

## TiO<sub>2-x</sub> 박막의 전기화학적 성질에 관한 연구

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(1985. 6. 24 접수)

## Studies on the Electrochemical Properties of TiO<sub>2-x</sub> Thin Films

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(Received June 24, 1985)

**요약.** 공기산화와 수증기 산화법에 의하여 TiO<sub>2-x</sub> 박막을 만들었고, 알곤 기체속에서 TiO<sub>2</sub> 단결정을 환원하였다. TiO<sub>2-x</sub> 박막의 전극 특성은 환원된 단결정 rutile의 특성과 거의 같았다. 산소가 용해된 전해질용액에서 측정된 TiO<sub>2-x</sub> 전극들의 전류-전압 곡선으로 부터 음극전류의 peak는 -0.8~-1.1V에서 나타났으며, 영볼트 근처의 TiO<sub>2-x</sub> 전극들의 음극전류는 공기로 포화된 용액에서 보다 질소로 포화된 용액에서 더 크게 나타났다. 시간에 따르는 전류 ( $i$ )의 변화는  $i_0 e^{-kt}$  식에 의존하였고 이때의 속도상수( $k$ )는  $k_0 [H^+]^n \exp(A\eta + \frac{E_a}{RT})$ 로 나타낼 수 있었다. 여기서 활성화에너지  $E_a$ 는 0.035~0.145V의 과전압에서는 4.6~4.8kcal/mole, 0.2~0.5V의 과전압에서는 1.6kcal/mole이고, 위식중의  $n$ 과  $A$ 는 0.035~0.145V에서 0.1과, 5.4~5.6/V, 0.2~0.5V에서는 0.04와 1.3/V이었다. 산소의 환원반응은 전체적으로 비가역 반응을 알았다.

**ABSTRACT.** A titanium oxide thin films were prepared by air oxidation and vapour oxidation and a TiO<sub>2</sub> single crystal was reduced by heating in an argon atmosphere. All the electrode characteristics of the TiO<sub>2-x</sub> thin films are not different from those of slightly reduced single crystal rutile. In cyclic voltammogram of oxygen containing electrolyte solution at TiO<sub>2-x</sub> electrodes, cathodic peaks were observed at between -0.8V and -1.0V vs. SCE. The cathodic current near OV vs. SCE in saturated solution with nitrogen was observed to be greater than in saturated solution with air. The chronoamperogram was represented by the equation of  $i = i_0 e^{-kt}$ , when the rate constant  $k$  was represented by the equation of  $k = k_0 [H^+]^n \exp(A\eta + E_a/RT)$ . The values of activation energy  $E_a$  were found to be 4.6~4.8kcal/mole in overpotential range of 0.035~0.145 V and 1.6kcal/mole in overpotential range of 0.2~0.5V. The values of  $n$  and  $A$  were found to be 0.1 and 5.4~5.6/V in range of 0.035~0.145V, and in range of 0.2~0.5V, to be 0.04 and 1.3/V, respectively. This can be interpreted as an totally irreversible reduction of oxygen.

### I. INTRODUCTION

The use of electrolyte-semiconductor junctions for the conversion of solar energy was first

demonstrated in the work on TiO<sub>2</sub> by Fujishima *et. al.*<sup>1-3</sup> The properties of rutile TiO<sub>2</sub> and its behavior as an anode in an electrochemical cell have received increasing attention recently.<sup>4-15</sup>

This interest stems from the work of Fujishima and Honda,<sup>1</sup> who suggested rutile as an agent for electrolytic splitting of water with photons supplying the necessary energy. Although the band gap of rutile is fairly large (3.0eV) allowing it to usefully capture only a small fraction of the energy available in sunlight, it is one of very few semiconducting materials considered sufficiently stable to resist corrosion when used as an electrode in an aqueous electrochemical cell.

In the present study,  $\text{TiO}_{2-x}$  thin films were prepared by air or water vapor oxidation of titanium sheet, and their electrochemical properties were elucidated.

