

Photo electrochemical study of ferrioxalate actinometry at a glassy carbon electrode

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Abstract

An alternative photo electrochemical approach of potassium ferrioxalate actinometry has been investigated via the amperometric detection of product (Fe^{2+}) formation at a glassy carbon electrode. The corresponding oxidation current response of $[\text{Fe}^{2+}]$ formed due to the photolysis of ferrioxalate, was monitored as a function of illumination time, which allowed the intensity of the illumination source to be determined. To validate this approach a parallel measurement to calculate the light flux was also carried out via monitoring the reactant (i.e. Fe^{3+}) disappearance with photolysis time.

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Keywords: Photo electrochemical; Liquid phase actinometry; Photolysis; Amperometric detection; Illumination intensity

1. Introduction

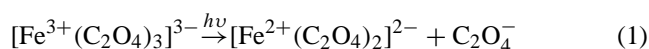
Since the outstanding scientific achievement of photo electrochemical splitting of water at an illuminated TiO_2 electrode, discovered by Fujishima and Honda [1], research efforts in this area has been diversified significantly to solve a variety of environmental problems, particularly of relevance to TiO_2 -sensitised advanced oxidation processes for the complete mineralisation of hazardous compounds employing either photochemical [2–6] or photo electrochemical strategies [7–10]. However, all the photochemical and photo electrochemical methodologies require the measurement of accurate output/intensity of the illumination source. Indeed, an important step in studying any photo process involves a proper demonstration of actinometry either by physical methods employing photosensitive detectors or by chemical methods employing chemical actinometers. Due to the high sensitivity, chemical actinometer has widely been used where the intensity measurement relies on a light induced chemical process for which the quantum yield is quantified accurately [11]. Hitherto, several photochemical actinometry systems have been explored in this regard [11–16], but potassium ferrioxalate actinometry developed by Hatchard and Parker [17] has been appeared as the

unique photochemical approach of liquid phase chemical actinometry. Moreover, due to its universal applicability few modified versions of this traditional actinometry have also been proposed in literatures [18–20].

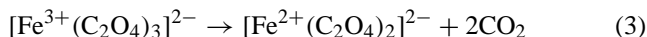
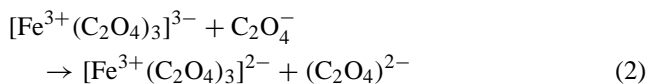
Although ferrioxalate actinometry offers a number of advantages [17,21,22], few drawbacks [14,23] of this conventional spectro-photochemical analysis system has led the researchers to find out alternative but straightforward ways of actinometer measurements. Particularly, developing electrochemical techniques of actinometry are now becoming a major concern to many research groups [24–28]. An electrochemical actinometry system of azo monolayer film was developed by Fujishima and co-workers [24–26], which facilitated in situ measurement of the light flux in both photochemical and photo electrochemical systems. Lingamurthy et al. [27] proposed a photo electrochemical study of riboflavin– Na_2EDTA as an actinometer. Recently, a micro electrochemical approach of ferrioxalate actinometer system has also been developed to quantify the light flux on the microscopic scale using scanning electrochemical microscopy (SECM) [28].

2. Measurement principle

Photolysis of aqueous solution of ferrioxalate in sulphuric acid proceeds according to the following stoichiometry [21].



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The preceding photo process produces one Fe^{2+} ion as a function of every Fe^{3+} ion lost and thus the conventional photochemical detection relies on the monitoring of product (Fe^{2+}) formation via the visible absorption spectroscopy of Fe^{2+} -phenanthroline complex at 510 nm [17] and the intensity of the UV-source is measured according to the following Eq. (4) [21]:

$$\text{intensity, } I(\text{quanta cm}^{-3} \text{ s}^{-1}) = \frac{d[\text{Fe}^{2+}]/dt}{\Phi} N_A, \quad (4)$$

where Φ represents the quantum yield which has a value of 1.21 [17] and $d[\text{Fe}^{2+}]/dt$ rate of formation of $[\text{Fe}^{2+}]$ in the photo process and $[\text{Fe}^{2+}]$ is usually calculated from Beer–Lambert's law and N_A the Avogadro number ($6.022 \times 10^{23} \text{ mol}^{-1}$).

