VOLTAMMETRTY OF METHYLENE BLUE IN AQUEOUS SOLUTION AT ITO GLASS ELECTRODE

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Introduction

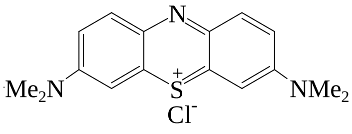
Besides its uses in the dye-sensitized solar cells as phot-anode indium tin oxide coated glass (ITO) is increasingly being used in the organic LED devices[1-4]. In a typical dye-sensitized solar cell ITO is coated with TiO_2 nanocrystals containing ruthenium sensitizer. An organic photoelectro-chemical cell[3] can be made by sandwiching solid polymer electrolyte (SPE) between polymer coated ITO and platinized ITO counter electrode. In such a cell liquid electrolyte can also be used instead of SPE. A polymer LED device has been reported[1]. It consists of several layers of polymer materials sandwiched between ITO anode and a metallic cathode. In another approach[2] organic layers are deposited on ITO followed by deposition of the metal layer that serves as cathode. There is an instance of organic photovoltaics[4], where ITO has been used as cathode and capped calcium as anode, giving open-circuit voltages >2 V.

In spite of the current trend in the use of ITO and the limitations of its use in aqueous system, particularly when dyes are to be studied as electroactive species, we have ventured to study some dyes systematically using ITO as the working electrode. The underlying idea is to see whether, ultimately, cheaper technology for dye-sensitized solar cells can be developed.

Compton and co-workers have studied methylene blue (MB) voltammetrically[5] and its use electroanalytically[6]. In our study of MB we have tried to maintain some conditions of these studies.

Experimental

A computerized electrochemistry system (Advanced Analytics, Virginia, USA, Model HQ-2040) consisting of rectangular (4 x 4 x 1 cm^3) three electrodes cell with ITO (7 x 50 x 0.6 mm cuvette slide, ITO coated both sides, $R_S \geq 10\ \Omega$/square) working electrode, Pt-wire auxiliary electrode and saturated Ag/AgCl reference electrode has been used. The electrodes were arranged in the order as mentioned. 10 mL solutions, and nitrogen purging were used. 0.1 M KNO_3 or KCl was used as supporting electrolyte, 0.2 M KH_2PO_4 was used to maintain pH in the range 3.5 to 6.5 and 0.1 M citric acid as electron donor. Methylene blue is $C_{16}H_{18}N_3S^+.Cl^-.3H_2O$ (99%). 160 W Xenon Arc source (Solar Light CO., USA), emitting only in the visible range, was used to illuminate through a light guide a specific electrode area. The experiments were done at ~28° C.



Methylene Blue (MB)

Results and discussion

The ITO working electrode was calibrated with 1.0 mM $[Fe(CN)_6]^{3-}$ against Ag/AgCl electrode in 0.1M KNO_3 solution. Ep_a and Ep_c for the Fe^{3+}/Fe^{2+} couple are 147 mV and 207 mV respectively.

MB in solution, at an appropriate pH (3.5-6.5), gives well-defined voltammograms showing complete reversibility involving two-electron transfer (Table 1). The half wave potential of the system increases with decrease in pH. These observations are in agreement with those found by Compton and others.[5,6] The slope of ip_c vs. $\nu^{1/2}$ plot decreases with increase in pH indicating the reduction of the apparent diffusion coefficient (*D*) of the electroactive species as pH increases. Repetition of the experiment between pH 3.5 to 6.5 did not show any change of current with time. Thus, the lowering of the diffusion coefficient cannot be due to fouling of the electrode. Charge transfer rate constant (k_f) also decreases with increase in pH of the solution. Table 2 shows that oxidative photocurrent is produced by light at the ITO electrode in MB solution containing citric acid (CA). On the other hand, photocurrent was not observed on illumination of the electrode in the MB solution alone.

Table 1. Voltammetric behavior of MB at ITO electrode at different pH

[MB] = 1.00 x 10^{-5}M

Scan rates (ν): 10, 20 and 50 mV/s respectively.

pH	$-E_{pc}$ mV	$-E_{pa}$ mV	ΔE_p mV	$-E_{1/2}$ mV	ip_a/ip_a
	114.0	4.00	110.0	59.0	1.01
3.5	115.0	4.50	110.5	59.8	0.98
	115.0	4.50	110.5	59.8	1.02
	155.0	46.0	109.0	100.5	1.01
4.3	156.0	47.0	110.0	100.5	1.00
	156.0	47.0	110.0	100.5	1.00
	162.0	60.0	102.0	111.0	1.00
5.0	162.0	60.5	101.5	111.0	1.01
	162.0	60.5	101.5	111.0	1.02

Table 2. Effect of illumination in the presence of citric acid

[MB] = 1.00 x 10^{-5}M , Scan rate 20 mV/s

[CA] = 0.10M

PH	$-E_{pc}$ mV	$-E_{pa}$ mV	ΔE_p mV	$-E_{1/2}$ mV	ip_c reduced (%)
		Before illumination			
5.22	220	104	116	162	0
6.33	256	140	116	198	0
		After illumination			
5.22	220	104	116	162	8
6.33	256	140	116	198	15

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