

ELECTROCHEMICAL PROCESSING OF SOLID WASTE

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SEMI-ANNUAL REPORT
JULY 1987

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(NASA-CR-181128) ELECTROCHEMICAL PROCESSING
OF SOLID WASTE Semiannual Report, Jul. 1987
(Texas A&M Univ.) 48 p Avail: NTIS HC
A03/MF A01

N87-25443

CSCL 07D

Unclas
G3/25 0082678

SUBMITTED TO

NASA JOHNSON SPACE CENTER
HOUSTON, TEXAS 77058

NASA GRANT - 1987 NAG - 192

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1.1 Electrochemical Recycling For Manned Space Exploration

This report describes an investigation of electrochemical waste treatment methods suitable for closed, or partially closed, life support systems for manned space exploration. The technique being investigated involves the electrolysis of solid waste where the aim is to upgrade waste material (mainly fecal waste) to generate gases that can be recycled in a space station or planetary base environment. This technique represents a means of converting waste materials to a more convenient form and bring about a reduction in amount of waste material needed to be stored during a mission. Furthermore, large quantities of hydrogen will be generated during the electrolysis which can be recycled to regenerate electrical energy in a fuel cell. This approach is aimed at minimizing the amount of resupply necessary to maintain manned space station leading to the development of recycling techniques that will facilitate manned exploration of deep space.

In the past, a number of electrochemical options have been put forward for waste management in closed environment life support systems. During the 1960's several promising studies were performed on biochemical fuel cells (1,2,3). In general, these devices utilize a living systems (microorganisms or purified enzymes) to effect partial degradation of the waste material. The products of the biological reactions are further

degraded in an electrochemical (fuel cell) system to provide chemicals that can be recycled, also electricity is generated for use in the space vehicle (4). Much of the research in this area was discontinued after 1970 even though some biochemical fuel cells were marketed commercially (see 5). Recent advances (6) seem to indicate that specialized biochemical fuel cells are candidate systems for use in life support and are worthy of further research.

More recently, the electrolysis of urine has been investigated as a means of water recovery and waste handling for application in space exploration (7,8) and demonstrated that carbon dioxide and nitrogen was regenerated electrochemically from organic waste.

The electrolysis of solid waste materials as a means of waste management for life support is a new concept. The concept under investigation was derived from work of 2 origins. Firstly, work performed by the present author (9) showed that complex polymers of biological origin such as starch and cellulose can easily be broken down to yield CO_2 with 100% current efficiency¹. Although the potential application of this discovery to solid waste management in space vehicles was noted at the time, there has been little follow-up to this work. A more complete account of scientific literature concerning biopolymer electrolysis will be given in Section 2.

¹current efficiency is the % of the total current that was involved in the formation of the product of interest

The second area of electrochemical research that has contributed to the concepts and methodology outlined in this report is the liquefaction and electrolysis of coal. Coal is a polymer derived from biological material that is quite insoluble but which, under the right conditions, can be broken down to CO₂ (10,11). This type of technology is highly relevant to the approach being undertaken in this report and an account of the scientific literature concerning coal electrolysis will be given in Section 2.

1.2 The Concept of Waste Electrolysis In Closed Life Support Systems

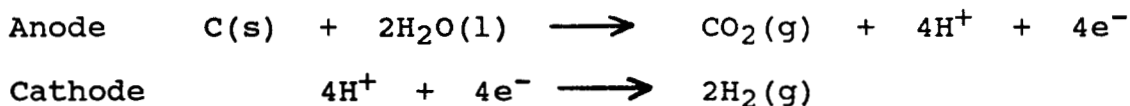
The purpose of this section is to outline the general features of electrolysis and to illustrate how, in principle, this concept may be adapted to function as an integral part of a regenerative life support system.

Electrolysis represents a means of driving chemical reactions using electrical energy from an outside power supply (see 12). During electrolysis, a continuous flow of electrons is maintained between two electrodes separated by an electrolyte. Electrons leave the cathode, at the electrode/electrolyte interface and at the second interface, the anode, electrons are taken up from particles in solution; these particles therefore become oxidized. The electrical circuit is completed by the two-

way ionic flow in the electrolyte. By controlling both the rate of electron transfer across the interface and the energy of the electrons it is possible to control the chemical transformations that are occurring each of which will occur when electrons of a specific energy are available. A particularly relevant description of this technique is given by Chum and Baizer (see 12 Chapter 2) who deal specifically with the techniques involved in biomass electrolysis.

Thus, the aim of this project is to degrade organic waste materials, mostly fecal waste, to CO_2 by oxidizing the waste in the anodic compartment of an electrochemical cell. The cathodic compartment will contain a strong acid and hydrogen will be evolved. The concept is illustrated schematically in Figure 1.

In general terms, the overall reactions will take the following general form:



It should be stressed that the bulk of the carbon undergoing oxidation will not be in its elemental state. Moreover, these reactions simulate the overall reactions and do not go into specific detail. It is indeed likely that there will be products of the oxidation other than those implied by the above formula especially since much of the waste material will be in the form of complex biological polymers (see section 2.1). Of particular

concern will be the synthesis of nitrogen-containing chemicals.

During biomass electrolysis, hydrogen will be evolved continuously from the cathodic compartment. It is likely, that hydrogen can be obtained in this manner at lower cell potentials than the reversible potential (ie 1.23 V) for the electrolysis of water. Indeed hydrogen can be obtained at potentials in the region of 0.8V using lignite slurry as anodic depolarizer (14). Thus, the supply of hydrogen, which can be used to generate electricity in efficient hydrogen/oxygen fuel cells, will off-set considerably the energy consumed in the electrolysis.

An important feature of this technique is that the potential at which the electrolysis is occurring can be selected (the method by which this is done is given later in the report) such that particular reactions can be enhanced. Since the type of waste to be degraded is likely to vary considerably during a mission (see Section 2.1), a flexible system can be adopted to provide the optimal potential for the degradation of the particular type of waste available. In addition, these reactions will be enhanced by the use of elevated temperatures (ie up to 100 °C). Even so, in comparison with incineration for example, electrolysis is a low temperature waste treatment method which possibly can be more easily engineered into a small space vehicle than higher temperature devices.

The technology being developed in this report is aimed at investigating a waste treatment method for all types of solid organic waste that are likely to accumulate in a space

environment during a manned mission. Urine and fecal waste will be major component of waste material accumulated during a manned mission and the chemical composition of the type of material is discussed below. Nevertheless, other types are waste material could be candidates for treatment by this method. Inedible material from higher plant components of a regenerative life support system could constitute a major source of waste in the future; the electrolysis of plant biomass is an established research area. Furthermore, plastics (used in food packaging etc.) based on biodegradable polymers such as cellulose, may be treated in this way.

It is worthwhile discussing what processes would utilize the CO_2 in a regenerative system since, these components would have to be integrated with the electrolysis system. Photosynthetic systems can be used to fix CO_2 and thereby act as a potential food source, however, the growth of higher plants (or photosynthetic microorganisms) in microgravity may not be feasible for some time. An alternative system exists which involves the regeneration of oxygen from CO_2 , for crew cabin resupply, by the Bosch reaction. Devices based on this principle are being fabricated at the present time for use in life support systems (15,16).

For deep space manned missions, where resupply becomes impractical, the recycling of nutrients will be a primary concern. The research approach described in this report has evolved to investigate the efficiency of recycling nutrients for

regenerative life support systems. An important consideration of this work is how to maximize the amount of material that can be recovered as reuseable compounds by this method. Along these lines the following questions are important: (a), to what extent electrolysis can be used to reduce the weight of the waste material? (b), is the electrolyzed waste less corrosive and less biologically active than untreated waste? (c), does the electrolysis eliminate the potentially pathogenic microorganism content of the waste?

2.1 The Chemical Nature of Fecal Biomass

A survey of the chemical nature of fecal matter has been carried out. It is clear that the components of fecal matter can vary enormously depending upon diet and from individual to individual. In general (see 17,18), fecal waste consists of 75% water and 25% solid matter. Of the solid matter, 30% is composed of bacteria, 20% is composed of fat, 10-20% is inorganic matter and 30% consists of undigested fiber material mostly cellulose. Fecal matter may also contain small amounts of protein, the dried constituents of digestive juices and bile pigments. The following table gives the formula for the chemical composition of some of the major components of fecal matter (19,20).

<u>Component</u>	<u>Formula</u>
Bacterial Cells	$\text{CH}_{1.666} \text{N}_{0.2} \text{O}_{0.27}$
Fat (eg oleic acid)	$\text{C}_{18} \text{H}_{34} \text{O}_2$
Fiber (eg cellulose)	$\text{C}_6 \text{H}_{10} \text{O}_5$
Protein (eg casein)	$\text{CH}_{1.92} \text{O}_{0.505} \text{N}_{0.23}$

It is important to note that this list does not include other constituents, such as chlorine and sulfur, which are likely to be present in significant amounts.

