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PRODUCTION OF CO AND CH_4 IN ELECTROCHEMICAL REDUCTION OF CO_2 AT METAL ELECTRODES IN AQUEOUS HYDROGENCARBONATE SOLUTION

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The total analysis of gaseous and soluble products was carried out in the electrochemical reduction of CO_2 (current density 5 mA cm^{-2}) on various electrode metals. $HCOO^-$ was predominantly produced at Cd, In, Sn, and Pb cathodes. Ag and Au principally gave CO. CH_4 was formed in an appreciable amount at Cu cathode.

Numerous papers have been published in connection with electrochemical reduction of carbon dioxide. Teeter and Van Rysselberghe,[1)] Hong,[2)] and Ito et al.[3)] reported that formate was exclusively produced in the cathodic reduction of CO_2 at metal electrodes (Hg, Au, Pb, Zn, Cd, Sn, and In) in aqueous inorganic salt solutions. However, these works were carried out without analysis of gaseous products. Frese and Leach[4)] reported that CH_4, CO, and CH_3OH were formed at Ru cathode, but the partial current for all these products did not exceed 0.3 mA cm^{-2}. No publication has reported total analysis of products (gaseous and soluble in electrolytes) in the electrochemical reduction of CO_2 at metal electrodes in aqueous inorganic salt solutions. Gaseous substances have not been reported as major products in metal electrode systems in aqueous electrolytes except by Frese and Leach.[4)]

Metal electrodes (Hg, Pb, Sn, and In) combined with aqueous tetraalkyl ammonium salt solutions gave formic, oxalic, and other carboxylic acids.[5,6)] Ikeda et al. showed that CO was formed in the cathodic reduction of CO_2 at Zn, Sn, In, and Pb electrodes with aqueous solutions of tetraalkyl ammonium salts.[7)] Metal elelctrodes in non-aqueous electrolyte solutions gave CO, oxalic, and formic acids.[8-11)]

Many authors described formation of CH_3OH, HCHO, HCOOH, CH_4, and CO in photoelectrochemical and electrochemical reduction of CO_2 at various semiconductor electrodes.[12-17)] However, Ito et al. pointed out that these substances were also produced in photochemical decomposition of epoxy resin in which semiconductors are mounted.[18)] They reported that only HCOOH was produced in the photoelectrolytic reduction of CO_2 at p-GaP.

Transition metal complexes were reported to catalyze cathodic reduction of CO_2 and to produce CO effectively.[19-22)]

The present communication reports the results of the total analysis of gaseous and soluble products from cathodic reduction of CO_2 at various metal electrodes. It is shown that CO and CH_4 are formed predominantly at Ag, Au, and Cu cathodes with current density 5 mA cm^{-2} in an aqueous hydrogencarbonate solution.

Zn, Cd, Sn, Pb, and In (purity 99.999-99.9999%) were melted and cooled in evacuated Pyrex tubes (i.d. 20 mm). The button-shaped electrodes prepared as above were mounted in polyester resin. Sheets of Au, Ag, Cu, Ni, and Fe (99.99%) were cut into 20 mm x 20 mm electrodes attached with a lead wire of same metal. Au electrode was etched in aqua regia before electrolysis experiments. Other metal electrodes were electrolytically polished unless otherwise stated. The solutions employed for this treatment were as follows. Concd H_3PO_4 for Cd, Zn, and Cu. $HClO_4$ + $(CH_3CO)_2O$ + H_2O for Sn, Pb, Ni, and Fe. Concd HNO_3 + CH_3OH for In. KCN + $K_4Fe(CN)_6$ + H_2O for Ag.

A conventional Pyrex H-type cell was employed in which the cathode compartment was separated from the anode by a sheet of cation exchange membrane (Selemion) donated by Asahi Glass Co. Ltd. The potential of cathode was measured with respect to an Ag/AgCl reference electrode. The electrode potential was corrected for the IR drop between the Luggin capillary tip and the cathode. The aqueous electrolyte of 0.5 M $KHCO_3$ was prepared from reagent grade chemicals and water which was doubly distilled from deionized water. The solution was purified by preelectrolysis with a 30 mm x 20 mm Pt black cathode at 2 x 10^{-2} mA cm^{-2} under purified N_2 gas for more than 20 h. The electrolysis were conducted at constant current at ambient temperature. Purified CO_2 was bubbled into the solution at ca. 100 ml min^{-1}. The solution was stirred by a magnetic stirrer during electrolysis. The exhaust gas from the cell was introduced to gas chromatographs. A molecular sieve 13X column and a Porapak N column were used for analysis of CH_4 and CO. CH_4 and CO were detected with an FID detector, where CO was converted to CH_4 before the detector. H_2 was analyzed with a molelcular sieve 5A column and a TCD detector. The limit of detection was 0.5 ppm for CO and CH_4, which corresponded to the current efficiency of 0.02% in the present experimental conditions. The products soluble in the solution were analyzed by ion chromatography and the permanganate titration technique. The flow gases N_2 and CO_2 were purified with activated copper columns and washing bottles containing chromic acid-sulfuric acid solution. N_2 further passed through a column of NaOH, and CO_2 through a washing bottle of $KHCO_3$ solution.

