distorted energy-band similar to the cathodic polarization. In order to let the electrons flow from Pt(L) to SnO_2(L), SnO_2, should have the ohmic contact or cathodic polarized state. The former is less probable, since the work-function of Pt is larger than that of SnO_2. There remains possible adsorption of some substances which bring about the cathodic polarization. Figure 5 shows the on-off behavior of ΔE and I in a thin-layer photocell. The electron-flow was SnO_2(L)→Pt(L), indicating that the discharged electrons from Sthn were captured by SnO_2 in the initial stage. The negative values in Fig. 5 represent the electron-flow of SnO_2(L)→Pt(L). The direction of electron-flow then reversed rapidly, *i.e.*, Pt(L)→SnO_2(L), ΔE and I reaching certain stationary values. By cutting off the illumination, ΔE and I increased temporarily toward (+)-side, showing the electron-flow to be Pt(L)→SnO_2(L), and then diminished rapidly. In this on-off behavior, the following should be noted:

1) the magnitude of temporary negative generation toward (−)-side of ΔE and I at on-illumination was larger than that of temporary positive generation toward (+)-side (Fig. 5) at off-illumination,

2) the temporary negative generation at on-illumination was scarecely observed after the second series of on-off recycles,

3) the temporary positive generation at off-illumination did not change with the repeated on-off recycles,

4) thn was strongly chemisorbed on the surface of SnO_2, which was almost constant at any off-illuminated state. The absorbed thn could be washed off with methanol, but not with water,

5) SnO_2 is activated only by UV-light (below 340 nm) to yield the anodic polarization, and is cathodic polarized state with the illumination of visible light, and

6) the SnO_2–Pt thin-layer photocell containing an aqueous solution of thn alone generated no dye-sensitized electricity under the illumination of visible light.

From the results, the reaction mechanism of the thn-Fe(II) system in these thin-layer photocells composed of SnO_2 and Pt is supposed to be as follows.
Firstly, a trivalent cation radical of Sthn at pH 1—4[7,8] encounters the surface of SnO_2, a real n-type semiconductor at this stage, and discharges. This may cause temporary negative generation at the on-illumination. The resulting monovalent cation of thn has smaller solubility than Sthn in water, and it will be adsorbed onto the SnO_2 electrode, which may cause the pseudo-cathodic polarization of SnO_2. However, further adsorption of thn, Sthn, and Lthn dissolved in the aqueous layer may occur on the surface of SnO_2 covered already with the dye (stuff). Thus we cannot determine which of the species thn, Sthn or Lthn covers the SnO_2

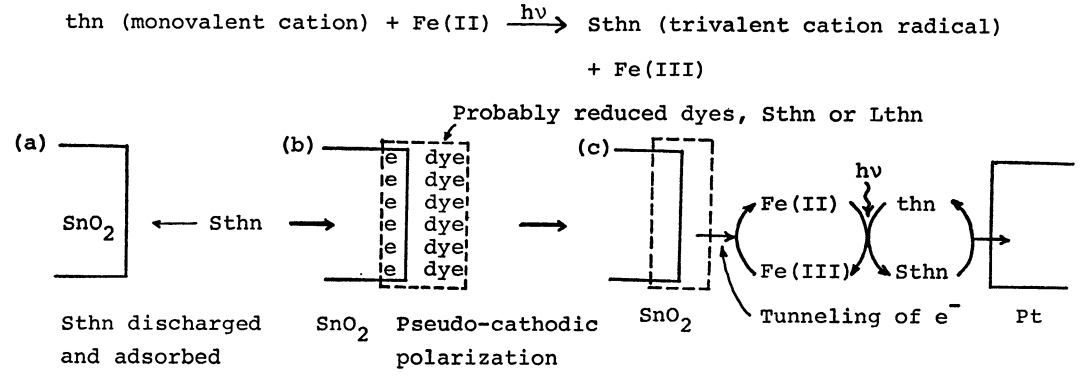


Fig. 6. Schematic representation of the role of SnO_2.

