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## ON THE SONO-VOLTAMMETRY CURVES OF POLYCRYSTALLINE PLATINUM ELECTRODE IN SULFURIC ACID SOLUTION

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### Abstract

The volumetric curve was characterized by current functions of large amplitude and formation peak potential of adsorption oxygen(O(a)) was disappeared with sonication. The reduction peak potential of O(a) shifted about 0.05 V to noble direction in saturated N<sub>2</sub> and air systems with addition of Cl<sup>-</sup> ion and sonication. The formation and ionization potentials of adsorption hydrogen(H(a)) had not been confirmed, and were not changed with sonication.

*Key words* : Voltammetry, Ultrasonic, Platinum, Sulfuric acid, Chloride ion.

### 1. INTRODUCTION

The collapse of cavitation bubbles in liquid generated shock wave pressure, liquid jet and water hummers pressure during to liquid jet. Sonication had been utilized mainly as a tool to accelerate heterogeneous processes and/or mass transport to electrode. Surface can be expected to raise the limiting currents attainable as results of reduction in the thickness of diffusion layer, and to improve quality in the electroplating and for the electrode pretreatment.

The physical and chemical properties of electrodeposited films affected with liquid jet<sup>(1)-7)</sup>. It was concluded as follows. The formation peak potential of O(a) was disappeared because degassing in solution was generated with cavitation and adsorption oxygen was disconnected from electrode with liquid jet. The current was more flowed as platinum oxide film on electrode decreased with shock wave pressure. The current functions of large amplitude change an apparent surface area of electrode as the amounts of adsorption of gas bubbles that generated with cavi-

tion reduced with liquid jet.

The present paper is to study the adsorption-desorption of hydrogen and oxygen, and addition of  $\text{Cl}^-$  ion in the course of potential cycling in order to find direct experimental.

## 2. EXPERIMENT

Fig. 1 shows the position of electrode and ultrasonic source. Test solution used  $100\text{cm}^3$  of 0.005, 0.05 and  $0.5\text{mol/dm}^3$   $\text{H}_2\text{SO}_4$ , and including  $0.002\text{mol/dm}^3$   $\text{Cl}^-$  ion. The cell measured  $5.0 \times 4.0 \times 7.0\text{cm}$  and, when containing  $100\text{cm}^3$  of solution, was covered glass, and immersed in ultrasonic tank (40 kHz, 100W). The cooling water maintained at 279 k in cooling bath with a thermostated refrigerator, and the cooling water circulated through the ultrasonic tank by a pump. The test solution maintained at 298 k during the measurement. The working and counter electrodes were

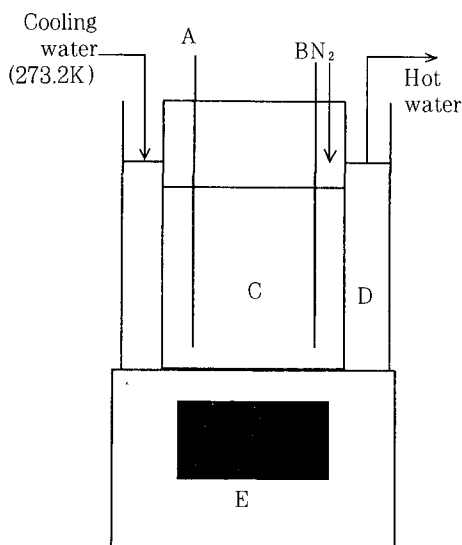


Fig. 1 The position of electrode and ultrasonic source

99.99% polycrystalline platinum plate and exposed active area of  $1.0 \times 1.0\text{cm}$  and  $2.5\text{cm} \times 4.0\text{cm}$ , respectively. The texture coefficients were {111} plane 35.0, {200} plane 52.7, {220} plane 11.0 and {311} plane 2.4. The distance between the electrode was 2.5cm. Surfaces polished with # 2000 emery paper and immersed in  $6\text{mol/dm}^3$   $\text{HNO}_3$  for several seconds, then rinsed with distilled water and air-dried before the experiments. Scan rate was  $100\text{mV/sec}$ . After cycle of 100 times, measurement started. All potentials had been given against the Ag/AgCl electrode in the saturated air and  $\text{N}_2$  systems.

