19-е заседание Общемосковского семинара по электрохимии

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Наноструктурные катализаторы на основе металлоорганических кластеров и координационных соединений для низкотемпературных топливных элементов

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- **Tolerant to methanol cathode electrocatalysts on the basis of organo-metallic clusters**
- **Bimetallic cathode electrocatalysts for H_2-O_2 FC on the basis of coordination compounds**
- **Bimetallic anode nanoelectrocatalysts on the basis of coordination compounds:**
  - catalyst on the basis Pt-Sn cluster for EtOH electrooxidation
  - catalysts on the basis coordination compounds for MeOH electrooxidation
- **Electrocatalysts on the basis Ni−Ru/ C and Ni−Ru−F/C alloys for direct borohydrides electrooxidation**

Tolerant to methanol cathode electro-catalysts on the basis of organo-metallic clusters

The aim of work

- The development of high active electrocatalysts for fuel cells

The maim principles

- homogenation by using of only one mixed-metal chalcogenide initial cluster for preparing of catalyst
- conservation of composition after thermodestruction of initial cluster on carbon support
- prevention of catalyst particles coalescence

The features of new catalysts

- a catalytical system contains a definite mixed-metal chalcogenide core MFeX, MMnX or homometallic M_nX_m core derived from initial clusters on an electrically conductive component such as conductive carbon, graphite, nanotubes, superfine diamond and others cariers.
- In nanosize electrocatalysts the metal chalcogenide core performs the role of catalyst and chalcogenide atoms may also act as bridges at electron transfer to oxygen molecule.

In a direct methanol fuel cell the reactions taking place at the anode, cathode, and the overall reaction are given below:

Anode reactions:

$CH_3OH \rightarrow COH_{ads} + 3H_{ads};$ (1)

anodic oxidation of adsorbed hydrogen :

$3H_{ads} \rightarrow 3H^+ + 3e;$ (2)

adsorption of some oxygen-containing species :

$3H_2O \rightarrow 3OH_{ads} + 3H^+ + 3e;$ (3)

interaction of the adsorbed species and their removal from the surface:

$COH_{ads} + 3OH_{ads} \rightarrow CO_2\uparrow + 2H_2O.$ (4)

The consecutive and parallel combination of the steps (1)–(4) gives overall anode reaction:

$CH_3OH + H_2O \rightarrow CO_2\uparrow + 6H^+ + 6e$ (5)

Cathode reaction:

$O_2 + 4H^+ + 4e \rightarrow 2H_2O$

Overall cell reaction: $CH_3OH + 1.5O_2 \rightarrow CO_2 + 2H_2O$

BACKGROUND

- **electrocatalysts - platinum or platinum-metal alloys on a substrate of carbon powder or the like;**

  U.S. Pat. Nos. 4,316,944; 4,822,699; 4,264,685; and 5,876,867.

- **metal-containing macrocyclic compounds - as fuel cell catalysts, include N_4– chelate compounds, such as phthalocyanines, porphyrins, and tetraazaannulenes**.

  U.S. Pat. No. 5,316,990 and Faubert et al., Electrochemica Acta, Vol. 43, pp.341-353, (1998).

- **Chevrel-phase materials with central octahedral metal cluster (M_6X_6) M-high valent transition metals X= S,Se,Te.**

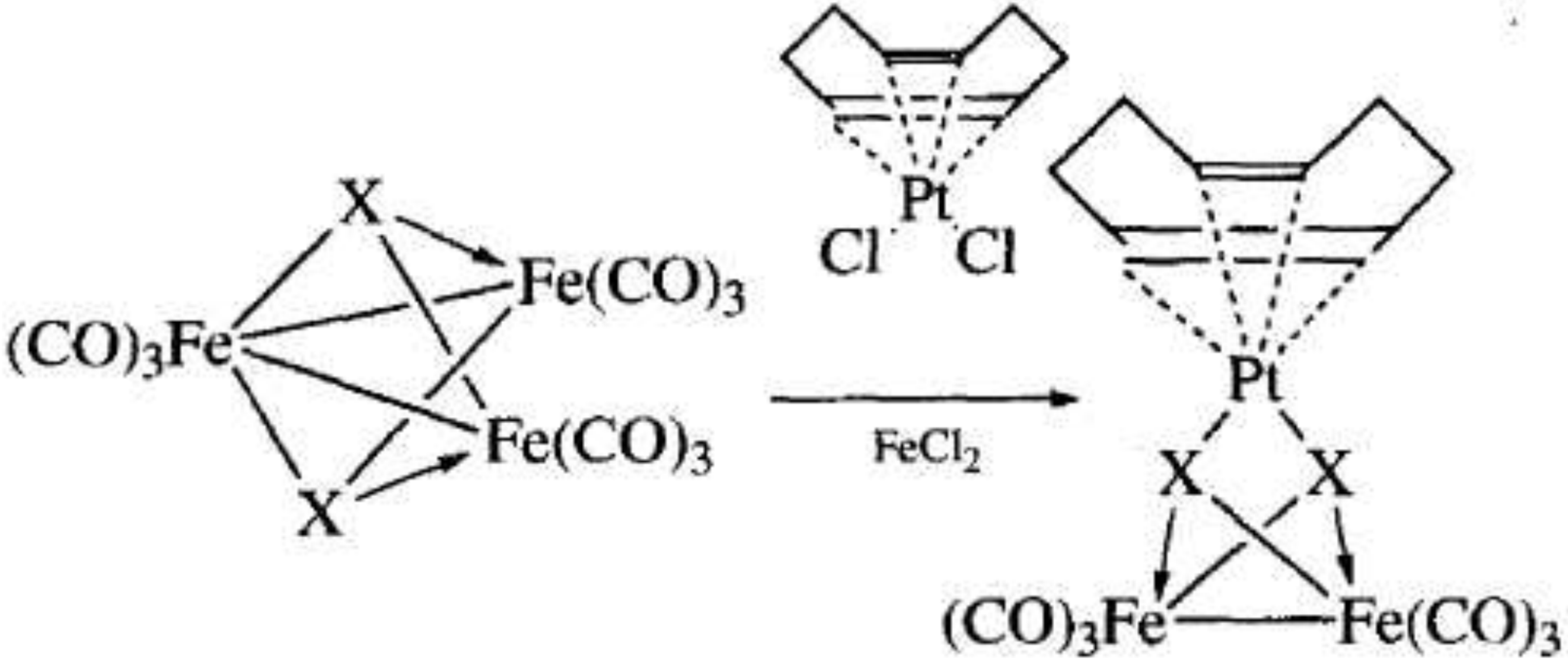
However, these catalysts had low activity and long-term stability.

- **systems on the basis of MoRuX where X = S, Se or Te, RuSe systems** (V. Trapp. P. Christensen, A. Hamnett, J. Chem. Soc. Trans., 92 (1996) 4311, R.W. Reeve, P. Christensen, A. Hamnett et al,

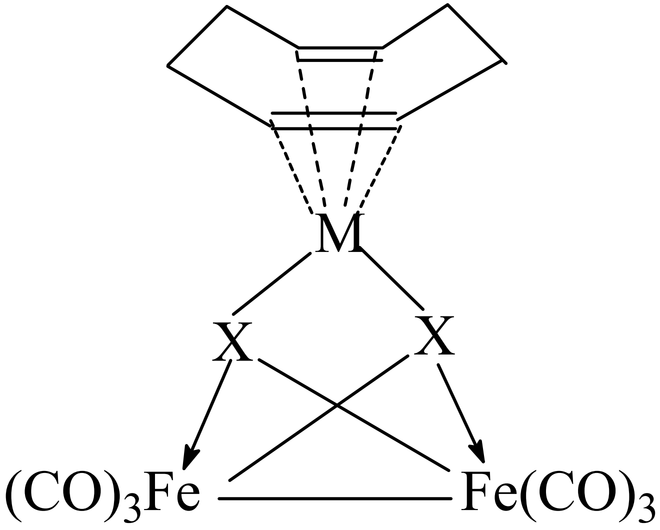
  J. Electrochem. Soc.,145 (1998) 3463; H. Tributsch, M. Bron, M. Hilgendorff et al,

  J. Appl. Electrochem. 31 (2001) 739-748);
- **The long-term stability of such cathodes is very low.**
- **The preparation of such material by pure catalytic methods is very difficult due to low reproducibility of described procedures.**

Tipical one-stage transmetallization reaction Pt-Fe chalcogenide clusters synthesis



The chemical structure of the cluster precursors used for preparation of the electrocatalysts



M = Pt; X = S, Se, Te

The final products of clusters thermolysis on carbon black have the composition $PtFe_2S_2$, $PtFe_2Te_2$, $PtFe_2Se_2$.

Pasynskii, A. A.; Semenova, N. I.; Torubaev, Yu. V.; Lysenko, K. A. Iron-Platinum interaction in (hexacarbonyldiiron)-[(π-diene)platinum] dichalcogenide clusters. Zhurnal Neorganicheskoi Khimii (2003), 48(8), 1299-1302.
Pasynskii, A. A.; Semenova, N. I.; Torubaev, Yu. V.; et al. Synthesis, molecular structures, and thermal decomposition of heterometallic (π-cyclooctadiene)platinum-bis(tricarbonyliron-μ3-chalcogenides)[Fe-Fe],(π− C8H12)Pt(μ3-X)2Fe2(CO)6,where X = S, Se, or Te. Russian Chemical Bulletin (Translation of Izvestiya Akademii Nauk, Seriya Khimicheskaya) (2001), 50(11), 2215-2220.

Summary of Syntheses of mixed-metal chalcogenides MFeX and homometallic MX clusters, where M = Pt, Ru, or Re; X = S, Se, Te

PRODUCT SYNTHESIZED	REACTANT	REACTANT	SOLVENT
$(CO)_6Fe_2S_2Pt(C_{10}H_{12})$ (1)	$Fe_3S_2(CO)_9$	$(C_{10}H_{12})PtCl_2$	THF
$(CO)_6Fe_2Se_2Pt(C_{10}H_{12})$ (2)	$Fe_3Se_2(CO)_9$	$(C_{10}H_{12})PtCl_2$	THF
□(π-Cyclooctadiene) platinum-bis(tricarbonyliron-μ3-sulfide)[Fe—Fe],(COD)Pt(μ3-S)$_2$Fe$_2$(CO)$_6$ (3)	$Fe_3S_2(CO)_9$	$(C_8H_{12})PtCl_2$	THF
□(π-Cyclooctadiene)platinum-bis(tricarbonyliron-μ3-selenide)[Fe—Fe],(COD)Pt(μ3-Se)$_2$Fe$_2$(CO)$_6$ (4)	$Fe_3Se_2(CO)_9$	$(C_8H_{12})PtCl_2$	THF
□(π-Cyclooctadiene)platinum-bis(tricarbonyliron-μ3-telluride)[Fe—Fe], (COD)Pt(μ3-Te)$_2$ Fe$_2$(CO)$_6$ (5) and tetracarbonyldiplatinum ditelluride, $(CO)_4Pt_2Te_2$ (6).	$Fe_3Te_2(CO)_9$	$(C_8H_{12})PtCl_2$	THF
$(C_8H_{12}PtCl)_2S$ (7)	Na(StBu)	$(C_8H_{12})PtCl_2$	THF
$(C_{10}H_{12}PtCl)_2Te$ (8)	NaPhTe	$(C_{10}H_{12})PtCl_2$	THF
$Fe_2RuS_2(CO)_{9.}$ (9)	$Ru_3(CO)_{12}$	$Ru(CO)_4(C_2H_4)$	Hexane
$Fe_2RuSe_2(CO)_{9.}$(10)	$Ru(CO)_4(C_2H_4)$	$Fe_2Se_2(CO)_6$	Hexane
Cp'Re(μ-CO)$S_2Fe_2(CO)_6$ (11) $(PPh_3)_2Pt[(C_5H_4S)Mn(CO)_3]_2$ (12)	Cp'Re$(CO)_3$ $(PPh_3)_4Pt$	$Fe_2S_2(CO)_6$ $[(C_5H_4S)Mn(CO)_3]_2$	THF THF

