MANGANESE-DIOXIDE ELECTRODE WITH A STABLE POTENTIAL

III. ION-EXCHANGE CHARACTERISTICS OF MANGANESE DIOXIDES

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The ion-exchange properties of various manganese dioxides have been investigated. It has been shown that synthetic ρ-, γ- and β-MnO_2 possess considerable proton capacity. Alterations of pH in cells containing manganese dioxides with different proton capacities have been investigated and a correspondence between the discharge curve and changes in pH established. These and earlier described anomalies in the cathodic reduction of the dioxides are explained by two competing processes taking place in the solution and in the solid phase, the rates of which depend from the pH of the electrolyte, which in turn is determined, amongst other factors, by the ion exchange properties of the manganese dioxide.

Based on the study of some physicochemical properties and the structure of synthetic manganese dioxides described in our previous publication [1] the assumption was made that the unusual electrochemical behavior of these dioxides [2] was related to the surface properties of the particles, primarily to their ion-exchange properties.

The ion-exchange characteristics of manganese dioxide have been investigated in a number of papers [4, 5]. These properties have been used to explain the reduction in pH of a salt electrolyte in contact with manganese dioxide [5]. It appears that only hydrated nonstoichiometric dioxides, for example δ-MnO_2 and γ-MnO_2, exhibit pronounced cation-exchange properties [6-9]. Buser and Graf [10] indicate that at the same specific surface area the exchange properties of α MnO_2 are 120 times stronger than of β-MnO_2. Morgan and Stumm [11] have found that the isoelectric point of colloidal manganese dioxide, which has an acidic character, corresponds to an electrolyte pH of 2.8.

This paper deals with the effect of ion-exchange properties on the discharge mechanism of manganese dioxide electrodes, whose characteristics have been described before [1, 2].

EXPERIMENTAL PART

The following procedure was used to determine the ion-exchange properties of manganese dioxides. Fifteen ml of electrolyte "E," containing 21% zinc chloride and 13.5% ammonium chloride [2] was added to one g manganese dioxide. The pH of the electrolyte was previously adjusted to the chosen value by the additon of hydrochloric acid or ammonia. The change in pH of the electrolyte was measured on an LPU-01 pH-meter after stirring for 30 min. The pH range of the solutions was chosen so that it included the isoelectric point of the dioxide in the given electrolyte, i.e., the solution in which no changes in pH took place after contact with the dioxide.

For the determination of the proton activity, those electrolytes in which a pH shift to the acid side occurred were titrated with a sodium hydroxide solution to bring the pH back to its initial value. The proton capacity of manganese dioxide, in gram-ions of hydrogen per gram of manganese dioxide, was calculated from the volume of sodium hydroxide solution used. The results are shown in Table 1. They show that all synthetic dioxides investigated have a relatively high proton capacity and cause a strong shift of electrolyte pH to the acid side. In the case of GAP and electrolytic γ-MnO_2 this shift is much smaller. Pyrolusite gives a pH shift of the basic side. This indicates lacking proton capacity and probably the presence of basic impurities.

From electron microscopic studies [2] it appears that the high proton capacity of synthetic manganese dioxides can be ascribed to the filar form of the particles having crystal faces with an increased chemisorbed water content. The observed differences in proton capacity led to the investigation of changes in electrolyte pH during discharge of the cells, made of various manganese dioxides.

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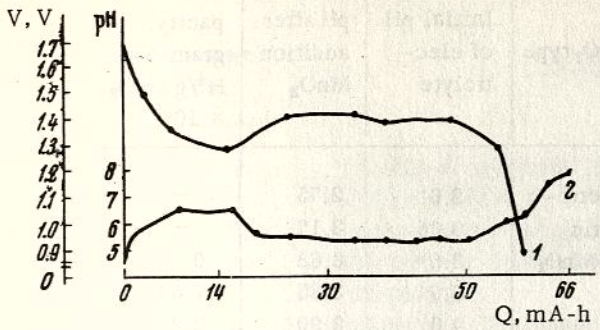


Fig. 1. Change in pH as function of electrode discharge. 1) Discharge curve, I = 0.4 mA/cm^2; 2) change in pH of potassium chloride solution after extraction of discharged active mass.

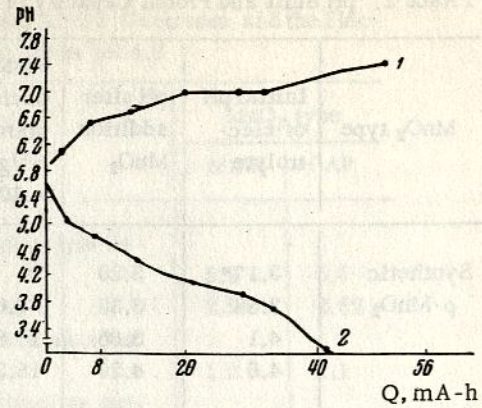


Fig. 2. Change in pH as a function of discharge degree of GAP (γ-MnO_2) electrode. 1) Change in pH of potassium chloride solution after treatment of discharge active mass; 2) discharge curve, I = 0.4 mA/cm^2.