## II. EXPERIMENTAL

### 1. Preparation of Ti-sheet

Titanium sheets ( $1 \times 1 \times 0.1 \text{ cm}^3$ ) used were Nilaco (Japan) 5-N purity titanium. Titanium sheets were polished with automatic crystal polisher (Model DS-701G, jasco) using alumina powder of  $0.2 \mu\text{m}$  size, etched in  $\text{CP}_4$  (mixed solution of  $\text{HNO}_3$ ; 50ml, glacial acetic acid; 30ml, HF; 30ml,  $\text{Br}_2$ ; 1 drop) for 1 minute, rinsed with the double distilled water and then with distilled isopropyl alcohol and dried in vacuum oven for 1 hour at  $50^\circ\text{C}$ .

### 2. Ar-gas purifier<sup>5</sup>

Argon (99.9%) was dried by passing through a  $\text{CaSO}_4$  column and a  $\text{Mg}(\text{ClO}_4)_2$  column and purified further by passing through a copper column filled with copper turnings kept at about  $300^\circ\text{C}$ , and stainless steel column filled with titanium turnings kept at  $850^\circ\text{C}$ .

### 3. Preparation of $\text{TiO}_{2-x}$ thin films<sup>5</sup>

#### (1) Air oxidation (AO)

The air oxidized titanium dioxide thin films were grown by heating titanium sheets in an electric furnace of SYBRON thermolyne 1300 furnace (U. S. A.) kept at  $800^\circ\text{C}$ , for 90 seconds,

then cooled to room temperature in a desiccator.

#### (2) Vapour phase oxidation in water vapour (VO)<sup>5</sup>

The  $\text{TiO}_{2-x}$  thin films were grown by passing water saturated argon gas over titanium sheets in an electrical furnace at temperature  $800^\circ\text{C}$ ,  $900^\circ\text{C}$ ,  $1140^\circ\text{C}$ , respectively, for 30 minutes, as explained below; Several Ti sheets were placed on top of a mullite combustion boat in the reaction tube ( $\phi$ ; 5cm, L; 35cm). After evacuating air in the reaction tube by a mechanical vacuum pump, the purified argon was passed through at the flow rate of 80ml/min for 2 hours and the temperature was raised as quickly as possible to the prescribed temperature.

The purified argon was saturated with water vapour by passing through distilled water and then passed at the flow rate of 50ml/min over titanium sheets for 30 minutes. The oxidized titanium sheets were removed from the furnace and cooled down to the room temperature in a desiccator.

#### (3) Designation of sample

In the present article, the temperature of oxidation followed by oxidizing atmosphere (AO for air oxidation and VO for vapour phase oxidation) in parentheses is used to designate the sample; for example, 800 (AO) represents the sample prepared by air oxidation at  $800^\circ\text{C}$  (AO).

#### (4) Reduction of single crystal rutile

$\text{TiO}_2$  single crystal rutile was reduced by heating it for 2 hours at  $1000^\circ\text{C}$  in gettered argon gas.

(5) The flat band potential ( $V_{fb}$ ) of the  $\text{TiO}_{2-x}$  thin film prepared by the above mentioned method was obtained to be  $-1.0 \sim -1.1$  V, and the value was the same with that reported by Bolts<sup>6</sup>.

The donor ionization energy ( $E_C - E_D$ ) was obtained to be  $0.1 \sim 0.3$  eV, and the value was

similar to that reported by Hoslor<sup>7</sup>.

#### 4. Electrodes for the measurement of the electrochemical properties

One side of TiO<sub>2-x</sub> was polished with sand paper of No.1500 and a copper lead(1×100×0.05mm<sup>3</sup>) was mounted on it with silver paste (silver:epoxy resin=7:1), and then covered with epoxy resin.

#### 5. Electrolyte cell

A cell for the measurements was prepared with a box(8.5×5×8cm<sup>3</sup>) made of acrylic plate (3mm thickness) with three electrodes(SCE, TiO<sub>2-x</sub>, and Pt) and a tube of air or nitrogen bubbling. The cell was divided into three compartments in order to maintain a constant laminar flow of electrolyte over the electrode.