Thermodestruction of clusters presented in table

The data of differential-thermal analysis of separated clusters are in accord with data of initial composition catalysts in surface layer obtaining by EDAX technique

$$(C_{10}H_{12})PtFe_2S_2(CO)_6 \xrightarrow[-C_{10}H_{12}]{100\text{–}135^\circ C} Pt\text{-}Fe_2S_2(CO)_6 \xrightarrow[-CO]{135\text{–}160^\circ C} PtFe_2S_2(CO)_5 \xrightarrow[-3CO]{205\text{–}380^\circ C} PtFe_2S_2(C)_2(O)_2,$$

cluster (1)

$$(C_{10}H_{12})PtFe_2S_2(CO)_6 \xrightarrow[-C_{10}H_{12}]{110\text{–}123^\circ C} Pt\text{-}Fe_2Se_2(CO)_6 \xrightarrow[-CO]{130\text{–}140^\circ C} PtFe_2Se_2(CO)_5 \xrightarrow[-3CO]{155\text{–}180^\circ C} PtFe_2Se_2(C)_2(O)_2,$$

cluster (2)

$$Fe_2PtS_2(C_8H_{12})(CO)_6 \xrightarrow[-C_8H_{12}]{100\text{–}145^\circ C} Fe_2PtS_2(CO)_6 \xrightarrow[-3CO]{145\text{–}175^\circ C} Fe_2PtS_2(CO)_3 \xrightarrow[-CO]{180\text{–}300^\circ C} Fe_2PtS_2(C)_2(O)_2,$$

cluster (3)

$$Fe_2PtSe_2(C_8H_{12})(CO)_6 \xrightarrow[-C_8H_{12}]{110\text{–}160^\circ C} Fe_2PtSe_2(CO)_6 \xrightarrow[-3CO]{165\text{–}185^\circ C} Fe_2PtSe_2(CO)_3 \xrightarrow[-CO]{200\text{–}330^\circ C} Fe_2PtSe_2(C)_2(O)_2,$$

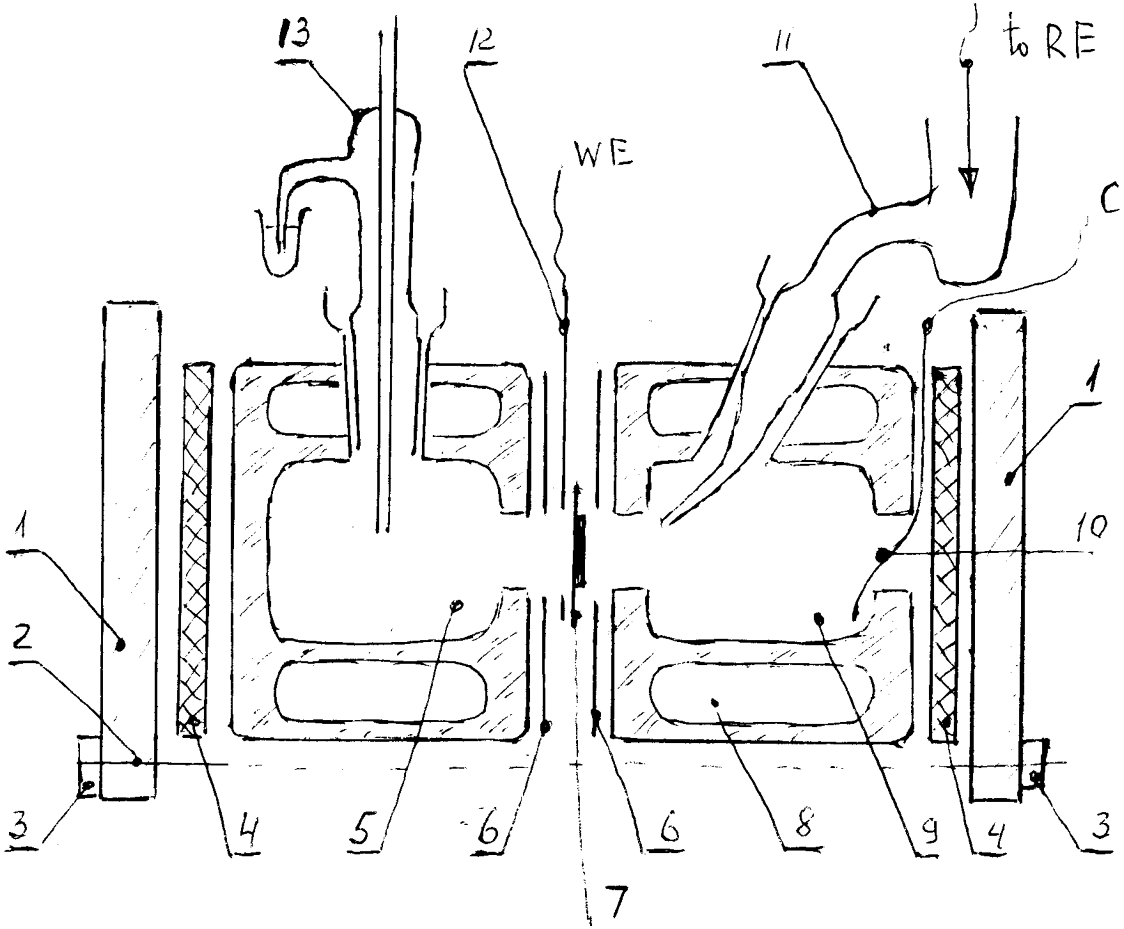
cluster (4)

$$Fe_2PtTe_2(C_8H_{12})(CO)_6 \xrightarrow[-C_8H_{12}]{120\text{–}155^\circ C} Fe_2PtTe_2(CO)_6 \xrightarrow[-3CO]{160\text{–}270^\circ C} Fe_2PtTe_2(C)_2(O)_2.$$

cluster (5a)

United States Patent Application*20070078052* Kind Code A1 Grinberg; Vitali Arkad'evich ; et al. April 5, 2007 Methanol tolerant catalyst material

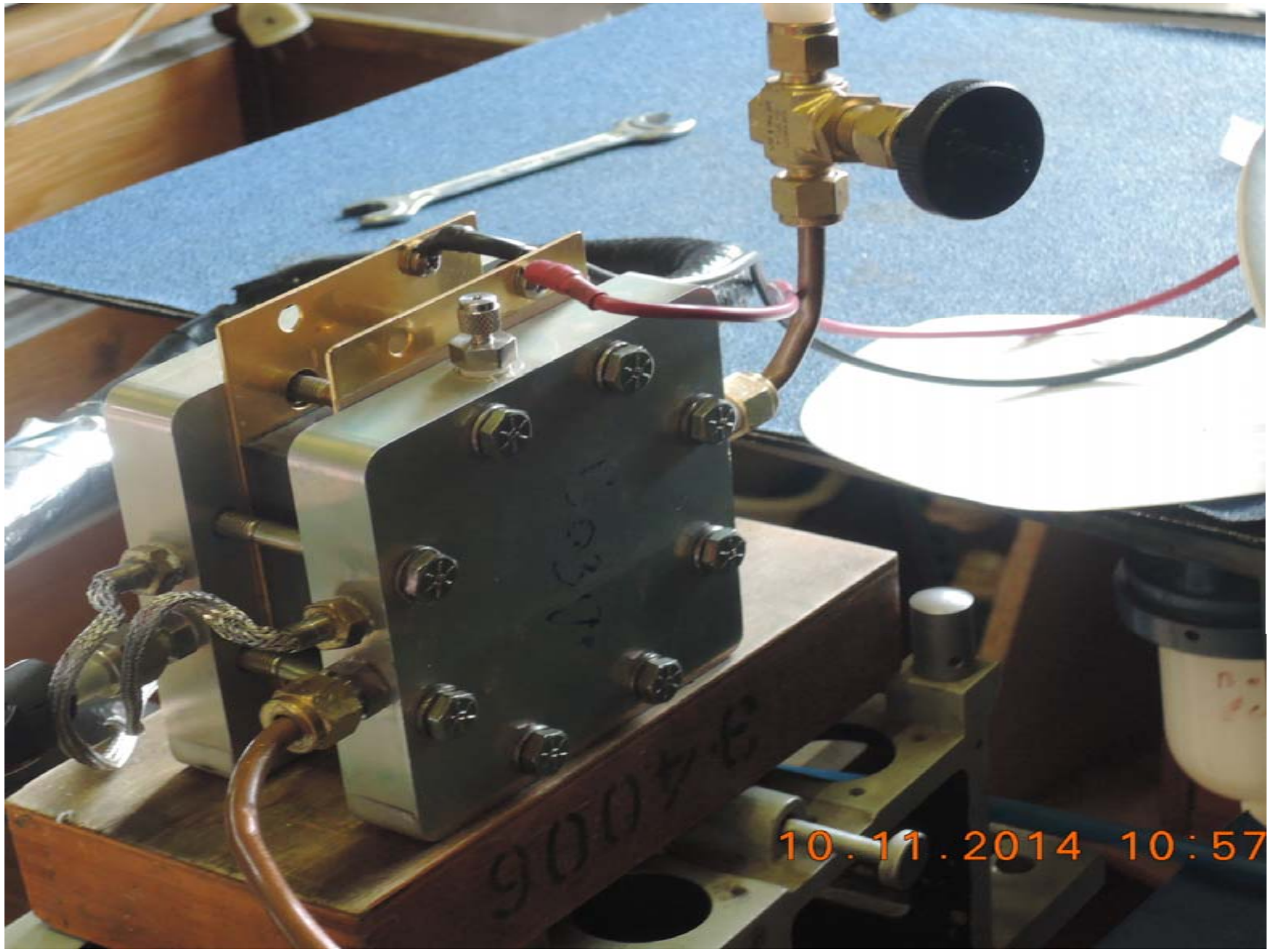
- Abstract
- Methanol tolerant catalyst material and method of its preparation are provided. These novel catalyst materials are based on organometallic clusters containing (i) a carbonyl group or a cyclic unsaturated hydrocarbon ligand group, and (ii) a chalcogen containing group selected from M.sub.nFe.sub.pX.sub.m, M.sub.nX.sub.m, M.sub.nCl.sub.pX.sub.m, or mixtures thereof wherein M=Pt, Ru or Re, X=S, Se or Te, and m, n and p=1 or 2. The catalyst materials are obtained by mixing together organometallic clusters of definite composition with an electrically conductive component in an organic solvent, subsequent removing of the solvent, and in a non-oxidizing environment, heat-treating the clusters adsorbed on the electrically conductive component at the temperature of at least 175.degree. C.
- Inventors:Grinberg; Vitali Arkad'evich; *(Moscow, RU)* ; Kulova; Tat'jana L'vovna; *(Moscow, RU)* ; Skundin; Alexander Mordukhaevich; *(Moscow, RU)* ; Pasynskii; Alexander Anatol'evich; *(Moscow, RU)* Correspondence Name and Address: E I DU PONT DE NEMOURS AND COMPANY;LEGAL PATENT RECORDS CENTER BARLEY MILL PLAZA 25/1128 4417 LANCASTER PIKE WILMINGTON DE 19805 USSerial No.: 245268Series Code: 11 Filed: October 5, 2005
- U.S. Current Class:502/150; 502/152; 502/159; 502/185 U.S. Class at Publication:502/150; 502/152; 502/159; 502/185 Intern'l Class: B01J 21/18 20060101 B01J021/18; B01J 31/00 20060101 B01J031/00*Foreign Application Data*
- DateCodeApplication NumberOct 5, 2004 RU2004129396



