

# STUDY OF THE ELECTROCHEMICAL OXIDATION OF MANGANESE(II) IONS TO MANGANESE DIOXIDE AND ITS CATHODIC STRIPPING USING ROTATING DISK AND ROTATING RING-DISK ELECTRODE

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*Dedicated to Professor Dr J. Zýka on the occasion of his 60th birthday.*

This work deals with the cathodic stripping peaks of manganese dioxide deposited on a disk electrode by pre-electrolysis. Coulometric and spectrophotometric methods and electrochemistry using a rotating ring-disk electrode are used to explain the formation of the more positive peak as a result of the reduction of nonstoichiometric oxygen formed in the manganese dioxide film on the disk electrode.

In addition to several authors<sup>1-5</sup>, who have discussed the voltammetric behaviour of manganese, Kublik<sup>6</sup> described two peaks obtained in the reduction of permanganate on a rotating platinum electrode. In a study dealing primarily with the analytical application of cathodic stripping voltammetry, Hrabánková<sup>7,8</sup> observed two cathodic peaks during stripping of a manganese dioxide film deposited from a dilute neutral solution of manganese(II) ions by anodic oxidation. On the basis of available experimental results, the author gave two possible explanations for the formation of two peaks: either a two-step reduction is involved,  $\text{Mn(IV)} \rightarrow \text{Mn(III)} \rightarrow \text{Mn(II)}$ , or the peaks depend on the formation of two layers or crystalline modifications<sup>9</sup> with different properties, which are reduced at different potentials.

This work deals with the use of a rotating disk electrode and a rotating ring-disk electrode which yielded results contributing to explanation of the formation of the more positive peak by the reduction of nonstoichiometric oxygen during the formation of various modifications of manganese dioxide.

## EXPERIMENTAL

### Reagents and Apparatus

The rotating disk electrodes were constructed by the method described by Beran and Opekar<sup>10</sup>. The disk diameters were as follows: platinum  $d = 7.210$  mm, gold  $d = 6.472$  mm, graphite

$d = 5.076$  mm. The platinum rotating ring-disk electrode<sup>11</sup> had disk and ring diameters of:  $r_1 = 3.144$  mm,  $r_2 = 3.227$  mm,  $r_3 = 3.666$  mm and theoretical collection efficiency of  $N_{\text{theor}} = 0.291$ . The auxiliary electrode was a platinum wire fixed in a tube terminated by a frit; the reference electrode was a K-401 saturated calomel electrode (Radiometer, Denmark), connected to the measuring cell by a salt bridge. The measurement was carried out using operational amplifiers connected as a three- or four-electrode polarograph or constant potential coulometer<sup>12</sup>. The work with the rotating disk electrode was carried out using the apparatus described by Opekar<sup>13</sup>. The apparatus for electrolyte exchange without interrupting the electric circuit consisted of a reservoir containing the base electrolyte with a pipe-shaped vessel placed in the electrolysis cell under the rotating electrode. After completion of the electrolysis, the pipe-shaped vessel was raised and the stop-cock to the reservoir was opened so that the solution from the reservoir flowed around the electrode and replaced the original solution. The original solution was simultaneously let out of the cell at the same rate. After exchange of about a five-fold amount of the solution, the curve corresponding to the stripping of the deposited film into the pure base electrolyte was recorded.

The voltammetric curves were plotted on a Bryans 20180/s  $x - y$  plotter (Great Britain); the pH was measured on a PHM 4 pH meter (Radiometer, Denmark). The temperature was maintained constant using a U1 thermostat (Mechanik Prüfgeräte, GDR). The spectrophotometric measurements were carried out using a Spekol instrument (Zeiss, Jena, GDR).

All the reagents were of *p.a.* purity. The nitrogen was purified to remove traces of oxygen by bubbling through an alkaline solution of sodium anthraquinone sulphonate. Borate buffer (0.1M) was prepared by mixing boric acid, sodium hydroxide and hydrochloric acid in a ratio corresponding to the required pH in the range 7–10. The solutions measured containing manganese(II) ions were prepared by suitable dilution of the stock solution of manganese sulphate ( $c(\text{MnSO}_4) = 0.01 \text{ mol l}^{-1}$ ).

