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CATHODIC REDUCTION OF CARBON DIOXIDE FOR ENERGY STORAGE^{*)}

By

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Abstract

The energy storage process is described on the basis of cathodic reduction of carbon dioxide to obtain liquid fuels such as formic acid or methanol. Three major problems associated with this process are briefly discussed; relatively low current density, high overvoltage and the gradual degradation of electrodes.

Supply demand gap of electric power needs effective ways of energy storage for load leveling. Energy storage of actual use is hydro pumped power station at present. Other methods of energy storage will be feasible in future, for example electrical, mechanical and thermal. We expect that energy storage devices based on chemical principles have many advantages; such as secondary batteries, hydrogen energy system and so on. Hydrogen is an excellent medium for energy storage. But hydrogen is gaseous, and is not convenient for handling. By the way, hydrogen can be combined with carbon dioxide to form methanol or formic acid, and the resultant liquid fuels are less expensive and more convenient for transport and storage.

Carbon dioxide is collected from exhaust gases of fossil fuel combustion, and is electrolytically reduced. The resultant fuels, methanol, formic acid and others, are fed to a fuel cell or a decomposer to generate hydrogen in response to demand. In addition to the advantage of energy storage, this process will contribute to fixation of carbon dioxide. Thus the discharge of carbon dioxide to environment will decrease, and the recent deleterious increase of atmospheric concentration of carbon dioxide will be suppressed.

We are studying feasibility of energy storage system with CO₂ reuse. There are several problems in relation to electrolytic reduction of CO₂. The first is low current efficiency; side reaction is hydrogen evolution. The

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second is high overvoltage; cathodic and anodic respectively. The third is gradual degradation of electrode. Now these three problems are briefly discussed below.

The pH potential diagram was constructed for the system CO_2 -water and related compounds at 25°C on the basis of the thermochemical data. (Fig. 1). The electroactive species of CO_2 cathodic reduction is molecular CO_2 , neither hydrogencarbonate ion nor carbonate ion as confirmed in this laboratory.¹⁾ CO_2 is reduced to formic acid or formate ion at metal electrodes in aqueous solutions without tetra-alkylammonium ions. The evolution of hydrogen competes with CO_2 reduction, and favorably proceeds in low pH

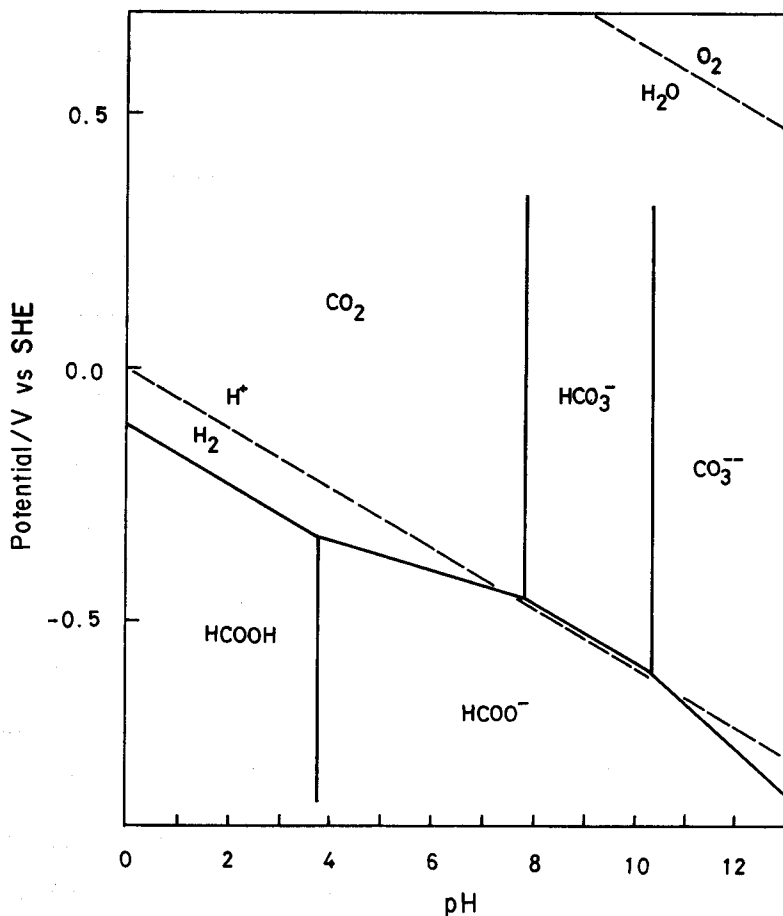


Fig. 1. pH-potential diagram of CO_2 and its related compounds. pH-potential relations for water are shown in broken lines — — —.

