NANOCOMPOSITE METAL - MANGANESE DIOXIDE CATALYST OF CATHODIC OXYGEN REDUCTION REACTION IN FUEL ELEMENT

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Introduction

For today a wind power and an inflow power, energies of atom, the sun and green plants are alternative to hydrocarbonic power. Hydrogen fuel as the alternative to hydrocarbon raw materials cannot be considered [1]. It is possible to consider hydrogen fuel as a parallel or specific power stream in comparison with hydrocarbon fuel. The increase in a resource of work of fuel hydrogen elements and decrease in their cost remain an actual problem of the present.

Obligatory link of a fuel element is the catalyst of electrochemical reactions, both on the cathode, and on the anode. As the catalyst of cathodic reduction of oxygen some platinum metals are widely used [2, 3]. Replacement of platinum metals by more accessible nanocomposite catalysts is economically and technically important stage.

Theoretical part

Among primary chemical energy sources air-zinc elements [4], in which air oxygen, as well as in a fuel oxygen-hydrogen element, are known as active substance of the cathode serves. In case of the air-zinc element electrodes with the advanced porous surface containing catalysts of reaction are applied to acceleration of some cathodic oxygen reduction reactions. It is known that manganese dioxide, activated coal, organic macrocycles, and silver are well catalysts in this kind of processes. For effective work of an oxygen electrode it is important not only a porous surface of the cathode, but also the developed surface of the catalyst included in it. Having increased catalyst surface, it is possible to increase quantity of the substance reacting in unit time on its surface. Besides it many facts are known that increasing catalytic activity is a direct consequence of increasing in degree of the catalyst fragmentation. It allows explaining falling of ignition temperature and changing of selectivity of the catalyst samples. To receive superfine firm catalysts it is possible several ways. One of them is a synthesis of colloidal solutions of the catalyst by means of chemical condensation [5].

In connection with abovementioned problems of acceleration of cathodic reduction of oxygen it is interesting to use some types of composite catalysts, which version are bimetallic catalysts on the basis of alloys of noble metals [6]. For example, it is very beneficial using of interfaced catalysts on a basis of nanoparticles of platinum and ferric oxide [7]. Thereupon the aim of the presented work is working out nanocomposite catalyst of cathodic oxygen reduction reactions in fuel elements on the basis of a combination of two colloidal fine substances: manganese dioxide and transition or noble metals.

In principal it is possible to synthesize such colloidal fine manganese dioxide by means of oxidation-reduction reaction [8]. Doping colloidal nanosystem of manganese dioxide particles by transition or noble metal atoms one can promote increasing of catalytic activity of manganese dioxide itself. Thus catalytic activity of transition or noble metals in oxidation-reduction reactions is known for a long time.

It is possible to synthesize the mixed catalyst by different way of nanotechnology assemblages, such as joint sedimentation manganese dioxide colloid and metals by means of method of consecutive electrochemical synthesis of specified substances or electrophoretic method.

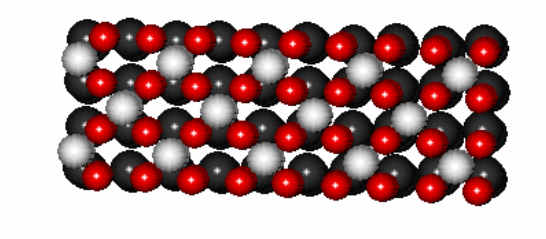
Results and discussion

The first stage of our exploration is devoted comparative analysis well-known crystal chemistry characteristics of manganese dioxide, transition and noble metals. Results of the analysis are sown by list-form at Tab.1.

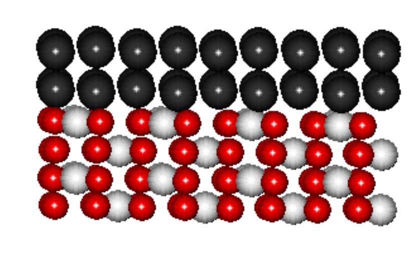
For manganese dioxide five crystal structures are known [9]. Belonging to tetragonal syngony the β-crystal structure is most steadinesses of them. Everything taken under consideration metals belong to cubic syngony. Some calculated parities of cell's key crystal chemistry parameters (for example, a and c) for manganese dioxide and transition metals, and, besides it, the account of diagonals of sides (d) allows to conclude that there is most favorable conformity of structures of metal and manganese dioxide for δ-manganese, cobalt, β-nickel, argentums, and aurums.

The next step is computer modeling of different interface combination of binary nanocomposite catalyst on a basis of nanolayers of manganese dioxide and previous selected transition or noble metals. Obtained by means of original package "Computational Nanotechnology" some results of modeling in particular case of silver - manganese dioxide nanocomposite catalyst interface are displayed on Fig. 1.

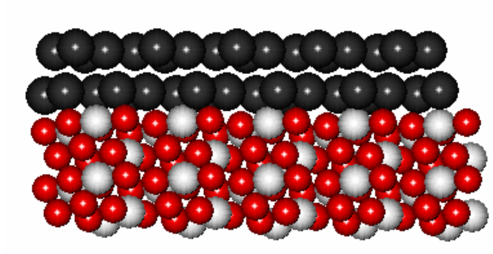
In figures the top view 1 (a) on the part of a manganese dioxide layer and two side views 1 (b), 1(c) on the nanocomposite catalyst's interface are shown. Thus the result of linkage a manganese dioxide layer with plane (110) silver is displayed.



(a)



(b)



(c)

Fig.1. Interface Ag-MnO_2:
(a) – top view; (b) – side view; (c) – side view; symbols black ball – Ag, red ball – O, white ball – Mn.

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Table1. - Crystal chemistry characteristics of substances

№	Substance	Lattice parameters, Å	d face of crystal (Me or MnO_2), Å	$a(MnO_2)/a(Me)$	$d(MnO_2)/a(Me)$	$a(Me)/c(MnO_2)$	$d(Me)/a(MnO_2)$	$d(Me)/c(MnO_2)$
1	β-MnO_2	4.380; 2.856	6.1943	-	-	-	-	-
2	Ag	4.0779	5.7787	1.07	1.52	1.43	1.32	2.02
3	Au	4.0781	5.7673	1.07	1.61	1.43	1.32	2.02
4	Ir	3.8389	5.4290	1.14	1.52	1.34	1.24	1.90
5	Pd	3.8902	5.5016	1.13	1.59	1.36	1.26	1.93
6	Pt	3.9237	5.5489	1.12	1.58	1.37	1.27	1.94
7	Rh	3.8043	5.3801	1.15	1.63	1.33	1.23	1.88
8	Co	3.5442	5.0123	1.24	1.75	1.24	1.14	1.76
9	β-Ni	3.525	4.9851	1.24	1.76	1.23	1.14	1.75
10	γ-Mn	3.8546	5.4512	1.13	1.61	1.35	1.24	1.91
11	δ-Mn	3.0744	4.3479	1.42	2.01	1.08	0.99	1.52

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