NANOCOMPOSITES BASED ON POLYCYCLOPHANOCTOLS AS ELECTRODE MATERIALS OF FUEL CELL

Altshuler H.N.[*], **Malyshenko N.V., Shkurenko G. Yu., Tryasunov B.G.**[(1)], **Ostapova E.V.**
Kemerovo division of Institute of Solid State Chemistry and Mechanochemistry SB RAS,
pr. Sovetsky, 18, Kemerovo, 650099 Russia
[(1)] Kuzbass State Technical University,
Vesennya st., 28, Kemerovo, 650026 Russia
[*]*Fax:+7 (3842) 36 37 66 E-mail: sorbent@kemnet.ru*

Introduction

Creation of highly effective fuel cell is impossible without application of new materials which would be active and selective catalysts in reactions of cathodic oxidation of fuel and anode reduction of oxygen. Highly disperse metals of platinum group, copper, nickel, silver are offered as catalysts of electrode processes. Increase of an overall performance of fuel cell should be promoted by optimum distribution of a liquid and gas in a electrode material, therefore electrode material should have porous structure and should contain hydrophilic fragments in a combination with water-repellented active layers [1]. Network polymers based on metacyclophanoctols are interest as a basis of metallocomposites, suitable for creation of fuel cell electrodes of new generation. Owing to presence of the belt generated by arene fragments, and hydrophilic assistants in metacyclophanoctols, network polymers on their basis at a molecular level combine hydrophilic and waterproof layers in the structure.

The purpose of the given work was research of the oxidation-reduction processes passing with participation of composites based on sulfonated polytetraphenylmetacyclophanoctol (PMC), containing nanoparticles and cations of metals: PMC-Pd^0-H^+; PMC-Pd^0-Cu^{2+}-H^+; PMC-Pd^0-Cu^0-H^+; PMC-Pd^0-Cu^0-Cu^{2+}-H^+; PMC-Pd^0-CuO-Cu^{2+}-H^+; PMC-Pd^0-CuO-Cu^{2+}; PMC-Pd^0-Ag^+-H^+; PMC-Pd^0-Ag^0-Ag^+-H^+.

Results and discussion

Test reactions which simulate the work of fuel cell electrodes of the electrochemical generator are chosen:

for a hydrogen electrode - reaction of creation of aniline by nitrobenzene hydrogenation at presence of PMC-Pd^0

$$3H_2 + C_6H_5NO_2 = C_6H_5NH_2 + H_2O \quad (1)$$

and reduction of copper or silver cations by hydrogen in a polymeric phase

$$H_2 + Cu^{2+} = Cu^0 + 2H^+, \quad (2)$$

$$H_2 + Ag^+ = Ag^0 + 2H^+; \quad (3)$$

for an oxygen electrode - oxidation of metal copper by oxygen in a polymeric phase

$$Cu^0 + ½\, O_2 = CuO. \quad (4)$$

Presence of protons at a polymeric phase promotes course of process

$$CuO + 2H^+ = Cu^{2+} + H_2O. \quad (5)$$

Reactions (1) – (4) were studied at the pressure of gases equal to 1 atmosphere, in 298-365 K interval of temperatures.

Structure of composites was determined by methods of the element analysis, ionic exchange, x-ray dispersion. Content of Pd^o in composites comprises 0,02 g in 1 g of dry polymer. The palladium in all composites according to x-ray dispersion is present only at a zero degree of oxidation. At absence of Pd^o the reactions (1) - (3) do not take place at the given conditions. Possibly, Pd^o in metallopolymer nanocomposite is the catalyst of oxidation - reduction processes (1) - (3).

Initial Cu^{2+} concentration is equal 2,6 mg-eq in 1 g of dry polymer. In connection with passing of reaction (5) copper cations content in a composite after several cycles of reduction and oxidation did not change. Initial concentration Ag^+ - 0.89 mg-eq in 1 g of dry polymer.

Kinetic curves of the oxidation-reduction processes proceeding with participation of nanocomposite, containing a palladium and copper are resulted in figure (*a*). Apparently, speeds of processes of reduction (2) and oxidation (4) are comparable and practically do not decrease with increase in number of reactionary cycles. The process of reduction proceeding with participation of nanocomposite, containing a palladium and silver, is carried out with higher speed, than process of oxidation (figure *b*).

