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Selective Formation of Formic Acid, Oxalic Acid, and Carbon Monoxide by Electrochemical Reduction of Carbon Dioxide

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Selective formation of formic acid, oxalic acid, and carbon monoxide by electrochemical reduction of carbon dioxide (CO_2) is demonstrated using several metallic electrodes in aqueous and nonaqueous electrolytes. The electrode metals catalyze the electrochemical reduction of CO_2 and are classified to three groups according to their main products from CO_2. In and Pb electrodes as well as Hg electrodes are useful for the selective formation of formic acid by electrochemical reduction of CO_2 in aqueous electrolytes. In the case of nonaqueous electrolytes, Pb, Hg, and Tl are useful for oxalic acid, and In, Zn, Au, and Sn electrodes are useful for carbon monoxide. Also, reaction mechanisms of CO_2 electrochemical reduction are discussed.

We have studied the electrochemical reduction of carbon dioxide, CO_2, to organic compounds using solid-state metallic electrodes. Then, we have also indicated that the reduction product of CO_2 in aqueous electrolytes is only formic acid at all electrodes examined such as Zn, In, Sn and Pb,[1-3] as well as at Hg as previously reported by other authors.[4-6] In the previous papers,[7,8] we reported that oxalic acid and carbon monoxide were mainly produced by the electroreduction of CO_2 at some metallic electrodes in nonaqueous electrolytes.

In the present work, a gastight cell with a cyclic gas flow system was used for electrolytic experiments, and the gaseous products in the gas phase were then determined in a manner similar to that used for the products in the electrolytes. According to the results in this work and those reported in the previous papers, we will discuss on the electrochemical reduction of CO_2 in aqueous and nonaqueous electrolytes, and also we will summarize the selective formation of formic acid, oxalic acid, and carbon monoxide from CO_2 by the electrochemical method.

Experimental

The working electrodes were prepared from solid-state metals such as Ti (99.3%), Cr (99.2%), Fe (99.9%), Ni (99.3%), Cu (99.99%), Zn (99.9999%), Nb (99.2%), Mo (99.95%), Pd (99.9%), Ag (99.99%), Cd (99.9999%), In (99.999%), Sn (99.999%), Pt (99.99%), Au (99.99%), Tl (99.99%), and Pb (99.99%) which were as pure as possible. These have employed as plate electrodes described in the previous papers[1-3] except for Au having a string shape. Hg was also used in liquid-state after distillation. A silver-silver chloride electrode and a bright platinum plate served as a reference electrode and an anode, respectively.

An electolytic cell for electroreduction of CO_2 in this work was almost the same structure as that reported in a previous paper[9] except for lacking of a quartz window. Namely, the cell made of Teflon was designed to separate the cathode chamber from the anode one with a cation-exchange membrane, Nafion 315, and also to be able to operate with a small volume of electrolyte, that is, 10 ml, for easy determination of the products. The cell was gastight and CO_2 gas was supplied with the cyclic gas flow system,[9] which was assembled from a mini peristaltic pump, a manometer, a gas sampler, and glass tubes.

Carbon dioxide gas was at first supplied into the catholyte of the cell from a CO_2 gas cylinder and exhausted through the cyclic gas flow system for 30 min. After the electrolytes was sufficiently saturated with CO_2 gas and the system was filled with CO_2, the line was closed to make it gastight. Thereafter, the gas in the system was circulated by the mini peristaltic pump at a rate of 1 ml min^{-1}.

Aqueous electrolytes, namely 0.1 M TEAP/H_2O (1 M = 1 mol dm^{-3}), were prepared from the synthesized tetraethylammonium perchlorate, TEAP, which was prepared from tetraethylammonium bromide, TEABr, and perchloric acid, and twice distilled water.

In order to prepare the nonaqueous electrolytes, propylene carbonate, PC, acetonitrile, AN, and dimethyl sulfoxide, DMSO, were employed as an aprotic solvent. The nonaqueous electrolytes, namely 0.1 M TEAP/PC, were prepared from synthesized TEAP and PC purified by Jasinski and Kirkland's method.[10] AN and DMSO were dried with unhydrous sodium sulfate (1.5 g l^{-1}) and then with Molecular sieve-4A (40 g l^{-1}). They were used without the other purification, although a little amount of the reduction products of some impurities in AN was found by high performance liquid chromatography.