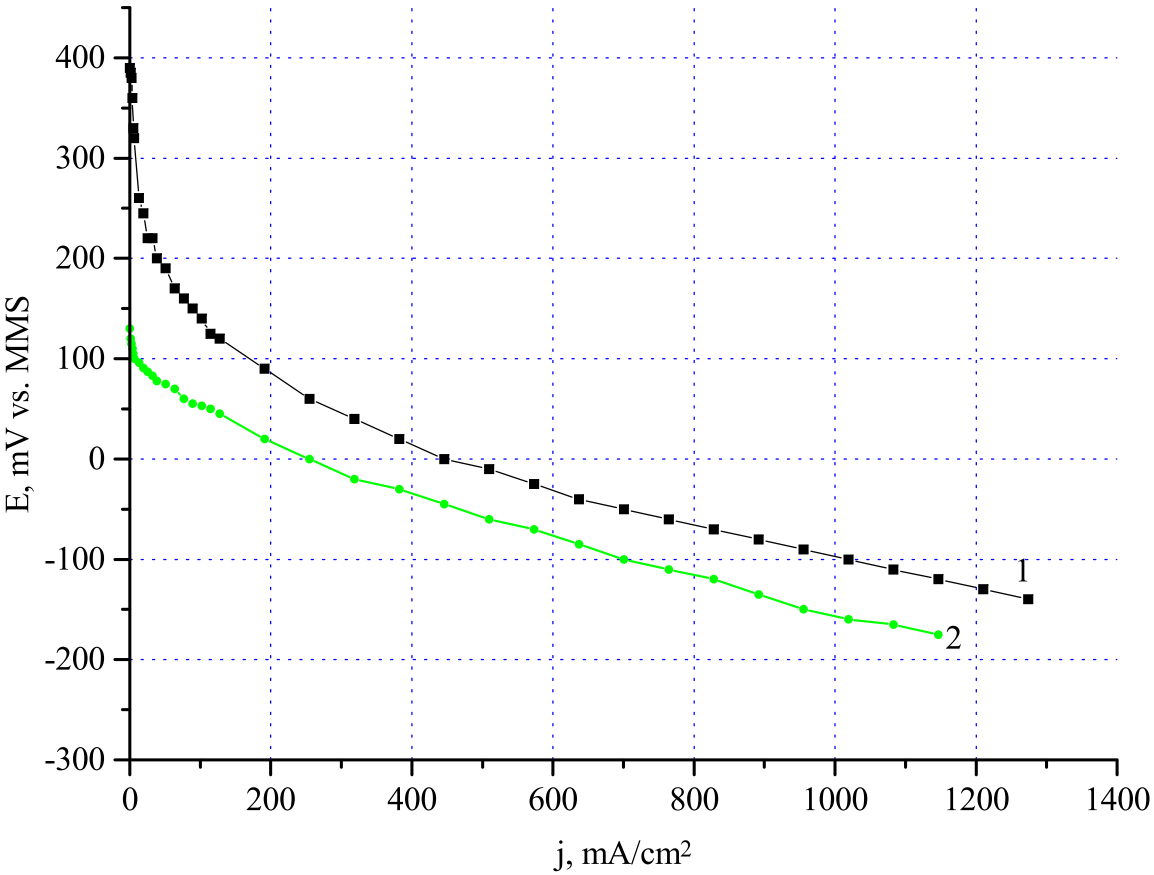
Sketch of two-compartment cell. 1 – assembling plate, 2 – screw, 3 – nut, 4 – rubber gasket, gas compartment, 6 – polyethylene gasket, 7 – working electrode, 8 – water-jacket, 9 – electrolyte compartment, 10 – counter electrode, 11 – liquid junction (salt bridge), 12 – current collector of the working electrode, 13 – gas

inlet-outlet

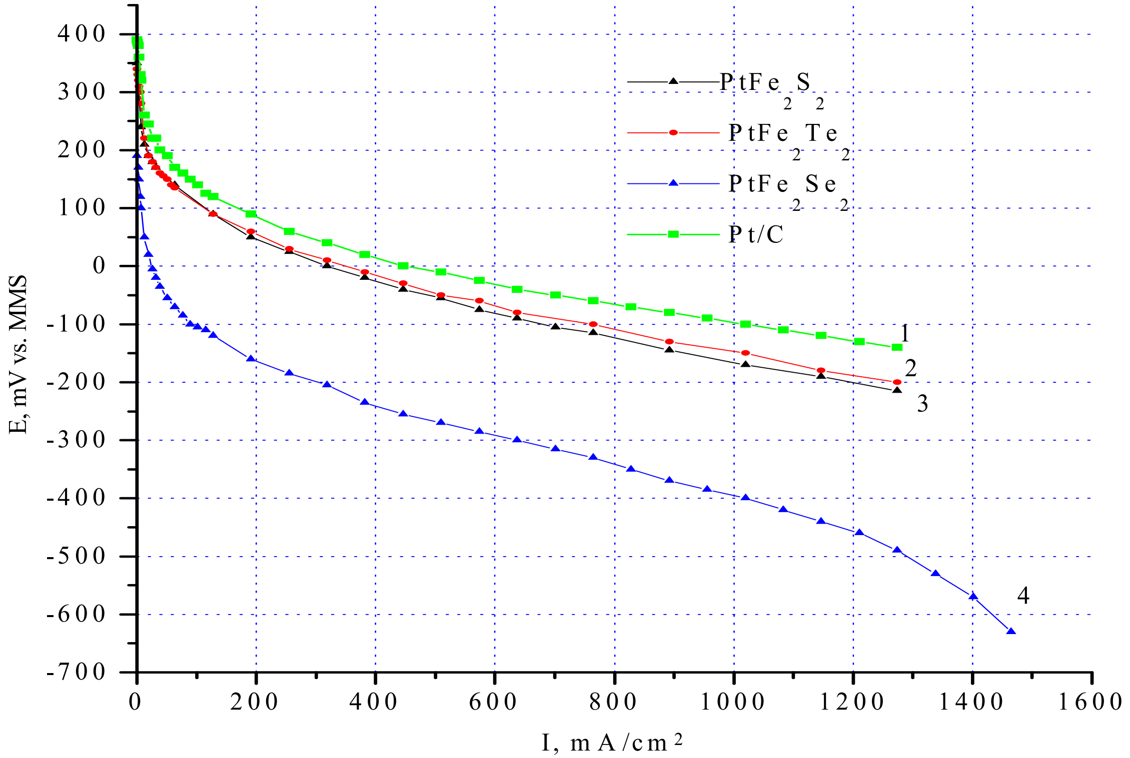
Laboratory HAFC and MeAFC setup



Galvanostatic polarization curves for the carbon-supported Pt electrode in 5 NH_2SO_4 saturated with O_2 (1), and in the presence 2M CH_3OH (2). (Pt- 0.5 mg/cm^2)

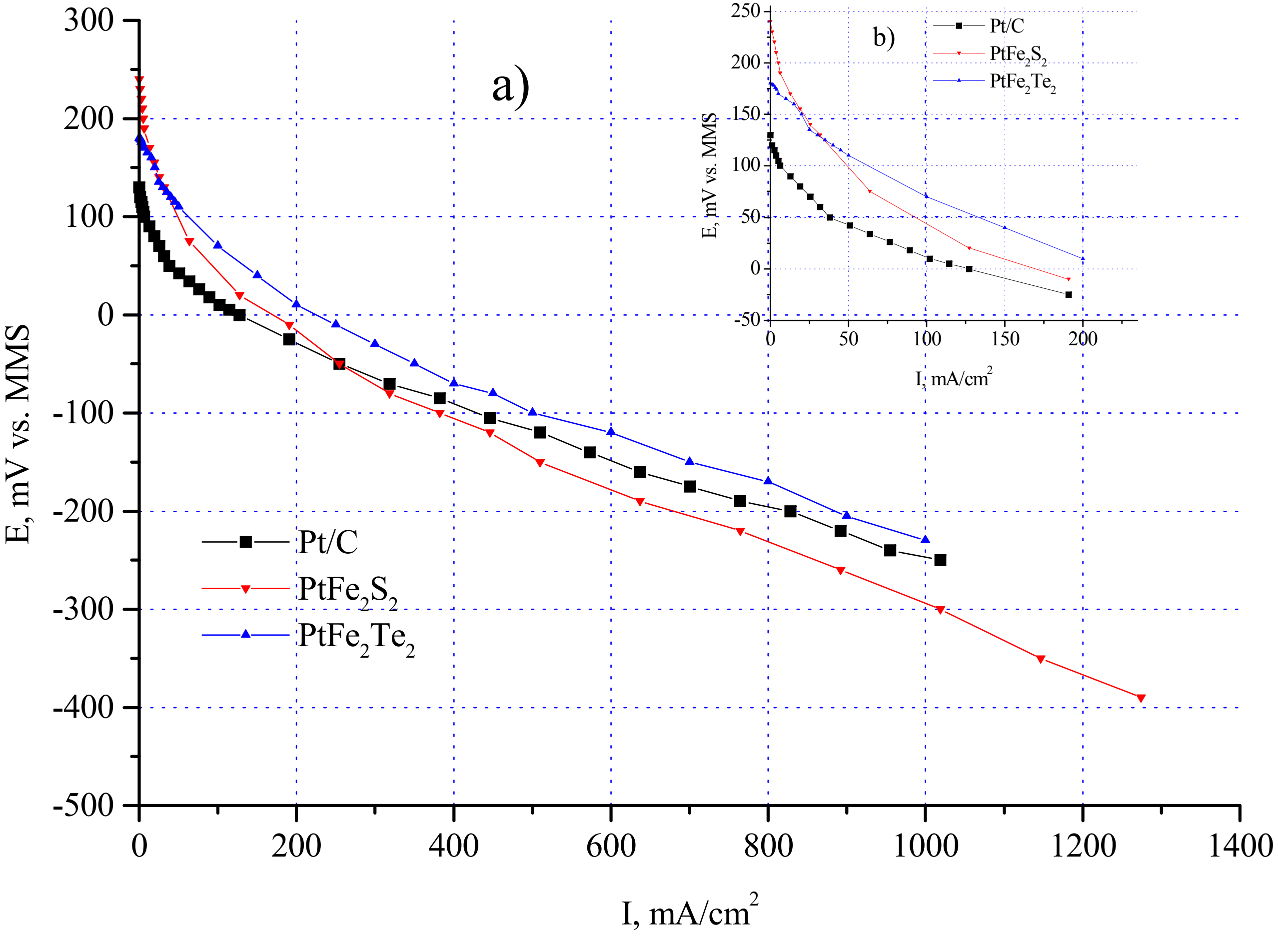


Galvanostatic polariztion curves for the carbon-supported Pt/C – 0.5 mg/cm^2 (1); $PtFe_2S_2$- 1.7 mg/cm^2 (2), $PtFe_2Te_2$ – 1.2 mg/cm^2 (3), $PtFe_2Se_2$ - 1.5 mg/cm^2 (4), electrodes in O_2-saturated 5N H_2SO_4

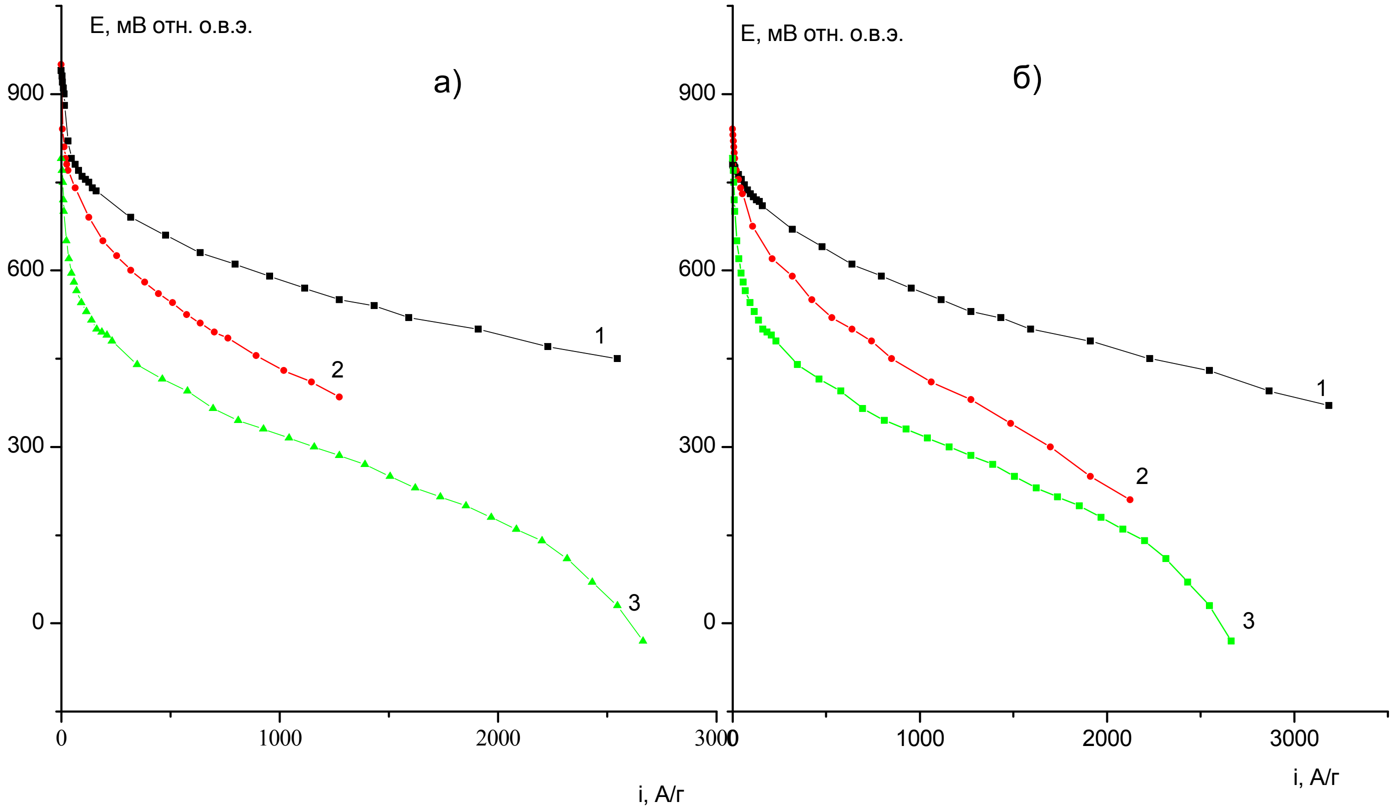


“Methanol tolerant catalyst material” ***Grinberg V.A., Kulova T.L., Skundin A.M., Pasynskii A.A.*** **// US Patent Application 20070078052, April 5, 2007.E I. du Pont de Nemours and Company**

