Results of works on creation of new generation fuel cells in Frumkin institute of physical chemistry and electrochemistry

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Intensive works on the creation of fuel cells (FC) are going at least within last 50 years. However up to now the commercialization of FC is insignificant and maintained by investment finance or governmental grants.

Profitable commercialization of FC depends in many instances on their successful competition with traditional power sources (including accumulating systems), motor machines for transport, electric power installations of low and middle power for production of electric energy and heat. This requires permanent improvement of FC and creation of their new generations with high parameters, lower price and convenient in service.

The works carrying out in A. N. Frumkin Instituteof Physical Chemistry and Electrochemistry (IPCE RAS) are concentrated on investigations and optimization of the most widespread low- and middle-temperature FC with working temperature up to 180°C destined for reserve and distributed systems of power supply. The main directions of these works are following:

- decrease of platinum delivery or refuse from its application;
- lowering or virtual elimination of need of special pretreatment of gaseous reagents;
- using hydrogen with CO admixtures;
- replacement of hydrogen by alternative liquid fuel, namely, ethanol (bioethanol).

IPCE RAS possesses necessary equipment and staff for conduction of studies and developments beginning with synthesis of new electrode materials to elaboration and optimization on their basis membrane-electrode assemblies (MEA) with size from 5 to 250 cm^2.

The main stages of these works are:

- synthesis of multicomponent electrocatalytical systems on the basis of organic and inorganic precursors of platinum and base metals;
- structural characterization of nanosystems by the complex of physicochemical methods;
- electrochemical testing activity, selectivity and tolerance of catalytic systems;
- corrosion express-testing of catalysts;
- MEA development and optimization on the basis of perfluorinated, hydrocarbonaceous and polybenzimidasole membranes;
- carrying out life tests of FC.

1. Low-temperature (60 – 80℃) hydrogen-air FC

1.1. Perfluorinated Fumion ® electrolytes and catalysts based on Pt

In low-temperature hydrogen-air FC, membranes and polymer electrolyte of German partner and catalysts based on platinum are used. The relatively low equivalent weight (900) in comparison with Nafion (1000) makes them less moisture-dependent. With the aim of decrease of platinum delivery, in IPCE RAS, the series of bi- and three-metallic catalysts PtM and PtM1M2 (M = Co, Cr, Ni) was developed with specific activity by 2–3 times higher in comparison with commercial monoplatinum catalysts E-TEK и HiSPEC. The synthesis is fulfilled with using cobalt and chromium organic precursors at temperature 850–900°C in rotor furnace Carboline.

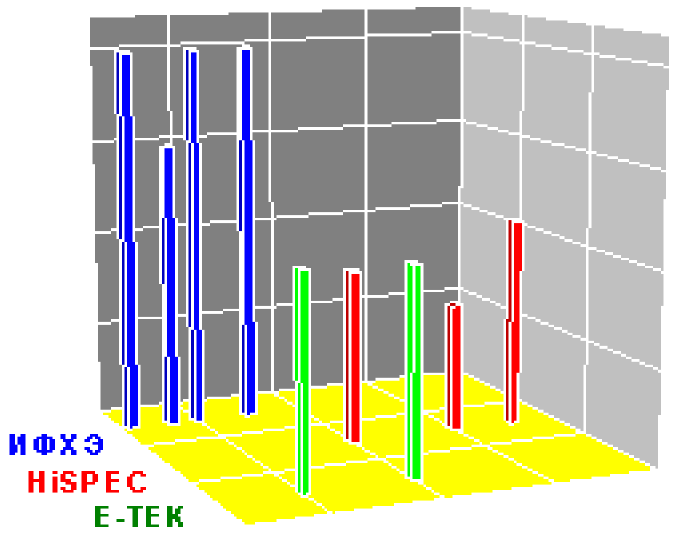

Fig. 1. Comparison of mass activity of PtCoCr catalyst (IPCE RAS) with commercial monoplatinum catalysts in oxygen reduction reaction