## 3. RESULTS AND DISCUSSION

$0.05\text{mol/dm}^3$   $\text{H}_2\text{SO}_4$

Fig. 2 and 3 show the voltammetric curves in  $0.005\text{mol/dm}^3$   $\text{H}_2\text{SO}_4$  and in the saturated  $\text{N}_2$  and air systems. The potential shifted to the noble direction. The voltammetric curves characterized by current functions of large amplitude. The curve in  $-0.2 \sim -0.05\text{V}$  vs. Ag/AgCl electrode indicated oxidation current with ionication

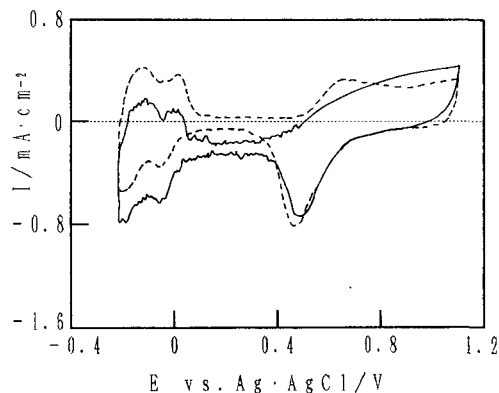


Fig. 2 The voltammetric curves in  $0.005\text{mol/dm}^3$   $\text{H}_2\text{SO}_4$  (Saturated  $\text{N}_2$  system).

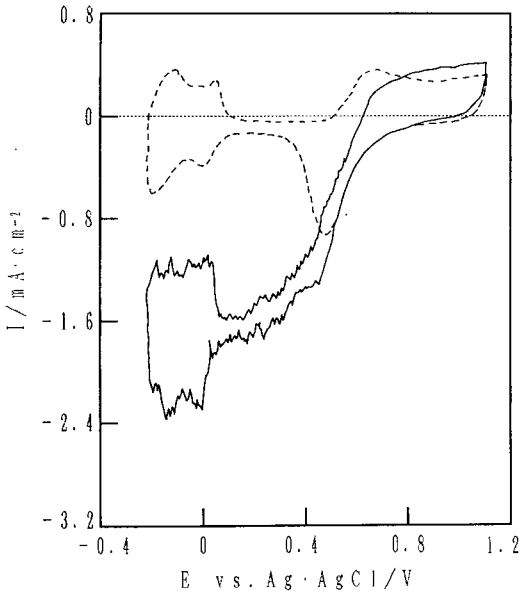
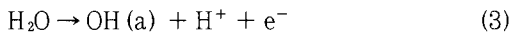
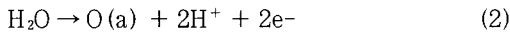


Fig. 3 The voltammetric curves in 0.005 mol/dm<sup>3</sup> H<sub>2</sub>SO<sub>4</sub> (Saturated air system)

of H (a).



The broad curve in the region of 0.5~1.1V vs. Ag/AgCl indicated with formation of O (a) from water.



Where, (a) means adsorption state. After the potential returned, the current curve at approximately 0.8 V was reduction of O (a). The curve at about 0.05V vs. Ag/AgCl was the formation of H (a). The two peaks observed in ionization of H (a), and H (a) of difference state existed. The peak potentials of formation and ionization of H (a) were not changed. The formation peak potential of O (a) disappeared and the reduction po-

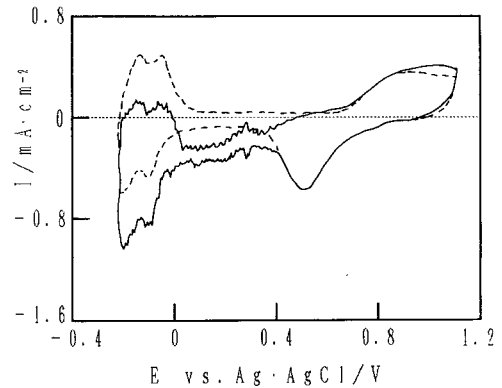


Fig. 4 The voltammetric curves in 0.005 mol/dm<sup>3</sup> H<sub>2</sub>SO<sub>4</sub>, 0.002 mol/dm<sup>3</sup> Cl<sup>-</sup> ion (Saturated N<sub>2</sub> system)

