

MnO₂ Nanoparticles as a Catalyst for the Air Electrode of a Zn/Air Battery

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Abstract— A form of electrolytic manganese dioxide obtained by us from fluorine-containing electrolytes was seen to produce the higher catalytic and electrochemical activity. The catalytic activity of the synthesized electrolytic manganese dioxide was designated as the constant of rate reaction to the decomposition of hydrogen peroxide. Quantum chemical calculations of the electronic structure of molecular cluster and adsorption complex were made to explain mechanism of the reaction. This material is characterized by the increased amount of structural defects. MnO₂ nanoparticles were synthesized and introduced as a catalyst for the air electrode of a Zn/air battery. The electrochemical property of the air electrodes containing MnO₂ nanoparticles is significantly associated with the shape and size of the nanoparticles. The independent comparative testing of the experimental samples of our power sources of 1142 size were 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 MnO₂/air – Zn system.

Keywords—*electrochemical synthesis; catalytic activity; nanoparticles; cathode catalyst; capacity*

I. INTRODUCTION

The specific capacity and power capability of metal-air cells strongly depend on the materials and structures of the air-breathing cathode. Many new cathode materials have been reported, particularly in the area of new catalysts for improving the battery efficiency. Catalysts are key materials that affect the capacity, cycle life and rate capability of such batteries. MnO₂-based compounds have been widely investigated as the cathode catalyst to improve the performance of the air-breathing cathode [1]. Different catalytic reactivity for the oxygen evolution reaction could be achieved for MnO₂ with different crystal structures and morphologies [2].

The structure and properties of manganese dioxide depend on the method of its synthesis. It was shown earlier [3], that electrolytic manganese dioxide which has been obtained from fluorine-containing electrolyte differs from the samples receiving by another methods. This material is characterized by the increased amount of structural defects. Such MnO₂ were synthesized and the properties were characterized. This study was motivated by the notion that the catalytic efficiency of oxides is highly dependent on their morphology, size and crystal structure [4,5].

II. RESEARCH METHODOLOGY

Electrolytic manganese dioxide (EMD) has been synthesized by electrochemical method from a manganese sulfate-containing electrolyte with additions of fluoride ion. The synthesis was carried out in a polyethylene cell without a diaphragm (stainless steel was a cathode and platinum was an anode) with current density 50-100 mA/cm² and temperature was 15-20°C. The chemical composition of oxides may be varied and successfully controlled by changing the conditions of electrochemical method of their production. The current density 50-100 mA/cm² 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 the catalysts for the electrochemical reduction of oxygen [6]. Quantum chemical calculations of the electronic structure of molecular cluster and adsorption complex were made to explain mechanism of the reaction.

The total conductivity and its ionic and electronic components were determined by the unipolar pulse method [7]. The microstructure of the powder was observed by electron diffraction analysis using an electron microscope (UEM-100).

The electrochemical performance of the air electrode containing MnO₂ nanoparticles was examined using a modified coin-cell, consisting of a cathode, an a malgamated zinc powder anode, a separator and an electrolyte of 9M KOH.

The testing of coin elements with the diameter of 11 mm and height of 4,2 mm has been carried out. The discharge test of manganese oxide compounds was performed at a constant external load at room temperature.

The cathode contained carbon, catalysts (MnO₂ nanoparticles) and a binder. 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.

III. RESULTS AND DISCUSSION

The catalytic activity of the synthesized electrolytic manganese dioxide (EMD) was designated as the constant of rate reaction to the decomposition of hydrogen peroxide. We used the following samples for comparison: EMD – 2 – has been synthesized by electrochemical method from a manganese sulfate-containing electrolyte with additions of sulfate-ion and CMD – chemical manganese dioxide from Pridneprovsky Chemical plant, Ukraine.

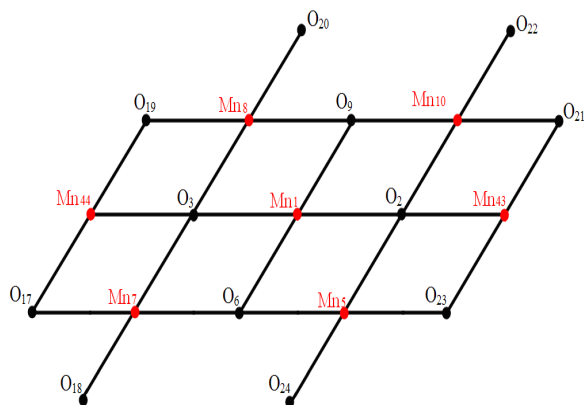
Table 1 is shown that EMD, which has been obtained from fluorine-containing electrolytes, differs from traditional types of MnO_2 obtained by another method.

