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AN ELLIPSOMETRIC STUDY ON THE SURFACE OF ANODE MATERIALS USED FOR THE KOLBE REACTION

By

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Abstract

Ellipsometric measurements have been made of surface films anodically formed on Pt, Au, and Pd in aqueous and nonaqueous acetate solutions. In nonaqueous solution where the Kolbe reaction occurs on all the anode materials used, no thick film was formed; the film thickness was of the order of 10 A in the potential region in which the Kolbe reaction took place. In aqueous acetate solution, the film thickness formed on Pt was also of the order of 10 A even in the potential region of O_2 evolution and Kolbe reaction. On Au and Pd in aqueous media, however, a phase oxide more than several tens angstrom thick was formed, and no Kolbe reaction took place. It is concluded that the formation of a phase oxide film which is formed on Au and Pd in aqueous acetate solution inhibits the advance of the Kolbe reaction.

Introduction

The Kolbe reaction in aqueous acetate solution proceeds efficiently on Pt anode at potentials more anodic than *ca.* 2.0 V, but not on Au and Pd anodes at any potentials[1-3]. However, in nonaqueous acetate solution, the Kolbe products were formed not only on Pt, but also on Au, Pd, and PbO_2 anodes at potentials above 2.1 V with more than 90% current efficiency[4]. This implies that the Kolbe reaction is affected not only by the nature of anode materials, but also by the presence of water[5,6]. In previous papers[7~11], the influence of water on the Kolbe reaction with various anode materials has been extensively examined in terms of the interfacial capacity and the polarization characteristics. However, no definite information was

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obtained on the surface state of anodes on which the Kolbe reaction occurs.

TOMILOV *et al.*[12] proposed that the electrode materials on which the Kolbe reaction takes place would have the following properties: (1) high oxygen overpotential, (2) negligible corrosion rate, and (3) the zero charge potential close to that of Pt.

Recently, ellipsometric studies on the surface film of Pt anodes in the Kolbe reaction system were reported by CONWAY[13] and by PARSONS and VISSCHER[14]. PARSONS *et al.* found no significant change in the optical properties of the surface film of Pt in H_2SO_4 solution, but found some change in acetate solution. They attributed such a change of the optical property of the surface to the incorporation of acetate in the surface film.

In the present study, ellipsometric measurements have been made of the surface film on Pt, Au and Pd anodes in acetate solutions in the presence or the absence of water in order to characterize the surface state of anode materials on which the Kolbe reaction is taking place.

Experimental

Ellipsometry. The ellipsometer used was of a standard type shown in Fig. 1. The light source was a helium-neon gas laser (Spectra Physics, model 155) of 632.8 nm in wavelength. The polarizer and the analyzer were Glan-Thompson prisms mounted in divided circles by which the azimuths of the polarizer and the analyzer could be measured to a precision of 0.01° with verniers. The compensator was a quarter-wave mica plate of which the fast axis was fixed at 45° orientation referred to the plane

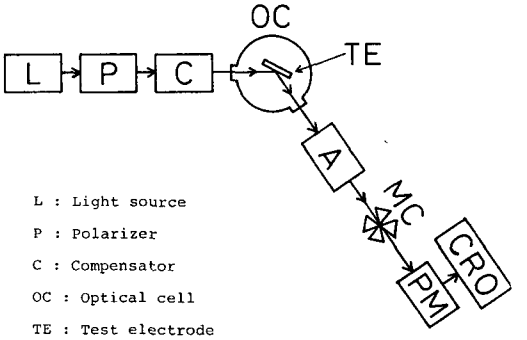

Fig. 1. Schematic diagram of ellipsometer.

of incidence. The light beam was chopped by a sector at 200 Hz. The intensity of the reflected light after passing through the analyzer was followed by a photomultiplier and a tuned amplifier, and displayed on a cathode-ray oscilloscope. The measurement was performed at a fixed angle of incidence of 64.45° by adjusting the azimuths of polarizer, P, and analyzer, A, to the extinguished position. The values of P and A were averaged over three measurements. Calculation was made by using a computer, FACOM 230-75, with the method after McCRACKIN *et al.*[15]

Cell. The electrolytic cell used is schematically shown in Fig. 2. It was a pyrex glass vessel of 100 ml capacity with two optical glass windows, 15 mm diameter and 2 mm thick, fixed by teflon screw joint at the angle of 128.90°. About 70 ml of solution was used in each run. The temperature was maintained at 20±0.5°C by circulating water in the jacket.

