# FACTORS DETERMINING ACTIVITY OF NONSTOICHIOMETRIC MANGANESE DIOXIDE IN MnO<sub>2</sub>, AIR - Zn SYSTEM

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## Introduction

Manganese dioxide is one of the most widely distributed electrode materials for power sources due to its low cost, low toxicity and relatively high electrochemical activity. It can be discharged at broad limits of temperatures. This electrode material found important applications in electrocatalysis and catalysis also.

The investigation of electrocatalytic activity of oxygen in MnO<sub>2</sub>, air - Zn system and factors determining it were the objects of the presented report. We have studied the samples of manganese dioxide of various origins. Among them were the samples synthesized from fluoride-containing electrolytes [1]. The discharge characteristics of mockups of 1142 size coin elements had been analyzed in accordance with the physical-chemical properties of manganese dioxide active layer.

## Experimental

Samples 1-3 of manganese dioxide studied in this work were electrosynthesized from electrolytes containing 0.1, 0.2, and 0.3M HF, respectively [1]; Sample 4 was electrolytic manganese dioxide of the EMD-2 brand synthesized in Georgia by OST-6-22-34-76; no. 5, obtained chemically (CMD); no. 6 was synthesized at the Pridneprovsk chemical plant by TU U 14312708.174-94. Our choice of fluoride-containing electrolytes for synthesizing manganese dioxide was by no means accidental. By using them, one can control the composition and properties of oxide compounds and produce them at high rates [2].

The obtained cathode materials were tested in the coin elements CR1142 (with a diameter of 11 mm and height 4.2 mm). The cathodic mass of a  $MnO_2$  -Zn system consisted of 85%  $MnO_2$ , 10% conductive additive, and 5% binder; the separator was polypropylene, the electrolyte was 9 M KOH. For zinc-air system with a manganese dioxide cathode containing the oxide under test, the negative electrode was of amalgamated zinc. The positive air electrode was prepared using a standard procedure. The reactive layer (70 wt % manganese dioxide and 30 wt. % of carbon black, 0.02 - 0.03 mm thick) was pressed onto the hydrophobic layer (a mixture of 70 wt % carbon black and 30 wt % polytetrafluoroethylene, pressed at 0.1 MPa). The pellet 11 mm in diameter was inserted into a coin element so that the hydrophobic layer touched the can, which served as a current lead. The electrolyte was 9 M KOH of analytical grade. The separator was made of

a PZ-100 film and an FOS paper (TU 6-09-1678-77).

The overall conductivity and its ionic and electronic components were determined by the unipolar-pulse method [3]. The catalytic activity of manganese dioxide in the hydrogen peroxide decomposition was estimated from the rate constant of this reaction by gasometry. Manganese dioxide pH values were determined using a standard procedure [1]. The x-ray diffraction of manganese dioxide was performed at a DRON-3 device with Mo K<sup>(2)</sup> radiation. The electron diffraction analysis was performed at a UEM-100 electron microscope. The thermogravimetric measurements were performed using a derivatograph of Paulic-Paulic-Erdey (Hungary).

## **Results and Discussion**

The results of chemical analysis are given in the table. Samples obtained from fluoride containing electrolytes have the largest content of  $Mn^{3+}$  and combined water including hydroxide groups of the surface. The X-ray and electron diffraction investigations showed that all samples except from no 5 ( $\partial_2$ -MnO<sub>2</sub> of stoichiometric composition) contain  $\gamma_{o-polimorph}$  as the main phase. Distinctive feature of electrolytic samples 1-4 is the low crystallinity and the presence of amorphous state in them. Moreover, samples 1-3 have the admixture of  $\mathfrak{O}$ -MnO<sub>2</sub>. Thus the chemical analysis data showed that samples obtained from fluoride-containing electrolytes have maximal structure disorder and nonstoichiometry.

