

The electrolytic reduction of carbon dioxide and monoxide for the production of carboxylic acids

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This work examines the possible production of carboxylic acids from inorganic feedstocks such as carbon dioxide and monoxide. The technique consists of dissolving the gas in a catholyte consisting of an organic solvent containing a tetraalkyl ammonium halide, separated by a cationic membrane from the aqueous sodium chloride anolyte. The performance of a number of cathode materials, catholyte formulations and cell designs have been investigated both at atmospheric and elevated pressure. It was found that the sole product was oxalic acid which was obtained with current efficiencies of over 50%. Current densities and hence space time yields were, however, disappointingly low.

1. Introduction

Due to the eventual depletion of crude oil as a source of organic chemicals great interest is being shown in alternative inorganic feedstocks. The use of electrolysis for this purpose is essentially a long term development since considerable technical difficulties still remain to be solved.

A previous investigation [1] had indicated that oxalic acid could be produced with current yields of about 70% by the reduction of carbon dioxide in a non-aqueous medium. The problem from the point of view of any industrial development was that current densities and hence space-time yields, i.e. amount of product per unit volume of reactor in unit time, were not high enough. The present work was undertaken in order to try and raise current densities by investigating the performance of a variety of electrode materials. Another, and complimentary, possibility was that by working at an elevated pressure, the higher concentration of carbon dioxide in the electrolyte would allow increased current densities. At the same time the effect on performance of different cell designs was also investigated.

2. Experimental

2.1. Cells

Four cell designs were employed in the present investigation.

2.1.1. A flanged glass cell. This cell was used for work at atmospheric pressure, the catholyte and anolyte being separated by a cationic membrane [2]. The cell's main feature was a high electrode area (discs of about 70 cm²) to catholyte volume (250 cm³) to facilitate quantitative analysis of products.

2.1.2. A filterpress type cell. This cell with electrode areas of 130 cm², flowing electrolyte and a cationic membrane [3] was used for work at atmospheric pressure.

2.1.3. A packed bed electrode cell. Frame dimensions of this cell [4] were 30 cm × 7.5 cm and the bed width in the direction of current flow was 2.5 cm. A feature of this cell was its high specific cathode area, the same electrolyte flow circuit being used as that employed for the cell of Section 2.1.2.

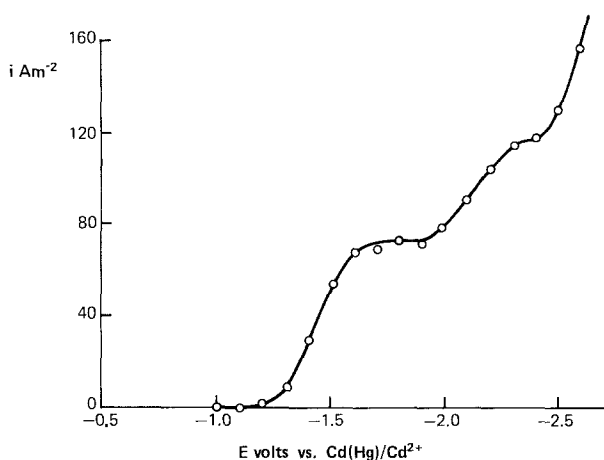


Fig. 3. Polarization curve for a lead cathode in an electrolyte of DMF saturated with TEAB and carbon dioxide. Cathode area 61 cm^2 .

convenient separation but also minimizes any further reduction. The reacting gas is bubbled through the catholyte throughout the experiment which is performed at ambient temperature.

3. Results and discussion

3.1. Work at atmospheric pressure

Before considering oxalic acid it should be mentioned that a considerable effort was employed, using a variety of catholyte formulations, cathode materials and operating conditions, in order to synthesize organic products other than oxalic acid. In this context, it is interesting to look at a typical polarization curve for a lead cathode in dimethyl formamide (DMF) saturated with carbon dioxide (Fig. 3). Two waves are clearly visible, the first being associated with the formation of

oxalic acid. Significant amounts of other organic products could not, however, be identified in the potential range of the second wave. None of the other cathode materials tried (Fig. 4) exhibited this second wave. Polarization curves in the absence of carbon dioxide showed no reduction waves prior to the onset of hydrogen evolution at the more extreme cathodic potentials.

