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*The influence of cell design and electrolysis parameters on the cathodic coupling of butadiene and carbon dioxide in acetonitrile. I. Undivided parallel plate configurations**

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The reduction of carbon dioxide in the presence of excess butadiene in acetonitrile leads to a mixture of carboxylic acids, pentenoic acids (two isomers), hexenedioic acids (two isomers) and decadienedioic acids (three isomers). The total current yield can exceed 60%. The current efficiency and the ratio of products are functions of both cell design and other electrolysis parameters. This paper reports studies of this coupling reaction in several undivided flow cells, where cyclindrical cathodes (lead-plated nickel gauze, reticulated carbon of various porosity, carbon felt) were surrounded by a platinum gauze anode. The electrolyte was ditetraethylammonium oxalate and/or tetraethylammonium formate so that the counter electrode reaction was the oxidation of the anions to CO_2 or $CO_2 + H^+$, respectively. This choice avoids solvent decomposition or other unwanted reactions at the anode, and may be helpful to the cathode chemistry by replenishing the cathode active species, CO_2, and possibly also creating a controlled supply of protons to the cathode.

1. Introduction

The economic success of most electrolytic processes is dependent on the choice of an appropriate design of cell. With electro-organic processes the cost of the cell is usually a very substantial part of the capital cost and a significant part of the total product cost [1–3]. Hence simple cell structures are advantageous and, for example, separators and membranes should be avoided when possible.

During the last twenty years many new cell designs have been described [3–6] and there have been comparisons based on space-time yield, energy consumption, etc. On the other hand, relatively few papers [7–9] have considered the influence of cell design on the product distribution and selectivity of electrosynthetic reactions. It is, however, clear that parameters such as electrolyte flow rate, electrode configuration and electrode material are important when dealing with complex chemical reactions coupled to the electron transfer. In addition, the counter electrode reaction must be handled in some way.

In this and a second paper [10] (which will consider cells where there is strong mixing between anode and cathode, e.g. a bipolar fluidized bed cell) the reaction of interest is the cathodic coupling of carbon dioxide and butadiene in acetonitrile. The reduction of carbon dioxide alone in aprotic solvents has been widely studied (see [11–14] and references therein) and it is generally accepted that the products are formed by a series of competitive reactions of the initially formed carbon dioxide anion radical. The formation of carboxylic acids by the cathodic reduction of mixtures of carbon dioxide and butadiene was first reported in two US patents [15, 16]. Similar chemical reductions

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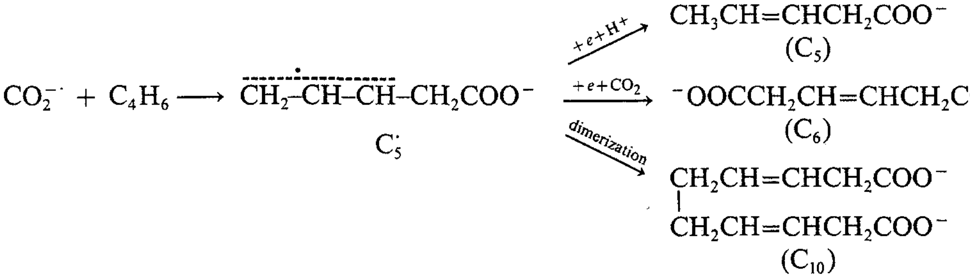
have also been described [17–21]. More recently, the electrochemical reduction of carbon dioxide and butadiene has been reinvestigated by a group at Shell [22, 23]. They showed that a mixture of C_5, C_6 and C_{10} carboxylic acids were formed, and suggested the mechanism

$$CO_2 + e \longrightarrow CO_2^{-\cdot}$$



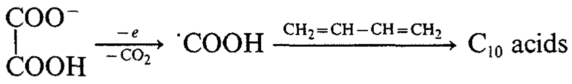
$$CO_2^{-\cdot} + C_4H_6 \longrightarrow \underset{C_5^{\cdot}}{\dot{C}H_2\text{–}CH\text{–}CH\text{–}CH_2COO^-} \begin{cases} \xrightarrow{+e+H^+} CH_3CH{=}CHCH_2COO^- \;(C_5) \\ \xrightarrow{+e+CO_2} {}^-OOCCH_2CH{=}CHCH_2COO^- \;(C_6) \\ \xrightarrow{\text{dimerization}} \begin{array}{l} CH_2CH{=}CHCH_2COO^- \\ | \\ CH_2CH{=}CHCH_2COO^- \end{array} \;(C_{10}) \end{cases} \quad (1)$$

where the isomers arise because of the two possible coupling sites and sites for reduction in the $C_5^{\cdot}$ radical. In fact the details of the mechanism are not clear and alternative routes from $C_5^{\cdot}$ to each of the products can be written. For example, the C_5 acid could result from H atom abstraction from the electrolysis medium, while the C_6 acid could well be formed by coupling of $C_5^{\cdot}$ with $CO_2^{-\cdot}$. Moreover, there is no definitive evidence as to whether this complex coupled chemistry occurs mainly via intermediates in a thin reaction layer close to the cathode surface (all the reactions are rapid) or whether the chemistry occurs predominantly between species adsorbed on the surface. In the former case the product distribution should depend strongly on mixing due to its influence on local concentrations, while if heterogeneous chemistry is important the choice of electrode material will be critical.