TABLE 4. CORRELATION OF THIN-LAYER PHOTOGALVANIC CELLS

Ref.	$[thn]_0$ (mol/l)	$[Fe(II)]_0$ (mol/l)	$[Fe(III)]_0$ (mol/l)	Vis-illumn (mW/cm²)	d[a] (mm)	ΔE (mV)	I (μA/cm)	Direction of e⁻
13)	10^{-3}—10^{-5}	10^{-2}	10^{-3}—10^{-5}	18.5	0.1	50—100	—	SnO_2(L)→Pt(L)
	10^{-3}—10^{-5}	10^{-2}	10^{-3}—10^{-5}	100	0.1	—	10—20	
This work	10^{-5}	5.0×10^{-2}	2.5×10^{-6}	10	2.0	80	0.07	Pt(L)→SnO_2(L)
	10^{-4}	5.0×10^{-2}	2.5×10^{-6}	10	2.0	80	0.4	

a) Distance between two electrodes.

electrode. When the solution was illuminated, the circuit closed and adsorption of dye (stuff) occurred, the species covering the SnO_2 electrode, formed by the photoredox reaction, was Sthn or Lthn rather than thn. Hence the direction of electron-flow was reversed as shown in Fig. 6(c). If this mechanism is valid, the experimental results 1)—4) and the effect of UV-light are understandable. The temporary negative generation of ΔE and I at the on-illumination in particular would be due to the initial stage of dye adsorption, which occurs only in the first on-off cycle, since the surface of SnO_2 is already covered with the dye (stuff) after the second cycle. The positive generation at off illumination was thus caused by the process of desorption of the dye (stuff) covering excessively the surface of SnO_2.

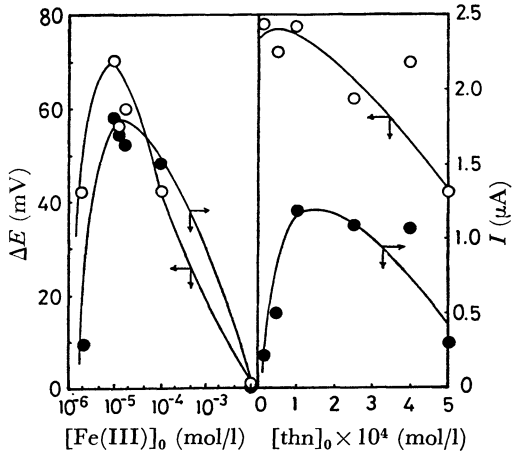


Fig. 7. Effect of $[Fe(III)]_0$ and $[thn]_0$ on ΔE and I of thn–Fe(II) systems. $[thn]_0=5.0\times10^{-4}$ mol/l in (a), $[Fe(OO)SO_4]_0=5.0\times10^{-2}$ mol/l, pH/l, pH 2.0-HCl aq, under N_2. (+) values indicate the electron-flow Pt(L)→SnO_2 (L).

Figure 7 illustrates the effect of $[Fe(III)]_0$ or $[thn]_0$ (subscript 0 indicates the initial concentration) on ΔE and I of the thn–Fe(II) aqueous systems studied by use of the thin-layer photocell (c). The dependence of ΔE and I on $[thn]_0$ is represented by a bell-shaped curve, the Δ values decreasing with $[thn]_0$. Under the conditions employed, $[thn]_0=5.0\times10^{-4}$ mol/l, $[Fe(II)]_0=5.0\times10^{-2}$ mol/l, the Δ value was almost 100%. The excess thn would decrease I due to the excessive adsorption of dye (stuff) onto SnO_2, and also decrease ΔE according to Nernst's equation:*

$$\Delta E = E_0 + 0.0592 \log\{([Sthn]/[thn][H^+])_A \times ([Fe(III)]/[Fe(II)])_C\}, \quad (5)$$

were A and C indicate the anodic and cathodic reactions, respectively. On addition of Fe(III), ΔE and I also showed the behavior represented by bell-shaped curves. At a low $[Fe(III)]_0$, the values increased due to the increased electron-exchange reaction and/or contribution of the $(\ )_C$ term in Eq. 6. The decrease in the values at high $[Fe(III)]_0$ was brought about by the increased short-circuit in solution or the increased bulk-backward reaction, which decreases the concentration of anode-active Sthn, and by the decrease of the dye-adsorption onto SnO_2. The direction of electron-flow reversed when the initial concentration of Fe(III) exceeded 10^{-2} mol/l. No quantitative discussions could be made due to the formation of thn-precipitates.