Electrodes. Pt, Au, and Pd sheets of 99.99% purity were machined to the size of 10×10×1 mm with a small tab. The electrodes were polished with emery paper up to No. 2000, degreased with ethanol, cleaned by immersion for 1 min in 1 N HNO_3 (Pt only), 1 N HCl (except for Pd), and washed with

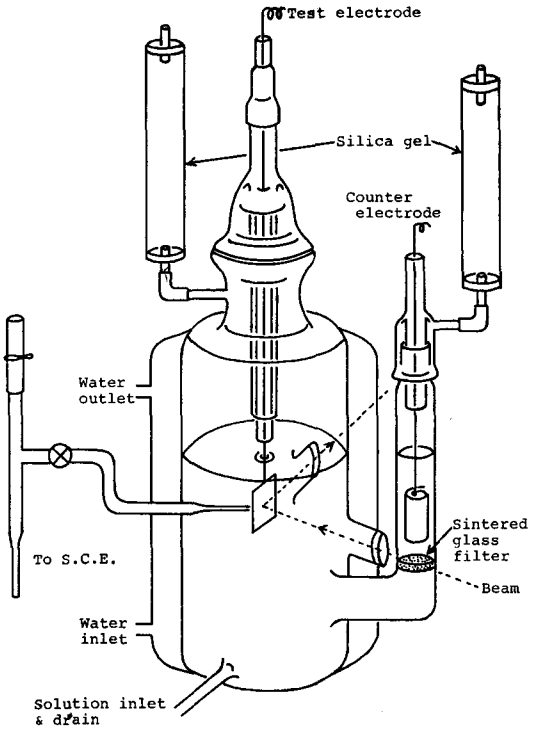

Fig. 2. Electrolytic cell.

distilled water. The counter electrode was of a smooth platinum foil. The electrode potential was measured with reference to a saturated calomel electrode (*SCE*), and was controlled by a Wenking potentiostat. In order to obtain an optical reference surface, the electrode surface was first reduced cathodically for 10 min at a constant potential (−0.6 V for Pt and Pd, and −0.8 V for Au) in the same solution, and then polarized anodically to various potentials at which optical measurements were made.

Solutions. The test solution was prepared from reagent grade chemicals and redistilled water. The nonaqueous acetate solution used was glacial acetic acid saturated with potassium acetate. Before preparation, glacial acetic acid was distilled after addition of fresh phosphorus pentoxide in order to eliminate water completely. Potassium acetate was dried under vacuum about 100°C for 10 hours. No water was then detected in the solution by Biltz's method. The aqueous acetate solutions used were equivolume mixtures of equimolar solutions of potassium acetate and acetic acid. The concentration of the aqueous acetate solutions was 0.5 M (pH 4.68) or 5 M (pH 5.22).

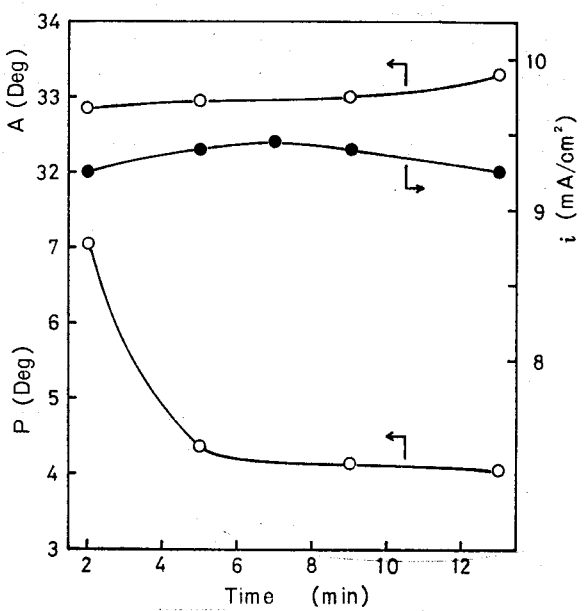

Fig. 3. Variation of P, A and current density with time during potentiostatic oxidation of Pd at +1.50 V in 5 M aqueous acetate solution. The specimen was pre-reduced at −0.60 V for 10 min.