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region, because the potential for H₂ evolution is nobler than that for CO₂ reduction. Hence the cathodic reduction of CO₂ is to be conducted at pH between 7 and 8, where CO₂ exists stably and H₂ evolution is not favored.

The electrolytic reduction of CO₂ at metal electrodes results in formic acid or formate ion in aqueous solutions. Since the reaction competes with hydrogen evolution, metals of high hydrogen overvoltage, such as indium, lead, tin, zinc and mercury, have been studied for application to the CO₂ reduction. The electrode properties measured in 0.5 M NaHCO₃ are summarized in Table 1. The electrode potentials for these metals are greatly cathodic as compared with the equilibrium potential. The current efficiencies are fairly good. On the basis of these values, energy conversion efficiency is tentatively estimated.

TABLE 1. Cathodes for CO₂ reduction; $\text{CO}_2 + \text{H}^+ + 2\text{e}^- \rightarrow \text{HCOO}^-$
Total current = 5.5 mA·cm⁻²

Electrode	Electrolyte	Electrode potential (SHE)	Current efficiency
In	0.5 M NaHCO ₃	-1.338 V	0.84
Pb	do.	-1.458 V	0.85
Sn	do.	-1.230 V	0.64
Zn	do.	-1.590 V	0.42
Hg	do.	-1.713 V*	1.00

Equilibrium potential for the above reaction; -0.45 V (at pH=7.8, where CO₂ at 1 atm is in equilibrium with 0.5 M NaHCO₃ at 25°C)

* extrapolated value

TABLE 2. Energy conversion efficiency of CO₂ electrolysis
 $\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{HCOO}^- + \text{H}^+ + 1/2\text{O}_2$ with use of In cathode

Theoretical decomposition voltage	1.22 V
Cathodic overvoltage	0.89 V
Anodic overvoltage	0.5 V
Total	2.6 V
Current efficiency	0.84
Energy conversion efficiency	0.39

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Table 2 gives energy conversion efficiency of CO_2 electrolysis with use of indium cathode. The theoretical decomposition voltage was calculated to be 1.22 V for the reaction



The cathodic overvoltage comes from Table 1, 0.89 V. The anodic overvoltage stems from the value obtained in industrial water electrolysis, *ca* 0.5 V. Summing up these figures, one obtains 2.6 V. Putting the current efficiency as shown before, one has 0.39 as the energy conversion efficiency. The value is relatively low; the reason comes from high overvoltages and relatively low current efficiency as mentioned before.

The third problem is the degradation of the electrode. The concentration of resultant formate ion increases during electrolysis, but the current efficiency falls gradually. The concentration of HCOO^- consequently reaches a certain plateau value; the values are not very reproducible. (Fig. 2). The decay of current efficiency is retarded, if the electrolyte solution is purified with preelectrolysis. The current efficiency is also remarkably improved with tetra-ethylammonium perchlorate used as an electrolyte.

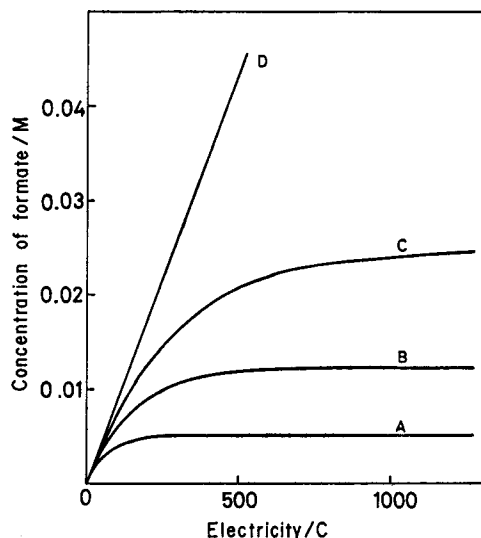


Fig. 2. The concentration of formate produced in the electrolytic reduction of CO_2 ; the electrode 3.6 cm^2 of In metal (5 N), the current density $5.5 \text{ mA} \cdot \text{cm}^{-2}$, the volume of the electrolyte 50 ml . The electrolyte solutions are $0.5 \text{ M Na}_2\text{HPO}_4$ (A), 0.5 M NaHCO_3 (B), 0.5 M NaHCO_3 preelectrolyzed (C) and $0.1 \text{ M (C}_2\text{H}_5)_4\text{NClO}_4$ (D).

