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Electrochemical Reduction of Carbon Dioxide at Various Metal Electrodes in Aqueous Potassium Hydrogen Carbonate Solution

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The electrochemical reduction of carbon dioxide at various metallic electrodes was carried out *potentiostatically* at 298 K in aqueous potassium hydrogen carbonate solution in order to make clear the electrocatalysis of metals in reduction of CO_2. It was found that metals used as electrodes are classified into four groups according to their main products from CO_2, i. e., metallic In, Sn, Hg, and Pb are selective for the production of formic acid; metallic Ag and Au are selective for the formation of carbon monoxide; metallic copper has the highest electrocatalytic activities in formation of hydrocarbons, aldehydes, and alcohols; and metallic Al, Ga, Group a, and Group VIII elements except Pd have scarce electrocatalytic activity in reduction of CO_2. Effects of the reduction potential on products from CO_2 were also examined in detail for Zn, In, and Au electrodes which have some interesting properties.

So far, many studies have been carried out on the electrochemical reduction of carbon dioxide at metal electrodes in both aqueous and nonaqueous electrolyte solutions. They have been reviewed in recent papers.[1–5)]

As was described in our early papers,[6,7)] we studied electroreduction of CO_2 at metallic Zn, Cd, In, Sn, and Pb electrodes in aqueous solutions of various inorganic salts and found occurrence of only formic acid in the solution phases. The gas phases were not analyzed for products.

Recently, Hori et al.[8)] have studied *galvanostatically* electrochemical reduction of CO_2 in aqueous $KHCO_3$ solution by means of several kinds of metal electrodes; the principal products are formic acid on Zn, Cd, Sn, and Pb, carbon monoxide on Ag and Au, and methane on Cu. They have also reported that considerable amounts of methane, ethylene, and alcohols are produced by the galvanostatic reduction of carbon monoxide at Cu electrode.[9)] From these findings they have suggested that the CO or CO-related species would play an important role in the formation of hydrocarbons and alcohols on the electroreduction of CO_2.

In our previous works[10,11)] we carried out *potentiostatic* reduction of CO_2 in nonaqueous salt solutions at various metallic electrodes and reported that oxalic acid is predominantly produced at Hg, Tl, and Pb, and carbon monoxide at Cu, Zn, In, Sn, and Au etc.

In the present work electroreduction of CO_2 was *potentiostatically* carried out at many kinds of metal electrodes in aqueous $KHCO_3$ solution in order to obtain insight into the electrocatalysis of metals for this reaction.

Effects of the reduction potential on products from CO_2 were also examined in detail at Zn, In, and Au metal electrodes.

Experimental

The working electrodes were prepared by using almost the same materials and procedures as described in the previous paper.[11)] Most of the electrodes had the shape of almost a square plate with the surface area of about 2 to 7 cm^2. The Rh and Re electrodes were of a wire type, and the Hg and Ga electrodes of a pool type. The Ru electrode was prepared by thermal decomposition of $RuCl_3$ on a graphite substrate at 873 K for 10 min under H_2 atmosphere. The purities of the electrode metals were as follows: Al(99.999%), Ti(99.5%), V(99.7%), Cr(99.2%), Fe(99.9%), Co(99.9%), Ni(99.9%), Cu-(99.9998%), Zn(99.99%), Ga(99.9999%), Nb(99.2%), Mo(99.95%), Rh(99.9%), Pd(99.95%), Ag(99.98%), Cd(99.9999%), In(99.999%), Sn(99.999%), Ta(99.95%), W(99.95%), Re(99.97%), Ir(99.9%), Pt(99.99%), Au(99.95%), and Pb(99.99%). Most electrodes were ordinarily polished with alumina powder (0.05 μm) and ultrasonically cleaned in twice-distilled water before use. Cu was electropolished.[12)] Zn was etched in 2 mol dm^{-3} HCl for 30 sec, and Au in aqua regia for 30 sec. Hg was purified by distillation. Ga was cleaned by cathodic treatment at −2.5 V in alkaline solution for 30 min.

A bright platinum plate of 6 cm^2 and an electrode of Ag–AgCl saturated with KCl served as an anode and a reference electrode, respectively.

An electrolytic cell made of Pyrex was employed. The catholyte was separated from the anolyte with a cation-exchange membrane, Nafion® 315. The cathode chamber was made gastight, and CO_2 gas was supplied with the cyclic gas flow system as described in the previous paper.[12)]

The electrolyte solution of 0.1 mol dm^{-3} $KHCO_3$ was prepared from the recrystallized $KHCO_3$ and twice-distilled water. The pH of the solution saturated with CO_2 was about 6.7 at 298 K.

