

The production of oxalic acid from CO_2 and H_2O

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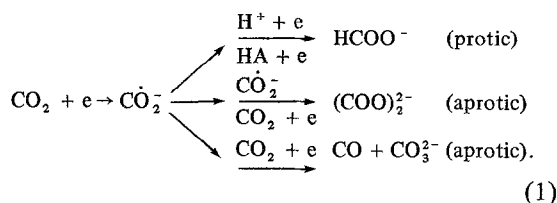
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Oxalic acid has been prepared on a preparative scale in an undivided cell with sacrificial anodes and an aprotic electrolyte. Optimum current efficiencies ($>90\%$) have been obtained in cells with zinc anodes, stainless steel cathodes and acetonitrile with tetrabutylammonium perchlorate as the electrolyte. Micro-pilot experiments revealed that a continuous electrochemical cell can be set up and that the reaction product can be removed by filtration. A complete process is designed by a combination of the oxalic acid production with a zinc electrolysis. No unwanted by-products appear, which is recently of increasing importance. Economic consideration shows that the process may become interesting in the future.

1. Introduction

Carbon dioxide is a waste product which is produced in large amounts by the natural carbon cycle as well as by a number of industrial processes. To make use of this by-product has for a long time been an aim of chemists: in the future with increasing CO_2 levels in the atmosphere the problem of production of useful organic chemicals from this carbon source will become increasingly relevant.

As it is a thermodynamically very stable compound ($\Delta H = -393 \text{ kJ mol}^{-1}$) it is not surprising that many efforts to dimerize the CO_2 molecule have been in vain, whereas the simple electrochemical reduction to formic acid has been known since the work of Royer over a century ago [1]. The low reactivity of CO_2 can be understood by its electronic structure [2]: all bonding and non-bonding molecular orbitals of the linear molecule are fully occupied whereas the lowest antibonding and therefore destabilizing molecular orbitals are not. As a consequence, only very powerful reducing agents such as electrons from a cathode or alkali metal amalgams are able to produce intermediates which either react with protons or proton donors to form formic acid, dimerize to oxalate ions, or disproportionate to carbon monoxide and carbonate:



Overall reactions of the kind listed in Equation 1 have been the subject of a number of kinetic investigations using polarographic or nonstationary methods [3–7], but the results cannot be used as a basis for an electrochemical process. It was Kaiser in this laboratory who first demonstrated the significance of the aprotic properties of the electrolyte in directing the electrochemical reduction towards oxalate and other higher carbon compounds [8]. At the same time, but independently, Baizer *et al.* also produced oxalate in a study of cathodic organic syntheses involving carbon dioxide [9]. Recently Savéant *et al.* published a thorough study of the reduction of CO_2 in dimethylformamide and dimethylsulphoxide on mercury and lead cathodes, in which complete product spectra have been evaluated [10].

2. Preparative and kinetic investigations

The following sections contain a selection of results which are relevant to process development.

Findings of a more basic or theoretical character are omitted and will be published elsewhere. From general considerations a great number of reaction parameters are important: the electrode material, the solvent, the supporting electrolyte, the water content of the electrolyte and the cell construction. To start with the latter, four basic design concepts have been investigated.

2.1. Basic cell design concepts

Fig. 1 shows four types of cell construction:

(a) The three-compartment cell. By using an anionic and cationic ion exchange membrane, an anode, a cathode and a middle compartment can be set up. The cathode compartment contains an aprotic electrolyte whereas the anode and middle compartments contain aqueous electrolyte. The anode reaction is oxygen evolution at a noble