Electrolyses in aprotic solvents are best carried out in undivided cells because the performance of membranes in such media falls well below that in aqueous solutions. In any case, membranes are expensive and lead both to greater cell complexity and a wider interelectrode gap. In order to use undivided cells, however, it is essential to devise a strategy where the counter electrode reaction is either innocuous or helpful to the desired conversion. Moreover, it is likely to be catastrophic if the counter electrode reaction leads to decomposition of the aprotic solvent or a large swing in the pH. There are several possibilities.

(a) Paired syntheses where different products are synthesized at the anode and cathode [24, 25]. Such systems are interesting but lead to additional problems in the product isolation stages,

(b) A more ambitious target is to form the same product at both electrodes. In fact, the system discussed in this paper is an example where this is theoretically possible. Kornienko *et al.* [26] have reported that the anodic oxidation of the mono-anion of oxalic acid in the presence of butadiene leads to three isomeric decadienedioic acids



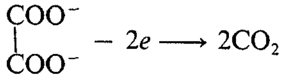
$$\begin{array}{l} COO^- \\ | \\ COOH \end{array} \xrightarrow[-CO_2]{-e} {}^{\cdot}COOH \xrightarrow{CH_2=CH-CH=CH_2} C_{10} \text{ acids}$$

Similarly the oxidation of a half ester of oxalic acid in the presence of butadiene has been reported to give the esters of the decadienedioic acids [27]. However, in both cases the yields were poor and the reactions have not been reproduced by other workers [22]. Clearly the formation of the same product at both electrodes is not commonly to be achieved.

(c) The counter electrode reaction may play an essential role in the cell chemistry (e.g. control the pH as in the epoxidation of propylene) [28] or aid the isolation of products (e.g. dissolving metal anodes where the resulting ions cause the precipitation of oxalic acid formed by reduction of carbon dioxide at the cathode) [29].

(d) The counter electrode reaction should be totally innocuous.

In this work we have used the approach of Van Tilborg and coworkers [30, 31] who suggested that when the desired reaction is a cathodic carboxylation, then an appropriate choice of anode reaction is the oxidation of oxalate and/or formate:



$$\begin{matrix} COO^- \\ | \\ COO^- \end{matrix} - 2e \longrightarrow 2CO_2$$

and

$$HCOO^- - 2e \longrightarrow H^+ + CO_2$$

The former leads to the formation of carbon dioxide, the electroactive species, at the cathode and hence may be regarded at least as totally innocuous and, perhaps, helpful if it leads to an increased current density. The oxidation of formic acid leads also to protons and hence might be employed to produce a controlled flux of protons to the cathode. This could influence the product distribution at the cathode.

This and a further paper [10] set out to discuss the influence of cell design and electrolysis parameters on the cathodic coupling of butadiene and carbon dioxide; the cells are undivided and the medium is anhydrous acetonitrile containing ditetraethylammonium oxalate and/or tetraethylammonium formate.

2. Experimental details

2.1. *Instrumentation*

Voltammograms were recorded using a Hi-Tek Instruments potentiostat, model DT 2101, a Hi-Tek Instruments Waveform Generator, model PPR 1, and Hewlett Packard X–Y recorder, model 7015 A. For the constant current electrosyntheses a modified Chemical Electronics potentiostat, type TR 70/2A, was used. The charge was measured by means of a laboratory-built electronic integrator. The products were analysed using a Varian gas chromatograph, model 3700, linked to a Varian chromatography data system, model CDS-111. The column (length, 2.3 m; diameter, 2.5 mm) was 10% OV 101 (BDH Chemicals Ltd) on 60–80 mesh Diatomite C-AAW-DMCS support (J.J's Chromatography Ltd). The carrier gas was N_2.

2.2. *Cells and electrodes*

The voltammetry was carried out in a three-electrode, two-compartment glass cell equipped with a vitreous carbon disc working electrode (area, 0.062 cm^2), a platinum wire counter electrode and a saturated calomel electrode (SCE) as reference electrode. In some experiments the working electrode was a platinum disc (area, 0.159 cm^2). Before each experiment the carbon or platinum disc was polished with 0.3 μm and 0.05 μm aluminium oxide (from Banner Scientific Ltd).

Most preparative electrolyses were carried out in the flow cell shown in Fig. 1a. Throughout the anode was a platinum gauze cylinder (height, 5.4 cm; diameter, 3 cm) and electrical contact was made via a platinum wire sealed through the glass wall of the cell. A series of cylindrical working electrodes was used. Each was held in the centre of the cell by glass spikes in the cell walls which acted as mechanical supports. Electrical contact was via a platinum wire through a joint in the cell top. The cell was also equipped with two gas inlets directly below the cathode and these were both used to introduce CO_2 during electrolyses.

The cathodes used during the study were as follows.