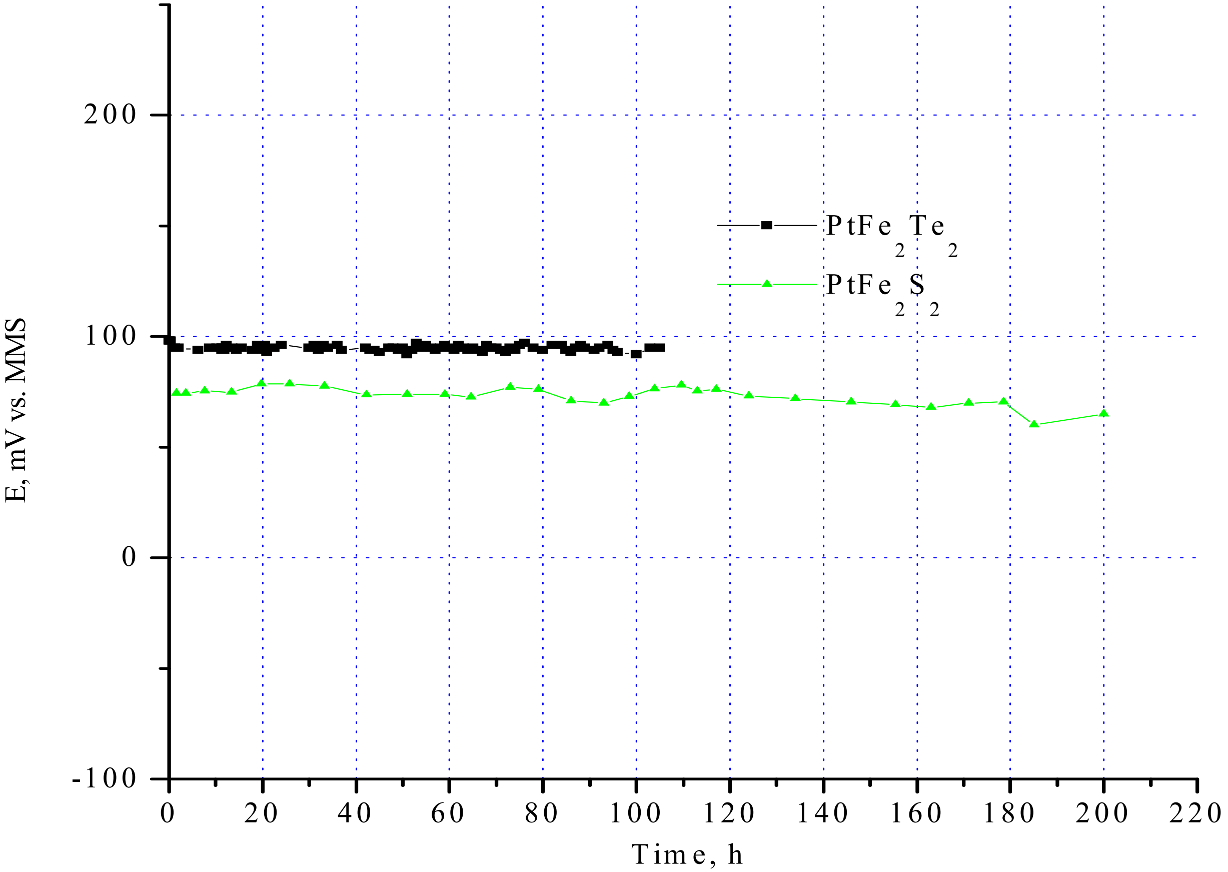
Galvanostatic polarization curves for the carbon-supported Pt - 0.5 mg/cm^2 (1), $PtFe_2S_2$ - 1.7 mg/cm^2 (2), $PtFe_2Te_2$ - 1.2 mg/cm^2 (3), electrodes in O_2-saturated 5N H_2SO_4 with 2M CH_3OH



Specific activities of catalysts (counting on Pt) from $PtFe_2Te_2$ (1), $PtFe_2S_2$ (2), and $PtFe_2Se_2$ (3) in absence (a) and in presence 2 M CH_3OH (б)



Results of prolonged test of the electrode with $PtFe_2Te_2$-catalyst (1.9 mg/cm^2) (1) and $PtFe_2S_2$ - catalyst (1.7 mg/cm^2) (2) at 80 ^{0}C in 5N H_2SO_4 with 2M CH_3OH (50 mA/cm^2)



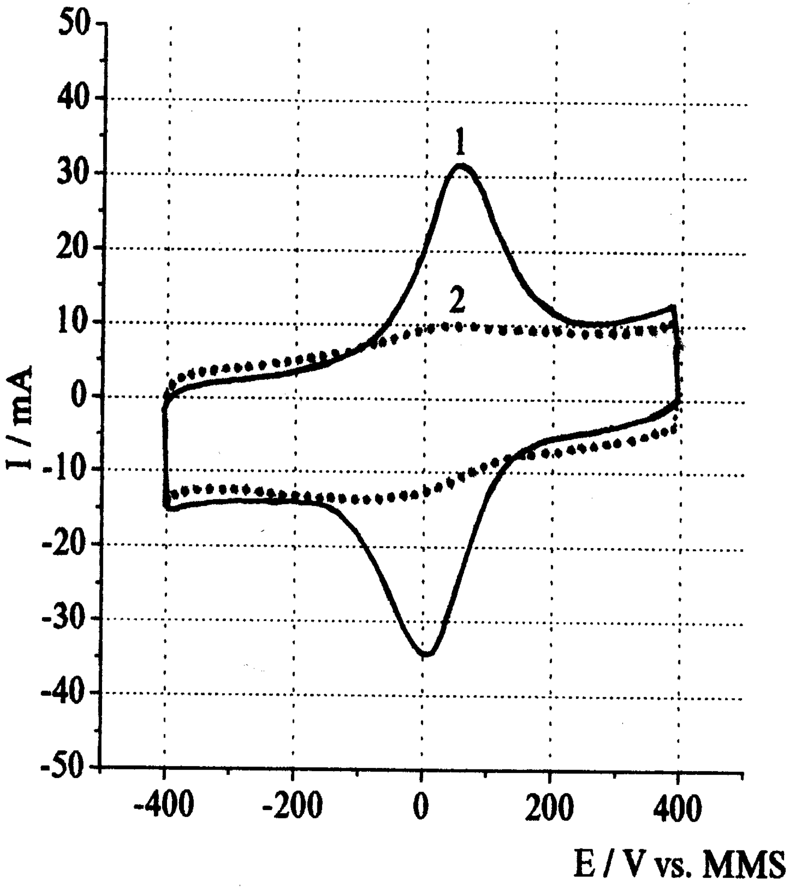
Testing of $PtFe_2Te_2$ catalyst in MeOH/air Fuel Cell

Specific power 50 mW/cm^2

at 0.3 V in 1M MeOH/air 70°C

. ***Law C.G., Grinberg V.A., Kulova T.L., Skundin A.M., Pasynskii A.A. //*** **US Patent Application 2007007011084, May 17, 2007. E. I. du Pont de Nemours and Company**

Comparison of CV for electrode with Pt-Fe-S catalyst before (curve 1) and after (curve 2) storage in an electrolyte for 1 hours

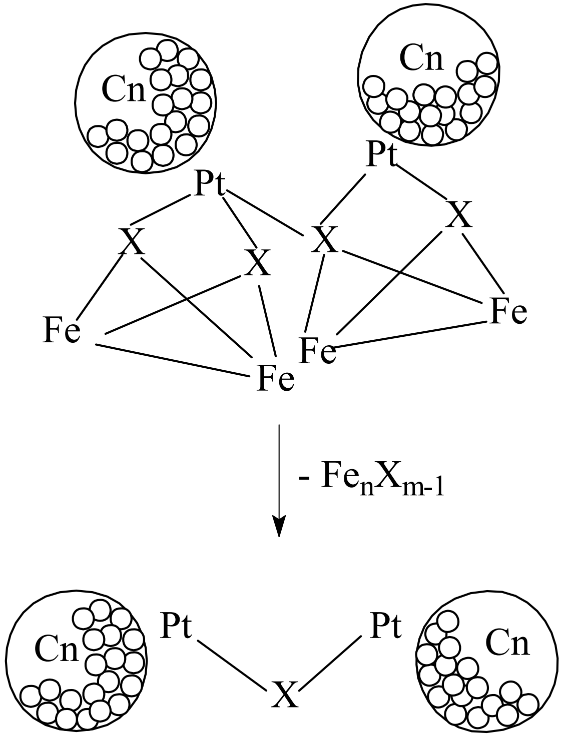


EDAX INVESTIGATION OF PtFeS CATALYSTS

- To check the suggestion that Iron leaches from the supported Pt-Fe-S catalyst, EDAX, energy dispersive analysis by X-ray, experiments were carried out. A comparison was made between a freshly prepared electrode and one that has undergone voltammetric studies. The results of the analysis confirm that iron leaches from the supported Pt-Fe-S catalyst samples. The surface composition of the freshly prepared sample had the following atomic percentages: %): Pt 14.23, Fe 39.66, S 43.01, Cl 2.16, Si 0.95. EDAX errors are ascribed to the presence of Cl and Si. Nominal atomic composition of $PtFe_2S_2$ is Pt 20, Fe 40, S 40; whereas, the real surface composition is Pt 0.71 Fe 1.98 S 2.15. EDAX results for the sample involved the voltammetry experiments, revealed only 2.72 atomic % iron, and in similar other samples no iron was seen.

- The scanning electron microphotography (SEM) obtained simultaneously with the EDAX confirmed a rather uniform distribution of the catalysts over the electrode surface.

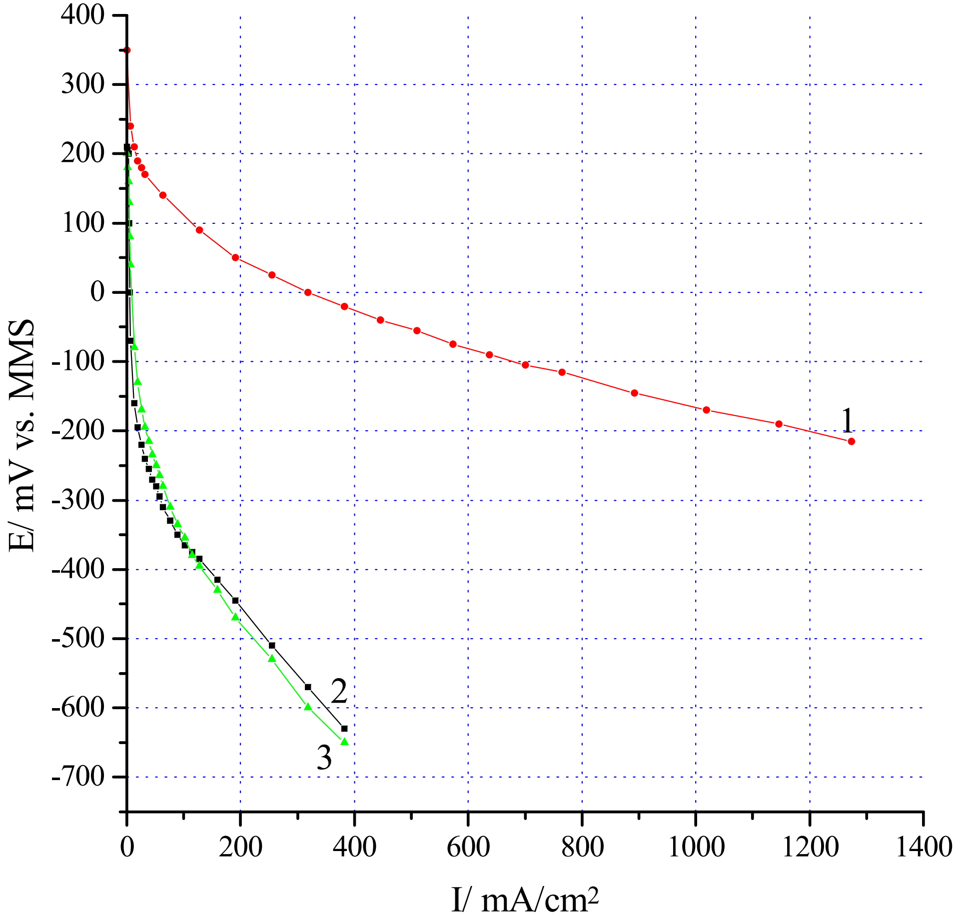
The scheme of oxygen catalytic reduction



