Electrochemical Reduction Products of Carbon Dioxide at Some Metallic Electrodes in Nonaqueous Electrolytes

Kaname Ito,* Shoichiro Ikeda, Nobuhiro Yamauchi, Takaya Iida, and Takehiko Takagi
Department of Applied Chemistry, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466
(Received May 4, 1985)

Synopsis. Regarding the electrochemical reduction of carbon dioxide in nonaqueous electrolytes, it has been clarified that the main products are oxalic acid at a Pb electrode and carbon monoxide at Sn and In electrodes. In the case of a Zn electrode, substantial amounts of oxalic acid, glyoxylic acid and carbon monoxide have been produced.

According to previous papers,[1-3] the electrochemical reduction products of carbon dioxide dissolved in aqueous electrolytes under either ordinary or high pressures were mainly formic acids at electrodes of indium (In), lead (Pb), tin (Sn), zinc (Zn), and cadmium (Cd).

We have reported in another paper[4] that for nonaqueous electrolytes consisting of dimethyl sulfoxide (DMSO) and tetraalkylammonium salts, such as $(C_2H_5)_4NClO_4$ (TEAP), the main product is oxalic acid at a Pb electrode. It was suggested that carbon monoxide should probably form at In, Sn, and Zn electrodes.

Therefore, in the present paper a cyclic gas flow system for supplying CO_2 to an electolytic cell was employed in order to determine gaseous products on the electrochemical reduction of carbon dioxide at various metallic electrodes. This was investigated in nonaqueous electrolytes using propylene carbonate instead of DMSO. The effects of various electrode metals and electrlytic conditions on the products are described.

Experimental

An electolytic cell made of Teflon was designed for separating a cathode chamber from an anode chamber with an ion-exchange membrane, Nafion 315. This system was made gas tight. The cyclic gas flow system was designed to use a peristaltic mini-pump, a gas sampler and a manometer for supplying CO_2 gas to a cell. Gaseous products in the cyclic gas were determined as well as products at various electrolytes.

Working electrodes were prepared from solid-state metals such as Pb (purity 99.99%), Sn (99.999%), In (99.999%), and Zn (99.9999%). These have been employed as described in previous papers.[1-4] The reference electrode utilized in the present work consisted of a silver silver chloride electrode with a (0.01 M LiCl+0.1 M TEAP)(1 M=1 mol dm^{-3})/ propylen carbonate solution saturated with AgCl. The potentials given in the present paper are with respect to this Ag/AgCl reference electrode.

Since commercially obtained guaranteed reagent propylene carbonate possessed various impurities, it was purified using Jasinski and Kirkland's method.[5] The catholyte and the anolyte each utilized 10 ml of a 0.1 M TEAP/ propylen carbonate nonaqueous electrolyte prepared from the synthesized TEAP[3] and purified propylen carbonate. The water content of the electrolyte was determined by Karl Fischer's titration method[6] to be 320 ppm.

Electrolytic experiments for a determination of the reduction products of carbon dioxide were carried out using working-electrodes with surface areas of 2.47 to 7.20 cm^2. After an electrolyte within a cell was sufficiently saturated with CO_2 gas and the system was substituted by CO_2 gas, it was closed and the enclosed gas was made to flow at a rate of 0.9 cm^3 min^{-1} using a peristaltic pump. The electrolytic current was potentiostatically flowed at 100 or 200 C (coulombs). The products in the electrolytes were qualitatively and quantitatively determined by high-performance liquid