tential of O (a) shifted to about -0.05V with sonication. In the sonication, current disturbed under 0.15V vs. Ag/AgCl. The current density shifted -0.3mA/cm<sup>2</sup> in the region of formation and ionization of H (a). The current density shifted in a negative direction under 0.75V, and shifted in a positive direction over 0.75 V vs. Ag/AgCl. Fig. 4 shows the effects of Cl<sup>-</sup> ion on the voltammetry in the saturated N<sub>2</sub> system. The formation peak potential of O (a) disappeared in the presence of Cl<sup>-</sup> ion with sonication. The curve in the range of reduction of O (a) had little effect with sonication. The current density shifted -0.4mA/cm<sup>2</sup> in the range of formation and ionization of H (a). Fig. 5 shows the effects of Cl<sup>-</sup> ion in the saturated air system. The formation peak potential of O (a) had not affected with air. The formation and reduction peak potentials of O (a) disappeared with sonication. In the sonication, the current density in region of formation and ionization of H (a) shifted -1.653 mA/cm<sup>2</sup>.

0.05 mol/dm<sup>3</sup> H<sub>2</sub>SO<sub>4</sub>

Fig. 6~9 show the voltammetric curves. The

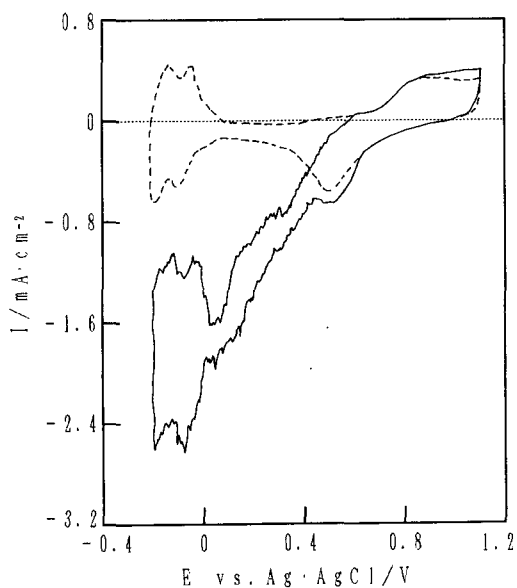


Fig. 5 The voltammetric curves in  $0.005 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$  containing  $0.002 \text{ mol/dm}^3 \text{ Cl}^-$  ion (Saturated air system)

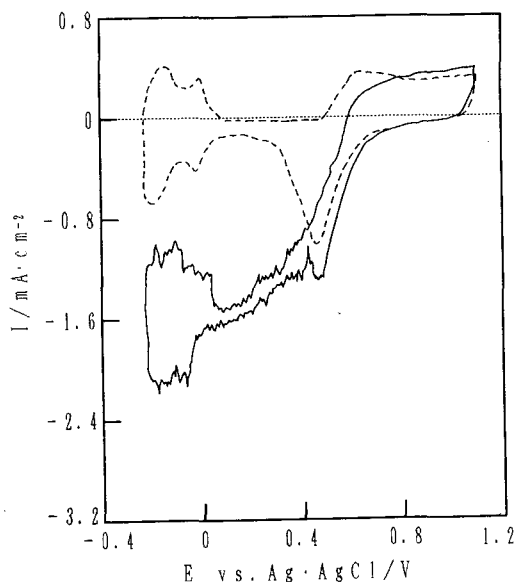


Fig. 7 The voltammetric curves in  $0.05 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$  (Saturated air system)

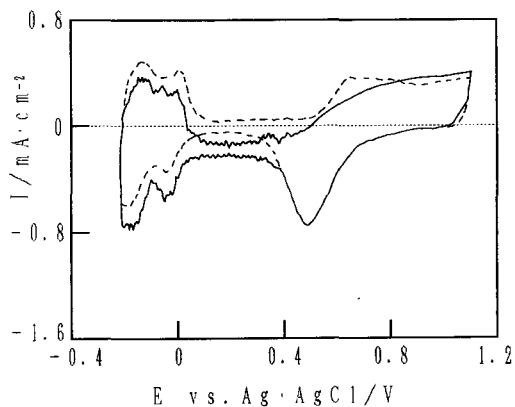


Fig. 6 The voltammetric curves in  $0.05 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$  (Saturated  $\text{N}_2$  system)