(a) A 60 ppi reticulated carbon cylinder, height 7.2 cm and diameter 2.1 cm. This was used for most experiments, but unfortunately the source of the material is unknown.

(b) Two cylinders identical to (a) but of height 3.5 cm and 1.75 cm.

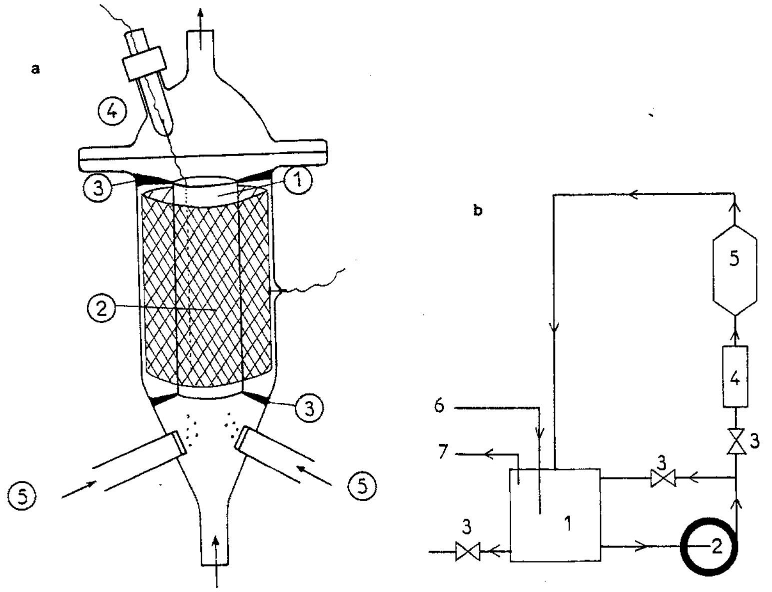


Fig. 1. (a) Electrolysis cell: 1, working electrode; 2, counter electrode; 3, working electrode support; 4, working electrode contact; 5, gas inlets. (b) Electrolyte flow circuit: 1, reservoir; 2, pump; 3, valve; 4, flow meter; 5, cell; 6, 7, gas inlet and outlet.

(c) Two cylinders, each of diameter 1.2 cm and height 7.2 cm, of 30 and 60 ppi reticulated carbon from the Electrosynthesis Co.

(d) A cylinder made from 6 mm graphite felt (Union Carbide Co) and held in position with a Teflon-coated gauze support.

(e) A nickel gauze (7 cm in height, 2.2 cm diameter, 15 wires per cm) cylinder plated with lead in a lead fluoroborate bath (W. Cannings and Co).

The flow diagram is shown in Fig. 1b. The electrolyte was pumped from a reservoir ($\sim 400\,\mathrm{cm}^3$) through a PTFE-lined magnetic pump (from Totton Electrical Sales Ltd) and a flowmeter (from Platon Furnishings Ltd) through the cell back to the reservoir. The flow was adjusted using two valves and a by-pass loop connecting the outlet of the pump and the reservoir. The connecting tubes were made of glass with polythene joints of minimum length. The reservoir was equipped with a tap and a gas inlet and outlet. The inlet was a long glass tube fitted with a sinter for a better gas distribution. It was used for deoxygenation of the electrolyte solution followed by saturation with a mixture of carbon dioxide and 1,3-butadiene for 1 h prior to every experiment. During an electrolysis only butadiene was introduced into the reservoir. The flow rates of both gases were controlled by flowmeters from Planton Furnishings Ltd which were calibrated for the viscosity of each gas.

To aid the interpretation of the data from the preparative electrolyses it was considered important to have some understanding of the mass transport regime in the cells. Hence current–voltage curves were recorded for the oxidation of ferrocyanide at each of the electrodes (a) to (e) in the flow cell; the electrolyte was $K_3Fe(CN)_6$ ($10\,\mathrm{mmol\,dm^{-3}}$) + $K_4Fe(CN)_6$ ($10\,\mathrm{mmol\,dm^{-3}}$) + KCl ($0.4\,\mathrm{mol\,dm^{-3}}$) in water. With the reticulated carbon cathodes the I–V curves show reasonable limiting current plateaux and, over the flow range 500–2000 $\mathrm{cm^3\,min^{-1}}$, plots of log I versus log (flow rate) have a slope of around 0.4, suggesting a reasonably laminar flow regime. The limiting currents, are, however, unexpectedly low; they are approximately proportional to the outer surface area of the cylindrical cathodes and the values of the limiting currents also correspond closely to those expected if only this outer surface were active. Hence it must be concluded that the cells behave essentially as undivided parallel plate configurations with laminar flow and that the inner surfaces of the carbon contribute little to the current.