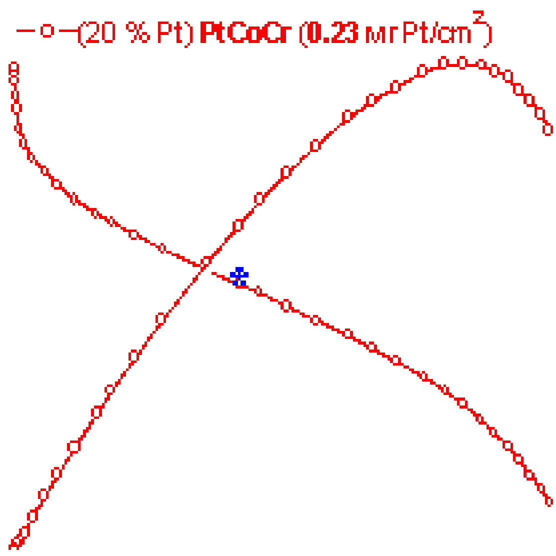

Fig.2. Discharge and specific power curves of hydrogen-air FC, MEA based on F-950 membrane; 65°C

The usage of high temperature synthesis ensures deep alloy-formation (the main phase Pt_3Co) and employment of organic precursors prevents to aggregation of nanoparticles of metallic phase.

The important peculiarity of synthesis is the formation of amorphous carbon which decorates metallic phase nanoparticles. It enhances their stability and results in hydrophobization of catalyst in whole.

Fig 1 represents the comparison of mass activity of three-metallic catalysts of IPCE and commercial catalysts in model conditions (0.5 M H_2SO_4, 60°C, rotating disk electrode, 100 μg/cm^2). As seen, that PtCoCr with 20 wt.%Pt corresponds to activity of 40 wt.%Pt and PtCoCr with 30wt.%Pt to activity of 60–70 wt.%Pt.

The formation of 3-layer MEAs with size of 25 cm^2 was performed by screen print method at EKRA printer and 5-layer MEAs were formed directly in cells which were tested at the stands Electrochem., Arbin, H-Power. It should be noted that in IPCE, MEA optimization method was developed which was based on measurements of electrochemical impedance. The method permits experimentally to distinguish kinetic, transport and ohmic losses.

Fig.2 shows discharge curves of MEAs with 0.4 mg/cm^2 of 40 wt.%Pt HiSPEC catalyst and 0.2 mg Pt/cm^2 of PtCoCr catalyst (IPCE). The discharge curves coincide. Therefore this permits to decrease in 2 times the amount of platinum when the parameters are constant. Life tests confirm the advantage of PtCoCr catalyst with comparison to monoplatinum one.

The usage of hydrogen obtained by reforming of organic fuel requires the tolerance of anodic catalyst to CO and CO_2 admixtures. In IPCE, anodic catalyst PtRuM (M = Co, Ni, Cr) with increased tolerance to CO and CO_2 is being developed.

Table 1. Discharge parameters of hydrogen-air FC with different catalysts without excess pressure at 65°C

Anodic catalyst	UFC at 0.4 A/cm^2	
	100%H_2	90%H_2+10%CO_2+50ppmCO
40wt.%Pt 20wt.%Ru	0.660	0.485
40wt.%Pt20wt.%Ru +5wt.%Co	0.700	0.570

Table 1 presents the data characterizing FC with bimetallic PtRu and three-metallic PtRuCo anodic catalysts in pure hydrogen and hydrogen with CO и CO_2 admixtures. As seen, the introduction of cobalt resulted in significant enhancement of tolerance of anodic catalyst to CO_2 and CO.

