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Electrocatalysis of anodic oxidation of ethanol

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Abstract. The results of fundamental and applied studies in the field of electrocatalysis of anodic oxidation of ethanol in fuel cells are considered. Features of the mechanism of ethanol electrooxidation are discussed as well as the structure and electrochemical properties of the most widely used catalysts of this process. The prospects of further studies of direct ethanol fuel cells with alkaline and acidic electrolytes are outlined. The bibliography includes 166 references.

I. Introduction

In recent years, the number of studies devoted to low-temperature fuel cells (FC) has increased; among these, a leading position belongs to the design of FC with direct oxidation of liquid organic fuels, particularly, aliphatic alcohols. The development of direct ethanol fuel cells appears to be the most promising firld. The direct ethanol fuel cells have the following advantages over FC operating on hydrogen fuel:

— since ethanol can be reproduced by biological systems in unlimited amount, it is possible to arrange an environmentally clean cycle of energy conversion;

— insofar as ethanol is used in some countries as a component of engine fuel, the already existing infrastructure of supply and distribution of liquid ethanol can be used.

The overall equation of ethanol electrooxidation is as follows:

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$$C_2H_5OH + 3H_2O \xrightarrow{pH < 7} 2CO_2 + 12e + 12H^+ \quad (1)$$

$$C_2H_5OH + 16HO^- \xrightarrow{pH > 7} 2CO_3^{2-} + 12e + 11H_2O \quad (2)$$

However, complete transformation of ethanol with the transfer of 12 electrons is never reached in practice. As a rule, at low temperatures, the reaction proceeds with preferential formation of incomplete combustion products, namely, acetaldehyde and acetic acid, in addition to a small amount of CO_2.

The central problem in improving the performance of direct ethanol FC is to attain stably high rates and completeness of the anodic process. The main factors determining these characteristics include the catalyst phase composition, the type of support and also parameters of the FC operation mode. To elaborate approaches towards development and optimization of catalysts, it is essential to study the kinetics of alcohol oxidation. Furthermore, it should be borne in mind that electrolyte pH has a substantial effect on the kinetics and mechanism of this process and, correspondingly, on the selection of the electrocatalyst.

Recently, the studies on the development of direct ethanol FC (below called simply ethanol FC) with both proton-conducting (acidic) polymer electrolytes and various types of alkaline electrolytes have been developed. These studies rely on the results of fundamental works on ethanol electrooxidation in the corresponding media. Note that back in the 1960s, when the studies in the field of alcohol FC were just started, the equal attention was paid to reactions of ethanol electrooxidation in acidic and alkaline electrolytes.[1–3] At present, a competitive FC of direct ethanol oxidation holds much promise due to the actively developing studies of anodic electrocatalysts and also as a result of development of corrosion resistant polymer electrolytes with high ionic conductivity.

Reviews devoted to the use of ethanol as a fuel usually embrace problems of the development of FC with either acidic[4] or alkaline electrolytes[5] without detailed comparative analysis. A recent review[6] devoted to the electrooxidation mechanism of ethanol (as one of C_2 alcohols) contains

neither the information on the preparation and investigation of practically important electrocatalysts nor the FC characteristics.

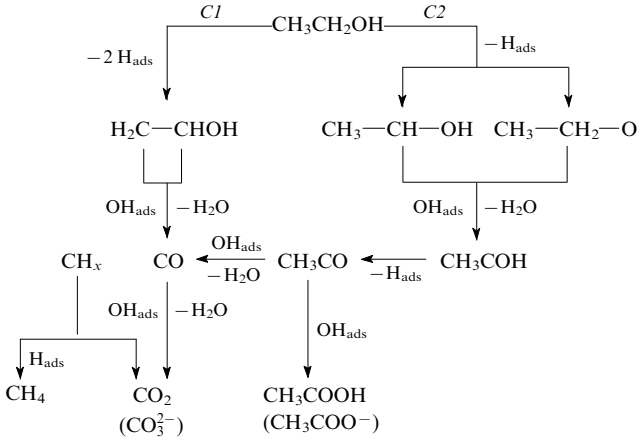
In the present review, the results of studies of ethanol electrooxidation both under model conditions and within a membrane–electrode assembly of a fuel cell are discussed and the reaction mechanisms in acidic and alkaline media are compared; also, the characteristics attained in FC with acidic and alkaline electrolytes are considered. The data on the ethanol electrooxidation obtained in the A N Frumkin Institute of Physical Chemistry and Electrochemistry of the Russian Academy of Sciences are analyzed together with information characterizing the state of the art in this field.

II. Specific features of the mechanism of ethanol electrooxidation

To date, a considerable volume of data has been accumulated on ethanol electrooxidation where platinum is used as the main electrode material.[6–14] When ethanol molecules interact with the platinum catalyst surface, various destruction processes occur (dehydrogenation, destruction of the molecule at the C–C bond and hydrogenation) to form a layer of adsorbed species of heterogeneous composition, which provides the formation of various electroxidation products. When studying ethanol chemisorption and electrooxidation, in view of the complex nature of these processes, in addition to electrochemical methods, it is necessary to invoke analytical techniques (particularly, gas and liquid chromatography) and certain physicochemical methods for analyzing the adsorbate composition.[6, 15, 16]

Scheme 1 illustrates the general multi-stage mechanism of ethanol oxidation under steady-state conditions in aqueous solutions of acidic and alkaline electrolytes.

Scheme 1



Since the C–C bond cleavage does not occur in all adsorbed species, the electrooxidation process represents a combination of sequential and parallel reactions to afford one- (pathway *C1*) and two-carbon products (pathway *C2*). Moreover, acetaldehyde formed in pathway *C2* can be further oxidized to CO_2.

Note that stages of dehydrogenation of ethanol and its chemisorption products involve oxygen-containing species (OH_{ads}).[9] At temperatures below 180–200 °C, partial reaction to form acetic acid represents a dead end.[11] According to certain data,[17] acetic acid is strongly adsorbed and blocks the active sites of platinum.

The rate and selectivity of ethanol oxidation are largely determined at the stage of chemisorption of alcohol molecules. In the study of ethanol adsorption and electrooxidation, an important role is played by measurements carried out upon bringing the substance into contact with the catalyst.[18–20] Under potentiostatic conditions, this is associated with measuring the non-steady-state current of ionization of hydrogen adatoms abstracted from an ethanol molecule upon its dehydrogenation. The formation of hydrogen upon dehydrogenation of organic compounds was experimentally observed for chemisorption processes on platinum,[2] palladium,[3] rhodium[19] and other platinum group metals. The current decreases as the electrode surface is being covered by organic species. In the initial period, the overall rate of substance electrooxidation is determined by the adsorption stage, whereas under steady-state conditions, it is determined by the stage of the removal of products.[20] When ethanol is brought into contact with the electrode at open circuit, the potential shifts to lower values down to the potential of the reversible hydrogen electrode (RHE). Then, due to hydrogenation of adsorbed species to form various hydrocarbons, the potential can shift to more positive values.[21]

Analysis of composition of ethanol chemisorption products and also of the mechanism of its further transformations is still an unsolved task in many aspects; moreover, the simultaneous consideration of literature data is complicated due to the use of different experimental techniques. The modern views on the mechanism of ethanol chemisorption are based on the results obtained by vibrational spectroscopy *in situ* (Table 1) and also by differential electrochemical mass spectrometry (DEMS). The latter technique provides indirect information on the adsorbate composition based on determination of volatile products of adsorbate reduction (methane and ethane) or oxidation (CO_2, acetaldehyde). Note that acetic acid, being the heavier oxidation product of ethanol, cannot be detected by DEMS; however, its formation rate can be determined by comparing the overall faradaic current with the partial rates of formation of all reaction products.[24] Among spectroscopic methods, the Fourier transform infrared spectroscopy (FTIRS) was applied widely. Together with DEMS,[25] this method made it possible to determine the major types of ethanol chemisorption products as far back as at the turn of the 1980s and 1990s. Later, the results obtained were refined and supplemented by the data acquired by surface enhanced Raman spectroscopy (SERS),[22] which simplifies the analysis of vibrational modes with frequencies $< 700\ cm^{-1}$ as compared with the FTIRS method. The sum-frequency generation spectroscopy (SFG) is also an efficient method to study adsorption.[16, 26, 27]

It was shown that ethanol adsorbs on the platinum surface by the oxygen atom of the OH group and also by the α-C atom (see Scheme 1). Based on the results of X-ray photoelectron spectroscopy, it was found[15] that on the Pt(111) surface, pure ethanol in the liquid phase is preferentially adsorbed through the oxygen atom (to form the ethoxy group). The presence of $CH_3CH_2O_{ads}$ as the main ethanol chemisorption product on the Pd(111) electrode was directly observed by high-resolution electron energy loss spectroscopy (HREELS).[28] At the same time, several authors assumed that in the first stage of ethanol adsorption, the hydrogen atom is abstracted from the α-C atom of the alcohol molecule to form the $CH_3–CHOH$ species. This

Table 1. Main types of ethanol chemisorption products on platinum in aqueous solutions according to data of various methods.[16, 17, 22, 23]

Method	Functional group or species	ν /cm^{-1} (see [a])	Potential range /V
SERS	CH_x	425	0.1 – 0.45
	CO (linear form)	500	0.1 – 0.7
FTIR	C – C – O (acetaldehyde mode)	933	0.3 – 1.0
	COOH (CO vibrations + OH distortion)	1280	0.6 – 1.0
SPAIRS, FTIR	CH_3 (distortion in acetaldehyde)	1355	0.1 – 0.9
SPAIRS	COOH (CH_3 distortion in acetic acid)	1385	0.1 – 0.9
SPAIRS, FTIR, ATR-SEIRAS	OCO (vibrations of adsorbed acetate ion)	1396 – 1420	0.2 – 0.9
ATR-SEIRAS	C=O (bond vibrations in adsorbed acetaldehyde and acetyl group)	1620 – 1635	−0.1 – 1.0
SPAIRS, FTIR	COOH or CHO (C=O vibrations)	1713	0.1 – 0.9
SPAIRS, FTIR, ATR-SEIRAS	CO (bridging form)		
SPAIRS, FTIR, ATR-SEIRAS, SERS	CO (linear form)	2050 – 2075	0.1 – 1.0
SPAIRS	O – C – O (asymmetrical vibrations)	2341	0.1 – 0.9

Notes. The following designations are used: SPAIRS is single potential alteration infrared spectroscopy, ATR-SEIRAS is attenuated total reflection surface enhanced infrared absorption spectroscopy; the rest abbreviations are explained in the text. [a] Frequency (IR), Raman displacement (SERS).

conclusion was made based on the results of DEMS studies which involved the use of tracers[29] and was indirectly confirmed by the weak adsorption of branched alcohols as compared with normal isomers.[30] It is generally accepted that the cleavage of the C – C bond is preceded by dehydrogenation of adsorbates to form acetaldehyde or an acetyl group (see Table 1, frequency range of 1396 – 1420 cm^{-1}). Note that acetaldehyde is characterized by lower energy of C – C bond cleavage as compared with ethanol.[14, 22]