2.3. *Chemicals*

CH_3CN (Fisons hplc/far UV grade) used for voltammetry was distilled from $KMnO_4$ and $MgSO_4$ under N_2 and stored over molecular sieves, 3 Å. For electrolyses the solvent was not distilled but was allowed to stand over molecular sieves for 24 h. The formate and oxalate salts were prepared from the acids and $(C_2H_5)_4NOH$; after evaporation of water, the salts were dried in a vacuum over P_2O_5. Periodically the salts were crushed and dried further until their water contents, estimated by NMR, were below 0.5 mol H_2O per mol of salt. The salts were extremely hygroscopic and were handled in a dry box. Carbon dioxide (BOC) and 1,3 butadiene (Exxon) were passed through molecular sieves, 3 Å, before passing into the cells. Molecular sieves (Sigma) were always freshly regenerated at 180° C.

2.4. *Extraction and analysis of products*

At the end of an electrolysis the acetonitrile was removed on a rotary evaporator and hexanoic acid was added to the residue as internal standard. The residue–standard mixture was dissolved in 100 cm^3 0.25 M aqueous NaOH and neutral products were extracted from the basic solution with three aliquots, $\sim 20\,cm^3$, of diethylether. The combined ether phases were dried and the ether was evaporated so that the amount of neutral products could be estimated by weighing. The aqueous basic solution was acidified with dilute sulphuric acid to a pH of about 2.5 and the acidic products were extracted five times with 20 cm^3 diethylether. After drying the combined ether extracts over anhydrous $MgSO_4$ and filtration, the solvent was evaporated and the residue was weighed to estimate the total amount of acidic products. For the analysis of the acidic products a fraction of the dried ether solution was evaporated to dryness and the carboxylic acids were redissolved in acetonitrile and silylated with bis(trimethylsilyl) trifluoroacetamide (Aldrich Chemical Co. Ltd) following the method described by Stelling *et al.* [32]. The mixture was heated in a sealed flask at 110° C for 10 min. After cooling, the esters were analysed by glc and their composition was checked by glc mass spectrometry. Current yields were calculated from the gas chromatograms by comparison of peak areas with those of the standards. The product distributions were also determined from glc assuming that the response factors for the different silylated acids depended only on the number of carbon atoms.

3. Results and discussion

3.1. *Preliminary studies*

Polarization curves were recorded at a scan rate of $2\,mV\,s^{-1}$ for the reduction of saturated solutions of carbon dioxide and/or butadiene under a variety of conditions. The parameters varied were solvent (CH_3CN, dimethylformamide, dimethyl sulphoxide, propylene carbonate), electrolyte (both anion, ClO_4^-, BF_4^-, Cl^-, $HCOO^-$, $(COO^-)_2$ and cation, Li^+, $(C_2H_5)_4N^+$, $(C_4H_9)_4N^+$) and electrode material (Pb, Zn, Sn, Cu, Fe, Cd and C).

Fig. 2 shows a typical pair of curves for a vitreous carbon disc electrode in CH_3CN containing $(C_2H_5)_4N^+\ HCOO^-$ (50 $mmol\,dm^{-3}$) and $[(C_2H_5)_4N^+]_2(COO^-)_2$ (50 $mmol\,dm^{-3}$). It can be seen that the reduction of CO_2 occurs more readily and at $10\,mA\,cm^{-2}$ the separation between the curves is about 200 mV; the I–E response for butadiene is, however, steeper and hence the separation is less at higher current densities. Moreover, if the experiment is extended to include more negative potentials, the reduction of CO_2 becomes mass transfer-controlled with a limiting current density of around $40\,mA\,cm^{-2}$. On the other hand, the polarization curve for C_4H_6 does not plateau because of the high solubility of the hydrocarbon in acetonitrile. When CH_3CN is saturated with various mixtures of $CO_2 + C_4H_6$ there is no evidence that the reduction of CO_2 is influenced by the presence

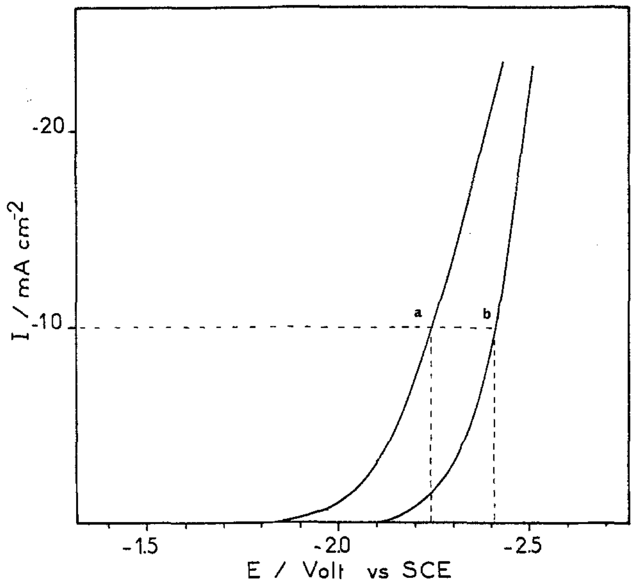


Fig. 2. Polarization curves for (a) CO_2 and (b) C_4H_6, both saturated in CH_3CN/0.05 mol dm^{-3} · $(Et_4N^+)_2(CO_2^-)_2$ + 0.05 mol dm^{-3} $Et_4N^+HCOO^-$. Vitreous carbon cathode, area 0.062 cm^2. Scan rate, 0.002 V s^{-1}.

of butadiene. Hence in this system there is little doubt that at current densities below the limiting current for CO_2 reduction, only CO_2 is reduced at the cathode surface.