The electrolytic experiment for CO_2 reduction was potentiostatically performed using a potentiostat and an electronic coulometer, Hokuto Denko; PS-303 and HF-201, respectively. Mainly, 100 coulombs were passed through the working electrode for each experiment.

The products in the gas phase were quantitatively determined using a gas chromatograph, Shimadzu; GC-3AH, having a TC detector on a column of activated charcoal using He gas as the carrier gas. On the other hand, the products in the electrolytes were sampled after the line was exposed to the atmosphere and then were determined using a high performance liquid chromatograph, Mitsumi (Atto); HSLC-022, having a RI detector and an UV detector on a column of Shodex Ion-Exchanger HC-125S using 1% H_3PO_4 aqueous solution as an eluent solution. Also a steam chromatograph, Ohkura Riken; SSC-1, having a FID detector on a column of G-0 (Chlomosolb 101), was used for determination of alcohols and aldehydes, although they were not observed at all in the present work.

Results and Discussion

In Aqueous Electrolytes. Table 1 shows all products obtained by electroreduction of CO_2 at potentials of −2.0 and −2.4 V vs. Ag/AgCl/sat'd KCl, using Zn, In, Sn, and Pb electrodes in 0.1 M TEAP aqueous electrolytes. It is evident from this table that carbon monoxide is produced even in aqueous electrolytes. Also the sum of the current efficiencies for formic acid, carbon monoxide, and hydrogen as a by-product is approximately 100%, so that they must represent all of the products obtained in this experiment.

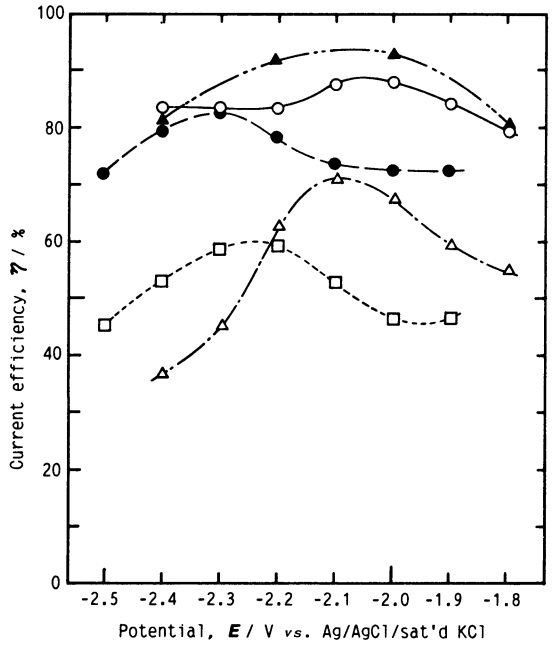

Fig. 1. Current efficiencies for formic acid formation at various metallic electrodes in 0.1 M TEAP/H_2O. Quantity of electricity passed: 100 C. ▲: Hg, ○: In, ●: Pb, △: Sn, □: Zn.

The current efficiencies for formic acid formation with respect to electrode potentials, when CO_2 has been reduced at various electrodes in 0.1 M TEAP aqueous electrolytes is shown in Fig. 1. In the case of In electrodes, the current efficiency went up to about 90% in the potential range of −2.0 to −2.1 V. Therefore, In electrode will be the most useful of the solid-state metallic electrodes for formic acid formation.

Figure 2 shows the current efficiencies for carbon monoxide formation under the same conditions as in Fig. 1. In the case of Zn electrodes, the current efficiency went up to about 36% in the potential range of −1.9 to −2.0 V even in the aqueous electrolyte.

In Nonaqueous Electrolytes. The brief results of electroreduction products of CO_2 obtained at In, Pb, Sn, and Zn electrodes in 0.1 M TEAP/PC electrolytes were already reported in the previous paper.[8] In the case of In electrodes, the efficiency for carbon