TABLE I. CHARACTERISTICS OF MANGANESE DIOXIDE SAMPLES

Sample	$K \cdot 10^4$, s^{-1}	$\sigma_0 \cdot 10^{-6}$, $Om^{-1}cm^{-1}$	$\sigma_{ion} \cdot 10^{-6}$, $Om^{-1}cm^{-1}$	σ_{ion}/σ_0 , %
EMD	2,15	10,8	2,8	26,6
EMD-2	1,27	8,5	0,6	7,7
CMD	1,83	8,9	1,3	14,4

The data (value K) shows that the catalytic activity tends to increase in the order EMD-2 → CMD → EMD.

In order to explain the mechanism of decomposition reaction of H_2O_2 on the surface of a heterogeneous catalyst MnO_2 , we performed quantum chemical calculations of the electronic structure of molecular clusters (MC) and adsorption complexes (AC): $Mn_{10}O_{23}H_{14}$ (K47), $Mn_{10}O_{23}H_{14} - H_2O_2$ (K47 H_2O_2), $Mn_{10}O_{22}H_{14}$ (K46), $Mn_{10}O_{22}H_{14} - H_2O_2$ (K46 H_2O_2), $Mn_{10}O_{22}H_{14} - H_2O_2 - HO^*$, $Mn_{10}O_{23}H_{14} - H_2O_2 - 2HO^*$. The electronic structure of manganese oxide was modeled by MC of composition $Mn_{10}O_{23}H_{14}$ (fig.1).


 Fig. 1. Fragment of model of the molecular cluster $Mn_{10}O_{23}H_{14}$

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

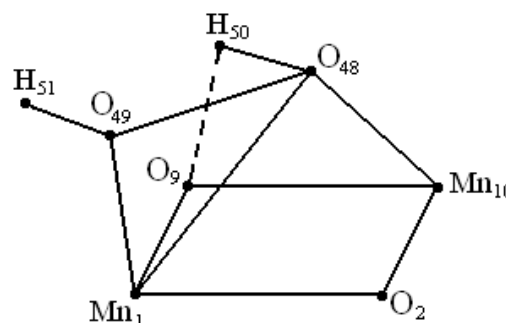
Stable adsorption complexes are formed on the surface of manganese oxide. The destabilization and dissociation of O - H in the adsorbed H_2O_2 molecule occurs under the influence of neutral anion radicals HO. This is shown by the results of the calculations of AK $Mn_{10}O_{23}H_{14} - H_2O_2 - HO^*$, $Mn_{10}O_{23}H_{14} - H_2O_2 - 2HO^*$. Overloading of the atoms takes place in the AK

$Mn_{10}O_{23}H_{14} - H_2O_2 - 2HO^*$ on the surface of the catalyst. As a result, the complex $Mn_{10}O_{23}H_{14} - H_2O_2 - 2HO^*$ is transformed into the complex $Mn_{10}O_{23}H_{14} - O_2 - 2H_2O$ and molecules of water and oxygen are desorbed.

The adsorption bond between H_2O_2 and the cluster $Mn_{10}O_{23}H_{14}$ is formed as a result of the interaction of cluster surface cations, peroxide atoms (Mn₁-O₄₉ bonds) and surface oxygen anions (O₉-H₅₀ bond) (Fig. 2, table 2).

 TABLE II. THE OPTIMIZED LENGTHS OF THE INTERCENTRAL BONDS R (A-B), Å AND THE BOND ORDERS P (A-B) IN AC $Mn_{10}O_{23}H_{14} - H_2O_2$

	Mn ₁ - O ₂	Mn ₁₀ - O ₂	Mn ₁₀ - O ₉	Mn ₁ - O ₄₉	H ₅₀ - O ₉	Mn ₁ - O ₉
$R(A-B)$, Å	1.992	2.074	1.928	2.073	1.739	1.965
$p(A-B)$	0.320	0.252	0.458	0.150	0.103	0.153


 Fig. 2. Fragment of the model of the adsorption complex $Mn_{10}O_{23}H_{14} - H_2O_2$

The dipole-dipole attraction makes an additional contribution to the energy of the adsorption bond between the H_2O_2 adsorbate and the cluster (table 3). The vacancy in oxygen in the MnO_2 catalyst causes a change in the electron density distribution between the power centers. 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_2O_2 adsorbate (table 4). The energy of the adsorption bond E_{ads} in the molecular clusters $Mn_{10}O_{23}H_{14} - H_2O_2$, $Mn_{10}O_{22}H_{14} - H_2O_2$ 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_2O_2 , the formation of a complex of the composition $Mn_{10}O_{23}H_{14} - H_2O_2 - HO^*$, the regrouping of atoms and the formation of a new complex $Mn_{10}O_{23}H_{14} - H_2O_2 - H_2O - O_2$. This reaction can occur if the adsorption bond between H_2O_2 and the catalyst is not broken off under the influence of electrolyte. Calculations show that the energy of the adsorption bond between H_2O_2 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.