X = S, Se, Te

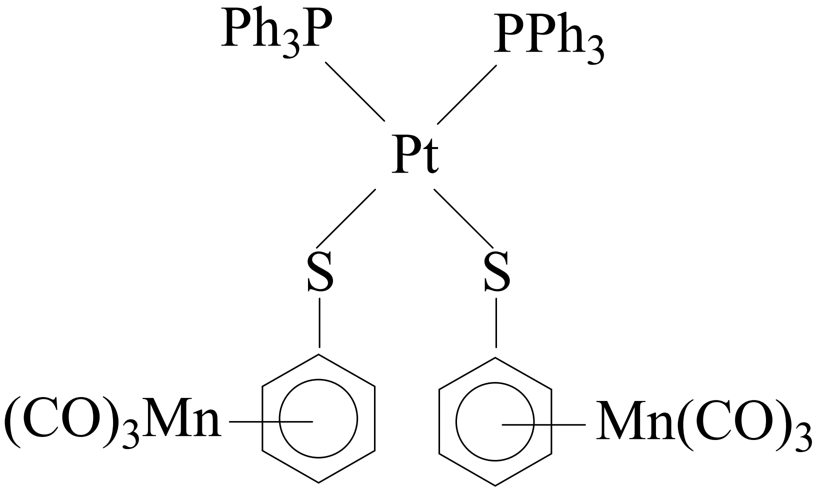
$$O{=}O + 4e + 4H^+ \longrightarrow 2H_2O$$

Polarization curves of oxygen reduction at the electrodes with Pt-Fe-S catalyst ($1.55\ mg/cm^2$, curve 1), Re-Fe-S catalyst ($1.38\ mg/cm^2$, curve 2), and Ru-Fe-S catalyst ($1.2\ mg/cm^2$, curve 3) in O_2-saturated 5N H_2SO_4



Preparation of catalyst on the basis of system PtS_2Mn_2

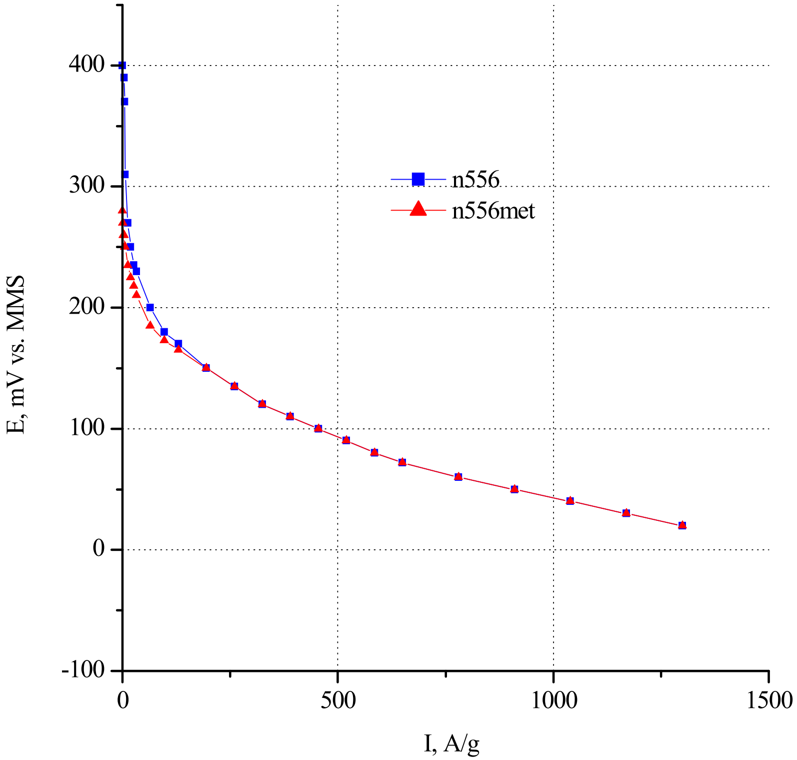
$$[(C_5H_4S)Mn(CO)_3]_2 + (PPh_3)_4Pt = (PPh_3)_2Pt[(C_5H_4S)Mn(CO)_3]_2$$



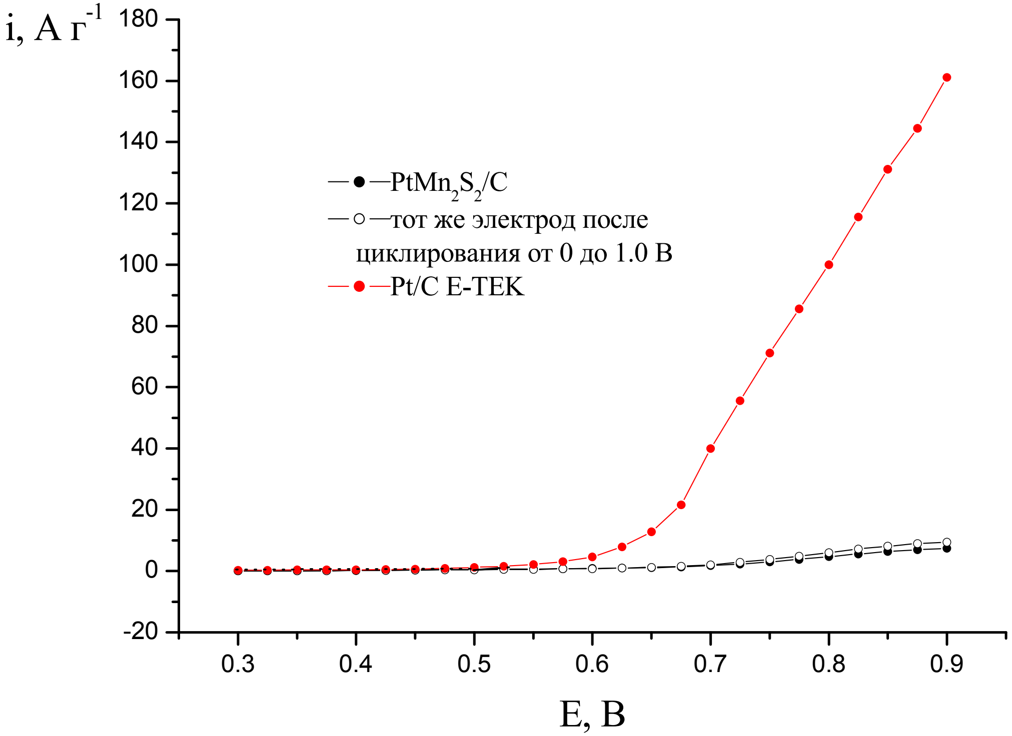
The final product of thermolysis on carbon black had a composition PtS_2Mn_2

A. A. Pasynskii, I.V.Skabitskii; Yu. V. Torubaev, The formation of Pt-S-Mn in triphenylphosphins complexes….. Russian Chemical Bulletin (Translation of Izvestiya Akademii Nauk, Seriya Khimicheskaya) (2005), (7), 1508-1511.

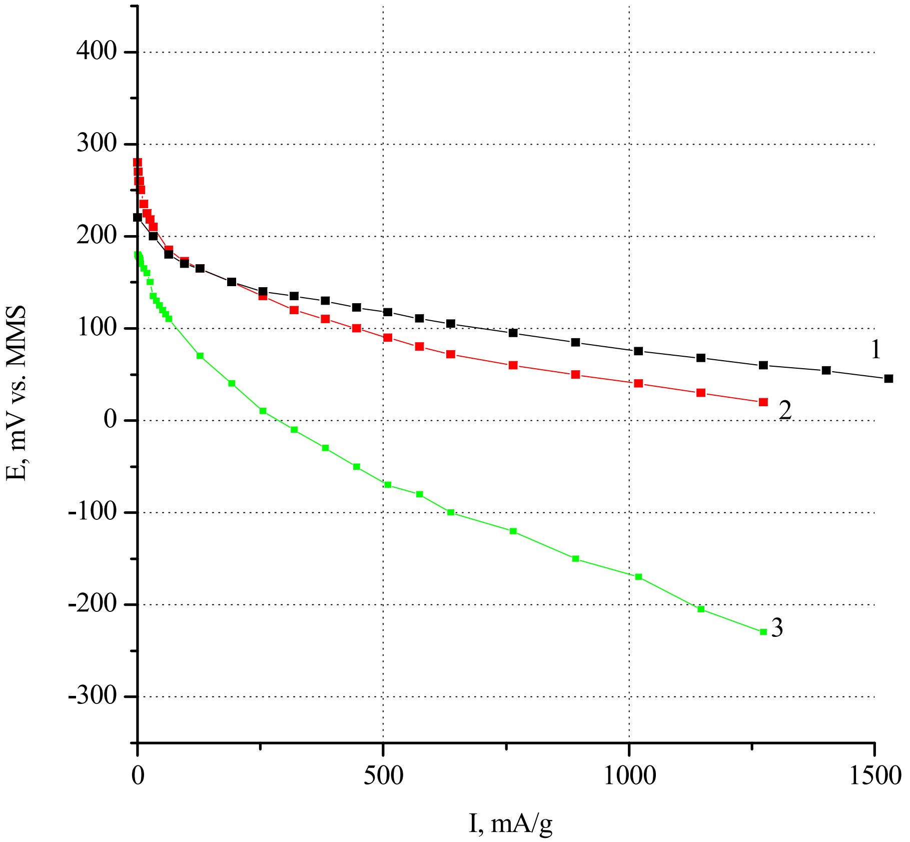
Polarization curves of oxygen reduction at the electrode with $PtMn_2S_2$ (blue) catalyst and in the presence of 1M CH_3OH(red) t= 25°C in O_2-saturated 5N H_2SO_4



Electrooxidation of 1 M CH_3OH on Pt/C E-TEK and $PtMn_2S_2/C$



Polarization curves of oxygen reduction at the electrodes with (1) Pt:P = 10:1 $PtMn_2S_2$(2) and $PtFe_2Te_2$ (3) catalysts in the presence of 1M CH_3OH t= 25°C in O_2-saturated 5N H_2SO_4



V.A. Grinberg, T.L. Kulova, A.M. Skundin, A.A. Pasynskii “Nanostructured cathode catalysts for DMFC”, //Elektrochimiya 2007.V.43 №.1.P.72-76 .