The galvanostatic electrolysis experiments were carried out at a constant current 5 to 5.5 mA cm^{-2} for 30 to 60 min. The electrode potential shifted to the negative direction for initial 3 to 5 min, but remained virtually constant thereafter. The variations of the potential for each individual electrolysis run are indicated with ± in Table 1.

CO, CH_4, and H_2 were produced in the reaction; these gaseous products appeared after the electrolysis started. The concentration of the gaseous products remained constant in the exhaust gas during the electrolysis. The product soluble in the electrolyte solutions was only formate ion for all the electrodes. The amount of formate ion obtained by ion chromatography agreed well with the results from the permanganate titration technique.

The faradaic efficiencies for the products are given in Table 1. They were

Table 1. Results of cathodic reduction of CO_2 at various electrodes

Electrode	Electrode potential (V vs. SHE)	Faradaic efficiency/ %, Lower limit/upper limit				
		$HCOO^-$	CO	CH_4	H_2	Total
Cd$^{a)}$	-1.66 ± 0.02	65.3/ 67.2	6.2/ 11.1	0.2	14.9/ 22.2	93/ 100
Sn$^{a)}$	-1.40 ± 0.04	65.5/ 79.5	2.4/ 4.1	0.1/ 0.2	13.4/ 40.8	94/ 110
Pb$^{a)}$	-1.62 ± 0.03	72.5/ 88.8	0.3/ 0.6	0.1/ 0.2	3.8/ 30.9	94/ 100
In$^{a)}$	-1.51 ± 0.05	92.7/ 97.6	0.9/ 2.2	0.0	1.6/ 4.5	93/ 102
Zn$^{a)}$	-1.56 ± 0.08	17.6/ 85.0	3.3/ 63.3	0.0	2.2/ 17.6	90/ 98
Cu$^{b)}$	-1.39 ± 0.02	15.4/ 16.5	1.5/ 3.1	37.1/ 40.0	32.8/ 33.0	87/ 92
Ag$^{b)}$	-1.45 ± 0.02	1.6/ 4.6	61.4/ 89.9	0.0	10.4/ 35.3	99/ 106
Au$^{b)}$	-1.14 ± 0.01	0.4/ 1.0	81.2/ 93.0	0.0	6.7/ 23.2	100/ 105
Ni$^{b)}$	-1.39	0.3	0.0	1.2	96.3	98
Fe$^{b)}$	-1.42	2.1	1.4	0.0	97.5	101

a) Current density: 5.5 mA cm^{-2}. b) Current density: 5.0 mA cm^{-2}. Concentration of $KHCO_3$: 1.0 mol dm^{-3} for Cu electrode and 0.5 mol dm^{-3} for other electrodes.

calculated on the basis of the number of electrons required for the formation of one molecule of the products from CO_2: 2 for $HCOO^-$, 2 for CO, 8 for CH_4, and 2 for H_2. The results obtained from several experiments are shown with the values of the lower and the upper limits. The total values of the faradaic efficiency were close to 100%. Hence the tabulated substances are the major products of the reaction.

The electrode metals are divided into several groups in accordance with the selectivity of the products. Cd, In, Sn, and Pb predominantly gave formate, although a small amount of CO and CH_4 was produced in addition to H_2. Zn gave formate and CO as major products. The reproducibility at Zn was poor; the faradaic efficiencies for CO increased from 3.3 to 63.3%, whereas formate decreased from 85.0 to 17.6%. The reason is still under investigation. Ag and Au gave principally CO with slight amount of formate. The gaseous products at Cu electrode contained significant amount of CH_4. H_2 was exclusively produced for Ni and Fe, but formate, CO, and CH_4 were formed slightly.

It is remarkable that CH_4 is selectively produced at Cu cathode, and CO at Ag and Au cathodes in the electrochemical reduction of CO_2. No publication has reported formation of CO and CH_4 in aqueous inorganic electrolytes at metal electrodes at considerable current density ($\geq$ 1 mA cm^{-2}).

The formation of CH_4 at Cu electrode was further investigated. Faradaic efficiency decreased appreciably without preelectrolysis of the electrolytes. A Cu electrode was etched in 7% HNO_3 aqueous solution before electrolysis instead of electrolytic polishing, which did not show a mirror like surface. The elctrode thus treated gave little difference in the faradaic efficiency of CH_4 formation. However, the production of CH_4 was remarkably suppressed in the presence of O_2 in the electrolyte. We are further investigating the effect of experimental parameters on the product distribution in the cathodic reduction of CO_2. The details of the results will be published elsewhere.

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