

ELECTROCHEMICAL REDUCTION OF CARBON DIOXIDE WITH AN ELECTRODE MEDIATOR AND HOMOGENEOUS CATALYSTS

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Summary

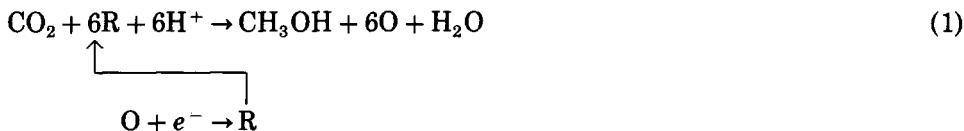
Carbon dioxide has been reduced catalytically to methanol with an electrode mediator and homogeneous catalysts, using a hydrogen fuel cell as an energy source to regenerate the active mediator. Thermodynamic assessment predicts that the reversible potential for the reaction $H^+ + e^- = \frac{1}{2} H_2$ should be more negative than that for the reaction $CO_2 + 6H^+ + 6e^- = CH_3OH + H_2O$ whenever a fuel cell with hydrogen as the fuel and CO_2 as the oxidant is feasible. As reaction proceeded, the pH of the catholyte rose but that of the anolyte dropped, until finally reduction of CO_2 ceased. Hence, adjustment of the pH values in both temperatures was necessary to maintain CO_2 reduction over long time periods.

Introduction

Although many methods for converting CO_2 have been proposed involving hydrogenation utilizing homogeneous [1, 2] and heterogeneous [3-5] catalysis, and photochemical reduction [6, 7], electrochemical methods have been most widely investigated [8-11]. In the electroreduction of CO_2 , the major products reported to date include carbon monoxide, formic acid, formaldehyde, methanol, methane and ethylene, whose formation is independent of the solvent and the nature of the electrode material employed [8]. In general, the electrochemical conversion of CO_2 requires large overpotentials and is somewhat lacking in selectivity toward the desired product. For these reasons, research has been directed toward improving these weaknesses.

We have developed a selective process for the conversion of CO_2 to methanol using homogeneous catalysts and electrode mediators [12-15]. The total reaction involved in CO_2 reduction may be represented by the following equation:

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where R and O refer to the reduced and oxidized forms of the electrode mediator, respectively.

Regeneration of the reduced form can be achieved by using external energy source to maintain reaction (1), with the mediator acting as an electron relay. Homogeneous catalysts are capable of making CO_2 electroactive through the formation of a coordinated intermediate. In the present study the reduced form of the electrode mediator was regenerated by means of a hydrogen fuel cell, and problems arising during prolonged reaction were investigated.

Experimental

The reduction of CO_2 was carried out with a fuel cell in which hydrogen and CO_2 were used as fuel and oxidant, respectively. A platinum gauze (86.2 cm^2) modified with Everitt's salt (ES, $\text{K}_2\text{Fe}^{\text{II}}[\text{Fe}^{\text{II}}(\text{CN})_6]$) was used as the cathode. ES is the reduced form of Prussian Blue (PB, $\text{KFe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]$), and coating onto the substrate was performed by the electrochemical method [16]. The anode was a platinized platinum gauze (40.3 cm^2), and the cathode and anode compartments were separated by a cation-exchange membrane. The electrode potential of the mediated cathode was measured *versus* the saturated calomel electrode.

The catalyst solutions were 0.1 M KCl solutions which included a metal complex and methanol. 1-Nitroso-2-naphthol-3,6-disulphonatocobalt(II), $[\text{Co}^{\text{II}}\{\text{C}_{10}\text{H}_4(\text{NO})(\text{OH})(\text{SO}_3)_2\}_2]$, and aquapentacyanoferrate(II), $\text{Na}_3[\text{Fe}(\text{CN})_5(\text{H}_2\text{O})]$, were used as the metal complexes. The initial pH value of the catalyst solution was adjusted to 2. The catalyst solution (300 cm^3) was transferred to the cathode compartment and CO_2 was bubbled during reaction. Methanol and water vapor evolved with exhausted CO_2 were first cooled with a condenser and then trapped with water (2°C). The solution in the anode compartment was 300 cm^3 of 0.1 M K_2SO_4 at various pH values, and hydrogen gas was always frothed.

The methanol produced was determined by both gas and steam chromatographic methods. A JGC-1000 gas chromatograph equipped with a thermal conductivity detector and a Porapak Q column was employed. The sampling procedure has been described previously [15]. Quantitative analyses of the methanol passed from the cathode to the anode compartment through the ion-exchange membrane, and captured using the water trap, were performed by means of a steam chromatograph with steam as the carrier gas, using a flame ionization detector and a Porapak R column.

