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Faiza Touati

Royal College of Surgeons in Ireland


John Cassidy

Technological University Dublin, john.cassidy@tudublin.ie

Kevin McGuigan

Royal College of Surgeons in Ireland

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A Novel TiO₂/PVC Composite for use in a Photoelectrochemical Cell.

Faiza Touati*, John Cassidy[†], Kevin G. McGuigan*,

*Department of Physiology and Medical Physics,

Royal College of Surgeons in Ireland,

123 St. Stephens Green,

Dublin 2.

Ireland

[†]School of Chemistry and FOCAS,

Dublin Institute of Technology,

Kevin Street,

Dublin 8.

Ireland

+ corresponding author: john.cassidy@dit.ie, ph 353-1-402-4779.

Abstract

A novel method of coating titanium dioxide on a glassy carbon electrode as a polyvinylchloride composite, is described. On illumination, there is an enhanced voltammetric current at this TiO₂/PVC composite in aqueous formic acid solution. This electrode is used as the basis of a formic acid fuel cell where oxygen is reduced at a platinum cathode. The system yields 100 μA cm⁻² for 0.01 mol dm⁻³ HCOOH in 0.1 mol dm⁻³ NaOH under illumination from a 150 W xenon lamp. The current without illumination is 0.5 μA cm⁻².

Keywords: Titanium Dioxide, Photoelectrochemistry, modified electrode

Introduction.

Fuel cells come in all shapes and sizes and some of the more efficient versions run at molten salt temperatures[1]. Others operate with well defined fuels based on hydrocarbon feedstocks that have been purified to remove sulphur. They are similar to a battery where there is a continuous supply of reagents: a fuel such as hydrogen, methane, methanol, or other organics along with a species capable of being reduced: oxygen is the compound of choice.

The most ideal system from an environmental standpoint, is that of a hydrogen /oxygen fuel cell where the product is water which avoids the production of CO₂ as a greenhouse gas.

Systems in place have been used for stand alone power plants for hospitals and transport such as an electric bus but typically these systems have yet to reach economic viability in an era where there is abundance of fossil fuels

Work in photochemistry work peaked in the 1980's where there was the prospect of using sunlight shining on suspensions of titanium dioxide in order to catalytically cleave water into hydrogen and oxygen [2-6]. In this way a clean and efficient method of producing hydrogen as a fuel was envisaged. However, there was a requirement to use a rather high energy light to achieve the splitting and it was not as efficient with visible light[6]. However suspensions of TiO₂ and immobilised TiO₂ have been used successfully to oxidise organic contaminants in waste waters when exposed to light[7-10]

The aim of this work involves the fusing of the two disparate areas of work to develop a fuel cell which is assisted with light. The primary aim is to employ this as a power source. At the anode, a coated composite layer of TiO₂ on carbon, organics will be oxidised when it is exposed to visible light, and at a porous platinum cathode oxygen from the air will be reduced. This novel device has the added advantage that it will reduce the chemical oxygen demand, COD, in waste water since the organic compounds will be mineralised.

There has been work previously carried out using systems which oxidised organic compounds while reducing metal cations; though their use as a fuel cell was not indicated. [11-13]. Although the photoelectrochemistry of TiO₂ layers [14] and immobilisation of TiO₂ in layers is well established, [15], their use in fuel cell technology has not been exploited to its full potential.

Experimental

Composite layers were prepared by preparing a suspension of TiO₂ (Degussa P25, 2.00 g dm⁻³) in tetrahydrofuran along with polyvinylchloride (0.07 g dm⁻³). This suspension was sonicated for 10 min and typically 0.171 cm³ of this suspension was coated on a glassy carbon electrode, (4 cm²) and the electrode dried at room temperature.