The experimental results of Clark and Eckert[13] and the present work are compared in Table 4. There is a large difference between the two I values if the direction of electron-flow is not taken into consideration. Since Clark and Eckert gave no details of the experimental procedure, it is difficult to find the reason for the difference. However, from the fact that (A) their I values are extraordinarily large for the thn-Fe(II) photogalvanic cells, and (B) we also observe a short-photocurrent of about 5 μA/cm² (or more) with the direction of SnO_2(L)→Pt(L) (under the conditions given in Table 4), the large I values they presented are considered to be short-photocurrent, or values obtained when the solution was pre-illuminated and the circuit then closed and I was measured. Especially, the phenomenon of (B) can be easily presumed from the on-off behavior shown in Fig. 5, in which the temporary negative generation, *i.e.*, the electron-flow SnO_2(L)→Pt(L), was observed at the on-illumination.

Thin-layer Photocells Composed of Gelatinized Thn-Fe(II) Systems. Since it was found that the electron-recycling in the thn-Fe(II) system mainly proceeds by the possible electron-exchange reaction between Fe(II)

TABLE 5. CORRELATION OF SEVERAL PHOTOGALVANIC CELLS

Systems of photocell	ΔE (mV)	I (μA)
(c) SnO_2/soln/Pt	70	1.82
(d) SnO_2/SS-gel/Pt	20	0.75
(e) SnO_2/SS-gel/membrane/Pt	29	0.30
(e) SnO_2/SS-gel/membrane×2/Pt*	32	0.53
(f) SnO_2/membrane/SS gel/Pt	6	0.23

$[thn]_0=5.0\times10^{-4}$ mol/l, $[Fe(II)SO_4]_0$ both in gel and membrane$=5.0\times10^{-2}$ mol/l, $[Fe(III)]_0$ both in gel and membrane$=2.5\times10^{-6}$ mol/l, *: $[Fe(III)]_0$ in membrane $=1.0\times10^{-5}$ mol/l. pH 2.0-HCl, under N_2. The direction of electron-flow was Pt(L)→SnO_2(L) in all cases.

* Nernst's equation is not correct in order to make quantitative discussions, since the equation does not take the formation of local cells into account. However, the equation is understandable for the qualitative discussions.

and Fe(III), the thin-layer photocells can be converted into some gel systems. Figures 1(c)—(f) illustrate the application of the thin-layer photocells. The results are summarized in Table 5. The semipermeable cellophane membrane having thickness 0.7—0.8 mm and porosity 24 Å was used for a diaphragm through which Fe(II) or Fe(III) permeates but not thn. In practice, thn permeated in a very small amount after 5 h. The most important facts are, (i) ΔE and I are very small in the SnO_2/wet membrane-[Fe(II)+Fe(III)]/gel-[thn+Fe(II)+Fe(III)]/Pt system, and (ii) in some extent larger ΔE and I were observed in the SnO_2/gel-[thn+Fe(II)+Fe(III)]/wet membrane-[Fe(II)+Fe(III)]/Pt system, in which the direction of electron-flow was Pt(L)→SnO_2(L). In the former system, there was no dye around SnO_2, since SnO_2 was attached to the membrane containing no dye. Hence SnO_2 is regarded as the real n-type semiconductor, which has an affinity for Sthn rather than for Fe(III). However, there existed only Fe(III) or Fe(II) around the SnO_2 electrode. Thus the former system is very disadvantageous as seen from the characteristics of SnO_2. In the latter system, SnO_2 can be converted into the pseudo-cathodic polarized state due to the adsorption of the dye (stuff), and consequently the cathodic reaction or the donation of electrons to Fe(III) is favorable on the SnO_2 electrode. However, it is very difficult to consider that Sthn, which cannot permeate to the Pt electrode through the cellophane membrane, discharges throughout the membrane. We consider the electron-recycling mechanism in the SnO_2/membrane/gel/Pt system to be as follows.

$$\underline{SnO_2} \longrightarrow (e^-) \longrightarrow$$

Pseudo-cathodic polarized by the adsorption of dyes.