## RESULTS

It was found that a borate buffer medium is optimal for the voltammetric measurements<sup>7,8</sup> of rotating disk and ring-disk electrodes. The best developed peaks for the reduction of manganese dioxide were obtained at pH  $\sim 7.2$ . After removal of oxygen, buffer solutions containing manganese(II) ions in a concentration between  $10^{-6}$  and  $10^{-4} \text{ mol l}^{-1}$  were usually electrolyzed for 3 min at a potential of  $+0.6 \text{ V}$  vs S.C.E. For constant potential coulometric measurements, the dependence of the disk current on time was measured simultaneously. Then the voltammetric curve of the dependence of the disk current on the potential from  $+0.6 \text{ V}$  to  $-0.06 \text{ V}$  (S.C.E.) was measured; after a change in the polarization, the anodic part of the curve was recorded. When the ring current was measured, the dependence of the ring current on the disk potential was recorded, where the potential of the ring electrode was maintained constant at a value of  $+0.5 \text{ V}$  (S.C.E.). Characteristic curves are given in Fig. 1.

The curve of the disk current vs the disk potential contains two cathodic peaks, the more positive at  $+0.35 \text{ V}$  (S.C.E.) and the more negative, larger at  $+0.07 \text{ V}$ . At  $c(\text{Mn}) < 10^{-5} \text{ mol l}^{-1}$ , the recording contains only the more negative peak and at  $c(\text{Mn}) > 10^{-5} \text{ mol l}^{-1}$  under the same conditions (preelectrolysis time) the second,

more positive peak begins to appear and the more negative peak begins to limit to a constant value. The peak height is dependent on the pre-electrolysis potential; the optimal value is 0.6 V (S.C.E.). The pH dependence also passed through a maximum at pH 7.2. The current increases by 4% per 1 K on increasing the temperature.

In an attempt to compare the efficiency of the anodic oxidation, the experiments with the disk electrode were carried out at three manganese concentrations. With three-minute electrolysis ( $E_D = +0.6$  V) the dependence of the anodic current on time was recorded and the amount of manganese dioxide was calculated from the curves obtained. The electrode was then removed from the solution and rinsed and the deposit on the disk was dissolved in hot nitric acid and hydrogen peroxide. This experiment was repeated five times and the solutions obtained were combined to yield a higher manganese concentration for further measurements. The hydrogen peroxide was then removed by boiling. The manganese was oxidized to permanganate by addition of sodium bismuthate and the permanganate was determined spectrophotometrically. The results obtained are given in Table I.

Cathodic stripping curves were recorded under the same conditions; two clearly developed peaks were observed. The average per cent ratio of the more positive peak to the more negative one was obtained by measuring the areas of both peaks. A value of 8.8% was obtained from twenty measurements; this value is in good agreement with the results in Table I.

The same results were obtained when using different material for the disk electrode

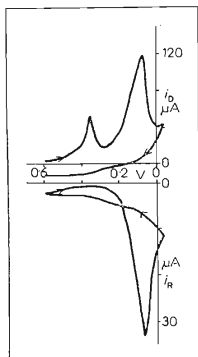


FIG. 1

The voltammetric curves of the ring ( $i_R$ ) and disk ( $i_D$ ) currents in dependence on the disk potential after deposition of manganese on the disk electrode as  $MnO_2$ , 0.1M borate buffer, pH = 7.2,  $c(Mn) = 10^{-4}$  mol  $l^{-1}$ , Pt rotating ring-disk electrode,  $\omega = 440$  rpm, polarization rate 440 mV  $min^{-1}$ , pre-electrolysis at the disk electrode, 3 min at  $E_D = +0.6$  V,  $E_R = +0.5$  V (S.C.E..)

(in addition to platinum, gold and glassy carbon were used), under the same conditions, *i.e.* the cathodic curves were identical with two peaks for the reduction of manganese dioxide.

## DISCUSSION

The existence of the more positive peak observed by Kublik<sup>6</sup> and Hrabánková<sup>7,8</sup> was discussed in detail only by the latter author, who gives two explanations for its formation. The explanation involving the existence of two crystalline layers, corresponding to the more negative and more positive peaks, is preferred by the author.

The temperature dependence excludes explanation of the positive peak by an adsorption effect, as a positive temperature dependence of the current of 4% per 1 K could not correspond to an adsorption reaction, which would have a negative temperature dependence.

The more positive peak could also correspond to specific behaviour of platinum as an electrode material. As, however, the curves obtained on gold and glassy carbon have shapes identical to those obtained on platinum, this possibility is excluded.