The light source was a 150 W xenon lamp powered by an Oriel 68806 basic power supply. Glassy carbon sheets (Tokai) and Platinum foil (Goodfellow) were silver epoxied (silver epoxy, Radionics, Dublin) to shielded copper wire and then encapsulated with Araldite (Radionics, Dublin). Carbon disks (diameter 3 mm, Metrohm), a saturated calomel electrode and a platinum wire formed the three

electrode one compartment cell for voltammetry. The potentiostat was a CHI model 602 linked to a PC. Current from the fuel cell was passed through a resistance (typically $1\text{k}\Omega$) and the voltage fed directly to a Recorderlab XYT chart recorder. The air electrode was taken from a mini fuel cell (Electro-chem-technic, 81 Old Road, Heddington, Oxford, UK) consisting of a porous platinum electrode of geometric area equal to 9.6 cm^2 . In order to simulate solar radiation , a filter, (Schott glass heat absorbing filter model KGO2, Melles Griot, Cambridge, U.K.) was used. Analysis of formic acid was carried out by HPLC using a Shimadzu LC-10 AS pump, Shimadzu SPD-10A Uv/Vis detector and the signal recorded on a Shimadzu C-R5A Chromatopac integrator. The column was C_8 , ($50\mu\text{m}$), $150 \times 4.6\text{ mm}$ (Phenomenex). The mobile phase was aqueous H_2SO_4 , $\text{pH} = 3.5$ with $\lambda = 210\text{ nm}$ as the detection wavelength.

Results and Discussion.

The classical use of TiO_2 coatings and suspensions involve both oxidation and reduction at the particle surface. An aim of this work which has proved successful elsewhere [16] is to separate the oxidation process and the reduction process in order to harvest the current for a useful purpose . Previously, oxidation of 4-chlorophenol was performed at the photoanode while reduction of oxygen occurred at the auxiliary electrode of a three electrode system[16].

In this work a device is proposed to remediate wastewaters by oxidising the organics and lowering the COD, while a corresponding level of reduction happens at the other electrode and the substrate is molecular oxygen. The model compound is formic acid which has clean fast electrochemistry . In addition simple organic acids are products

of the decomposition of organic compounds in landfills and are frequently found in leachates.

Figure 1 shows the open circuit potential transient on exposure to light from the xenon arc source. The electrode was a carbon disk of diameter 3 mm coated with a composite layer of PVC and TiO₂. The negative shift of potential, characteristic of TiO₂ layers can be seen and the magnitude of the shift is not as big as can be found when oxygen is removed from solution. The negative shift in potential is due to promotion of electrons to the conduction band of the TiO₂. Oxygen, if present acts as an efficient electron acceptor for the photogenerated electrons. It can be seen in Figure 1 that this electrode, which can be prepared readily, behaves in a manner similar to other methods of layer deposition such as from Ti(IV) n-butoxide deposits [17], Ti metal oxidation or annealed TiO₂ nanoparticle deposits on indium tin oxide [12]. As such the presence of the PVC as a binder does not affect its behaviour and there is no annealing step required for an adherent layer. The PVC does not affect the electrical contact between the TiO₂ particles and the underlying carbon electrode. In order to optimise the coating thickness, different quantities of the TiO₂/PVC suspension (1, 2, 3, 4, μL) were applied to a carbon disk electrode and it was found that the best voltammetric response was obtained using 3 μL.

Figure 2 shows the cyclic voltammogram of a carbon disk modified with the PVC / TiO₂ composite in a three electrode system, in ambient laboratory light (A) and when exposed to light from the xenon arc lamp (B). It can be clearly seen that there is an enhancement of the current over a wide range of potentials associated with the enhanced oxidation of formic acid in solution. It can be seen that even though the TiO₂ is immobilised by PVC, that there still is an easy access of HCOOH to the electrode. An aim of this work is to harness this current along with facilitating the

removal of the organic material from the solution.. A proposed mechanism of the formic acid oxidation at the illuminated electrode is