#### 6. Electrolyte solution

Saturated NaOH(sp. grade) solution was prepared with distilled water and left for about 30 days to allow deposition of Na<sub>2</sub>CO<sub>3</sub> and other impurities contained in sodium hydroxide. The supernatant was diluted to 1M NaOH solution. Various buffer solutions were prepared according to Table 1.

#### 7. Measurement of cyclic voltammograms

Cyclic voltammograms were observed using a potentiostat<sup>4</sup> with a sensitive current amplifier (OP 07) and recorded on X-Y recorder(Graphtec WX4301-H); measurement was made after finishing air or nitrogen saturation and the results are shown in Fig. 1~3.

#### 8. Measurement of chronoamperograms

The chronoamperograms were measured to obtain the instantaneous current  $i_0$  and rate constant  $k$  of the TiO<sub>2-x</sub> electrodes at various temperature (273K, 288K, 298K, 308K), pH(8.6, 10.0, 12.0, 13.6), and overpotentials in the saturated electrolyte solution with air or nitrogen.

The variation of current with time was obtained using a potentiostat<sup>4</sup> and recorded on

X-Y recorder as shown in Fig.4,5.

### III. RESULTS AND DISCUSSION

#### 1. Cyclic voltammetry of oxygen containing 1 M NaOH solution

The values of potential ( $E_{pa}$ ) responding to

Table 1. Buffer solution at 25°C

pH	8.6	10.0	11.0	12.0
0.05M NaHCO <sub>3</sub> (mL)	50	50	50	50
0.1M NaOH(mL)	—	10.7	21.8	26.6

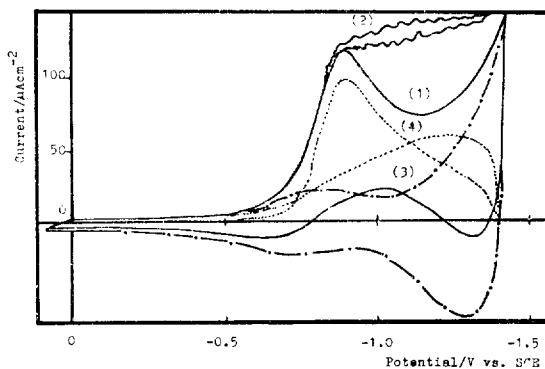


Fig.1. Cyclic voltammograms of 900(VO) TiO<sub>2-x</sub> electrode in 1M NaOH solution at  $v=65\text{mV/sec}$ . (1); After air saturation, (2); With air bubbling, (3) After N<sub>2</sub>-gas saturation, (4); Oxygen only.

$$(i_{pa} - i_{pn}) / \mu A$$

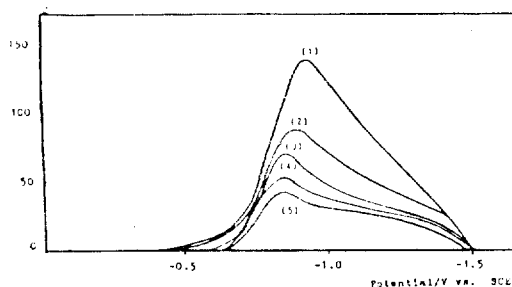


Fig.2. Cyclic voltammograms of 1140 (VO) according to various scan rates in 1M NaOH solution.  $v/\text{mVsec}^{-1}$  = (1) ; 65, (2) ; 31, (3) ; 15, (4) ; 8.6, (5) ; 4.5.

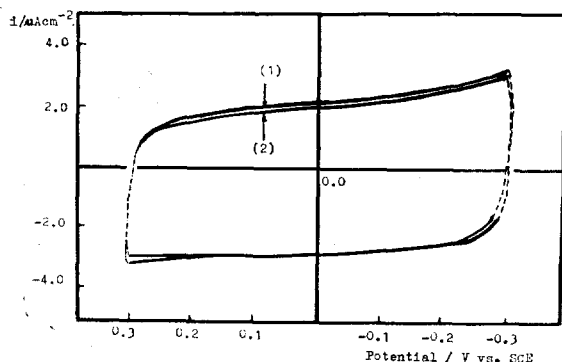


Fig. 3. Cyclic voltammogram of 1140(VO)  $\text{TiO}_{2-x}$  electrode in 1M NaOH solution at  $v=31\text{mV/sec}$ . (1) ; After  $\text{N}_2$ -gas saturation, (2) ; After air saturation.

