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THE CHARACTERISTIC OF γ-MANGANESE DIOXIDE ELECTRODE IN ACIDIC SOLUTIONS IN THE PRESENCE OF COMPLEXANES

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By using γ-manganese dioxide (MnO_2) as an indicator electrode, the electrode-reaction of ethylenediaminetetraacetic acid (EDTA) and other complexanes was investigated. A characteristic cathodic peak of manganese dioxide which increases in the presence of complexanes was observed.

The use of γ-MnO_2 as a counter electrode to obtain a highly positive potential in the short-circuited amperometric titration of chromate and vanadate with iron(II) was reported by one (Fujinaga) of the authors[1]. Recently, similar oxide electrodes used as an indicator electrode in the amperometric titration of metals with complexanes have been reported[2]; the anodic current due to the oxidation of complexanes on the electrode was utilized for the detection of the end point of the titrations. The electrode-reaction of complexanes at a metal oxide electrode has been investigated only in the case at a lead dioxide electrode by Tallant et al.[3]. Presently, the voltammetric behavior of the MnO_2 electrode in acidic solutions in the presence of EDTA or other complexanes was investigated. As the results, some phenomena which have been unreported were observed. The present letter describes the characteristic cathodic peak of the MnO_2 electrode which increases in the presence of complexanes.

The MnO_2 electrode was prepared by the electrolytic oxidation of manganese sulfate on a platinum microelectrode in acidic solution[4,5]. All voltammetric measurements were carried out 25°±0.2°C without deaeration of solution. A silver-silver chloride reference electrode (SSE) and a platinum counter electrode were used.

Figure 1 shows the cyclic current-voltage curves of the solutions of EDTA in 0.1 mol dm^{-3} HNO_3 at the MnO_2 electrode and at the platinum electrode. In the Figure, a characteristic cathodic peak at +1.02 V vs.SSE was first observed. And, two anodic peaks at +1.18 V and +1.24 V vs.SSE or the coalesced one anodic peak were observed. The sharp cathodic peak is due to the reduction of manganese dioxide and the process is accelerated by the addition of EDTA. In accordance with the results, the following reaction scheme of the cathodic process is assumed:

$$MnO_2 + H^+ + e^- \longrightarrow MnOOH \quad (1)$$

$$MnOOH + H_3Y^- \longrightarrow MnY^- + 2H_2O \quad (2)$$

where H_3Y^- denotes EDTA (pH 1.5). Such a phenomenon in the cathodic process has

not been seen in the case of the lead dioxide electrode[3]. In the anodic process, the anodic peak at +1.18 V corresponds to the reoxidation of manganese complex to form manganese dioxide as in the case at the lead dioxide electrode[3], and the anodic peak at +1.24 V corresponds to the oxidation of EDTA to form decarboxylation products and the peak height increases with the increase of EDTA concentration. Therefore, in the presence of high concentration of EDTA these two peaks coalesce to form one peak.

The effect of EDTA concentration on the anodic and cathodic peak heights at the MnO_2 electrode was investigated. The heights of both the anodic and cathodic peaks are directly proportional to the EDTA concentration. By the measurement of cathodic peak height, it is possible to determine EDTA of the concentration down to 1×10^{-4} mol dm^{-3}.

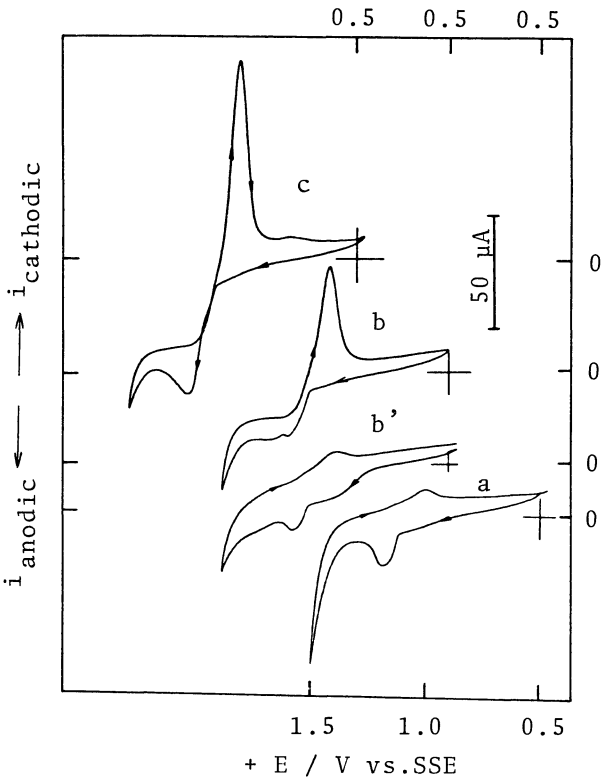

Figure 1 Cyclic current-voltage curves of EDTA in 0.1 mol dm^{-3} HNO_3 solution and the sweep rate, 3.3 mV s^{-1}. Curves a, 0; b, 1.0; c, 2.0 mmol dm^{-3} EDTA at MnO_2 electrode and b', same as b but at Pt electrode.

The voltammetric behavior of iminodiacetic acid (IDA), nitrilotriacetic acid (NTA) and diethylenetriaminepentaacetic acid (DTPA) at the MnO_2 electrode was also examined in 0.1 mol dm^{-3} HNO_3 solution. The specific height of cathodic peak at +1.02 V increases in the order of IDA < NTA < EDTA < DTPA.

References

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