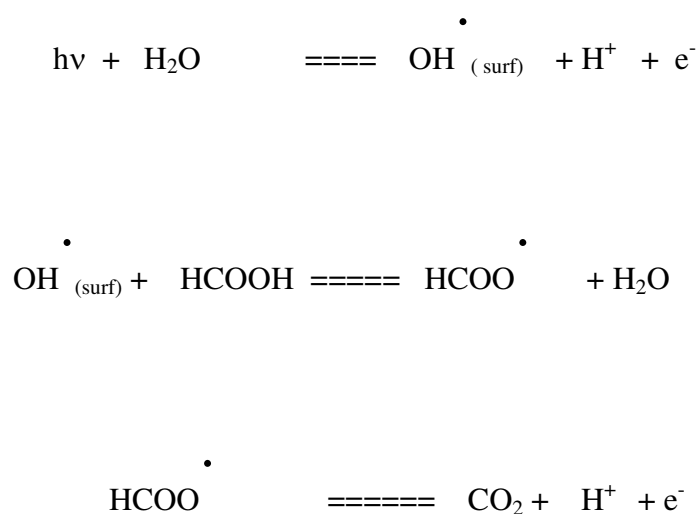


Figure 3 shows the current transient when a glassy carbon electrode plate (area = 4 cm²) is modified with a PVC/TiO₂ composite. Even at a moderate applied potential of 0.1 V, there is a dramatic increase in the current which appears to be a steady state kinetically controlled current. This photo-enhanced current has a rapid response and the limiting current is found to follow a Tafel behaviour with a linear relationship between ln(i) and the applied potential, E . There is considerable enhancement of the current making the proposal of a fuel cell a possibility.

When an optical filter, used to simulate solar radiation was employed, the current levels are typically 75% of those without the filter. Therefore it should be possible to use this system in practice using sunlight.

Figure 4 shows the behaviour of a fuel cell consisting of a TiO₂/PVC composite on a carbon plate (4 cm²) linked to an air electrode. On exposure to light there is an enhancement of the current even though there is only a small level of background

electrolyte. This cell was used to generate the data presented in Table 1. Notable features of Table 1 are as follows

(a) There is considerable enhancement of the current for the TiO_2/PVC composite on exposure to light in both formic acid and traditional methanol fuel cells which is not seen in the case of a platinum electrode as anode.

(b) There is a greater current using formic acid compared to methanol, when the electrode is exposed to light. This is markedly the case for relatively low concentrations of formic acid (0.01 mol dm^{-3}) compared to 5% Methanol with 0.1 mol dm^{-3} NaOH as electrolyte.

(c) Although the highest currents were obtained for high electrolyte concentrations, reasonable currents were obtained for 1.5 mmol dm^{-3} NaOH (currents that are 75% of the level of current for 0.1 mol dm^{-3} NaOH). This would be an important aspect for practical use where the electrolyte concentrations in natural samples may be low.

Figure 5 shows the decrease in the concentration of formic acid monitored chromatographically as a function of time for a fuel cell with a carbon electrode (4 cm^2) coated with the TiO_2/PVC composite as an anode and a Pt electrode (1 cm^2) as cathode. Typically the current level dropped from $70 \mu\text{A}$ to $10 \mu\text{A}$ over a period of 2 hours. The integral of the current yields a charge which would predict a decrease in formic acid concentration to $0.01 \text{ mmol dm}^{-3}$ after 120 minutes. This does not correlate well with the experimental results showing that the current generated is not specifically through the oxidation of formic acid. The concentration decreases linearly indicating a zero order reaction as has been found previously for HCOOH [12]. When a similar HCOOH solution was exposed to, there was no decrease in formic acid concentration over a period of two hours.

Conclusions.

This work describes the behaviour of electrodes coated using a simple method of casting a TiO₂ / PVC composite layer without any need for annealing.

A fuel cell with this novel electrode along with an air electrode can be operated in solutions where the electrolyte concentration is very small. This makes the system ideal for environmental samples.

Work needs to be carried out on the efficiency of the conversion using strong ambient sunlight to determine whether the cell is viable on a practical basis. A cell configuration would need to be designed to take into account high concentrations of organics to ensure that they do not absorb the light before it reaches the electrode surface.

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Figure Legends.

Figure 1. Open circuit potential transient for a carbon disk ($d = 3\text{mm}$) coated with PVC/TiO₂ composite. Potential measured with respect to a saturated calomel electrode. The solution is formic acid (10 mmol dm^{-3}) and the light source is 150W xenon lamp. The solution equilibrated with air.

Figure 2. Cyclic voltammogram for an electrode described in Figure 1 in 6 mmol dm^{-3} HCOOH in 13 mmol dm^{-3} KCl. (A) in ambient laboratory light and (B) exposed to 150W xenon lamp. Scan rate = 100 mVs^{-1}

Figure 3. Current transient at a carbon sheet (geometric area = 4 cm^2), where the electrode in a three electrode system was held at 0.1 V vs SCE on exposure to light from xenon light. The solution is 1 mmol dm^{-3} HCOOH in 0.1 mol dm^{-3} KCl.

