Electrochemical Reduction of CO_2 to Hydrocarbons with High Current Density in a CO_2-Methanol Medium

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We reported that CO and methyl formate were the major products in the electrochemical reduction of highly concentrated CO_2 in a CO_2-methanol medium when tetrabutylammonium salts were used as supporting salts. Here we report that CO_2 is reduced efficiently to hydrocarbons when tetraethylammonium perchlorate is used as the salt. CO_2 reduction proceeds with a current efficiency of 89.7 % at *1 A·cm*$^{-2}$, indicating sufficient mass-transfer of CO_2 even at such a high current density.

High current density is a topic of great interest in electrochemical reduction of CO_2. Utilization of gas diffusion electrodes[1-3] and electrolysis in aqueous systems under high pressure of CO_2[4-9] have been reported. In order to obtain a high current density, we have conducted the electroreduction of highly concentrated CO_2 in a CO_2-methanol medium. Mole fraction of CO_2 (χ) is 0.34 at 4.0 MPa and 0.94 at 5.8 MPa.[10] Supply of CO_2 to the electrode is sufficient so that CO_2 reduction proceeds with high current density and efficiency.[11,12] We have also reported the effects of the supporting salt on the reaction.[13] The electrochemical reduction of such concentrated CO_2 may be called "the electrochemical reduction of *liquid* CO_2."

Reduction product is also an important matter. In aqueous ambient systems, two-electron transfer products such as CO and formic acid are formed at most of metal electrodes. Hydrocarbon formations are more interesting in the electrochemical reduction of CO_2, since multi-electron transfer is required in the process. Among various metals, only Cu shows the remarkable electrode activity of hydrocarbon formation in the electrochemical reduction of aqueous CO_2.[14,15] In the electrochemical reduction of concentrated CO_2 in the CO_2-methanol medium, major products are still two-electron transfer products of CO and methyl formate ($HCOOCH_3$) at a Cu electrode, when tetrabutylammonium (TBA) or lithium salts are used as supporting electrolytes.[13] We report here that CO_2 is efficiently reduced to hydrocarbons with high current density in a CO_2-methanol medium when *tetraethylammonium* salt is used.

A working electrode used was a copper wire of 0.5 cm^2, which was donated by Sumitomo Electric Industry (purity >99.999 %). A counter electrode used was a platinum wire. The working electrode was etched electrochemically in concentrated H_3PO_4 before use. Tetrabutylammonium tetrafluoroborate (TBAT, Aldrich), tetrabutylammonium perchlorate (TBAP, Tokyo Kasei) and tetraethylammonium perchlorate (TEAP, Tokyo Kasei) were used as supporting salts. Carbon dioxide was introduced into 1.0-ml methanol containing 0.1-M supporting salt. Electrolyses were performed in a one-compartment cell in a pressure-tight apparatus (13.2 ml), at 298 or 293 K, at 0.1 and 4.0 MPa, galvanostatically with a potentio-galvanostat (HA-501, Hokuto Denko). After the electrolysis, reaction products were quantitatively analyzed by gas chromatography. Details were described in the previous paper.[12]

Results of the electrolyses are presented in Table 1. Carbon monoxide, methane and ethylene were determined to be CO_2 reduction products by $^{13}CO_2$-$^{12}CH_3OH$-$(^{12}C_2H_5)_4NClO_4$ and $^{13}CO_2$-$^{12}CH_3OH$-$(^{12}C_4H_9)_4BF_4$ experiments. Ethane was formed with about 1-% efficiency when TEAP was used. This compound was also confirmed to be a CO_2 reduction product, although it was not shown in Table 1. One-fifth to one-third of methyl formate was $H^{12}COO^{12}CH_3$ even in the $^{13}CO_2$ experiments. However, its current efficiency was tentatively calculated on the basis that all of detected $HCOOCH_3$ is a CO_2 reduction product.

When TBAT is used as a supporting electrolyte and χ is 0.007, H_2 is the main product at 500 mA·cm^{-2}. The low efficiency of CO_2 reduction indicates that CO_2 reduction is limited by mass-transfer process of CO_2. Total current efficiency of CO_2 reduction to hydrocarbons is 9.3 %. At χ=0.33, CO_2 reduction proceeds with the efficiency higher than 90 %. Carbon dioxide is reduced to CO and $HCOOCH_3$ mainly. Hydrocarbon formation is inefficient in the whole range of current density from 0.8 to 500 mA·cm^{-2}.[12]

