A Saur Vidyut Kosh – Solar Photogalvanic Cell-II

M. SHARON, S. G. SHARAN, A. SINHA AND B. M. PRASAD

Dept. of Chemistry, I.I.T., Bombay

THIONINE/Fe^{2+}/Fe^{3+} system has been studied and is found to become non-reversible after 30 minutes of exposure in solar rays. A detailed study is made on Fe^{3+}/I_2/Rh-B system. This cell is fully reversible in solar photons and gives 40-35 mV potential. The cell can be charged within 29 minutes and is fully reversible. The rate of discharge in dark is slow. The mechanism of photo-reaction is discussed. The role of Rhodamine-B dye has also been explained. It is postulated that this type of cell can be used to give a bias potential, required for the electrolysis.

AFTER the pioneering work of Robinowitch (1-3), on the Fe^{2+}/Fe^{3+}/Thionine system, there has been a large number of publications on the photogalvanic cell using a variety of photosensitive dyes, Most of these galvanic cells are basically concentration cells. A change in concentration of chemicals is maintained by exposing one half-cell to a suitable light, while keeping other half-cell in the dark. In presence of a photosensitive dye, a chemical present in the illuminated half cell gets oxidised and a concentration difference of this chemical is maintained between the two half-cells, which gives rise to a potential in this type of cell. Invariably an artificial source of light such as xenon-lamp or iodine-quartz lamp or tungsten lamp have been used for these experiments. A curiosity, therefore arises as to whether these dyes (e. g. thionione, Rhodamine-B etc.) would work in the same fashion. if they are exposed to Sun-light, because the latter has photons from near u, v. to i. r. spectrum. Therefore, our first object was to repeat the published work of Clark[9], Peter[10], Tadayoshi[7], Rabinowitch[1-3] Hardwick[4-5] and Ainsworth[6] using the solar rays directly to see whether these would work in Sun-light.

Rideal[11] and Kistakowsky[12] have shown that a mixture of ferrous ammonium sulfate, ammonium sulphate, potassium iodide in H_2SO_4 (1×10^{-2}N) when irradiated with a light source (Hg-lamp), gives ferric which oxidizes iodide ion and the process in found to be reversible. Chta et al[13] have also shown the feasibility of such photochemical reaction in splitting of water. However, no report is availabie to show the effect of a photosensitive dye on this chemical reaction. Because in Fe^{2+}/I_2 system, iodine is the only species which can absorb photons near the visible region (352 nm) of the spectrum and as the concentration of iodine decreases due to the formation of iodide ions, the efficiency of conversion will also gradually decrease. On the other hand if some suitable dyes are used which can absorb the photons of visible regions and could transfer its energy to the Fe^{2+}/I_2 system, without itself being oxidised or reduced, then perhaps the efficiency of photoconversion of Fe^{2+}/I_2 would increase. We have tried Rhodamine-B and thionine dyes for this chemical reaction.

EXPERIMENTAL

A. R. grade chemicals were used without any further purification. Thionine was purified by the method discussed elsewhere[9]. Rhodamine-B was used without any further purification.

Design of Photogalvanic Cell : A cell as shown in Fig. 1 was constructed. This was made

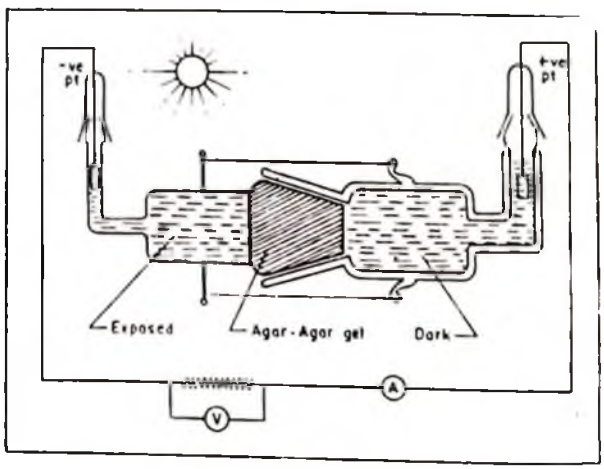


Fig. 1 A solar cell to study the photochemical reactions and to measure the potential developed due to such reactions

out of a pair of B-34 cone and socket. The cone was filled with Agar-Agar gel in saturated KCl. One compartment was blackened by a black paint. The platinum electrodes were used in the two half-cells. A solution whose photogalvanic effect was to be studied was added into the two half-cells. This

cell was directly exposed by Sun-light. The current and potential were measured at different time of irradiation.