This conclusion also applies to the other solvents, electrolytes and electrode materials, although the potential difference between the polarization curves at 10 mA cm^{-2} varies in the range 0.04 to 0.34 V. In acetonitrile, the choice of both electrode material and electrolyte influences the reduction potential ($E_{I=10\,mA\,cm^{-2}}$) of carbon dioxide. The latter effect is surprising, but the replacement of $(C_4H_9)_4N^+$ by $(C_2H_5)_4N^+$ causes a positive shift of 50 mV while the $(C_2H_5)_4N^+$ salts of BF_4^-, ClO_4^-, $(COO^-)_2$ and $HCOO^-$ led to $E_{I=10\,mA\,cm^{-2}}$ values of -2.39 V, -2.24 V, -2.30 V and -2.10 V, respectively (all measured with a lead cathode). The reduction potential for C_4H_6 also shows a small dependence on the electrode and electrolyte, and perhaps these data should be taken as an indication of the importance of adsorption in these reductions. Cyclic voltammetry confirmed that the reductions of CO_2 and C_4H_6 were always irreversible.

The anodic oxidation of oxalate and formate in aprotic solvents has not been widely investigated [30, 31, 33, 34] and hence cyclic voltammetry was used to check the characterization of these reactions at platinum and carbon in CH_3CN (see Figs 3–5). Oxalate gives a single, irreversible but diffusion-controlled oxidation peak, with E_p = $+0.37$ V and $+0.68$ V at platinum and vitreous

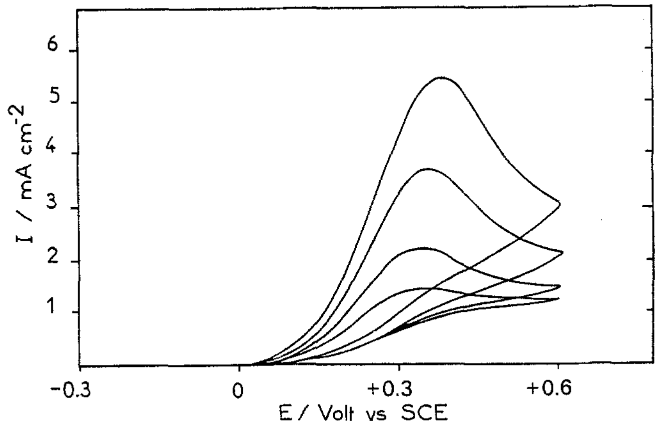


Fig. 3. Cyclic voltammogram on platinum (0.159 cm^2) in CH_3CN/0.1 mol dm^{-3} Et_4NClO_4. Tetraethylammonium oxalate (27 mmol dm^{-3}), scan rates 0.02, 0.05, 0.1 and 0.2 V s^{-1}.

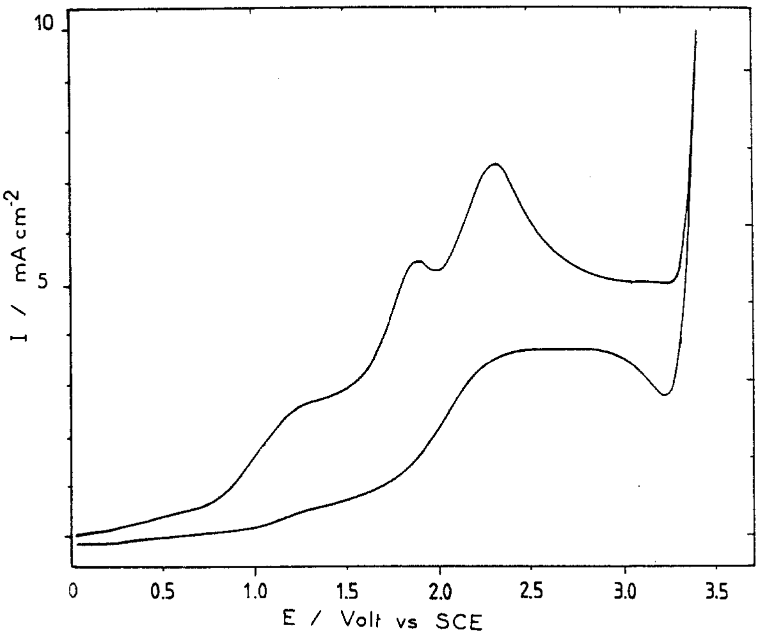


Fig. 4. Cyclic voltammogram on platinum (0.159 cm^2) in CH_3CN/ 0.1 mol dm^{-3} Et_4NClO_4. Tetraethylammonium formate (45 mmol dm^{-3}), scan rate 0.2 V s^{-1}.