Figure 4. A fuel cell consisting of a glassy carbon electrode coated with the composite acting as an anode (area = 4 cm^2) along with a porous air electrode as cathode in a one compartment cell with a solution of 1 mmol dm^{-3} HCOOH and 1.5 mmol dm^{-3} NaOH. The transient is on exposure to light causes a rapid rise in current.

Figure 5. Decrease in HCOOH concentration in a fuel cell consisting of a TiO₂/PVC anode (4 cm^2), a cathode which is a Pt sheet (1 cm^2) in 15 cm^3 of solution, exposed to 150 W xenon lamp.

Table 1. Current density of a fuel cell where the anode is either a TiO₂ /PVC composite or a Pt sheet with an air cell electrode as cathode, either exposed to light (Y) or not (N)

Anode	Electrolyte	Substrate	Light	Current density ($\mu\text{A cm}^{-2}$)
Pt	0.1 M NaOH	5% MeOH	Y	< 1
Pt	0.1 M NaOH	5% MeOH	N	< 1
Pt	0.1 M NaOH	0.01M HCOOH	Y	22
Pt	0.1 M NaOH	0.01MHCOOH	N	20
Pt	1.5×10^{-3} M NaOH	5% MeOH	Y	< 1
Pt	1.5×10^{-3} M NaOH	5% MeOH	N	<1
Pt	1.5×10^{-3} M NaOH	0.01M HCOOH	Y	20
Pt	1.5×10^{-3} M NaOH	0.01M HCOOH	N	20
C/TiO ₂ /PVC	0.1 M NaOH	5% MeOH	Y	45
C/TiO ₂ /PVC	0.1 M NaOH	5% MeOH	N	2
C/TiO ₂ /PVC	0.1 M NaOH	0.01M HCOOH	Y	100
C/TiO ₂ /PVC	0.1 M NaOH	0.01M HCOOH	N	0.5
C/TiO ₂ /PVC	1.5×10^{-3} M NaOH	5% MeOH	Y	28
C/TiO ₂ /PVC	1.5×10^{-3} M NaOH	5% MeOH	N	3.5
C/TiO ₂ /PVC	1.5×10^{-3} M NaOH	0.01M HCOOH	Y	75
C/TiO ₂ /PVC	1.5×10^{-3} M NaOH	0.01M HCOOH	N	3.5