RESULTS AND DISCUSSION

(A) *Ferrous/Thionine System :* It is depressing to note rhat none of the experiments reported on Fe^{2+}/Fe^{3+}/Thionine system by various authors ([1,4,6,7,9,10]) could be reproduced in the solar rays. It was observed that after half an hour of continuous exposure to the Sun-light, the entire colourless solution of exposed half-cell turned purple blue. This solution could not be used for recycling process, even after keeping the solution in dark for one day. However, addition of water to the solution bleached this system momentaly, but the solution again turned purple blue after long exposure. These experiments were tried at the concentrations suggested[1-13] i. e. Fe^{2+} (1×10^{-2}M), Fe^{3+} (1×10^{-3} M), Thionine (1×10^{-5}M) at pH = 3. A similar observation has been recently reported by Kamat et al[14], who observed that by raising the temperature of the exposed compartment, the potential of the cell decreased to almost zero. Their results would suggest that when the exposed half-cell is kept in Sun for longer period, the solution gets heated and thus shows decrease in potential. However, this does not explain as to why the solution becomes purple in colour and why the solution does not follow its reversible cycle even after keeping in dark for a day.

It is possible that with the solar photons some secondary reactions might be getting initiated which inactivates thionine for the oxidation of Fe^{2+} to Fe^{3+}. This will also be temperature dependent. Because of this Kamat could observe this behaviour even with artificial light. Addition of water (as observed by us) may be disturbing the dynamic equilibrium of the secondary reaction, which makes the thionine to show its reversible behaviour tempo arily.

Isabel and Harriman[15] have studied the system by the flash photolysis experiment and report that there are two types of reactions which might throw the reduced thionine back into the original thionine, i. e.

$$2TH^{\bullet}_2 \text{ (semi thionine)} \rightleftharpoons TH^{+} + TH^{\bullet}_3 \text{ (fast process)} \quad (1)$$
Thionine Leucothionine

$$TH^{\bullet}_3 + Fe^{3+} \rightleftharpoons TH^{\bullet}_2 + H^{+} + Fe^{2+}$$
(slow process) (2)

where the main reaction being

$$Fe^{2+} + H^{+} + TH^{\bullet} \rightleftharpoons Fe^{3+} + TH^{\bullet}_2$$

Those two processes might form a cyclic reaction. However, one has to confirm that whether such reaction would continue to occur in dark as well.

(F) *Ferrous/Iodine System :* A solution of Fe^{2+}, Fe^{3+}, I^- and H_2SO_4 with various possible concentration combination were made and transferred to the two half-cells of the photogalvanic cell (Fig. 1). One compartment was exposed to sunlight and I-V characteristics were measured for each mixture. The maximum current and potential obtained by various combinations are given in Table I. The experiment was tried with thionine and rhodamine-B dyes. Thionine did not work with this system. However, application of rhodamine-B dye helped in getting the maximom potential in a shorter period (Table I). From Table I it is obvious that Fe^{3+} (1×10^{-2}M), Fe^{2} (1×10^{-2}N) KI (1×10^{-2} N), Rhodamine-B (1×10^{-6} N) and H_2SO_4 (0.1 N) are the best combination to get the maximum power. Therefore, for all subsequent experiments, a mixture containing these concentrations were tried.

In Fig. 2, the rate of charging of the cell is shown, which suggests that within half an hour the cell can be fully charged. In Fig. 3 the effect of light and dark on the solution with and without Rhodamine is shown. This figure shows that the dark reaction is not as fast as light reaction. Rhodamine-B increases the photocurrent as well as reduces the rate of dark reaction. In Fig. 4, the reproducibility of the cell is shown. Even after 12 days one gets the same power characteristics from the cell. This suggests that there is no degradation of the chemical even after 12 days of the operation. The cell gives open circuit voltage of 40–45 mV and maximum current of 20μ A. The lower current is because of the high internal resistance of the cell.

Rhodamine-B helps in increasing the photoresponse of Fe^{2+}/I_2 system, because the former has λ_{max} at 550 nm (whereas iodine has λ_{max} at 352nm), and Sun-rays has maximum intensity between 450-550 nm. Furthermore, Rhodamine-B might be acting as photosensitizer i.e. it gets excited be

