

## MANGANESE DIOXIDE AS A CATHODE CATALYST IN METAL-AIR CELLS

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The main attention in the present work has been given to the development of composites based on electrolytic manganese dioxide and their practical application in metal-air cells. Electrolytic manganese dioxide which has been obtained from fluorine-containing electrolytes differs from traditional types of  $MnO_2$  obtained by another method. This material is characterized by the increased amount of structural defects. This is established by complex of different physical-chemical methods.

The catalytic activity of the synthesized electrolytic manganese dioxide was designated as the rate constant of reaction to the decomposition of hydrogen peroxide. Quantum chemical calculations of the electronic structure of molecular cluster and adsorption complex were made to explain the mechanism of the reaction. The form of electrolytic manganese dioxide obtained by us from fluorine-containing electrolytes was seen to produce a higher catalytic and electrochemical activity. This is favored in turn by a large dividend in discharge characteristics of chemical power sources. Independent comparative testing of the experimental samples of our power sources of 1142 size was carried out. It was shown that power sources with the manganese dioxide cathode catalyst obtained from fluorine-containing electrolyte (sample EMD) have 20 % higher capacity in the  $MnO_2$ /air – Zn system.

Cathode materials represent a major technology challenge in rechargeable metal-air battery development [1]. The specific capacity and power capability of metal-air cells strongly depend on the materials and microstructures of the air-breathing cathode. A high performance cathode should be able to provide: good electronic and ionic conductivity; fast oxygen diffusion and stable electrode integrity. It should also have an efficient catalyst supported by a high surface area substrate, similar to that in a proton exchange membrane fuel cell. Many new cathode materials have been reported, particularly in the area of new catalysts for improving the battery efficiency.

In 2006 Bruce et al. [2] demonstrated high-energy-density metal-air cells using a porous carbon cathode with electrolytic manganese

dioxide. Since that time, MnO<sub>2</sub>-based compounds have been widely investigated as a cathode catalyst to improve the performance of the air-breathing cathode. In their study, they found that different catalytic reactivity for the oxygen evolution reaction could be achieved for MnO<sub>2</sub> with different crystal structures and morphologies.

The structure and properties of manganese dioxide depend on the method of its synthesis. It was shown earlier [3], that electrolytic manganese dioxide obtained from fluorine-containing electrolyte differs from the samples fabricated by other methods. This material is characterized by an increased amount of structural defects.

Therefore, the main attention in the present work has been given to the development of composites based on such electrolytic manganese dioxide and their practical application in metal-air cells.

### **Research Methodology**

Electrolytic manganese dioxide (EMD) was synthesized by the electrochemical method from a manganese sulfate-containing electrolyte with additions of the fluoride ion. The synthesis was carried out in a polyethylene cell without a diaphragm (stainless steel was a cathode and platinum was an anode) at a current density of 50-100 mA/cm<sup>2</sup> and a temperature of 15-20°C. The current density 50-100 mA/cm<sup>2</sup> was applied to obtain powders.

We investigated the behavior of EMD in the decomposition reaction of hydrogen peroxide. This reaction is a model in the study of the activity of catalysts for the electrochemical reduction of oxygen. Quantum chemical calculations of the electronic structure of molecular cluster and adsorption complex were made to explain the mechanism of the reaction.

The testing of coin elements with a diameter of 11 mm and a height of 4.2 mm was carried out. The discharge test of manganese oxide compounds was performed at a constant external load at room temperature. Manganese dioxide compounds were mixed thoroughly with Carbon Black and binder (Teflon suspension). The composition of a hydrophobic layer was as follows: 70% Carbon Black and 30% PTFE. The composition of active layer was as follows: 70% catalyst and 30% Carbon Black. The experimental electrodes were made by pressing this paste to a current collector. The resulting active material was pressed at 0,1 MPa into the test cells.

### **Results and Discussion**

The catalytic activity of the synthesized electrolytic manganese dioxide (EMD) was designated as the rate constant of reaction to the decomposition of hydrogen peroxide. We used the following samples for

comparison: EMD-2- was synthesized by the electrochemical method from a manganese sulfate-containing electrolyte with additions of sulfate-ion and CMD – chemical manganese dioxide from Pridneprovsky Chemical plant, Ukraine.

Table 1 shows the constants for different samples.