TABLE III. CHARGE ON ATOMS AND DIPOLE MOMENT (μ) OF CLUSTERS AND ADSORPTION COMPLEXES: $Mn_{10}O_{23}H_{14}$ (K47), $Mn_{10}O_{22}H_{14}$ (K46), K47- H_2O_2 , K46- H_2O_2

	K47	K46	K47- H_2O_2	K46- H_2O_2
μ	4.891	10.119	4.975	8.430
Mn_1	+2.206	+0.309	+2.315	+0.574
O	-1.357	-	-1.358	-
O_3	-1.323	-1.319	-1.321	-1.327
Mn_5	+1.736	+1.909	+1.718	-1.829
O_9	-1.258	-1.224	-1.319	-1.295
Mn_{10}	+1.743	2.341	+1.759	+2.218

TABLE IV. THE TOTAL ENERGY (E) AND THE ENERGY OF THE ADSORPTION BOND (Eads) OF ADSORPTION COMPLEXES: $Mn_{10}O_{23}H_{14}-H_2O_2$, $Mn_{10}O_{22}H_{14}-H_2O_2$

Adsorption complexes	E, a.o.e.	Eads, KJ / mol (eV)
$Mn_{10}O_{23}H_{14}-H_2O_2$	-13376.532	-133.371 (1.382)
$Mn_{10}O_{22}H_{14}-H_2O_2$	-13301.880	-172.227 (1.735)

The rate of formation of the complex $Mn_{10}O_{23}H_{14} - H_2O_2 - 2HO^*$ will increase with increasing concentration of HO^* radicals in solution. The process $O^- + H^+ \rightarrow HO^*$ is realized when there is a defect in the solution of the MnO_2 catalyst. This is due to the O^- anions detached from manganese cations. Due to this process, the concentration of neutral radicals of HO increases and the reaction rate increases.

The conductivity of these samples was studied too (table 1). 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, great number defects. The ionic conductivity may be criteria of the catalytic activity. The sample EMD has the highest ionic conductivity. This material is characterized by the increased amount of structural defects. This is established by complex of different physico-chemical methods, which was demonstrated in our earlier publications [8]. The rate of electrochemical solid state reduction which was determined by current density is 2-5 times higher for nonstoichiometric compounds. The particle size of the powder decreases with increasing current density and the number of crystallization centers increases. This leads to additional distortions of the microstructure - the appearance of various surface defects. A high current density causes deformation of the crystallites, as a result of which they take a villiform-type particles (table 5). The parameters of the unit cell are calculated. Indication of the parameters of the crystallographic cell for $\gamma-MnO_2$ was carried out in the orthorhombic cell along the main reflections [9]. EMD is encapsulated from two

phases - $\gamma-MnO_2$ and $\alpha-MnO_2$. The main phase is $\gamma-MnO_2$, and the impurity phase is $\alpha-MnO_2$. 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.

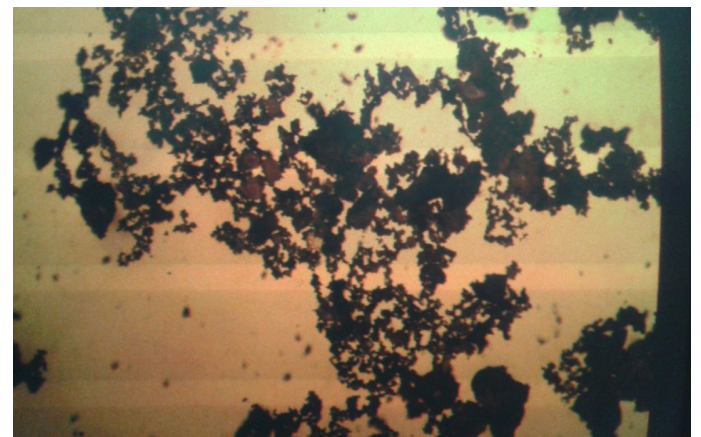
TABLE V. STRUCTURAL PARAMETERS OF MANGANESE DIOXIDE

Sample	Modification	a, nm	b, nm	c, nm	Particle size, nm·nm
EMD	γ, α	0,4566	0,9256	0,2879	Villiform-type ~10x200
EMD-2	γ	0,4568	0,9247	0,2877	Cube-type ~90x50
CMD	γ, α	0,4350	0,9403	0,2831	villiform-type ~20x200

Electron microscopy was employed to investigate the shapes of the samples. This study has indeed shown that the crystallites of manganese dioxide obtained from a fluorine-containing electrolyte have a villiform-type. The villiform-type EMD particles were formed by a nucleus covered with numerous micrometer-sized nanorods (fig.3,a). 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. Cube-type EMD-2 nanoparticles have a homogeneous cubic morphology (fig.3,b).