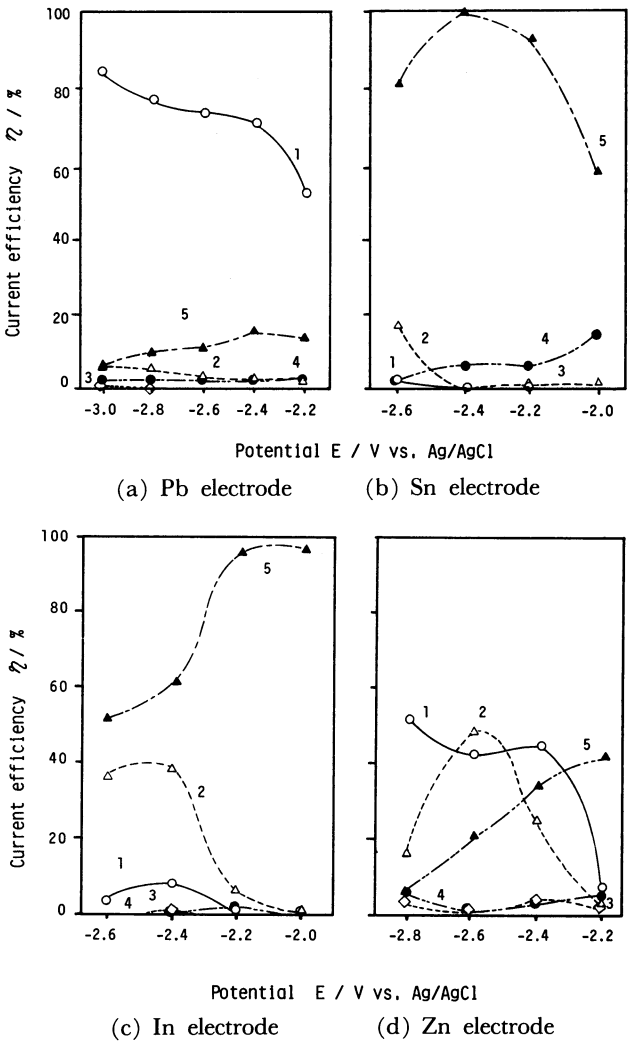

Fig. 1. Current efficiencies of electroreduction products of CO_2 in the cases of Pb(a), Sn(b), In(c), and Zn(d) electrodes.
Electrolyte: 0.1 M TEAP/propylen carbonate, Quantity of electricity passed: 100 C (a) or 200 C (b, c, d).
Curve 1 (—○——): Oxalic acid, 2 (-△---): Glyoxylic acid, 3 (--◇---): Glycolic acid, 4 (-●----): Formic acid, 5 (—▲—·—): Carbon monoxide.

chromatgraphy. Gas chromatgraphy was used to determine the gaseous products in the cyclic gas. This equipment and the operating conditions were similar to that described in a previous paper.[4]

Results and Discussion

The electrochemical reduction products in both the electrolyte and the cyclic gas were determined. The obtained results are illustrated in Fig.1 as current efficiencies of products with respect to certain potentials (−2.0 to −3.0 V) for each electrode.

When a Pb electrode was employed, the main product was oxalic acid and the current efficiency increased to *ca.* 80% at −3.0 V, as shown in Fig. 1-(a). The efficiencies for formic, glyoxylic and glycolic acids were less than 5% in a potential range of −2.2 to −3.0 V, though 6 to 15% for carbon monoxide. On the other hand, when a Sn electrode was employed, the main product was carbon monoxide and its current efficiency increased to *ca.* 100% at −2.4 V, as shown in Fig. 1-(b). Other products had relatively lower efficiencies. In the case of an In electrode, as shown in Fig. 1-(c), the main product was also carbon monoxide at every potential measured; however, the current efficiencies, though *ca.* 95% in the potential range of −2.0 to −2.2 V, decreased to below 60% at potentials less than −2.4 V. Also, glyoxylic acid, instead of carbon monoxide, was produced with a current efficiency of *ca.* 40%. In the case of a Zn electrode, as shown in Fig. 1-(d), oxalic acid, glyoxylic acid and carbon monoxide were produced with substantial current efficiencies. According to these results, it has been experimentally comfirmed that carbon monoxide is the main product for Sn and In electrodes. This was not comfirmed in a previous paper.[4]

Consequently, although Saveant *et al.*[7] have reported that the production of oxalic acid by the electroreduction of carbon dioxide in a nonaqueous electrolyte was mainly dependent on the current densities from experimental results using only Pb and Hg electrodes, it may be concluded that the electroreduction products for carbon dioxide are primarily dependent on the electrode metals employed. Then, the main products are oxalic acid at a Pb electrode and carbon monoxide at Sn and In electrodes. Also, the current efficiencies regarding the products at each electrode are affected by the electrode potentials.

References

1) K. Ito, T. Murata, and S. Ikeda, *Bull. Nagoya Inst. Tech.*, **27**, 209 (1975).
2) K. Ito, S. Ikeda, and M. Okabe, *Denki Kagaku*, **48**, 247 (1980).
3) K. Ito, S. Ikeda, T. Iida, and H. Niwa, *Denki Kagaku*, **49**, 106 (1981).
4) K. Ito, S. Ikeda, T. Iida, and A. Nomura, *Denki Kagaku*, **50**, 463 (1982).
5) R. J. Jasinski and Kirkland, *Anal. Chem.*, **39**, 1663 (1967).
6) K. Muroi, *Bunseki*, **1979**, 74.
7) C. Amatore and J. M. Saveant, *J. Am. Chem. Soc.*, **103**, 5021 (1981).