

# Hydrogenation of CO<sub>2</sub> on the cathodized tungsten trioxide/polyaniline/polyvinylsulfate-modified electrode in aqueous solution

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## Abstract

A tungsten trioxide (WO<sub>3</sub>)/polyaniline (PAN)/polyvinylsulfate (PVS)-modified electrode has been characterized by the in situ FTIR reflection spectroscopic method, and applied to the electroreduction of CO<sub>2</sub> in aqueous solution. Carbon dioxide is hydrogenated through the reaction with the adsorbed hydrogen atoms generated on the cathodized electrode, and the reduction intermediates (COOH<sub>ads</sub>, CHO<sub>ads</sub>) are reoxidized at the potentials close to the first and second oxidation potentials of PAN. The prolonged potentiostatic reduction of CO<sub>2</sub> led to the formation of lactic acid, formic acid, ethanol, and methanol under low overpotential. © 1997 Elsevier Science B.V.

*Keywords:* Tungsten trioxide; Polyaniline; Polyvinylsulfate; FTIR; Carbon dioxide; Hydrogenation

## 1. Introduction

The chemical conversion of CO<sub>2</sub> to more valuable substances is a very important subject in connection with the mitigation of the concentration of green-house gas in the atmosphere. Many conversion processes are proposed, including the hydrogenation at high temperature or in supercritical condition and the electrochemical or photochemical reduction. However, a matter of importance in the chemical conversion of CO<sub>2</sub> is to achieve it under an input

energy as low as possible to avoid a secondary generation of CO<sub>2</sub>. In this regard, the electrochemical process, occurring at room temperature, is promising except that it requires a large overpotential and affords only less valuable products such as HCOOH or CH<sub>4</sub>. To move ahead with the electrochemical process, these problems should be settled, and it is necessary to construct a well-designed electrode system. Generally, an overpotential more than 1 V is required to reduce CO<sub>2</sub> on a metal electrode [1]. This requirement is attributed to the difficulty of the generation of anion radical (CO<sub>2</sub><sup>-</sup>) that is the precursor in the reduction reaction of CO<sub>2</sub> on a metal electrode. Hence, in order to mitigate

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the requisite overpotential, it is expected to find out a reduction route taking place without  $\text{CO}_2^-$ . For this purpose, various electrocatalysis are valid [2–5] in that the chemical activation of  $\text{CO}_2$  and the stabilization of reduction intermediates can be brought about by the reaction with a suitable catalyst.

In spite of these works, there is still much to do to design better catalysis in terms of overpotential and the worth of reaction products. We have developed a mediated electrode system that permits to reduce  $\text{CO}_2$  to  $\text{C}_1$  or  $\text{C}_3$  compound at a potential close to a thermodynamic one, which is a modified electrode with two layered films consisting of an inorganic conductor and a conducting polymer doped with a metal complex [6–8]. In those works, Prussian blue (PB) and polyaniline (PAn) were used as the inorganic conductor and the conducting polymer, respectively. The existence of these two layered films in addition to a fixed metal complex is very important for the efficient reduction of  $\text{CO}_2$ . The mediated reduction of  $\text{CO}_2$  proceeds through the activated state in which the electrophilic carbon atom of  $\text{CO}_2$  is bound to the amino group of PAn and the basic oxygen atom coordinates to the central metal of the complex, and the role of the inner PB film is to supply active adsorbed hydrogen atoms [7]. In the present study, tungsten trioxide and PAn were used as the two layered film, and polyvinylsulfate (PVS) was doped onto the PAn film instead of a metal complex. As found previously [9], PVS is not undoped from the PVS-confined electrode during the cathodic polarization, and operates to suppress the hydrogen evolution at negative potentials. This property is very important for the electrochemical reduction of  $\text{CO}_2$  in aqueous solution since it is in competition with hydrogen evolution. An optimum electrode for the reduction of  $\text{CO}_2$  should be the system in which active adsorbed hydrogen atoms are most effectively provided to hydrogenate  $\text{CO}_2$  at a potential as positive as possible but the coupling of the adsorbed atoms is minimized.