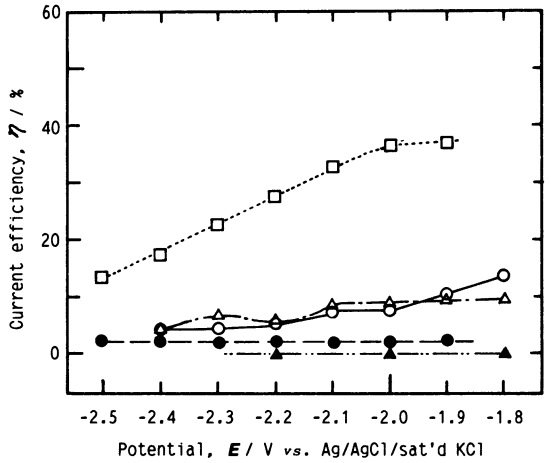

Fig. 2. Current efficiencies for carbon monoxide formation at various metallic electrodes in 0.1 M TEAP/H_2O. Quantity of electricity passed: 100 C. ▲: Hg, ○: In, ●: Pb, △: Sn, □: Zn.

Table 1. Electrochemical Reduction Products of CO_2 at Various Electrodes in 0.1 M TEAP/H_2O under Normal Pressure
Quantity of Electricity; 100 C

Cathode	Potential V	HCOOH		CO		H_2		$\eta_1+\eta_2$	$\eta_1+\eta_2+\eta_3$
		n_1/μmol	η_1/%	n_2/μmol	η_2/%	n_3/μmol	η_3/%	%	%
In	−2.0	454	87.6	35	6.8	25	4.9	94.4	99.1
	−2.4	431	83.2	22	4.2	69	13.2	87.4	100.6
Pb	−2.0	377	72.9	10	2.0	81	15.6	74.9	90.5
	−2.4	409	78.9	11	2.1	74	14.3	81.0	95.3
Zn	−2.0	241	46.6	185	35.6	64	12.4	82.2	94.6
	−2.4	277	53.4	89	16.8	183	35.2	70.2	105.4
Sn	−2.0	350	67.5	47	9.1	155	29.9	76.5	106.4
	−2.4	192	37.1	22	4.2	329	61.6	41.3	102.9

n and η represent the produced amount and the current efficiency of each product, respectively.

Table 2. Relationship between Water Content and Current Efficiency of Products Obtained by CO_2 Electroreduction at −2.6 V vs. Ag/AgCl/(0.01 M LiCl+0.1 M TEAP)/PC in 0.1 M TEAP/PC Quantity of Electricity; 100 C

Cathode	Water added Weight %	Current efficiency/%				$\eta_1+\eta_2+\eta_3+\eta_4$ %
		Oxalic acid, η_1	Glyoxylic acid, η_2	Formic acid, η_3	Carbon monoxide, η_4	
Pb	0.0	73.3	3.4	2.2	11.0	89.9
	0.83	9.8	0.0	56.9	14.4	81.1
	4.2	trace	0.0	72.8	8.6	81.4
In	0.0	0.1	0.0	1.3	85.3	86.7
	0.83	0.0	0.0	33.3	57.8	91.1
	4.2	0.0	0.0	63.6	20.0	83.6

Initial water content of 0.1 M TEAP/PC is 0.032%.

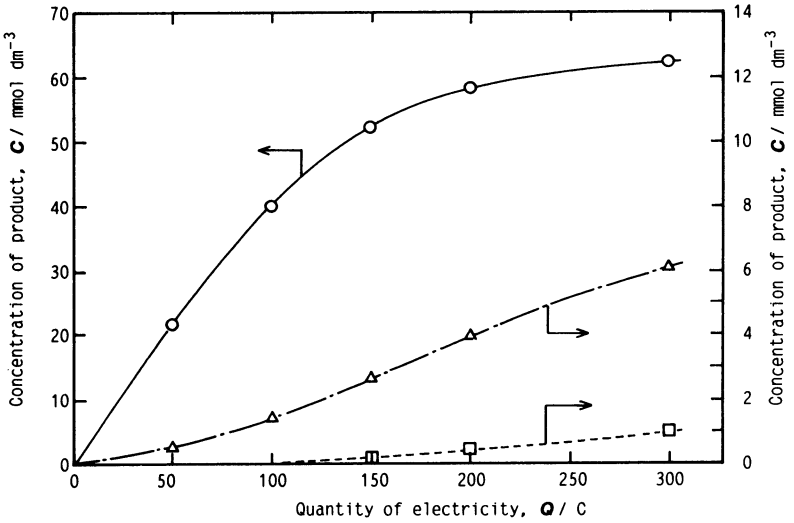

Fig. 3. Carboxylic acid formation at Pb electrode in 0.1 M TEAP/PC at −2.8 V vs. Ag/AgCl/(0.01 M LiCl+0.1 M TEAP)/PC. ○: Oxalic acid, △: glyoxylic acid, □: glycolic acid.

monoxide went up to 90% at −2.8 V, while the efficiency for formic acid and oxalic acid were very small. Therefore, an In electrode was suitable for selective production of carbon monoxide from CO_2 in nonaqueous electrolyte.