In several publications,[9, 31, 32] various bridging species were proposed as intermediates of the formation of one-carbon products; nonetheless, they could not be detected by *in situ* methods. Acetic acid as the oxidation product of acetyl along pathway *C2* (see Scheme 1) is mainly detected by the OCO (ν = 1396 – 1420 cm^{-1}) and COOH or CHO modes (ν = 1713 cm^{-1}). As products of C – C bond cleavage, the CO-like adsorbates (CO_{ads}) and CH_x species were reliably detected.[22] It should be stressed that the term 'CO-like adsorbates' is conditional because even CO adsorption gives species of various compositions,[33] which are generally detected at potentials > 0.1 V due to the blocking effect of adsorbed hydrogen (H_{ads}) at lower potentials.[34] In the potential range of 0.2 – 0.6 V, the main part of CO_{ads} species (in both linear and bridging form) contain an α-C atom and, hence, they are dehydrogenation products of the CH_2OH fragment of the ethanol molecule. The species CH_x formed by the β-C atom can be either oxidized to CO_{ads} as the potential increases to 0.45 V (acidic medium)[22] or reduced to methane at potentials < 0.2 V.[35] Note that in an alkaline medium on polycrystalline platinum, the potential of the onset of β-CO_{ads} formation is shifted far in the positive direction as compared with the analogous value for the acidic medium.[26, 27]

The regularities of ethanol adsorption and electrooxidation mechanism are determined by several factors among which mention should be made of electrolyte pH, parameters of electrode polarization, the catalyst phase composition and characteristics of its microstructure. Figure 1 shows the typical potentiodynamic voltammograms of ethanol electrooxidation recorded on platinum in acidic and alkaline electrolytes. It is noteworthy that at potentials below 0.7 – 0.8 V, the current in the anodic branch is higher in the alkaline medium than in acidic medium. In a wide potential range, the curve is characterized by a considerable hysteresis; moreover, the cyclic voltammogram (CV) demonstrates three current peaks in the acidic medium and two peaks in the alkaline medium. It was shown[36, 37] that the regions of inhibition of electrooxidation of organic compounds mainly coincide with the oxygen adsorption regions in the supporting electrolyte solution. Moreover, on the RHE scale, the potentials of maxima and minima are independent of pH and depend little on the presence of oxygen-containing anions (SO_4^{2-}, ClO_4^-, *etc.*[38, 39]) in the electrolyte.

In the studies of oxidation of simple organic compounds, particularly, methanol, the ratio of the heights of current peaks in the forward (anodic) and reverse (cathodic) CV scans $\left(i_a^{max}/i_c^{max}\right)$ in the potential range of < 1 V is often considered as the preliminary indication of catalyst stability with respect to the poisoning action of intermedi-

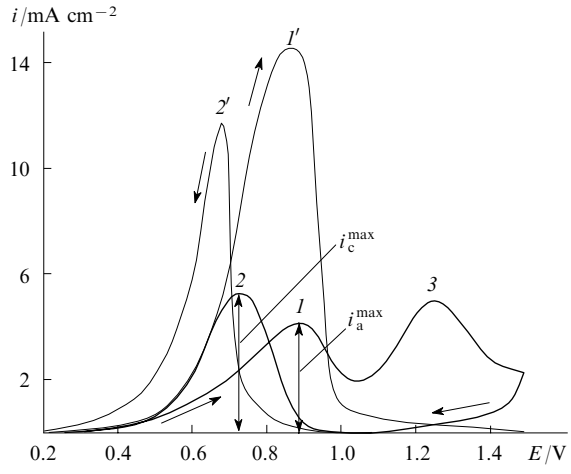


Figure 1. Cyclic voltammograms of ethanol oxidation in acidic (*1* – *3*) and alkaline (*1′*, *2′*) media.[14]
0.5 M EtOH solution, potential scan rate w = 50 mV s^{-1}, T = 20 °C. Arrows indicate the potential scan direction.

ates and also of the attained selectivity of this process with respect to CO_2.[40] It is assumed that the peak in the reverse scan corresponds to oxidation of organic adsorbates formed in the forward scan. Correspondingly, a higher ratio i_a^{max}/i_c^{max} points to the good tolerance of the catalyst to strongly chemisorbed substances and to a relatively high yield of CO_2. Moreover, these conclusions correspond to conditions far removed from the steady state and sometimes depend on the scan rate and cycling limits. It should be noted that for ethanol oxidation, the above approach appears to be insufficiently correct, because a part of formed adsorbed species fail to be oxidized to CO_2 at low temperature. Furthermore, the height of peaks 2 and 2′ in Fig. 1 also depends on the possibility of reduction of oxides formed on the catalyst surface at high anodic potentials.

The composition of ethanol eletrooxidation products on platinum in various potential regions was studied by the DEMS and *in situ* spectroscopic methods (Table 2), which made it possible to plot partial polarization curves of product formation. To avoid the repetition of close results, the table shows the data obtained on platinum by varying experimental conditions and catalyst composition. The partial curves of the formation of acetic acid and acetaldehyde have maxima, which are, most often, located similarly with respect to the overall current peaks (see Fig. 1). Carbon dioxide is detected mainly in the CV anodic scan. The partial curve of CO_2 formation in both acidic and alkaline electrolytes passes through a maximum located approximately in the same potential range as the maximum in the CV anodic scan. Also, methane is detected resulting from both hydrogenation of ethanol in the hydrogen potential region and chemisorption of aldehyde (as CH_3^+) in the oxygen region.

Peak *3* observed in the CV recorded in an acidic electrolyte (see Fig. 1) can be attributed to oxidation of the acetaldehyde formed.[14] Acetic acid is the main product of this process. According to certain data,[38] the absence of peak *3′* in the alkaline electrolyte is due to blocking of the active sites of chemisorption of organic compounds by strongly adsorbed oxygen species.

Table 2. Ethanol electroxidation products on platinum in a wide potential range.

c	Medium	*T*/°C	Method	Reaction product							Ref.
				$CO_2(CO_3^{2-})$		MeCOH		MeCOOH ($MeCOO^-$)		CH_4	
				ΔE/V	Q_F (%)	ΔE/V	Q_F (%)	ΔE/V	Q_F (%)	ΔE/V	
Catalyst: 20% Pt/C in the amount of 0.14 mg cm^{-2}											
0.1	acidic	20	DEMS	0.5 → 0.9 [a]	2.7	0.4 → 1.1 [a]	37	0.4 → 1.1 [a]	60	0.4 → 1.1 [a]	24
						0.4 ← 0.9 [a]		0.4 ← 1.1 [a]		0.6 ← 0.9 [a]	24
										0.0 ← 0.2 [a]	24
Catalyst: platinum foil											
0.1	acidic	20	DEMS	0.6 → 1.3 [a]	–	0.4 → 1.1 [a]	–	–	–	0.5 → 1.1 [a]	35
						1.0 → 1.6 [a]				1.1 → 1.6 [a]	35
						0.3 ← 0.8 [a]				0.4 ← 0.8 [a]	35
										0.0 ← 0.2 [a]	35
0.01	alkaline	20	DEMS	0.4 → 0.8 [a]	–	0.4 → 0.8 [a]	–	–	–	0.4 → 0.8 [a]	35
						0.3 ← 0.8 [a]				0.3 ← 0.8 [a]	35
										0.1 ← 0.2 [a]	35
Catalyst: 40% Pt/C in the amount of 8 mg cm^{-2}											
0.01	acidic	90	DEMS	0.3 → 1.0 [a]	96.5	0.2 → 1.2 [b]	0	–	3.5	0.1 → 0.7 [a]	13
						0.0 ← 1.2 [c]				0.0 ← 1.4 [a]	13
Catalyst: platinum film on silicon											
0.1	acidic	20	ATR-SEIRAS	0.35 → 0.65 [b]	–	–	–	0.35 → 0.65 [a]	–	–	17
								0.2 ← 1.0 [a]			17
Catalyst: 40% Pt/C in the amount of 0.09 mg cm^{-2}											
0.1	acidic	20	DEMS	0.55 → 0.7 [b]	1.5 – 2.1	–	43.1 – 50.0	–	50.0 – 54.8	–	41
Catalyst: Pt(111)											
0.1	acidic	20	FTIR	0.5 → 1.2 [a]	–	0.4 → 1.2 [d]	–	0.4 → 0.8 [b]	–	–	34
						0.0 ← 1.2 [a]		0.0 ← 0.9 [a]			34
Catalyst: Pt in the amount of 4 mg cm^{-2}											
9	acidic	175	DEMS	0.3 → 0.55 [b]	24.3	0.3 → 0.55 [b]	75.7	–	–	–	42
				0.3 ← 0.55 [d]		0.3 ← 0.55 [d]					

Notes. The following designations were used: *c* is ethanol concentration /mol litre^{-1}; ΔE is potential range in which the reaction product is formed in forward (→) and reverse (←) CV scans; Q_F is faradaic efficiency of the partial reaction determined at the ethanol concentration of 0.1 mol litre^{-1}. The character of the partial curve of reaction product formation in the ΔE potential range: [a] curve passes through a maximum; [b] ascending dependence of the rate of product formation on the potential; [c] the absence of dependence; [d] descending dependence.

The approaches to elucidation of the nature of the limiting stage of ethanol electrooxidation are based on the analysis of slopes of the corresponding steady-state polarization curves and also on consideration of the reaction rate as a function of pH with regard to the data on the nature of adsorbed substances and selectivity of the overall reaction. In the general case, the process of ethanol electrooxidation includes the following key stages:[11, 37, 43, 44]

$$H_2O \rightleftharpoons OH_{ads} + H^+ + e$$

$$CH_3CO_{ads} + OH_{ads} \xrightarrow{k_1} CH_3COOH \quad (3)$$

(see Scheme 1, pathway *C2*)

$$CO_{ads} + OH_{ads} \xrightarrow{k_2} CO_2 + H^+ + e \quad (4)$$

(see Scheme 1, pathway *C1*)

At potentials <0.4 V, the reaction rate may be limited by stage (3) and/or (4). Note that the stage of C–C bond cleavage (due to the low reaction selectivity in pathway *C2*) is not the rate-limiting stage of the overall process.[45] The majority of scientists consider stage (3) to be rate-limiting. The question of limitation of a process rate by stages involving electron transfer can be solved by analyzing the slopes of polarization curves and also the dependence of the overall reaction rate on the pH. As was shown,[14] the rate of ethanol electrooxidation in the potential range of 0.1–0.4 V is virtually independent of pH in the 2–11 range. Hence, on the RHE scale,

$$\frac{dE}{dpH} = 0,$$

which formally corresponds to slowing down of the chemical reaction.

As the potential increases, the reaction rate in the alkaline medium increases more sharply as compared with the acidic medium (see Fig. 1), which is attributable to the increase in the rates of parallel reactions that proceed by pathways *C1* and *C2*:

— pathway *C1*: in alkaline electrolytes, the species OH_{ads} that are involved in the oxidation of products of C–C bond cleavage are formed at lower potentials as compared with acidic electrolytes; correspondingly, at the same potentials, the rate of reaction (3) is higher due to higher surface coverage by one of reactants;

— pathway *C2*: at pH > 11, the ethanol molecule is deprotonated to form the ethoxy anion and the latter is adsorbed on the catalyst in the presence of OH_{ads}

$$CH_3CH_2OH + HO^- \longrightarrow CH_3CH_2O^- + H_2O$$

$$CH_3CH_2O^- + OH_{ads} \longrightarrow CH_3CHO_{ads} + e + H_2O$$

For comparison, it should be noted that in the acidic medium, the formation of CH_3CHO_{ads} requires abstraction of two protons from the molecule

$$CH_3CH_2OH \longrightarrow CH_3CHO_{ads} + 2e + 2H^+$$

The selectivity of ethanol electrooxidation substantially depends on the crystallographic orientation of the platinum surface in the catalyst. As regards the C–C bond cleavage, areas with high-index orientation are most active. The Pt(110) face exhibits the maximum selectivity with respect to CO_2 in the acidic medium [23, 24, 46]

For highly disperse catalytic systems including those formed on various supports, the catalyst amount per unit electrode surface area is an important parameter. In addition to activity, one should also consider the microstructure of the catalytic layer (first of all, its porosity and the size distribution of pores) and also the flow rate of the alcohol solution through this layer. Electrodes with thin catalyst layers (<1 mg cm^{-2}) are generally characterized by low selectivity with respect to CO_2 (see Table 2). As the catalyst amount increases, the degree of conversion also substantially increases. This is associated both with the increase in the number of adsorption sites per unit surface and with the increase in the time the alcohol molecules and intermediate products stay in the active layer volume.[13] An analogous effect was observed upon slowing down of fuel mixture circulation and also with the transition to ethanol oxidation under potentiostatic conditions.