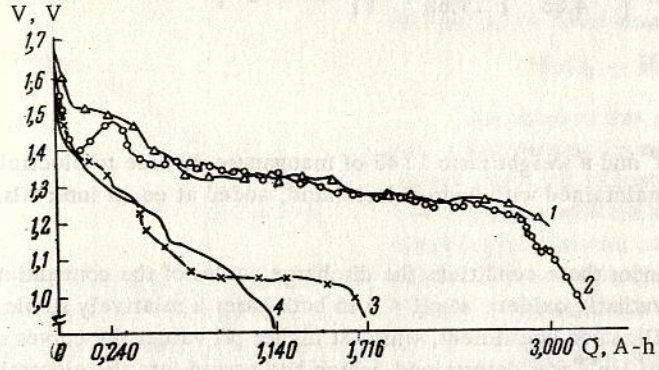


Fig. 3. Discharge curves of ρ-MnO_2 electrode in excess electrolyte at various pH. I = 0.4 mA/cm^2. 1) Electrolyte "E," pH 3.2; 2) electrolyte "E," pH 4.6; 3) 13.5% ammonium chloride solution, pH 7.0; 4) potassium hydroxide solution, 560 g/liter.

The amount of electrolyte in the investigated cells is small and it is present mainly in the active mass [2]. Therefore, to establish changes in electrolyte pH during operation of the cell, the change in pH of a 0.1 N potassium chloride solution was measured, used to extract the positive active mass, discharged to a given capacity. The pH of the solution was previously adjusted to 4.6. The solution was taken from the calculated 15 ml per gram of manganese dioxide (referring to the undischarged electrode). The potassium chloride solution was chosen instead of electrolyte "E," because the former solution had no buffering properties and showed a minimal influence on the actual pH of the cell.

Figures 1 and 2 show the pH changes in the solutions as a function of capacity to which the cells were discharged. For easier interpretation of results the discharge curves of the cells are also shown. Curves are presented only for GAP and ρ-MnO_2 because other dioxides, belonging to the two groups under consideration give analogous results. As shown by Figs. 1 and 2, during discharge of the conventional manganese dioxides a gradual increase of pH to 7.5 is observed, corresponding to a gradual potential drop. In the case of synthetic dioxides corresponding changes in electrolyte acidity are observed in the region of potential drop and the pH levels out at about 5.

To show the existence of a relationship between pH changes and the form of discharge curves, the manganese dioxide electrodes prepared in the form of "cocoons" were discharged in an excess of electrolyte "E," at various pH.

TABLE 1. pH Shift and Proton Capacity of Various Manganese Dioxides

MnO_2 type	Initial pH of electrolyte	pH after addition MnO_2	Proton capacity, gram-ions $H^+/g\ MnO_2 \times 10^{-5}$	MnO_2 type	Initial pH of electrolyte	pH after addition MnO_2	Proton capacity, gram-ions $H^+/g\ MnO_2 \times 10^{-5}$
Synthetic	3.17*	3.20	0	Electro-	2.6	2.75	–
ρ-MnO_2	3.58	3.33	6.00	lytic	3.05	3.17	–
	4.1	3.65	17.62	γ-MnO_2	3.6*	3.63	0
	4.6	4.20	18.37		3.7	3.85	1.50
					4.0	3.90	2.25
Synthetic	2.55	2.75	–		4.6	4.30	5.25
γ-MnO_2	2.85*	2.83	–				
	4.1	3.70	13.87	GAP,	3.2	3.40	–
	4.6	4.35	18.00	γ-MnO_2	3.6*	3.60	0
					4.1	4.00	2.25
Synthetic	2.55	2.80	–		4.6	4.48	3.00
β-MnO_2	2.85*	2.83	0				
	4.1	3.70	13.12	Pyrolusite,	3.6	3.78	–
	4.6	4.35	17.62	β-MnO_2	4.8	4.95	–

*Isoelectric point.

A current density of 0.4 mA/cm^2 and a weight ratio 1 : 45 of manganese dioxide to electrolyte was used in the experiments. Electrolyte pH was maintained with hydrochloric acid, added at equal intervals. The results are shown in Figs. 3 and 4.

The results indicate that under these conditions the discharge curves of the conventional manganese dioxides do not differ from those of the synthetic oxides: at pH < 5 in both cases a relatively stable manganese dioxide potential is observed and a high utilization coefficient, while at higher pH values the curves start decreasing. After discharge at pH 4.6 the amount of Mn^{2+} was determined, which had passed into the electrolyte during discharge. The results obtained are presented in Table 2 and show that under these conditions the discharge for both dioxides type takes place through the solution with the formation of Mn^{2+}.