Here we define the selectivity of hydrocarbon among CO_2 reduction products (γ_{HC}) as follows:

$$\gamma_{HC} = \frac{\eta_{CH_4} + \eta_{C_2H_4}}{\eta_{CO} + \eta_{HCOOCH_3} + \eta_{CH_4} + \eta_{C_2H_4}}$$

where η refers to the current efficiency of each product. The values of γ_{HC} are 29.0 % at χ=0.007 and 6.9 % at χ=0.33 with TBAT electrolyte. These results show that CO_2 reduction to hydrocarbons is less efficient under higher concentration of CO_2. Hara et al. reported recently that product distribution of CO_2 reduction in an aqueous high pressure system depends on a flux of CO_2 to the electrode; selectivity of hydrocarbons is low when CO_2 is supplied excessively to the electrode.[9] The main product in their system is CO when the electrolyte solution is stirred under a diffusion-control condition, while it is CH_4 without stirring. In our system, as described above, CO_2 reduction is controlled by the mass-transfer process of CO_2 at χ=0.007, while the mass transfer of CO_2 is sufficiently high at χ=0.33.[12] Our result of lower hydrocarbon selectivity at χ=0.33 is, therefore, consistent with the result of Hara et al., and is also interpreted as the effect of mass-transfer process of CO_2 to the electrode. When TBAP was used as a supporting electrolyte, the main products were also CO and $HCOOCH_3$.

When TEAP was used as a supporting electrolyte, on the other hand, efficient formation of methane and ethylene was observed with a good reproducibility. The hydrocarbon selectivity (γ_{HC}) amounts to 48.9 ± 5 %. Concentration of CO_2 and diffusion coefficient of CO_2 in TEAP system may not be considerably different from those in TBAP system. Therefore, the observed change in the product distribution can be attributed

Table 1. Current Efficiency of Products (η) and Selectivity of Hydrocarbon (γ_{HC}) in the Electrochemical Reduction of CO_2 in a CO_2-Methanol Medium at a Cu Electrode [a]

Salt	χ^b	j^c	η / %						γ_{HC}
		$mA \cdot cm^{-2}$	H_2	CO	CH_4	C_2H_4	$HCOOCH_3$[g]	Total	%
TBAT	0.007[d]	500	63.6	13.0	8.5	0.8	9.7	95.6	29.0
TBAT	0.33[e]	500	4.0	46.4	3.4	2.6	34.6	91.0	6.9
TBAP	0.33[e,f]	200	9.7	48.1	7.6	5.2	25.4	96.0	14.8
TEAP	0.33[e]	200	6.5	24.1	40.7	9.0	27.7	108.2	48.9
TEAP	0.33[e]	1000	9.3	40.9	15.8	6.9	22.0	99.0	25.3

[a]Electrolyses were performed at 25 °C. [b]Mole fraction of CO_2 at 25 °C, from ref. 10. [c]Current density at a Cu cathode. [d]1 atm. [e]40 atm. [f]Electrolysis was conducted at 20 °C. Mole fraction will be slightly larger than 0.33. [g]Current efficiency of $HCOOCH_3$ was calculated on the basis that all of detected $HCOOCH_3$ was the CO_2 reduction product (see the text).

to the effect of the cation of supporting salt. We previously reported that the electroreduction of CO_2 in a CO_2-methanol medium with a TBA salt yields CO chiefly, while that with a lithium salt yields $HCOOCH_3$ mainly. We concluded that hydrophobic atmosphere of TBA ion and hydrophilic atmosphere of Li ion are advantageous for CO and $HCOOCH_3$ formations, respectively.[13] Here, in the present study, even a slight change in the alkyl chain length of tetraalkylammonium cation affects the reaction significantly. At the present stage, we cannot explain such a drastic effect of a small difference in the salts.

Another important characteristic observation here is that total efficiency of CO_2 reduction remains higher than 90 % and the efficiency of CO_2 reduction to $HCOOCH_3$ also remains around 25 %. Only CO production decreases and hydrocarbon formation increases, when TBAP is replaced by TEAP. It is considered that CO_2 is reduced to hydrocarbons through CO in the electrochemical reduction of CO_2.[15] Our observation indicates that the use of TEAP instead of TBAP does not affect $HCOOCH_3$ and H_2 formations remarkably, but significantly affects the hydrocarbon formation process from CO.

In the TEAP electrolyte solution, current density could be increased up to 1 $A \cdot cm^{-2}$ (Table 1). Even at such an extremely high current density, the reduction of CO_2 proceeded with a current efficiency of about 90 %, indicating that CO_2 was still supplied sufficiently. The partial current density of CO_2 reduction amounted to 897 $mA \cdot cm^{-2}$. This value is larger than that in industrial electrolysis such as chloralkali industry (200 $mA \cdot cm^{-2}$ at an anode) and aluminum refinement (700 $mA \cdot cm^{-2}$ at an anode).

Current efficiencies of CH_4 and C_2H_4 formations in aqueous $KHCO_3$ medium at ambient condition are reported to be 29.4 and 30.1 %, respectively.[15] Similar result was also reported in an aqueous high pressure system.[9] The present result demonstrates that Cu also shows the excellent electrode activity on CO_2 reduction to hydrocarbons in the high rate electroreduction of concentrated CO_2 in a CO_2-methanol medium.

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