However, the necessity of a number of analytical manipulations has already been accounted as a limitation of this approach [23]. In contrast, recently straightforward in situ photo electrochemical approaches of ferrioxalate actinometry has been developed to quantify the absolute light flux in static and flowing solutions, employing SECM [28] and channel flow method with electrochemical detection (CFMED) [29], respectively. Both the strategies developed focused on the monitoring of the disappearance of the reactant (Fe^{3+}) amperometrically via the reduction mechanism. However, in order to investigate a parallel amperometric monitoring to follow up in situ the product (Fe^{2+}) formation, which would be beneficial to measure the intensity directly via Eq. (4), the present approach described in this paper is adapted as an alternative way of electrochemical actinometer measurement using this well known *potassium ferrioxalate liquid phase actinometry*.

3. Experimental

3.1. Chemicals

Potassium trisoxalato ferrate(III) and 1,10-phenanthroline were obtained from Alfa Aesar while sulphuric acid was from BDH (UK). The substrate solutions were prepared in $0.05 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ using doubly distilled deionised water.

3.2. Photo electrochemical arrangement

The photo electrochemical cell (250 cm^3 , made of quartz) employed for this study consisted of a Teflon lid with drilled holes to hold the electrodes. The electro chemical set-up followed the conventional three-electrode arrangement. A glassy carbon electrode of 3 mm diameter (BAS Technicol,

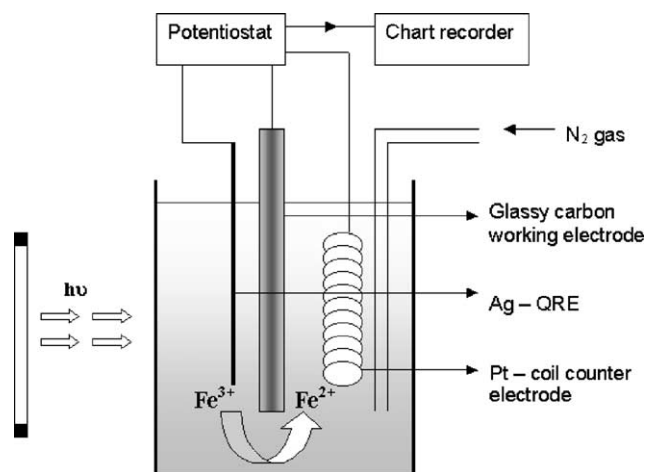


Fig. 1. Photo electrochemical set-up for the study of ferrioxalate actinometry.

UK) was served as the working electrode while a Pt-coil and a Ag-wire (1 mm diameter) were used as the counter and reference electrodes, respectively. All the electrodes were connected with a potentiostat and the cyclic voltammetry responses were recorded on a chart recorder. An aqueous solution of $6.0 \times 10^{-6} \text{ mol cm}^{-3}$ potassium trisoxalato ferrate(III) in $0.05 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ was photolysed using a mercury lamp ($\lambda = 420 \text{ nm}$), taking extra care to avoid any possibility of initial conversion of Fe^{3+} to Fe^{2+} which can cause due to room light [14]. Due to the high visible light sensitivity of ferrioxalate red coloured photographic safe light was used in the room. Since the presence of O_2 can affect the photolysis of ferrioxalate [30], prior to the execution of experiment, ferrioxalate solution was degassed for enough time and a gentle stream of nitrogen was continued into the solutions during the measurements, which ensured uniform distribution of product formation in the solution. The formation of $[\text{Fe}^{2+}]$ was monitored at different illumination time intervals (typically from 60 to 600 s) via the cyclic voltammetry (CV) at the glassy carbon electrode at a scan rate of 50 mV/s . A schematic of experimental set-up is shown in Fig. 1.

In order to determine the diffusion coefficient of Fe^{2+} , 25 cm^3 of ferrioxalate solution of same concentration (as above) was photolysed for enough long time to achieve complete reduction to Fe^{2+} and the cyclic voltammetry was recorded with a variation of scan rate ($10\text{--}200 \text{ mV s}^{-1}$). Necessary spectrophotometric analysis was performed (using Shimadzu UV-160A UV-Vis spectrophotometer) following the conventional method of Hatchard and Parker [17].