**Table 1** Chemical analysis data, surface OH-groups content (OH<sub>surf</sub>), catalytic activity of H<sub>2</sub>O<sub>2</sub> decomposition as the rate constant (*k*), acidity values of MnO<sub>2</sub> surface (pH), ionic conductivity value ( $\sigma_{ion}$ )

Sample	1	2	3	4	5	6
Mn <sup>3+</sup> (%)	5.36	7.38	5.36	1.77	1.74	1.74
OH <sub>suf</sub> (%)	2.8	2.9	3.2	1.1	0.2	1.3
10 <sup>5</sup> k (s⁻¹)	21.7	19.7	18.1	10.0	3.0	18.1
pH− MnÓ₂	2.49	2.97	3.74	4.24	5.70	3.71
10 <sup>-6</sup> σ <sub>ion</sub> (Ω <sup>-1</sup> .cm <sup>-1</sup> )	2.8	2.9	3.2	0.6	0.1	1.3
σ <sub>ion</sub> (%)	26.6	23.8	21.6	7.7	3.3	14.4

The coin elements of zinc - air power sources with the cathode containing in its active mass sample No. 1, which has the maximal nonstoichiometry, displays the best discharge characteristic (Fig. 1). The discharge parameters of elements based on samples no. 2 and 3 are somewhat worse, and those based on sample no. 4 are still worse. Similar results were obtained for power sources elements based on the alkaline system  $MnO_2$  - Zn [1]. Capacity of 1142 zinc-air coin elements correlates well with the ionic conductivity value of manganese dioxide samples as shown in Figure 2.



*Fig.1* Discharge curves of zinc-air coin elements (load 500 ohm; cathodes based on samples No. 1-4 and 6)



Fig. 2 Dependence of discharge capacity of zinc-air coin elements on the ionic conductivity component of samples No. 1-4 and 6.

As mentioned in [1] manganese dioxide belongs to solid acids. Brønsted acidity of such OH-groups can be estimated as the result of exchange between protons of the surface and salt solution cations. The surface of manganese dioxide contains predominately hydroxide groups dissociated as Brønsted centers. To estimate evidently low concentration of Lewis centers at the surface the further investigation by the potentiometic titration method should be performed.

The acidity of manganese dioxide samples surface OH-groups vary in the range of pH to within 2.5 -5.7 in accordance with pH value measurements (table). The less active samples 4 - 6 comparing with the samples 1 - 3 have higher values of pH (but lower than 7) and minimal content of  $Mn^{3+}$ . It can be expected that the large content of  $Mn^{3+}$  ions in samples 1 - 3 will strongly influence the dissociation of surface hydroxide groups although the analysis of the surface acidity shows that Brønsted centers are the hydroxide groups of the four-valenced manganese.  $Mn_2O_3$  possesses predominately basic behaviour and has considerably higher values of acidity (pH > 7) as shown in [1]. This observation agrees with approach proposed in [1] that EPR signal width is proportional to the  $Mn^{3+}$  content in the bulk of the manganese dioxide as result of the "double exchange" interaction of  $Mn^{4+} - O - Mn^{3+}$  ions into the crystal lattice of manganese dioxide.

## Conclusions

The catalytic activity in the hydrogen peroxide decomposition and the electrocatalytic oxygen reduction rate increase with growth of defects concentrations of manganese dioxide structure. The defects of manganese dioxide can be judged from its ionic conductivity, pH value and the widening of an EPR signal. In the bulk the redox pairs Mn<sup>3+</sup>/Mn<sup>4+</sup> of the oxygen octahedrons, fixed in the lattice by the OH-groups, are the main defects in electrochemically-active manganese dioxide obtained from fluoride-containing electrolytes but the surface of such samples contain predominately four-valenced manganese ions. Probably, active sites at the surface could be Brønsted centers of the four-valenced manganese participated in the "double exchange" and ionic charge transfer simultaneously. This conclusion confirms the discharge parameters of the zinc-air coin elements with cathodic material based on the obtained manganese dioxide.

## References

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