Turning now to the production of oxalic acid, Table 1 summarizes results using cell 2.1.1. with a variety of electrode materials. Other cathode materials tried (not shown in Table 1) included silver and glassy carbon. The catholyte consisted of DMF saturated with tetraethyl ammonium bromide (0.18 M) and carbon dioxide approximately 0.2 M [10]. The catholyte was separated by an Ionac cationic membrane from the anolyte, which consisted of a 1 M aqueous solution of sodium chloride. The anode was graphite in all cases.

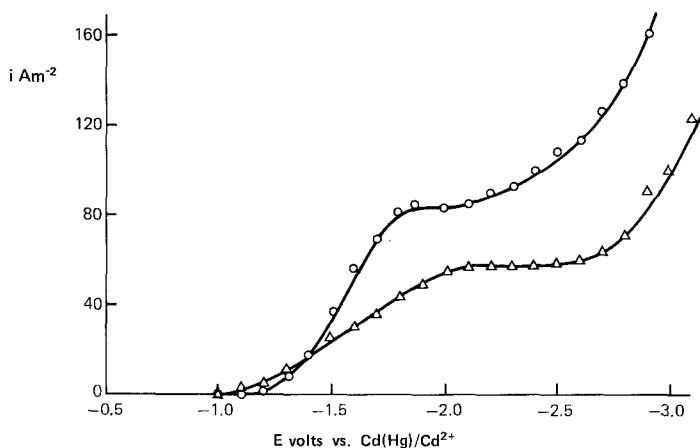
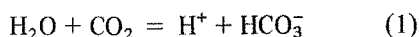


Fig. 4. Polarization curves in an electrolyte of DMF saturated with TEAB and carbon dioxide. \circ — amalgamated lead cathode, area 59.5 cm^2 ; \triangle — cadmium cathode, area 66 cm^2 .

Table 1. Current efficiencies as a function of electrode materials and current density at atmospheric pressure

Cathode material	Current density ($A m^{-2}$)	Current efficiency (%)
Lead	100	31
	200	35
Lead amalgam	100	51
	200	29
Stainless steel	50	25
Cadmium	30	21
	80	22
Aluminium	100	25
Copper	100	9
Zinc	100	23
	200	16

The isolated solid sodium oxalate contained substantial amounts of sodium bicarbonate formed by the reaction between carbon dioxide, water and sodium ions transported across the membrane, according to the equations:



The water content of the catholyte arising from the transport of the hydrated sodium ion is critical, too high a water content ($> 5\%$) resulting in significantly lower current efficiencies. Under these circumstances hydrogen gas could be seen to be evolved. This was also true at higher current densities.

Looking at Table 1 current densities are an order of magnitude lower than one would ideally like. In addition a problem that had to be solved was that using either lead, or the less desirable lead amalgam, in DMF resulted in the formation of a black deposit on the cathode which contaminated the oxalic acid product. The problem became more severe at higher current densities, the deposit probably being formed by solvent attack of the electrode surface. The remaining metals did not suffer from this problem, but current efficiencies were rather low.

In order to find a way of avoiding the attack of DMF on the lead electrode, a number of alternative solvents were investigated. These included the following:

- 1-methylpyrrolidine: no improvement was found
- propylene carbonate: resulted in very low current efficiencies and additionally, due to

its high boiling point, the solvent proved difficult to remove from the oxalic acid product

- acetonitrile: saturated with tetraethyl ammonium bromide, this solvent proved marginally superior to DMF when using a lead electrode. Thus at a current density of $200 A m^{-2}$, the current efficiency was 46% without any attack on the cathode. Unfortunately, going to a higher current density ($500 A m^{-2}$) again produced the black deposit.

Having had little success in avoiding electrode attack at higher current densities by means of a solvent change, attempts were now made to reach the same objective by the use of different cell designs. Polarization curves produced with a stainless steel rotating disc electrode (Fig. 5) indicated that current densities were mass transport dependent. Cells of Sections 2.1.2. and 2.1.3. employing a flowing electrolyte should therefore prove superior in performance to that of the cell in Section 2.1.1., used so far.