**Table 1.** Characteristics of Manganese Dioxide Samples

Sample	EMD	CMD	EMD-2
$K \cdot 10^4, c^{-1}$	2.50	1.83	1.27

Table 1 shows that the EMD obtained from fluorine-containing electrolytes differs from traditional types of  $MnO_2$  obtained by another method. The data (value K) shows that the catalytic activity tends to increase in the order EMD-2→CMD→EMD. This material is characterized by an increased amount of structural defects. This is established by a complex of different physical-chemical methods, which was demonstrated in our earlier publications [4]. EMD is encapsulated from two phases- $\gamma$ - $MnO_2$  and  $\alpha$ - $MnO_2$ . The last phase distinguishes this sample from the others and adds defects. It is shown that crystalline structure with a large number of defects has a higher catalytic and electrochemical activity.

The conductivity of these samples was studied as well (Table 2). As a result, all these samples possess mixed conductivity - ionic and electronic, and the ionic one is due to the presence of defects. Its contribution into overall conductivity ranges from 4 to 20% depending on the nature of oxide and conditions of the electrochemical synthesis. The overall conductivity is approximately by a factor  $10^2$  greater than that of stoichiometric compounds of the same metals. These compounds are of great interest as cathodic and catalytic active materials.

Nonstoichiometric oxide compounds show disorder of crystal structure, a great number of defects. The ionic conductivity may be a criterion for the catalytic activity. The sample EMD has the highest ionic conductivity.

**Table 2.** The overall and the ionic conductivity of samples

Sample	$\sigma_o \cdot 10^{-6}, \text{OM}^{-1} \cdot \text{cm}^{-1}$	$\sigma_{\text{ion}} \cdot 10^{-6} \text{OM}^{-1} \text{cm}^{-1}$	$\sigma_{\text{ion}}/\sigma_o, \%$
EMD	10.8	2.8	26.6
EMD-2	8.5	0.6	7.7
CMD	8.9	1.3	14.4

Scanning electron microscopy was employed to investigate the shapes of the samples [5]. Cube-type EMD-2 particles have a homogeneous cubic morphology. The villiform-type EMD particles were formed by a nucleus covered with numerous micrometer-sized rods (Fig.1). In comparison with the length, the diameter of the rod was very small. It is interesting that the villiform - type EMD has a rough surface.



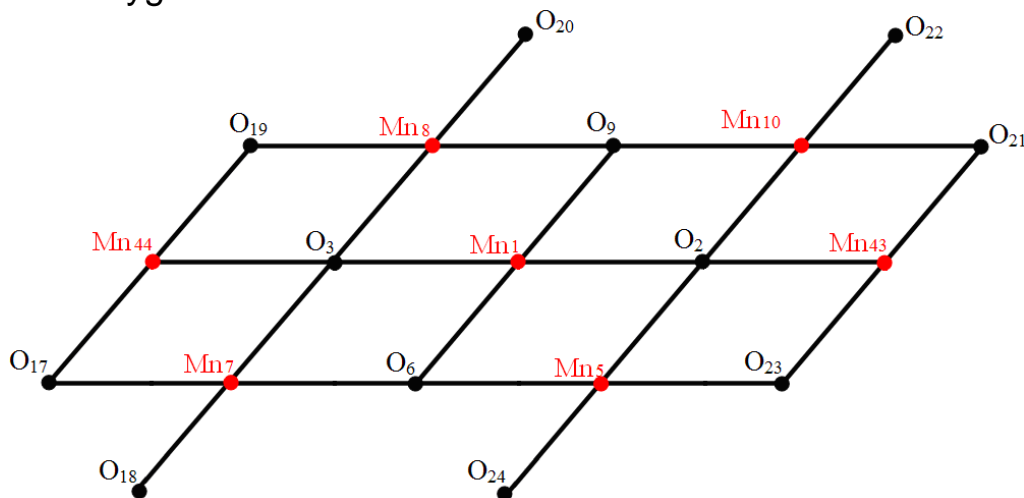
**Fig 1.** Micro particles of manganese dioxide obtained from fluorine – contained electrolyte at the magnification x 600

The electrochemical property of the air electrodes containing  $\text{MnO}_2$  particles is significantly associated with the shape and size of the particles. It appears that the capacity of electrodes containing villiform - type particles is superior to that of electrodes containing cube-type particles. This is probably due to the relatively sufficient pore space between active catalytic sites, which stores a large amount of reaction products.