Since the objective of this work is to electrolyze cellulose and bacteria which together make up about 60% of fecal matter the structure of some of the polymers likely to be present is given in Figure 2. Of particular interest is the type of polymers associated with bacteria where much is associated with cell wall material. The supporting cell wall of a typical gram-negative has an outer layer of proteins, phospholipids and lipopolysaccharides (21). The lipopolysacchides usually present consist of a glucoseamine disaccharide esterified with C₁₂, C₁₄ and C₁₆ fatty acids. Other constituents include a branched chain of glucose, galactose and of N-acetyl glucoseamine. These components are attached to a supporting "skeleton" of the peptidoglycan murein which makes up 10% of the dry weight in gram-negative bacteria (30-70% of the dry weight in gram-positives).

2.2 Biomass Electrolysis

Considerable research has been conducted into the electrolysis of biomass that has originated from plant material. In this section, aspects of the electrochemistry of biopolymers (ie polysaccharides) will be reviewed since a significant

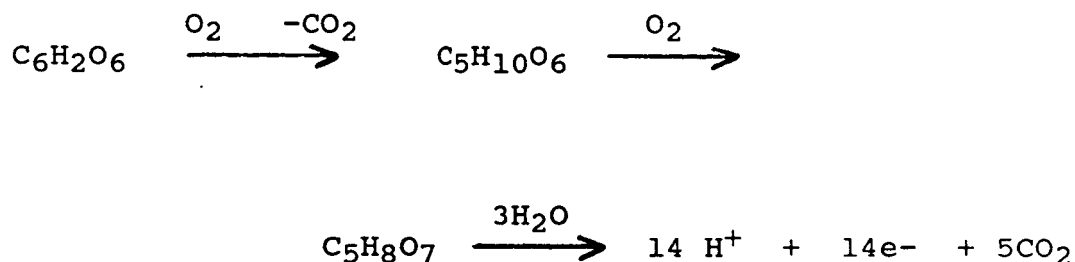
proportion of fecal biomass will be constituted by this type of material.

A number of older studies are worthy of comment beginning with Oertel (22) who showed that cellulose dissolved in 16% potassium chloride can be degraded into lower molecular weight entities. By varying electrolyte concentration, current density and time, gel gums with adhesive properties could be obtained. Cellulose electrolysis in 0.5 M H_2SO_4 saturated with $[(\text{NH}_4)_2\text{SO}_4]$ also led to considerable degradation of cellulose (23). Hemicelluloses have been degraded in 5M NaOH (2% wt/wt) to CO_2 and H_2O and at the cathode, pure hydrogen was evolved (24). Neuberg (25) has investigated the electrolysis of 60 organic compounds including starch, mannitol and raffinose and found that after many days of electrolysis, the polymers were fragmented into their constituent sugars. The production of hydrogen by glucose-depolarized water electrolysis has been proposed using Pb-Ru anode leading to glucose oxidation at less anodic potentials (26).

Of particular relevance to the present work is the investigation performed by Bockris et al concerning the possibility of utilizing plant waste materials based on polysaccharides as oxidants in fuel cell systems (9). Initially, simple carbohydrates were investigated such as sucrose, cellobiose (β -D-glucose dimer) and glucose. The electrolysis was performed in 40% H_3PO_4 /5N NaOH at temperatures 80-100°C. A platinized platinum gauze (52 cm^2) was used as the anode. It was

found that the reactivity decreased for molecules of increasing complexity. Nevertheless, it was found that cellulose can be broken down to CO₂ with a current efficiency of around 100% and that 2 faradays were involved in the evolution of 1 mol of CO₂.

The following stoichiometric equation for the reaction was suggested; the monomer glucose is shown for simplicity.



In this scheme, 2.3 farads would be used per mole of CO₂ evolved, which agrees with experimental results. These workers drew attention to this concept as a possible means of waste management for space vehicles.

2.3 Coal Electrolysis

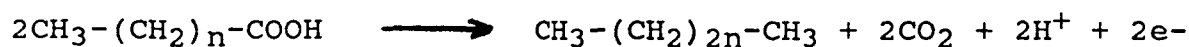
The technology associated with the electrolysis of coal is relevant to the present project. Coal is a complex and insoluble polymer that is in some ways similar to the types of waste material that are the subject of this report, therefore, studies of coal electrolysis represent a guide to biomass electrolysis.

Coal electrolysis represents a means of obtaining hydrocarbon fuels and hydrogen (10,11,14,27). The technique usually involves placing a coal slurry in the anodic compartment of an electrochemical cell (11). During the electrolysis the coal is oxidized to organic compounds in solution some of which are of potential value as fuels (10,11). In addition, hydrogen is evolved from the cathode (14). Initial work on lignite slurry showed that the evolution of hydrogen occurred at potentials about 60% lower than those normally required for water electrolysis and that no oxygen evolution was observed (14). These workers paid little attention to the anodic products. Subsequent work has shown that the high oxidation currents were due to the oxidation of dissolved Fe^{2+} (28). Furthermore Park (29,30), discovered a secondary reaction, the oxidation of coal particles by Fe^{3+} in solution; the Fe^{3+} produced in the reaction was subsequently reoxidized to Fe^{3+} at the electrode surface. Recent work by Taylor et al has provided further information concerning the use of redox couples to mediate the oxidation of coal slurry (31).

Work performed in this laboratory showed that hydrocarbons (C_{18} - C_{19}) are formed in the anodic compartment during oxidation after the electrolysis had been performed for 5 hours (11). Platinum electrodes were used and the lignite was present at a concentration of 0.6g/ml and electrolyzed in 5M sulfuric acid.

Current/potential measurements (see section 3) were performed to determine the potentials for the maximum oxidation rate of the

coal prolonged electrolysis was then performed at these potentials. An assessment of the reaction taking place are likely to include the Kolbe reaction given below.



This reaction involves the dimerization of 2 organic molecules and gives rise to CO_2 . The reversible potential for the Kolbe reaction for acetic acid/acetate is -0.40 V but at higher temperatures reduction in the overpotential may occur (11).

However, after prolonged electrolysis of several days, no compounds were detected in solution having been oxidized to CO_2 (11).

Major research areas concerning coal electrolysis are (a) methods to improve solubility of coal and, (b) the use of redox mediators to enhance the oxidation process in solution.

3.1 Rationale Behind Present Technical Approach

The survey of fecal biomass (section 2.1) demonstrates the complex nature of this type of human waste; furthermore the relative proportions of the major constituents will vary between individuals and during the course of a mission on a day-to-day basis. Nevertheless, the four major components of fecal biomass have been identified as lipid, bacteria, cellulose (fibre) and protein. The approach being undertaken at present is to take each of these individual components in turn and establish the optimal conditions for CO₂ regeneration. From this approach, a fundamental understanding of parameters such as, current density, cell potential, electrolyte composition, temperature and pretreatment procedures can be established thereby enhancing CO₂ production from each of the constituent chemical groups. Although electrochemical oxidations of organic material has been studied extensively, in all experiments, the complete oxidation of the organic to CO₂ is always avoided. Moreover, most studies of this type aim to partially degrade the material (eg plant biomass or coal) to obtain intermediates that may be of commercial value. The work plan below describes the technical approach to developing electrochemical methods for generating CO₂ from waste material; the plan also represents the order in which the tasks are being performed.

3.2 Lipid Electrolysis

To establish methods for CO₂ generation from organic compounds, the following model compounds will be investigated: (a) acetate; (b) propionate; (c) oxalic acid; (d) caprilic acid; (e) palmitic acid; and (f) oleic acid. The rationale behind this approach is to begin with simple molecules and progress to more complicated ones such as oleic acid which is typical of some chemicals found in fecal matter. The experimental techniques that will be used, as-well-as the rationale behind their use, are described below.

Current/Voltage Studies

In these experiments the change in current (i) as a function of potential (E) will be determined. Specifically, the applied potential on the working electrode will be increased (in a positive direction) at a constant rate and the corresponding values of current are recorded. A plot of i versus E will show current peaks corresponding to the potential at which the maximum rate of oxidation of the organic substance is occurring. These experiments will be performed for each of the compounds given above. This method represents a convenient means to screen material (eg.to determine appropriate reaction conditions); the electrolysis can then be performed at the potentials determined for the reaction.

Constant Current/Constant Potential Electrolysis

These experiments are performed over longer time periods than the voltammetry described above. Constant potential electrolysis is where the working electrode (ie the anode in these experiments) is maintained at a constant potential, and the magnitude of the current, as a function of time, is measured. Using this method, the number of Faradays required to complete the electrolysis of 1 mole of substrate can be determined. Also, selective oxidation of different chemical species can be performed. During constant current electrolysis, the potential of the working electrode will vary with time as the concentration of substrate decreases; thus, selective oxidation (or reduction) would be difficult. Therefore, batch electrolysis at constant current can give quite different products than constant potential electrolysis.

Product Analysis

The gaseous products resulting from electrolysis will be analyzed using gas chromatography. From a quantitative assessment of the reaction products, coupled with information of the current that has flowed during the electrolysis, the current efficiency for CO₂ production can be assessed. Information concerning the reaction mechanism can be obtained in this way. Analysis of the constituents of the liquid phase will be performed when complex materials (eg higher fatty acids are being

electrolysed.