Results and discussion

Figure 1 summarizes schematically the catalytic reduction of CO_2 with a hydrogen fuel cell. The net charge transfer occurring at the anode and cathode are represented as reactions (2) and (3), respectively.



As described above, the assistance of homogeneous catalysts and an electrode mediator is indispensable for the activation process depicted as reaction (3). Homogeneous catalysts M capture CO_2 and convert it into an electroactive intermediate. This species is reduced to methanol by reaction with the reduced form R of the electrode mediator which is regenerated using the hydrogen fuel cell.

Thermodynamic assessment predicts that the reversible potential of reaction (2) should be more negative than that of reaction (3) whenever a fuel cell with hydrogen as the fuel and CO_2 as the oxidant is feasible. In the present study, the initial pH value of the catholyte was fixed at 2, and it was necessary that the pH value of the anolyte should be higher than 1.7. The reaction mechanism proposed is given in Fig. 2 where Everitt's salt was used as the electrode mediator [14, 15]. The reduction of CO_2 is induced by the oxidation of ES to PB:

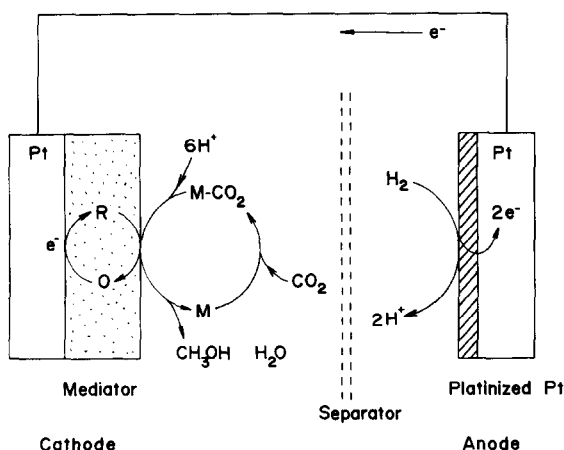
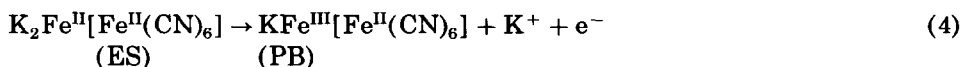


Fig. 1. Schematic representation of the catalytic reduction of CO_2 using a hydrogen fuel cell with CO_2 as the oxidant.

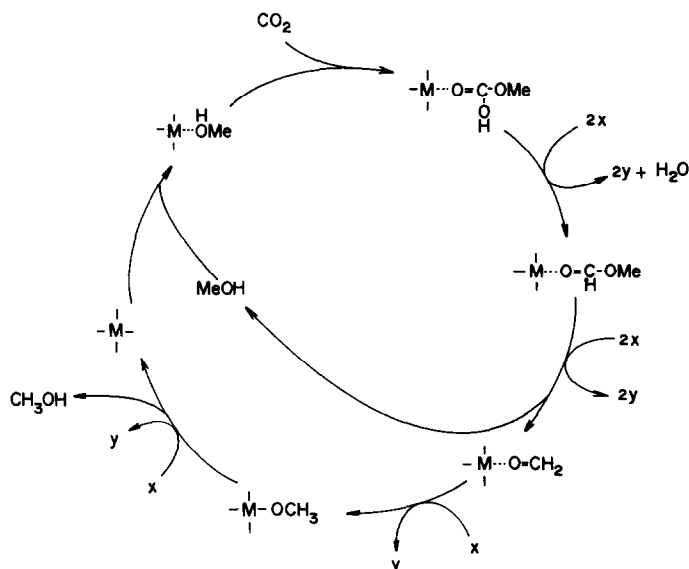


Fig. 2. Reaction scheme for the reduction of CO_2 ($x = ES + H^+$; $y = PB + H^+$).

The metal complex capable of operating as a homogeneous catalyst should have a relatively high stability constant and at least one vacancy (really associated with a water molecule) in its coordination shell [14]. The position of the vacancy in the metal complex serves as the active site in the catalytic process. A coordination bond is first formed between the central metal and the primary alcohol, CO_2 inserts into this bond and the coordinated species is reduced to methyl formate by reaction with ES. Methyl formate is further reduced to formaldehyde and MeOH, and finally to methanol, by ES. Gas chromatograms for the catholyte showed no accumulation of intermediates, methanol being the only product of the reduction reaction of CO_2 .