In dilute ethanol solutions, the main reaction products are CO_2 and acetic acid, the yield of CO_2 reaching its maximum ($\sim$30%) for the ethanol concentration of <0.1 mol litre^{-1} (Ref. 11); however, as the ethanol content increases up to 1 mo litre^{-1}, acetaldehyde becomes the predominant reaction product. This can be explained by the competitive chemisorption-induced decrease in the surface coverage by oxygen species involved in the ethanol and acetaldehyde oxidation in concentrated alcohol solutions. The assumption that the alcohol chemisorption products are oxidized exclusively to CO_2 can be considered as generally accepted.[7, 8, 47] One of the most probable reasons for the decrease in the yield of CO_2 with increase in ethanol concentration is the formation of weakly bound species which are oxidized preferentially to acetaldehyde and acetic acid.[8] The portion of the current spent in reactions with C–C bond cleavage increases on going from acidic to alkaline medium. In the potential region of hydrogen adsorption, this may almost double the yield of methane (according to data on the Pt–Ru system[48]). In turn, the yield of CO_2 for FC with alkaline electrolyte can reach 55% as opposed to 2% for a FC with proton-conducting electrolyte, which operates under similar conditions (anode potential 0.8 V, $T = 60$ °C, EtOH concentration 0.1 mol litre^{-1}, individual Pt catalyst).[49] The mechanism of the decrease in the yield of CO_2 on going from alkaline to acidic media is not yet entirely clear. Probably, this can be explained by the acidic properties of acetaldehyde, which is deprotonated in the alkaline medium. In addition, as was mentioned above, the energy of C–C bond cleavage in the acetaldehyde molecule is lower than in the ethanol molecule.

One of the main methods of enhancing the selectivity of the process of ethanol electrooxidation to CO_2 is to carry out the reaction at high temperature. According to certain data,[13] at 90 °C and higher, the yield of CO_2 can be >90%. At the same time, at a high ethanol concentration (>8 mol litre^{-1}), the degree of ethanol oxidation to CO_2 fails to exceed 25% even at 175 °C.[42]

The comparative analysis of the regularities of adsorption and oxidation of ethanol on platinum in acidic, alkaline and carbonate media [10, 14, 47, 50] made it possible to identify the following relationships. Irrespective of pH, the CO-like adsorbates are the predominant product of dissociative chemisorption of ethanol. The ethanol oxidation rate in the potential range <0.4 V is limited by the stage of

interaction of chemisorption products with OH_{ads}. According to Lai and Koper,[50] one of the main factors that determine the changes in the catalyst activity when going from acidic to alkaline media is the difference in the oxidation rate of β-CH_x adsorbates in the polycrystalline platinum surface regions with different crystallographic orientation. In the alkaline electrolyte, the oxidation of CH_x to CO_{ads} starts at potentials < 0.1 V on Pt(110) and only at 0.55 V on Pt(111). In the acidic electrolyte, CH_x oxidation proceeds at the same rate on all low-index faces up to potentials of ~ 0.45 V. The above peculiarity can explain the higher yield of CO_2 at low potentials in the alkaline medium as compared with acidic electrolytes. At the same time, taking into account that CO oxidation is accelerated on going from the acid to the alkali,[51] a similar effect can be inferred for CO adsorbates formed from alcohols.

On the whole, these assumptions correspond to the SFG spectroscopy data on the adsorption and electrooxidation of ethanol on polycrystalline platinum in alkaline and acidic media.[26, 27] The shift of the intensity maximum of β-CO lines from 0.35 V (acidic electrolyte) to 0.9 V (alkaline electrolyte) (Fig. 2) can be due to the preferential (111) orientation of the catalyst surface, which complicates the CH_x oxidation in alkalis as compared with acids. However, in the former case, the oxidation of CO_{ads} to CO_2 proceeds faster at the same potentials.

The main disadvantages of individual platinum catalysts as a part of the anode in ethanol FC are the low oxidation rate of alcohol chemisorption products (primarily due to the small number of active sites accessible for adsorption of OH species and water) and also insufficient selectivity of the overall process with respect to CO_2. Taking this into account, the primary avenue of the development of platinum-based catalysts for ethanol oxidation is the quest for multicomponent systems that would provide the optimal catalytic effect and larger extent of reaction. The mechanism of ethanol oxidation on these multicomponent materials is often explained in terms of bifunctional catalysis.[52 – 54] In the platinum active sites, dissociative adsorption of ethanol takes place, the promoting component ('less noble' metal or oxide) serving as the donor of active oxygen which oxidizes organic adsorbates. A criterion of efficiency of these catalysts is the ability of the promoter to undergo dissociative adsorption (in acidic electrolytes) or chemisorb OH groups (in alkaline electrolytes). Wang *et al.*[55] obtained the following series of activity with respect to chemisorption of water:

$$Cu < Pd < Rh < Pt < Ru < Sn.$$

Taking into account this relationship makes it possible to explain the enhanced activity of catalytic systems Pt – Sn and Pt – Ru as compared with individual platinum in the ethanol oxidation reaction. Among the factors determining the activity of composite systems, mention should be made of the decrease in the energy of the adsorbate–platinum bond due to the so-called ligand effect, *i.e.*, the changes in the platinum electronic structure,[46, 55] the formation of an alloy with a modified lattice parameter[56] and also the redistribution of platinum and additional components in the bulk or on the surface of the catalyst.[57]

The key role in the development of multicomponent catalysts is given to the quest for metals (or oxides) that can promote platinum. The promoting element should, on the one hand, be oxidized relatively easily at low anodic potentials and, on the other hand, be stable in the electrolyte medium. Approaches towards the design of catalyst systems with the use of density functional theory (DFT), the Mote Carlo method, and other methods based on model concepts on the effect of the catalyst electronic structure and the reaction layer composition are being developed (see reviews[58, 59]). A kinetic model of CO oxidation on the Pt – Ru catalyst has been proposed, which relates the catalytic effect of this system to the enhanced mobility of CO adsorbates. Also, problems of modelling and optimiziation of more complex reactions including ethanol oxidation are discussed. In connection with this, noteworthy is the approach to selection of binary catalyst compositions which is based on the data on segregation of system components and variations in the d-electron energy upon the formation of the catalytic system. At the same time, the transition from modelling to scientifically substantiated prognoses of properties of potential catalysts is still inefficient and it is the subject of further studies.

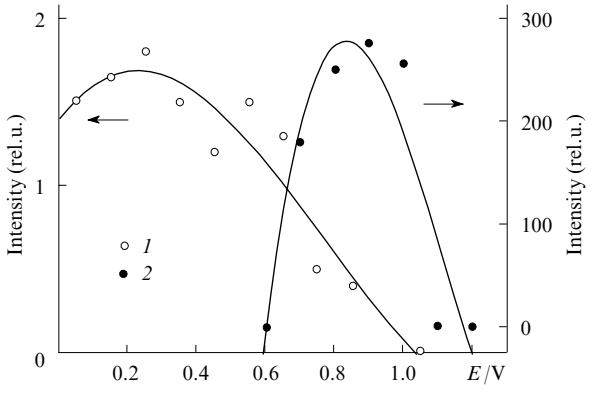


Figure 2. Intensity of β-CO spectral lines *vs.* potential during ethanol oxidation on polycrystalline platinum.
Electrolyte: (*1*) 0.5 M EtOH + 0.1 M $HClO_4$ (Ref. 26), (*2*) 0.5 M EtOH + 0.1 M NaOH (Ref. 27).

III. Synthesis and properties of catalysts of ethanol electrooxidation

The main trend in the perfection of direct ethanol fuel cells is the development of highly efficient anodic catalysts. In a review,[6] it was reasonably noted that the studies on developing such catalysts substantially differ from the studies on elucidating the mechanism of catalytic reactions due to involvement of the material science component. Among the most important requirements which should be fulfilled in order to provide successful operation of anodic catalysts in direct ethanol FC, the following factors deserve mention:

— the high and stable activity per unit catalyst mass or volume (up to 50 mA mg^{-1}, or 125 mA cm^{-3} at $E < 0.4$ V); the chief line in solving this problem is to form nanosized catalytic systems on disperse supports;

— an acceptable value of the faradaic utilization factor of ethanol, *i.e.*, the number of electrons given by one ethanol molecule (> 6 electrons per molecule); this problem is solved, on the one hand, by developing multicomponent catalysts and, on the other hand, by optimizing the FC

structure and operation conditions (electrolyte type, temperature, fuel delivery and removal of oxidation products);

— a corrosion stability that provides a sufficient service life; the components of nanostructured catalysts, *i.e.*, metals, oxides, alloys and also support materials, should be selected with due attention paid to the FC working conditions.

Whereas the results of model studies of the mechanisms of ethanol adsorption and oxidation were obtained back in the 1980–1990s by optical and other *in situ* techniques, the main achievements in the field of electrocatalysts for FC were made only in the past decade. Insofar as the characteristics of ethanol electrooxidation are to a large extent determined by the catalyst morphology, one of the most important problems is the development of efficient methods for the manufacture of catalysts, providing the formation of catalytic systems with desired microstructure characteristics.

1. Methods of the preparation of catalysts

The methods of the preparation of catalysts for ethanol electrooxidation can be subdivided into the following groups:

— chemical reduction of precursors in the liquid medium;

— methods of electrochemical deposition and galvanic displacement;

— colloid methods (first of all, polyol and Bonnemann methods);

— thermochemical method.

Most of catalysts are synthesized by the chemical reduction. It is used to produce catalysts based on platinum, palladium, ruthenium, and also of multicomponent systems based on platinum group metals and various oxides.[60–62] Usually, for nucleation and growth of the active phase, a reducing agent is added to a precursor solution or suspension brought in contact with the substrate material. The process is autocatalytic and continues on the emerging catalyst surface. The size, the specific surface area and the phase composition of the resulting particles are determined, to a large extent, by characteristics of the reducing agent. Particularly, the use of metal borohydrides in the synthesis of the Pt–Sn system provided more extensive reduction as compared with the use of alcohols in the polyol method.[63]

A method of electrochemical formation of catalysts is based on the deposition of platinum and other transition metals from solutions of their salts onto various supports. A version of this method is the galvanic displacement of a 'less noble' element by a 'more noble' one. The advantages of the electrochemical method include more accurate control over the amount of deposited catalyst and the possibility of forming layers of metal adatoms on the surface of the support material and also on the pre-formed sublayer of the catalyst active phase. At the same time, this method fails to provide uniform catalyst layers on the surface of porous supports, which is necessary for the formation of active layers on the FC electrodes.