Conditions for Substrate Oxidation

For each of the test compounds given above, the following parameters will be varied to obtain information on the optimal conditions for CO₂ regeneration: (a) temperature; (b) pH; (c) supporting electrolyte; and, (d) current density.

3.3 Cellulose & Protein Electrolysis

Polymers like cellulose that are based on polysaccharides will be make up a large proportion of solid material in feces. Experiments will be conducted which are based on the methodology described in the previous section to determine the conditions for CO₂ generation (ie current/voltage studies, electrolysis & product analysis). Given that these large molecules are less electroactive than those molecules discussed in the previous section, pretreatment procedures to enhance material solubility will be important. In particular, the choice of electrolyte may be crucial; for instance, it has been shown that the reactivity of carbohydrates is higher in alkaline rather than in acid media (9) and cellulose, used in this study, was more soluble in alkali.

3.4

Bacteria Electrolysis

Bacteria will constitute a large fraction of human fecal matter. Chemically, bacteria will be made up of complex biological polymers, much of which will be associated with the cell wall material. The planned approach is to conduct experiments on the electrolysis of bacterial cultures. Bacteria which are typical of the flora of human gut (eg. Escherichia coli) will be grown and harvested. The growth phase of the bacteria will be monitored since most of the bacteria present in fecal matter are likely to be in stationary growth phase. The research plan is to use the methodology described above to determine ways to oxidize bacterial material to CO₂. Methods to enhance the solubility of the bacterial components will be applied. In particular, the conventional means to bring about extensive structural disruption of intact bacteria is to subject the cell suspension to ultrasonic bombardment. A Fischer sonic 150 dismembrator will be used, a few minutes exposure to this type of treatment is usually sufficient to bring about extensive fragmentation of the cell wall and membrane components of bacteria. Prolonged sonication may greatly enhance the fragmentation and solubility of the polymeric material rendering it suitable for electrolysis.

3.5 Electrolysis of Fecal Material

Prior to the electrolysis of fecal material, experiments will be performed on mixtures of lipid, bacteria, cellulose and protein to represent typical contents of feces. The research will be performed using the methods developed in the experiments described above to optimize pretreatment and reaction conditions for CO₂ generation. Fecal material will then be electrolyzed; the reaction conditions will be an appropriate combination of those that have been developed in the aforementioned research approach. In section 2.3, the use of redox couples to enhance the electrochemical breakdown of coal was described (see 31). These compounds which may be inorganic eg $\text{Fe}^{2+}/\text{Fe}^{3+}$, $\text{Ce}^{3+}/\text{Ce}^{4+}$, $\text{Cu}^{2+}/\text{Cu}^{2+}$ or organic eg methylviologen or its derivatives may effect homogeneous oxidation reactions. These mediators will become reoxidized at the electrode and will recirculate in the electrolyte. Thus tests will be performed to determine if the presence of these mediators increase the oxidation current significantly.

Throughout these experiments, attention will be paid to (a) side reactions that occur and, (b) what nitrogen-containing products are formed. Furthermore, material from the liquid phase will be analyzed. Dry weight of the liquid phase will be assessed both before and after electrolysis to determine the extent to which the material has be degraded and the products in the liquid phase will be assessed after the completion of

electrolysis. This analysis of the residual material will be important in determining if the residual solid waste can be stored in a convenient form (ie. is in a less corrosive form and has minimal biological activity).

4.1 Reaction cell

The electrochemical cell that has built for these experiments is shown in Figure 4. It is constructed mostly from glass and is suitable for the collection and analysis of gaseous products and for the analysis of the reaction mixture. Water condensers are located above both the anodic and cathodic compartments to prevent the loss of volatile compounds. Before use, the cell and auxiliary glass-ware was soaked overnight in nitric acid solution which was followed by washing with triple-distilled water.

4.2 Electrodes

Three electrodes have been used as working electrodes, a large platinum gauze (100 cm²), a platinum foil (26 cm²) and a platinum wire (0.292 cm²). A platinum wire was used as counter electrode and a calomel electrode served as reference.

The platinum electrodes were cleaned by immersion in aqua regia followed by rinsing in triple-distilled water.

4.3 Equipment

A PYNE potentiostat (Model R.D.E.4) was used in the voltammetric and electrolysis studies described below; A schematic representation of the apparatus used in this investigation is shown in Figure 3. Current vs potential curves and current vs time curves were recorded on a Hewlett. Packard. XY recorder (model 7044.B). Gaseous phase CO₂ concentration as well as the concentration of other gaseous products (eg carbon monoxide, methane and ethane) was determined using a Varian (model 3400) gas chromatograph with a Carbosieve II column with a TDC detector. Helium was the carrier gas. Chromatograms were recorded using a H.P.3390A integrator which provided digital readouts of the retention times and integrated areas of the different peaks.

Liquid phase CO₂ concentration was determined from experimental values of CO₂ solubility from values given in the literature. Carbon dioxide solubilities at different temperatures, pH and pressures were obtained (see 36,37,38). To determine the concentration of CO₂ (assuming that the liquid phase is saturated before CO₂ is evolved in the gas phase) a value of 0.147 g of CO₂ per 100 g of solution was used.

4.4 Electrolyte solutions

Solutions were made up from triply distilled water using reagent grade chemicals.

4.5 Experiments on p-Phenylene diamine

These experiments were performed to establish procedures for conducting electrolysis on organic material and to test the performance of the reaction cell and equipment. The aim is to conduct both constant current and constant potential electrolysis on para-phenylene diamine (PPD) to determine the number of electrons involved in the overall oxidation of this compound.

Test procedures

Constant current electrolysis was performed with an electrode of large surface area, on a solution containing a known concentration of PPD; three stages are involved. Initially, potential sweeps of a solution of PPD is performed to establish the potential at which the oxidation occurs. In the second stage, the potential of the working electrode is set to the value corresponding to the oxidation peak for PPD (as determined by the above procedure) and the change in current with time is recorded on a strip chart recorder. The value of the current reaches a steady state (or limiting current) which is noted. The third

stage involves the constant current electrolysis. The value of the current for electrolysis is set approximately 3 times less than the value determined for the limiting current.

The procedure for constant potential electrolysis involves two stages only. Voltage sweeps are first performed to determine the oxidation peak for PPD as above. The next stage involves performing the electrolysis at that potential and the amount of current passed during the electrolysis is followed on a strip chart recorder.

In both these types of electrolysis, the amount of PPD oxidized during the experiment is monitored. This is achieved by placing a smaller electrode into the anodic compartment alongside the working electrode, however, the smaller electrode is connected to a potentiostat so that voltage sweeps can be performed. For simple charge transfer reactions where both the reactant and the product are soluble, the current peak for the reaction (i_p in amp cm^2 at 25°C) is related to the concentration of reactant according to the following equation (32).

$$i_p = 2.72 \times 10^5 \quad n^{3/2} \quad D^{1/2} \quad C^0 \quad v^{1/2}$$

where D is the diffusion coefficient, C^0 is the concentration in moles, v is the sweep rate in volts sec^{-1} (n is assumed to be 2 in this test procedure). Thus, in this procedure to determine

concentration, the electrolysis is halted briefly from time to time and potential sweeps are made using a second working electrode; since this electrode is small, negligible amounts of PPD are oxidized by this measurement. The decrease in peak height with increased time of electrolysis enables the amount of PPD being oxidized to be determined.

Results

All experiments were performed on a 2.0 mM solution of PPD containing 0.05M H_2SO_4 and 0.1M Na_2SO_4 . The electrolysis was performed using a platinum gauze working electrode (100 cm^2). A second working electrode (0.29 cm^2) of platinum was placed in the anodic compartment to determine the change in concentration of PPD.

For the constant current electrolysis, the potential sweep measurement (see Fig 5) showed that the oxidation peak of PPD occurred at 0.81 (vs NHE). The limiting current density at this potential (determined after 7.5 seconds) was 0.2 mA cm^2 . The solution was removed, the electrodes and reaction cell was cleaned thoroughly and a fresh solution was introduced. Constant current electrolysis was performed at a current density of 0.066 mA cm^2 . The change in concentration of PPD with time of electrolysis was determined from potential sweep measurements performed using the second working electrode. These results are shown in Fig 6.