The electroreduction of CO_2 was potentiostatically carried out with a potentiostat, HA-301 (Hokuto Denko) and an electronic coulometer, HF-201 (Hokuto Denko). The quantities of electricity passed were 30 to 50 coulombs. After electrolysis the reduction products were analyzed both by gas chromatography and by high performance liquid chromatography, as was described previously.[12)] All the experiments were carried out at 298 K.

Results and Discussion

Some typical results obtained in the electrolysis of CO_2 at various electrodes at −1.6 V are given in Table 1. The products detected are $HCOO^-$, CO, CH_4, C_2H_4, C_2H_6, and H_2. The main product at metallic electrodes of Group-a elements is H_2, which is evolved by competitive reaction with the CO_2 reduction. There is also indication of the formation of small amounts of CO at Ti(Group IVa) Nb, Ta(Va), W(VIa), and Al, Ga(IIIb).

At the metals of Group VIII elements the faradaic efficiencies for H_2 evolution are close on 100% except that at Pd, where the efficiency for CO formation is 12.5% and the sum of efficiencies for all products reaches only 46%. This finding in the case of Pd suggests that the substantial amount of evolved H_2 is absorbed by Pd. Small amounts of hydrocarbons are formed at all the metals of Group VIII; the faradaic efficiencies at Co and Ni are especially higher than those at the other metals of Group VIII. The formation of the hydrocarbons has also been reported by Azuma et al.[12]

The highest catalytic activities for the production of hydrocarbons, alcohols, and aldehydes are observed at the Cu electrode. The results have been discussed in detail in the previous paper.[13]

CO is formed selectively at Au and Ag electrodes. Hg, In, Sn, and Pb electrodes are selective for the formation of $HCOO^-$. The considerable amounts of CO and $HCOO^-$ are detected at Zn and Cd electrodes.

In order for the electrocatalytic activities of the metals to be easily understood, the relationships between the positions for the electrode metals on the Periodic Table and the faradaic efficiencies for the products at −1.6 V are visualized in Figs. 1 and 2. These figures suggest that the electrode metals are roughly classified into four groups on the basis of the catalytic activities for the reduction of CO_2; the metals such as Hg, In, Sn, and Pb make a first group, which is selective for the formation of $HCOO^-$. A second

Table 1. Faradaic Efficiencies for Electrochemical Reduction Products of CO_2 at Various Metallic Electrodes at −1.6 V vs. Ag/AgCl Sat'd KCl in 0.1 mol dm^{-3} $KHCO_3$ Aqueous Solution at 298 K[a]

Group	Electrode metal	I_d	Faradaic efficiency/%						
		mA cm^{-2}	$HCOO^-$	CO	CH_4	C_2H_4	C_2H_6	H_2	Total
IVa	Ti	1.9	n	1.6	0.03	t	t	100	102
Va	V	4.4	n	1.1	0.03	t	t	86	87
	Nb	9.6	n	0.7	0.02	t	t	97	98
	Ta	3.2	n	0.9	0.04	t	t	90	91
VIa	Cr	20.8	n	n	0.07	t	0.01	99	99
	Mo	24.6	n	n	0.01	t	t	103	103
	W	21.9	n	1.9	0.06	t	0.01	102	104
VIIa	Re	b)	n	n	0.04	t	t	98	98
VIII	Fe[c]	15.8	n	n	0.09	t	0.03	104	104
	Co	23.0	n	n	0.26	0.03	0.10	102	102
	Ni	2.8	n	n	2.29	0.26	0.48	93	96
	Ru[d]	10.2[e]	n	n	n	n	n	111	111
	Pd	3.6	n	12.5	0.01	t	t	29	42
	Ir	b)	n	0.6	0.13	t	0.01	99	100
	Pt[c]	3.2	n	n	0.03	t	0.01	99	99
Ib	Cu	4.3	t	3.6	23.10	40.00	0.06	16	83(104[f])
	Ag	1.5	n	64.7	0.03	t	t	28	93
	Au	41.3	6	15.8	n	n	n	86	107
	Au[g]	3.8	n	81.5	n	n	n	23	105
IIb	Zn	0.6	20	39.6	t	t	t	40	100
	Cd	0.8	39	14.4	0.05	0.01	0.01	39	92
	Hg	0.3	94	n	0.04	0.03	0.03	6	100
IIIb	Al	0.8	n	n	0.58	0.04	0.11	99	100
	Ga	4.5	n	5.9	t	n	n	91	97
	In	2.3	69	7.5	0.09	0.01	0.02	25	101
IVb	Sn	3.8	63	7.3	0.01	t	t	26	97
	Pb	0.4	50	3.4	0.05	t	t	41	94

a) n: Under detection limit, t: Trace amount (<0.01%). b) Not measured. c) Cathode potential (−1.4 V vs. Ag/AgCl). d) Cathode potential (−1.0 V vs. Ag/AgCl). e) Calculated from the area of the substrate. f) Other reduction products included. g) Cathode potential (−1.25 V vs. Ag/AgCl).