$$\begin{pmatrix} Fe(II) \\ Fe(III) \end{pmatrix} \begin{pmatrix} thn \\ Sthn \end{pmatrix} \begin{pmatrix} Fe(II) \dashrightarrow Fe(II) \\ Fe(III) \dashleftarrow Fe(III) \end{pmatrix}$$

$h\nu$ (wavy arrow)

Electron-exchange

The reaction in a gel — The reaction in a wet membrane

$$\longrightarrow (e^-) \longrightarrow Pt \qquad (6)$$

As the use of membrane brought about the increase of internal resistivity to yield small ΔE and I values, a single-gel system was examined. Figure 8 illustrates the effect of $[Fe(III)]_0$ or $[thn]_0$ on ΔE and I observed by use of the thin-layer photocell (d) as in the SS (50 wt%)-gel systems. Although, the whole values were smaller than those in Fig. 7, similar bell-shaped curves were obtained. It is important that the dependency of $[Fe(III)]_0$ is more clearly recognized in Fig. 8 than in Fig. 7, *i.e.*, the direction of electron-flow reversed at high $[Fe(III)]_0$ as SnO_2(L)→Pt(L).

Figure 9 shows the effect of $[Fe(III)]_0$ on ΔE and I in the PVA (50 wt%)-gel systems. The values of ΔE and I showed similarly a maximum point of 82 mV at $[Fe(III)]_0=10^{-4}$ mol/l and of 0.85 μA at $[Fe(III)]_0=3.0\times10^{-5}$ mol/l, respectively, which were large enough

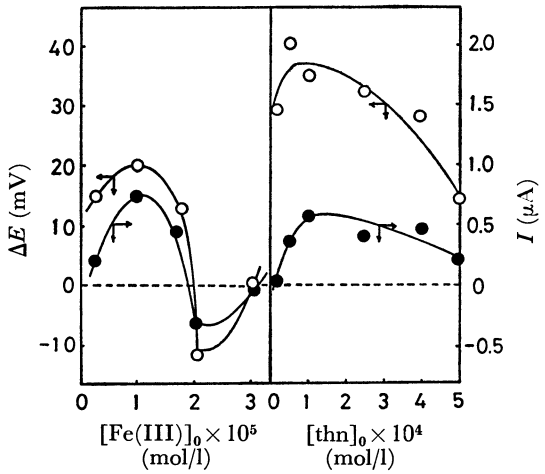


Fig. 8. Effect of $[Fe(III)]_0$ and $[thn]_0$ on ΔE and I of SS(thn–Fe(II))-gel systems. In SS 50 wt% gel, other conditions are the same as in Fig. 7.

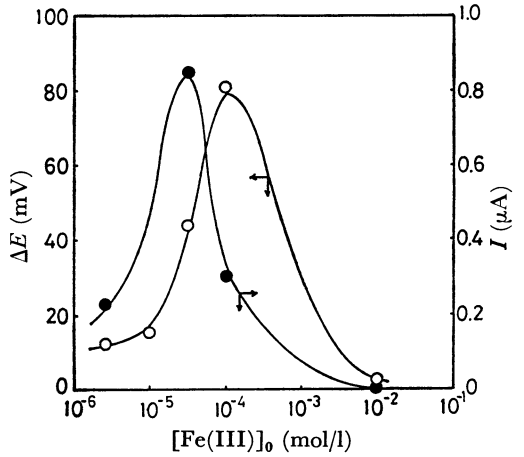


Fig. 9. Effect of $[Fe(III)]_0$ on ΔE and I of PVA(thn–Fe(II))-gel systems. In PVA 50 wt% gel, other conditions are the same as in Fig. 7.

as compared with the corresponding aqueous systems due to the excellent electron-recycling or electron-exchange reaction attributed to the role of the intra-macromolecular hydrogen bonds.