The electrochemical property of the air electrodes containing MnO_2 nanoparticles is significantly associated with the shape and size of the nanoparticles. 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.

The independent comparative testing of the experimental samples of our power sources of 1142 size were 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 MnO_2 /air - Zn system, table 5.



a)

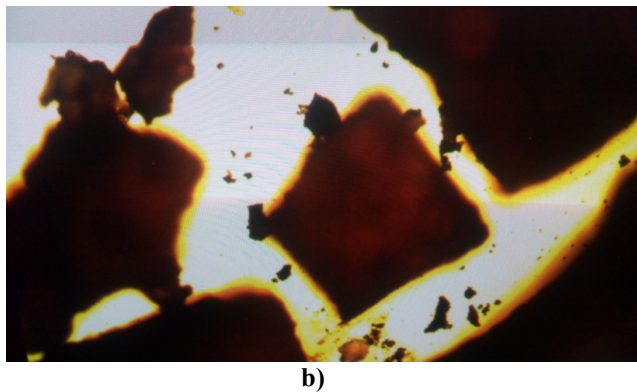


Fig. 3. Nanoparticles of manganese dioxide obtained from fluorine-containing (a) and sulfate (b) electrolytes

It appears that the capacity of electrodes containing villiform - type nanoparticles is superior to that of electrodes containing cube-type nanoparticles. This is probably due to the relatively sufficient pore space between active catalytic sites, which stores a large amount of reaction products [10].

The higher rate of mass transfer in nonstoichiometric oxides make it possible to operate a discharge current density

TABLE VI. NOMINAL CAPACITY (C_{nom}), 1142 - SIZE $\text{MnO}_2/\text{AIR} - \text{Zn}$ CELL BASED ON VARIOUS MnO_2 SAMPLES

Sample	EMD	CMD	EMD-2
C_{nom} , mAh	110-115	95-97	75-77

of the order of 2 – 5 mA/cm² which is several times greater than with usual oxide. Thus, the purposeful disordering of structure of a cathode material of manganese dioxide allows to utilize such power sources in extreme conditions – for element discharge at a low resistance (from 0,3 kOm). This result indicates that electric parameters of power sources are in agreement with data on the degree of deviation from stoichiometric composition.

We compared the discharge characteristics of chemical current sources with cathode material based on the samples under study. The results are shown in fig. 4.

From the data presented, it can be seen that the best discharge characteristic has a chemical current source with a cathode based on the sample EMD. The discharge characteristics of chemical current sources with cathode materials based on the samples EMD-2 and CMD have worse indicators. The obtained electrical parameters of the current source with the catalyst - manganese dioxide from the fluorine-containing electrolyte are at the level of the world analogues.

IV. CONCLUSIONS

MnO_2 nanoparticles were synthesized and introduced as a catalyst for the air electrode of a Zn/air battery. A form of electrolytic manganese dioxide obtained by us from fluorine-containing electrolytes was seen to produce the higher catalytic and electrochemical activity. This material is characterized by the increased amount of structural defects.

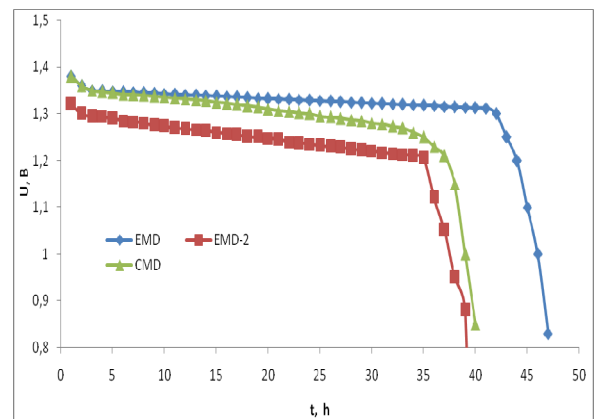


Fig. 4. Discharge curves of $\text{MnO}_2/\text{air} - \text{Zn}$ (1142 cell size) power sources at the low load 500 Ohm per cell

The number of lattice defects in MnO_2 structure increased the discharge capacity. The electrochemical properties of the air electrodes containing MnO_2 nanoparticles were found to be highly dependent on the type of MnO_2 nanoparticles. The electrode containing villiform-type MnO_2 nanoparticles showed a higher discharge capacity. Power sources with the manganese dioxide cathode catalyst obtained from fluorine containing electrolyte (sample EMD) have 20 % higher capacity in $\text{MnO}_2/\text{air} - \text{Zn}$ system.

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