carbon, respectively (at 0.2 V s^{-1}). On repetitive cycling of the potential between − 0.5 V and + 1.0 V the peak shifts positive by 100 mV and the addition of small quantities of water causes a 200 mV positive shift of oxalate oxidation. The voltammetry of formate is more complex. Fig. 4 shows that formate leads to three irreversible oxidation peaks at + 1.3 V, + 1.9 V and + 2.2 V at platinum and the addition of trace water leads to an enhancement of the first peak. The origin of the peaks was not studied in detail, but it is clear that formate oxidation does not commence until + 0.8 V. It was also expected [35] that the carboxylic acid products would not oxidize until potentials well positive to + 1.0 V, and this was confirmed by running a cyclic voltammogram on a product extract from a preparative electrolysis (see Fig. 5). Hence it was concluded that the difficulty of oxidation increases along the series oxalate < formate < product acids. Even so, it is not possible to rule out the possibility that, at least under some circumstances, anode poisoning or contamination by water would lead to a change in this order observed on clean surfaces.

Acetonitrile was chosen as the solvent for preparative electrolyses because its relative stability and ease of removal make it a good medium for synthesis. From the above experiments it was concluded

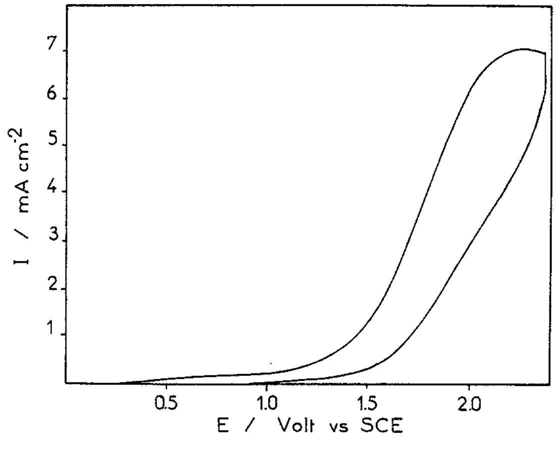


Fig. 5. Cyclic voltammogram on platinum (0.159 cm^2) in CH_3CN/0.1 mol dm^{-3} Et_4NClO_4. Electrolysis acid extract (200 mg in 20 cm^3), scan rate 0.2 V s^{-1}.

that ditetraethylammonium oxalate and/or tetraethylammonium formate were suitable electrolytes for the cathodic coupling of CO_2 and butadiene, and that the anions are suitable electroactive species for the anode which should avoid product oxidation when the electrolysis is carried out in an undivided cell. Carbon appears to be one of several possible cathode materials and was chosen for most experiments because it was available in several forms. A few experiments were carried out with a lead cathode to allow comparison with earlier work [22, 23]. Platinum was used as anode material throughout this work, although carbon again seems to be a possible choice.

3.2. *Preparative studies*

A large number of experiments were carried out in the undivided flow cell shown in Fig. 1. In all cases the products were almost entirely a complex mixture of carboxylic acids, although the work-up procedure included the isolation and estimation by weight of the neutral products (e.g. oligomers and polymers of butadiene) and these never exceeded 10% of the acidic products. The two isomeric pentenoic acids (hereafter called the C_5 acids), two hexenedioic acids (C_6 acids) and three decadienedioic acids (C_{10} acids) predicted by Equation 1 accounted for 80–100% of the total acidic product observed by glc. It will be shown that the ratio of $C_5:C_6:C_{10}$ products varies markedly with some experimental parameters, and the purpose of the studies was to optimize the current yield for the coupling of CO_2 and C_4H_6 and to seek conditions which favoured the formation of C_5, C_6 or C_{10} acids. The ratio of isomers of each product, however, did not vary markedly with electrolysis conditions and these are reported in Table 1.

3.2.1. Electrode material. Tables 2 and 3 report data from electrolyses carried out at reticulated carbon and lead electrodes. It can be seen that the current efficiency is better at carbon and also that the product distribution is quite different. While the yields of C_5 acids are similar, the ratio $C_{10}:C_6$ is in the range 1 to 3 at carbon but 0.35 to 0.65 at lead. Indeed the major product can be the C_{10} acids at carbon and the C_6 acids at lead. The low current yield of carboxylic acids and the dominance of C_6 product at a lead cathode was also reported by Van Tilborg and Smit [23] and was confirmed in another cell in our laboratory, an undivided cell with a rotating lead cathode.

It should be noted, however, that the exact type of carbon used for the cathode is also critical. A few experiments were caried out with reticulated carbon (both 30 and 60 ppi) from a different source and while the current efficiency remained high (50%), the product distribution was similar to that at lead, i.e. $C_5:C_6:C_{10} = 37:45:18$. Moreover, the product distribution using a cathode cylinder made from carbon felt was also similar with $C_5:C_6:C_{10} = 36:52:12$. (All the data in this paragraph is quoted with $I \simeq 45\,\mathrm{mA\,cm^{-2}}$ and an electrolysis charge of 600 C — see below.)