Hrabánková<sup>8</sup> suggested that the more positive peak could correspond to reduction of Mn(IV) to Mn(III). This idea, as well as the suggestion that two layers are formed, which would be reduced at two different potentials, are contradicted by experiments with the rotating platinum ring-disk electrode. If the products passing into solution are formed in the potential region of the more positive peak, they would have to be recorded on the ring electrode. However, our experiments indicated that no current corresponding to oxidation of divalent or trivalent manganese is observed at the ring electrode in the potential region of the more positive peak (+0.5 V *vs* S.C.E.); these valence forms would be reoxidized to manganese dioxide at the potential

TABLE I

Comparison of the amount of deposited MnO<sub>2</sub> found in coulometric and spectrophotometric measurements

c, Mn mol l <sup>-1</sup>	MnO <sub>2</sub> , found in µg		A, %
	coulom. meas.	spectrophot. meas.	
1.5 · 10 <sup>-4</sup>	3.049	2.784	8.69
1 · 10 <sup>-4</sup>	2.067	1.895	8.32
8 · 10 <sup>-5</sup>	1.61	1.626	9.19

of the ring electrode,  $E_R = +0.5$  V. An anodic peak was obtained only in the potential region of the negative cathodic peak ( $+0.07$  V vs S.C.E.); this ring peak corresponds to the oxidation of manganese (II) ions formed by reduction of manganese dioxide at the disk. It was simultaneously demonstrated in these experiments that the electrode process on the disk is purely of convectational diffusion character, as the theoretical collection efficiency of the rotating ring-disk electrode calculated on the basis of its geometric parameters ( $N_{\text{theor}} = 0.291$ ) is in good agreement with the experimentally determined collection efficiency for the given system ( $N_{\text{exp}} = 0.305$ ).

It was found in the coulometric oxidation of manganese(II) ions to manganese dioxide and in the chemical dissolution of the deposit of manganese dioxide from the electrode and its spectrophotometric determination that the amount of  $\text{MnO}_2$  found in the coulometric measurements is larger than the amount of manganese determined spectrophotometrically (Table I). This difference is practically identical for the three measurements described. Simultaneously, it was found that this difference (an average of 8.7%) corresponds to the size of the small positive peak expressed as the ratio of its area to that of the large, more negative peak (*i.e.* 8.8%). It can be concluded on the basis of these measurements and of the information given by Brenet<sup>14-16</sup>, who carried out an X-ray study of the modifications of  $\text{MnO}_2$  and structural changes of  $\text{MnO}_2$  to  $\text{Mn}_2\text{O}_3$  or  $\text{Mn}_3\text{O}_4$ , that oxygen is reduced in the region of the potential of the more negative peak: oxygen is in excess over the stoichiometric amount of manganese dioxide. Manganese dioxide can generally be expressed by the formula  $\text{MnO}_{1+x}$ , where  $x$  varies in dependence on the activity of proton defects in the crystal lattice of the oxide, *i.e.* on the activity of the oxygen ions. Indirect evidence in support of this statement can be found in the results obtained on the ring-disk electrode, where no ring current was obtained in the region of the more positive peak, as oxygen is reduced at the disk electrode to electroinactive water or hydroxide ions.

#### REFERENCES

1. Mašín V.: *Thesis*. Charles University, 1967.
2. Farsang G., Tomczányi L.: *Acta Chim. (Budapest)* 52, 123 (1967).
3. Huber C. O., Lemmert L.: *Anal. Chem.* 38, 128 (1966).
4. Brainina C. Z.: *Zh. Anal. Khim.* 19, 810 (1964).
5. Monier H., Zinke K.: *Z. Anal. Chem.* 240, 32 (1968).
6. Kublík Z.: *J. Electroanal. Chem. Interfacial Electrochem.* 5, 450 (1963).
7. Hrabánková E., Doležal J., Mašín V.: *J. Electroanal. Chem. Interfacial Electrochem.* 22, 195 (1969).
8. Hrabánková E.: *Thesis*. Charles University, 1969.
9. Micka K.: *Chem. Listy* 65, 225 (1971).
10. Beran P., Opekar F.: *Chem. Listy* 65, 855 (1971).
11. Beran P., Opekar F.: *Chem. Listy* 68, 304 (1972).

12. Beran P., Opekar F., Štulík K.: *Instrumentální analytické metody*, p. 292, 190, 301. Published by Státní pedagogické nakladatelství, Prague 1977.
13. Opekar F., Beran P.: *J. Electroanal. Chem. Interfacial Electrochem.* 32, 49 (1971).
14. Brenet J.: *Proceedings of the 8th International Congress CITCE*, p. 394. Butterworths, London 1958.
15. Brenet J.: *C. R. Acad. Sci.* 246, 2469 (1958).
16. Traore K., Brenet J.: *Z. Elektrochem.* 63, 563 (1959).

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