In Fig. 3, the concentration of methanol formed and the electrode potential at the cathode are plotted as a function of the pH value of the solution in the anode compartment. As expected thermodynamically, CO_2 is not reduced to methanol at pH values lower than 1.7. The formation of methanol increases as the pH of the anolyte is increased. This finding may be explained by the shift in the cathode potential to a negative value as the pH value of the anolyte increased. However, the yield of methanol formed decreased in the fuel cell as the anolyte became more alkaline, which is attributable to the lower solubility of the hydrogen gas and the slower oxidation rate for reaction (2).

The results obtained for the reduction of CO_2 with the hydrogen fuel cell on varying the initial pH value of the anolyte from 6 to 1.65 or 1.40 are shown in Table 1. In this table, the initial and final pH values of the anolyte, the metal complexes added to the catholyte, the electric charge passed (Q),

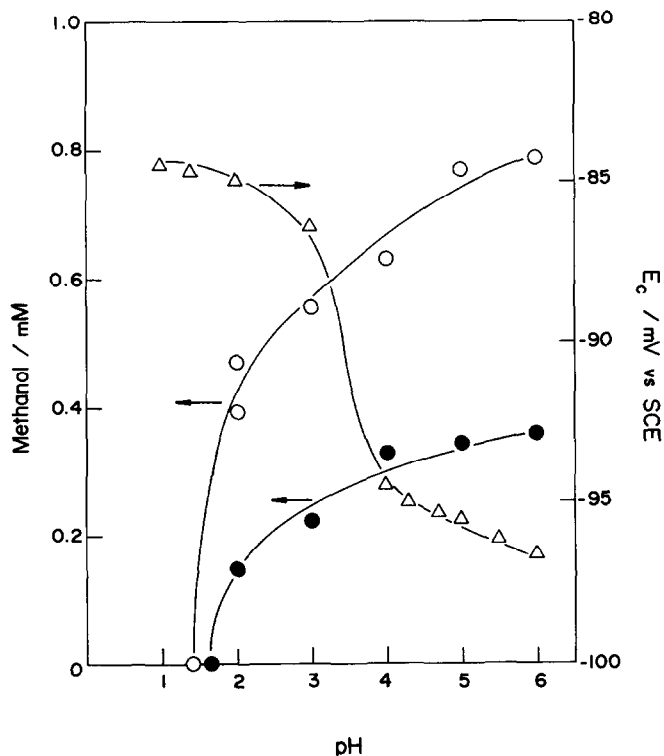


Fig. 3. Plots of methanol formation and cathode potential *versus* pH value of the anolyte. Catholyte, 0.1 M K_2SO_4 solution (initial pH = 2) containing (○, △) 15 mM 1-nitroso-2-naphthol-3,6-disulphonatocobalt(II) or (●) 15 mM pentacyanoferrate(II) and 20 mM methanol. Reaction time, 5 h.

the concentration of methanol produced and the current efficiency for methanol formation (η) are listed. Both metal complexes lead to the reduction of CO_2 with relatively high current efficiency. The current efficiencies are higher with anolytes of higher pH values in the hydrogen fuel cell, with no formation of methanol at pH values of 1.65 and 1.40. As the reaction advanced, the pH of the catholyte rose while that of the anolyte dropped, until finally CO_2 reduction ceased. This, in order to achieve prolonged reduction, it was necessary to regulate the pH values in both compartments.

The concentration of added metal complex affects methanol formation in the manner listed in Table 2. An increase in the concentration of the metal complex results in an increase in CO_2 reduction and leads to higher current efficiency. This effect is more conspicuous in the presence of 1-nitroso-2-naphthol-3,6-disulphonatocobalt(II) than aquapentacyanoferrate(II), because the activity of a metal complex as a homogeneous catalyst is related to the value of its stability constant [14].