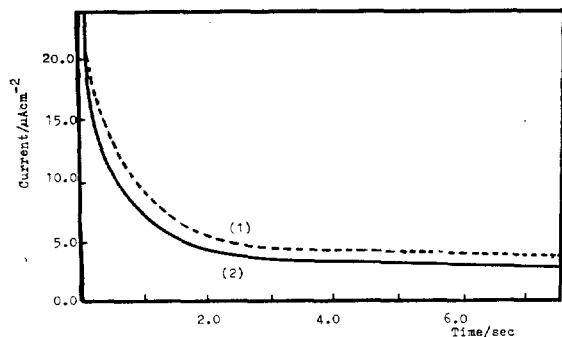


Fig. 4. Chronoamperogram curve of 1140 (VO)  $\text{TiO}_{2-x}$  electrode in 1M NaOH solution at  $-0.5\text{V}$  overpotential. (1) ; After  $\text{N}_2$ -gas saturation, (2) ; After air saturation.

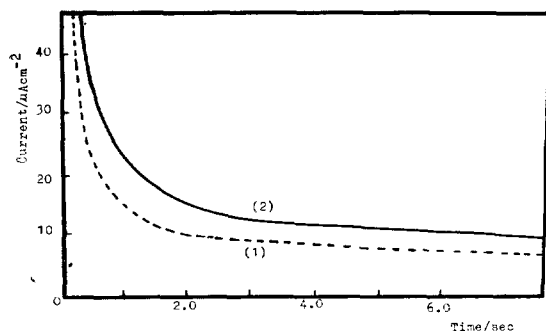


Fig. 5. Chronoamperogram curve of 1140(VO)  $\text{TiO}_{2-x}$  electrode in 1M NaOH solution at  $-0.7\text{V}$  overpotential. (1) ; After  $\text{N}_2$ -gas saturation, (2) ; After air saturation.

current peak obtained from the cyclic voltammogram of the  $\text{TiO}_{2-x}$  electrodes at various scan rates were observed between  $-0.80 \sim -1.10\text{V}$

vs. SCE in 1M NaOH electrolyte solution (Table 2) and shifted to the negative potential when the scan rate became faster, as shown in Fig. 2.

During the air bubbling, the cathodic currents were influenced from  $-0.7\text{V}$ , which is near peak potential, as shown in Fig. 1. Therefore these cathodic peak currents were the ones resulted from the reduction of oxygen in electrolyte solution.

The plot of  $i_p - i_{pN}/A$  vs.  $\sqrt{v}$  shows that the peak current increased linearly according to the square root of the scan rate (Fig. 6).

The relationship between the peak current

Table 2. The values of  $i_p$  and  $E_p$  from the cyclic voltammograms according to scan rates in 1M NaOH solution.

Sample	Area ( $\text{cm}^2$ )	Scan rate ( $\text{mV sec}^{-1}$ )	Peak current ( $\mu\text{A}/\text{cm}^2$ )			Peak voltage/ $-V$
			$i_{p_a}$	$i_{pN}$	$i_{p_a} - i_{pN}$	$E_p$
Single crystal	0.200	65.0	140.4	38.9	101.5	1.05
		31.0	82.0	21.0	61.0	1.03
		15.0	65.0	14.0	51.0	1.03
		8.6	50.0	11.0	39.0	1.00
800 (AO)	0.774	65.0	149.8	43.9	105.9	0.89
		31.0	108.0	22.7	85.3	0.87
		15.0	76.7	14.2	62.5	0.85
		8.6	61.5	9.6	51.9	0.84
800 (VO)	0.833	65.0	165.6	32.8	132.8	0.87
		31.0	115.7	20.9	94.8	0.86
		15.0	81.0	12.6	68.4	0.83
		8.6	64.7	10.8	53.9	0.82
900 (VO)	0.732	65.0	177.3	44.2	133.1	1.10
		31.0	104.7	24.5	80.2	1.05
		15.0	83.5	15.8	67.7	1.01
		8.6	63.8	1.05	53.3	0.98
1140 (VO)	0.822	65.0	207.5	48.6	158.9	1.11
		31.0	123.3	35.7	87.6	1.08
		15.0	97.4	29.1	68.3	1.05
		8.6	73.3	25.5	47.8	1.02