## 2. Experimental

Cyclic voltammetric and potentiostatic electrolysis experiments were performed with a platinum substrate modified with  $\text{WO}_3$ ,  $\text{WO}_3/\text{PAn}$  or  $\text{WO}_3/\text{PAn}/\text{PVS}$  films. A platinum plate with surface area of 2.0 or 3.6  $\text{cm}^2$  was mechanically polished with alumina, sonicated for 10 min, and then pretreated by electrolyzing at +2.5 V (vs. Ag/AgCl) in 0.1  $\text{mol dm}^{-3}$  (= M)  $\text{H}_2\text{SO}_4$  solution. The pretreatment was repeatedly carried out until a CV curve became reproducible in the potential range between  $-0.2$  and  $+1.25$  V. The  $\text{WO}_3$  film was first immobilized on the Pt plate in the following way. The tungsten solution was prepared by dissolving tungsten powder in a 30% hydrogen peroxide solution, and the excess hydrogen peroxide was decomposed with a platinum-black-coated platinum foil [10]. The electrodeposition of  $\text{WO}_3$  onto the Pt plate was formed from a 50 mM tungsten solution by the potentiostatic electrolysis at  $-0.45$  V (vs. Ag/AgCl) for 15 min. A two layered film electrode, Pt/ $\text{WO}_3$ /PAn, was made by depositing PAn on the Pt/ $\text{WO}_3$  electrode from a 0.2 M aniline + 0.05 M KCl solution of pH 1 by the repetitive potential cycling at the scan rate of 100  $\text{mV s}^{-1}$  in the potential range between  $-0.2$  and  $+0.9$  V. A fully modified electrode was finally obtained by immersing the Pt/ $\text{WO}_3$ /PAn electrode in a neutral buffer solution of 0.025 M  $\text{KH}_2\text{PO}_4$  + 0.025 M  $\text{Na}_2\text{HPO}_4$  for 30 min to take out the chloride ions incorporated during the electrodeposition of PAn, and then immersed in a 20 mM PVS (calculated in terms of monomer concentration) in which the electrodeposition of PVS was carried out at a constant potential of  $+0.6$  V for 50 min. All chemicals used were of analytical grade, and the degree of the polymerization of PVS (Wako) was about 1500.

The potentiostatic reduction of  $\text{CO}_2$  was conducted with the prepared electrode in a gas tight H-type electrolysis cell containing KCl and  $\text{KHSO}_4$  solutions of various pH's. The pH value of the solution was regulated throughout the

electrolysis with a pH controller (NPH-600ND type). The volume of the catholyte after the electrolysis was 85–95 cm<sup>3</sup>, which was precisely measured. CO<sub>2</sub> (Iwatani, 99.7% purity) was purified by the repeated freeze–pump–thaw cycles. The reaction gas was circulated with a pump through the cathode compartment above the level of the solution. The reference electrode used was a Ag/AgCl/1 M KCl electrode, and the counter electrode was a platinum plate with a large surface area.

Aqueous products were found both in the solution and within the coated film, and determined by the same procedure as that noted before [7] using a Shimadzu organic acid analyzer (LC-10AD type) and a steam chromatograph (Ohkura SSC-1). Gaseous products were analyzed with a Shimadzu GC-8AIF or a GC-8AIF gas chromatograph. The reaction products adsorbed on the modified electrode were determined with a Fourier transform infrared (FTIR) reflection spectrometer. The characterization of the two layered films with the doped PVS was carried out by the in situ FTIR method, and the experimental way and spectroelectrochemical cell used were described previously [8].

