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ELECTRODE REACTION OF EDTA AT LEAD DIOXIDE ELECTRODE IN AQUEOUS SOLUTIONS OF DIFFERENT pH

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Ethylenediaminetetraacetic acid (EDTA) at lead dioxide (PbO_2) electrode gives two anodic waves and one cathodic wave in the pH range 4 ∿ 9 (one anodic wave and one cathodic wave at pH lower than 4). The anodic main-wave and the cathodic wave increase with the EDTA concentration. The anodic pre-wave appears only at pH higher than 4.

Tallant and Huber[1)] investigated the voltammetry of EDTA at lead dioxide electrode. Fujinaga and Yoshimura[2)] described previously the electrolytic behavior of acetylacetone in aqueous solution at electro-deposited PbO_2 electrode as an indicator electrode. The present paper describes the electrode reaction of EDTA at the PbO_2 electrode in the wide pH range.

The β-lead dioxide (PbO_2) electrode was prepared by the electrolytic oxidation of lead nitrate on a platinum microelectrode (10.2 mm^2) [2)]. All voltammetric measurements were carried out at (25±0.2)°C without deaeration of solution. A saturated calomel electrode (SCE) was used as a reference electrode.

No anodic or cathodic wave was obtained for the cyclic current-voltage curve of 0.1 $mol\,dm^{-3}$ KNO_3 solution at the PbO_2 electrode (Figure 1-a). On addition of EDTA, the anodic wave at +1.05 V and the cathodic wave at +0.85 V were obtained (Figures 1-b, c and d), and the heights of the two waves were proportional to the EDTA concentration down to 1×10^{-4} $mol\,dm^{-3}$. Accordingly, the determination of EDTA is possible by the measurement of the anodic or cathodic wave with the PbO_2 electrode. The anodic and cathodic waves are probably attributable to the following electrode reaction:

$$PbO_2 + H_2Y^{2-} + 2H^+ + 2e^- \rightleftharpoons PbY^{2-} + 2H_2O ,$$

where H_2Y^{2-} denotes EDTA. The reaction is expected to be faster in the presence of EDTA than in the buffer solution alone because of the formation of the stable lead (II) chelate.

Interestingly, an anodic pre-wave at +0.70 V before the main-wave appeared at pH higher than 4 in the presence of EDTA; This pre-wave was not observed by Tallant and Huber who used the lead dioxide-plated electrode (by the linear potential sweep method)[1)]. Effects of pH on the two anodic waves in aqueous solutions of 2.0 $mmol\,dm^{-3}$ in EDTA and 0.1 $mol\,dm^{-3}$ in KNO_3 were investigated (Figure 2). The sum of heights of the two anodic waves (wave height a + b) was found to be almost constant

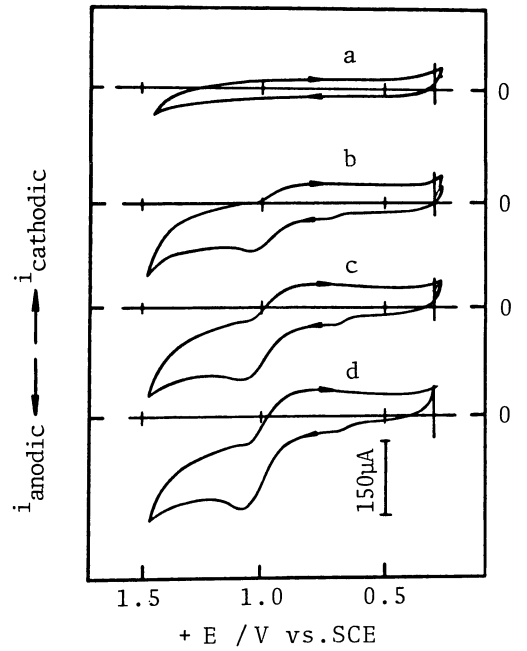

Figure 1 Cyclic current-voltage curves of EDTA at PbO_2 electrode in 0.1 mol dm^{-3} KNO_3 solution(pH 4.4) and the sweep rate, 30 mV s^{-1} Concn. EDTA: curves a,0; b,1.0; c,2.0; d, 3.0 mmol dm^{-3}.

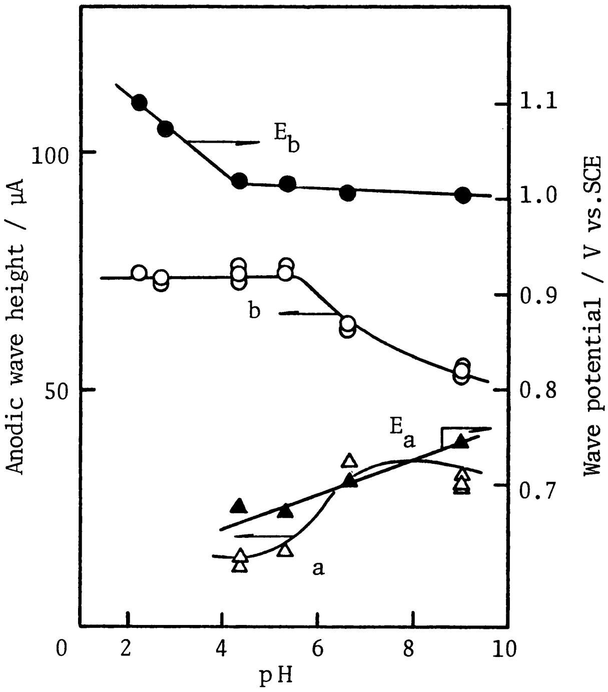

Figure 2 Effect of pH on the anodic pre-wave(a) and anodic wave(b) heights and the wave potentials (E_a, E_b) of 2.0 mmol dm^{-3} EDTA in 0.1 mol dm^{-3} KNO_3 (pH-adjusted) solution at PbO_2 electrode and the sweep rate, 30 mV s^{-1}.

over the whole pH range tested. The anodic pre-wave potential (E_a) shifted by +23 mV/pH at pH higher than 4, and the anodic main-wave potential (E_b) shifted by -45 mV/pH and -2.8 mV/pH at pH lower and higher than 4, respectively. This result suggests that the electrode reaction of EDTA at the PbO_2 at pH lower than 4 differs from that at pH higher than 4. The above reaction may take place at pH lower than 4. On the other hand, the anodic reaction at pH higher than 4 is considered to consist of two steps corresponding to the two anodic waves. The further study is under way.

References

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