$i_{p_a}$ ; in air saturated solution,  $i_{pN}$ ; in nitrogen saturated solution,  $i_{p_a} - i_{pN}$ ; Oxygen only.

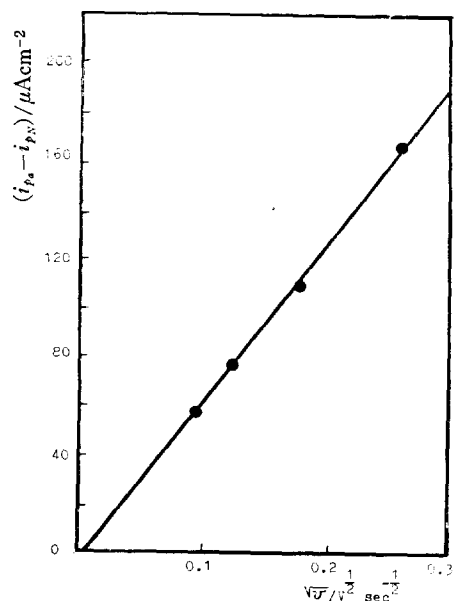


Fig. 6. Plot of  $i_p - i_{pN}$  vs.  $\sqrt{v}$  from the cyclic voltammograms of the 900(VO)  $TiO_{2-x}$  electrode in 1M NaOH solution.

and scan rate shows as the following

$$i_p/A = 2.99 \times 10^5 n(\alpha n_a)^{1/2} C^* D_o^{1/2} v^{1/2} \quad (1)$$

where,  $i_p$ ; the cathodic peak current ( $\mu A$ ),

$A$ ; the area of electrode,

$n$ ; the number of electrons per molecule oxidized or reduced,

$\alpha$ ; the transfer coefficient,

$n_a$ ; the number of electrons involved in the rate determining step,

$C^*$ ; bulk concentration of oxygen,

$D_o$ ; diffusion coefficient of oxygen,

$v$ ; the scan rate.

## 2. Cyclic voltammetry of 1 M NaOH solution without oxygen

Cyclic voltammogram curves in saturated 1 M NaOH electrolyte solution with nitrogen showed that the peak current  $i_{pN}$  increased linearly with the scan rates from the plot of  $i_{pN}$  vs.  $v$  (Fig. 7).

The linear dependence of peak currents on scan rate was indicative of an influence of adsorption on the electrode reaction. These

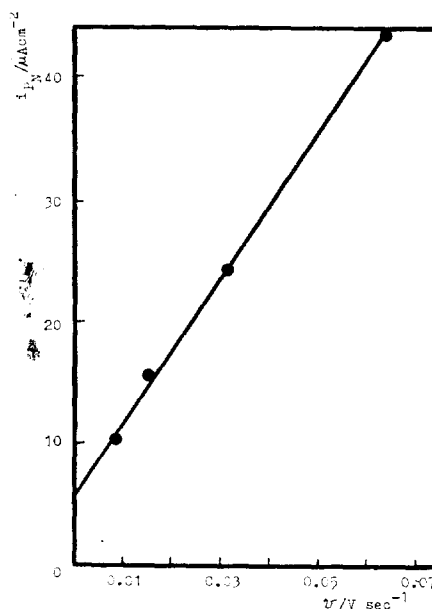


Fig. 7. Plot of  $i_{pN}$  vs.  $v$  from the cyclic voltammograms of the 900(VO)  $TiO_{2-x}$  electrode in 1M NaOH solution.

results were in agreement with those reported by Parkinson *et al.*<sup>17</sup>

Thus, reduction of oxygen at  $TiO_{2-x}$  electrode is to be described as totally irreversible process.