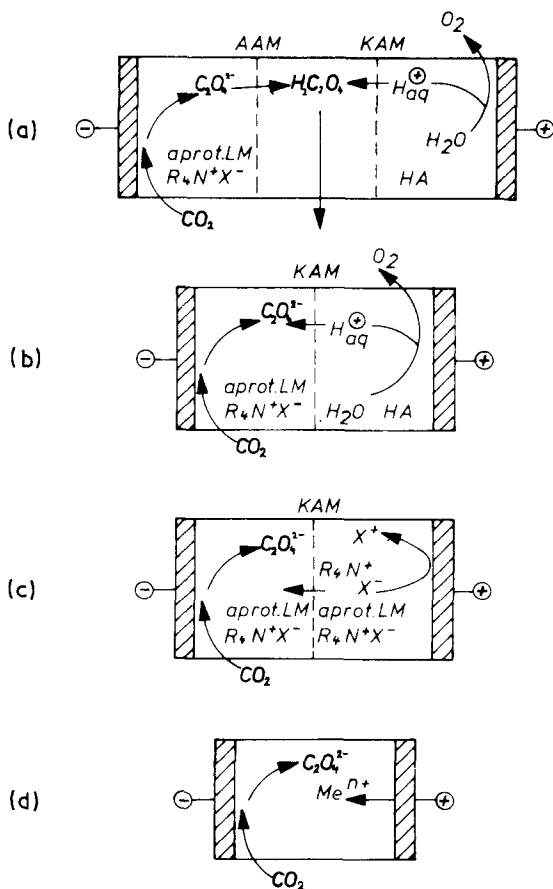


Fig. 1. Development of cell construction, (a)–(d). AAM: anionic ion exchange membrane, KAM: cationic ion exchange membrane, aprot. LM: aprotic solvent.

metal. Most of the results in [8] were obtained with this cell arrangement. The disadvantages of the three-compartment cell are the instability with time because of interdiffusion of the aqueous and aprotic electrolyte and the high cell voltage as a consequence of the two membranes.

(b) The two-compartment cell. This construction only contains a cationic ion exchange membrane with an aprotic and an aqueous electrolyte. The cell voltage is lower but the time stability is still poor. The anode reaction again is oxygen evolution.

(c) The two-compartment cell with aprotic catholyte and anolyte. This design has the disadvantage that there are no suitable anode reactions, the anolyte being anodically oxidized at noble metal electrodes. A typical cell design for a two-compartment cell is shown in Fig. 2. It consists of cylindrical segments with a stainless steel (18% Cr–8% Ni) cathode, a glass frit as the CO_2 inlet, a cation exchange membrane (Nafion 415) and a platinum anode. The advantages of such an arrangement are: low IR drop, a large and adjustable ratio of electrode area/electrolyte volume, homogeneous current distribution and easily exchangeable electrodes and membranes.

(d) The undivided cell with sacrificial anodes. As a final design undivided cells with aprotic electrolyte and an anodically dissolving metal have been used. As will be shown in Section 3, this cell design could become the basis for a continuous electrochemical process.

2.2. Results of experiments on a preparative scale

A great number of experiments have been performed to improve the current efficiency by suitable choice of the electrode material, electrolyte, charge (electrolysis time) and cell type. Most of the experiments have been made in cells of the kind shown in Fig. 2.

The solvents and supporting electrolytes were reagent grade with subsequent further purification according to the following methods. Tetraalkylammonium salts: recrystallization from alcoholic solution and drying in vacuum at $100^\circ C$. Propylene carbonate: drying with molecular sieves and distillation. Dimethylformamide: distillation and drying with molecular sieve. Butyrolactone, acetic anhydride and acetone: drying with

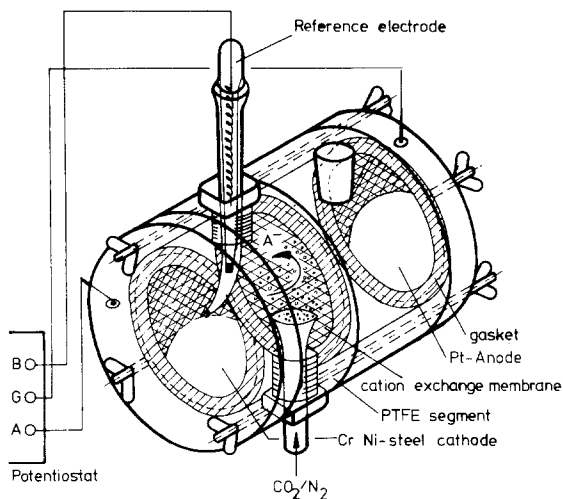


Fig. 2. Divided cell for preparative experiments.

molecular sieve. Analysis was carried out as follows: water determination by the Karl Fischer method; oxalate analysis by manganometric titration and i.r. spectroscopy; higher carbon compounds have been determined by esterification and subsequent gas chromatography.

