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Prospects of Low-Temperature Platinum-free Fuel Cells

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Abstract — Results of research on the development of platinum-free cathode PdM (M = Co or Fe) and anode catalysts PdM (M = Ru, Mo, Au) and RuM (M = Co, Ni, Fe), deposited onto disperse carbon material, are presented. The developed catalysts are shown to be practically feasible for membrane electrode assemblies for low-temperature hydrogen–air and ethanol–air fuel cells. A platinum-free alkaline ethanol–air fuel cell is first developed.

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The potential of the Frumkin Institute of Physical Chemistry and Electrochemistry of the Russian Academy of Sciences in hydrogen energy research is based on deep traditions of basic research formed over more than 70 years of Institute's history. Research into fuel cells has been initiated by Academician A.N. Frumkin who headed the Institute in 1939. The present publication presents the results of activities on the development of platinum-free cathode and anode catalysts and their based membrane electrode assemblies (MEAs) for low-temperature hydrogen–air and ethanol–air fuel cells (FCs).

Fuel cells with working temperatures of up to 200°C relate to the most advanced group of power sources and have various applications (transport, stationary power sources, portable electronic devices), various installed capacitiesy (from μW to MW), and various fuels (hydrogen, liquid hydrocarbons, etc.). According to manufacturer's estimations [1], expanded use of FCs will be possible when their cost will reach $100–200 per kW rated power.

The basic current-forming reactions in low-temperature fuel cells are cathodic reduction of oxygen:

$$O_2 + 4H^+ + 4\bar{e} \rightleftarrows 2H_2O \quad (1)$$

and anode oxidation of hydrogen and simple alcohols:

$$H_2 \rightleftarrows 2H^+ + 2\bar{e}, \quad (2)$$

$$CH_3OH + H_2O \rightleftarrows CO_2 + 6H^+ + 6\bar{e}, \quad (3)$$

$$C_2H_5OH + 3H_2O \rightleftarrows 2CO_2 + 12H^+ + 12\bar{e}. \quad (4)$$

Now platinum and its based systems are considered the most suitable catalysts for these reactions, especially in fuel cells with solid polymeric proton-conducting electrolytes (SPFCs). However, as seen from Table 1, a catalyst can have a reasonable cost determined by the quantity of the catalyst only when a pure hydrogen is used. With a real hydrogen gas obtained by hydrocarbon conversion, the catalyst cost sharply increases, since platinum is poisoned by carbon oxide impurities. The cost of platinum catalysts in case of direct methanol oxidation is especially high.

Palladium is double as abundant in the Earth's crust than platinum and gold [3], and it is one of the most expensive precious metals (Table 2) promising for FC applications. The estimated recoverable resources platinum are about 40000 tons, and those of palladium are 50 times higher [3]. In view of the significant rise in the prices of platinum group metals, major manufacturers of MEAs have recalculated the cost of components (gas diffusion layers, active layers, membranes, and bipolar plates) and stacks for power devices. These data will be published in the near future. However, comparing data in Tables 1 and 2, we can conclude that the share of active layers and

Table 1. Prices of platinum catalyst (E-TEC) per 1 kW SPFC for various fuels [2]

Fuel	Price, Euro/kW
H_2, pure	45
H_2, decomposition of methanol	1000–2000
H_2, decomposition of propanol	1000–5000
CH_3OH in SPFC	~20000

Table 2. Abundances of precious metals [3] and their cost [4]

Metal	Abundance in the Earth's crust, wt %	Cost, USD/year	
		January 2006	May 2006
Au	4.3×10^{-7}	16.1	16.8
Pt	5.0×10^{-7}	33.6	39.3
Pd	1.0×10^{-6}	9.2	12.4
Rh	1.0×10^{-7}	128.3	160.7
Ir	1.0×10^{-7}	6.4	11.9
Ru	5.0×10^{-7}	2.8	5.6

precious metal catalysts in the cost MEAs and FCs as a whole has sharply increased. This circumstances makes research into replacement of platinum catalysts still more urgent.

No one of individual metals is capable of replacing platinum because of kinetic or corrosion restrictions, especially in acid electrolytes. Therefore, a general solution of the task to lower consumption of platinum or its full replacement can be provided by the synthesis of binary systems PtM, PdM, and RuM (M = Ni, Co, Fe, Cr, W, etc.). The IPCE RAS is working in both these directions. The present paper focuses on prospects for development of platinum-free low-temperature fuel cells.