## 3. Chronoamperometry and Tafel plot

The cyclic voltammograms near 0 volt vs. SCE show that the cathodic current is greater in saturated electrolyte solution with nitrogen than in the saturated electrolyte solution with air (Fig. 3). To elucidate the nature of the current near 0 volt, the chronoamperometric study was carried out as follows:

(1) Determination of instantaneous current<sup>18</sup>

A different approach to the evaluation of the activation controlled reaction rate from measurements taken under mixed activation and diffusion control is to consider the two processes as consecutive steps in a reaction sequence. The measured current density from the chronoamperometry may then be written in the form

$$\frac{1}{i} = \frac{1}{i_{ac}} + \frac{\sqrt{t}}{K} \quad (2)$$

where  $K$  is a potential dependent quantity given by

$$K = nFD\frac{1}{2} C^* \pi^{-\frac{1}{2}} (1 + \xi\theta)^{-1}$$

Therefore the activation controlled current density  $i_{ac}$  may be evaluated by plotting  $\frac{1}{i}$  vs.  $t^{\frac{1}{2}}$  and extrapolating back to  $t=0$ .

The current-time relation follows equation (2) when  $O_2$  is reduced at the electrode as shown in Fig. 8. However, when  $O_2$  was completely removed from the electrolyte solution,  $\frac{1}{i}$  vs.  $t^{\frac{1}{2}}$  plot did not give straight lines (Fig. 9). Since the current in such cases was proportional to the scan rate in cyclic voltammetry, an exponential decay of current  $i = i_0 e^{-kt}$  was tried and found to represent the experimental result quite well, as shown in Fig. 10.

The slope  $k$  obtained by plotting  $\ln i$  vs.  $t$  was regarded as the function of  $k = k^0 [H^+]^n \exp \left( A\eta + \frac{E_a}{RT} \right)$ .

where  $k$ : the rate constant

$n$ : the exponent of concentration of hydrogen ion

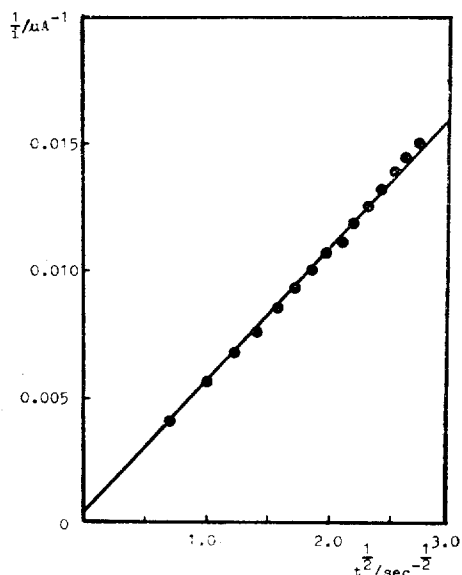


Fig. 8. Plot of  $\frac{1}{i}$  vs.  $t^{\frac{1}{2}}$  from the chronoamperometry of the 900 (VO)  $TiO_{2-x}$  electrode in air saturated 1M NaOH solution at  $-1.0V$  overpotential.

$A$ : the constant

$E_a$ : the activation energy

(a) From the Arrhenius plot shown in Fig. 11, the activation energies ( $E_a$ ) are summarized in Table 3. The magnitude of  $E_a$  (1.6~4.7 kcal/mole) indicates that the current is associated

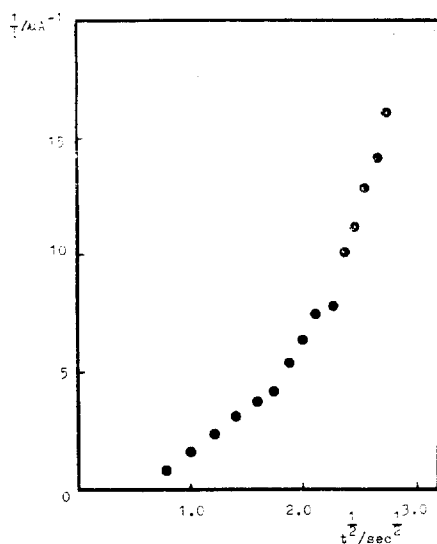


Fig. 9. Plot of  $\frac{1}{i}$  vs.  $t^{\frac{1}{2}}$  from the chronoamperometry of the 900 (VO)  $TiO_{2-x}$  electrode in  $N_2$ -gas saturated 1M NaOH solution at  $-0.06V$  overpotential.

