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BRIEF COMMUNICATION

C_1 ELECTROCHEMISTRY : ELECTROSYNTHESIS OF OXALIC ACID FROM CARBON DIOXIDE

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Oxalic acid has been synthesized from carbon dioxide as its zinc salt on a preparative scale in an undivided cell with soluble anodes like zinc and lead cathode in dimethyl formamide medium with tetrabutyl ammonium perchlorate as supporting electrolyte. The yield efficiency is around 85% with a current efficiency of about 80%. Formation of some oxidisable organic product from reduction of oxalic acid is also indicated.

Key words: Electrosynthesis, C_1 electrochemistry, oxalic acid, reduction of carbon dioxide

INTRODUCTION

Reduction of carbon dioxide by electrochemical and photoelectrochemical methods has been studied extensively [1–6]. This reduction reaction has several attractive features. Due to the depleting resources of oil and other fossil fuels, alternative energy sources have to be tapped particularly from abundant resources such as carbon dioxide and water. Also, effective utilisation of carbon dioxide helps reduce its content in the atmosphere for pollution hazards. Carbon dioxide can be reduced to a number of important organic chemicals, such as formic acid, methanol, oxalic acid, etc [6] and may be coupled with organic halides [7], alkenes [8], carbonyls [9] and schiff's base [10] to produce valuable carboxylated products of commercial interest.

Carbon dioxide is a thermodynamically very stable molecule reduction of which requires high overpotential. Wide spectrum of products are formed depending on various electrochemical parameters like electrode, reaction medium, etc; in aprotic solvents, formatiion of oxalic acid is reported on stainless steel cathode [11].

In this paper, a simple and convenient electrochemical method for the preparation of oxalic acid from carbon dioxide using lead cathode is reported.

EXPERIMENTAL

A high purity lead sheet (4cm (dia) x 9cm(h)) bent in a cylindrical fashion was cleaned with nitric acid, washed thoroughly with distilled water, dried and then used as the cathode. A high purity zinc sheet (3.5cm (dia) x 9cm(h)) also bent cylindrically was cleaned in the similar way and used as the anode. Laboratory grade dimethyl formamide (DMF) was dried and used as the solvent. Tetrabutylammonium perchlorate (Fluka) was used as the supporting electrolyte. A simple double walled glass cell was fabricated with provision for introducing anode, cathode, thermometer, stirrer and gas inlet. A solution of 0.1M tetraalkylammonium salt in DMF was used as the reaction medium. Carbon dioxide gas from a commercial cylinder was purified by passing through heated copper turnings and solvent supporting electrolyte. Purified carbon dioxide was passed for 20 minutes at the flow rate of 4 litres per minute into the solvent medium contained in a glass cell at 293K. The dissolved carbon dioxide was estimated as barium carbonate gravimetrically using barium chloride solution. Electrolysis was carried out at 323K.

After electrolysis, a white or in some cases black solid settled at the bottom of the cell which was filtered, washed thoroughly with water to remove DMF and dried. The white solid was analysed as zinc oxalate. The zinc oxalate was decomposed with dilute sulphuric acid and the oxalic acid formed was estimated volumetrically using permanganate.

RESULTS AND DISCUSSION

When a number of experiments were carried out on the reduction of CO_2 in DMF with stainless steel cathode, oxalic acid was not formed as the major product as reported [11], but constituted only 2-5% of the product. On the other hand, zinc carbonate was obtained as the major product. It seems now that on stainless steel cathode, even under aprotic condition, carbon dioxide anion radical formed by 1e transfer undergoes diproportionation to carbon monoxide and carbonate.

$$CO_2 + e \longrightarrow CO_2^{\cdot-} \qquad \ldots (1)$$

$$CO_2^{\cdot-} \xrightarrow{CO_2+e} CO + CO_3^{2-} \qquad \ldots (2)$$

Alternatively, lead was examined as cathode material. On lead cathode, a pure white solid was obtained which was characterised to be zinc oxalate. From zinc oxalate, oxalic acid content was estimated. At low current densities (0.5 $A.dm^{-2}$ to 1 $A.dm^{-2}$), oxalic acid is obtained in 85% yield and the current efficiency is also around 80%. When a higher current density is employed, a black solid is obtained. This black solid becomes white on washing with water or on exposure to atmosphere. Both the black and white solid always contained about 20% of other oxidisable organic compounds. On lead electrode, it is believed that the product undergoes dimerisation according to the following scheme.

At cathode: $$CO_2 + e \longrightarrow CO_2^{\cdot-} \qquad \ldots (3)$$

$$2\ CO_2^{\cdot-} \longrightarrow (CO_2^-)_2 \qquad \ldots (4)$$

At anode: $$Zn \longrightarrow Zn^{2+} + 2e \qquad \ldots (5)$$

Overall: $$Zn^{2+} + (CO_2^-)_2 \longrightarrow ZnC_2O_4 \qquad \ldots (6)$$

The decomposition reaction is

$$ZnC_2O_4 + H_2SO_4 \longrightarrow ZnSO_4 + H_2C_2O_4 \qquad \ldots (7)$$

CONCLUSION

Reduction of carbon dioxide in DMF medium with a lead cathode and a zinc anode gives oxalic acid in good yield. Studies on the

effect of various experimental conditions as well as large scale synthesis are under way.

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