3.2.2. Current density. Increasing current density leads to an improvement in current yield and a small change in product distribution (see Tables 2 and 3). At reticulated carbon the current yield

Table 1. Products from the cathodic coupling of butadiene and carbon dioxide

Product	*Ratio of isomers*	*Major isomer*[a]
C_5	1:25	3-pentenoic acid
C_6	1:5	3-hexenedioic acid
C_{10}	1:5:10	linear 3,7-decadienedioic acid

[a] Structures determined by NMR and mass spectroscopy [36].

Table 2. Electrolyses of CO_2 + C_4H_6 in $CH_3CN/[(C_2H_5)_4N^+]_2\ (COO^-)_2$ (0.04 mol dm^{-3}) + $(C_2H_5)_4N^+\ HCOO^-$ (0.04 mol cm^{-3})

Cell current (A)	Current density $(mA\,cm^{-2})$[b]	$\frac{(C_5 + C_6 + C_{10}) \times 100}{\text{all acid products}}$ (%)[c]	Current yield of $C_5 + C_6 + C_{10}$ (%)[d]	Ratio of products (%)		
				C_5	C_6	C_{10}
0.05	1	95	32	39	25	36
0.15	3.1	97	23	40	27	33
0.30	6.2	96	45	42	24	34
0.50	10.4	97	46	35	27	38
0.90	19	99	50	36	21	43
2.00	42	98	58	36	15	49
2.00[a]	84	97	63	39	31	30
2.00[a]	168	99	62	33	26	41

Cathode, cylinder of 60 ppi reticulated carbon, diameter 2.1 cm and height 7.2 cm. Anode, platinum gauze cylinder, diameter 3 cm. Electrolyte volume, 300 cm^3. Charge passed, 600 C. Gas flow rates both 80 cm^3 min^{-1}. Solution flow rate 1000 cm^3 min^{-1}.

[a] Electrodes of reduced height.

[b] Assuming only outer surface of cathode cylinder is active.

[c] Based on peak areas from glc trace.

[d] By comprison of peak areas on glc with those of internal standards.

exceeds 60% at the highest current densities while there is a trend to increasing C_{10} acids with increasing current density at least up to 42 mA cm^{-2}. At lead the maximum current efficiency is only 33% but the C_6 and C_{10} acids show a small increase with the higher current densities. These changes might be predicted since the concentration of radical intermediates, both $C_5^{\cdot}$ and $CO_2^{-\cdot}$ will increase under conditions of high current density.

3.2.3. Charge passed. Several electrolyses at the reticulated carbon cathode were carried out to various charges and the electrolyte was then analysed. Table 4 shows the results and it can be seen that although the current efficiency drops with charge passed, the ratio of products remains quite constant. The behaviour of the carbon felt cathode is again quite different, see Table 5; in particular the yield of C_{10} acid drops sharply during the electrolysis. Indeed, it is clear that the C_{10} acids are being lost from the electrolyte, but we have not been able to explain why this should happen in the case of this cathode material alone. There is, however, little doubt that the electrode becomes covered with polymer during the electrolysis since it becomes impossible to maintain the cell current during the latter stages of the experiment. This emphasizes that the form of carbon is important in determining the cathode behaviour.

Table 3. Electrolyses of CO_2 + C_4H_6 at lead-coated nickel gauze cathode[a]

Cell current (A)	Current density $(mA\,cm^{-2})$	$\frac{(C_5 + C_6 + C_{10}) \times 100}{\text{all acid products}}$ (%)	Current yield $C_5 + C_6 + C_{10}$ (%)	Product Distribution (%)		
				C_5	C_6	C_{10}
0.1	4	83	12	44	35	21
0.5	20	97	24	40	45	16
1.0	40	99	33	34	40	26
2.0	80	99	30	32	45	23

[a] Cathode diameter 2.2 cm and height 7 cm. For other details see Table 2.

Table 4. Influence of charge passed on the reduction of $CO_2 + C_4H_6$ at reticulated carbon cathode[a]

Charge (C)	$\frac{(C_5 + C_6 + C_{10}) \times 100}{\text{all acid products}}$ (%)	Current yield $C_5 + C_6 + C_{10}$ (%)	Ratio of products (%)		
			C_5	C_6	C_{10}
300	95	43	49	12	39
600	98	33	46	10	44
1200	89	34	56	10	34
2400	86	28	51	11	38

[a] $I = 42\,\text{mA cm}^{-2}$. Other conditions as Table 2.

3.2.4. Electrolyte flow rate. The data in Table 6 demonstrate that, at least over the range investigated ($500-2000\,\text{cm}^3\,\text{min}^{-1}$), the electrolyte flow rate has no influence on either the current efficiency or the product spectrum. This would seem to be strong evidence that the rate determining steps in this cathodic coupling process occur between species adsorbed on the electrode surface.

3.2.5. Concentration of carbon dioxide. The experiments reported in Table 7 were an attempt to study the effect of carbon dioxide concentration in the electrolyte, since the butadiene concentration, although also changing, is always very much higher. The effect of reactant concentration, in any case, seems very small.