### 3. Results and discussion

As shown in Fig. 1, the performance of the CV curve is changed extremely by the surface modification. At the Pt/WO<sub>3</sub> electrode, the redox peak due to WO<sub>3</sub> is seen at about –0.2 V with the adsorption/desorption peak of hydrogen at a more negative potential. The modification of this electrode with PAN led naturally to the appearance of the redox current due to PAN, but the redox peak of WO<sub>3</sub> became negligible although the smaller current owing to the adsorption/desorption of hydrogen is still observed. At the fully modified electrode, the redox current of WO<sub>3</sub> was further diminished and the hydrogen evolution was suppressed.

Fig. 2 shows in situ FTIR reflection spectra of a Pt/WO<sub>3</sub> electrode. In this figure, the IR

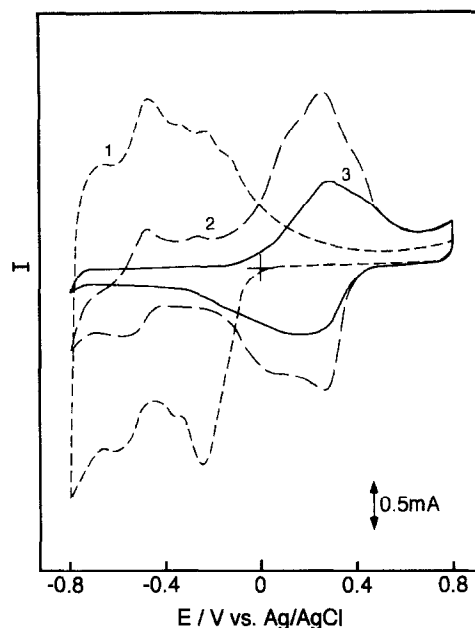


Fig. 1. Cyclic voltammograms of Pt/WO<sub>3</sub> (1)-, Pt/WO<sub>3</sub>/PAN (2)-, and Pt/WO<sub>3</sub>/PAN/PVS (3)-modified electrodes at the scan rate of 100 mV s<sup>-1</sup> in a 0.5 M KCl solution.

intensity is represented by  $\Delta R/R$  in the normalized form:  $\Delta R/R = [R(E_s) - E(E_b)]/R(E_b)$  where  $R(E_s)$  and  $R(E_b)$  are the reflected intensities measured at the sample and base potentials, respectively. Upward peaks in  $\Delta R/R$

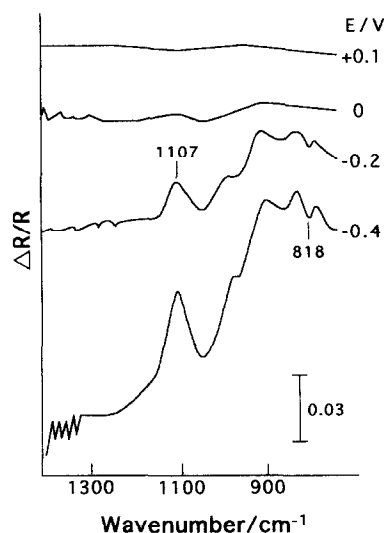


Fig. 2. In situ FTIR reflection spectra of a Pt/WO<sub>3</sub> electrode in a 0.1 M KCl solution of pH 4. The potential was stepped from +0.25 V (base potential) until –0.4 V.

spectra represent absorption from a substance that decreases in concentration in a thin layer formed at the IR window (silicon disk)/solution interface upon the potential shift from the base value to the sample, and reversely a downward peak refers to a species that gains in concentration in the thin layer. As seen from Fig. 2, two distinct peaks directed upward and downward at 1107 and 818  $\text{cm}^{-1}$ , respectively, appear at  $-0.2$  V or more negative potentials. They are both enhanced in each direction as the potential is stepped to more negative values. The wavenumber of 1107 and 818  $\text{cm}^{-1}$  can be assigned to  $\text{W}^{\text{VI}}=\text{O}$  and  $\text{W}^{\text{V}}-\text{O}$  stretching vibration, respectively [11]. Hence, the cathodic current around  $-0.2$  V at the Pt/ $\text{WO}_3$  electrode in Fig. 1 is attributable to the reduction of  $\text{W}^{\text{VI}}\text{O}_3$  to  $\text{HW}^{\text{V}}\text{O}_3$ .