Redox-potentials of suspend electrodes on the basis of PMC-Pd^0, PMC-Pd^0-Cu^0, PMC-Pd^0-CuO, submerged in water solutions of the electrolytes are measured in the environment of argon, oxygen and hydrogen concerning saturated Cl^-/AgCl,Ag electrode.

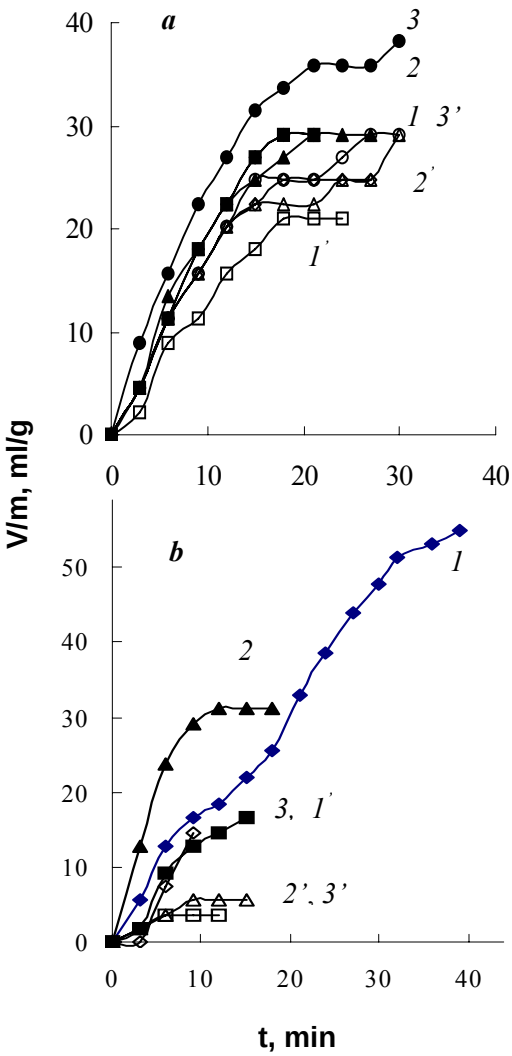

Fig. 1. Dependence of absorption H_2 or O_2 by nanocomposite, containing a palladium and copper (*a*), a palladium and silver (*b*) from time at 353 K. *1, 2, 3* - a serial number of operation of reduction, *1', 2', 3'* - a serial number of operation of oxidation.

Operational characteristics of suspend electrodes containing metallopolymer nanocomposites based on polymetacyclophanoctols are resulted in the Table 1.

Conclusions

Oxidation-reduction reactions with participation of metallocomposites based on polycyclophanoctols, simulating work of fuel cell

Table 1. Operational characteristics of suspend electrodes containing metallopolymer composites on the basis of polymetacyclophanoctols.

Parameter	Nanocomposite	
	PMC-Pd^0-H^+	PMC-Pd^0-Cu^O-Cu^{2+}
Appearance	Spherical grains of dark brown color	
Effective diameter of grain, cm	$(1.0 \pm 0.5)\cdot 10^{-2}$	
Humidity, %	10	
Content Pd^0, g/g	0.02	
Dispersity Pd^0, nm	25±5	
Redox-potential $E^0_{H^+/H_2}$, V	0.596	0.526
Catalytic activity - in reaction (1), mol H_2/min·g Pd	$1.1\cdot 10^{-2}$	
- in reaction (2), mol H_2/min·g Pd	$5.0\cdot 10^{-3}$	
- in reaction (3), mol H_2/min·g Pd	$3.7\cdot 10^{-3}$	
- in reaction (4), mol O_2/min·g Pd		$3.45\cdot 10^{-3}$

are studied. In connection with that in fuel cell an exchange current on an oxygen electrode on some orders below, than on a hydrogen electrode, using of copper containing composites on a polycyclophanoctol matrix, possessing high catalytic activity in reactions of oxidation in the capacity of electrode materials can improve operational characteristics of electrochemical generators.

The authors would like to thank the Russian Foundation for Basic Research for financial supporting of this work (project 07-03-96030).

References

1. Bagotsky V.S. A new electrochemical source of energy. Zhurn. Ross. Khim. Ob-va im. D.I. Mendeleeva. 1971;16(6): 685-690 (in Rusian).