A compilation of selected results from experi-

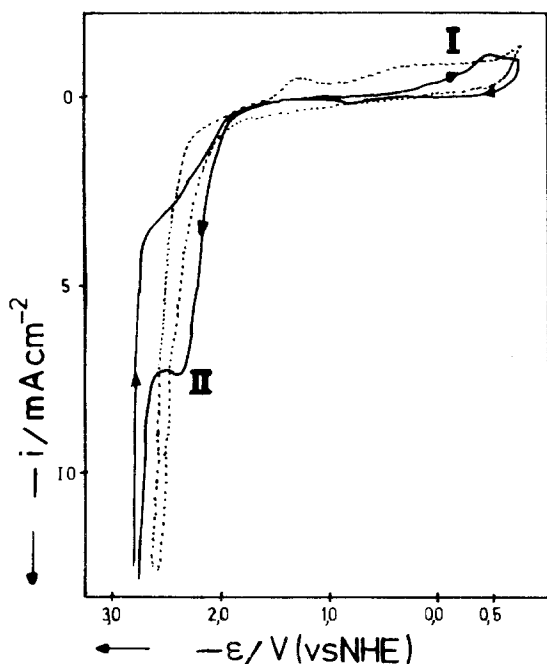


Fig. 3. Cyclic voltammogram of the system CrNi-steel/acetoneitrile + 0.2 M Bu₄NClO₄ at room temperature. Full curve, with CO₂; dotted curve, without CO₂. I, reoxidation peak; II, reduction peak. Sweep rate: 0.1 V s⁻¹.

ments at ambient temperature is shown in Table 1 [11]. It is evident that the current efficiencies increase remarkably with change of cell type from the three-compartment cell to the undivided cell and by the use of Al and Zn as anodes. A high water content leads to low current efficiencies as is to be expected. It seems also that stainless steel is sufficiently effective as a cathode material whereas platinum mainly leads to CO + CO₃²⁻ [8]. In conclusion, the use of an undivided cell with zinc anodes and acetonitrile with tetrabutylammonium perchlorate as electrolyte proved to be the optimum system for the process described in Section 2.4.

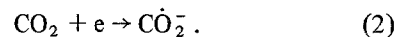
2.3. Kinetic investigations

Extensive experimental results have been evaluated to obtain information on the mechanism of the reactions involved. Besides quasi-stationary current potential curves, cyclic voltammograms were taken and ring-disc experiments were made.

An important question in elucidating the reaction mechanism is whether any intermediates are produced from CO₂. Fig. 3 shows a cyclic voltammogram of the system stainless steel/acetoneitrile + 0.2 M Bu₄NClO₄ at room temperature. From the curves it can be seen that there exists a cathodic (II) and a small anodic peak (I) which can be attributed to a low life-time, oxidizable intermediate. An analogous result is obtained with ring-disc experiments (Fig. 4). The system differs from that above (solvent: DMF; cathode: Pb), but this should not give rise to major differences. If CO₂ is cathodically reduced, an anodic peak appears on the gold ring electrode provided the cathode potential is sufficiently negative.

From these results and the findings in Section 2.4 the following conclusions can be drawn:

(a) The primary step is a charge and mass-transfer (mixed) controlled reaction at a sufficiently cathodically polarized electrode; it leads to the radical ion CO₂^{-•} according to



(b) After the primary electron transfer a chemical step follows which is a combination reaction [11]; it occurs in the bulk of the electrolyte and is most probably the reaction of a radical ion with CO₂ according to an ECE mechanism, as has been con-

Table 1. Selected results from preparative electrolyses at room temperature. (Further results with Zn anodes are given in Section 3.)