In situ reflection spectra of Pt/ $\text{WO}_3$ /PAN and Pt/ $\text{WO}_3$ /PAN/PVS electrodes are shown in Fig. 3A and B, respectively. At the Pt/ $\text{WO}_3$ /PAN electrode, the upward peaks at 1345 and 1153  $\text{cm}^{-1}$  that increase with shifting the potential to more negative values are assignable to the C–N stretching and C–H deformation vibration of the semiquinoid form of

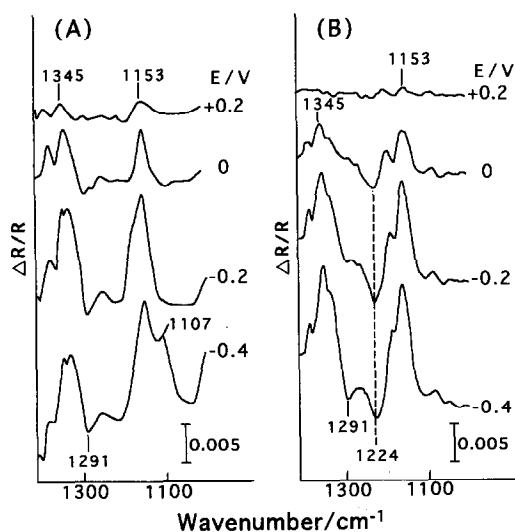


Fig. 3. In situ FTIR reflection spectra of Pt/ $\text{WO}_3$ /PAN (A) and Pt/ $\text{WO}_3$ /PAN/PVS (B) electrodes in a 0.1 M KCl solution of pH 4. The potential was stepped from  $+0.25$  V (base potential) to until  $-0.4$  V.

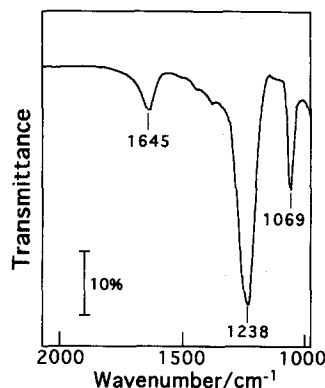


Fig. 4. Ex situ FTIR spectrum of poly(vinylsulfate) powder.

PAN [12], and the downward peak at 1291  $\text{cm}^{-1}$  is attributed to the C–N stretching vibration of the benzenoid form of PAN. It is therefore confirmed that the cathodic reduction of PAN causes the structural change from the semiquinoid form to the benzenoid and that the decrease of the cathodic current at the Pt/ $\text{WO}_3$ /PAN electrode in the potential range between 0 and  $-0.4$  V (Fig. 1) reflects the formation of non-conducting benzenoid PAN. On the other hand, the existence of PVS at the fully modified electrode can be certified from the peak at the wavenumber of 1224  $\text{cm}^{-1}$  in Fig. 3B. This peak was identified by comparing with ex situ FTIR spectrum of PVS powder. Fig. 4 is the spectrum of PVS obtained by the KBr method, and the wavenumber of 1238  $\text{cm}^{-1}$ , corresponding to 1224  $\text{cm}^{-1}$  in Fig. 3B, is assignable to the asymmetric vibration of  $\text{SO}_3$  [13]. As seen from Fig. 3B, the potential-dependence of PAN is much smaller and the peak due to  $\text{WO}_3$  is not observable, suggesting that the electrochemical reduction of PAN as well as  $\text{WO}_3$  is considerably restrained at the fully modified electrode in agreement with the polarization behavior of this electrode (Fig. 1, curve 3).