Results

Fig. 3 shows a typical change in ellipsometric parameters, P and A, together with anodic current, as a function of oxidation time for Pd electrode polarized at 1.5 V in 5 M aqueous acetate solution. Both P and A initially changed with time to some extent, but approached nearly steady values after 5 min-polarization. Similar behaviour was also observed with Pt and Au electrodes in aqueous or nonaqueous solution. The P and A values at 5 min-polarization were therefore taken as the representative ones at a given polarization condition.

Fig. 4 shows the loci of the change in P and A (δP and δA) relative to the reference values which were obtained with a cathodically reduced surface for Au in the course of potentiostatic oxidation at various potentials in the nonaqueous and 5 M aqueous solution. In the nonaqueous solution, a straight line can be drawn on the figure to fit experimental points within the experimental error. Such a straight line could also be obtained with Pt and Pd in the nonaqueous solution and with Pt electrode even in aqueous media where the Kolbe reaction proceeds. In aqueous solutions, however, the locus obtained on Au and Pd shows a large deviation from a straight line, especially in δP, in the potential region in which the oxygen evolution reaction takes place.

Fig. 5 shows δP and anodic current as a function of potential for Pt and Pd electrodes in 0.5 M aqueous acetate solution. It is seen that the

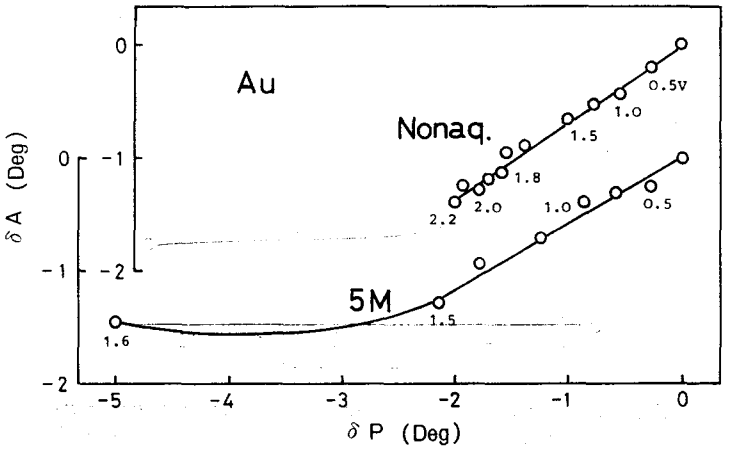

Fig. 4. Change in P and A with potential for Au in 5 M aqueous and nonaqueous acetate solutions. Figures along the curve indicate the potential.

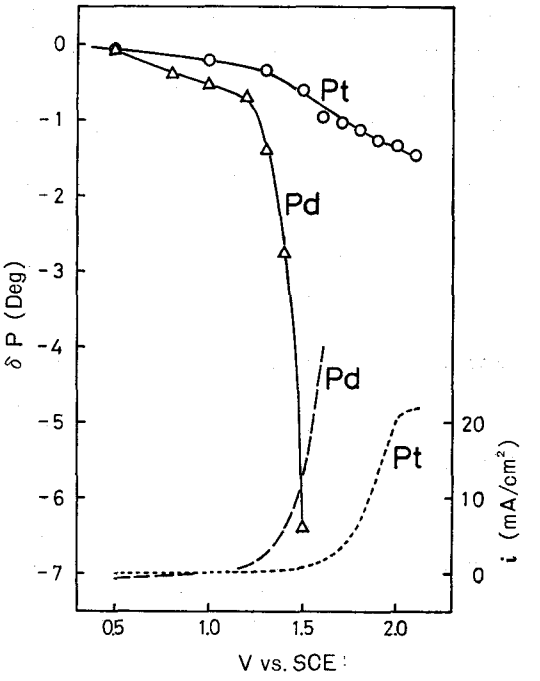

Fig. 5. Change in P and current density with potential for Pt (○, ···) and Pd (△, – –) in 0.5 M aqueous acetate solution.