The colloid methods of catalyst production, in contrast to conventional chemical reduction, employ various stabilizers, which are added to the reaction mixture to promote the dispersion of metal particles and prevent them from agglomeration.

In the polyol process, alcohols perform the functions of reducing and stabilizing agents and also of the reaction medium.[63–65] The most popular reagent is ethylene glycol, due to its low cost and low toxicity and also to the possibility of removing its oxidation products from the catalyst surface without additional heating (the process is usually carried out at temperatures from 160 to 190 °C). The use of the polyol process for the catalyst formation on carbon supports makes it possible to obtain systems with rather narrow particle size distribution. The average particle size can be <2 nm (according to data for the Pt–Sn/C system[66]). For comparison, the reduction of platinum and tin precursors by a metal borohydride generally produces coarser particles (>3 nm[63]).

When catalysts are prepared by the Bonnemann methods, the precursors (metal salts) in a dry aprotic solvent are reduced by tetraalkylammonum triethylborate, which also serves as the stabilizer.[67] According to several reviews,[68–70] this method can be used for preparation of all major types of catalysts for alcohol oxidation with the preset ratio of active components and the low degree of their alloying. However, the necessity of using high temperatures for the removal of the stabilizer after the catalyst preparation (>300 °C) restricts the use of the Bonnemann method as the alternative to the polyol method.

In the thermochemical method, metal salts or their complexes with organic ligands, which, as a rule, are deposited on the support, are reduced in a hydrogen atmosphere at elevated temperatures (from 300 to 900 °C). This method is often employed for deposition of metals the ions of which have low reducing capacity and also for the synthesis of multicomponent systems with the aim to attain a high degree of alloying throughout the metal phase bulk In some cases, the thermochemical method can provide a narrower size distribution of catalyst particles than low-temperature methods. However, high temperatures favour coarsening of particles which is accompanied by the loss of some of catalyst active sites.[68]

2. Structure and electrochemical characteristics of platinum-based catalysts for ethanol oxidation

As mentioned above (see Section II), one of the main challenges for the design of anodic platinum-based catalysts for ethanol FC is the development of highly efficient multicomponent systems. The rate of ethanol electrooxidation in the acidic medium can be increased by introducing such elements as Sn, Ru, Rh, Pd, Ni, Mo, W into the platinum catalyst. The activity of binary systems per unit platinum weight decreases in the following sequence:[56, 66, 71]

$$\mathrm{Pt–Sn} > \mathrm{Pt–Ru} > \mathrm{Pt–W} > \mathrm{Pt–Pd} > \mathrm{Pt}.$$

The majority of publications were devoted to the preparation and investigation of Pt–Sn and Pt–Ru binary catalysts and also of multicomponent systems based on them.[72]

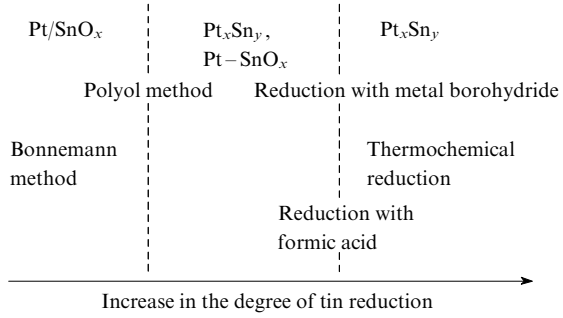
The bimetallic system Pt–Sn has an extremely low enthalpy of formation [for example, for intermetallic compound Pt_3Sn, this quantity is -50.2 kJ mol^{-1} (Ref. 73)]; in this system, five intermetallic compounds are formed, namely, Pt_3Sn, PtSn, Pt_2Sn_3, $PtSn_2$, $PtSn_4$.

The Pt_3Sn phase has the fcc lattice and can be considered as the interstitial tin phase in the platinum lattice.[74]

Depending of the preparation process, the Pt–Sn systems used as FC catalysts can form an alloy (as a rule, Pt_3Sn), occur in the non-alloyed state (Pt–SnO_x), or form a partially alloyed state (a mixture of Pt_xSn_y alloy and SnO_x

oxide) (Scheme 2).[60, 63, 69, 75, 76] A separate type of Pt – Sn catalysts is formed by systems in which platinum is modified by tin adatoms.

Scheme 2



There is no general consensus on the optimal relative content of components in the Pt – Sn system and also on the required ratio of metallic (alloyed) and oxidized tin. As was found in many studies, the maximum activity corresponds to the atomic ratio Pt : Sn ~ 3 : 1 (Fig. 3), which formally coincides with the thermodynamically stable Pt_3Sn phase composition. It is known that carbon-containing alcohol residues do not virtually adsorb on tin;[32] hence, the stages of the electrooxidation remain unchanged when going from platinum to the Pt – Sn system. At the same time, it was shown that depending on the catalyst phase composition, the mechanism of tin promoting action can change.[69] For the Pt – SnO$_x$ system, the non-stoichiometric tin oxides become donors of oxygen species, in particular, at potentials lower than that of the beginning of adsorption of these species on platinum. As a result, the reaction zone is supplied with active OH groups, which take part in oxidation of carbon residues of alcohol molecules (first of all $MeCO_{ads}$) adsorbed on platinum. In connection with this, the results by Jiang *et al.*[44] deserve attention. According to their data, in the acidic medium under conditions of deficiency of OH species on the catalyst surface, the activity ratio of Pt – Sn to individual Pt calculated per unit true surface of platinum is substantially higher than in the alkaline electrolyte.

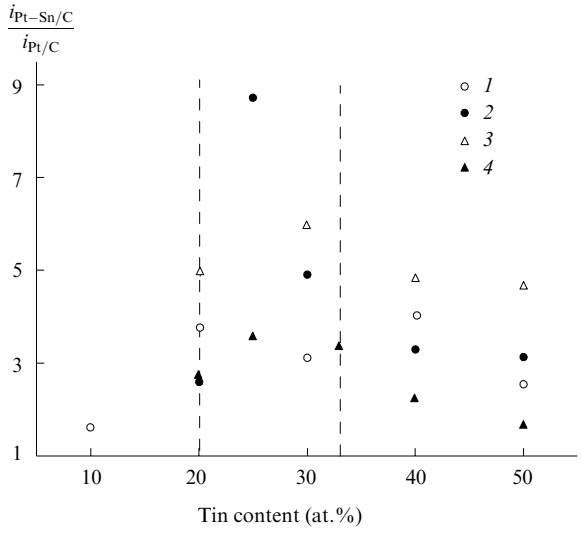


Figure 3. Activity ratio of Pt – Sn/C and Pt/C catalysts (calculated per catalyst mass) in ethanol electrooxidation as a function of the atomic fraction of tin in the Pt – Sn system.
The dashed lines confine the optimal tin content region. Activities correspond to the first anodic maximum in the potentiodynamic curve. $w = 20$ mV s^{-1}, electrolyte: 0.5 M EtOH + 0.5 M H_2SO_4, $T = 40$ °C. (*1–4*) data obtained in Refs 32, 75, 77 and 78, respectively.

For Pt – Sn catalysts with a higher degree of alloying, the increase in the activity of individual platinum is attributed, as a rule, to the ligand effect. According to the data by Vigier *et al.*,[43] insertion of tin into the platinum lattice favours the mobility of adsorbed CO species, which makes easier their oxidation and desorption. Tin adatoms were found to exert a positive promoting effect on the faces of platinum single crystals[46, 79–81] and also on Pt/C and Pt_3Sn/C catalysts.[82] Tin atoms deposit preferentially on the edges of platinum crystal faces (terraces) which are characterized by high CO coverage. On the one hand, this favours the adsorption of OH groups and, on the other hand, this decreases the specific (per unit surface area) number of platinum active sites, which become blocked by strongly adsorbed organic species. Several groups of authors[46, 81] have shown that at low anodic potentials, the degree of ethanol oxidation can be increased due to partial decoration of platinum single-crystal steps (sites that are most active with respect to the C – C bond cleavage) by tin or ruthenium adatoms.

The variation of the phase composition of the Pt – Sn system also affects the selectivity of the ethanol electrooxidation to CO_2. According to certain data,[83, 84] for a metal oxide catalyst, the yield of CO_2 was 2 – 3 times higher as compared with the corresponding alloy, because platinum with invariable lattice parameter ensures the geometry favourable for the C – C bond cleavage. The optimal ratio between the metallic (alloyed) and oxidized (non-alloyed) tin is determined by the temperature of the experiment and the potential.[85] At low temperatures and low potentials, the oxidation rate of ethanol chemisorption products increases with the increase in the tin oxide content. At an elevated temperature and potential > 0.5 V, the electrooxidation rate increases with the increase in the percentage of alloyed tin. The highest activity (per unit true surface area) was exhibited by a catalyst with the maximum content of the Pt_3Sn phase (62% with respect to the total mass of platinum and tin). It was shown[56] that the increase in the tin content in the Pt – Sn system induced the increase in the FC power density to reach the maximum (P_{max}) at the total tin content of 33 at.% and the working temperature of 60 – 90 °C. The decrease in P_{max} observed at higher tin contents can be explained by the partial blocking of platinum active sites by tin-containing components.

It deserves mention that irrespective of the phase composition, the fraction of processes that follow pathway *C1* (see Scheme 1) is higher for the Pt – Sn system than for individual platinum.[69, 75, 76] The main catalytic effect upon the introduction of tin into the platinum catalyst consists of acceleration of the partial reaction along pathway *C2* to afford acetic acid.

The important stage in the development and optimization of platinum-containing catalysts for ethanol FC is comparative analysis of the regularities of ethanol adsorption on platinum and on multicomponent materials. The deviations in the rates and selectivities of ethanol electro-

oxidation on Pt, Pt–Ru and Pt–Sn catalysts are largely determined by the differences in the binding energy of ethanol chemisorption products and water with the surface. At potentials of 0–0.06 V, the surface coverage with organic species is higher for binary catalytic systems than for individual platinum, because the bond energy of H_{ads} with the surface is lower. This agrees with the higher yield of hydrogenation products of ethanol (both methane and ethane) on individual platinum as compared with Pt–Sn.[84] As the potential shifts to more positive values, the platinum surface is freed from strongly bound hydrogen, which results in fast accumulation of dissociative adsorption products of ethanol, particularly, linearly bound CO_{ads}. The lower surface coverages with carbon monoxide for Pt–Ru and Pt–Sn catalysts cannot be explained by the faster oxidation of one-carbon species on these catalysts than on platinum, bearing in mind the low yield of CO_2. Probably, for binary systems, the preferential adsorption of two-carbon species, which are bound more weakly to platinum than CO_{ads}, takes place.

An integrated study of electrochemical properties of Pt/C, Pt–Ru/C and Pt–Sn/C systems carried out at the Frumkin Institute of Physical Chemistry and Electrochemistry of the Russian Academy of Sciences[75] demonstrated the relationship between the degree of alcohol oxidation and regularities of ethanol adsorption and kinetics of oxidation under both steady-state and non-steady-state conditions. By using pulsed electrochemical techniques, it was found that the addition of ruthenium or tin into a platinum catalyst leads to the preferential adsorption of weakly bound organic species with enhanced reactivity.[75] The main oxidation products of such species, namely, acetaldehyde and acetic acid, are formed faster (calculated per unit true surface of the catalyst) as compared with individual platinum. However, this somewhat decreases the contribution of the reaction that proceeds with the C–C bond cleavage and is possible only for strongly adsorbed species. When alcohol is chemisorbed on individual platinum and forms strong adsorbates, a larger quantity of electricity should be consumed in the dehydrogenation process than in the case of the Pt–Sn system (Fig. 4). At the same time, the rate of oxidation of organic adsorbates is higher on the Pt–Sn catalysts.