Cyclic voltammograms of a fully modified electrode are shown in the solutions with  $\text{N}_2$  (a) and  $\text{CO}_2$  (b) in Fig. 5 where the electrode was precatodized for each time before the measurement of CV curves. In the presence of  $\text{N}_2$ , the CV curve bore a close parallel to a typical

doping/undoping behavior of the PAN film itself [14] as the precathodizing time was prolonged: there are two redox couples of  $I_{a1}$  to  $I_{c1}$  and  $I_{a2}$  to  $I_{c2}$  at +0.25 and +0.45 V, respectively. In the presence of  $\text{CO}_2$ , however, the situation is quite different: an anodic peak ( $I'_a$ ) around -0.35 V becomes evident and the increase of  $I_{a2}$ ,  $I_{c2}$ , and  $I_{c1}$  with the cathodizing time is negligible although  $I_{a1}$  increases with time. The increase of  $I_{a1}$  is not accompanied with that of the corresponding cathodic peak ( $I_{c1}$ ), meaning that the increase of  $I_{a1}$  is mainly caused by the reoxidation of a product generated in the cathodic reduction of  $\text{CO}_2$  and the anodic doping of anions onto PAN is considerably suppressed. The potential corresponding to  $I_{a1}$  is +0.25 V, and the probable substance to be oxidized is  $\text{COOH}_{\text{ads}}$  [15].

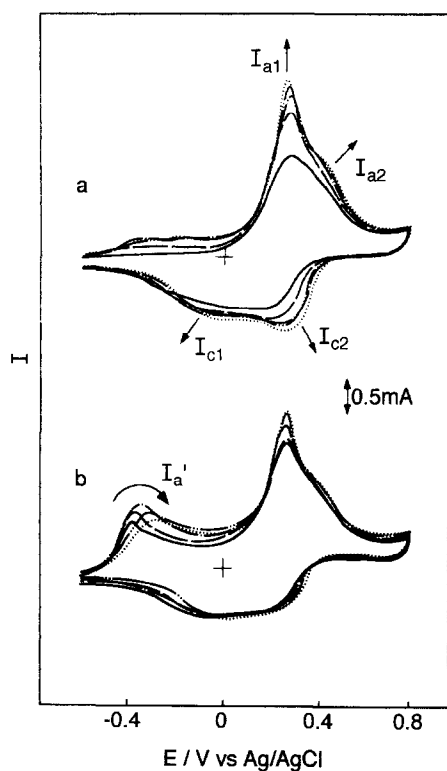


Fig. 5. Cyclic voltammograms of a Pt/WO<sub>3</sub>/PAN/PVS electrode in 0.5 M KCl solutions of pH 4 saturated with N<sub>2</sub> (a) and CO<sub>2</sub> (b). The electrode was precathodized at -0.6 V for each time prior to the measurement of the CV curve: 1 min (—), 2 (— — —), 10 (- - -), 40 (- · - · -), 60 (· · ·). Potential scan rate, 100 mV s<sup>-1</sup>.

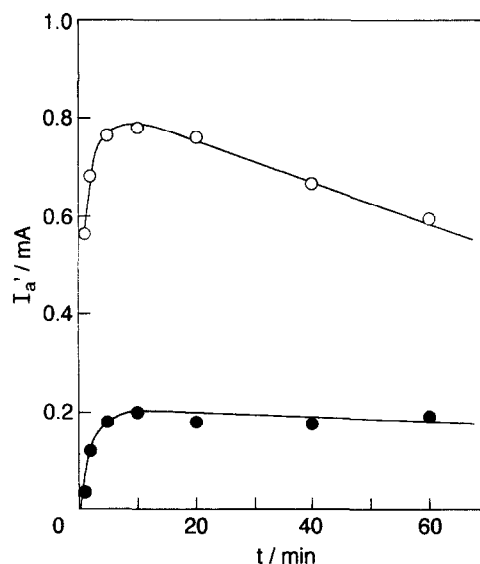


Fig. 6. Relationship between  $I'_a$  (Fig. 5b) and the cathodizing time. The electrode was precathodized at -0.6 V in 0.5 M KCl solutions with N<sub>2</sub> (●) and CO<sub>2</sub> (○).