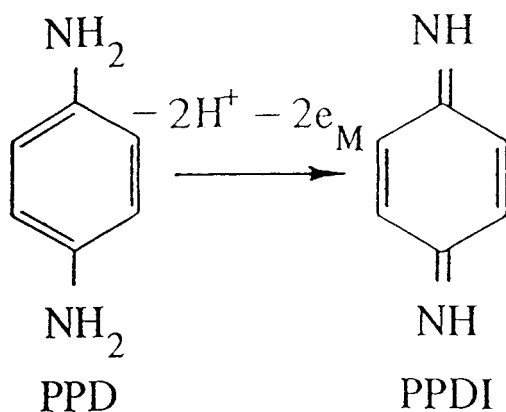
The results were calculated for the change in concentration

that occurred after 5 minutes of electrolysis. The number of moles oxidized (N) was calculated as 0.1×10^{-4} . The number of moles of substrate oxidised per mole electrons (n) is calculated below, where F is the Faraday constant, i is the current in amps, and t is the duration of electrolysis in seconds .

$$n = \frac{I \times t}{N \times F} = \frac{6 \times 10^{-3}}{0.1 \times 10^{-4}} \times \frac{3 \times 10^{-2}}{96500}$$

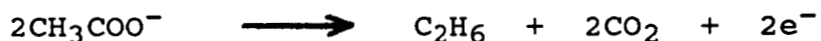
$$n = 1.86$$

This results suggests that 2 electrons are involved in the oxidation of one molecule of PPD. Similar results were obtained for the constant potential electrolysis. This suggests that the following reaction is taking place.



5.1 Acetate Electrolysis

Acetate represents a model compound for the study of CO₂ generation from organic compounds. These experiments aim to establish the optimal conditions for electrochemical CO₂ generation by the Kolbe reaction that involves the dimerization of 2 carboxylic acids and is given below (see 33).



Procedures

The experiments described below involve potential sweeps (ie cyclic voltammetry), steady state current determinations and constant current electrolysis. These techniques were described in the previous section. However in the experiments described below, the steady state current densities were performed by first sweeping the potential of the working electrode between 0.24 V and 1.24 (vs NHE) for several minutes to establish a clean platinum surface and remove oxide the oxide layer from the surface. The potential was then held at 1.24 V momentarily and the potential with then stepped up to the measuring potential. At this point, the current is monitored on an XY recorder in time

mode. The value of the steady state current was noted for a number of different potentials.

In these experiments, the current efficiencies were obtained by comparing the number of moles of each of the products of the Kolbe reaction, with the number of moles of electrons taken up. The products were analyzed quantitatively using gas chromatography.

Results

These experiments were conducted on a solution of 0.1M sodium acetate and 0.1M acetic acid. Figure 6 shows a cyclic voltammogram of the above solution. Before recording the voltammogram, the potential of the working electrode was swept continuously between -0.25 and 1.25 V (vs NHE) for 30 mins to activate the platinum surface; the solution was nitrogen-saturated. No current peaks due to the oxidation of acetate are detectable using this technique.

Using the method for determining limiting currents described above, the limiting current densities for a number of potentials has been determined. Figure 7 shows the logarithm of current density against potential for 3 concentrations of acetate. For the highest concentrations, the Tafel slope has an upper and a lower part; the transition between the parts of the curve occurs at around 2.2 V (vs SCE).

Constant current electrolysis was performed at 2 different current densities corresponding to points on the upper and lower

parts of the Tafel slope. The products of the electrolysis performed at 8 mA cm^2 , as analyzed by gas chromatography, are shown in Figure 8A where CO_2 and ethane are the main products. Also methane is formed in small amounts. In contrast, the electrolysis performed at a lower current density of 1 mA cm^2 gives rise to no ethane (see figure 8B) where the main products would seem to be oxygen and CO_2 with small amounts of CO being formed. Nitrogen was used to purge the reaction chamber and the gas collecting apparatus before the experiment and therefore is always present in the analysis. The potential of the working electrode did not deviate significantly during the course of the electrolysis. These results are summarized in table 1 which also shows the current efficiencies for CO_2 and ethane production under each of the reaction conditions.

It is clear from these results that the dimerization of acetate to form ethane and CO_2 is associated with high current densities (also see 34); at these high potentials the formation of oxygen is suppressed. The potential at which the Kolbe reaction becomes significant is sometimes called the crucial potential, in general, it occurs between 2.1 and 2.8 V (vs NHE) and may be different for different carboxylates (35).

5.2 Propionic Acid Electrolysis

Current potential transients have been performed on propionate at one concentration. The solution contained 1M propionic acid in 1M NaClO₄. A plot of log current against working electrode potential is shown in Figure 9. Constant current electrolysis was performed at 1 mA cm² and the gaseous product analysis is shown in Figure 10. The results show that this current density does not favour in Kolbe reaction since little CO₂ and ethane is evolved and that oxygen is being evolved in significant quantities. Experiments are under way to determine the products formed during electrolysis at higher current densities.

PERSONNEL

This material was prepared by: Dr John O'M. Bockris, Distinguished Professor and Principal Investigator; Dr G. Duncan Hitchens, Research Associate and member of the Regenerative Concepts (RECON) Group of TAMU; Dr Lamine Kaba, Research Associate.

ACKNOWLEDGEMENT

The authors would like to acknowledge that the guidance given to them by Mr Oran Nicks and by other members of the Space Research Center at TAMU has been invaluable.

FIGURES

Options for Waste Treatment
Electrolysis

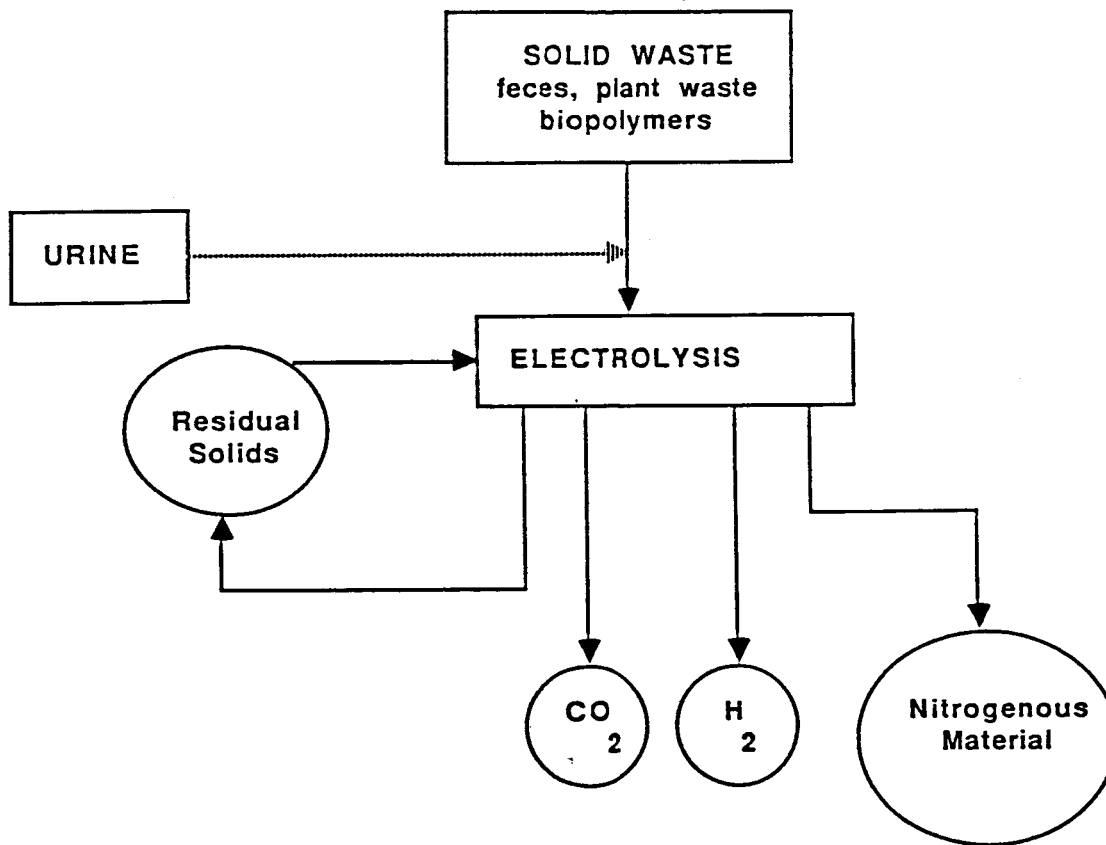
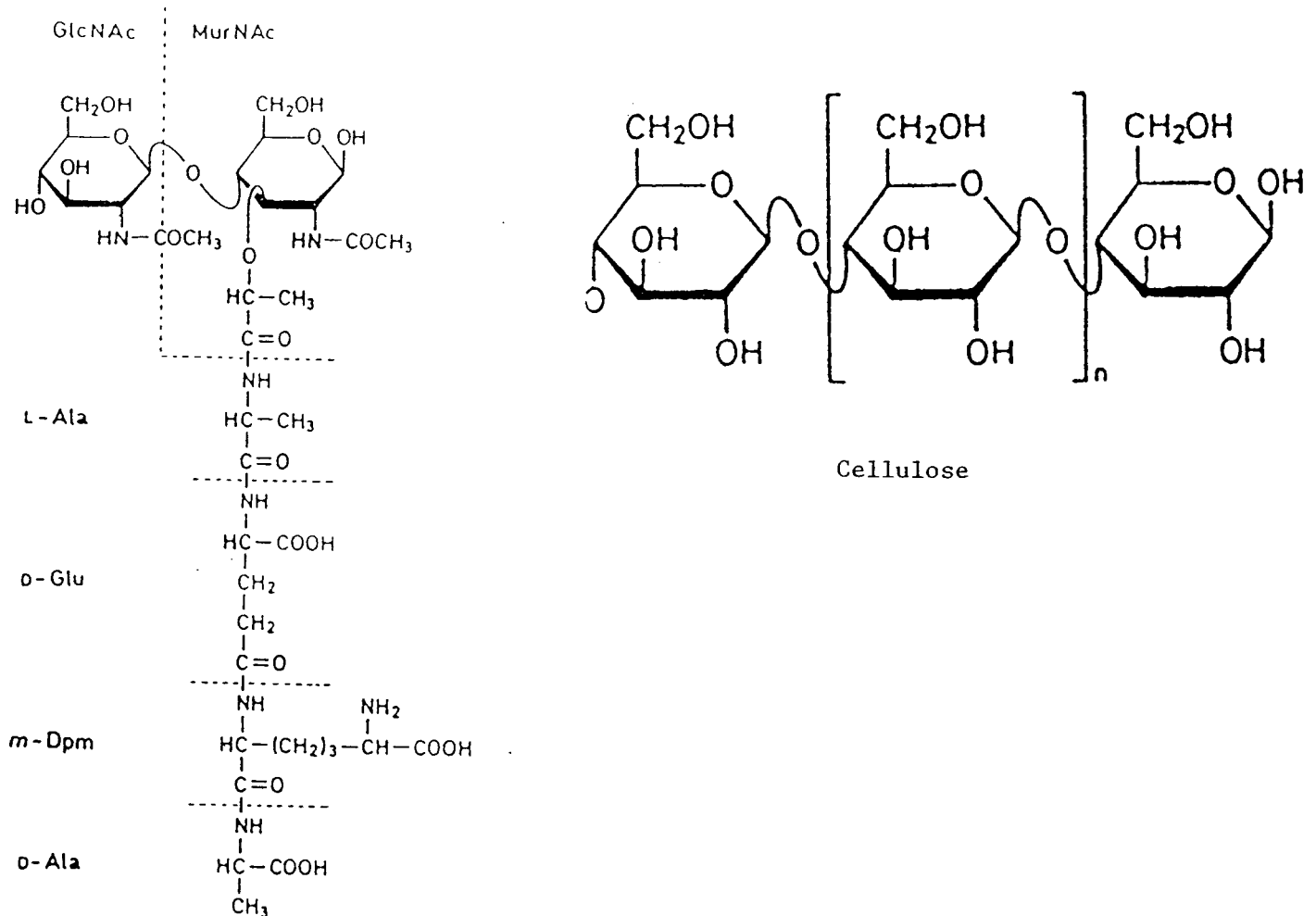