Experiments with the filterpress type cell were performed using a stainless steel cathode and two catholyte formulations, namely, DMF or acetonitrile, saturated with tetraethyl ammonium bromide. Current densities in both cases were still low ($150 A m^{-2}$), but current efficiencies were significantly higher than those

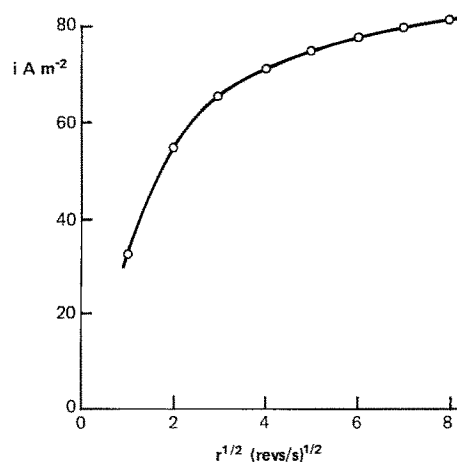


Fig. 5. Increase in current density with rotation speed for a stainless steel rotating disc cathode, area = $0.283 cm^2$, in an electrolyte of DMF saturated with TEAB and carbon dioxide and at an electrode potential of $-2.2 V$ vs $Cd(Hg)/Cd^{2+}$.

quoted in Table 1, namely, 54% and 51%, respectively for the two electrolytes.

Anticipated advantages of using the packed bed cell were not only good mass transfer characteristics, but a hope that the presence of a large specific electrode area would enable one to work at a low current density and yet obtain reasonable space time yields. A disadvantage of this type of three-dimensional electrode was its uneven electrode potential distribution which could lead to unwanted by products. Using DMF saturated with tetraethyl ammonium bromide and a bed of lead shot in contact with a stainless steel current feeder, resulted in a current efficiency of only 20% at a feeder current density of only 70 A m^{-2} . In addition problems arose in getting the solid product out of the packed bed electrode, but worse was that the product was heavily contaminated with lead. Stainless steel particles making up the bed might have provided a partial solution to the problem, but ball bearings, the only material readily available, proved to be prohibitive in price.

3.2. Work at elevated pressure

Table 2 gives results for the production of oxalic acid at a pressure of 690 kN m^{-2} . The latter was maintained by bubbling carbon dioxide continuously into the cell of Section 2.1.4., thereby also providing agitation of the electrolyte. The catholyte had a formulation identical with that for the runs in Table 1, the anode again being graphite and the membrane Ionac. The anolyte was an aqueous solution of 1 M sodium

chloride. All runs were of two hour duration at a constant current density.

Comparing results in Table 2 for the lead cathode with those at atmospheric pressure, it is evident that the elevated pressure produces higher current efficiencies but unfortunately the cathode is still attacked at the higher current density. The lead amalgam performed best in terms of an absence of any black deposit but a limit of 500 A m^{-2} was set by the onset of the decomposition of the DMF to dimethylamine. On balance stainless steel appeared to be the most satisfactory of all the cathode materials looked at in the present work.

3.3. Reduction of CO and mixtures of CO and CO₂

Carbon monoxide and mixtures of carbon monoxide and dioxide were subjected to the techniques applied to carbon dioxide alone, both at atmospheric and at elevated pressure (690 kN m^{-2}). Experiments with carbon monoxide on its own gave no identifiable organic products. This reinforces the finding that no products arose from the electrolysis of the base electrolyte and DMF. Mixtures of carbon monoxide and dioxide gave oxalic acid, but in reduced yields. It was concluded that under the conditions of the experiments carbon monoxide was not reduced.

4. Conclusion

Extensive work has shown that so far the only reduction product of carbon dioxide in a non-aqueous medium was oxalic acid. A major problem was provided by the solvent attack of the working electrode and the resulting limitation to the current densities that could be maintained. Elevated pressure operation did result in some improvement of the situation. A combination of a stainless steel cathode and a flowing electrolyte resulted in the best current efficiencies observed.

Carbon monoxide gave no organic reduction product under the experimental conditions used in the present work.

Table 2. Current efficiencies as a function of electrode material and current density at 690 kN m^{-2} pressure

Cathode material	Current density (A m^{-2})	Current efficiency (%)
Lead	200	58
	500	44
Lead amalgam	50	25
	100	51
	200	40
	300	34
	400	37
	500	30
Stainless steel	100	38
	200	36
Cadmium	200	18
Zinc	500	9

Acknowledgements

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