The value of  $I'_a$  (Fig. 5) in the solutions with CO<sub>2</sub> and N<sub>2</sub> is plotted versus the cathodizing time in Fig. 6. As seen from this figure, the initial value of  $I'_a$  in the presence of CO<sub>2</sub> is about four times as large as that in the presence of N<sub>2</sub>, suggesting a larger amount of adsorbed hydrogen atoms in the former solution. This is probably caused by CO<sub>2</sub> hindering the adsorption of anions (Cl<sup>-</sup>) to permit protons to enter the coated films, which is supported by the fact that the doping of anions to the PAN film was very difficult in the presence of CO<sub>2</sub> as noted above. The drop of  $I'_a$  in the solution with CO<sub>2</sub> reflects the decrease of the number of H<sub>ads</sub> atoms owing to the consumption by the reaction with CO<sub>2</sub> and the adsorption of the product (COOH<sub>ads</sub>). This trend was more conspicuous at lower pH (Fig. 7).

Cyclic voltammograms of a modified electrode in KHSO<sub>4</sub> and KCl solutions are shown in Fig. 8A and B, respectively. The CV curves in KHSO<sub>4</sub> are fairly different from those in KCl: the adsorption/desorption peak ( $I'_a$ ) of hydrogen and the peak of  $I_{a2}$  at the potential of about +0.6 V are evidently seen. The fact that the peak of hydrogen adsorption is much more dis-

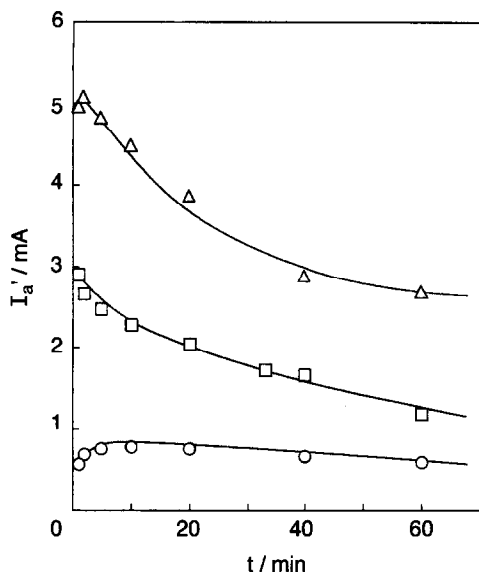


Fig. 7. Relationship between  $I'_a$  and the cathodizing time. The electrode was precathodized at  $-0.6$  V in  $0.5$  M KCl solutions of various pH's saturated with  $\text{CO}_2$ : pH, 2 ( $\Delta$ ); 2.5 ( $\square$ ); 4 ( $\circ$ ).

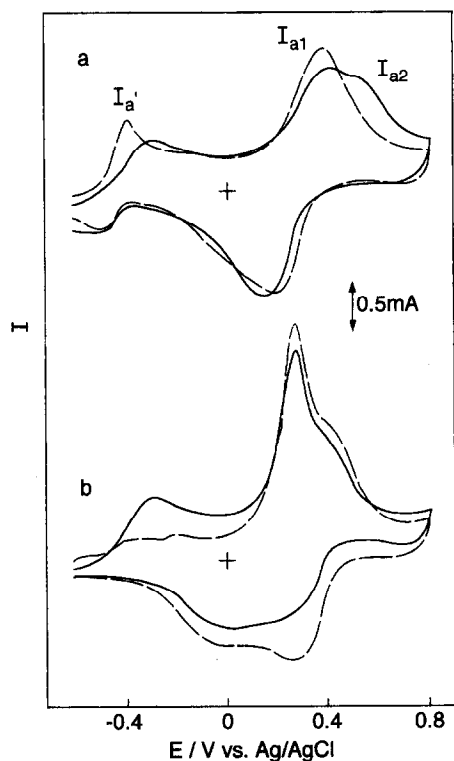


Fig. 8. Cyclic voltammograms of a Pt/ $\text{WO}_3$ /PAN/PVS electrode in  $0.5$  M  $\text{KHSO}_4$  (a) and  $0.5$  M KCl (b) solutions of pH 4 saturated with  $\text{N}_2$  (---) and  $\text{CO}_2$  (—). The electrode was precathodized at  $-0.6$  V for 5 min before the measurement of the CV curve. Potential scan rate,  $100$   $\text{mV s}^{-1}$ .