The value of the mole ratio of methanol generated and methanol added prior to electrolysis is plotted *versus* reaction time in Fig. 4, where the results

TABLE 1

Experimental results for methanol yield, electric charge (Q), current efficiency (η), and initial and final pH values of anolytes^a

Run No.	Anolyte pH value		Catholyte ^b	Q (C)	Methanol yield (mmol dm ⁻³)	η (%)
	Initial	Final				
1	6.0	3.07	A	112.3	0.657	102
2	5.0	3.01	A	111.9	0.655	102
3	4.0	2.87	A	109.6	0.570	90.3
4	3.0	2.67	A	100.1	0.484	84.0
5	2.0	1.78	A	134.1	0.279	36.1
6	1.65	1.68	A	136.2	(-0.009)	—
7	6.0	2.97	B	97.3	0.357	63.7
8	5.0	2.83	B	100.2	0.343	59.5
9	4.0	2.67	B	86.1	0.327	65.9
10	3.0	2.42	B	105.6	0.220	36.2
11	2.0	2.01	B	105.2	0.148	24.4
12	1.40	1.49	B	119.9	(-0.011)	—

^aAnolyte, 0.1 M K₂SO₄ with various initial pH values.

^bCatholyte (300 cm³) contained (A) 15 mM 1-nitroso-2-naphthol-3,6-disulphonatocobalt(II) or (B) 15 mM pentacyanoferrate(II) and 20 mM methanol. Reaction time, 5 h.

TABLE 2

Experimental results for methanol yield, electric charge (Q) and current efficiency (η) obtained in the presence of various concentrations of (A) 1-nitroso-2-naphthol-3,6-disulphonatocobalt(II) and (B) pentacyanoferrate(II) and 20 mM methanol^a

Catholyte Type	Concn. (mmol dm ⁻³)	Q (C)	Methanol yield (mmol dm ⁻³)	η (%)
A	1.0	89.7	0.324	62.7
A	2.0	99.2	0.465	81.4
A	5.0	112.3	0.657	102
A	15	125.1	0.787	109
A	20	141.8	0.857	105
B	0.5	40.4	0.089	38.3
B	1.0	51.3	0.079	26.7
B	2.0	49.2	0.193	68.1
B	5.0	68.1	0.249	63.5
B	15	97.3	0.357	63.7
B	20	111.5	0.425	66.2

^aReaction time, 5 h. Anolyte, 0.1 M K₂SO₄ of initial pH value 6.0.

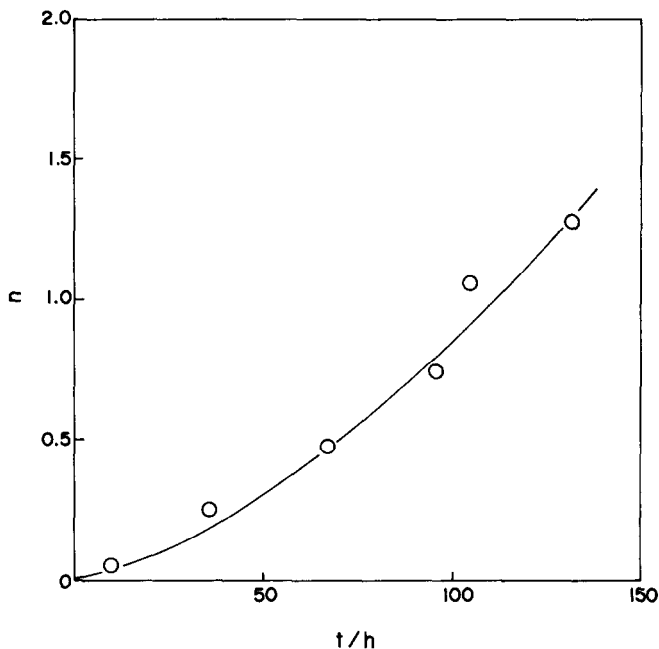


Fig. 4. Plot of n versus reaction time, where n is the molar ratio between methanol produced and methanol added at the beginning of electrolysis. Catholyte (initial pH = 2) included 15 mM 1-nitroso-3,6-disulphonatocobalt(II) and 0.2 mM methanol. Anolyte was 0.1 M K_2SO_4 with an initial pH value of 6. The pH values of the catholyte and anolyte were regulated to ca. 2 and 6 by adding concentrated HCl and KOH solutions, respectively, every 10 h.

from experiments in which the pH values of the anolyte and catholyte were adjusted to ca. 2 and 6 by adding concentrated HCl and KOH solutions, respectively, every 10 h are depicted. The molar ratio exceeds a value of unity after 110 h, while the molar ratio versus reaction time curve is concave suggesting that the reduction of CO_2 is catalytic. The electrode mediator used here suffered no degradation during reaction.

Thus, CO_2 can be reduced catalytically to methanol using a hydrogen fuel cell. However, adjustment of the pH values in both compartments is required in order to maintain CO_2 reduction over prolonged periods of time.

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