δP decreases with a rise of the potential on both the electrodes but the magnitude is larger for Pd than for Pt, and that Pd shows a steep decrease in δP at potentials above *ca.* 1.2 V where the oxygen evolution reaction is occurring, while Pt shows only a slight decrease even at potentials where the Kolbe reaction proceeds extensively. Such a large decrease in δP was also observed with Au electrode in aqueous solution as is exemplified in Fig. 4. Since δP and δA are quite sensitive to the formation and growth of surface layers formed under polarization, the decrease in δP and δA is considered to be due to the formation of an adsorbed layer or a phase oxide on the surface as will be discussed later.

For such an electrode-electrolyte system where the δP–δA plot falls in a straight line as Au in nonaqueous solution (Fig. 4), it is reasonable to assume that a film grows on the electrode surface in the potential region investigated. Based on the assumption, calculations were performed to determine the optical constants of the film formed on Pt and Au by taking into account the optical constants of oxides of Pt and Au found in the literatures[14,16,17]. For Pd electrode, analogous calculations were made

over a probable range of optical constants as no data have been reported. The optical constants thus determined are summarized in Table 1. For Au and Pd electrodes in aqueous solution in which the δP–δA plot shows a large deviation from a straight line, the optical constants could not be

TABLE 1. Optical constants of anodic films

anode	Concn. (M)	Potential (V *vs. SCE*)	Optical constants ($n-ik$)
Pt	0.5	0.5~2.1	$3.3-0.8\,i$
	5	0.5~2.0	$3.3-0.6\,i$
	Nonaq.	0.5~2.4	$3.3-0.4\,i$
Au	0.5	0.5~1.6	$0.3-(0.5\sim0.6)\,i$
	5	0.5~1.6	$0.3-(0.6\sim0.8)\,i$
	Nonaq.	0.5~2.2	$0.3-0.5\,i$
Pd	0·5	0.5~1.5	$3.4-(1.2\sim0.4)\,i$
	5	0.5~1.5	$3.4-(0.7\sim0.3)\,i$
	Nonaq.	0.5~2.1	$3.4-0.4\,i$

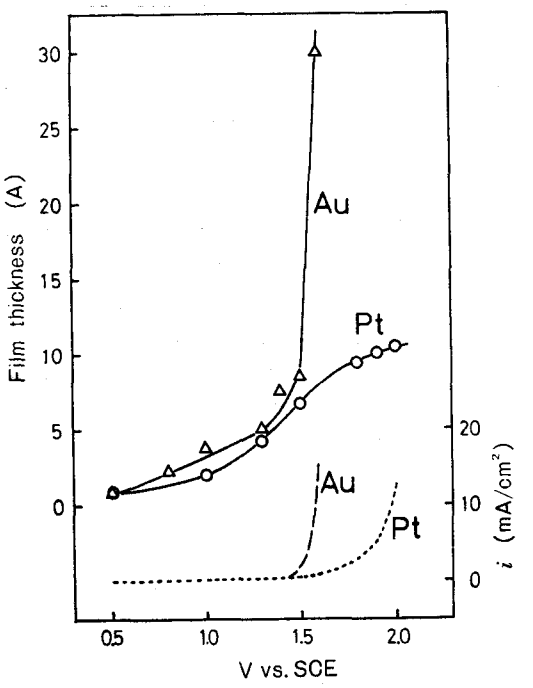

Fig. 6. Dependence of film thickness and current density on potential for Pt (○, ···) and Au (△, - -) in 5 M aqueous acetate solution.

determined uniquely. These were therefore assigned by assuming that the film was growing without any significant change in the real part of optical constants. The results are also shown in Table 1. It may be read from Table 1 that on Pt the imaginary part of optical constants, so-called extinction coefficient k, tends to decrease with increasing acetate concentration.