Acceleration of the ethanol electrooxidation process on going from Pt to Pt–Sn can be explained in terms of both the ligand effect and the bifunctional catalysis. Due to changes in the electronic properties of platinum, the reactivity of adsorbates on platinum within the binary system increases, resulting in acceleration of the overall reaction. At the same time, higher affinity of the Pt–Sn catalyst (as compared with individual platinum) with respect to oxygen species promotes acceleration of the oxidation of organic species according to the bifunctional mechanism. Based on the results obtained, it was concluded[75] that one way to further advance the catalysts is to find more complex multicomponent systems with the optimal balance between the bond energy and reactivity of adsorbed species.

According to the generalization presented in a reviews,[86] a promising trend is the development of three-component systems such as Pt–Sn–Ru, Pt–Ru–W or Pt–Sn–Rh. According to results of some studies,[87,88] the introduction of rhodium into platinum-containing catalysts enhances the selectivity of ethanol electrooxidation with respect to CO_2, while an acceptable level of activity per catalyst unit mass is

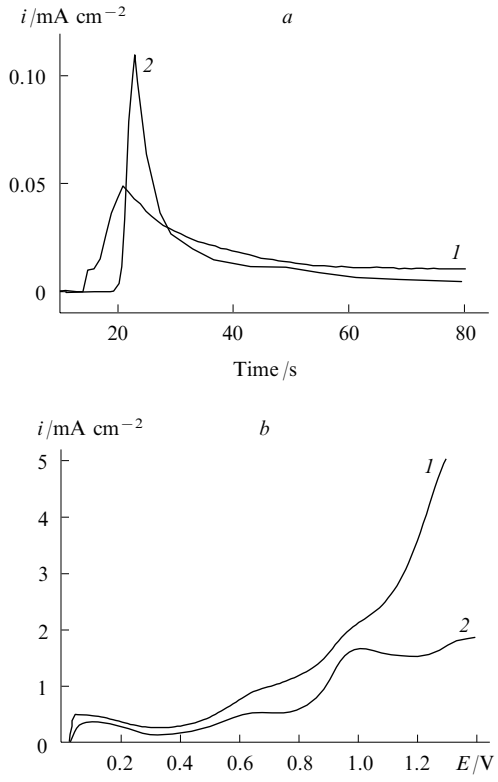


Figure 4. Chronoamperograms measured at the potential of 0.4 V (*a*) and pulse curves (w = 1000 mV s^{-1}) measured after chronoamperograms (*b*) on catalysts of 40% Pt–Sn/XC-72 (*1*) and 40% Pt/XC-72 (*2*).
Catalysts are applied on a model electrode of pyrolytic graphite in the amount of 100 g cm^{-2}, the current is normalized to the specific surface area of platinum. The quantity of electricity consumed in ethanol dehydrogenation /C cm^{-2}: (*1*) 0.28, (*2*) 0.40; electrolyte: 0.1 M EtOH + 0.5 M H_2SO_4, T = 20 °C.

retained. Koval *et al.*[88] have synthesized a Pt–Sn–Rh catalyst by the method of galvanic displacement with the successive formation of platinum and rhodium monolayers on the surface of carbon black-supported SnO_2. The mechanism of polyfunctional catalysis for Pt–Sn–Rh was interpreted by employing DFT calculations. It was assumed that in the catalytic system under consideration, the role of tin oxide consists of formation of sites for immobilization of oxygen species, which frees platinum and rhodium for the adsorption and oxidation of ethanol molecules. Correspondingly, ethanol is dehydrogenated on platinum, while rhodium provides the cleavage of the C–C bond and oxidation of CO_{ads} and tin oxides serve as the donors of OH_{ads} groups.

A series of studies[89–91] devoted to ethanol oxidation on the Pt–Sn–Ce catalyst reported a higher activity of this material per platinum unit mass as compared with Pt–Sn or elemental platinum, which can be explained both in terms of bifunctional catalysis and based on the assumption that the Pt–CO_{ads} bond energy decreases due to the ligand effect.

3. Non-platinum catalysts in ethanol electrooxidation

Studies on the development of non-platinum anodic catalysts are aimed, on the one hand, to reduce the cost of FC

and, correspondingly, of the generated power and, on the other hand, to achieve higher and more stable performance parameters of alcohol electrooxidation as compared with platinum catalysts. Attention is paid to problems of using platinum group metals that are less difficult-to-obtain and expensive than Pt and to investigation of the alcohol electrooxidation on catalysts containing no platinum group metals. The majority of these studies were devoted to ethanol electrooxidation in the alkaline medium. This is caused by the following factors:

— in acidic electrolytes, platinum is the most active individual metal; for alkaline media, the activity series is as follows: Pd > Pt > Ru;

— due to acceleration of processes of dissociative chemisorption and electrooxidation of ethanol in the alkaline medium, a higher rate of electrooxidation can be reached for a low content or even in the absence of platinum group metal on the electrode;

— the range of catalytic systems can be extended due to lower corrosivity of alkaline electrolytes as compared with acidic electrolytes.

The first studies on ethanol electrooxidation on catalysts involving transition metals and their compounds date back to the 1960–1970s.[3,92] At present, the list of non-platinum materials used includes, in addition to elements of the iron triad, compounds of copper, titanium, zirconium, tungsten, *etc.*[93–95] However, only few non-platinum catalysts provide a noticeable acceleration of the reaction at low temperatures. In particular, nickel oxide electrodes are widely known to be capable of serving as the mediator of ethanol oxidation to acetate. The process is accompanied by the reversible redox transition $Ni^{III} \rightleftarrows Ni^{II}$ and is accelerated with the increase in the alkali concentration

$$4\,NiOOH + CH_3CH_2OH + HO^- \longrightarrow CH_3COO^- + 4\,Ni(OH)_2$$

A review[6] mentions the possibility of C–C bond cleavage during ethylene glycol oxidation on nickel. The Italian company Acta has developed efficient nanosized catalytic systems Ni–Fe–Co for ethanol electrooxidation;[96,97] however, their structural characteristics and the methods of their synthesis are unavailable.

To date, only binary systems involving palladium and ruthenium approach platinum catalysts in efficiency. In view of commercialization of ethanol FC, of special interest are the studies on the design of ruthenium-containing catalysts, because ruthenium is 8–9 times less expensive than platinum.

The majority of palladium-based catalysts used in ethanol electrooxidation in the alkaline medium were already comprehensively surveyed.[5] Note the following most typical characteristics of these systems:

— ethanol adsorption on palladium is accompanied by active dehydrogenation of alcohol molecules, the rate of this process being limited by oxidation of chemisorption products;

— as on platinum, acetic acid (in the acetate form) is the main product of ethanol electrooxidation on palladium and the yield of CO_3^{2-} is < 5%;

— in terms of the bifunctional mechanism, the rate of acetate formation can be substantially increased by promoting palladium with various metals and oxides (among these systems, Pd–NiO_x is the most efficient, which can be explained by the ability of nickel oxide to oxidize organic compounds and CO[98]).

The problem of enhancing the stability of platinum catalysts was considered in publications[99,100] devoted to various phases of the Pd–Au system. Their activity in the ethanol electrooxidation in the alkaline medium was shown to decrease in the sequence

$$Pd/C > Pd_3Au/C > Pd_7Au/C > PdAu/C;$$

However, a different sequence was observed for stability of their characteristics attained, namely,

$$PdAu/C > Pd_3Au/C > Pd_7Au/C > Pd/C.$$

As regards the resistance to the poisoning action of ethanol oxidation products, the Pd–Au system substantially surpasses the commercial platinum catalyst. The increased stability can be explained, on the one hand, by a decrease in the rate of palladium poisoning when the latter is alloyed with gold and, on the other hand, by the synergistic effect, *i.e.*, the changes in the electronic structure of components upon formation of a catalytic material with new properties. Within the framework of the latter explanation, it was assumed[100] that palladium forms active sites for alcohol dehydrogenation in the alkaline medium; moreover, the oxidation, at least, partial of the chemisorption products proceeds on the gold surface

$$CO_{ads} + Au-OH_{ads} \longrightarrow Au-CO-OH \longrightarrow$$
$$\longrightarrow Au-COOH \longrightarrow Au + CO_2 + H_2O$$

This scheme was confirmed by the results of numerous studies which demonstrated the high activity of gold in the CO electrooxidation.[101] However, these results disagree with other data[14] which demonstrated the low activity of gold with respect to ethanol adsorption and oxidation with the C–C bond cleavage.

Ruthenium compounds as the active components of catalysts of ethanol electrooxidation were first considered by Shieh and Hwang.[102] When considering ethanol electrooxidation in the alkaline medium on ruthenium oxide, these authors have found that Ru^{VII}/Ru^{VI} redox pairs formed on the RuO_2 surface take part in the alcohol electrooxidation. Later, the RuO_2–Ni catalyst which surpassed metallic nickel as regards the activity in the alkaline medium was developed.[103] The next step in this direction was the development of the Ni–Co–Ru metal oxide system, which exhibited the highest activity per catalyst unit mass. At the same time, the degree and the rate of ethanol electrooxidation achieved with the use of catalysts based on oxidized ruthenium forms give no way of considering these catalysts as the efficient substitute for platinum-containing catalysts in the FC anode.

In view of the development of an efficient ethanol FC with catalysts containing no platinum, the results on new electrocatalysts based on metallic ruthenium promoted by transition metal oxides seem to be more encouraging.[104–109] With the use of the thermochemical method of formation of binary systems Ru–MO_x (M = Ni, Fe, Co, V, Cr) on the surface of carbon supports, a series of catalysts were synthesized which surpassed platinum and palladium as regards their specific activity in ethanol electrooxidation in the alkaline medium (Table 3). According to structural studies by X-ray diffraction, X-ray photoelectron spectroscopy, transmission electron microscopy, ruthenium (the

Table 3. Activity of various catalysts at potentials of 0.33 and 0.43 V in ethanol electrooxidation.[104, 105, 109]

Catalyst	Potential 0.33 V		Potential 0.43 V	
	mA per mg of noble mertal	mA per mg of the catalyst	mA per mg of noble mertal	mA per mg of the catalyst
15% $Ru_{68}Ni_{32}O_x$/XC-72	47.9	5.6	111	13.0
20% $Ru_{70}Cr_{30}O_x$/XC-72	41.5	6.8	90.2	14.8
20% $Ru_{60}V_{40}O_x$/XC-72	48.0	7.2	107	16.0
20% Pd (E-TEK)	17.5	3.5	85.0	17.0
20% Pt (E-TEK)	31.0	6.2	57.5	11.5

Note. The activity was determined in the anodic branch of the quasisteady-state curve; $w = 5$ mV s^{-1}, electrolyte: 1 M EtOH + 2 M KOH, $T = 60$ °C.

active component) mainly occurs in the catalytic systems in the metallic state, while the promoting components are in their oxidized states; moreover, surface regions of ruthenium are partly covered with the oxide phase. The catalysts are characterized by a rather narrow particle size distribution with the average size being 2 to 5 nm.[109] An important advantage of Ru – MO_x/C catalysts over the systems based on platinum and palladium is the high yield of CO_2 (in the carbonate form) upon ethanol electrooxidation (up to 80% for the Ru – NiO_x/C system of the optimal composition). The catalytic effect of Ru – MO_x systems was confirmed by analyzing the kinetic data on ethanol electrooxidation, the attained degree of electrooxidation (based on the data of liquid and gas chromatography) and the specific features of ethanol adsorption acquired by the methods of adsorption displacement and fast potentiodynamic pulses.[110, 111]