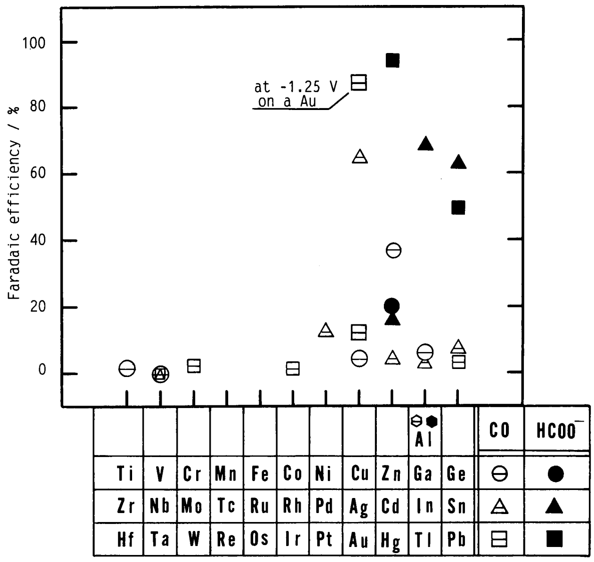

Fig. 1. Relationship between the positions of electrode metals in the periodic table and the faradaic efficiencies for CO and $HCOO^-$ formation at −1.6 V vs. Ag/AgCl in 0.1 mol dm^{-3} $KHCO_3$ aq solution at 298 K.

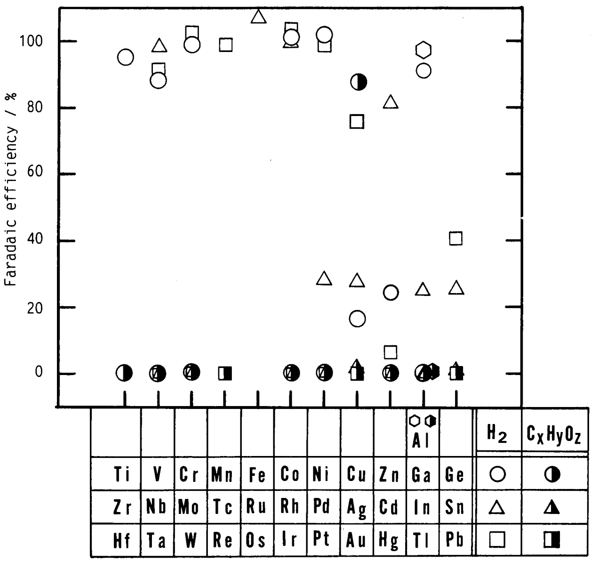

Fig. 2. Relationship between the positions of electrode metals in the periodic table and the faradaic efficiencies for H_2 and hydrocarbon formation at −1.6 V vs. Ag/AgCl in 0.1 mol dm^{-3} $KHCO_3$ aq solution at 298 K.

group consists of Ag and Au, whose main product is CO. A third group is Cu, which has the highest electrocatalytic activities in the formation of hydrocarbons, aldehydes, and alcohols. The metals of a fourth group such as Al, Ga, Group a, and Group VIII elements except Pd have little activities in reduction of CO_2. There are several exceptions in the present classification. For example, the Zn and Cd metals have intermediate properties between a first group and a second one. The behavior of Pd is uncommon, as described above.

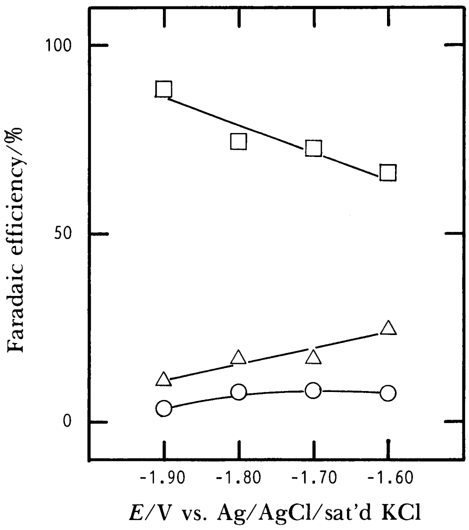

Fig. 3. The faradaic efficiency-potential curves for formation of CO (○), $HCOO^-$ (□), and H_2 (△) in 0.1 mol dm^{-3} $KHCO_3$ aq solution on In electrode at 298 K.