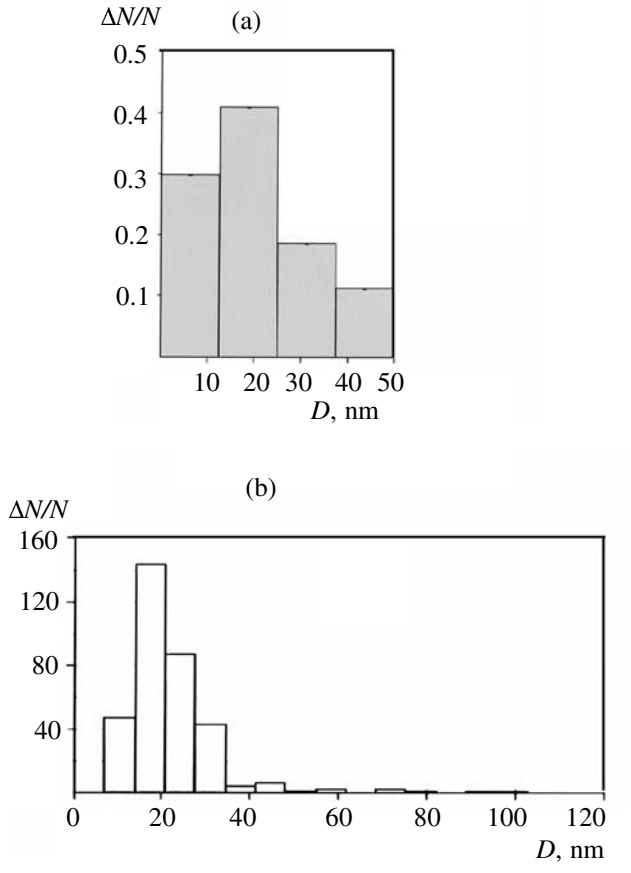

Fig. 1. Histograms of particle-size distribution for catalysts on XC72: (a) PdCo (50 : 50) and (b) PdFe (75 : 25).

HYDROGEN–OXYGEN (AIR) FUEL CELL

In low-temperature (up to 90°C) hydrogen–air FCs, the oxygen reaction is limiting, and it is achievement of appropriate cathode characteristics which is responsible for the greatest consumption of platinum catalysts. Sovadogo et al. [5] in their basic work provided evidence for the utility of Pd alloys as binary catalysts for cathode reduction of oxygen. Cobalt, iron, and chromium are perspective components of binary systems PdM for electrolytic reduction of O_2. We developed a method of high-temperature synthesis of binary Pd-containing catalysts on a disperse support. Organic precursors on XC72 soot were used to synthesize nanosized PdCo [6] and PdFe systems comparing in electrocatalytic activity with platinum catalysts and possessing acceptable corrosion resistance. Figure 1 shows the histograms of particle-size distribution for PdCo/C and PdFe/C catalysts. These systems feature wide particle-size distributions peaking nearly 15–20 nm.

Analysis of structural data points to alloy formation in both cases, the concentrations of cobalt and iron in the alloys with palladium are 10–15 at %. The polarization oxygen reduction curves measured on a rotating disk electrode (RDE) and a rotating ring–disk electrode (RRDE) for binary systems PdM and a platinum catalyst point to similar cathode oxygen reduction mechanisms. In case of binary catalysts PdM, the slope of the polarization curve becomes sharper ($\partial E/\partial \log I$) at more negative potentials compared to deposited platinum. This makes the discharge curves for FCs with Pt and PdM cathodes to come closer together at potentials below 0.6 V.

Selectivity measurements for the electrochemical reduction of oxygen to water on RRDEs with binary catalysts [7] showed that in the practically important potential range 0.8–0.5 V the percentage of hydrogen peroxide in the solution does not exceed 5%.

Corrosion testing the PdCo/C system in sulfuric acid for 200 h revealed a good stability of the catalyst and preservation of its catalytic activity. Figure 2 compares data on the change of the catalytic activity of PdCo on XC72 soot on acid treatment. With increasing duration of corrosion testing, the specific