Hydroquinone (H_2Q) is a good reductant in the photoredox reaction with thn. The electrode active species are Sthn (anode) and benzoquinone (BQ) or semi-quinone radical (cathode) in this system. Vigorous stirring of the solution is necessary in order to keep the constant ΔE and I when the double-Pt type photocell as shown in Fig. 1(a) is used. This suggests that the electron-recycling in solution probably proceeds only by the transportation of the cathode active species. Figure 10 illustrates the effect of $[BQ]_0$ on ΔE and I in the SnO_2/thn–PH_2Q-gel/Pt system. The spontaneous decrease in ΔE and I indicates that there is no electron-exchange reaction between PH_2Q and BQ, while ΔE and I increase with $[BQ]_0$ in the SnO_2/thn–PH_2Q–SS-gel/Pt system, when a small amount of BQ is added (Fig. 11). The side hydroxyl groups of SS act the bridging reagent between H_2Q and BQ or semi-quinone residues to increase ΔE and I. PH_2Q is very easily oxidized by molecular oxygen, and the PVA–PH_2Q

TABLE 6. CORRELATION OF THIN-LAYER PHOTOGALVANIC CELLS UNDER THE MOST APPROPRIATE CONDITIONS

Photocell	$[thn]_0$(mol/l)	$[Reductant]_0$(mol/l)	$[Additive]_0$(mol/l)	ΔE (mV)	I (μA)	pH
(c)	1.0×10^{-4}	Fe(II), 5.0×10^{-2}	Fe(III), 2.5×10^{-6}	80	1.20	2.0
(c)	5.0×10^{-4}	Fe(II), 5.0×10^{-2}	Fe(III), 1.0×10^{-5}	70	1.82	2.0
(d), SS	1.0×10^{-4}	Fe(II), 5.0×10^{-2}	Fe(III), 2.5×10^{-6}	40,	0.50	2.0
(d), SS	5.0×10^{-4}	Fe(II), 5.0×10^{-2}	Fe(III), 1.0×10^{-5}	20	0.75	2.0
(d), PVA	5.0×10^{-4}	Fe(II), 5.0×10^{-2}	Fe(III), 1.0×10^{-4}	82	0.45	2.0
(d), PVA	5.0×10^{-4}	Fe(II), 5.0×10^{-2}	Fe(III), 3.0×10^{-5}	45,	0.85	2.0
(d), PH_2Q	5.0×10^{-2}	PH_2Q, 50 wt% gel	None	22	0.48	4.0
(d), SS	1.0×10^{-4}	PH_2Q, 5.0×10^{-2}	BQ, 1.0×10^{-4}	17	0.03	4.0
(d), SS	1.0×10^{-4}	PH_2Q, 5.0×10^{-2}	BQ, 1.0×10^{-3}	15	0.05	4.0
(e), SS	5.0×10^{-4}	Fe(II), 5.0×10^{-2}	Fe(III), 2.5×10^{-6} a) Fe(III), 1.0×10^{-5} b)	32	0.53	2.0
(f)	5.0×10^{-4}	Fe(II), 5.0×10^{-2}	Fe(III), 2.5×10^{-6}	6	0.23	2.0

a) in SS-gel. b) In membrane with double thickness, direction of electron-flow Pt(L)→SnO_2 (L).

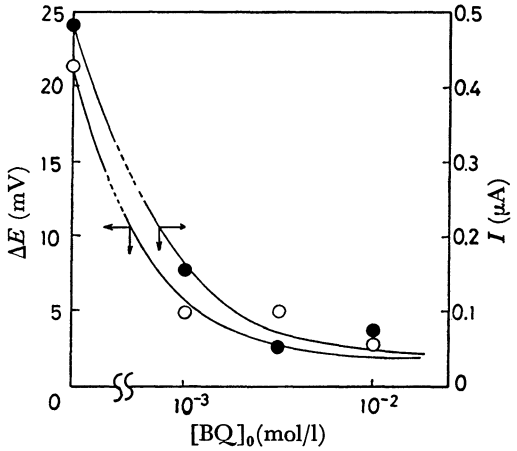


Fig. 10. Effect of $[BQ]_0$ on ΔE and I of PH_2Q(thn)-gel systems. $[thn]_0=5.0\times10^{-2}$ mol/l, PH_2Q 50 wt%-gel, pH 4.0-HCl aq under N_2. (+) values indicate the electron-flow Pt(L)→SnO_2(L).