On the other hand, at a Pb electrode, the main product became oxalic acid, and the current efficiencies increased at more negative potentials and went up to 84% at −3.0 V. In this case, detectable amount of glyoxylic acid was produced and the efficiency went up to 7% at −3.0 V, while carbon monoxide increased at relatively noble potentials and the efficiency went up to 13% at −2.2 V. These results indicated that Pb electrodes were suitable for selective production of oxalic acid.

Figure 3 shows the concentration of oxalic acid, glyoxylic acid, and glycolic acid, with respect to the quantity of electricity passed, when electrolytic reduction of CO_2 has been performed at −2.8 V, using Pb electrodes in 0.1 M TEAP/PC nonaqueous electrolytes. The concentration of oxalic acid increased almost linearly up to 150 C and thereafter the rate of increase slowed. The concentration of glyoxylic acid then progressively increased, and after 150 C passed, glycolic acid also began to be produced.

These facts suggest that glyoxylic acid and glycolic acid are psoduced by the further reduction of oxalic acid obtined in the electrochemical reduction of CO_2.

Table 2 shows the relationship between the water content in nonaqueous electrolytes and the electroreduction products of CO_2. In the case of Pb electrodes, as mentioned above, oxalic acid was the main product in 0.1 M TEAP/PC electrolyte having an initial water content of 0.032%, while increasing the water content to 0.83 or 4.2% causes an extreme decrease in oxalic acid and an increase in formic acid.

In the case of In electrodes, increasing the water content causes a decrease in carbon monoxide and also an increase in formic acid. In both cases of 4.2% water content, formic acid becomes the main product in-

stead of oxalic acid or carbon monoxide.

The above mentioned results demonstrate that the main products of CO_2 electroreduction in nonaqueous electrolytes are oxalic acid at Pb electrodes and carbon monoxide at In electrodes. In order to clarify the function of these electrode metals, various electrodes were prepared from many kinds of metals and the current efficiencies for oxalic acid and carbon monoxide production were measured using these electrodes in 0.1 M TEAP/PC, 0.1 M TEAP/DMSO, and 0.1 M TEAP/AN nonaqueous electrolytes, respectively. The water content of each electrolyte determined by Karl Fischer's method was 294, 883, and 206 ppm, respectively.

Figures 4, 5, and 6 show the relationships between the position on the periodic table for the metals employed and the current efficiencies for oxalic acid and carbon monoxide formations in these electrolytes, respectively. These figures indicate that these metals are divided into three groups. The first group is the metals of Group A in the periodic table, such as Fe, Cr, Mo, and Ti; the electrodes prepared from such metals contribute to the production of substantial amounts of oxalic acid and carbon monoxide. The second group is VIII and B group metals except for Pb, Tl, and Hg; the electrodes of these metals contribute to the selective production of carbon monoxide, of which the current efficiencies at In and Zn electrodes go up to 90% and oxalic acid production is very small. The third group consists of Pb, Tl, and Hg, and such metal electrodes contribute to selective production of oxalic acid in spite of the B group metal. The current efficiency for oxalic acid production at the Pb electrode goes up to 80% and carbon monoxide production is very small. The Hg electrode belongs to this group, because it does not produce hydrogen at all similarly to the other IIB, IIIB, and IVB group metals as shown in Table 3, although its production rates of ox-

