— Communication —

Electrochemical Reduction of CO₂ on the Low Index Planes of Platinum in Acetonitrile

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Structural effects on the rate of CO₂ reduction were studied on the low index planes of Pt (Pt(111), Pt(100) and Pt(110)) using macro-electrolysis in acetonitrile containing 0.1 M (M = mol dm⁻³) tetraethyl ammonium perchlorate. CO₂ was reduced at -3.1 V (vs. Ag/Ag⁺) with the concentration of water controlled at 25 ± 2 mM. Oxalic acid was the main reduction product on each electrode. Formic acid and trace of CO were also produced. The order of the partial current density of oxalic acid formation is Pt(110) < Pt(111) < Pt(100): the partial current on Pt(100) is twice as high as that on Pt(110).

Key Words : Acetonitrile, Pt Single Crystals, Carbon Dioxide, Macro-electrolysis

1 Introduction

Electrochemical reduction of CO₂ is one of the noteworthy methods to convert CO₂ to hydrocarbons and alcohols at room temperature and ambient pressure.^{1,2)} Revealing the surface structures enhancing the catalytic activity for CO₂ reduction is important for developing electrocatalysts reducing CO₂ with less activation energy. Pt electrodes are useful for this purpose, since well-defined surfaces of Pt can be prepared easily according to Clavilier *et al.*³⁾

Adsorbed hydrogen atoms on Pt electrodes reduce CO₂ to adsorbed CO in aqueous solutions.^{4,5)} The initial rates for the CO₂ reduction depend on the crystal orientation remarkably: Pt(111) < Pt(100) < Pt(110),⁶⁻⁸⁾ where the initial rate on Pt(110) is 200 times as high as that on Pt(111).⁹⁾ However, no reduction product of CO₂ is desorbed from the Pt electrodes.¹⁰⁾

Non-aqueous solutions have wider polarizable potential range than water. The reduction products of CO₂ differ from those in aqueous solution: a Pt polycrystal electrode gives oxalic acid and CO in organic solvents, such as dimethyl sulfoxide and acetonitrile.¹¹⁾ In this communication, we report the orientation dependence of the catalytic activity for CO₂ reduction on the low index planes of Pt single crystal electrodes (Pt(111), Pt(100) and Pt(110)) in acetonitrile (AN).

2 Experimental

Single crystal electrodes of Pt were prepared according to Clavilier *et al.*³⁾ Crystals were oriented using the reflection beam of He-Ne laser from (111) and (100) facets on the surfaces,¹²⁾ and mechanically polished with diamond slurry down to 0.125 micrometer. The surface areas of the electrodes are 0.179 cm² (Pt(111)), 0.185 cm² (Pt(100)) and 0.201 cm² (Pt(110)).

The single crystal electrodes were annealed in H₂/O₂ flame and cooled in Ar/H₂ atmosphere prior to each electrochemical measurement. The surface was protected with a droplet of ultrapure water during the transfer, and rinsed with purified AN 3 times before inserting into the electrolytic cell. All the electrochemical measurements were done in the hanging meniscus configuration.

The cell was composed of three compartments. The compartment of working electrode was separated from those of counter and reference electrode using glass filter and ground glass cock, respectively. The counter electrode was Pt wire and the reference electrode was Ag/Ag⁺ (0.01 M (M = mol dm⁻³) AgNO₃ in AN). All potentials were referred to Ag/Ag⁺.

Special grade AN was further purified by distillation. The electrolyte, tetraethyl ammonium perchlorate (TEAP: (C₂H₅)₄NClO₄), was purified by recrystallization. The purity of Ar and CO₂ was 99.9999 %.

The concentration of water was controlled at 25 ± 2 mM by adding ultrapure water into AN, measured with gas chromatography. The macro-electrolysis of CO₂ was conducted in the closed system at -3.1 V (vs. Ag/Ag⁺) with the solution stirred at 100 rpm until the electricity reached 3.4 C. The reduction products were analyzed using gas chromatography and liquid chromatography after electrolyses.