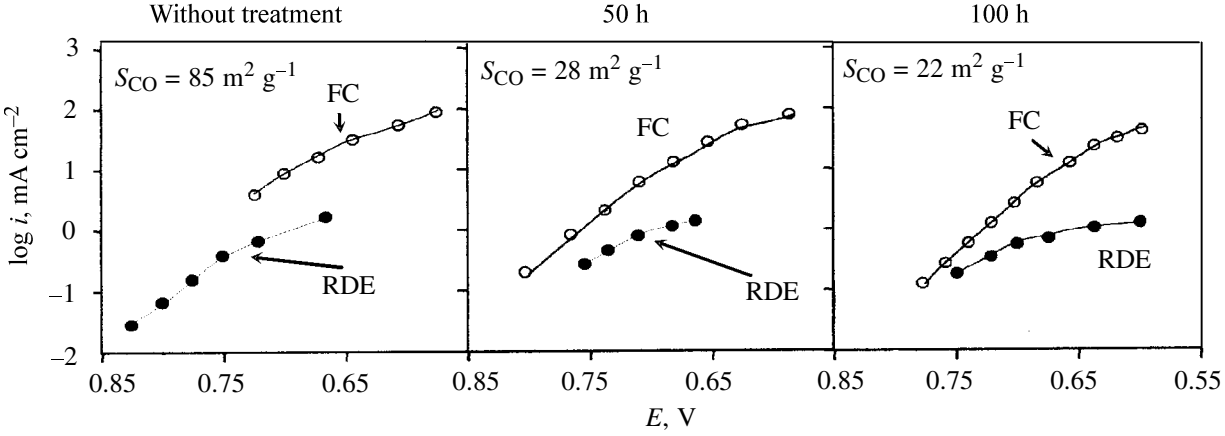

Fig. 2. Effect of the duration of acid treatment on the electrocatalytic activity of the PdCo/C catalyst in a FC cathode and on an RDE.

surface of the metal phase, according to CO oxidative desorption data, tends to slightly decrease. This is caused by dissolution of nonalloyed palladium. Therewith, the activity of the catalyst (RDE) and electrodes on its basis (FC) changes only slightly.

Anode binary catalysts on the basis of palladium are more resistant to poisoning with impurities in the hydrogen gas obtained from organic fuels. After standard purification, the hydrogen gas contains 50–150 ppm of CO and 20–70 vol% of CO_2.

Figure 3 shows the poisonous effect of carbon oxides (70 ppm of CO or 20 vol% of CO_2) on the characteristics hydrogen–air FCs with an E-TEC commercial Pt/C catalyst. To develop a platinum-free catalyst resistant to CO poisoning, three binary palladium systems PdRu, PdMo, and PdAu were synthesized and studied at the ICPE RAS [8]. Table 3 lists metal particle sizes (by X-ray diffraction and X-ray photoelectron spectroscopy) are presented and data on the effect of CO on the exchange current of the hydrogen reaction (by electrochemical impedance spectroscopy, 0.5 M H_2SO_4, 60°C) on palladium catalysts in comparison with the E-TEC platinum catalyst. The exchange current of the hydrogen reaction with binary systems is slightly lower than with platinum, and they are much more resistant to poisoning. The reasons for the enhanced CO resistance of palladium-containing binary systems could be explained on the basis of a combined structural and electrochemical research. Alloy formation in the PdRu system facilitates oxidative desorption of CO. At a 1:1 Pd:Ru atomic ratio, the CO desorption peak potential shifts to the negative range by more than 0.4 V, which attenuates the sensitivity to CO (Fig. 4).

In the PdMo system, no alloy formation takes place, and palladium particles are decorated by molybdenum oxide. Like with PtMo [9], the accelerated oxidation of adsorbed CO is caused by functioning the Mo_4 + /Mo_6 + couple. The alloy formation and decoration of palladium with gold nanoparticles sharply decrease the quantity of adsorbed CO, since the maximum CO absorptivity on Au is no higher than 0.2.

It is the strong adsorption of CO and CO_2 in the vicinity of the equilibrium hydrogen potential on platinum leads to poisoning of the latter, when contaminated hydrogen is used in FCs. Unlike platinum, palladium does not adsorb CO_2 [10], which was confirmed by electrochemical impedance spectroscopy. The PdRu system effectively replaces platinum on operation with hydrogen contaminated carbon oxides. With an XC72 + PdRu anode catalyst, CO impurities

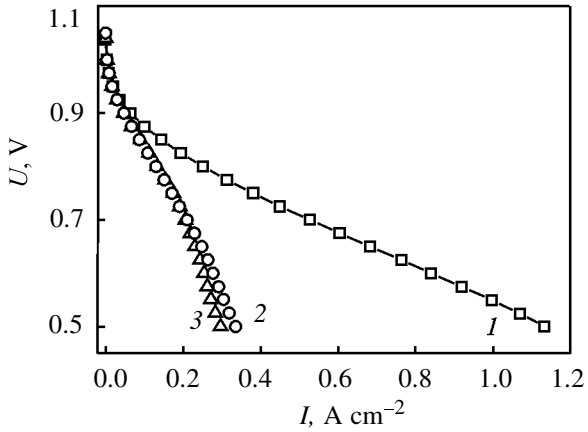

Fig. 3. Discharge curves of a hydrogen–air FC with hydrogen of various purity: Nafion-117 membrane, E-TEK platinum catalyst, 80°C; (*1*) H_2; (*2*) H_2 + 70 ppm CO; and (*3*) H_2 + 20 vol% CO_2.

