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Carbon Dioxide Fixation by Electrolysis of Aqueous Hydrogencarbonate Solution. Reduction to Formic Acid at a Mercury Cathode

Hiroki FUJIWARA, Akinori KONNO, and Tsutomu NONAKA*
Department of Electronic Chemistry, Tokyo Institute of
Technology, 4259 Nagatsuta, Midoriku, Yokohama 227

Carbon dioxide liberated by introduction of anodically-generated acid into an aqueous cathodic solution of sodium hydrogencarbonate was efficiently (65% current efficiency) reduced to formic acid at a mercury cathode in a divided cell with a cation-exchanging membrane.

In recent years, electrochemical reduction of carbon dioxide has received much interest and been frequently reported. For instance, Hori *et al.*1) tested various kinds of metals as cathode materials in a carbon dioxide-saturated solution and reported that product-selectivity and current efficiency were greatly affected by the materials.

Because alkali treatment of exhaust and waste gases containing carbon dioxide in low contents is one of useful methods for recovering carbon dioxide, it should be desired to develop efficient procedures for the electroreductive fixation of carbonates. However, Rysselberghe *et al.*2) suggested that carbonates are not polarographically electroreducible. On the other hand, Iwahara *et al.*3) suggested the possibility of the reduction of hydrogencarbonate to formic acid at a mercury cathode. This problem has been given an answer by Hori and Suzuki;4,5) namely, carbon dioxide dissociated from hydrogencarbonate can be reduced, but limiting current density for the reduction must be extremely low because of the very small dissociation constant.

Thus, an auxiliary acid is necessary to liberate carbon dioxide in concentration high enough to be reduced at a practically reasonable current density in carbonate solutions. In this work, it was aimed to use anodically-generated acid as the auxiliary acid for liberating carbon dioxide from a hydrogencarbonate solution. A principle to realize this purpose is illustrated in Fig. 1. This principle is applicable to the reduction giving products more acidic than carbonic acid, judging from the overall stoichiometry.

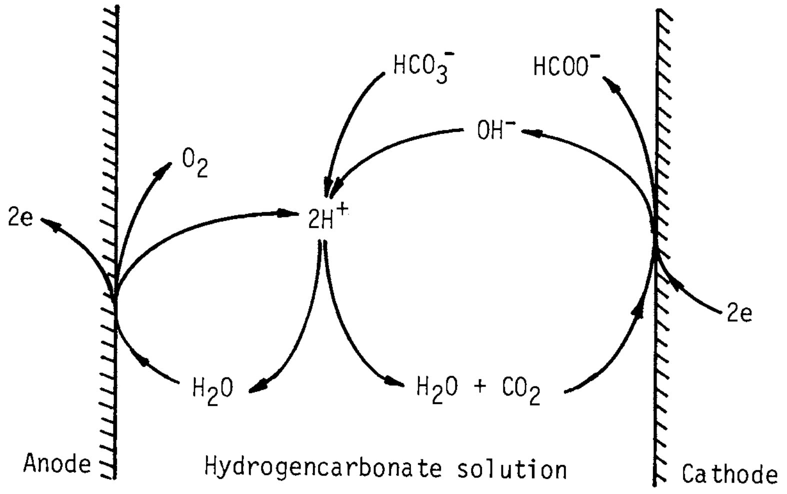

Fig. 1. Schematic illustration of a principle for reduction of hydrogencarbonate to formate.

The reduction to formic acid at a mercury cathode was examined as a test reaction in divided and undivided cells in this work. No carbon dioxide gas was introduced into the cells in order to indicate clearly that carbon dioxide derived from hydrogencarbonate in the solution was certainly reduced.