4. Results and discussion

Due to enough illumination of ferrioxalate solution, Fe^{3+} has photoreduced to Fe^{2+} completely following the equation,



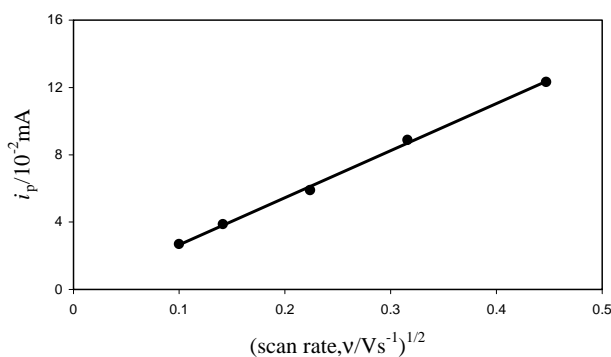


Fig. 2. Randles–Sevcik plot for the determination of diffusion coefficient of Fe^{2+} .

and the diffusion coefficient of Fe^{2+} was calculated using the Randles–Sevcik equation for a reversible process:

$$i_p = (2.69 \times 10^5) n^{3/2} A C D^{1/2} v^{1/2} \quad (6)$$

where i_p is the peak current, n the number of electron involved in the electrode process = 1, A the area of the electrode (cm^2), C the concentration of $Fe^{2+} = 6.0 \times 10^{-6} mol cm^{-3}$ (also confirmed via spectrophotometric analysis [17]), D the diffusion coefficient ($cm^2 s^{-1}$) of Fe^{2+} and v denotes the scan rate ($V s^{-1}$). A plot of peak current (for Fe^{2+} oxidation) as a function of square root of scan rate was constructed as shown in Fig. 2, which

yielded a straight line as predicted and from the slope of the line value of diffusion coefficient of Fe^{2+} is obtained as $6.03 \times 10^{-6} cm^2 s^{-1}$.

Since upon illumination ferrioxalate solution follows the reduction process forming Fe^{2+} , the present investigation focuses on the amperometric detection of product formation at different irradiation time intervals. An increasing fashion of the oxidation peak current (inset plot of Fig. 3) is observed with the increase of illumination time duration, obviously indicating a gradual increase in $[Fe^{2+}]$ formation as the photolysis proceeds. As longer the illumination time, more Fe^{3+} become engaged in the photo process. This indicates a reasonable sensitivity of the present approach adapted herein. Since the peak current (i_p) is directly proportional to the analyte concentration (Eq. (6)), using the values of diffusion coefficient of Fe^{2+} and the peak current response, the concentration of Fe^{2+} formed with the corresponding illumination time was achieved. Fig. 3 represents the dependency of $[Fe^{2+}]$ formed with illumination period. Clearly, the plot in Fig. 3 appeared in a linear fashion, which is consistent with the measurement of traditional photochemical approach developed by Hatchard and Parker [17]. The rate of $[Fe^{2+}]$ formation was obtained as, $4.0 \times 10^{-10} mol cm^{-3} s^{-1}$, from the gradient of the plot and this value allows the absolute output of the illumination source to be determined from Eq. (4) as $1.99 \times 10^{14} quanta cm^{-3} s^{-1}$.

The above approach was further validated by a parallel cathodic investigation where the reduction peak current of