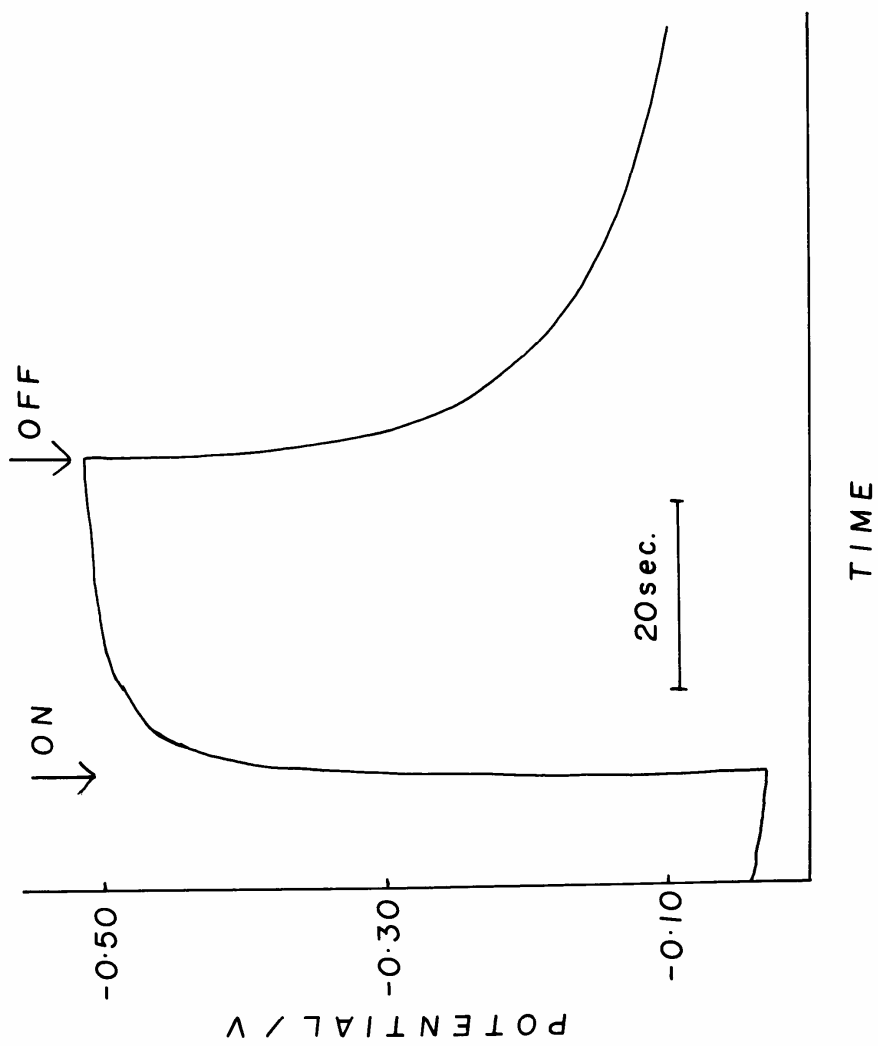


Figure 1

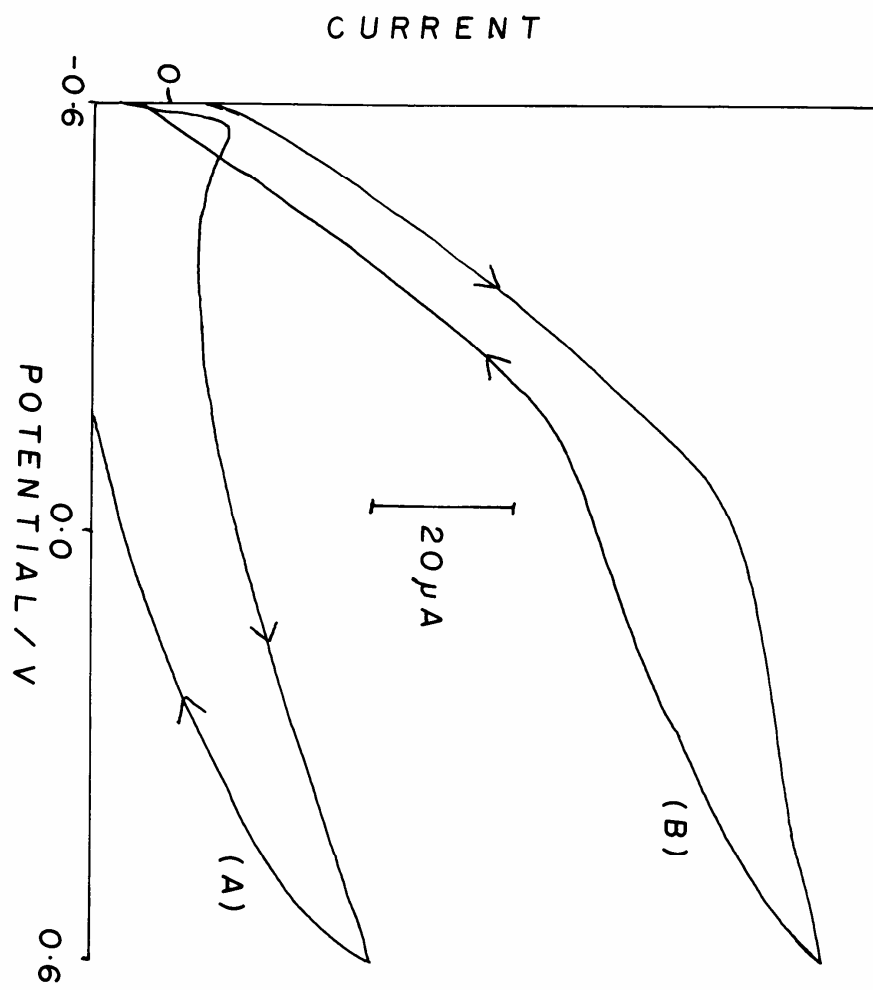