TABLE 1

No. obs	Conc. of Fe^{+2} in Molarity	Conc. of Fe^{+3} in Molarity	Conc. of I^- in Molarity	Conc. of Rh(B) in Molarity	Max. current in Micro Amphere	Max. potential in Milli volts	Time of attaining max. current in minutes	Time of decay in minutes
1	2×10^{-2}	1×10^{-3}	1×10^{-1}	2.5×10^{-6}	7.5	20	12	12
2	2×10^{-2}	1×10^{-3}	1×10^{-1}	—	7.5	18	12	—
3	1×10^{-2}	1×10^{-1}	1×10^{-1}	2.5×10^{-6}	—	—	—	—
4	1×10^{-2}	1×10^{-2}	1×10^{-2}	5.0×10^{-6}	10-13	35-45	10.25	170
5	1×10^{-2}	1×10^{-3}	1×10^{-3}	2.5×10^{-6}	0.25	60	—	—
6	2×10^{-2}	1×10^{-3}	1×10^{-1}	5.0×10^{-6}	8	25	15	—
7	1×10^{-2}	1×10^{-2}	1×10^{-1}	5.0×10^{-4}	2	—	7	—
8	1×10^{-2}	1×10^{-2}	1×10^{-2}	2.5×10^{-6}	11.13	40	11-30	—
9	1×10^{-2}	1×10^{-2}	1×10^{-2}	1×10^{-4}	12	—	12-25	—
10	1×10^{-2}	1×10^{-2}	1×10^{-2}	1×10^{-5}	—	—	—	—
11	1×10^{-2}	1×10^{-2}	1×10^{-2}	1×10^{-6}	12-13	37.5	14	—
12	1×10^{-2}	1×10^{-2}	1×10^{-2}	—	11.5	37.5	15	—
13	1×10^{-1}	1×10^{-1}	1×10^{-1}	5.0×10^{-6}	8	2	30	—
14	1×10^{-1}	1×10^{-1}	1×10^{-2}	3.0×10^{-6}	13	37.5	45	—
15	1×10^{-2}	1×10^{-2}	1×10^{-3}	1.0×10^{-6}	2-3	—	15	60

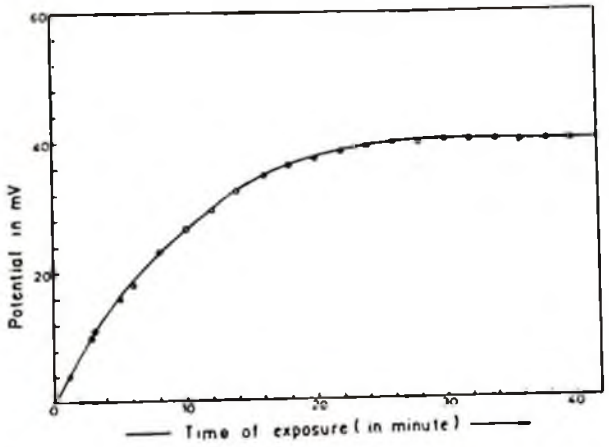


Fig. 2 Change of potential with time of irradiation with solar photons

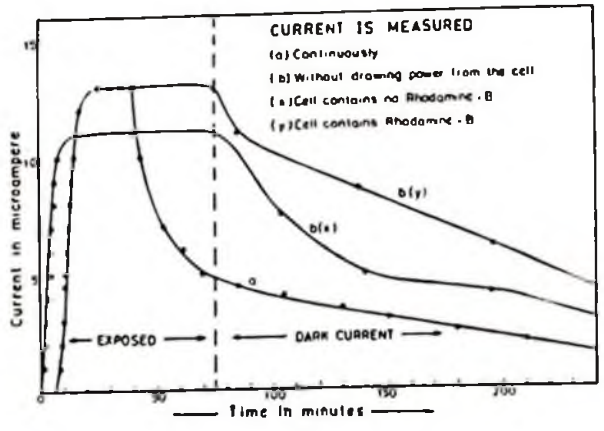


Fig. 3 Current characteristics of the Saur Vidyut Kosh using Fe^{+3}/I_2 system

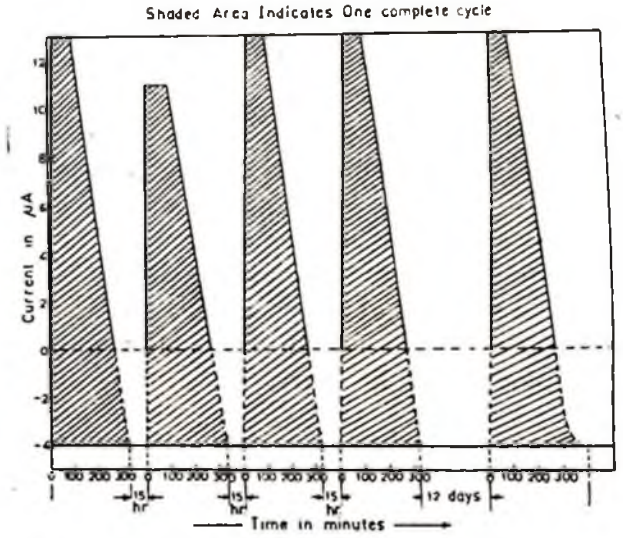


Fig. 4 Current characteristics for repetitive exposures — Dark cycles

solar radiations and transfers its energy to I_2 as well as to Fe^{+2} as suggested below :