In order to explain the mechanism of decomposition reaction of  $\text{H}_2\text{O}_2$  on the surface of heterogeneous catalyst  $\text{MnO}_2$ , we have performed quantum chemical calculations of the electronic structure of molecular clusters (MC) and adsorption complexes (AC):  $\text{Mn}_{10}\text{O}_{23}\text{H}_{14}$  (K47),  $\text{Mn}_{10}\text{O}_{23}\text{H}_{14} - \text{H}_2\text{O}_2$  (K47 $\text{H}_2\text{O}_2$ ),  $\text{Mn}_{10}\text{O}_{22}\text{H}_{14}$  (K46),  $\text{Mn}_{10}\text{O}_{22}\text{H}_{14} - \text{H}_2\text{O}_2$  (K46 $\text{H}_2\text{O}_2$ ),  $\text{Mn}_{10}\text{O}_{22}\text{H}_{14} - \text{H}_2\text{O}_2 - \text{HO}^*$ ,  $\text{Mn}_{10}\text{O}_{23}\text{H}_{14} - \text{H}_2\text{O}_2 - 2\text{HO}^*$ . The electronic structure of manganese oxide was modeled by MC of composition  $\text{Mn}_{10}\text{O}_{23}\text{H}_{14}$  (Fig. 2).

The quantum chemical calculations of the electronic structure of MC and AC were performed with the full optimization of the usual structural parameters.

Stable adsorption complexes are formed on the surface of manganese oxide. The destabilization and dissociation of O - H in the adsorbed H<sub>2</sub>O<sub>2</sub> molecule occurs under the influence of neutral anion radicals HO. This is shown by the results of the calculations of AK Mn<sub>10</sub>O<sub>23</sub>H<sub>14</sub>-H<sub>2</sub>O<sub>2</sub>-HO\*, Mn<sub>10</sub>O<sub>23</sub>H<sub>14</sub>-H<sub>2</sub>O<sub>2</sub>-2HO\*. Overloading of the atoms takes place in the AK Mn<sub>10</sub>O<sub>23</sub>H<sub>14</sub>-H<sub>2</sub>O<sub>2</sub>-2HO\* on the surface of the catalyst. As a result, the complex Mn<sub>10</sub>O<sub>23</sub>H<sub>14</sub> - H<sub>2</sub>O<sub>2</sub> - 2HO\* is transformed into the complex Mn<sub>10</sub>O<sub>23</sub>H<sub>14</sub> - O<sub>2</sub> - 2H<sub>2</sub>O and molecules of water and oxygen are desorbed.



**Fig 2.** Fragment of model of the molecular cluster Mn<sub>10</sub>O<sub>23</sub>H<sub>14</sub>

The vacancy in oxygen in the MnO<sub>2</sub> catalyst causes a change in the electron density distribution between the power centers (Table 3). The polarization of the cluster increases and the dipole moment increases. This causes an increase in the energy of the adsorption bond between the cluster and the H<sub>2</sub>O<sub>2</sub> adsorbate. The energy of the adsorption bond E<sub>ads</sub> in the molecular clusters Mn<sub>10</sub>O<sub>23</sub>H<sub>14</sub>-H<sub>2</sub>O<sub>2</sub>, Mn<sub>10</sub>O<sub>22</sub>H<sub>14</sub>-H<sub>2</sub>O<sub>2</sub> is as follows: 133.737 kJ / mol (1.382 eV) and 172.227 kJ / mol (1.735 eV).

The reaction is multistage. It consists of: the stage of formation of a bond between the catalyst and H<sub>2</sub>O<sub>2</sub>, the formation of a complex of the composition Mn<sub>10</sub>O<sub>23</sub>H<sub>14</sub>-H<sub>2</sub>O<sub>2</sub>-HO\*, the regrouping of atoms and the formation of a new complex Mn<sub>10</sub>O<sub>23</sub>H<sub>14</sub>-H<sub>2</sub>O<sub>2</sub>-H<sub>2</sub>O-O<sub>2</sub>. This reaction can occur if the adsorption bond between H<sub>2</sub>O<sub>2</sub> and the catalyst is not broken off under the influence of electrolyte. Calculations show that the energy of the adsorption bond between H<sub>2</sub>O<sub>2</sub> and the cluster with a defect is greater than the bond energy in the absence of defects. The probability of the reaction on the catalyst with defects is greater.

The rate of formation of the complex Mn<sub>10</sub>O<sub>23</sub>H<sub>14</sub> - H<sub>2</sub>O<sub>2</sub> - 2HO\* will increase with increasing concentration of HO\* radicals in solution. The process O<sup>-</sup> + H<sup>+</sup> → HO\* is realized when there is a defect in the solution