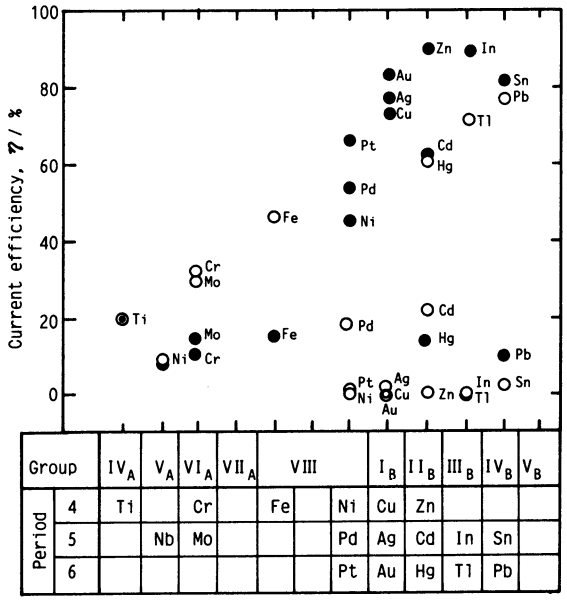

Fig. 4. Current efficiencies for oxalic acid or carbon monoxide formation from CO_2 at various electrodes in 0.1 M TEAP/PC at −2.8 V vs. Ag/AgCl/(0.01 M LiCl+0.1 M TEAP)/PC. Quantity of electricity passed: 100 C. O: Oxalic acid, ●: carbon monoxide.

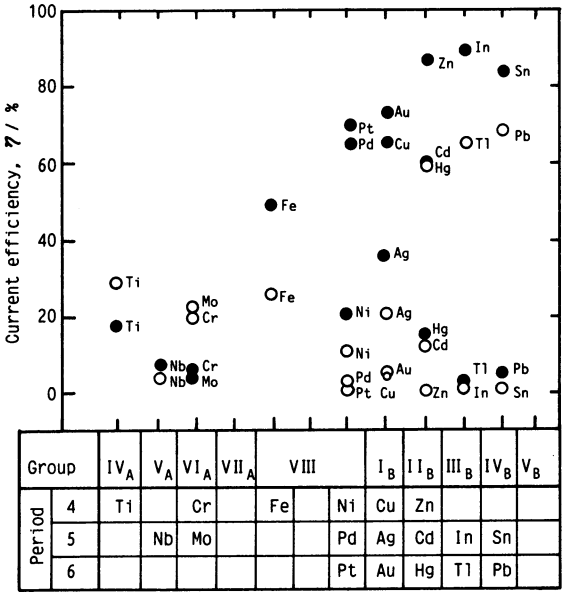

Fig. 5. Current efficiencies for oxalic acid or carbon monoxide formation from CO_2 at various electrodes in 0.1 M TEAP/DMSO at −2.8 V vs. Ag/AgCl/(0.01 M LiCl+1 M $LiClO_4$+ 0.1 M TEAP)/DMSO. Quantity of electricity passed: 100 C. O: Oxalic acid, ●: carbon monoxide.

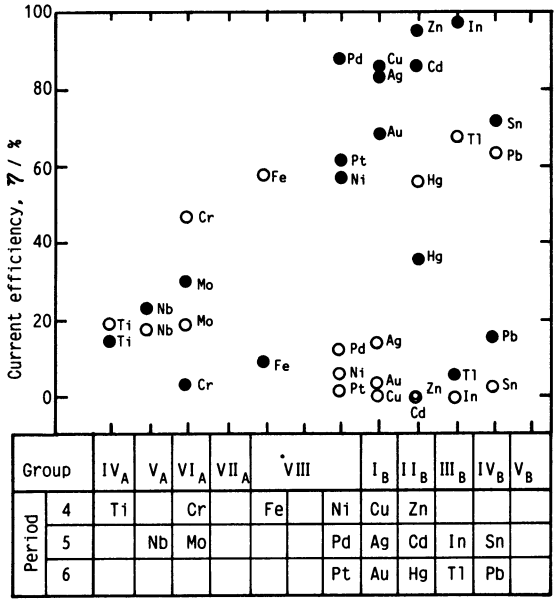

Fig. 6. Current efficiencies for oxalic acid or carbon monoxide formation from CO_2 at various electrodes in 0.1 M TEAP/AN at −2.6 V vs. Ag/AgCl/(0.01 M LiCl+0.1 M TEAP)/AN. Quantity of electricity passed: 100 C. O: Oxalic acid, ●: carbon monoxide.