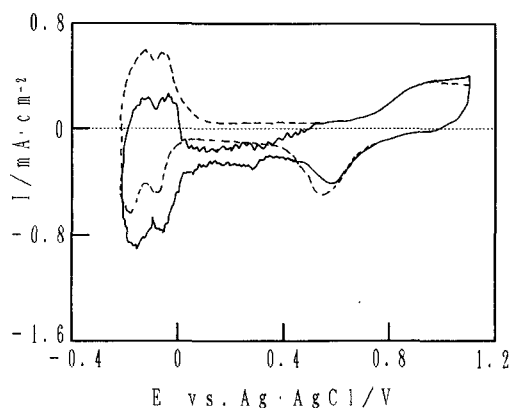


Fig. 8 The voltammetric curves in  $0.05 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$ ,  $0.002 \text{ mol/dm}^3 \text{ Cl}^-$  ion (Saturated  $\text{N}_2$  system)

formation peak potential of O (a) disappeared in the saturated  $\text{N}_2$  and air systems and addition of  $\text{Cl}^-$  ion with sonication. Voltammetric curve shifted  $-1.75 \text{ mA/cm}^2$  in the H (a) region. In the addition of  $\text{Cl}^-$  ion, the effect of  $\text{Cl}^-$  ion was

same  $0.005 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$  in the saturated  $\text{N}_2$  and air systems. The reduction peak potential of O (a) shifted about  $-0.04 \text{ V}$  in the saturated  $\text{N}_2$  system and  $-0.03 \text{ V}$  in the saturated air system with addition of  $\text{Cl}^-$  ion. The curve characterized

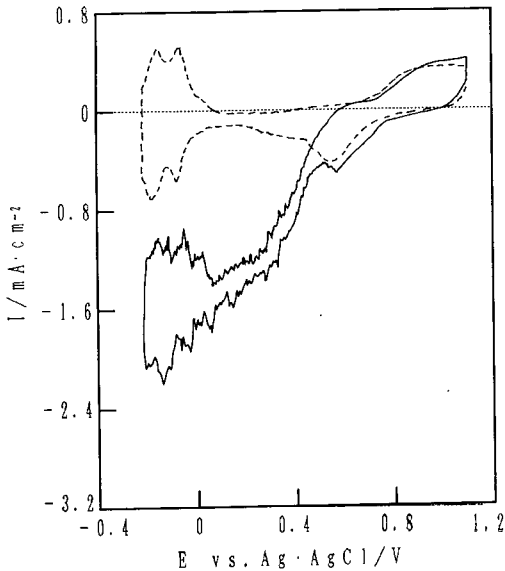


Fig. 9 The voltammetric curves in  $0.05 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$  containing  $0.002 \text{ mol/dm}^3 \text{ Cl}^-$  ion (Saturated air system)

by current functions of large amplitude under  $0.45 \text{ V vs. Ag/AgCl}$ . It was estimated that the formation and ionization potentials of H (a) had not been confirmed, and were not changed with sonication. The curve shifted in a negative direction under  $0.75 \text{ V}$ , and shifted in a positive direction over  $0.85 \text{ V vs. Ag/AgCl}$  in the saturated air system comparing that in the saturated  $\text{N}_2$  system.

$0.5 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$

Fig. 10~13 show the voltammetric curves. The formation peak potential of O (a) disappeared in the saturated  $\text{N}_2$  and air systems and addition of  $\text{Cl}^-$  ion with sonication. The reduction peak potential of O (a) shifted about  $-0.04 \text{ V}$  in the saturated  $\text{N}_2$  system and  $-0.03 \text{ V}$  in air system with addition of  $\text{Cl}^-$  ion. The peak potential of oxygen desorption shifted about  $-0.05 \text{ V}$  in the saturated  $\text{N}_2$  system with sonication. The curve

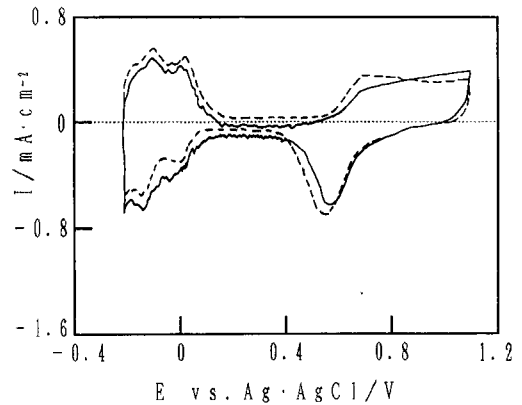


Fig. 10 The voltammetric curves in  $0.5 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$  (Saturated  $\text{N}_2$  system)