1.2. Perfluorinated electrolytes Nafion® and catalysts based on Pd

The works on replacement of platinum electrocatalysts by cheaper metals of platinum group, namely, Pd and Ru, are one of the most important directions of electrochemical science and technology in FC domain. Thereby, it is necessary the worthful level of parameters and high enough corrosion stability. In IPCE, the series of cathodic (PdM (M = Co, Cr)) and anodic (PdM (M=Ru, Mo, Au)) non-platinum catalysts were developed. By their parameters, developed catalysts for the present are inferior to catalysts based on platinum but possess acceptable corrosion stability and anodic catalysts are tolerant to CO and CO_2 admixtures in hydrogen gas. Fig. 3 represents parameters of a number of catalysts based on Pd indicating the significant enchancement of corrosion stability of bi- and three-metallic systems in comparison with palladium. This speaks about their prospectivity for using in FC. At present, in hydrogen-oxygen FC, maximal power 0.26 W/cm^2 was achieved at application of catalysts based on Pd and Nafion 212 membrane.

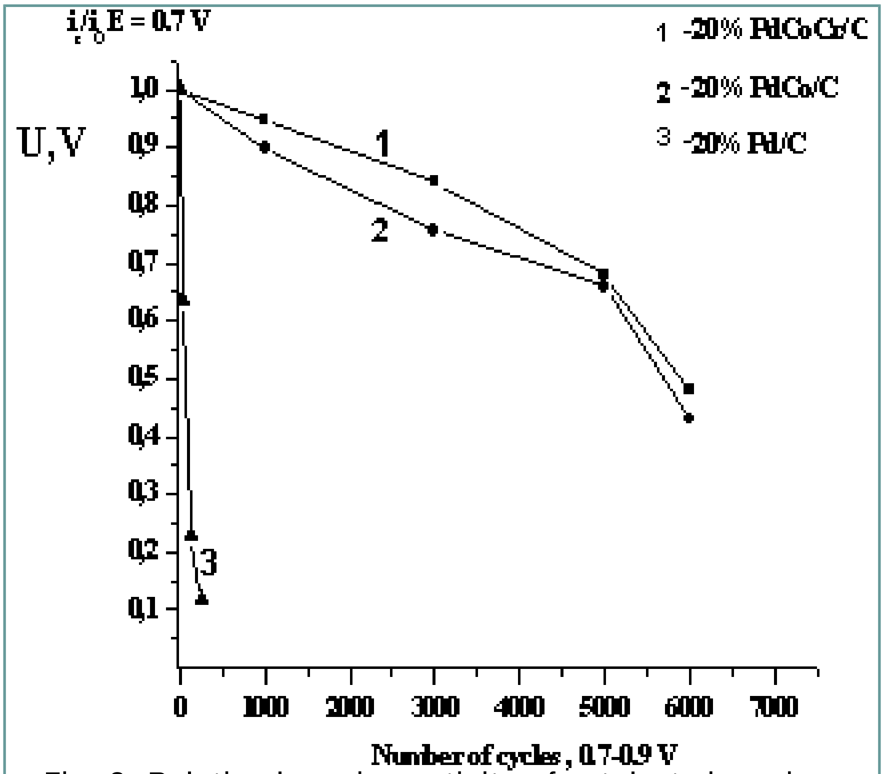

Fig. 3. Relative lowering activity of catalysts based on palladium as a function of number of cycles in potential interval 0.7–0.9 B. 0.5 M H_2SO_4; 20°C

2. Middle-temperature FC with polymer electrolyte based on polybenzimidasole (PBI)

Polybenzimidasoles are large enough polymer group. These polymers differ by high temperature and chemical stability. They withstand the stay in oxidative or reductive atmosphere for a long time at temperature up to 400°C. In studies in IPCE RAS, OM-PBI polymer developed in OOO "NIC"NEP" was used.

The doping of membrane-separators made from this polymer was performed in 85% H_3PO_4 at 140–150°C during 20–30 hours. Acid content in membranes after doping was about 8.5 molecules per one structural unit of polymer. Specific ionic conductivity of polymer at 160°C achieved 10–40 mSm cm^{-1} when high mechanical properties are constant (elastic modulus 75 MPa).