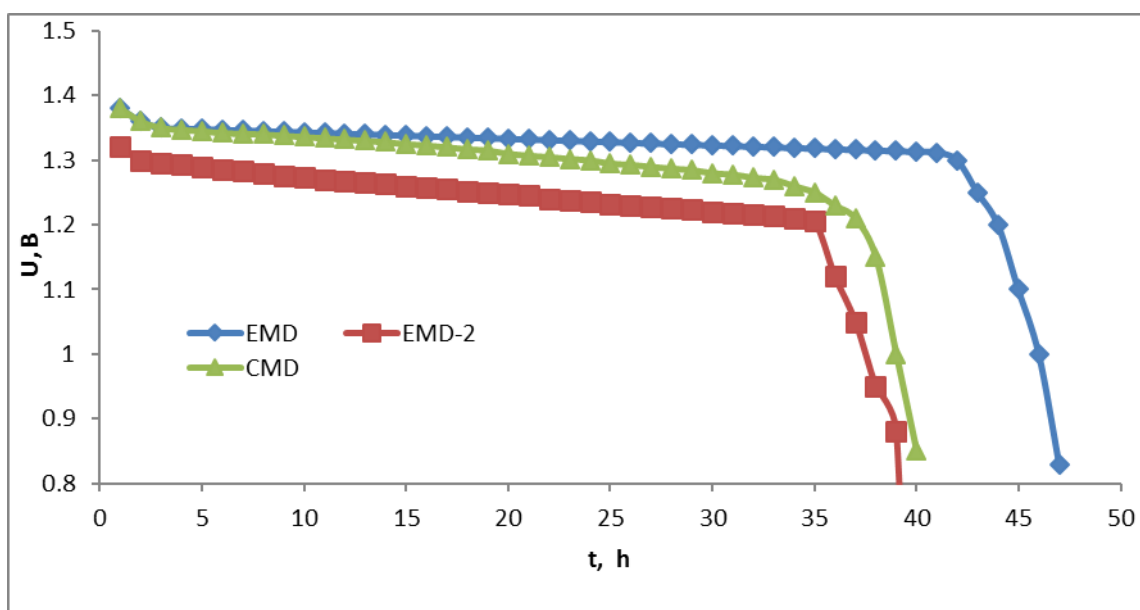
of the MnO<sub>2</sub> catalyst. This is due to the O<sup>-</sup> anions detached from the manganese cations. Due to this process, the concentration of neutral radicals of HO increases and the reaction rate increases.

**Table 3.** Charge on atoms and dipole moments of  $\mu$ , D clusters and adsorption complexes Mn<sub>10</sub>O<sub>23</sub>H<sub>14</sub>(K47), Mn<sub>10</sub>O<sub>22</sub>H<sub>14</sub>(K46), K47 - H<sub>2</sub>O<sub>2</sub>, K46 - H<sub>2</sub>O<sub>2</sub>

Atoms↓	K47	K46	K47 - H <sub>2</sub> O <sub>2</sub>	K46 - H <sub>2</sub> O <sub>2</sub>
Mn <sub>1</sub>	+2.206	+0.309	+2,315	+0,574
O <sub>2</sub>	-1.357	-	-1,358	-
O <sub>3</sub>	-1.323	-1.319	-1.321	-1.327
Mn <sub>5</sub>	+1.736	+1.909	+1.718	+1.829
O <sub>9</sub>	-1.258	-1.224	-1.319	-1.295
Mn <sub>10</sub>	+1.743	2.341	+1.759	+2.218
$\mu$	4.891	10.119	4.975	8.430

EMD is more catalytically and electrochemically active. This is favored in turn by a large dividend in discharge characteristics of chemical power sources. The testing of coin elements has been carried out. The discharge test of manganese oxide compounds was performed at a constant external load at room temperature (Fig. 3).

The independent comparative testing of the experimental samples of our power sources of 1142 size were carried out.



**Fig.3.** Discharge curves of MnO<sub>2</sub>/Air – Zn (1142 cell size) power sources at the low load 500 Ohm per cell

It was shown that power sources with the manganese dioxide cathode catalyst obtained from fluorine containing electrolyte (sample EMD) have 20 % higher capacity in MnO<sub>2</sub>/Air – Zn system (Table 4).

**Table 4.** Nominal capacity, mA·h, 1142 - size MnO<sub>2</sub>/air – Zn cell based on various MnO<sub>2</sub> samples

Sample	EMD	CMD	EMD-2
C <sub>nom</sub> , mA·h	110-115	95-97	75-77

### Conclusions

A form of electrolytic manganese dioxide obtained by us from fluorine-containing electrolytes was seen to produce a higher catalytic and electrochemical activity. This material is characterized by an increased amount of structural defects. The number of lattice defects in MnO<sub>2</sub> structure increased the discharge capacity. Power sources with the manganese dioxide cathode catalyst obtained from fluorine containing electrolyte (sample EMD) have 20 % higher capacity in the MnO<sub>2</sub>/air – Zn system.

### References

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