S

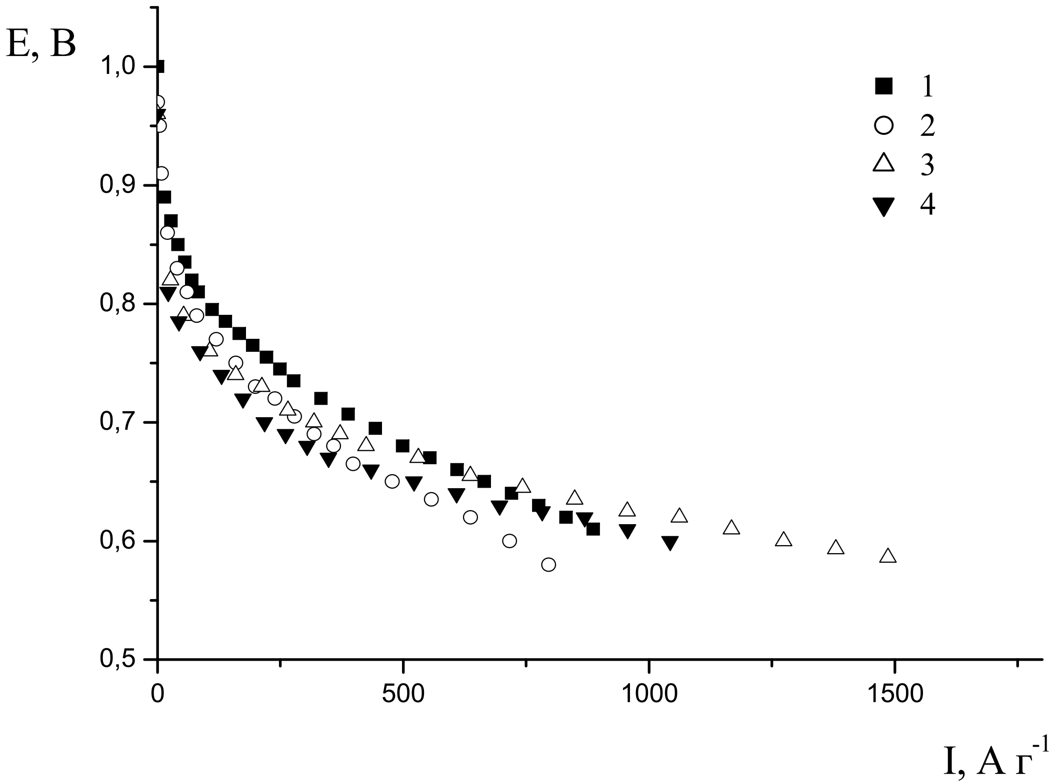
Bimetallic cathode electro-catalysts for H_2-O_2 FC on the basis of coordination compounds

Pt-Cr　Pt-Co　Pt-W　Pt- Fe　Pt-Mn　Pt-Ni

Preparation of Binary Catalysts on the basis coordination compounds

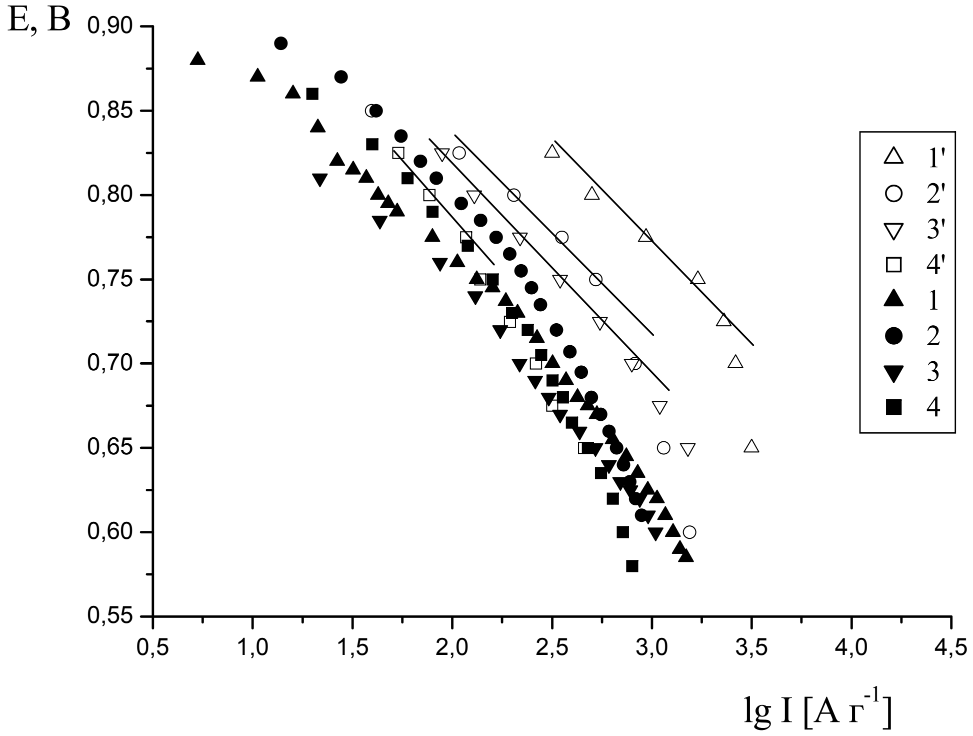
- Ethoxy dicyclopentadiene–platinum–ethoxide **$(C_{10}H_{12}OC_2H_5)2Pt_3(OC_2H_5)_4$** was chosen as the initial platinum compound for synthesis of heteroorganometallic precursors. Coordination complexes of cobalt, chromium, tungsten, iron, manganese, and nickel were used as its partners, namely: **$Co_2(CO)_6(HOCH_2CCCH_2OH)$, $[C_5H_5Cr(CO)_3]_2$, $[C_5H_5W(CO)_3]_2$ $[CpFe(CO)_2]_2$, $HOOCC_5H_4Mn(CO)_3$, $(\alpha\text{-pic})2Ni(OOCCMe_3)_2$.**
- 1) sonication of highly dispersed Ketjen Black (the specific surface area 600 m^2 g^{-1}) in absolute tetrahydrofuran (THF), 2) dropwise addition of the corresponding mixed precursors solution in THF, 3) sonication, 4) drying at 100^{o}C under vacuum, 5) annealing at 500^{o}C in a hydrogen atmosphere for 45 min, 6) cooling in the atmosphere of a high–purity argon. The obtained catalysts contained 30 wt.% of the metals and 70 wt.% of the carbon black. The atomic ratio of the metals in binary systems was close to 1:1.

The polarisation curves of oxygen reduction on GDE electrodes with the catalysts: 1- Pt/C E-TEK, 2- Pt-W/C, 3-Pt-Cr/C, 4-Pt-Co/C.

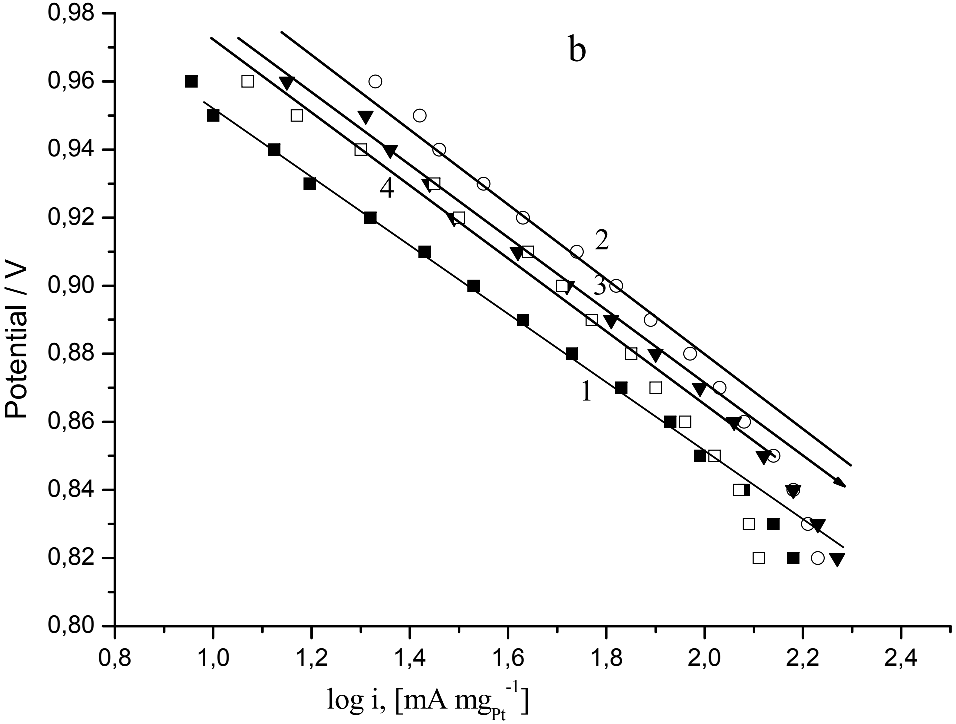


V.A. Grinberg, T.L. Kulova, N.A. Mayorova, O.A.Khazova et al.
“Nanostructure cathode catalysts for hydrogen-oxygen fuel cells”,
Elektrohimiya 2007. V.43 №.1. P. 77-86

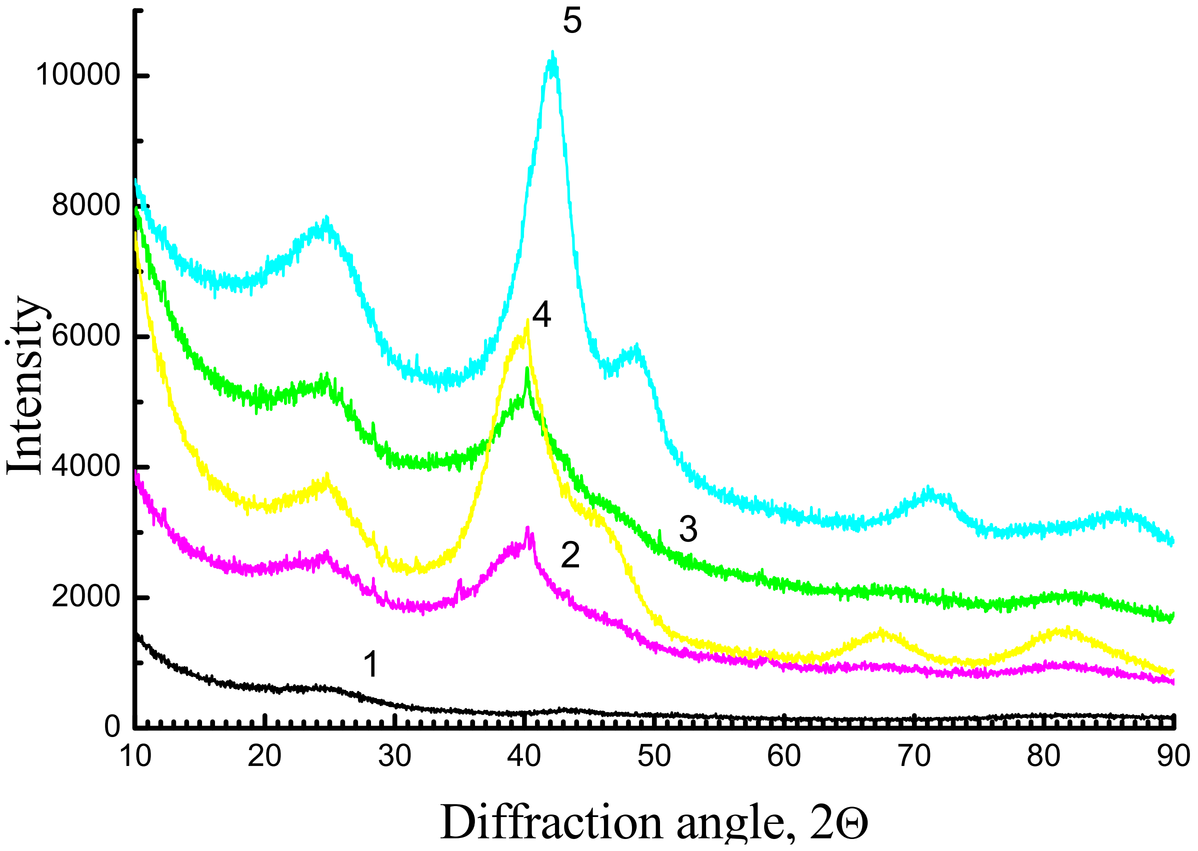
Tafel plots for currents oxygen reduction on GDE (1-4), and for kinetic currents calculated from the measurements on TFRDE (1’-4’):1,1’- Pt-Cr/C, 2, 2’ – Pt/C E-TEK, 3,3’ – Pt-Co/C, 4,4’- Pt-W/C.



Voltammograms (a) and Tafel plots (b) of the oxygen reduction at Pt/C (1), PtFe/C (2), PtMn/C (3), and PtNi/C (4) in 0.5 M H2SO4 solution saturated by oxygen at the atmospheric pressure measured at the potential sweep rate 5 mV s–1 and the electrode rotation rate 2000 rpm. Platinum loading for all electrodes is 21 μg cm^{-2}.