Table 3. Structural characteristics and oxidation parameters of pure hydrogen and hydrogen with CO admixture on various catalysts synthesized on soot. Metal content 20 wt %

Catalyst	Phase	Particle size, nm	$i_0^{H_2}$, A g^{-1} metal	$i_0^{H_2+CO}/i_0^{H_2}$
Pt (E-TEC)	Pt	2.8	4400	0.24 (226 ppm)[a]
PdRu (50:50)	Alloy, Pd, Ru	3–5	1476	0.50 (500 ppm)
PdMo (70:30)	Pd	14–18	1570	0.55 (500 ppm)
PdAu (70:30)	Alloy, Au, Pd	6.0	1640	0.60 (500 ppm)

[a] Parenthesized are CO contents in hydrogen.

Table 4. Properties of various catalytic systems for alcohol electrooxidation. Metal content 20 wt %, support XC72 soot

Catalytic system	Average particle size, nm	Specific activity (A g^{-1} cat.)[a] and optimal composition for oxidation		
		CH_3OH	C_2H_5OH	$C_3H_5(OH)_3$
Pt, E-TEC	3–4	70	1.5	29
Ru	4–8	1.5	3.0	35
Pd	6–14	15	–	–
PtRu, E-TEC	3–5	68 (50:50)	–	–
PdRu	4–6	38 (50:50)	10 (50:50)	–
RuCo	6	2 (84:16)	18 (84:16)	30 (84:16)
RuNi	2.5–3,5	1.9 (68:32)	21 (68:32)	57 (92:8)
RuFe	4–6	2.9 (80:20)	16 (84:16)	20 (84:16)
RuFePd	7–8	19.5 (78:18:4)	22 (78:18:4)	–

[a] Activity was measures at E 0.43 V; electrolyte 8 M KOH + 4 M alcohol; 60°C.

in hydrogen only slightly impair FC characteristics. The development of binary catalysts on the basis of palladium initiated activities on development of a platinum-free FC. As a result, MEAs were designed and partially optimized in FC prototypes.

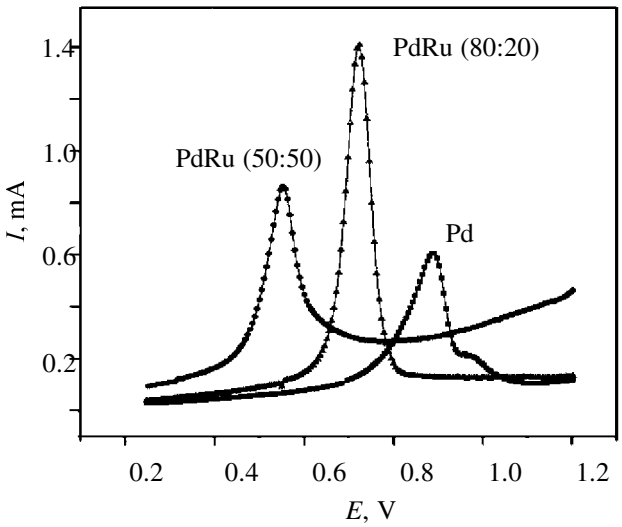

Fig. 4. Voltage–current CO desorption curves for catalysts deposited on XC72: 0.5 M H_2SO_4; 60°C. Values in parentheses are the metal atomic ratios.

ETHANOL–OXYGEN (AIR) FUEL CELL

Application of alkaline electrolytes allows extension of the range of metals suitable for platinum-free binary catalytic systems. This is caused by milder, in terms of corrosion, conditions and acceleration of the cathode reduction of oxygen of [11] and simple alcohols [12] in alkaline electrolytes in comparison with acidic. The example of electrooxidation of three alcohols: methanol, ethanol, and glycerol, was used at the ICPE RAS to demonstrate for the first time the effective use of binary systems RuM, where M = Pd, Fe, Co and Ni. Nanosized catalysts active in the oxidation of alcohols could be synthesized by thermochemical methods (Table 4).