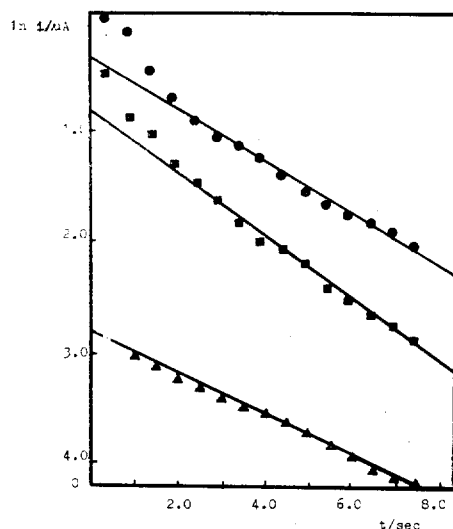


Fig. 10. Plots of  $\ln i$  vs.  $t$  from the chronoamperometry of the 900 (VO)  $TiO_{2-x}$  electrode in  $N_2$ -gas saturated 1M NaOH solution. overpotential =  $\bullet$ ;  $-0.1V$ ,  $\blacksquare$ ;  $-0.06V$ ,  $\blacktriangle$ ;  $+0.015V$ .

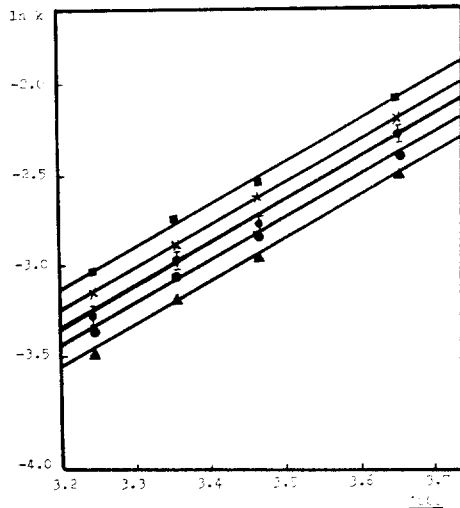


Fig. 11. Plot of  $\ln k$  vs.  $\frac{1000}{T}$  for 1140(VO)  $\text{TiO}_{2-x}$  electrode in  $\text{N}_2$ -gas saturated carbonate buffer (pH=10.0). overpotential(mV) = ■; 35, ×; 55, ○; 75, ●; 95, ▲; 145.

Table 3. The values of  $E_a$  from the plot of  $\ln k$  vs.  $1/T$  plot

Sample	pH	Single crystal	1140(VO)			
		13.6	13.6	12.0	10.0	8.6
35	4.6	4.7	4.7	4.7	4.7	4.8
55	4.6	4.7	4.7	4.7	4.7	4.8
75	4.6	4.7	4.7	4.7	4.8	4.8
95	4.5	4.7	4.7	4.7	4.7	4.7
145		4.8	4.8	4.8	4.8	4.7
200		1.6				
300		1.6				
400		1.6				
500		1.6				

( $E_a$ /kcal mole<sup>-1</sup>).

with adsorption.

(b) The values of  $k$  obtained in various pH solutions plotted in regard to pH (Fig. 12). The exponent of concentration of the hydrogen ion ( $n$ ) was obtained from the slope (Table 4). The values of  $n$  obtained are smaller than unity. Thus, the adsorbed species is very likely to be hydrogen ion.