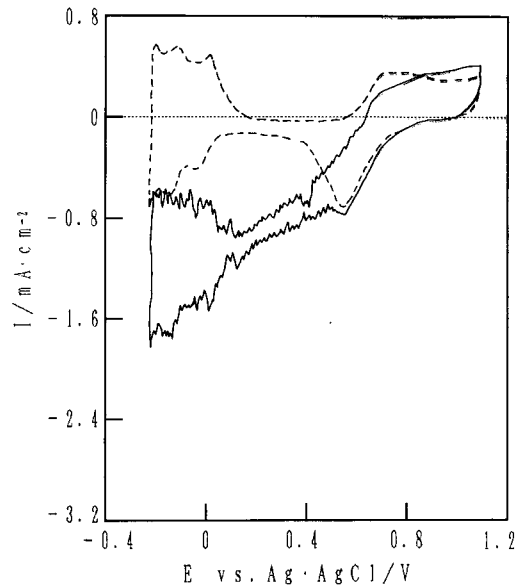


Fig. 11 The voltammetric curves in  $0.5 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$  (Saturated air system)

characterized by current functions of large amplitude under  $0.45 \text{ V vs. Ag/AgCl}$ . The displacement in current density was smaller comparing with that of  $0.005$  and  $0.05 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$ . The formation and ionization potentials of H (a) had not been confirmed, and were not changed with sonication.

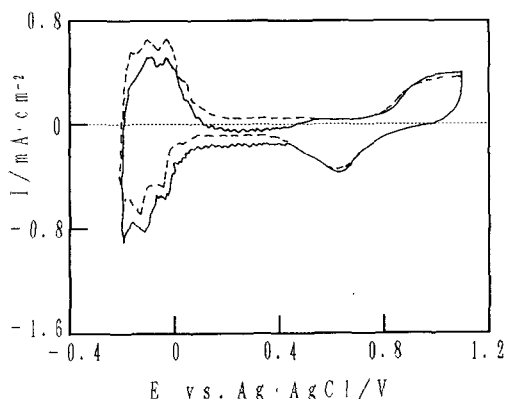


Fig. 12 The voltammetric curves in  $0.5 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$  containing  $0.002 \text{ mol/dm}^3 \text{ Cl}^-$  ion (Saturated  $\text{N}_2$  system)

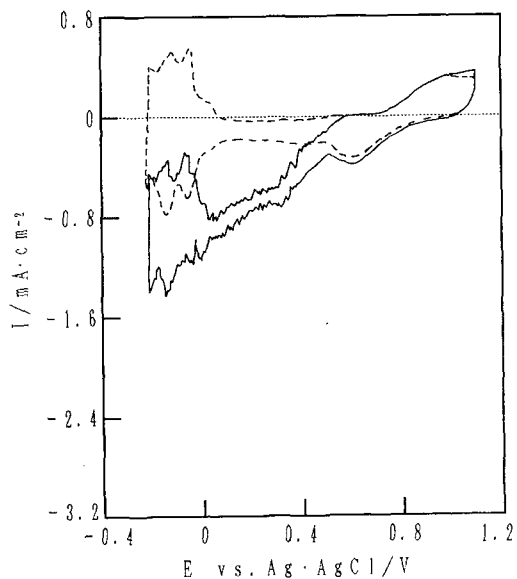


Fig. 13 The voltammetric curves in  $0.5 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$  containing  $0.002 \text{ mol/dm}^3 \text{ Cl}^-$  ion (Saturated air system)

#### 4. CONCLUSION

The formation peak potential of O (a) disappeared because degassing in solution generated with cavitation, and adsorption oxygen disconnected from delctrode with liquid jet. The current was more flowed as platinum oxide film on electrode decreased with shock wave pressure. The current functions of large amplitude change an apparent surface area of electrode as the amounts of adsorption of gas bubbles that generated with cavitation reduced with liquid jet.

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