The most important results were obtained with the electrooxidation of ethanol. Ethanol is a promising liquid fuel for direct oxidation in low-temperature FCs. Its specific energy is 8.05 kW kg^{-1} against 6.1 kW kg^{-1} for methanol. Ethanol is ecologically safe, and it is produced from biologically renewable raw materials. The key problem in the realization of effective ethanol oxidation is to develop electrocatalytic systems providing C–C bond cleavage and high

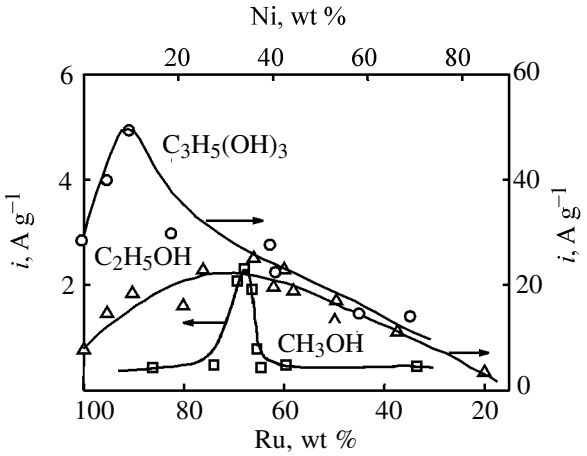

Fig. 5. Effect of the metal atomic ratio of the catalytic activity in alcohol oxidation. Catalyst 20 wt% RuNi on XC72; 60°C; E 0.43 V; 8 M KOH + 4 M alcohol.

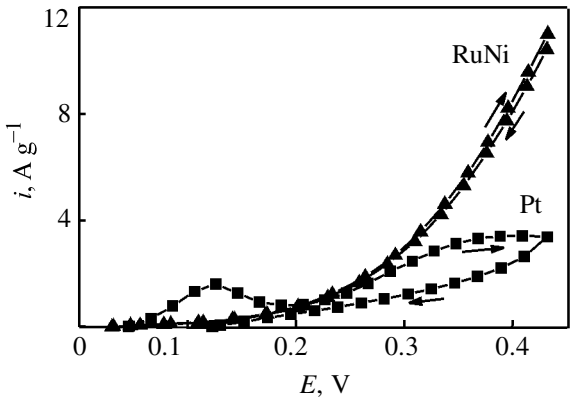

Fig. 6. Polarization ethanol oxidation curves: 60°C; 4 M KOH + 4 M C_2H_5OH; catalysts 20 wt% Pt and 20 wt% RuNi (68 : 32) on XC72.

Faraday's alcohol oxidation factors. In the case of platinum catalysts, the final reaction products in acid solutions and in SPFCs are acetaldehyde or acetic acid [13]. The yield of CO_2 does not exceed 5% [14]. Thus, the Faraday's ethanol utilization factor for an SPFC does not exceed 30%. Therewith, the acetic acid formed is strongly adsorbed and poisons the catalyst. In alkaline electrolytes, the use of catalysts RuM (M = Ni, Fe, Co) [15] provides an essentially deeper ethanol oxidation and, under optimal operating conditions of the anode in an alkaline FC, the Faraday's factor is 70–80%. Table 5 gives typical results of the chromatographic determination of the yield of CO_2 during operation of an alcohol anode in an alkaline FC.

The dependence of the rate of alcohol oxidation on the Ru : M ratio for Fe-, Co-, and Ni-containing systems is a peaked curve. The optimal compositions of the catalytic systems are listed in Table 4 (in parentheses). Figure 5 depicts, as an example, data for the RuNi system. Compared to platinum, the latter system not only provides faster reaction with ethanol, but also qualitatively changes the character of the polarization curve: hysteresis disappears and the current density in the practically important potential range increases (Fig. 6).

According to X-ray diffraction and X-ray photoelectron spectral data, alloys formation scarcely occurs in RuM systems (M = Ni, Co, Fe) under the chosen synthesis conditions. Nanoparticles are decorated by oxides, specifically nickel oxide. Nickel functions to disperse ruthenium and, probably, to facilitate C–C bond cleavage. The highest activity, depending on the structure of the catalyst, is observed at an optimum dehydrogenation, C–C bond cleavage, and fragment afteroxidation rate ratio.