Figure 2

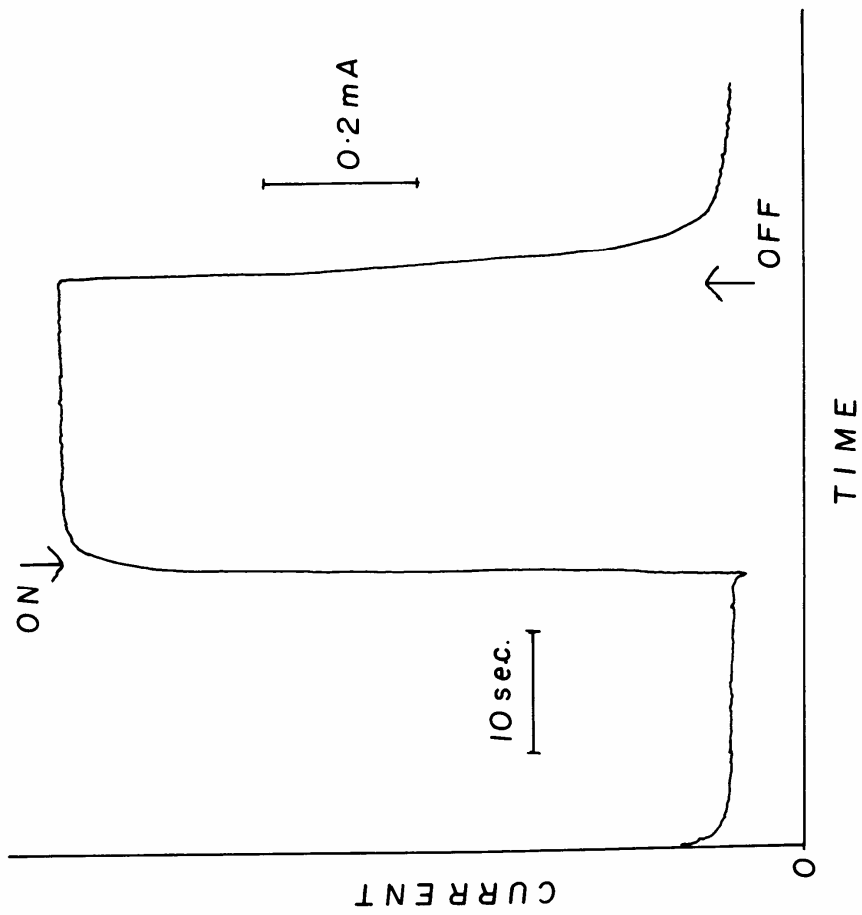


Figure 3