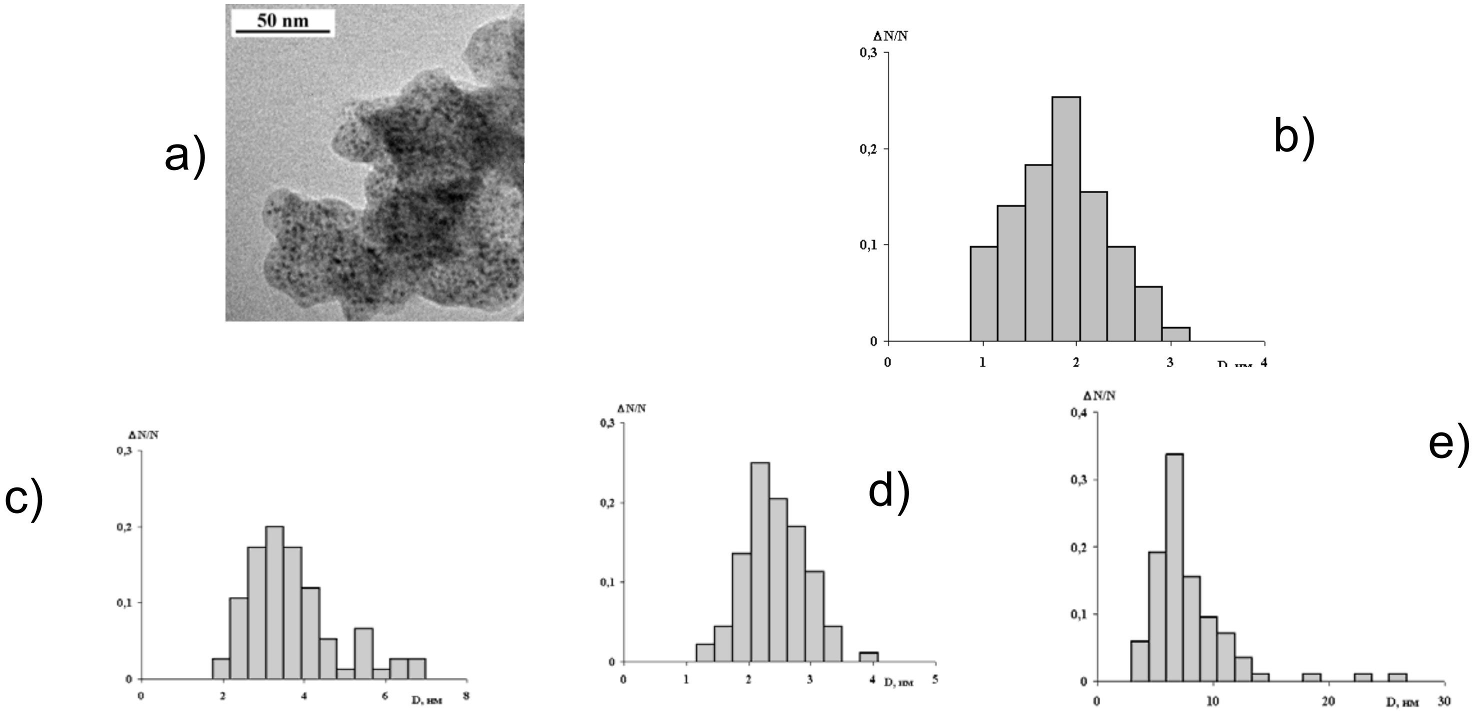


X-ray diffraction patterns: 1 - carbon support; 2 - PtMn/C; 3 - PtFe/C; 4 - Pt; 5 - PtNi/C



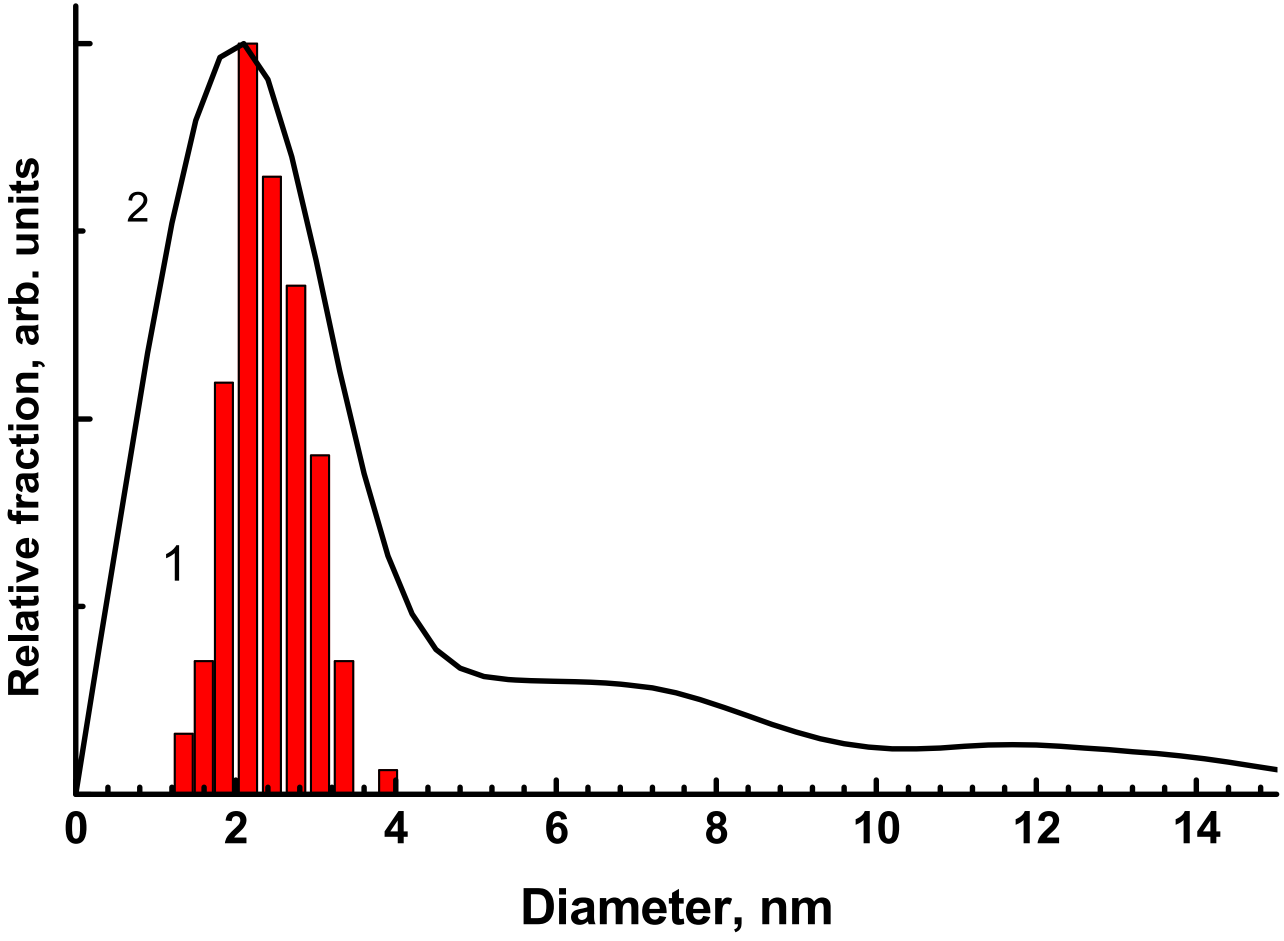
Metallic particles and phases with composition Pt_3Fe, PtFe, $PtMn_3$, PtMn, $Pt_{0.63}Mn_{0.37}$, Pt_3Ni and some other Pt-Ni compounds were detected.

Catalysts of particle size distribution

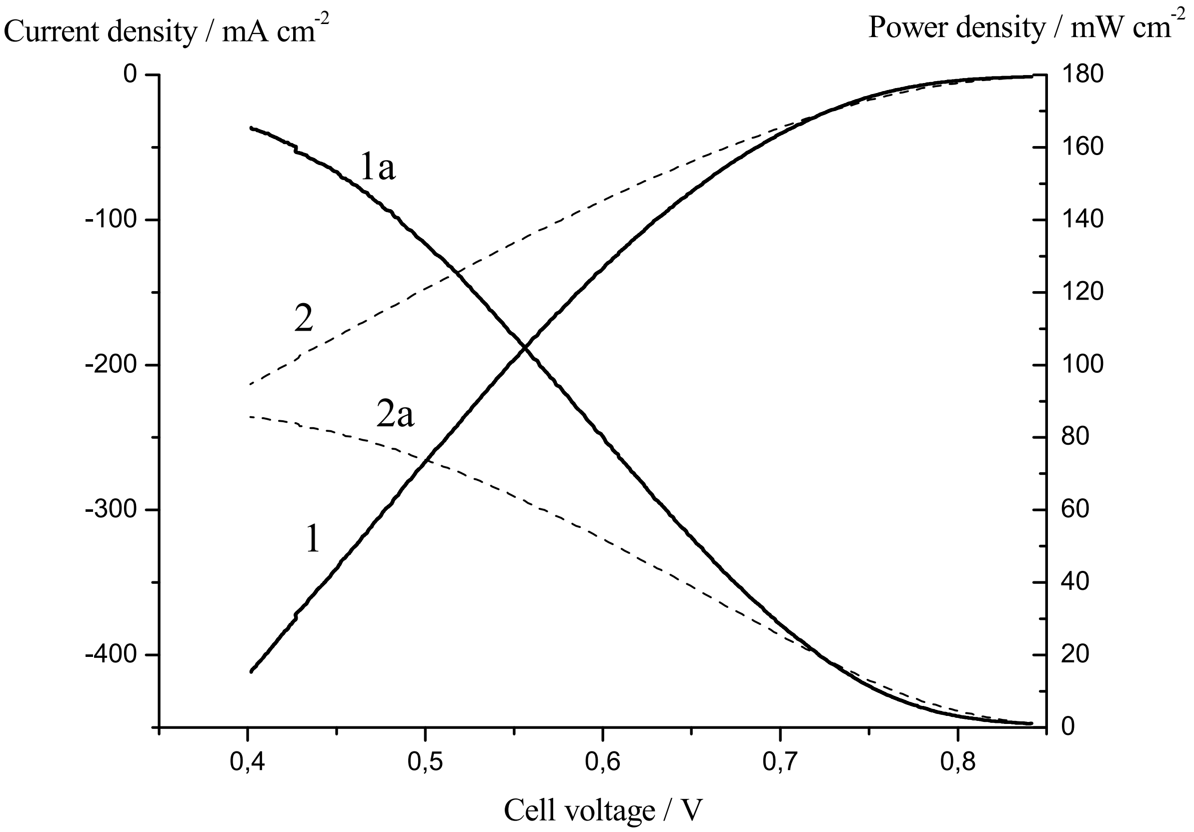


Microphotograph of Pt/C sample (a) and histograms of particle size distribution (b-e) for (b) Pt/C, (c) PtFe/C, (d) PtMn/C, and (e) PtNi/C.

Comparison of particles size distribution extracted from TEM (histogram) and from SAXS (solid curve) data for PtMn/C sample: 1 -TEM; 2 - SAXS

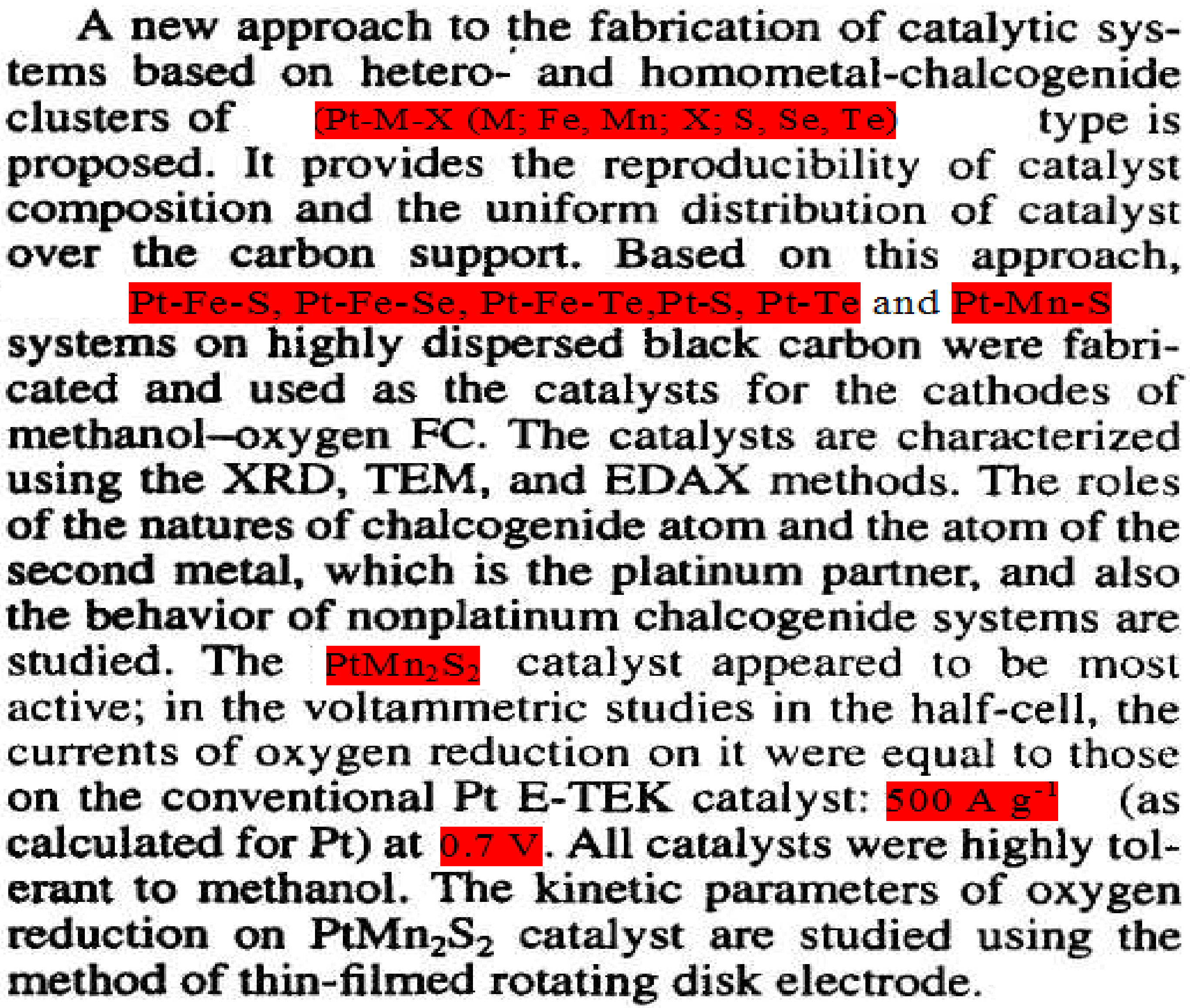


Dependences of current density (1, 2) and power density (1a, 2a) on the unit fuel cell voltage for MEA with PtFe/C (1, 1a) or commercial Pt/C (2, 2a) cathode catalyst and Nafion 212 membrane measured at room temperature in a laboratory HAFC setup.