Figure 7 gives a scheme of the MEA in an ethanol–air FC, with the electrode surface area 10 cm^2. The two-layer hydrophobized cathode made of acetylene soot [16] is promoted by a CoN_4 system [17] tolerant to ethanol. The RuNi binary system synthesized on XC72 soot [15] was used on the anode. A necessary element of the MEA design is a polybenzimidazole (PBI) composite membrane formed on the anode surface and separating the circulating alkaline electrolyte (8 M KOH) and fuel mixture (4 M aqueous ethanol). For operation with this fuel mixture, PBI should also be introduced, as a polymeric electrolyte, in the anode.

Even though the cathode catalyst is resistant to ethanol, the penetration of the latter to the cathode can render it inoperative. Rigid requirements for the separating membrane prompted special research on its optimization. Electroconductivity (σ, S cm^{-1}) and alcohol permeability (DK, cm^2 s^{-1}) are two the most important characteristics of a polymer membrane, which determine its efficiency in a direct ethanol FC. As the integral characteristic of a membrane one can

Table 5. Electrooxidation of 3 M ethanol on an anode with a RuNi catalyst

E, V (RHE)[a]	I, A	Q, C	Yield of CO_2, %
0.40	0.38	1410	34.0
0.30	0.18	1430	53.0

[a] Electrolyte 8 M KOH; 75°C.

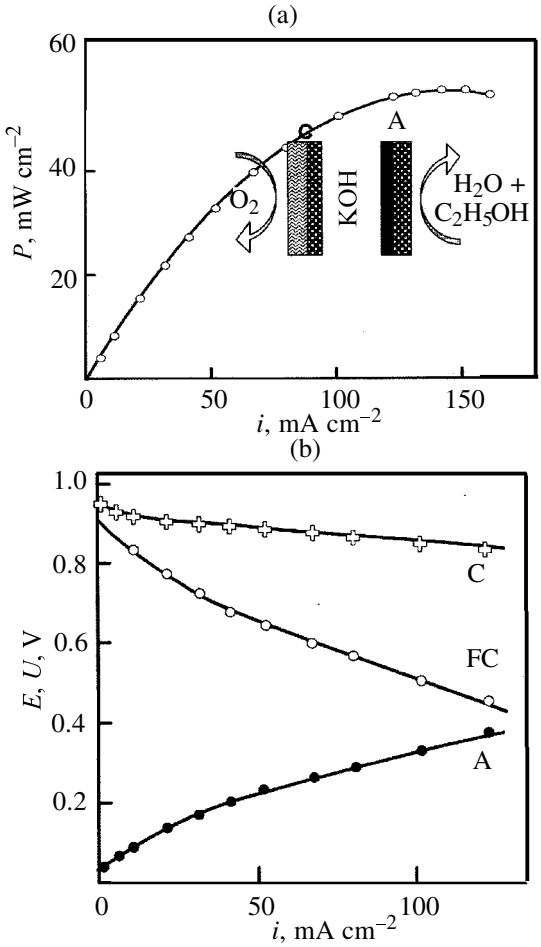

Fig. 7. Characterisitcs of an ethanol–air fuel cell with a composite PBI membrane: (a) scheme of MEA and specific power of FC in 8 M KOH + 4 M C_2H_5OH; cathode CoN_4/C; anode RuNi (68 : 32)/C; and (b) plot of cathode and anode potentials and TC voltage vs. current density.

use the ratio $\varphi = \sigma/DK$ [18]. The higher φ, the more suitable is the given polymer. Polybenzimidazole doped with alkali is preferred over Nafion.

Partial optimization of the anode/membrane assembly allowed fairly high characteristics to be attained at a moderate temperature (60°C). At the current density of 150 mA cm^{-2} (Fig. 7), the specific capacity is 60 mW cm^{-2}. At a continuous (~150 h) discharge of a 2.5-W prototype charging device, the Faraday's ethanol utilization factor was about 80%.

CONCLUSION

Over the last two years a real possibility for the creation of effective substitutes of platinum in low-temperature FCs has been demonstrated at the IPCE RAS. The hydrogen-air solid polymer fuel cells with palladium-containing catalysts and ethanol–air alkaline FCs have been prototyped for the first time and are still unprecedented.

The presented data have grown out of efforts of a big team of researchers to whom the authors bring their sincere and profound gratitude. We should also express gratitude to the organizations which have shown interest and supported these works: Presidium of the Russian Academy of Sciences, "GMK Noril'skii nickel" OJSC; Independent Power Technologies JSC, BMBF (Germany, "Effective Oxygen Reduction for Electrochemical Energy Conversion" Network Program), NEDO (Japan, International Cooperation Research Program for Energy and Environmental Protection).

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