Table 3. Electrochemical Reduction Products of CO_2 at Various Electrodes at −2.8 V vs. Ag/AgCl/(0.01 M LiCl+0.1 M TEAP)/PC in 0.1 M TEAP/PC. Quantity of Electricity; 100 C

Group	Cathode	Amount of products, n/μmol				
		Oxalic acid	Glyoxalic acid	Formic acid	Carbon monoxide	Hydrogen
IV_A	Ti	103	6	22	104	235
V_A	Nb	39	4	42	35	256
VI_A	Cr	165	5	23	58	189
	Mo	153	Trace	28	72	212
VIII	Fe	239	None	7	81	115
	Ni	1	None	43	237	228
	Pd	113	None	16	269	None
	Pt	5	None	40	345	90
I_B	Cu	3	None	Trace	388	Trace
	Ag	7	Trace	11	401	10
	Au	1	None	19	431	72
II_B	Zn	2	None	Trace	465	None
	Cd	112	20	8	327	None
	Hg	312	5	6	92	None
III_B	In	1	None	12	462	None
	Tl	365	5	11	16	None
IV_B	Sn	10	5	18	424	None
	Pb	397	15	13	54	None

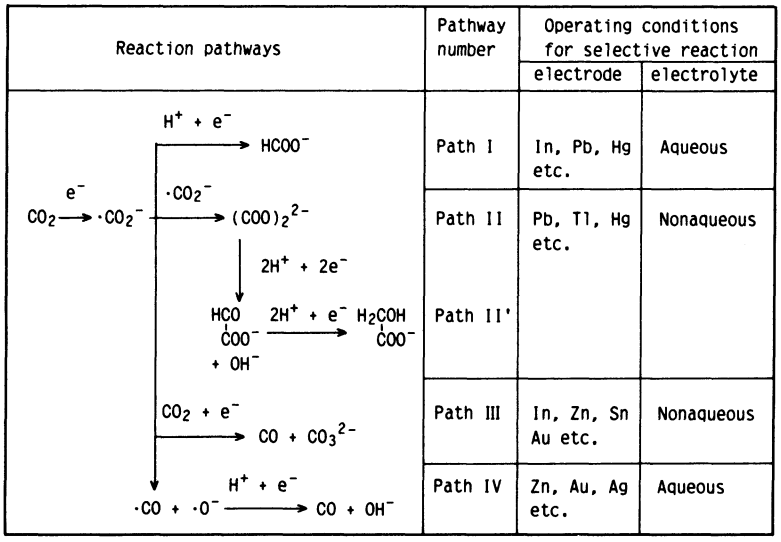

Fig. 7. Reaction pathways in electrochemical reduction of CO_2 under various conditions.

alic acid and carbon monoxide are like to those of the Fe electrode of which hydrogen production is in the order of 100 μmol for 100 C passed.

Such behavior of these metal electrodes has also been observed in the other nonaqueous electrolytes using AN and DMSO as aprotic solvents. Results were almost similar to that in the case of PC. Slight differences are thought to be due to the water content of them and electrode potentials.

Reaction Pathways. Figure 7 shows the reaction pathways in the electroreduction of CO_2 and the operating conditions for each pathway to proceed selectively. These reaction pathways may proceed competitively, but the reaction rate of each pathway is dependent upon the electrode metals and the electrolytes.

Namely, in Pass I, the reduced CO_2 anion radical reacts with proton or water molecule in aqueous electrolytes to produce formic acid. This reaction is competitive with the hydrogen evolution reaction (HER), so metals having higher overvoltages for HER, such as In, Pb, and Hg, are useful for the formic acid formation by Pass I.[1,2,11]

In nonaqueous electrolytes, if CO_2 anion radicals remained for a somewhat longer time at the surface of electrode metals such as Pb, Hg, and Tl, they would react together on the surface to produce an oxalate ion.[2,3,7,8] Thereafter the oxalate ion will be further reduced to produce glyoxalate, glycolate anions, etc. (Pass II′). These passes also observed at Pb electrodes in aqueous electlolytes.[3] If CO_2 anion radicals easily desorb from the surface of metals, such as Zn, Sn, and Au, they are attacked by CO_2 molecules near at the surface or in the bulk to disproportionate producing carbon monoxide and carbonate ion passing an intermediate anion radical (Pass III).[8,12] This mechanism also accounts for the production of carbon monoxide at some metals, such as Zn, in aqueous electrolytes.[13]

If metals are more attractive to CO_2 anion radicals, such as Zn, Au, and Ag, a dissociative adsorption mechanism of CO_2 anion radicals or molecules, Pass IV, may also be proposed to account for the carbon monoxide production in aqueous electrolytes.[9,13]

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