Catholyte	Cathode		Anolyte	Conditions			Results			Type of cell			
	Solvent	Electrolyte		C_{H_2O} (g dm ⁻³)	i (mA cm ⁻²)	$-\epsilon_k$ (V) (Ag/Ag ⁺)	U (V)	Q (A s)	β (%)		E_s (kW h kg ⁻¹)		
PC		0.3 M Bu ₄ NClO ₄	> 10	S	Pt	0.1 M H ₂ SO ₄ /H ₂ O	5	—	20	7500	12	99	Three compartments
DMF		0.3 M Bu ₄ NClO ₄	100	S	Pt	1 M NaCl/H ₂ O	5	—	5	7200	9	33	Two compartments, aprotic/protic
PC		0.3 M Et ₄ NClO ₄	40?	Pb	Pt	0.1 M NaCl/H ₂ O	5.1	2.7	6.5	7240	10	38.7	
PC		0.2 M Bu ₄ NClO ₄	0.38	S	Pt	See catholyte	6	—	20–16	1000	32	33	Two compartments, aprotic/aprotic
PC		0.2 M Et ₄ NCl	0.34	S	Pt		5.6	—	10	1030	55	10.8	
DMF		0.2 M Et ₄ NCl	< 0.4	S	Al		5	2–3	5	1000	76	3.9	
Ac		0.2 M Bu ₄ NBr	> 1	Pb	Al		8	—	23–30	997	49	30.4	
EA		0.1 M Et ₄ NF	0.4	S	Al		5.1	2–3	8–90	918	0.1	—	
BL		0.2 M Et ₄ NCl	0.6	S	Al	5	3–4	12	1300	50	14.29		
PC			0.4	S	Al	Identical with catholyte	5	—	2.6–3	1440	68	2.6	Undivided, aprotic
DMF		0.2 M Et ₄ NCl	0.9	S	Al		5.7	—	11	1440	56	11.6	
DMF			0.9	S	Al		10.1	—	3.1	1370	81	2.3	
DMF			0.8	Pb	Al		5.2	2.5	1.8	1120	78	1.4	
Ac		0.3 M Bu ₄ NBr	0.45	Pb	Al		5.6	—	4	996	46	5.2	
DMF			0.35	S	Zn	5	—	2.7	610	72	2.2		
AN			0.06	S	Zn	5	—	4.5	312	68	3.9		
AN		0.2 M Bu ₄ NClO ₄	0.19	S	Zn	5	—	4.3	1200	72	3.6		
AN			0.12	S	Zn	5	—	4.3	600	87	2.9		

Key:

PC propylene carbonate
 DMF dimethylformamide
 Ac acetone
 AN acetonitrile
 EA acetic anhydride
 BL γ -butyrolactone

S high-alloy steel
i current density
 $-\epsilon_k$ cathode potential
 U cell voltage
 Q charge
 β current efficiency with respect to oxalate
 E_s specific energy.

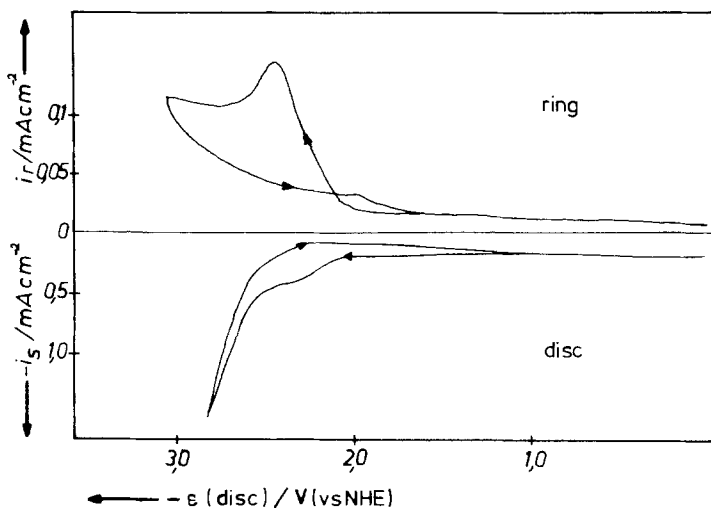
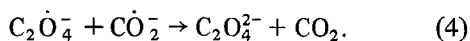
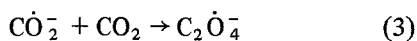
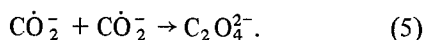