3 Results and Discussion

Voltammograms of the prepared Pt single crystals were measured in 0.5 M H₂SO₄ for confirming the orientation. Each electrode gave the same voltammogram as reported by Clavilier *et al.*^{3,13)}

Figure 1 shows the voltammograms of the low index planes of Pt in 0.1 M TEAP/AN saturated with Ar. The potential is held at 0 V initially. Each surface gives the cathodic current of the hydrogen evolution

Fig. 1 Voltammograms of Pt(111), Pt(100) and Pt(110) in 0.1 M TEAP/AN saturated with Ar. Scanning rate: 0.050 V s⁻¹.

due to the decomposition of water in AN, when the potential was swept from 0 V to the negative direction. When the potential was swept positively after the negative polarization, Pt(111) and Pt(100) give anodic peaks at -1.0 and -1.2 V, respectively, whereas Pt(110) shows no peak. The orientation dependence of the voltammogram in 0.1 M TEAP/AN is less remarkable than that in aqueous solutions; no electrode provides the peaks of the hydrogen adsorption and desorption that are observed in 0.1 M HClO₄. AN is adsorbed to single crystal electrodes of Pt and blocks the site for hydrogen adsorption.¹⁴⁻¹⁶ The adsorption of AN may attenuate the orientation dependence of the voltammograms of the Pt electrodes.

Table 1 shows the results of the macro-electrolysis of CO₂ at -3.1 V. Each surface gives oxalic acid as a main product. Formic acid and trace of CO are also produced. These products definitely originate from CO₂, since control experiments conducted in Ar saturated solution produced only H₂.

The catalytic activity for CO₂ reduction was measured by the sum of the partial current densities of the reduction products of CO₂, such as oxalic acid, formic acid and CO. The activity depends on the crystal orientation, and the following order of the activity is obtained: Pt(110) < Pt(111) < Pt(100). The partial current density of oxalic acid on Pt(100) is nearly twice as high as that on Pt(110), and that of formic acid on Pt(100) is 3 times higher than that on Pt(110). In 0.1 M HClO₄, the initial rate of the reduction of CO₂ of Pt(110) is 200 times as high as that of Pt(111). Orientation dependence of the rate of the CO₂ reduction in AN is much lower than that in aqueous solutions. Pt(110), which has the highest activity in aqueous

solutions, gives the lowest partial current for CO₂ reduction in AN.

The difference of the orientation dependence between AN and aqueous solution can be attributed to the difference of the reduction mechanism of CO₂: adsorbed hydrogen atoms on Pt reduce CO₂ to adsorbed CO in 0.1 M HClO₄,^{4,5} whereas Pt electrode in AN reduces CO₂ mainly to oxalic and formic acid. Another possible factor affecting the different structural effects is the following. Systematic study using stepped surfaces of Pt suggests that pseudo-4-fold bridged site characteristic of (110) is the surface structure suitable for CO₂ reduction in aqueous solutions.¹⁷ The pseudo-4-fold bridged site provides characteristic redox peaks at 0.12 V (RHE) in the voltammogram in 0.1 M HClO₄. In TEAP/AN, however, Pt(110) electrode does not give such peaks as shown in Fig. 1. This result suggests that some adsorbates are strongly adsorbed to the pseudo-4-fold bridged site in TEAP/AN. IRRAS studies show that AN¹⁵ and CO^{18,19} is adsorbed to Pt single crystal electrodes in AN at -1.2 and -1.5 V, respectively. Adsorbed AN and CO may prevent CO₂ from approaching the active site and attenuate the structural effects on the catalytic activity in AN. In 0.1 M HClO₄, neither CO nor AN is adsorbed on the electrode surface at the initial stage of the CO₂ reduction; thus the initial rates depend on the orientation remarkably.

It is striking, however, that the catalytic activity still depends on the orientation of the electrodes on which AN and CO are strongly adsorbed. The electrons transferred through the adsorbate layer will reduce CO₂; the difference of the adsorbate structure may cause the orientation dependence of the CO₂ reduction. The origin of the structural effects will be studied in detail using IRRAS and STM.

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Table 1 Partial current density of the reduction products at -3.1 V (Ag/Ag⁺). Current efficiency is also shown in parenthesis. (A) + (B) + (C) presents the sum of the partial current densities of the reduction products from CO₂, such as (COO⁻)₂, HCOO⁻ and CO.

	Partial current density/mA cm ⁻² (current efficiency/%)					(A)+(B)+(C)
	(COO ⁻) ₂ ^(A)	HCOO ⁻ ^(B)	CO ^(C)	H ₂	total	
Pt(100)	4.3 (73)	1.2 (19)	5.7 × 10 ⁻² (0.8)	0.71 (9.4)	6.3 (102)	5.6 (93)
Pt(111)	3.2 (57)	0.49 (8.8)	9 × 10 ⁻³ (0.2)	1.7 (31)	5.4 (97)	3.7 (66)
Pt(110)	2.3 (74)	0.42 (13)	1.5 × 10 ⁻² (0.5)	0.32 (10)	3.1 (98)	2.7 (88)

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