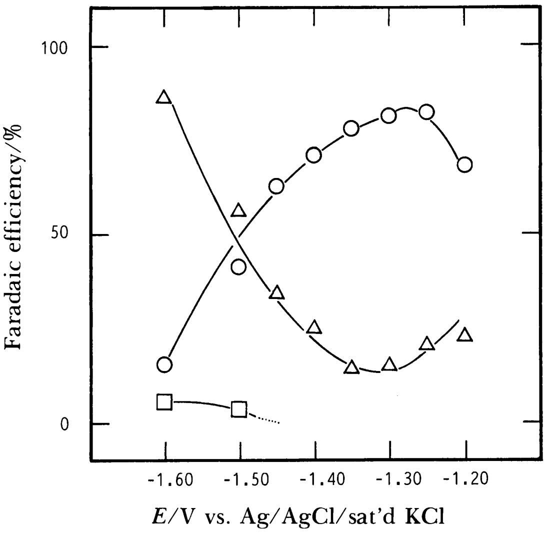

Fig. 4. The faradaic efficiency-potential curves for formation of CO (○), $HCOO^-$ (□), and H_2 (△) in 0.1 mol dm^{-3} $KHCO_3$ aq solution on Au electrode at 298 K.

Figure 3 shows the dependencies of the faradaic efficiencies on the reduction potentials for the formation of $HCOO^-$, CO, and H_2 at the In electrode of a first group. It is seen that the efficiency for the formation of $HCOO^-$ gradually increases as the electrode potential becomes more negative and finally reaches more than 80% at maximum. On the other hand, the efficiency for the CO formation is not so much affected by the variation of electrode potentials.

Figure 4 illustrates also the dependencies of the faradaic efficiencies on the reduction potentials at the Au electrode of a second group. The electrode

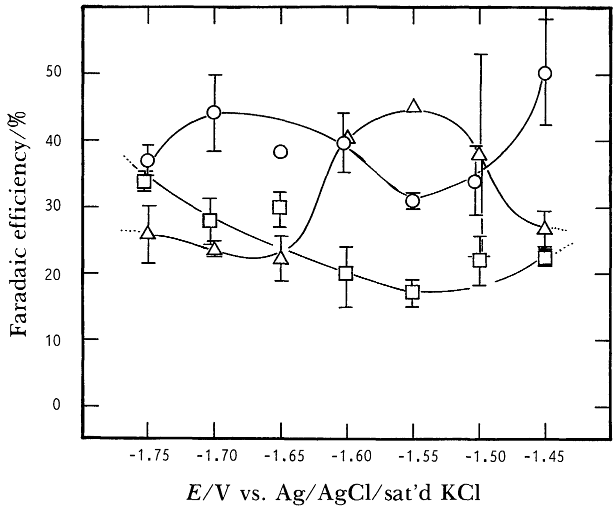

Fig. 5. The faradaic efficiency-potential curves for formation of CO (○), $HCOO^-$ (□), and H_2 (△) in 0.1 mol dm^{-3} $KHCO_3$ aq solution on Zn electrode at 298 K.

produces predominantly CO. It is apparent that the faradaic efficiency for the CO formation increases from −1.20 V, passes through a maximum of 83% at −1.25 V, and then gradually decreases as the electrode potential becomes more negative. This result agrees with that reported by Hori et al.[8,14]

It is seen from Fig. 5 that the behavior of the Zn electrode in reduction of CO_2 is complicated. It is clear that the more negative the electrode potential is, the higher the efficiency for the $HCOO^-$ formation. The reproducibility of the efficiencies for H_2 and CO formation is not good. The complicated behavior of the Zn electrode would be caused by the oxide or hydroxide layer formed on the electrode surface. Detailed investigation of the behavior at the Zn electrode is now in progress in our laboratory.

Finally, the reduction products at various electrodes in aqueous $KHCO_3$ solution were compared with those in nonaqueous propylene carbonate, acetonitrile, and dimethyl sulfoxide solutions of tetraethylammonium perchlorate where it was found that the metals are classified into three groups according to their main products from CO_2, i.e., a group selective for the production of CO, one for the production of $(COO^-)_2$, and one for the production of both CO and $(COO^-)_2$.[11] Among Hg, Pb, In, and Sn of a first group which produce selectively $HCOO^-$ in the aqueous solution, the former two metals are effective for the formation of $(COO^-)_2$ in the nonaqueous solutions, while the latter two are effective for the CO formation. The Ag and Au electrodes classified into a second group in the aqueous solution produce selectively CO in both aqueous and nonaqueous solutions. The Cu electrode, which has the highest catalytic activities for the production of hydrocarbons, aldehydes, and alcohols in the aqueous solution, produces only CO in the nonaqueous solutions. The metals of Group a and Group VIII, which are classified into a fourth group and evolve H_2 in the aqueous solution, produce considerable amounts of both CO and $(COO^-)_2$ in the nonaqueous solutions. Exceptions among Group VIII elements are Ni, Pd, and Pt. Ni and Pt, which evolve H_2, and Pd, the behavior of which is uncommon in reduction of CO_2 in the aqueous solution, are selective for CO formation in the nonaqueous media.

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