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An Experiment Using A Simple Photoassisted Fuel Cell Designed to Remediate
Wastewater

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Introduction.

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 [1-5]. 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[5]. Doped TiO_2 layers have been used in a three electrode system for formic acid degradation[6].

In this work, the system uses an electrode coated with TiO_2 to oxidise organic compounds, along with an air electrode as a cathode where oxygen reduction occurs. In this case the light source is a tungsten source which is readily available and safe in comparison with UV sources. This practical demonstrates that it is possible to directly degrade organics in wastewater, assisted with light, and will also generate a current. So there is an advantage from two fronts. One is the lowering of chemical oxygen demand, COD and the other is the yield of current which may be used for a purpose such as preventing corrosion in remote pipelines.

Experimental

Composite layers were prepared by preparing a suspension of TiO_2 (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 0.162 cm^3 of this suspension was coated onto a glassy carbon electrode, (3.8 cm^2) and dried at room temperature.

The light source was a standard 60 W Tungsten lamp (Tesco, Dublin), Glassy carbon sheets (Tokai) and Platinum foil (Goodfellow) were silver epoxied 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, Oxford, UK) consisting of a porous platinum electrode of geometric area equal to 9.6 cm^2 . 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.

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 where the substrate is molecular oxygen. The model compound for degradation 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 cyclic voltammogram of a carbon disk modified with the PVC / TiO_2 composite in a three electrode system, in ambient laboratory light (A) and when exposed to light from the 60 W tungsten 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. Furthermore, even though the TiO_2 is immobilised by PVC, that there still is an easy access of HCOOH to the electrode.

Figure 2 shows the photoactive behaviour of a fuel cell consisting of a TiO_2/PVC composite on a carbon plate (3.8 cm^2) linked to an air electrode. On exposure to light there is an enhancement of the current. The current increases from $4 \mu\text{A}$ to $26 \mu\text{A}$ on exposure to the light which is not as energetic as UV light, typically used in photoelectrochemistry[7]

Figure 3 shows the decrease in the concentration of formic acid monitored chromatographically as a function of time for a fuel cell with a carbon electrode (3.8 cm^2) coated with the TiO_2/PVC composite as an anode and a Pt electrode(4 cm^2) as cathode. Typically the current level changed from $0.2 \mu\text{A}$ to $0.9 \mu\text{A}$ over a period of 4 hours. The concentration decreases linearly indicating a zero order reaction as has been found previously for HCOOH [7]. When a similar HCOOH solution was not exposed to light, there was no decrease in formic acid concentration over the same period.

Discussion and Conclusion.

This work describes the behaviour of electrodes coated using a simple method of casting a $\text{TiO}_2 / \text{PVC}$ composite layer

A fuel cell with this novel electrode along with an air electrode can be operated in solutions with a readily available light source.

This system demonstrated that even with quite low energy light sources, that an enhancement of the oxidation efficiency is possible. This would encourage the development of systems in sunny climates, where there is continuous sunshine; (obviously not Ireland!). Much work has to be done for the development of optimised

cell configurations that would be compatible with large water masses. Most simply the device would float on the surface of the water in order to employ the sun's radiation and work is ongoing in the area.

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Figure Legends.

Figure 1. Cyclic voltammogram for a carbon disk electrode (area = 0.071 cm^2 in a solution on 6 mmol dm^{-3} HCOOH in 0.1 mol dm^{-3} KCl. (A) in ambient laboratory light, (B) exposed to 60 W tungsten lamp, scan rate = 100 mVs^{-1}

Figure 2 A fuel cell consisting of a glassy carbon electrode coated with the composite acting as an anode (area = 3.8 cm^2) along with a porous air electrode as cathode in a one compartment cell with a solution of 10 mmol dm^{-3} HCOOH and 0.1 mmol dm^{-3} KCl. The transient is on exposure to light causes a rapid rise in current.

Figure 3 Decrease in HCOOH concentration (initial concentration = 0.01 mol dm^{-3}) in a fuel cell consisting of a TiO_2/PVC anode (4 cm^2), a cathode which is a Pt sheet (4 cm^2) in 15 cm^3 of solution, exposed to 60 W tungsten lamp.