Fig. 4. Results from ring-disc electrode experiments in the system dimethylformamide + 0.2 M Bu₄NClO₄ at room temperature. Ring: Au; disc: Pb. Potential sweep rate at the disc: 0.1 V s⁻¹; angular velocity: 52.36 rad s⁻¹.

cluded by Bewick from a spectroscopic study [7]



Other authors (Savéant *et al.* [11]) favour the purely radical dimerization corresponding to an EC mechanism



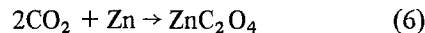
Diagnostic criteria and more experimental material with respect to these two possibilities will be published elsewhere [12].

2.4. Micro-pilot experiments on the electrochemical step in a complete oxalic acid process

To develop a complete process, experiments have to be focused on the electrochemical reaction, although other steps may also be of importance. The following problems have to be solved: (a) the electrochemical step must be continuous, (b) a suitable anodic reaction in aprotic solvents must be found, and (c) the reaction product should be easily separable.

Experiments were performed in a laboratory-size loop containing all the relevant parts for a large-scale design (Fig. 5). The loop had an overall content of 1 dm³ and consisted of a parallel-plate cell with a CrNi-steel cathode and a zinc anode, a pump, a heat exchanger, a CO₂ inlet and finally provision for product separation. The electrolyte had the following composition: acetonitrile + 0.2 M Bu₄NClO₄.

Both step-wise and continuous experiments revealed that the aims cited above can be met. The precipitation of insoluble zinc oxalate according to the overall cell reaction



proved to be possible, with the reaction product removed by filtration.

The dependency of the current yield on the amount of charge (Fig. 6) and current density (Fig. 7) is most interesting. It can be seen that increases in both the amount of charge (i.e. time of electrolysis up to 100 h) and the current density increase the current yield, which rises to more

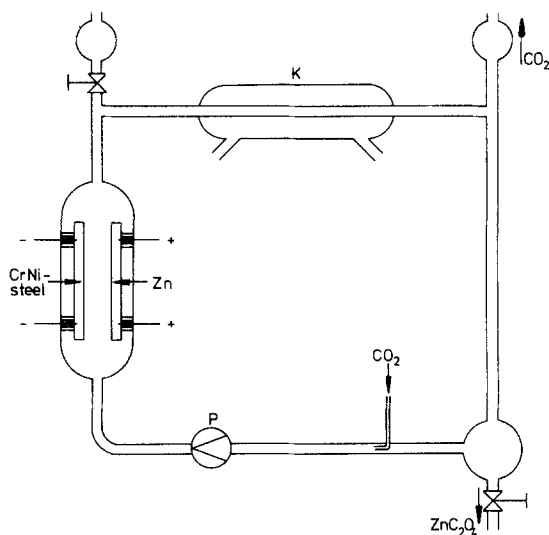


Fig. 5. Scheme of the micro-pilot loop. K, Cooler; P, pump.

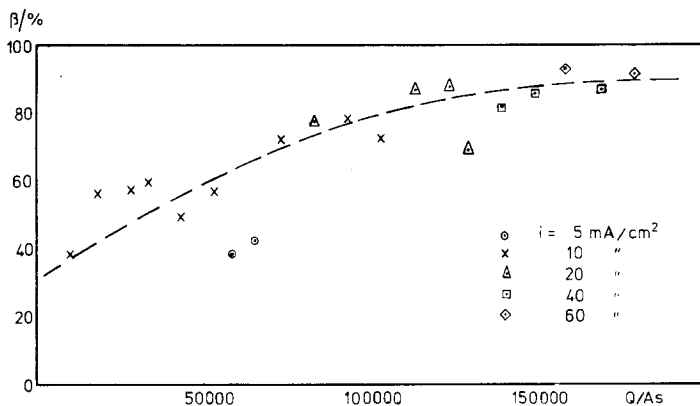


Fig. 6. Current yield and amount of charge (150 000 A s) in acetonitrile + 0.2 M Bu_4NClO_4 . Anodes: Zn; cathodes: CrNi-steel.

than 90%. For the amount of charge this is a completely unexpected finding since yields of organic electrochemical reactions tend to diminish because of aging effects. The increase of the current yield with rising current density can be easily explained by the postulated ECE or EC mechanism: higher current densities increase the concentration of the radical ion intermediate and, as a consequence, the recombination rate leading to oxalate ions is increased. It is important from the point of view of electrochemical engineering that these high current yields were obtained in nonpurified electrolytes. Therefore no special drying procedures are necessary. The analysis of the product revealed only oxalate but no higher carboxylic acids. The difference between the cathodic current yield obtained and 100% is due to cathodic hydrogen and formate production.