FIGURE 1

SOME BIOLOGICAL POLYMERS OF FECAL BIOMASS



Structure of the Murein of E. Coli

A typical bacterial cell wall component

L-Ala : L alanine acid

D-Glu : D glutamic acid

m-Dpm : m diamino pimelic acid

D-Ala : D alanine

GlcNAc : N-acetyl glucosamine

MurNAc : N-acetyl muramic acid

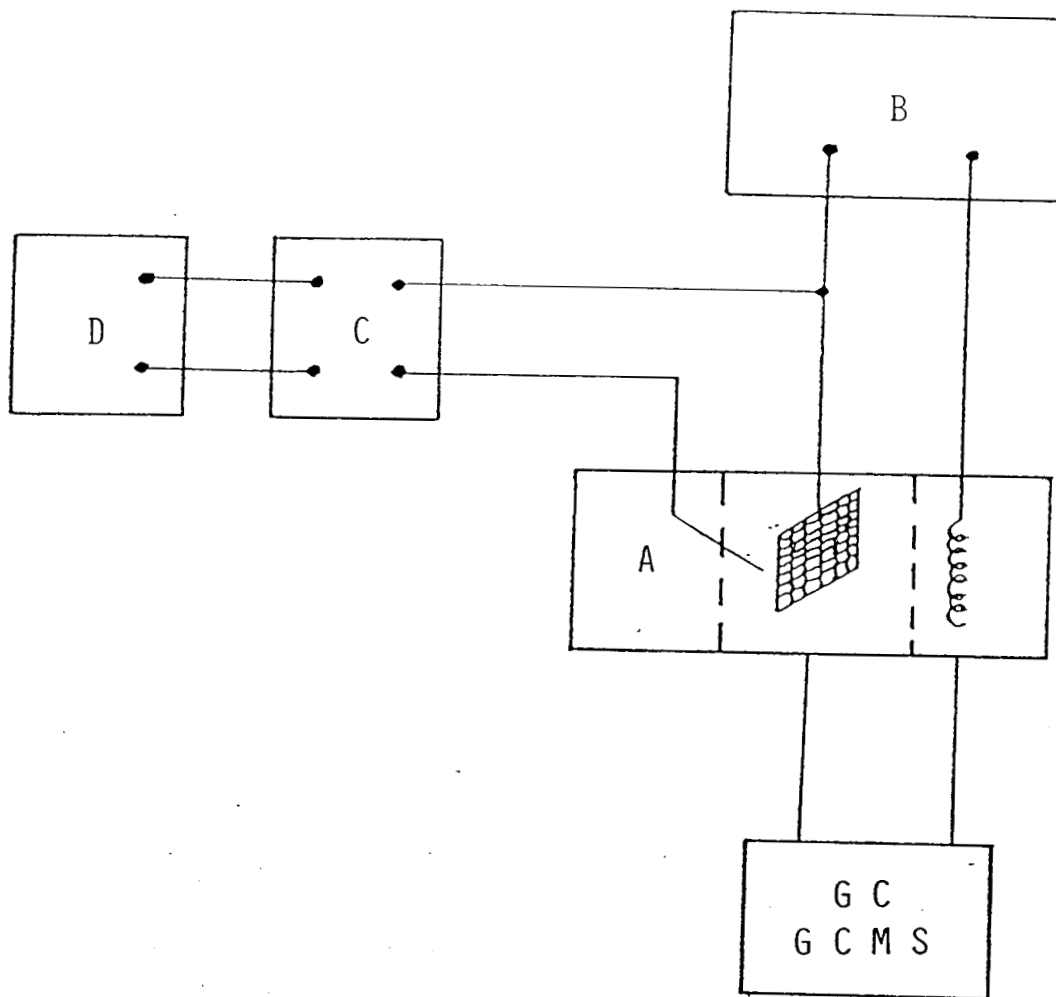
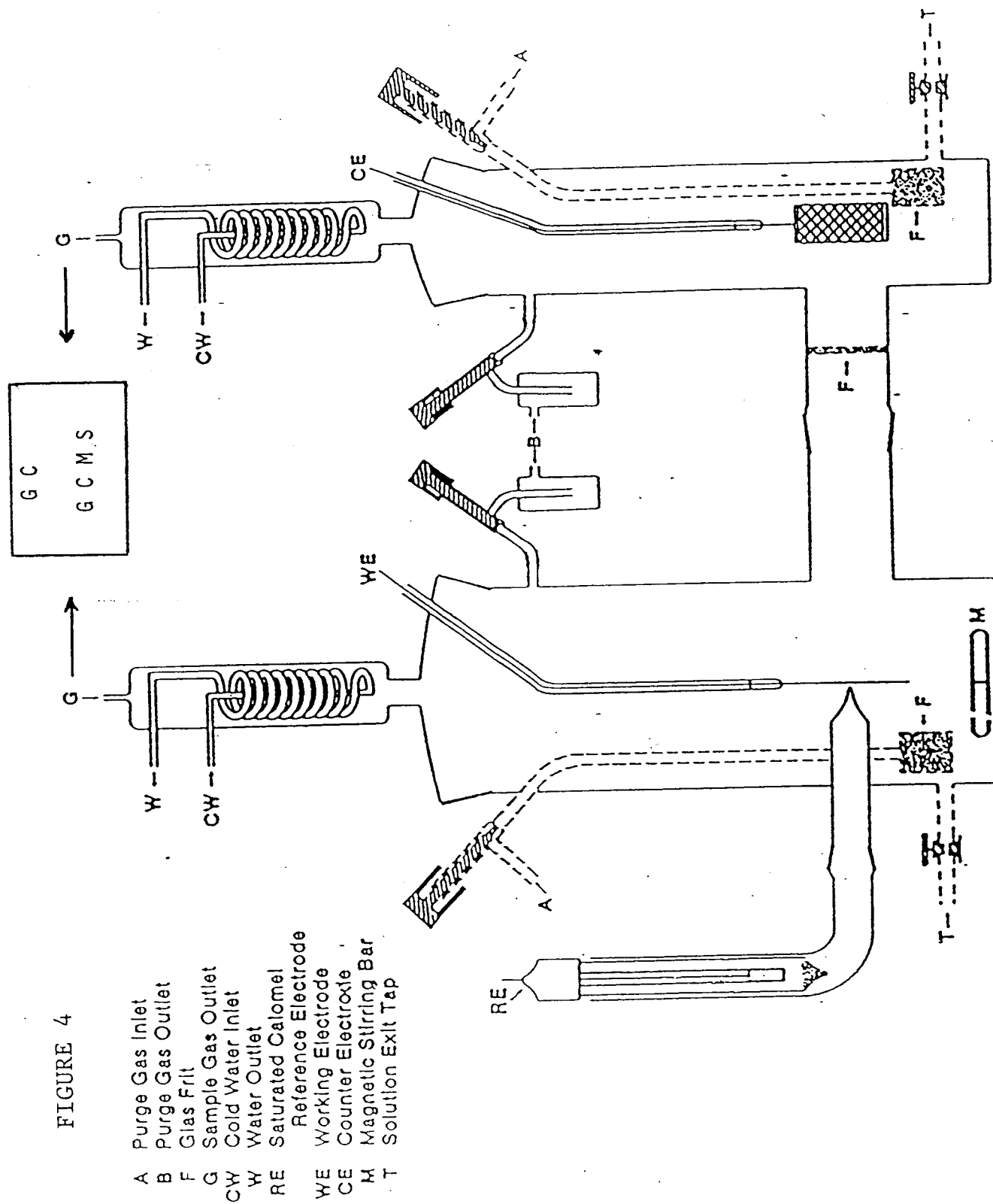