DISCUSSION OF RESULTS

In previous papers [1, 2] it was shown that the unusual electrochemical behavior of the investigated dioxides cannot be explained on the basis of structural characteristics alone. The important conclusion can be drawn from ion-exchange properties that all synthetic dioxides, unlike those investigated earlier, have a pronounced effect on the salt electrolyte, present in limited quantity, maintaining in it a relatively low pH. Based on this fact a correct explanation of the investigated phenomenon can be given if the initial hypothesis is abandoned that a solid-phase mechanism is the only possible course a reaction can take in the salt solution. Literature data [5, 12] and our own measurements confirm, that the discharge of any dioxide at pH < 5 goes through the solution with the formation of Mn^{2+}. However, heterolyte formation takes place after reaching its solubility product [13] and after overcoming difficulties in the formation of nuclei of the new phase [14]. It was observed only in discharges in a limited electrolyte volume. When the pH is shifted to the alkaline side the Mn^{2+} formation rate is sharply reduced and the solid phase process becomes dominant with the formation of Mn^{3+}. Therefore, the cathodic reduction of synthetic dioxides can be explained in the following way for the conditions investigated (limited volume of electrolyte, consisting of zinc chloride and ammonium chloride, zinc anode, relatively low current densities - down to 1 mA/cm^2).

To the minimum in the valley of the discharge curve the electrode process follows the equation

$$MnO_2 + 4H^+ + 2e \rightarrow Mn^{2+} + 2H_2O. \quad (1)$$

TABLE 2. Amount of Manganese Compounds Present in the Electrodes and the Electrolye before and after Discharge in Excess Electrolyte at pH 4.6

Serial no.	Analysis	MnO_2 type	
		ρ-MnO_2	GAP
1	Amount of manganese dioxide in electrolyte before discharge, g	5.2	5.5
2	Current passed through electrode, A-h	2.52	2.52
3	Amount of manganese dioxide in electrode after discharge, g	1.2	1.1
4	Amount of MnO_2 passed into the electrolyte during discharge, g	4.0	4.0
5	Percent of theory, based on $MnO_2 \rightarrow Mn^{2+}$, %	102	97.2

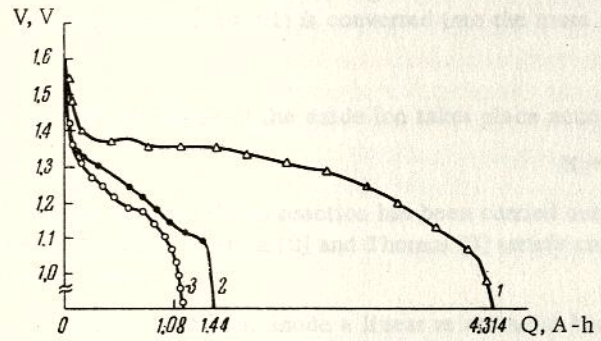


Fig. 4. Discharge curves of GAP (γ-MnO_2) electrode in excess electrolyte at various pH. I = 0.4 mA/cm^2. 1) Electrolyte "E," pH 3.2; 2) electrolyte "E," pH 5.8; 3) potassium hydroxide solution, 560 g/liter.

It is followed by alkalization which is suppressed by the anodic character of the dioxide and by a buffering action of the electrolyte, if present. At this stage apparently the following process takes place simultaneously in the solid phase

$$MnO_2 + H^+ + e \rightarrow MnOOH. \quad (2)$$

The share of this process increases with increasing pH. After passing through the minimum on the discharge curve the intensity of heterolyte crystal formation is already sufficient for its precipitation rate to become bigger than the overall rate of the electrode processes. The cell's electrolyte again becomes acidic according to the equation

$$MnO_2 + Mn^{2+} + Zn^{2+} + 2H_2O \rightarrow ZnO \cdot Mn_2O_3 + 4H^+. \quad (3)$$

In this stage the electrode process already follows not only Eqs. (1) and (2) but also equation

$$2MnO_2 + Zn^{2+} + 2e \rightarrow ZnO \cdot Mn_2O_3. \quad (4)$$

In the stable part of the discharge curve the overall electrode process is fully characterized by Eq. (4), and the overall process in the cell by the equation

$$2MnO_2 + Zn \rightarrow ZnO \cdot Mn_2O_3. \quad (5)$$

This scheme is not valid for the conventional dioxide types because in the first discharge stage of such dioxides a low proton capacity is followed by a sharp pH shift to the alkaline side. As a result of this shift process (1) is abruptly slowed down allowing only the processes in the solid phase to proceed according to Eq. (2).

The principle of concurrent processes in the solid phase and through the solution, depending on electrolyte pH, can be applied more generally to the interpretation of anomalies in the electrochemical behavior of conventional manganese dioxides.

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