(c) The values of  $k$  at various overpotentials

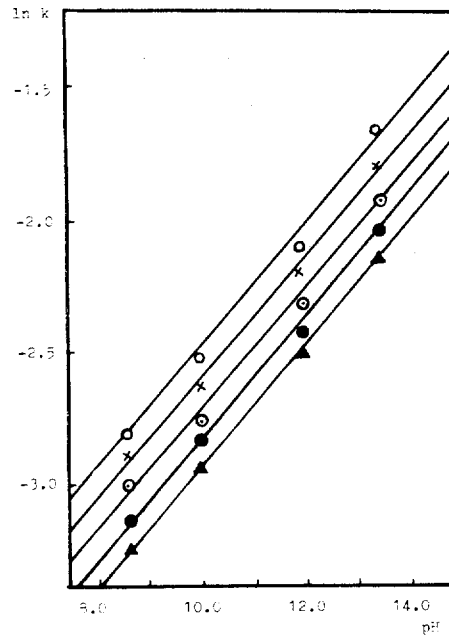


Fig. 12. Plots of  $\ln k$  vs. pH for 1140(VO)  $\text{TiO}_{2-x}$  electrode at 288K. overpotential(mV) = ○; 35, ×; 55, ○; 75, ●; 95, △; 145.

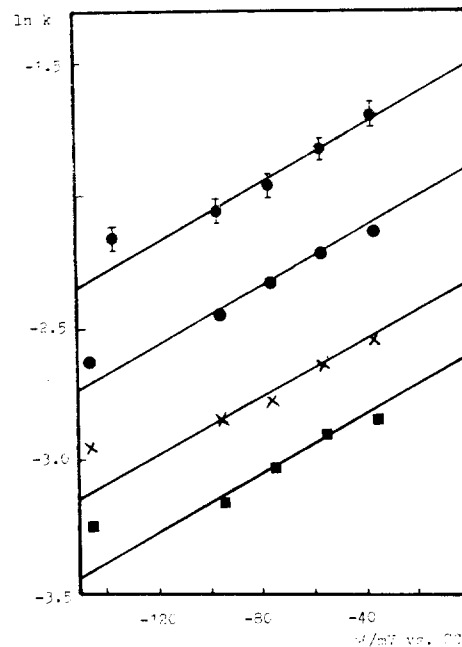


Fig. 13. Plots of  $\ln k$  vs.  $\eta$  for 1140(VO)  $\text{TiO}_{2-x}$  electrode in  $\text{N}_2$ -gas saturated various buffer at 288K. pH = ■; 8.8, ×; 10.0, ●; 12.0, ○; 13.5.

Table 4. The values of  $n$  and  $A$  for a single crystal(S.C) and 1140(VO)  $\text{TiO}_{2-x}$  Electrode

Sample $\eta$ -mV pH Temp.	A/V(from $\ln k$ vs. $\eta$ plot)						n(from $\ln k$ vs. pH plot)								
	S. C	1140(VO)					S. C			1140(VO)					
	a	a	b	a			35	75	145	35	75	145	200	300	500
	13.6	13.6	13.6	12.0	10.0	8.6									
273	5.4	5.5	1.3	5.6	5.6	5.6	0.1	0.1	0.1	0.1	0.1	0.1	0.04	0.04	0.04
288	5.4	5.6	1.3	5.6	5.5	5.5	0.1	0.1	0.1	0.1	0.1	0.1	0.04	0.04	0.04
298	5.4	5.6	1.3	5.5	5.5	5.6	0.1	0.1	0.1	0.1	0.1	0.1	0.04	0.04	0.04
308	5.4	5.6	1.3	5.5	5.5	5.6	0.1	0.1	0.1	0.1	0.1	0.1	0.04	0.04	0.04

a;  $\eta$ =at 35~145mV range, b;  $\eta$ =at 200~500mV range.

are plotted in regard to  $\eta$  (Fig. 13). The constants ( $A$ ) were obtained from the slope (Table 4).

### ACKNOWLEDGEMENT

This work was supported by a grant from the Ministry of Education, Republic of Korea. The authors would like to thank the Ministry of Education for financial support of this work.

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