tinct in  $\text{KHSO}_4$  than in KCl indicates that the hydrogen adsorption is easier in the former solution; in other words,  $\text{Cl}^-$  ions are more strongly adsorbed, disturbing the adsorption of protons. In the same manner as the case of  $I_{a1}$ , the increase of  $I_{a2}$  is not attended by that of the corresponding current of  $I_{c2}$ , and the enhancement of  $I_{a2}$  is attributable not to the oxidation of PAN but to the oxidation of another reduction product of  $\text{CO}_2$ . The probable species would be  $\text{CHO}_{\text{ads}}$  that was assumed as a product in the electrochemical oxidation of formic acid or methanol at the potential of about  $0.8$  V (NHE) [16].

The values of  $I'_a$  and  $I_{a2}$  measured in  $\text{KHSO}_4$  solution saturated with  $\text{CO}_2$  are plotted versus the cathodizing time in Fig. 9. The decrease of  $I'_a$  links with the increase of  $I_{a2}$ , indicating that the reaction of adsorbed hydrogen atoms with  $\text{CO}_2$  causes the decrease of  $I'_a$  and the reoxidation of the reduction product causes the increase of  $I_{a2}$ .

The prolonged potentiostatic electrolysis of  $\text{CO}_2$  with various electrodes was carried out, and the yields of the products are shown in Table 1. No reduction product except formic

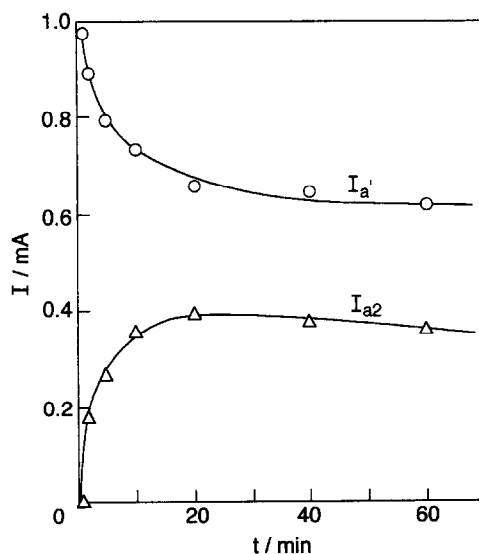


Fig. 9. Relationship between  $I'_a$  or  $I_{a2}$  and the cathodizing time. The CV curves were measured with a fully modified electrode in a  $0.5$  M  $\text{KHSO}_4$  solution of pH 4 saturated with  $\text{CO}_2$ .

Table 1

Yields of the products obtained from the electrochemical reduction of CO<sub>2</sub> on various electrodes at a constant potential of -0.6 V in a 0.5 M KCl solution<sup>a</sup>

Run	Electrode	Products ( $\mu\text{mol dm}^{-3}$ )				$Q^b$ (C)	$\eta^c$ (%)
		methanol	ethanol	lactic acid	formic acid		
1	Pt	0.3	0.3	0.0	2.8	1173.3	0.0
2	Pt/WO <sub>3</sub> /PAN	0.7	1.7	6.2	0.2	38.9	2.2
3	Pt/WO <sub>3</sub> /PAN/PVS	1.3	1.5	13.7	5.2	61.2	3.0
4 <sup>d</sup>	Pt/WO <sub>3</sub> /PAN/PVS	0.2	0.2	0.0	0.0	79.9	0.0

<sup>a</sup> WO<sub>3</sub>, tungsten trioxide; PAN, polyaniline; PVS, polyvinylsulfate; electrolysis time, 24 h.