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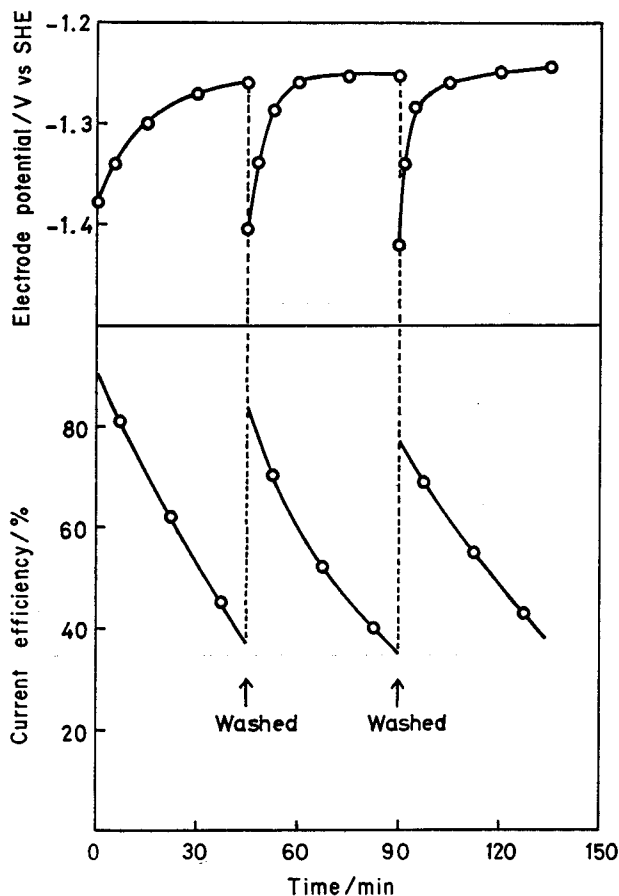


Fig. 3. The variation of the electrode potential and current efficiency of CO_2 reduction at 5 N In electrode with current density $5.5 \text{ mA}\cdot\text{cm}^{-2}$. The electrolyte is 0.5 M Na_2HPO_4 . The arrows (\uparrow) indicate the interruption of electrolysis and the washing of the electrode with 2 N HNO_3 and distilled water.

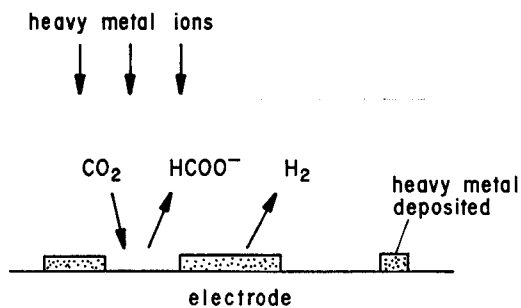


Fig. 4. The model of degradation of the electrode.

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Figure 3 shows the variation of the electrode potential and the current efficiency of CO_2 reduction at 5 N indium metal. The current efficiency goes down, and the electrode potential rises with time. The electrolysis is interrupted and the electrode is washed with 2 N HNO_3 and distilled water. Then the current efficiency is recovered and the potential becomes cathodic again.

These experimental facts suggest that the deterioration of the electrode may be ascribed to contamination of electrodes with heavy metals. A very

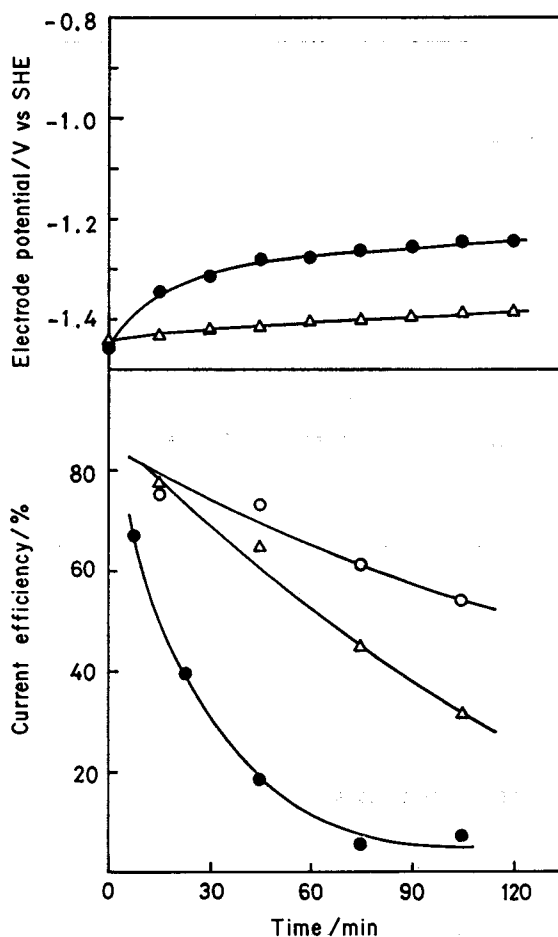


Fig. 5. The variation of the electrode potential and current efficiency with time. In electrode with current density $5.5 \text{ mA}\cdot\text{cm}^{-2}$.

