Electrocatalytic Generation of C_2 and C_3 Compounds from Carbon Dioxide on a Cobalt Complex-immobilized Dual-film Electrode

Kotaro Ogura,* Kenichi Mine, Jun Yano and Hideaki Sugihara

Department of Applied Chemistry, Yamaguchi University, Ube 775, Japan

The electrocatalytic reduction of CO_2 on a Prussian blue–polyaniline dual film electrode on platinum including immobilized 2-hydroxy-1-nitrosonaphthalene-3,6-disulfonatocobalt(II) in aqueous solution leads to the formation of lactic acid, ethanol, acetone and methanol at a low overpotential (−0.6 V *vs.* standard calomel electrode) under ambient conditions.

It is known that the electrochemical reduction of carbon dioxide with metal electrodes gives various products including formate, oxalate, CO or CH_4. However, this reduction can be achieved only at highly negative potentials, and hence considerable attention has been devoted to reducing the required overpotential. For this purpose, metal complexes of nitrogen macrocycles[1–3] or bipyridine[4,5] have been extensively studied. The overpotential can be decreased to some extent in this way, but it nevertheless remains high and in most cases reduction products other than CO or formate are seldom observed. We report here an electrocatalytic process for CO_2 fixation with the formation of more complex molecules including C_3 compounds. CO_2 was reduced at a much lower overpotential than hitherto achieved, on a metal complex-immobilized dual-film electrode in aqueous solution.

The dual film was composed of Prussian blue (PB) and polyaniline (PAN). The PB film was first electrodeposited on a platinum plate (15.6 cm^2) from an aqueous solution of iron(III) chloride (0.01 mol dm^{-3}) and potassium hexacyanoferrate(II) (0.01 mol dm^{-3}).[6] The average surface concentration of the film was about 2.5×10^{-7} mol cm^{-2}. The PAN film was then deposited by repeated potential cycling in CO_2-saturated aqueous potassium sulfate (pH 1) containing aniline (0.1 mol dm^{-3}).[7] A metal complex was further immobilized on the PAN film; 2-hydroxy-1-nitrosonaphthalene-3,6-disulfonatocobalt(II) (CoL_2) was immobilized from aqueous solution *via* electrochemical doping by anodizing the modified electrode at +0.6 V *vs.* standard calomel electrode (SCE) for 50 min. CO_2 was electroreduced at a constant potential using the prepared modified electrode in 0.5 mol dm^{-3} KCl solution. The pH of the solution controlled at 2.0 throughout the electrolysis (NPH-660 ND type pH controller), by addition of 0.5 mol dm^{-3} aqueous KCl, the pH of which was adjusted to 0 with concentrated HCl. Gaseous products were analysed with Shimadzu GC-8AIT or a GC-8AIF gas chromatograph on molecular sieve 5A or Porapak Q. An Ohkura SSC-1 steam chromatograph with a flame ionization detector and a Porapak R column and a Hitachi 655A high performance liquid chromatograph with a UV monitor and a GL-C610H column were employed to analyse the aqueous samples.