FIGURE 3

BLOCK DIAGRAM FOR GALVANOSTATIC CIRCUIT
 A- CELL; B- GALVANOSTAT; C- IMPEDANCE-
 MATCHING UNIT; D- OSCILLOSCOPE OR STRIP-
 CHART RECORDER

FIGURE 4



SCHEMATIC DIAGRAM OF THE ELECTROLYSIS CELL

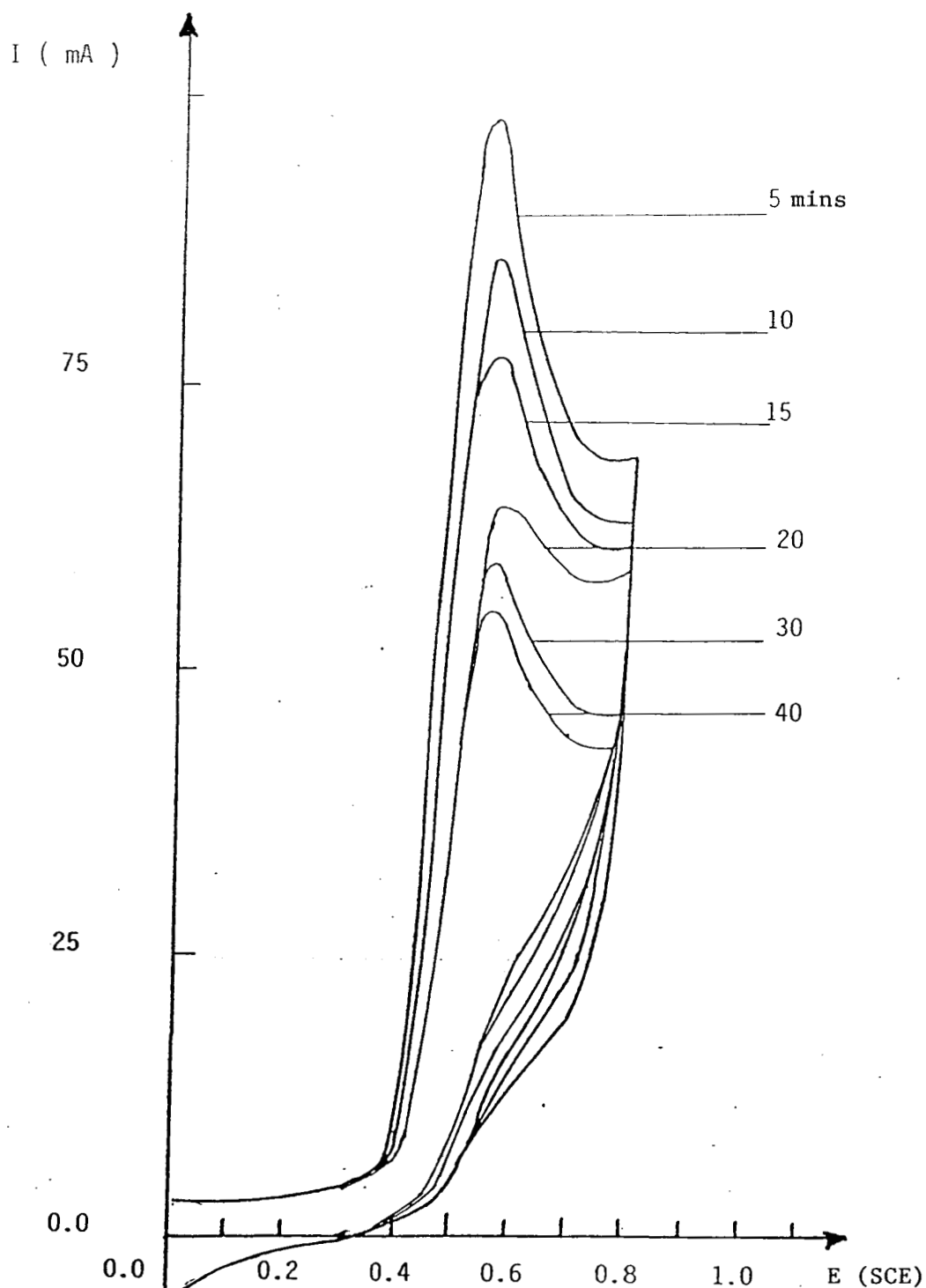


Fig 5

CYCLIC VOLTAMMOGRAM OF 2 mM P-PHENYLENE DIAMINE
IN 0.05 M H_2SO_4 , 1M Na_2SO_4 , SWEEP RATE 40 mVs^{-1}

ELECTRODE AREA $= 0.29 \text{ cm}^2$ (SCE 0.0V = 0.24V NHE)

change in concentration of para-phenylene diamine with time
in minutes is shown.