The cell voltage and the ohmic drop have been determined as a function of the current density (Fig. 8). The linear characteristics of the cell

voltage are not only due to the ohmic drop in the electrolyte but also to a linear polarization behaviour of the electrodes. This observation cannot be explained at the present time. Since the electrode separation was 6 mm during these experiments a decrease in distance could well give further reduction of the cell voltage. At a current density of 80 mA cm^{-2} the reaction product formed a weakly adherent deposit at the electrodes with a consequent increase in the cell voltage. This effect could be overcome by higher flow velocities in the cell.

3. Design of a complete process

As is well known in electrochemical engineering, the central electrochemical cell is only a small part of a complete process. Therefore a set of additional steps has been designed to form a closed material cycle for the oxalic acid process [13]. The principle of the proposal for this new

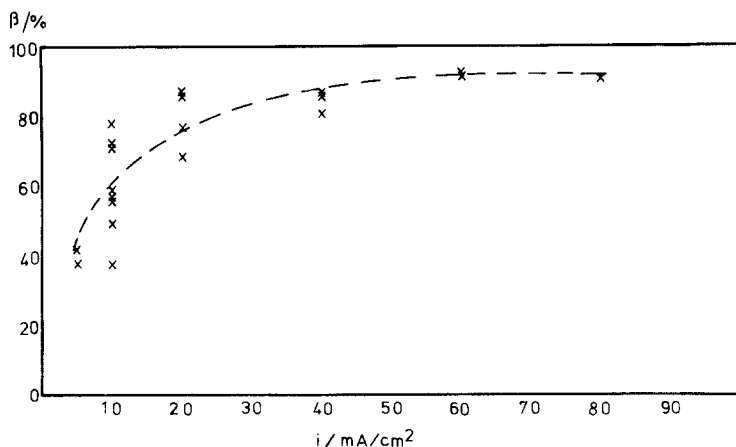


Fig. 7. Current yield as a function of current density (from Fig. 6).

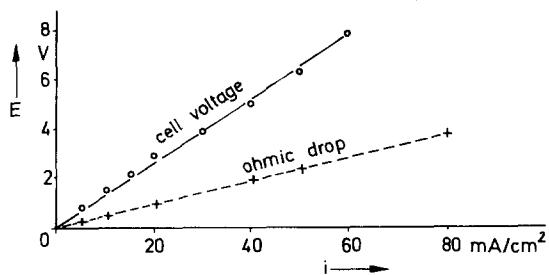
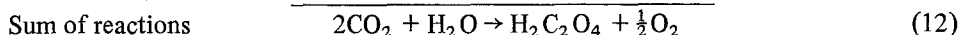
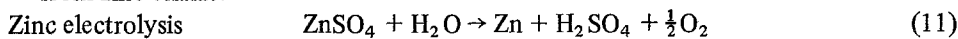
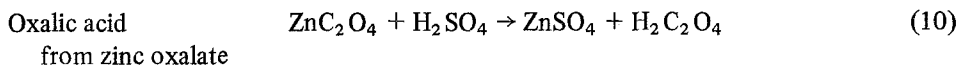
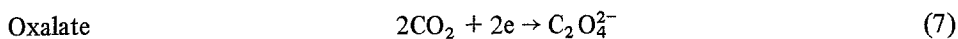


Fig. 8. Cell voltage and ohmic drop versus current density; system: see Fig. 6.

process is the combination of the oxalic acid production with a zinc electrolysis. The stoichiometry of cell steps leads to the following set of equations:



After the oxalate electrolysis and separation of product, a liquid/liquid extraction follows and the resulting zinc sulphate is recycled into a zinc electrolysis.