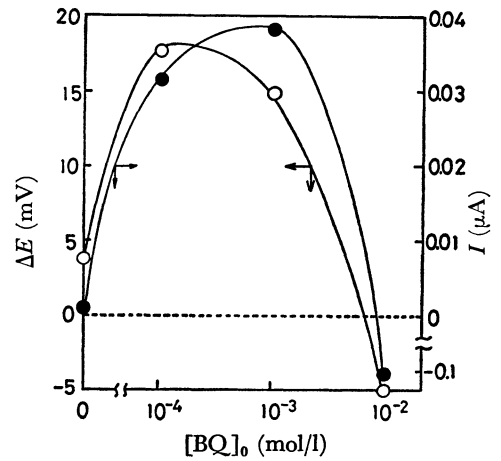


Fig. 11. Effect of $[BQ]_0$ on ΔE and I of SS(thn-PH_2Q)-gel systems. $[thn]_0=1.0\times10^{-4}$ mol/l, $[PH_2Q]_0=5.0\times10^{-2}$ mol/l, SS 50 wt%-gel, pH 4.0-HCl aq, under N_2. (+) values indicate the electron-flow Pt(L)→SnO_2(L).

system could not be examined.

The ΔE and I values under the most appropriate conditions in all the systems are summarized in Table 6. The ability to generate the photo-induced electricity in the PVA system is remarkable. It is noteworthy that the values and the direction of electron-flow in these thin-layer photocells composed of SnO_2 and Pt are very sensitive toward the experimental conditions, *i.e.*, the ration of $[thn]_0/[Reductant]_0$, or their absolute concentration, *etc.*, being balanced at the very critical and delicate situation.

Thin-layer Photocells Composed of Polymeric Thn-Membrane. A remarkable polymer effect in the photogalvanic property of the cationic thn-polymer-Fe(II) systems has been reported.[12] Large ΔE and I values were obtained due to the prohibition of the short-circuit in solution or the bulk-backward reaction between Sthn and Fe(III). The cationic thn-polymer in a gel or membrane state would generate much larger ΔE and I.

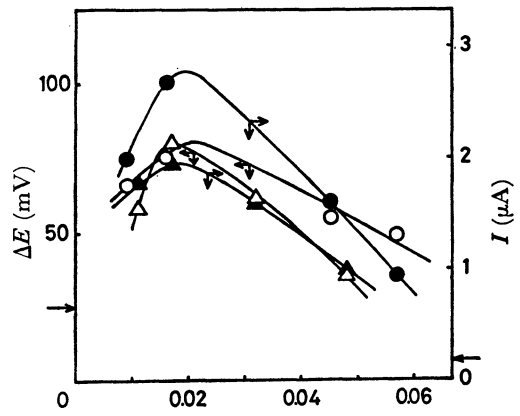


Fig. 12. Relationship between the thickness of BQEthn-film and ΔE, I in thin-layer photocell. (○,●); BQEthn 23%, (△,▲); BQEthn 19%. $[Fe(II)SO_4]_0=5.0\times10^{-2}$ mol/l, $[Fe(III)]_0=2.5\times10^{-6}$ mol/l, pH 2.0-HCl aq, under N_2.

BQEthn of the prescribed structure carrying cationic charges has been prepared, in which it is somewhat crosslinked with thn nuclei and is insoluble in water and soluble in methanol or *N,N*-dimethylformamide, and can thus be cast to a film from a methanol solution. Figure 12 illustrates ΔE and I of the BQEthn–Fe(II) systems cast between SnO_2 and Pt electrodes and swolled by the Fe(II) aqueous solution. Thus, the distance between two electrodes changes with the thickness of the film. The values ΔE and I show maxima at about 0.02 mm thickness of the film, and the direction of electron-flow is also Pt(L)→SnO_2(L). The decrease in the values with thicker films is probably due to the potential barrier formed by excess BQEthn. Hence the BQEthn of x (degree of incorporation of thn nuclie, see Experimental)=23% shows larger values than that of x=19%, since the former requires a smaller amount of polymer than the latter, when the active thn concentration is kept constant. The BQEthn of x=23% shows absorpbance of about 0.3 at the 0.02 mm thickness, the influence of light-scattering being corrected in the measurement. The ΔE and I values of the thn–Fe(II) aqueous system possessing the same absorbance are also indicated by arrows in Fig. 12. The polymer systems shows much larger values than those of the monomeric solution system.

By utilizing the electron-exchange reaction and several polymer systems, the photogalvanic cells consisting of aqueous solutions could be converted into solid-phase cells without any remarkable decrease of the photo-induced electricity.

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