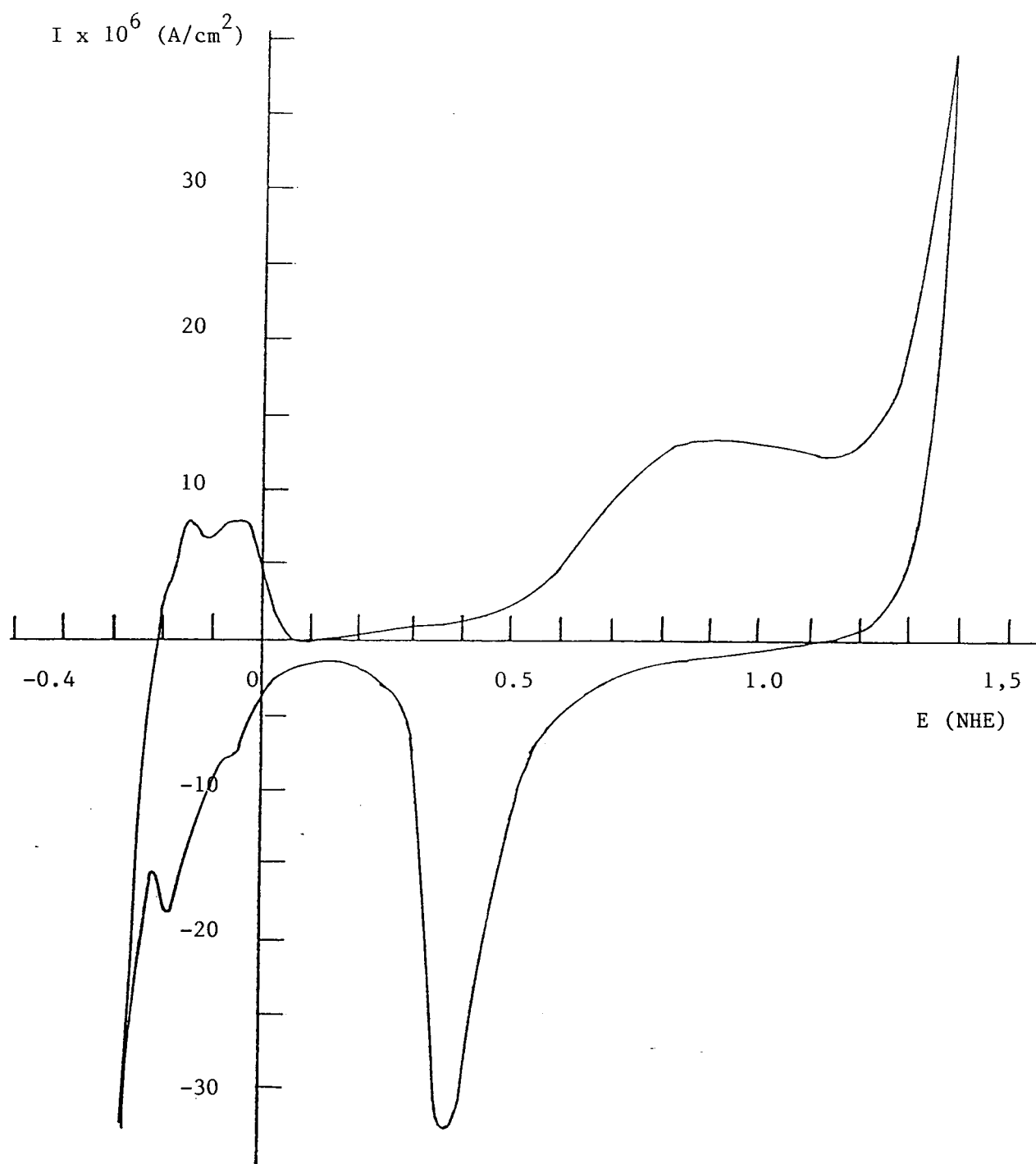


Fig 6

Cyclic Voltammogram for the oxidation of 1M Acetic acid in 1M Sodium acetate

Sweep rate = 10 mVs^{-1} ; $t = 20^\circ\text{C}$

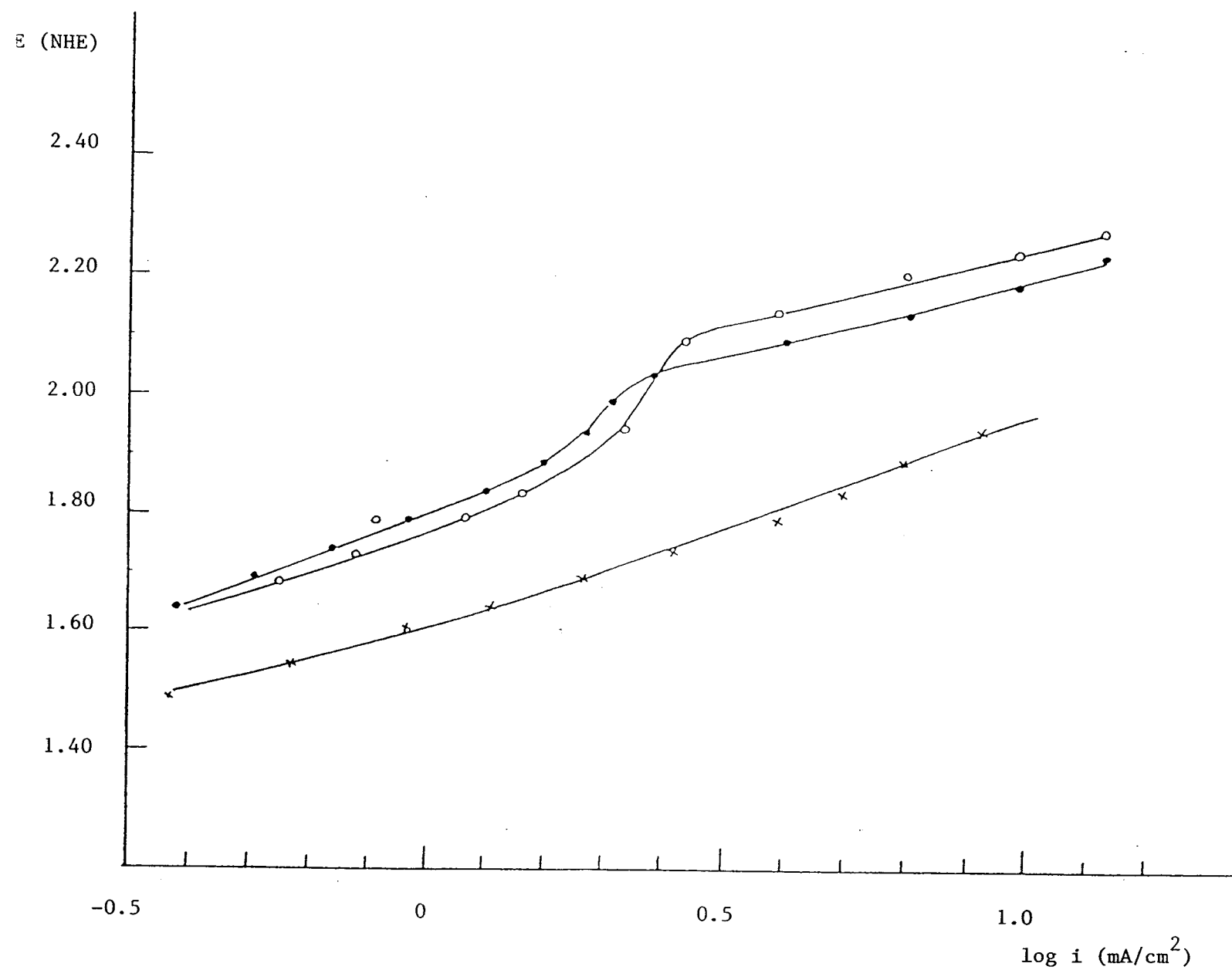


Fig 7

Anode potential against log current density curves on Platinum

● Solution 1M in sodium acetate and acetic acid; ○ 0.5 M; × 0.1M; at 20 °C

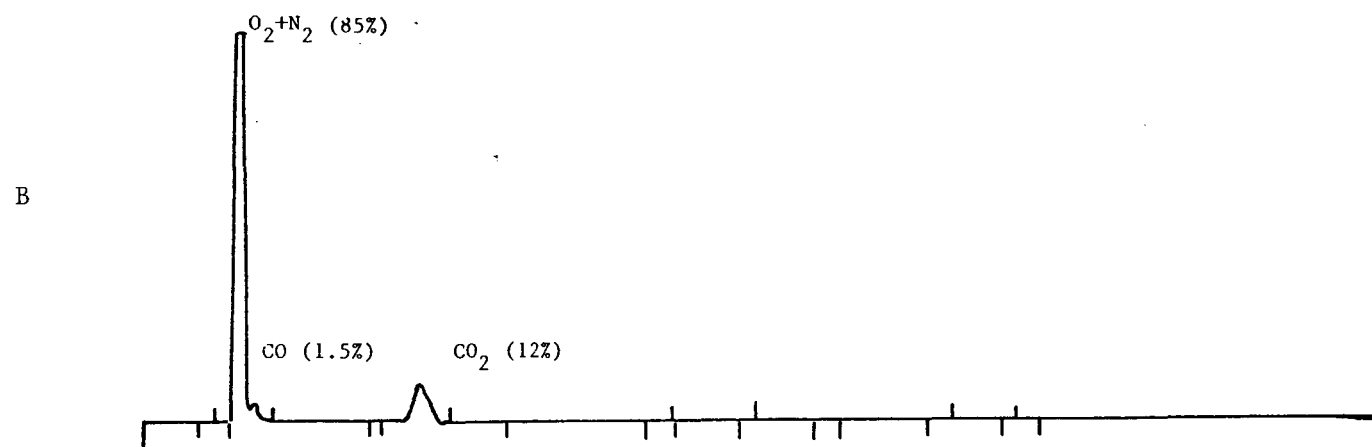
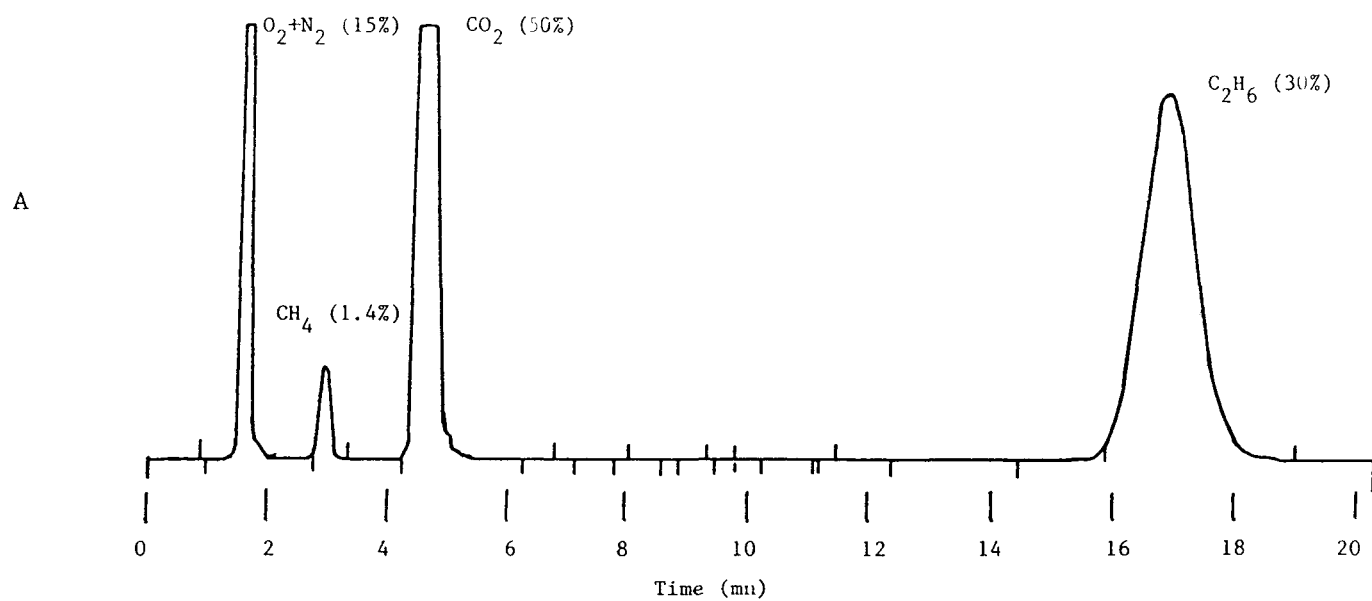