3.2.6. Electrolyte and added water. The first two entries in Table 8 compare the products when the electrolyte is oxalate and when it is a mixture of oxalate and formate. It can be seen that the addition of formate leads to an increase in the quantity of C_{10} product. A similar effect has been noted with a mercury-covered lead cathode [22]. It has been proposed [36] that the change of product distribution results from the influence of protons formed at the anode from the oxidation of formate. It is suggested that the rate of dimerization of two $C_5^{\cdot}$ radicals is reduced by the electrostatic repulsion of the two carboxylate groups, and that the presence of proton leads to protonation of one or both of the carboxylate groups and hence to more rapid dimerization. In our experiment it must be noted, however, that the electrolyte contains both oxalate and formate, and our preliminary studies clearly show that only oxalate oxidation would be expected at these current densities. On the other hand, it was also noted in those studies that anode passivation may well occur on an electrolysis timescale and hence the anode may take up a potential where formate oxidation occurs.

The final entry in Table 8 shows that with a reticulated carbon cathode the electrolysis products are not strongly affected by the addition of a low concentration of water. This is in contrast to the influence of water on electrolyses at lead, reported by Van Tilborg and Smit [23] and also observed in our experiments with a rotating lead cathode.

Table 5. Influence of charge passed on the reduction of $CO_2 + C_4H_6$ at carbon felt cathode[a]

Charge (C)	$\frac{(C_5 + C_6 + C_{10}) \times 100}{\text{all acid products}}$ (%)	Current yield $C_5 + C_6 + C_{10}$ (%)	Ratio of products (%)		
			C_5	C_6	C_{10}
300	94	61	24	42	34
600	98	39	36	52	12
1150	98	28	44	53	3

[a] $I = 48\,\text{mA cm}^{-2}$. Other conditions as Table 2.

Table 6. Influence of electrolyte flow on the reduction of CO_2 + C_4H_6 at reticulated carbon cathode[a]

Solution flow rate ($cm^3\,min^{-1}$)	*Current yield $C_5 + C_6 + C_{10}$ (%)*	*Ratio of products (%)*		
		C_5	C_6	C_{10}
500	52	44	15	42
1000	58	36	16	48
2000	56	39	15	47

[a] $I = 42\,mA\,cm^{-2}$. Other conditions as Table 2.

4. Conclusions

Although the cathodic coupling of carbon dioxide and butadiene is clearly a complex reaction with products being formed by competing reaction pathways, it can be carried out with some success even in a simple undivided cell. While the anode reactions chosen, i.e. the oxidation of oxalate and/or formate, can influence the product distribution, they do not prevent a reasonable current efficiency for the coupling. The products identified never account for all the charge passed at the cathode and it may be that some of the carbon dioxide is reduced to oxalate. Such oxalate formation would lead to no net change in the electrolyte composition (assuming only oxalate oxidation at the anode) but only a loss in current efficiency.

Hence in the electrolysis systems studied, the current efficiency can exceed 60% and conditions have been found where the major products are pentenoic acids (58%), hexenedioic acids 53% or decadienedioic acids (49%). Moreover, the conditions for each product could be refined further (see also other cell designs) [10]. The factors influencing the product distribution most strongly are the choice of electrode material and electrolyte with some effect of current density. On the other hand, the electrolyte flow rate and carbon dioxide concentration have no influence.

We now believe that the complex chemistry between $CO_2^{-\cdot}$ and C_4H_6 occurs largely on the electrode surface between adsorbed intermediates. In support of this view, we would offer the following evidence.

(a) The absence of polybutadiene polymers. In homogeneous reactions involving radical intermediates, butadiene normally polymerizes to a considerable extent.

(b) The absence of an influence of electrolyte flow rate on the product distribution.

(c) The strong dependence of the product distribution on the choice of electrode material, even the type of carbon.

(d) The variation in the reduction potentials for CO_2 and C_4H_6 with the electrode material and both anion and cation of the base electrolyte (double layer effects?).

(e) The strong difference between the reticulated carbon and lead with respect to the addition of

Table 7. Influence of gas feed ratio on the reduction of CO_2 + C_4H_6 at the reticulated carbon cathode[a]

Gas flow rates ($cm^3\,min^{-1}$)		*Current yield $C_5 + C_6 + C_{10}$ (%)*	*Ratio of products (%)*		
CO_2	C_4H_6		C_5	C_6	C_{10}
80	80	58	36	15	49
80	40	61	40	14	46
80	160	49	46	7	47

[a] $I = 42\,mA\,cm^{-2}$. Other conditions as Table 2.

Table 8. Influence of electrolyte flow on the reduction of CO_2 + C_4H_6 at reticulated carbon cathode[a]

Electrolyte ($mol\,dm^{-3}$)	Current yield $C_5 + C_6 + C_{10}$ (%)	Ratio of products (%)		
		C_5	C_6	C_{10}
oxalate (0.1)	33	58	22	20
oxalate (0.04) + formate (0.04)	33	46	10	44
oxalate (0.04) + formate (0.04) + H_2O (0.1)	30	52	9	39

[a] $I = 42\,mA\,cm^{-2}$. Other conditions as Table 2.

water. If the chemistry occurred in the aprotic solvent phase, surely the influence of added water must be similar.

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