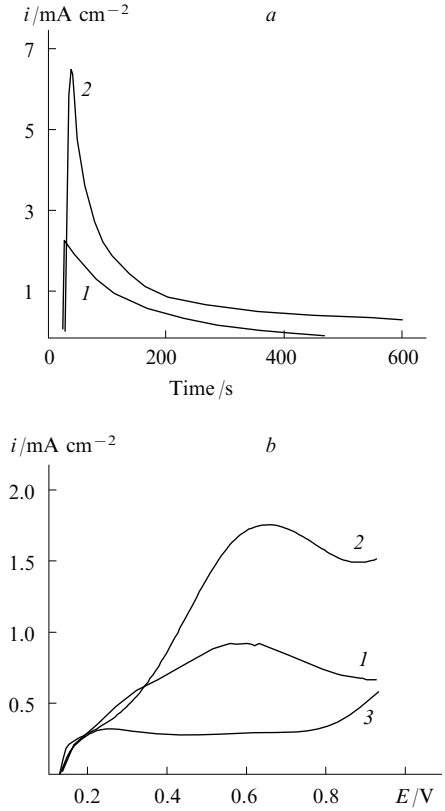


Figure 5. Chronoamperograms at the potential of 0.13 V (*a*) and pulse curves ($w = 500$ mV s^{-1}) recorded after chronoamperograms (*b*) on catalysts with 15% Ru/XC-72 (*1*) and 20% Ru – VO_x/XC-72 (*2*) and also background curve ($w = 500$ mV s^{-1}) for 20% Ru – VO_x/XC-72 (*3*).
Catalyst is applied on a model nickel grid electrode in the amount of 1 mg cm^{-2}, current is normalized to the specific surface area of ruthenium. The quantity of electricity required for alcohol dehydrogenation /C cm^{-2}: (*1*) 0.24, (*2*) 0.52; electrolyte: 0.2 M EtOH + 1 M KOH, $T = 60$ °C.

It was shown that upon the introduction of a transition metal into the ruthenium catalyst, the specific surface area of the catalyst decreases while the rate and degree of ethanol dehydrogenation increase due to the active feed of the reaction zone with OH groups generated by the oxide phase. These factors as well as the longer time needed to attain the steady-state coverage with organic species as compared with platinum at the same potentials increase the probability of the C – C bond cleavage upon adsorption. A comparison of Fig. 4 and Fig. 5 shows that in contrast to Pt – Sn, the use of the Ru – VO_x system ensures both a higher degree of ethanol dehydrogenation and a higher rate of its subsequent oxidation (as compared with characteristics of individual platinum and ruthenium, respectively). The Ru : M ratio optimal as regards the degree and rate of ethanol electrooxidation is ~2 : 1 irrespective of the nature of the promoting component. These studies demonstrated the prospects of the development of multicomponent catalysts of ethanol oxidation which would provide the high rate of CO_2 formation as a result of changing the energy of ethanol interaction with the catalyst surface.

4. Catalyst supports

The development of highly efficient supports for catalysts pertains to the most important routes of optimization of processes in low-temperature fuel cells. On the one hand, the support material affects the microstructural properties of the catalyst active phase (the first group of parameters) and, on the other hand, it determines the macrokinetics of the electrode process when the catalyst operates within a FC electrode (the second group of parameters). The first group involves parameters developed mainly in the stage of catalyst formation, *i.e.*, the porosity, the surface area, the particle size distribution and the phase composition. Parameters of the second group describe how the support affects the catalyst performance depending on conditions of mass transfer of electrode reaction components and also the electron conductivity of the active layer as a function of support characteristics.

To date, the following main groups of support materials have been proposed and studied:

— carbon materials that embrace various blacks, activated carbons, graphenes, diamond-like structures including those doped with various elements; nanomaterials, nanotubes, nanocones, nanofibres, *etc.*;[112, 113]

— oxides, nitrides and carbides of various elements;[93, 114, 115]

— conducting materials based on organic polymers (polyaniline, polypyrrole, polythiophene, *etc.*).[116, 117]

An increase in the specific surface area of the carbon support was shown [111] to be accompanied by the increase in the activity and specific surface area of Ru_2Ni/C, a catalyst of ethanol electrooxidation in the alkaline medium (Fig. 6). Thus, transition to supports with higher specific surface areas increases the number of active sites formed; hence, the catalyst utilization factor also increases. The increase in the metal phase degree of dispersion upon the increase in the carbon support specific surface area can be explained by the stabilizing effect of the support during the catalyst preparation by the thermochemical method. At the same time, the kinetics and the mechanism of ethanol oxidation are probably the same for all supports, as evidenced, on the one hand, by the invariance of the optimal ratios of catalyst components and, on the other hand, by similar slopes of the corresponding polarization curves in the potential range under consideration (Fig. 7).

Despite the highly developed surface and the high conductivity of furnace blacks, they contain a small number of mesopores, which complicates the access of reactants to the catalyst and the removal of CO_2 formed during the FC operation. Moreover, electrochemical oxidation of a black can occur, resulting in the detachment of metal catalyst particles from the support.[118] In connection with this, alternative supports for electrocatalysts, first of all, carbon nanotubes and nanofibres, are being explored. As regards their use in electrocatalysis, the carbon nanomaterials should combine characteristics such as highly developed surface and mesoporous structure, corrosion resistance and high conductivity. Physicochemical characteristics and methods used for synthesis and preliminary treatment of nanomaterials that serve as catalyst supports have already been summarized.[119, 120] Below, we consider the main results on their use in ethanol electrooxidation.

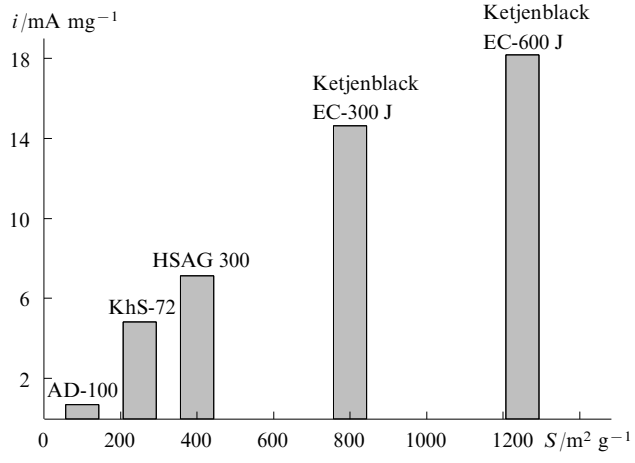


Figure 6. Dependence of specific activity of a 20% Ru_2Ni/C catalyst on the specific surface area of the support.[111]
The catalyst is applied on the model electrode of pyrolytic graphite in the amount of 100 g cm^{-2}. Activity is determined in the anodic branch of a quasisteady-state curve (w = 5 mV s^{-1}) at the potential of 0.5 V; electrolyte: 1 M EtOH + 2 M KOH, T = 40 °C.

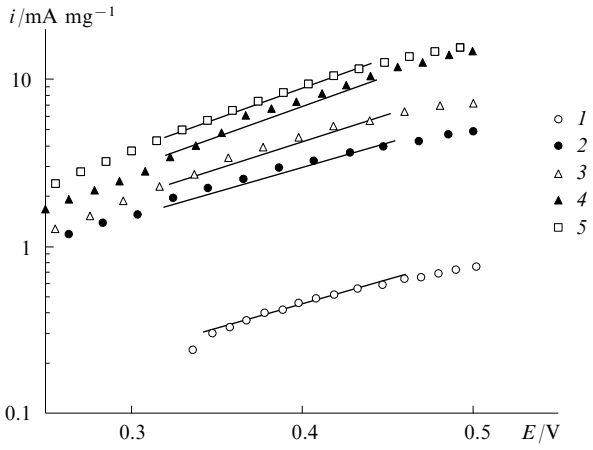


Figure 7. Polarization curves characterizing the ethanol oxidation on 20% Ru_2Ni catalysts formed on various supports.[111]
Catalysts are applied on a model pyrolytic graphite electrode in the amount of 100 g cm^{-2}. Anodic branch, 5 mV s^{-1}, electrolyte: 1 M EtOH + 2 M KOH, T = 40 °C. Support (black): (*1*) AD-100, (*2*) XC-72, (*3*) HSAG, (*4*) EC-300, (*5*) EC-600.

The problems associated with the formation of catalysts for ethanol FC with acidic electrolytes were discussed in several publications.[121 – 126] The majority of studies were aimed at the development of multicomponent systems based on platinum. First of all, we consider the results of our studies along this line.[121, 122] The Pt – Sn catalysts formed on pyrolytic carbon materials by a modified polyol method demonstrated the higher performance in ethanol electrooxidation as compared with commercial platinum-containing catalysts and also with similar systems formed on XC-72 black.

Efficient Pd and Pd – Ni catalysts were formed on the surface of multi-walled nanotubes and carbon nanofibres to be used in alkaline ethanol FC. [127, 128] An active catalyst was synthesized by electrodeposition of a monolayer of nickel particles on multi-walled nanotubes pretreated with nitroaniline.[129] A positive effect was also obtained when multi-walled nanotubes were used as the supports for $Ru-VO_x$ catalysts.[130, 131] The optimized system $Ru-VO_x$/multi-walled nanotubes exhibited a higher activity per catalyst unit mass as compared with $Ru-VO_x/XC-72$.

When developing metal/oxide composite systems, the possibility of using oxide supports as an alternative to carbon materials was often considered. One of the main advantages of oxides over carbon blacks is the combination of electronic and ionic conductivity, which reduces the ohmic losses at the formation of considerably thick catalytic layers. Moreover, in contrast to carbon materials of supports, oxides exhibit high hydrophilicity, which facilitates the control over mass exchange processes in the membrane – electrode assembly of the fuel cell. The use of SnO_2 as the support made it possible to synthesize a platinum catalyst with the average particle size of $\sim$ 2.5 nm and the

activity resulting from its bifunctional properties. This material surpassed the Pt/C catalyst as regards stability and activity per unit mass or unit surface area of platinum.[114] The formation of a platinum catalyst for ethanol oxidation with a support made of the composite SnO_2/carbon nanotubes was reported.[132] The stability of platinum catalysts was found[133] to be higher on supports based on TiO_2-promoted carbon materials, because water molecules structurally bound to the oxide could take part in oxidation of ethanol chemisorption products.