FIGURE 8

GC Analysis of the gases produced during Acetic acid oxidation

A- Acetic acid 1M in Sodium acetate 1M; current density $8mA/cm^2$

B- Acetic acid 1M in Sodium acetate 1M; current density $1mA/cm^2$

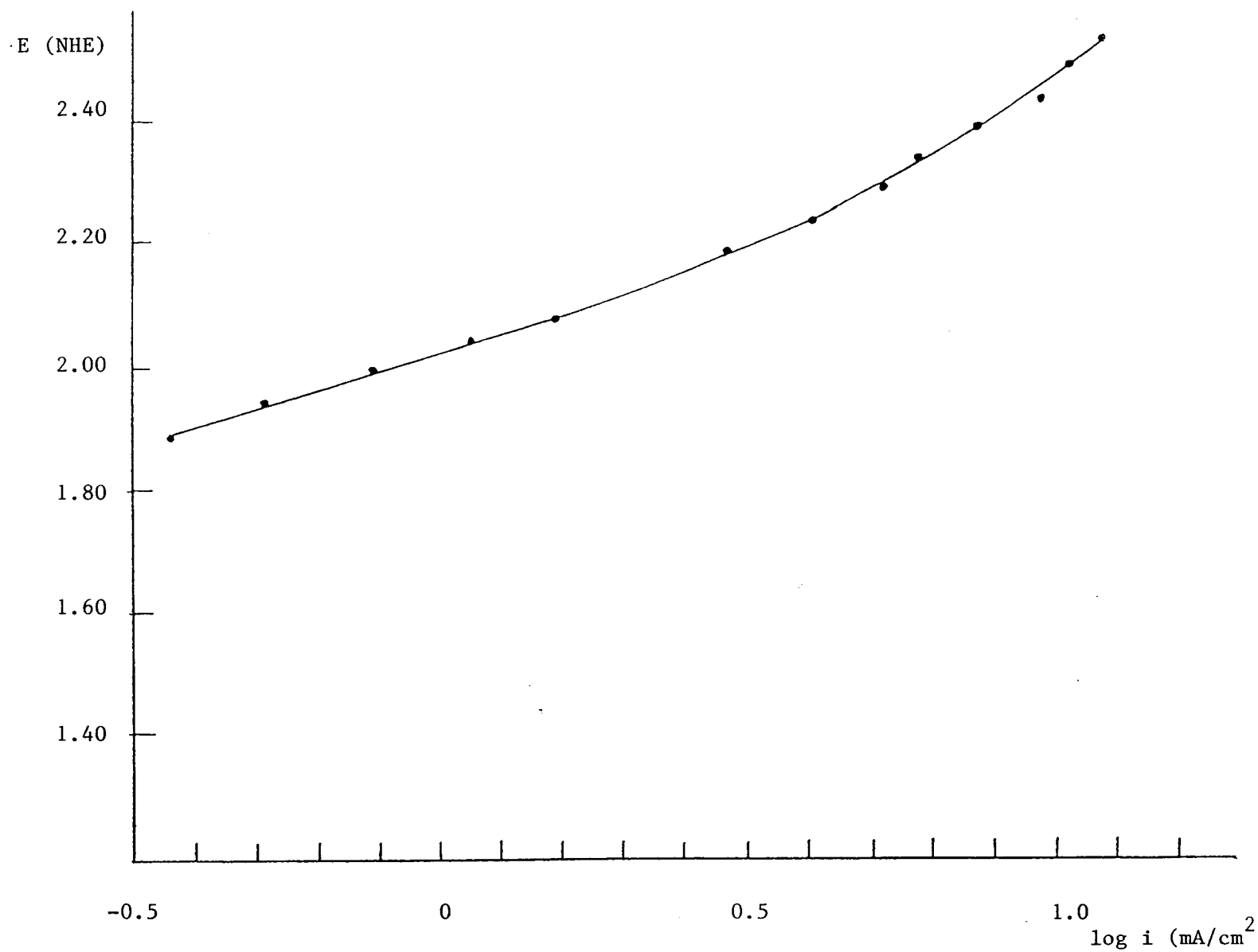


FIGURE 9

Anode potential against log current density curve on Platinum

1M Propionic acid in 1M Sodium perchlorate at 20°C

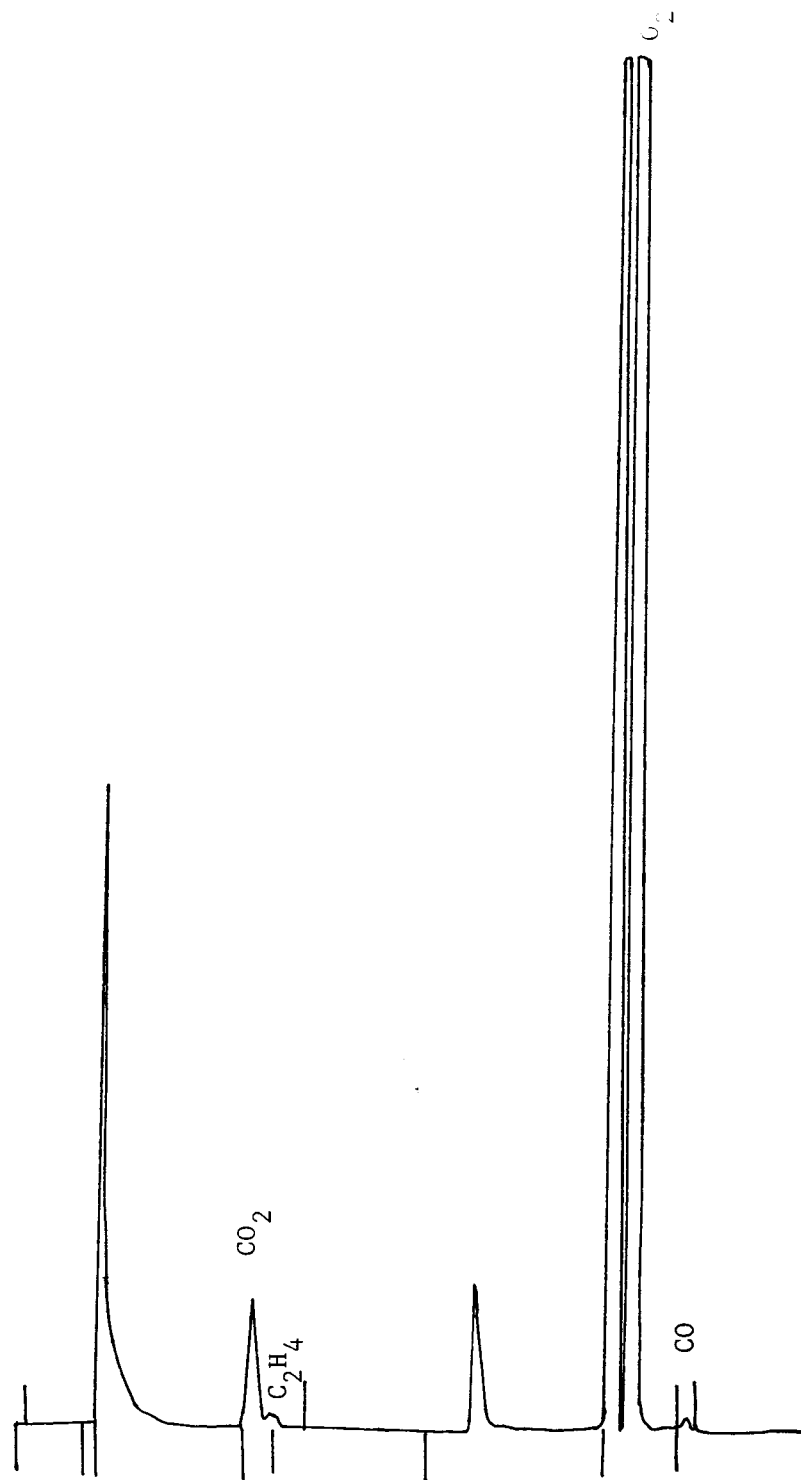


FIGURE 10

GC Analysis of the gases produced during Propionic acid oxidation

Propionic acid 1M in NaClO_4 1M; current density mA/cm^2

TABLE 1

Electrode material	Concentration of electrolyte	Current density mA/cm ²	Anode potential V(NHE)	% of		Current efficiency of Ethane & CO ₂ formation %
				CO ₂	O ₂ C ₂ H ₆	
Pt	1M	1	2.1	12	79 0	0 10
		8	2.5	50	- 30	50 30

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