It is interesting to note that no unwanted by-products appear, as is often the case with organic electrochemical processes. Another important point is the similarity of the overall reaction with the photosynthesis in nature, which also starts with CO₂ + H₂O and forms carbohydrates and oxygen.

Preliminary experiments show that in principle

the different steps of the process can be realized according to the flow sheet in Fig. 9. The process starts with the oxalate electrolysis which is performed in an electrolyte loop with a filter for separation of the solid zinc oxalate. The zinc oxalate is transferred into a dissolver which is fed by sulphuric acid from the zinc electrolysis. The solution containing ions of oxalate, sulphate, zinc and hydrogen is extracted by an organic solvent which separates the oxalic acid from the zinc sulphate. Experiments with ethanol and a concentrated mixture of the dissolver product showed a satisfying separation effect. The aqueous phase is transferred into the zinc electrolysis cell and the alcoh-

holic oxalic acid solution is finally evaporated to form dry oxalic acid.

The whole process consists of four cycles: the aprotic electrolyte, the zinc cycle, the sulphuric acid cycle and the alcoholic extraction cycle. The mass balance in the idealized case shows only input of carbon dioxide and water and output of oxalic acid and oxygen. The energy input comprises the electrical energy for the oxalate and zinc electrolysis, the separation energy for the extractor and the evaporator and various mechanical energies for pumping, mixing, etc.

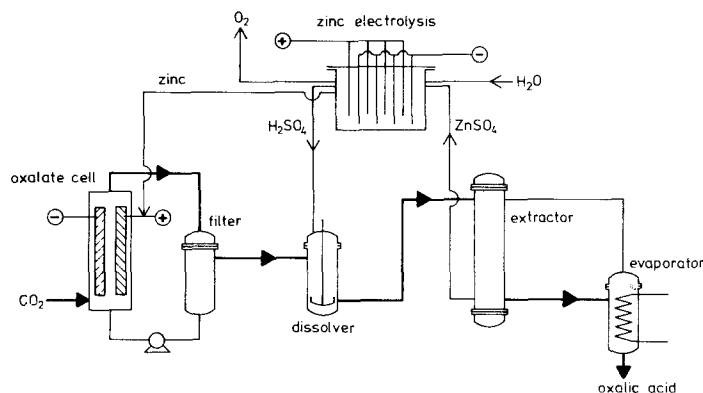
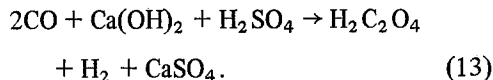


Fig. 9. Flow sheet of the proposed process.

4. Economic considerations

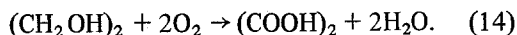
At the present time the main oxalic acid production processes are [14]:

(a) The thermal decomposition of calcium formate via sodium formate with the following overall reactions:



(b) The oxidation of propylene by nitric acid.

(c) The catalytic oxidation of glycol [15]



The first process is the classical one: it consists of a number of steps with yields (based on CO) between 80 and 90%. It inevitably leads to the formation of calcium sulphate as an unwanted by-product, with an associated disposal problem. Processes (b) and (c) are based on petrochemicals, (b) having a yield of approximately 80%. No specific information has been published on the 'one-step' process (c) (the starting material is the petrochemical, ethylene) [15].

In principle the electrochemical process neither poses waste disposal problem, which is now of increasing economic significance, nor does it involve petrochemicals. If a cost estimate is made on the basis of 80% current efficiency, 90% material efficiency, 1 kA m⁻² current density, 4 V cell voltage and a production capacity of 2000 t y⁻¹, a production cost of approximately DM200 per 100 kg oxalic acid is obtained. This number has the same magnitude as the selling price of oxalic acid (in West Germany, 1979). Therefore economic production is not possible at

this time. However, it is to be expected that with increasing price of petrochemicals and coal-based raw materials (carbon monoxide) the process may become economically interesting in the near future. In countries with lower oxalic acid prices the outlook is less promising.

Acknowledgement

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