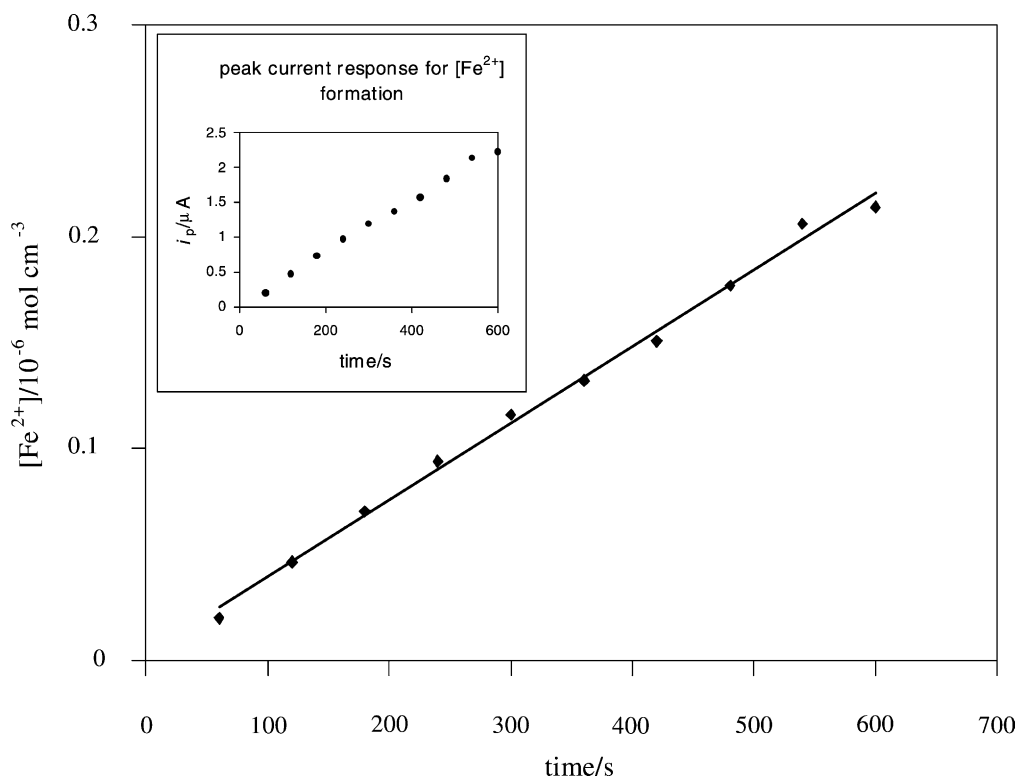


Fig. 3. Dependence of photogenerated $[Fe^{2+}]$ formation with illumination time.

Fe^{3+} was monitored with photolysis time. Prior to illumination, the current response of bulk solution of ferrioxalate (under deoxygenated condition) was recorded via CV and the diffusion coefficient of Fe^{3+} was determined from Eq. (6) as $5.49 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. This value is quite reasonable with that observed by Fonseca et al. [28]. A number of measurements of illumination current for the reduction process were then followed at regular time intervals. This approach also showed a linear decay of reduction current as the illumination proceeds. Using the known values of the parameters in Eq. (6), the reduction peak current responses were converted to $[\text{Fe}^{3+}]$. A depletion rate of $4.6 \times 10^{-10} \text{ mol cm}^{-3} \text{ s}^{-1}$, was achieved for this case, which satisfies the anodic rate (i.e. oxidation of photogenerated Fe^{2+}). This observation also ensures that the present photo electrochemical measurement follows a reasonable pathway where anodic and cathodic reaction rates are balanced, which is also expected from the electrochemical point of view. However, following the alternative way of intensity measurement via the reactant disappearance rate [21] (i.e. $I = ((d[\text{Fe}^{3+}]/dt)/\Phi)N_A$), the intensity of the illumination source was calculated as $2.28 \times 10^{14} \text{ quanta cm}^{-3} \text{ s}^{-1}$ which is very close to that obtained via the monitoring of product $[\text{Fe}^{2+}]$ formation.

5. Conclusion

The well known liquid phase potassium ferrioxalate actinometer system has been used to determine the absolute light output of a mercury lamp ($\lambda = 420 \text{ nm}$) via an alternative photo electrochemical approach where the preceding photo process is monitored through the increasing of oxidation peak current (responsible for the formation of $[\text{Fe}^{2+}]$) as a function of illumination time. Recording the reduction peak current with photolysis time also validated the approach. The intensity values obtained by monitoring both the product formation and reactant depletion were in close agreement, which indicates that the approach adapted here is quite reasonable.

Acknowledgements

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