The H-type divided and beaker-type undivided cells were left open to the atmosphere, unless stated otherwise. The former was equipped with a glass frit disc (G-4) or a cation-exchanging membrane (Nafion 427). A mercury pool cathode (Diameter, 2.5 cm) and a platinum plate (Area, 8 cm^2, unless stated otherwise) were used. A sodium hydrogencarbonate solution (0.8 mol dm^{-3}, 50 cm^3) was used as the catholyte for the divided cell or as the electrolyte for the undivided cell. The solution was agitated by a magnet bar floating on the mercury pool cathode, unless stated otherwise. Electrolysis was galvanostatically (Cathodic current density, 10 mA cm^{-2}) carried out by passing 2500 C (0.6 F(1 F = 96480 C) $mol(HCO_3^-)^{-1}$) in an ice bath. Formic acid was analyzed by HPLC (SCR 101-H column, 0.1% H_3PO_4).

Electrolytic results are summarized in Table 1. Runs 1 and 2 were performed in the divided cell with a glass frit diaphragm as control experiments for comparison with Runs 3 - 6. A high current efficiency (75%) for formic acid was obtained when carbon dioxide gas was introduced into the catholyte during the electrolysis (Run 1), while the efficiency decreased significantly to 3% without introduction of the gas (Run 2). These results are equivalent to those reported previously.[1)]

Table 1. Electrolytic reduction of sodium hydrogencarbonate solution to formic acid at a mercury cathode

Run	Cell	Diaphragm	Current efficiency/%
1[a,b]	Divided	Glass frit	75
2[a]	Divided	Glass frit	3
3[c]	Undivided	-	29
4[c,d]	Undivided	-	42
5[c,e]	Divided	Nafion 427	38
6[c,e,f]	Divided	Nafion 427	65

a) Anolyte, 0.8 mol dm^{-3} $NaHCO_3$. b) CO_2 gas was introduced into the catholyte during electrolysis through a bubbling tube. c) A small amount (1 mmol) of H_2SO_4 was added to the electrolyte (catholyte) before electrolysis. d) A small anode (Area, 0.8 cm^2) was used. e) Anolyte, 1 mol dm^{-3} H_2SO_4. f) The capillary tube and the catholyte was agitated by a motor-driven propeller and a magnet bar.

Undivided cell electrolysis resulted in a very poor efficiency similarly to Run 2. However, a fairly good efficiency (29%) could be obtained, when a small amount (1 mmol) of sulfuric acid was added to the electrolyte before electrolysis to liberate initially carbon dioxide from hydrogencarbonate used (Run 3). This value of efficiency corresponds to 9% yield of formic acid based on the starting hydrogencarbonate, while sulfuric acid added must liberate carbon dioxide corresponding to only 2% of the hydrogencarbonate. Therefore, it is clearly verified that carbon dioxide liberated from hydrogencarbonate by anodically-generated acid is reduced to formic acid. The efficiency increased when an extremely small anode compared with the cathode was used (Run 4). This fact suggests that formic acid once formed is consumed by the anodic oxidation, probably to carbon dioxide.[6)] Hence, the undivided cell electrolysis should give much higher efficiencies in cases where reduction products are not oxidized anodically.

To prevent the oxidation of formic acid and transport smoothly the anodically-generated acid to the cathode chamber, another type of divided cell with a cation-exchanging membrane (Nafion 427) was used. The addition of sulfuric acid seemed to be also necessary in this cell. Unexpectedly, electrolysis (Run 5) in this cell gave a rather lower efficiency than that in Run 4, though higher than that in Run 3. It was observed that carbon dioxide bubbles were formed at the cathode side of the membrane and did not dissolve immediately in the catholyte. Thus, the bubbles might escape to the atmosphere passing through the catholyte. In Run 6, the cathode chamber was closed with a rubber stopper and the catholyte was strongly agitated by both a magnetic bar and a motor-driven propeller,and consequently a high efficiency of 65% could be obtained. It is noticeable that this value of efficiency is comparable to that in Run 1 which was operated under bubbling of carbon dioxide gas. The efficiency seems to be governed by not only electrochemical factors but also chemical engineering ones such as fluidics of electrolyte, geometry of cell assembly, character of membrane and gas-tightening system of propeller shaft. Optimization of these factors should be made from a practical aspect in a case where this electrolytic system is industrialized.

According to the overall stoichiometry (Fig. 1), this system developed should be also applicable to a variety of carbon dioxide reductions giving acidic products[7-14] other than formic acid.

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