IV. The state-of-the-art of the research of direct ethanol fuel cells

The main routes in the design of low-temperature FC of direct ethanol oxidation involve the development of highly active stable catalysts and also the optimization of the electrolyte composition. In these works, several peculiarities of this type of FC, which determine the basic difference of these investigations from the studies on the development of hydrogen – air FC, should be taken into account:

— the anodic reaction in an ethanol FC is slow; as a rule, the faradaic efficiency of ethanol utilization in acidic solutions is $<40\%$ and approaches 80% only in alkaline solutions;

— the anodic reaction rate can be increased by increasing the temperature of the fuel mixture to >80 °C; however, this is accompanied by an increase in the deactivation rate of the cathodic catalyst due to acceleration of ethanol crossover to the cathode space; and, moreover, the pressure cannot be varied without limitations determined by the ethanol solution boiling temperature;

— the cathodic reaction rate in acidic solutions decreases due to catalyst poisoning with ethanol that penetrates into the cathode space as a result of the crossover effect, and this also leads to the loss of fuel;

— taking into account the low activity of cathodic and anodic systems in alcohol – air FC, considerable amounts of catalysts should be used, which increases the active layer thickness thus aggravating transport complications; moreover, when alcohols are used as the fuel, the stability of a solid polymer electrolyte is lower than in the case of hydrogen fuel;

— integrated optimization of the cathode, the anode and the membrane – electrode assembly as a whole is necessary, which is explained by specific conditions of FC operation where ethanol solution is fed to the anode; the anode active layer should have a mesoporous structure to provide efficient delivery of ethanol solution and the removal of carbon dioxide. As compared with the hydrogen – air FC, the use of liquid fuel ensures sufficient wetting of the membrane and eliminates the necessity of preliminary wetting of the oxidant, because the required humidity at the cathode is maintained by water formed in oxygen reduction.

The pursuit for the advancement of direct ethanol FC is stimulated by achievements in the mathematical simulation of the corresponding processes[134] and also by the development of new construction materials and ion-exchange membranes.[135, 136] The type of electrolyte used is the decisive factor which determines the FC architecture and characteristics and also the choice of catalytic systems and operation conditions.

The use of solid polymer electrolyte (membrane) provides spatial separation of the cathode and the anode at a minimum distance between them, which makes it possible to minimize ohmic losses (virtually completely determined in this case by the membrane electric resistance) and forms prerequisites for FC miniaturization. The main requirements to membranes are their chemical and electrochemical stability at low permeability to ethanol ($<10^{-6}$ mol cm^{-2} min^{-1}), high ionic conductivity (>0.08 S cm^{-1}) and low cost. An additional requirement is low crossover of dissolution products of platinum-modifying metals (M = Ru, Sn, *etc.*) from the anode to the cathode when Pt – M catalysts are used at the anode.[137]

At the formation of the membrane – electrode assembly, as a rule, the 'catalytic ink' is prepared, *i.e.*, a suspension of catalyst powder in a solution of a polymer electrolyte (ionomer) and a stabilizer of suspension, to be later spread over the gas-diffusion layer made of graphitized paper or metal grid. For spreading the catalytic ink, many methods are used such as brushing,[138] spraying,[139] screen printing.[140] Ink is applied on the gas-diffusion layer and then the resulting electrodes are pressed to the membrane. The formed membrane – electrode assembly is fixed between the cathodic and anodic current-collector plates which have channels in the zone of their contact with the gas-diffusion layer for the delivery of reactants and the removal of reaction products.

Typically, the membrane – electrode assemblies for ethanol FC use large amounts of platinum at the anode, namely, 3.0 mg cm^{-2} and above. Even for catalysts with 40 mass % (and more) of metal, the anodic layers are considerably thick and comparable with the gas-diffusion layer. This determines the necessity of adding large amounts of ionomer into the active layer in order to create acceptable conditions for ion transport and porosity sufficient for the delivery of the liquid reactant and the removal of gaseous products (CO_2). One of possible versions is the formation of active layers both with hydrophobic (gas-outlet network) and hydrophilic (liquid and electron transport network) pores.[141] Nonetheless, even using special methods for the anodic active layer formation, it is much more difficult to provide the access of the liquid fuel to the catalyst as compared with gaseous fuel. Thus, to overcome the transport limitations is a challenge for development of the active layer at the anode.

The working conditions of direct ethanol FC are constantly affected by ethanol that has penetrated through the membrane, which is critical for unloaded FC. The main way to overcome this difficulty is to develop a membrane with low permeability to fuel; to enhance the stability of FC operation, and ethanol-tolerant cathodic catalysts are also required.[122]

The working parameters of an ethanol FC have also certain specific features. The boiling temperature of rectified alcohol (95.57% ethanol) is 78.15 °C and, although FC use preferentially 1 – 2 M ethanol solutions (at higher concentrations, the ethanol crossover to the cathode space considerably increases), operation of such systems at temperatures >90 °C is only possible at elevated pressures in the fuel cell (to prevent boiling). This complication can be overcome by using liquid alkaline electrolytes.

1. Membranes for alcohol – air fuel cells

Depending on the type of conduction, membranes of direct alcohol FC can be classified as cation- and anion-exchange electrolytes; porous membranes filled with liquid electrolyte

are also being distinguished. The most frequently used membranes are those of the first type which include first of all commercial perfluorinated membranes Nafion (manufactured by Du Pont), various Nafion-based composite membranes and non-fluorinated (hydrocarbon) membranes.

Despite their high ionic conductivity (>0.1 S cm^{-1}), commercial membranes Nafion (particularly, Nafion 115 with the thickness of 125 μm) have several drawbacks when used in direct alcohol FC, namely, high crossover of alcohol and dissolution products of ruthenium, high cost, operating temperature limitations (<80 °C) and strict requirements as regards wetting. These drawbacks are partly eliminated in the thick membrane Nafion 117 (thickness 175 μm). The use of composite fluorinated membranes with inorganic additives extends the range of working temperatures and suppresses the alcohol crossover. The most popular method for improving direct alcohol FC is their modification with silicon compounds. For membranes with silicon additives, the operating temperature increases to 150 °C. Nafion membranes containing 10%–20% diphenylsilicon [142] have the nanolayer microstructure, which prevents the alcohol crossover. The possibilities of forming a layered structure in order to eliminate the crossover were studied by several authors (for example, see Ref. 143). The multilayer structure may involve layers with different proton conductivity or consist of polymers with different equivalent masses.

Non-fluorinated polymer membranes for FC for the direct oxidation of alcohols (first of all, methanol) are also called 'hydrocarbon' membranes and can be subdivided into three main groups:[144]

— composite membranes with modified organic components;

— acid-base membranes with modified polymer chains;

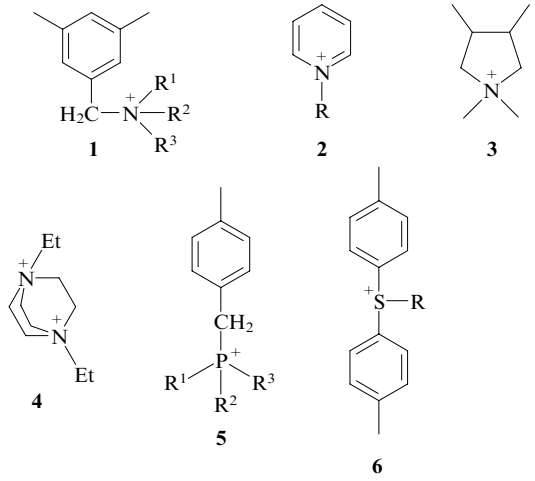
— acid-base membranes synthesized from monomer units.

Polyvinyl fluoride films modified with SiO_2 and treated with 60% H_2SO_4 have nanopores measuring 1.5–3 nm; in Nafion membranes of similar thickness, the pore size is 3 nm.[145] For smaller pores, the alcohol crossover is weaker (in the case under consideration, it is weaker by almost one order of magnitude as compared with Nafion membranes). Membranes can operate in the temperature range of 0–90 °C; they are thermally stable up to 120 °C and cheap. Membranes based on sulfonated poly(3-methylphenoxy)phosphazene are characterized by high conductivity and low diffusion coefficient of ethanol (1.6×10^{-8} cm^2 s^{-1});[146] moreover, they are chemically stable and mechanically strong. It was also assumed [147, 148] that the low permeability of hydrocarbon membranes to ethanol (as compared with Nafion) is due to the presence of a larger number of branched narrow water channels with dead ends. It should be noted that hydrocarbon membranes are, on average, three times cheaper than fluoropolymer membranes. However, both perfluorinated and hydrocarbon membranes have insufficiently long service life, first of all, in units working at elevated temperatures and pressures. When passing to hydrocarbon membranes, the decrease in the alcohol crossover to the cathode space is accompanied by a decrease in the proton conductivity. The corresponding ionomer solutions have not yet been developed, which makes it difficult to form active layers based on hydrocarbon membranes.

Alcohol–air FC with alkaline electrolytes usually employ anion-exchange membranes or membrane separators of the matrix type. The latter membranes separate the FC electrodes; the conductivity of such membranes is associated with the presence of the alkaline solution in the pores. The alcohol–air FC employ rather often separating membranes based on alkali-resistant asbestos, polybenzoimidazole (PBI), polyvinyl alcohol (PVA) and polypropylene. PBI-based membranes impregnated with alkaline solutions are characterized by the high thermal stability and chemical resistance.[108] Their conductivity increases with the increase in the alkali concentration and is 5×10^{-5} to 10^{-1} S cm^{-1} (see Ref. 5), *i.e.*, it approaches characteristics of Nafion 117 membranes. The permeability of PBI-based membranes to ethanol is two orders of magnitude lower as compared with Nafion membranes.[149] The rate of ethanol crossover through a PBI membrane reaches its maximum at the alkali concentration of 3.5 mol litre^{-1} and then decreases as the latter increases. A substantial drawback of separating membranes is the non-uniform distribution of their conductivity throughout the bulk

In order to achieve the uniform distribution of conducting zones throughout the membrane bulk, topical is the development of anion-exchange membranes with incorporated ionogenic groups (structures **1**–**6**). Yet another advantage of FC with anion-exchange membranes is weakening of alcohol crossover, because in this case, the alcohol transfer to the cathode space occurs under conditions of counter-flow of HO^- ions.

Structures **1**–**6**



Quaternized polysulfone is the basis of most anion-exchange membranes.[150] Such membranes are stable in a 2 M NaOH solution up to 40 °C. In 1 M KOH, membranes of quaternized poly(ether sulfone) remain stable up to 70 °C.[151] Despite the lower conductivity as compared with Nafion (0.04 S cm^{-1} at room temperature), the mentioned membranes are characterized by relatively low permeability to ethanol. These and other types of anion-exchange membranes were surveyed.[5, 136] The alcohol–air FC with alkaline electrolytes employ most often commercial anion-exchange membranes manufactured by Tokuyama and Solvay S.A. companies. However, the information on their composition and structure is limited.[136]

On the whole, the general drawbacks of anion-exchange membranes include their lower ionic conductivity as com-

pared with Nafion 117, which is associated with the lower mobility of OH groups compared with protons, and high sensitivity of membrane characteristics with respect to the level of wetting.[5] In addition, membrane stability under conditions of high alkali concentrations at elevated temperatures should be increased.

2. Characteristics of direct ethanol fuel cells

The analysis of published results of tests has shown that irrespective of the electrolyte type used, the functional characteristics of direct ethanol FC are determined, first of all, by the electrocatalysis of the anodic reaction. Both in acidic and alkaline media, on going from individual metal catalysts to multicomponent catalysts, the power density and open-circuit voltage increase (Table 4). The observed increase of these characteristics is usually attributed to acceleration of the anodic reaction along pathway *C2*. At the same time, binary systems in alkaline electrolytes [104, 105, 109] (in some cases, in acidic electrolytes [13]) can provide a high yield of CO_2.