MEAs with working size of 25 $см^2$ were developed and partially optimized with application of commercial gas-diffusion layers (GDL) and platinum catalysts on carbon support.

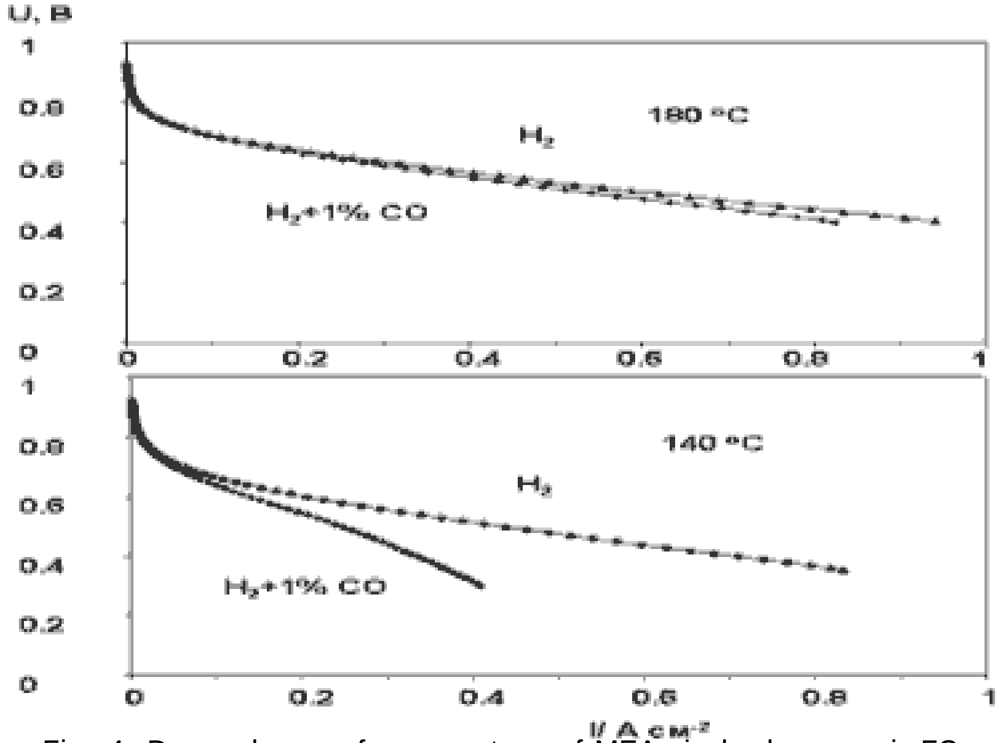

Fig. 4. Dependence of parameters of MEAs in hydrogen-air FC with PBI membrane on temperature and CO admixture in hydrogen gas. Pt content in electrodes is 0,6 mg cm^{-2}

Fig. 4 shows the influence of CO admixture in hydrogen and temperature on MEAs discharge curves

Advantage of FC with working temperature 160–180°C is absence of necessary in moistening of gases and possibility to use hydrogen with significant CO content. The main difficulty in realization of such a FC is the development of polymer electrolyte and MEAs architectonics ensuring the maintenance of phosphoric acid concentration.

3. Fuel cells for direct ethanol oxidation.

Ethanol (bioethanol) is the most prospective reagent as alternative fuel to hydrogen in low-temperature FC. In IPCE RAS, ethanol-air FC are being developed and optimized as on the basis of anion-exchanged and proton-exchanged membranes. For alkaline electrolytes, catalysts RuM (M = Ni, Cr, V) were synthesized. They ensure practically full oxidation of ethanol. A number of cathodic catalysts as platinum and nonplatinum ones highly tolerant to organic fuel was also synthesized. On the basis of perfluorinated and hydrocarbonaceous membranes, FC were developed with anodic Pt_3Sn catalyst and cathodic PtBi catalyst and specific power 60–70 mW/cm^2 at temperature 70°C and alcohol concentration 2 M.

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