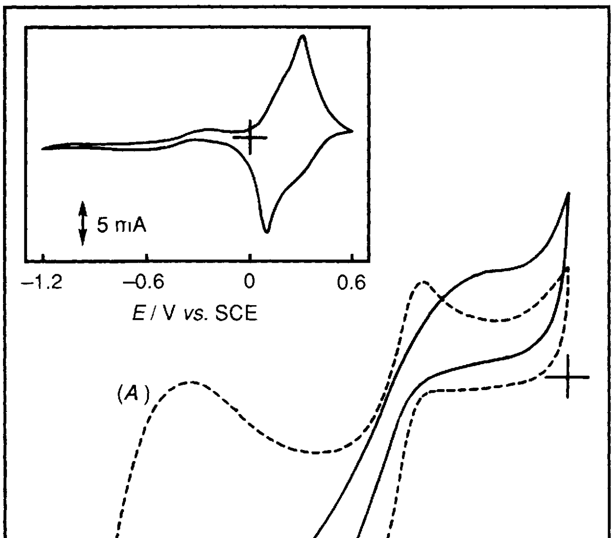

Fig. 1 Cyclic voltammograms at a dual-film electrode including immobilized 2-hydroxy-1-nitrosonaphthalene-3,6-disulfonatocobalt(II) for 0.5 mol dm^{-3} aqueous KCl (pH 2) saturated with (*A*) N_2 and (*B*) CO_2; Scan rate 100 mV s^{-1}. The inset shows the i–E curve (with the same electrode) in CO_2-saturated solution.

Table 1 Electroreduction of CO_2 on various electrodes[a]

Electrode[b]	E/V (*vs.* SCE)	Q/C	Products/μmol dm^{-3}[c]			
			MeOH	EtOH	Me_2CO	$MeCH(OH)CO_2H$
A	−0.6	266	0 (−)	0 (−)	0 (−)	0 (−)
B	−0.6	342	0 (−)	0 (−)	1 (0.2)	0 (−)
C	−0.6	71	4 (0.3)	15 (2.4)	4 (0.8)	21 (3.4)
D	−0.6	240	4 (0.1)	33 (1.6)	5 (0.3)	16 (0.8)
E	−0.6	83	4 (0.3)	22 (3.0)	5 (0.9)	16 (2.2)
F	−0.6	372	10 (0.2)	39 (1.2)	11 (0.5)	59 (1.8)

[a] 0.5 mol dm^{-3} aqueous saturated with CO_2; concentration of CO_2, 0.03 mol dm^{-3}; pH, 2.0; reaction time, 24 h. [b] Naked and modified electrodes: A, naked Pt; *B*, Pt–PB; *C*, Pt–PAN; *D*, Pt–PB–PAN; *E*, Pt–PAN–CoL_2; *F*, Pt–PAN–PB–CoL_2. [c] The numerical value in parentheses indicates the current efficiency (%).

A typical current–potential curve is shown in the inset in Fig. 1. The anodic (+0.38 V *vs.* SCE) and cathodic (+0.1 V) peaks are ascribed to the oxidation and reduction of Everitt's salt (ES, reduced form of PB), the ES–PB couple. The catalytic effect of the electrode mediator is apparent from Fig. 1. A catalytic current is evident when CO_2 is present. For the N_2-saturated solution, a reversible wave due to hydrogen deposition giving chemisorbed hydrogen is seen at E° −0.4 V.[8] The electroreduction of CO_2 takes place at a slightly more negative potential than that for the formation of H_{ads}. The disappearance of the cathodic peak due to H_{ads} suggests that the chemisorbed hydrogen is continuously consumed to reduce CO_2 before H_{ads} is accumulated to a critical concentration corresponding to the current peak in the solution without CO_2.

The reduction products obtained by prolonged potentiostatic electrolysis with various electrodes are listed in Table 1. No product was detected on the naked (*A*) and PB-modified (*B*) platinum electrodes except for a trace of acetone with the latter electrode. The modification of the platinum electrode by PAN (*C*), PB–PAN (*D*) and PAN–CoL_2 (*E*) led to formation of lactic acid, ethanol, acetone and methanol. The generation of these products was further facilitated on the modified electrode (*F*) fabricated by combining PB, PAN and CoL_2. It is remarkable that a C_3 compound such as lactic acid is produced from CO_2 reduction at a low overpotential under ambient conditions. In all cases except with a naked electrode, a negligible amount of methane and acetaldehyde was detected.

The products shown in Table 1 were found both in the solution and within the coated film, and the values listed are the sum of both amounts. The species within the film were extracted in hot water, and their quantities were determined by the same method as described above. A high percentage of lactic acid was found within the coated film, presumably resulting from the reduction of CO_2 incorporated during the electrodeposition of PAN into the film. Accordingly, the present result indicates the possibility that CO_2 molecules incorporated into an organic film can be reduced to C_3 or more novel substances.

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