On average, the performance characteristics of ethanol FC with liquid alkaline electrolytes are higher than in the case of proton-conducting electrolytes. According to model concepts on the anodic reaction mechanism, the higher open-circuit voltage observed in alkaline electrolytes points, first of all, to a greater degree of ethanol dehydrogenation. The power density increases with the increase in the alkali concentration, which is most clear in the low potential range corresponding to the kinetic region of the anodic reaction.[5] However, the wider use of alcohol FC with alkaline electrolytes is limited by the following factors:

— high alkali concentrations induce decomposition of the majority of polymer membranes and reduce the service life of components of the FC structure;

— in the CO_2 formation zone in alkaline solutions, the carbonization of electrolyte takes place, which is accompanied by deposition of carbonates on electrodes;

— when a system contains concentrated alkali solutions, the estimated overall characteristics of the FC degrade; also, it is necessary to organize the storage and delivery of alkaline electrolytes.

Only few studies with results of long-term service-life tests of direct ethanol FC are published. According to Shen *et al.*,[162] a 15% power loss of ethanol FC with the membrane – electrode assembly based on a Nafion 115 membrane and catalysts of Pt (cathode) and Pt–Sn (anode), which was observed in 60-h tests, is due to catalyst degradation. By the methods of X-ray diffraction and transmission electron microscopy, the coarsening of particles after the service-life tests was observed preferentially for the cathodic catalyst. Zhou *et al.*[154] achieved stable operation of a FC with an anode based on Pt–Sn (9 : 1) catalyst, while the FC voltage was kept at a level of 0.3 V for at least 14 days. As the load increased, the anode potential also increased, which resulted in irreversible oxidation of tin and degradation of FC characteristics.

Long-term (220 h) continuous tests of stability were carried out at the constant voltage of 0.5 V in full-scale membrane–electrode assemblies with the surface area of 50 cm^2 (Fig. 8). [75, 76] The results demonstrated stability of characteristics in time. In the loaded state, the current per unit geometric surface area of the electrode was $\sim$50 mA cm^{-2}, which corresponded to the power of $\sim$1.2 W. For FC with non-platinum catalysts, sufficiently

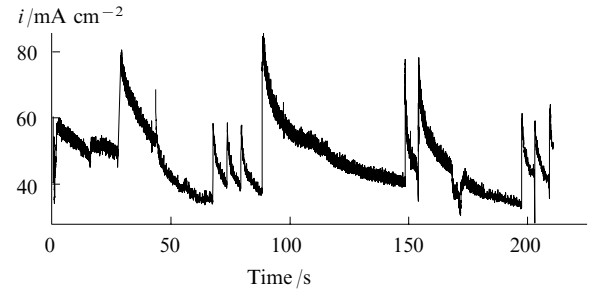


Figure 8. Current *vs.* time dependence at the voltage of 0.5 V, measured during testing a membrane – electrode assembly with the surface of 50 cm^2 (current is normalized to the geometric surface area of the anode).[76]
1 M EtOH solution, T = 75 °C, p_{O_2} = 2 atm; cathodic catalyst: 40% Pt (E-TEK) in the amount of 1.5 mg cm^{-2}; anodic catalyst: Pt–Sn (3 : 1, 40% Pt) in the amount of 3.5 mg cm^{-2}.

stable work of the membrane–electrode assembly was observed for 150 h at the voltage of 0.55 V (Fig. 9). The results obtained have shown that even at this stage of studies, portable ethanol–air FC can be developed in both acidic and alkaline electrolytes.

In recent years, studies on modifying conventional direct ethanol FC were being actively developed with the aim of enhancing the FC efficiency. In view of this, mention should be made of the development of a medium-temperature ethanol FC (up to 145 °C),[163] the studies on the prospects of using mixed-composition fuels [with addition of methanol [164] or metal borohydride (alkaline FC) [165]], and also the attempt to obtain the maximum FC characteristics by changing the oxidant (O_2 by H_2O_2).[166] It should be noted that the majority of these studies are of interest first of all as prospecting model investigations because, as a rule, the practical efficiency of systems proposed was not discussed.

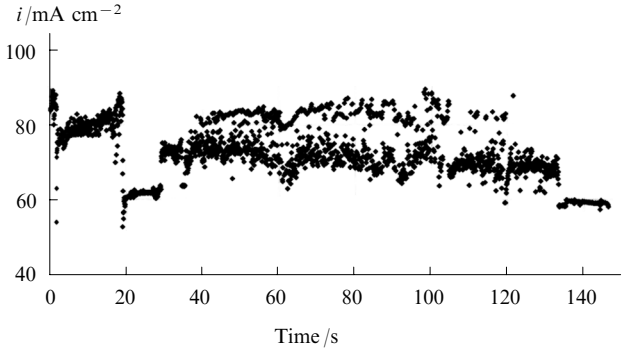


Figure 9. Current *vs.* time dependence at voltage of 0.5 V recorded during testing of a membrane–electrode assembly with the surface area of 25 cm^2 (current is normalized to the geometric surface area of the anode).
Electrolyte: 2 M EtOH + 3 M KOH, T = 65 °C, air oxygen (without excess pressure) as oxidant; on the cathode, catalyst PP CoTMPP in the amount of 7.0 mg cm^{-2}; on the anode, catalyst of 40% Ru–VO_x/XC-72 in the amount of 9.9 mg cm^{-2}; fuel consumption 4.5 ml min^{-1}.

Table 4. Characteristics of ethanol – oxygen FC with various types of membranes and catalysts.

Membrane – electrode assembly composition			Amount of platinum-group metal /mg cm^{-2}		Testing conditions					OCV /V	P_{max} /mW cm^{-2}	Ref.
cathode	membrane	anode [a]	at the cathode	at the anode	T /°C	p_s /atm	p_a /atm	c_s /mol litre^{-1}	c_a /mol litre^{-1}			
40% Pt/C	Nafion 117	Pt – Sn (9 : 1, 30%)/C	2.0	2.0	90	3	2	1	0	0.80	53	32
	Nafion 117	Pt – Sn (5 : 1, 30%)/C	2.0	1.0	110	1	1	1	0	0.77	45	152
50% Pt/C	Nafion 115	Pt – Sn (5 : 1, 20%)/C	1.0	2.0	90	–	2	1	0	0.78	58	153
20% Pt/C	Nafion 115	Pt – Sn (1 : 1, 20%)/C	1.0	1.33	90	–	2	1	0	0.82	52	154
	Nafion 115	Pt – Ru (1 : 1, 20%)/C	1.0	1.33	90	–	2	1	0	0.70	28	154
40% Pt/C	Nafion 117	Pt – Sn (9 : 1, 60%)/C	2.0	3.0	80	3	1	2	0	0.70	27	155
	Nafion 117	Pt – Sn – Ru (86 : 10 : 4, 60%)/C	2.0	3.0	80	3	1	2	0	0.70	50	155
Pt (black)	Nafion 115	Pt – Ru (1 : 1, (black)	3.0	3.0	90	2	0	1	0	0.65	30	156
Pt – Ru (black) + Pt – Sn	Nafion 115	Pt – Ru (black) + Pt – Sn (3 : 1, 45%)/C	3.7	2.5 + 1.7	90	0	2	1.5	0	0.85	96	157
40% Pt (E-TEK)	Nafion 117	Pt – Sn (3 : 1, 40%)/XC-72	1.2	2.5	75	0	2	2	0	0.77	60 – 80	75, 76
	Nafion 117	Pt – Sn (3 : 1, 40%)/CNT	1.2	2.5	85	0	2	1	0	0.74	52	75, 76
20% Pt/C	PBI/KOH	Pt – Ru (1 : 1, 45%)/C	1.0	2.0	90	–	–	2	2	0.95	61	158
Pt (black)	Tokuyama	Pt – Ru (black)	3.0	3.0	20	–	–	4	7	0.88	58	159
			3.0	3.0	20	–	–	4	0	0.67	6	159
Fe – Co	Tokuyama	Pd (4%) – (Ni – Zn)/C	0	1.0	25	–	0	~2.2	2	0.80	61	160
HYPERMEC™			0	1.0	80	–	0	~2.2	2	0.90	170	160
	Tokuyama	Pd (30%)/C	0	3.0	40	–	–	3	5	0.85	58; 42 [b]	99
		PdAu (3 : 1, 30%)/C	0	3.0	40	–	–	3	5	0.85	58; 52 [b]	99
		Pd (3.8%)/MWNT	0	1.0	25	–	–	~2.2	2	0.70	25	161
			0	1.0	80	–	–	~2.2	2	0.83	73	161
		Pd (20%)/C	0	1.0	60	–	–	3	5	0.80	66	162
		PdNi (2 : 3, 20%)/C								0.90	90	162
		Ni – Fe – Co HYPERMEC™	0	0	40	–	–	3	7	0.74	60	97
PP CoTMPP/XC-72	Nafion 117	Ru – VO_x (3 : 2, 20%)/XC-72	0	1.5	60	0	0	4	6	0.95	56	108, 109
	PBI/KOH	Ru – VO_x (3 : 2, 20%)/XC-72	0	3.4	80	0	0	2	3	0.92	125	108, 109
	PBI/KOH	Ru – VO_x (3 : 2, 20%)/XC-72	0	4.4	80	0	0	2	4.5	0.89	167	108, 109

Note. The following designations are used: p_s is ethanol pressure; p_a is alkali pressure; c_s is ethanol concentration; c_a is alkali concentration, OCV is the open circuit voltage, CNT is carbon nanotubes; PP CoTMPP/XC-72 is the pyropolymer of cobalt tetra(*p*-methoxyphenyl)porphyrin of carbon black; MWNT are multi-walled nanotubes. [a] in parentheses, the ratios of components and the contents of Pt, Pd, Ru in the overall catalytic systems are shown and also, for Ru – VO_x catalysts, the sum of mass fractions of ruthenium and vanadium is given; [b] P_{max} values before (the first value) and after (the second value) 288-h tests of stability.

V. Conclusion

Direct ethanol fuel cells pertain to the most promising electrochemical current generators. Numerous studies were devoted to the following aspects of the development of ethanol FC: the synthesis of highly active electrocatalysts, the formation of chemically stable polymer membranes, and the optimization of the structure of the membrane – electrode assembly and FC as a whole. At the same time, the main problem in designing direct ethanol FC, namely, the achievement of stably high rates of ethanol electrooxidation for the maximum reaction selectivity with respect to CO_2, is still unsolved. This problem is of special importance for fuel cells with proton-conducting polymer electrolytes, which are most often considered as the alternative to chargeable batteries used as power sources in portable electronic devices.

At present, there are no catalysts capable of providing a sufficient degree of conversion at room temperature.[14] To keep operating a medium-temperature FC that provides the necessary degree of ethanol oxidation, additional equipment should be used, which reduces the efficiency of the system as a whole. In a low-temperature (80 – 90 °C) ethanol FC with a liquid alkaline electrolyte, the yield of CO_2 can reach 80%. In alkaline ethanol FC, due to acceleration of ethanol dissociative adsorption and oxidation in the reaction layers containing OH groups and also due to the lower corrosive resistance as compared with acidic electrolytes, the successful use of non-platinum metal oxide catalysts is possible. However, the high rate of CO_2 formation in the presence of alkali leads to irreversible accumulation of carbonates in the fuel mixture. Moreover, the high rate and the acceptable degree of the anodic process are attained, as a rule, only in concentrated alkaline solutions. This determines the enhanced requirements to chemical stability of membranes used and also to mechanical strength of FC structural elements.

To solve the above problems, further upgrading of structural materials for ethanol FC is necessary, which is possible only based on further detailed elaboration of views on the mechanisms of ethanol adsorption and electrooxidation in various media and the properties of polymer membranes and also on the microscopic structure of potential catalysts.

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