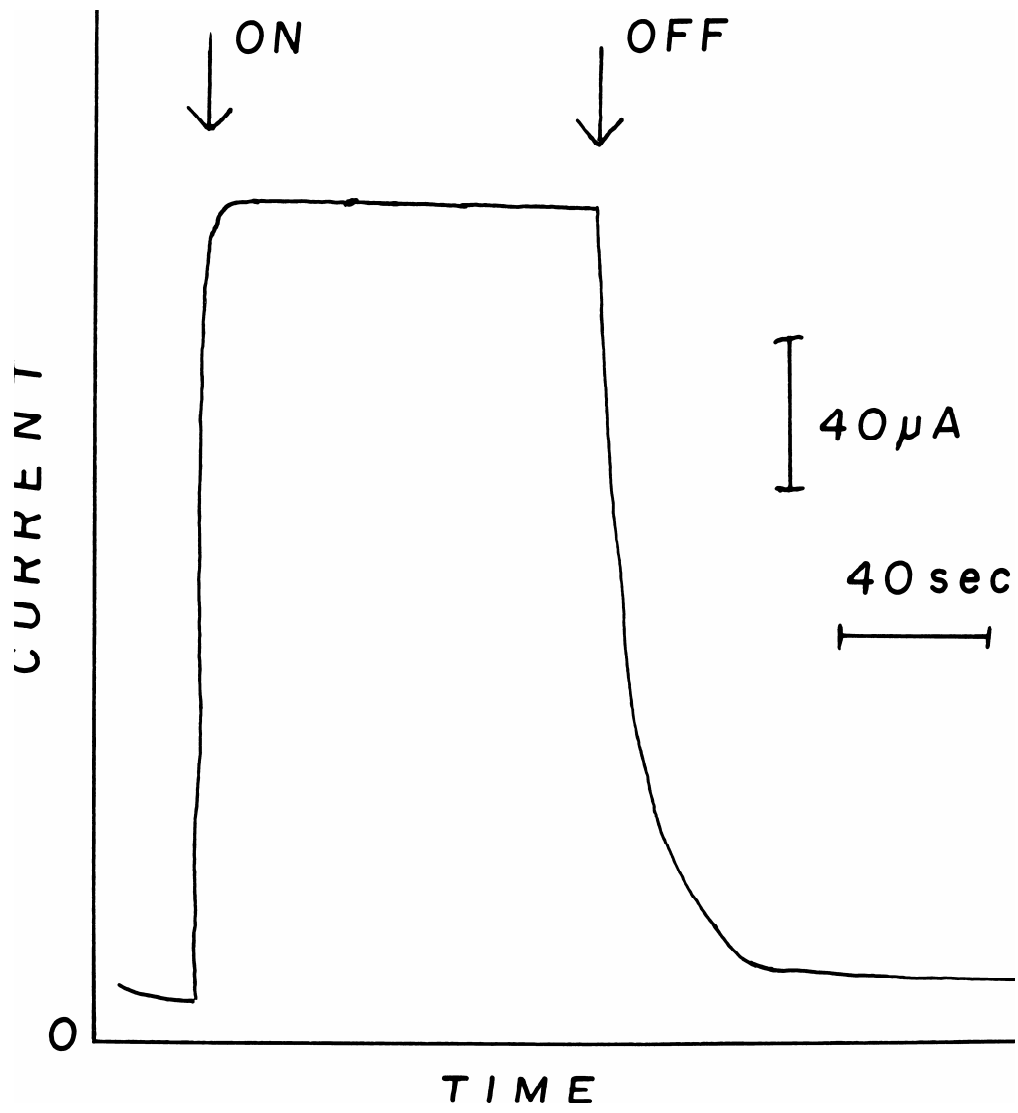


Figure 4

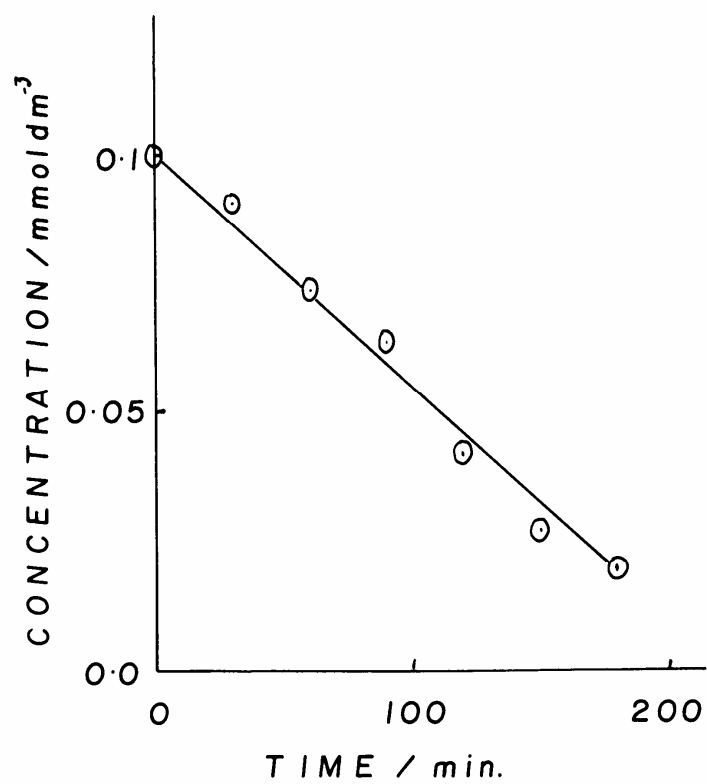


Figure 5