By using the optical constants in Table 1, the film thickness formed on the electrodes was calculated. Typical examples of the results of calculation for Au and Pt electrodes in 5 M acetate solution are plotted in Fig. 6 as a function of potential; the anodic current is also shown for comparison. It can be seen that on Au electrode an abrupt change in the film thickness occurred with onset of the oxygen evolution reaction, leading to formation of a phase oxide film which became several tens angstrom thick with increasing anodic current. A similar figure was also obtained with Pd electrode in aqueous solution. On the other hand, the film thickness on Pt electrode was of the order of ten angstrom even at potentials where the Kolbe reaction took place where a slight dependence of the film thickness on the acetate concentration was found. In nonaqueous solution, a surface film was also formed on Pt, Au and Pd, but its thickness did not exceed 10 A even in the potential region of Kolbe reaction.

Discussion

The experimental results have shown that the film formed on Au and Pd electrodes does not grow thicker than 10 A in nonaqueous solution, but becomes more than several tens angstrom thick in aqueous solutions with increase of a potential. On the contrary, the thickness of the film formed on Pt is of the order of 10 A irrespective of the solutions used even in the potential region in which the Kolbe reaction proceeds. The film growth is thus different for different anode materials and solutions and it is suggested that the electrode on which the film growth occurs extensively is not favorable to the Kolbe reaction.

In aqueous solutions, it is seen on Au (Fig. 6) and also on Pd that a steep increase of the current due to the O_2 evolution reaction, which occurs at 1.5 V with Au and at 1.3 V with Pd, is accompanied by a steep increase of the surface film thickness. The surface films formed on Au and Pd are likely to be oxides, and their formation may be written as,

$$2Au + 3H_2O = Au_2O_3 + 6H^+ + 6e, \qquad E_0 = 1.457 - 0.0591pH$$

and

$$Pd + H_2O = PdO + 2H^+ + 2e, \qquad E_0 = 0.897 - 0.0591pH$$

It is thermodynamically possible that these oxides form at potentials more noble than 0.938 V (*vs. SCE*) for Au_2O_3 and more noble than 0.378 V for PdO in 0.5 M aqueous acetate solution (pH=4.68). Further, color of the Au surface in aqueous media clearly changes to reddish brown (Au_2O_3) after polarization, but not in nonaqueous solution. It seems therefore reasonable to conclude that a phase oxide is formed in aqueous media.

In the case of Pt in aqueous solution (Fig. 6), however, the film thickness of the surface does not exceed 10 A even in the Kolbe reaction region. CONWAY *et al.*[5,6] proposed that the surface of Pt in aqueous acetate solution was covered by a dipole barrier-layer, suggesting that the surface film is not a phase oxide but a thin adsorption layer. The thickness of the order of 10 A therefore may be regarded as representing an adsorption layer rather than a phase oxide film.

The optical constant of the film on Pt is found to vary with acetate concentration. Namely, the extinction coefficient k of the film on Pt (Table 1) decreases as the water content in the solution becomes smaller. This means that the film is more transparent when the acetate concentration is greater, suggesting that CH_3COO^- or $CH_3COO^\cdot$ is incorporated into the film. PARSONS *et al.*[14] have also found that the extinction coefficient of the film on Pt in aqueous acetate solution decreases with the rise of potential, and suggested an incorporation of acetate in the film at noble potentials.

In the nonaqueous solution, the surface film thickness on Pt, Au, and Pd did not appreciably differ among each other, and is of the same order of magnitude as that on Pt in aqueous media. The surface state in this case should thus be analogous to that of Pt in aqueous media. It appears likely from the present study that the film on the anode surface on which the Kolbe reaction is taking place is an adsorbed layer of less than 10 A thick, probably consisting of oxygen and acetate. On the anode materials on which the film growth proceeds extensively to form a phase oxide, it is considered that the O_2 evolution reaction dominates over the Kolbe reaction. This may result from the difference in electronic properties between Au_2O_3 or PdO and PtO as suggested by HOARE[18].

Further work is required before one has the complete understanding of the role of surface layers on the catalytic activity for the O_2 evolution reaction and the Kolbe reaction.

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