$$Rh\text{-}B \xrightarrow{h\nu} Rh\text{-}B^* \quad \ldots 1$$

$$I_3^- + Rh\text{-}B^* \longrightarrow I_3^{-*} + Rh\text{-}B \quad \ldots 2$$

$$Fa^{2-} + Rh\text{-}B^* \longrightarrow Fe^{-3} + Rh\text{-}B \text{ (oxidised)} \quad \ldots 3$$

$$I_3^{-*} + Fe^{2} \longrightarrow Fe^{+3-} + \tfrac{1}{2}I_2 + 2I^- \quad \ldots 4$$

$$Rh\text{-}B^* + \tfrac{1}{2}I_2 \longrightarrow Rh\text{-}B + \tfrac{1}{2}I_2^* \quad \ldots 5$$

$$\tfrac{1}{2}I_2^* + Fe^{2} \longrightarrow Fe^{3+} + I^- + \text{heat} \quad \ldots 6$$

$$Rh\text{-}B^* + Rh\text{-}B \longrightarrow Rh\text{-}B + \text{heat} \quad \ldots 7$$

Quickenden[16] has shown the possibility of reaction (3) by using a tungsten lamp, but this reaction does not occur in solar rays, because we could not get photopotential with Fe^{2}/Fe^{3+}/Rh-B system with solar photon. The results shown in Table I agrees with this.

It is clear from Table I that whenever I^{+} ion concentration is greater than the Fe^{2-}, the solution gives a lower power and after a prolonged exposure, the solution becomes yellow, showing the production of iodine (reaction-4), whereas when the concentration of all the species are same except Rhodamine-B (1×10^{-6}M) then one gets the maximum power probably due to reactions 1, 2, 4 and 6. The exposed half-cell becomes pink coloured (due to the colour of Rhodamine-B).

Such type of cell would not have any advantage to generate power for general purpose. However, it can be used for applying a bias potential to semiconductor electrode for splitting water by photoelectrolytic process[13].

Acknowledgement

The authors are thankful to Mr. C.R. Das, Co-ordinator for Procuring grant and a fellowship from Tata Energy Research Instjtute, Bombay without whlch this work could not be carried out.

REFERENCES

1. E. Rabinowitch, *J. Chem. Phys.*, 8 (1940) 535-559.
2. E, Rabinowitch, *Ibid.*, 8 (1940), 560-566.
3. K. G. Mathai and E. Rabinowitch. J. *Phy. Chem.*, 66 (1962) 663-664.
4. R. Hardwick, J. *Am. Chem. Soc.*, 80 (1958) 5667-73.
5. R. Hardwlck, J. *Phys. Chem.*, 66 (1962) 349-350.
6. S. Ainsworth, J. *Phys. Chem.*, 64 (1960) 715-722.
7. Tadayoshi Sakata, Yasuhiro Suda, Jirro Tanaka and Hiroshi, Tsubumura, J. *Phys. Chem.* 81 (1977) 537-542.
8. D. E. Hall, J. A. Eckert, N. N. Lichtin and P. D. Wildes, J. *Electro. Chem. Soc.*, 123 (1976) 1705-7.
9. W. D. K. Clark and J. A. Eckert, J. *Solar Energy*, 17 (1975) 147-150.
10. Petar, D. Wildes, Karen, T. Brown, Morton Z. Hoffman Norman N. Lichlin and Date E Hall, J. *Solar Energy*, 19 (1977) 579-582.
11. E. K. Rideal and E. G. Williams, J. *Chem. Soc.*, 127 (1925) 258.
12. G. B. Kistiakowsky, J. *Am. Chem. Soc.*, 49 (1977) 976.
13. T. Ohta, S. Asakura, M. Yamaguchi, N. Kamiya, N. Gotoh and T. Otagawa, *Int. J. Hydrogen Energy* 1 (1976) 113-116.
14. V. Kamat, Ph.D. Thesis, Bombay University, 1978.
15. M. Isabel C. Ferreira and Anthony Harriman, J. *Chem. Soc. Faraday Transc. I*, 73 (1927) 1085-1091.
16. Terence I. Quickenden Gek Kim Yim, J. *Solar Energy*, 91 (1977) 283-289.