<sup>b</sup>  $Q$ : total electric charge passed during the electrolysis.

<sup>c</sup>  $\eta$ : current efficiency for the reduction of CO<sub>2</sub>.

<sup>d</sup> N<sub>2</sub> was saturated to the electrolyte instead of CO<sub>2</sub>.

acid was obtained with a bare platinum electrode. The modification of Pt with WO<sub>3</sub>/PAN-layered films led to the formation of ethanol and lactic acid. A fully modified electrode gave most abundant amounts of lactic acid, formic acid, methanol, and ethanol. It is noted that a C<sub>3</sub> compound such as lactic acid was produced by the electrochemical reduction of CO<sub>2</sub> on such modified electrode. The prolonged electrolysis was also performed in the solution with N<sub>2</sub>, but there was no detectable amount of carbon-con-

taining species. It is therefore confirmed that the carbon source of the products is CO<sub>2</sub>.

The reduction products within the coated film were identified by the FTIR reflection method. The spectra of the fully modified electrode before and after the electrolysis in CO<sub>2</sub>-saturated solution are shown in Fig. 10. The absorption peaks at the wavenumber of 1600 and 1500 cm<sup>-1</sup>, appearing both before and after the electrolysis, are attributable to the NH vibration of PAN. After the electrolysis, several new peaks are observed, and these are assignable to CO<sub>2</sub> (2350 cm<sup>-1</sup>), -CONH- (3400, 1650, 1530 cm<sup>-1</sup>), C-CH<sub>3</sub> (2900 cm<sup>-1</sup>), and >CH-OH (1340 cm<sup>-1</sup>). These absorption peaks suggest the involvement of the observed products in the coated film. Especially the existence of the -CONH- group indicates a linkage of the amino nitrogen of PAN to the carbon atom of CO<sub>2</sub>, reduction intermediate, and/or products. The reduction of CO<sub>2</sub> given in Table 1 was carried out at the potential of -0.8 V vs. Ag/AgCl, and it is noteworthy that the overpotential for the reduction of CO<sub>2</sub> as well as the usefulness of products was much improved in aqueous solution.

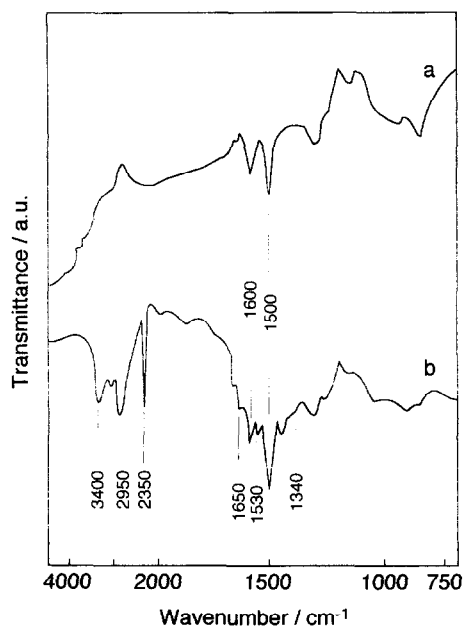


Fig. 10. FTIR reflection spectra of a fully modified electrode before and after electrolysis in a 0.5 M KCl solution of pH 4 saturated with CO<sub>2</sub>.

#### 4. Conclusions

In situ FTIR reflection spectra of a Pt/WO<sub>3</sub>/PAN/PVS electrode were measured, and the electrode was applied to the electrocat-

alytic reduction of CO<sub>2</sub> in aqueous solution. The reduction of CO<sub>2</sub> was achieved through the reaction with the adsorbed hydrogen atoms generated on the cathodized electrode, and the –CONH– group was found in the mediated film. The prolonged potentiostatic reduction of CO<sub>2</sub> led to the formation of C<sub>1</sub>–C<sub>3</sub> compounds under low overpotential.

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