△: 0.5 M NaHCO_3 .

○: 0.5 M NaHCO_3 preelectrolyzed.

●: 0.5 M $\text{NaHCO}_3 + 1.85 \times 10^{-6} \text{ M Fe}^{2+}$.

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small amount of heavy metal ion exists in the solution as impurities. These heavy metal ions are deposited on the electrode surface. (Fig. 4). The hydrogen overvoltage at the heavy metals will be relatively low. Hydrogen evolution will dominate at the surface covered with these heavy metals. CO₂ is reduced only at the surface not covered with heavy metal. The contaminated part of electrode with heavy metals gradually develops and the

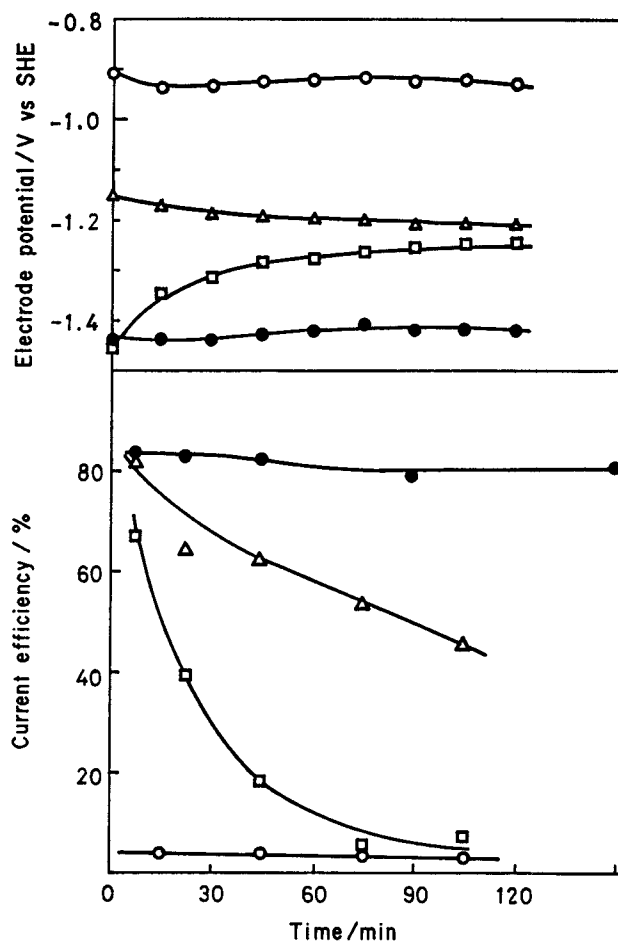


Fig. 6. The variation of the electrode potential and current efficiency with time. Current density $5.5 \text{ mA} \cdot \text{cm}^{-2}$.

- : 0.1 M TEAP with In electrode.
- △ : 0.1 M TEAP + $1.85 \times 10^{-6} \text{ M Fe}^{2+}$ with In electrode.
- : 0.5 M NaHCO₃ + $1.85 \times 10^{-6} \text{ M Fe}^{2+}$ with In electrode.
- : 0.1 M TEAP with Fe electrode.

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current efficiency of CO_2 reduction will be lowered.

Figure 5 shows the variation of current efficiency with time. If ferrous ions are added to NaHCO_3 electrolyte solution, the decay of the current efficiency is accelerated. This fact verifies the above explanation.

Figure 6 shows the results of CO_2 reduction in TEAP (tetra-ethyl ammonium perchlorate) solution. If the electrolysis is conducted in TEAP solution with indium electrode, the current efficiency remains constant. Then the effects of TEAP as electrolyte are studied in detail. If ferrous ions are added to TEAP solution, the current efficiency gradually decreases. But the decay rate is much retarded as compared with NaHCO_3 solution. If CO_2 reduction is conducted with iron sheet electrode in TEAP solution, the current efficiency remains very low constant value.

The reason why the current efficiency does not fall in TEAP solutions may be explained by the following two mechanisms:

- 1) H_2 evolution hardly takes place on the electrode surface covered with TEA ion, even if the electrode is partially contaminated with heavy metal.

- 2) Discharge of heavy metal ion is hindered on TEA covered electrode. The electrode is kept free from heavy metal contamination for long time.

These two mechanisms would probably work. Among two mechanisms, the second one seems to contribute more significant effect in this case. Because the current efficiency at iron electrode in TEA solution is very low. Thus, once heavy metals cover the electrode, the hydrogen evolution will take place more easily.

Reference

- 1) Y. Hori and S. Suzuki, submitted for publication.