V.A. Grinberg, V.V. Emets, N.A. Mayorova, A.A. Pasynskii et al., Coordination compounds as the precursors for preparation of nanosized platinum or platinum-containing mixed-metal catalysts of oxygen reduction reaction // Coordination chemistry 2015 (in press)

CONCLUSIONS



A new approach to the fabrication of catalytic systems based on hetero- and homometal-chalcogenide clusters of (Pt-M-X (M; Fe, Mn; X; S, Se, Te) type is proposed. It provides the reproducibility of catalyst composition and the uniform distribution of catalyst over the carbon support. Based on this approach, Pt-Fe-S, Pt-Fe-Se, Pt-Fe-Te,Pt-S, Pt-Te and Pt-Mn-S systems on highly dispersed black carbon were fabricated and used as the catalysts for the cathodes of methanol–oxygen FC. The catalysts are characterized using the XRD, TEM, and EDAX methods. The roles of the natures of chalcogenide atom and the atom of the second metal, which is the platinum partner, and also the behavior of nonplatinum chalcogenide systems are studied. The $PtMn_2S_2$ catalyst appeared to be most active; in the voltammetric studies in the half-cell, the currents of oxygen reduction on it were equal to those on the conventional Pt E-TEK catalyst: 500 A g^{-1} (as calculated for Pt) at 0.7 V. All catalysts were highly tolerant to methanol. The kinetic parameters of oxygen reduction on $PtMn_2S_2$ catalyst are studied using the method of thin-filmed rotating disk electrode.

- The specific activity system Pt-Mn-S/C in the presence of 1 M MeOH reach 110 A g^{-1} Pt, and for catalyst Pt-P /C 44–100 A g^{-1} Pt in relationship from ratio Pt-P under potential 0.85 B vs. (r.h.e)
- On the basis of coordination compounds developed high active catalysts for hydrogen-oxygen FC: Pt-Cr; Pt-Co; Pt-W, Pt-Fe, Pt-Mn, Pt-Ni.
- Under voltage 0.6V specific currents of Pt-Co/C reach 1200 A g^{-1}, Pt-Cr/C – 1500 A $g^{-1.}$

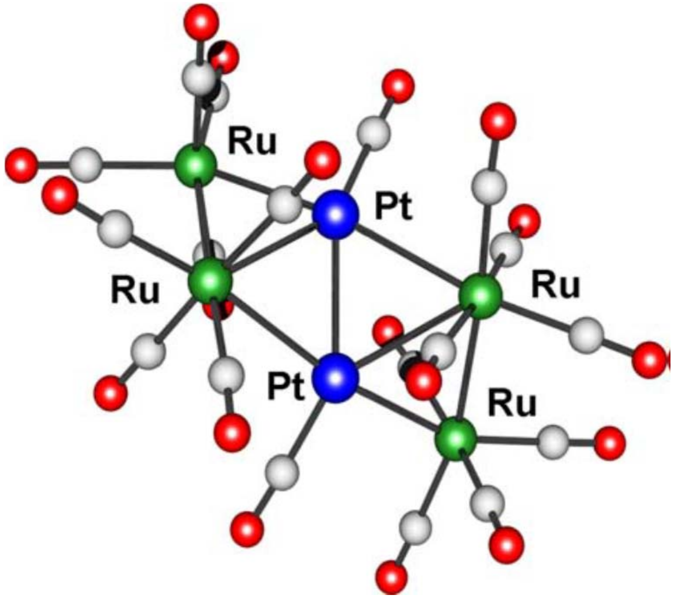
Bimetallic anode nanoelectrocatalysts on the basis of organo-matallic clusters

Nanocatalysts on the basis of clusters Pt–Ru/C nanocomposites

- 1. J. T. Moore, J. D. Corn, D. Chu, R. Jiang, D. L. Boxall, E. A. Kenik, and C. M. Lukehart (2003). Chem. Mater. 14, 505. Synthesis and Characterization of a Pt_3Ru/Vulcan Carbon Powder Nanocomposite and Reactivity as a Methanol Electrooxidation Catalyst.
- 2. D. L. Boxall, G. A. Deluga, E. A. Kenik, W. D. King, and C. M. Lukehart (2001). Chem. Mater. 13, 891. Higher Activity Electrocatalyst for Methanol Oxidation
- 3. W. D. King, J. D. Corn, O. J. Murphy, D. L. Boxall, K. C. Kwiatkowski, S. R. Stock, and C. M. Lukehart (2003). J. Phys. Chem. B. 107, 5467. Pt-Ru and Pt-Ru-P/Carbon Nanocomposites: Synthesis, Characterization, and Unexpected Performance as Direct Methanol Fuel Cell (DMFC) Anode Catalysts.
- Department of Chemistry, Vanderbilt University, Nashville, Tennessee, USA.

Molecular structure

$Pt_2Ru_4(CO)_{18}$

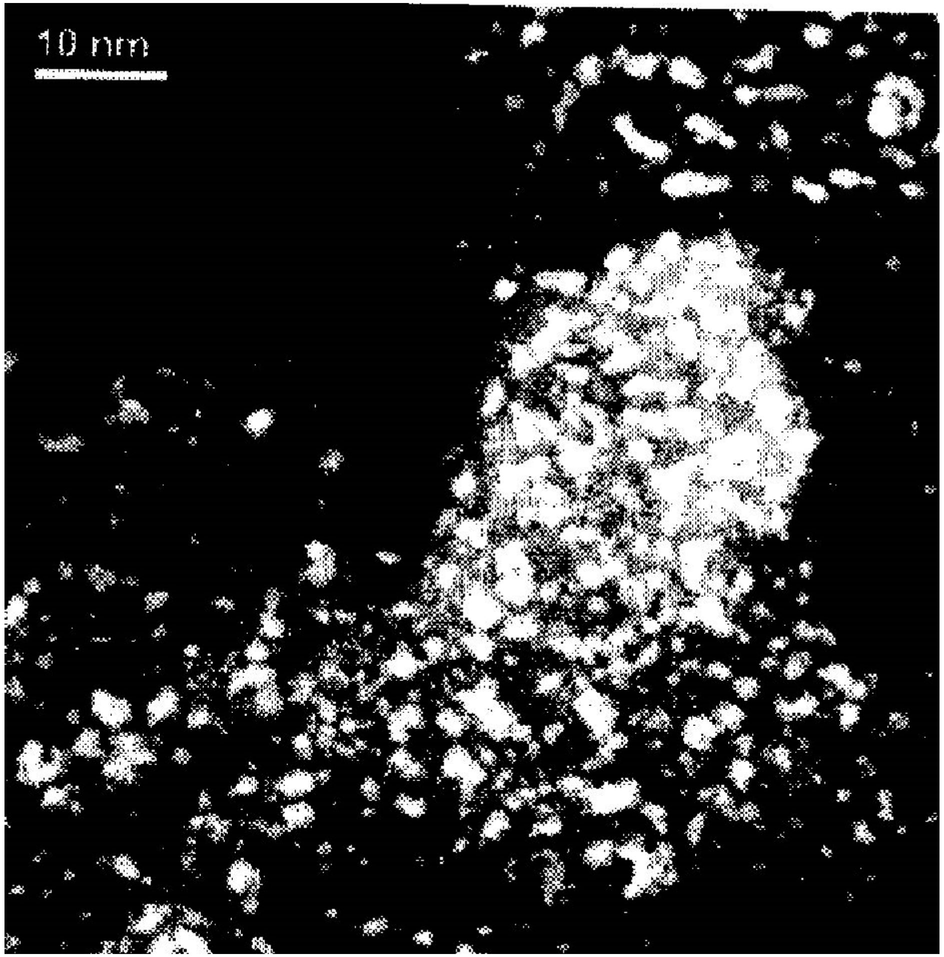


The molecular structure of $Pt_2Ru_4(CO)_{18}$

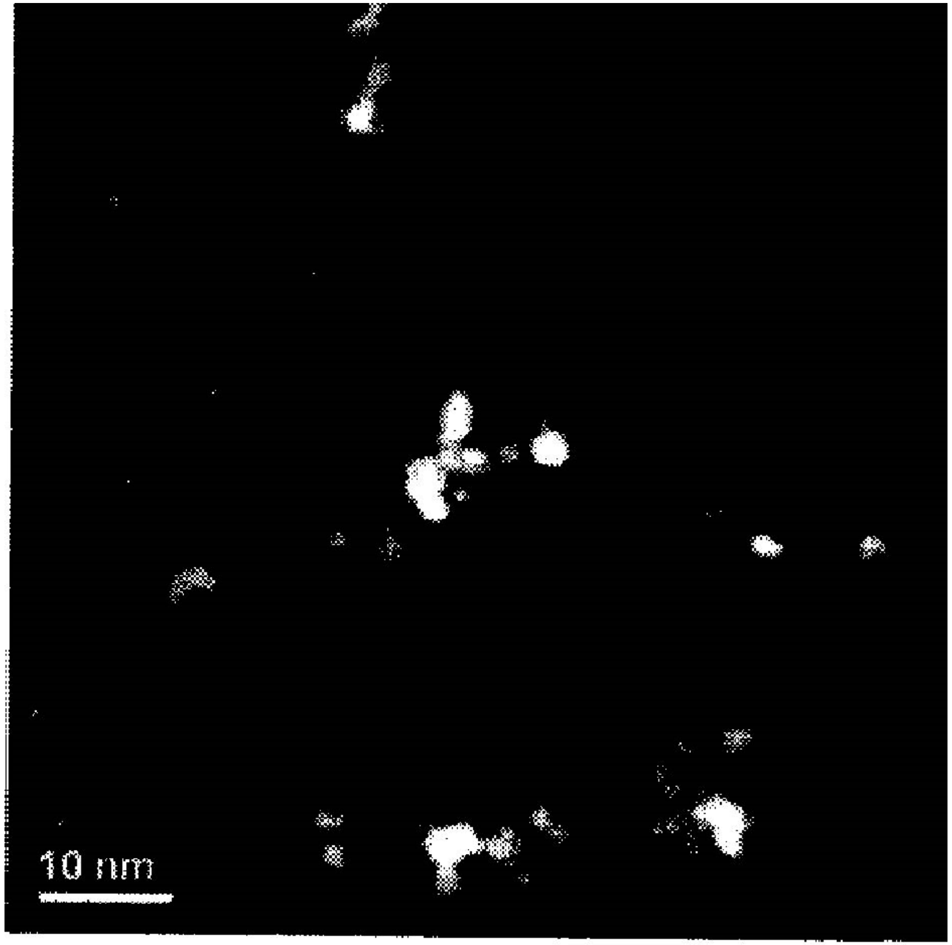
Brenda L. Garcıŕa, Burjor Captain, Richard D. Adams, Ana B. Hungria,
Paul A. Midgley, Sir John Meurig Thomas, and John W. Weidner //
J. Clust. Sci. 2007. V. 18. P. 121. Bimetallic Cluster Provides a Higher Activity
Electrocatalyst for Methanol Oxidation.

Department of Chemistry and Biochemistry, University of South Carolina,
Columbia, SC 29208, USA.

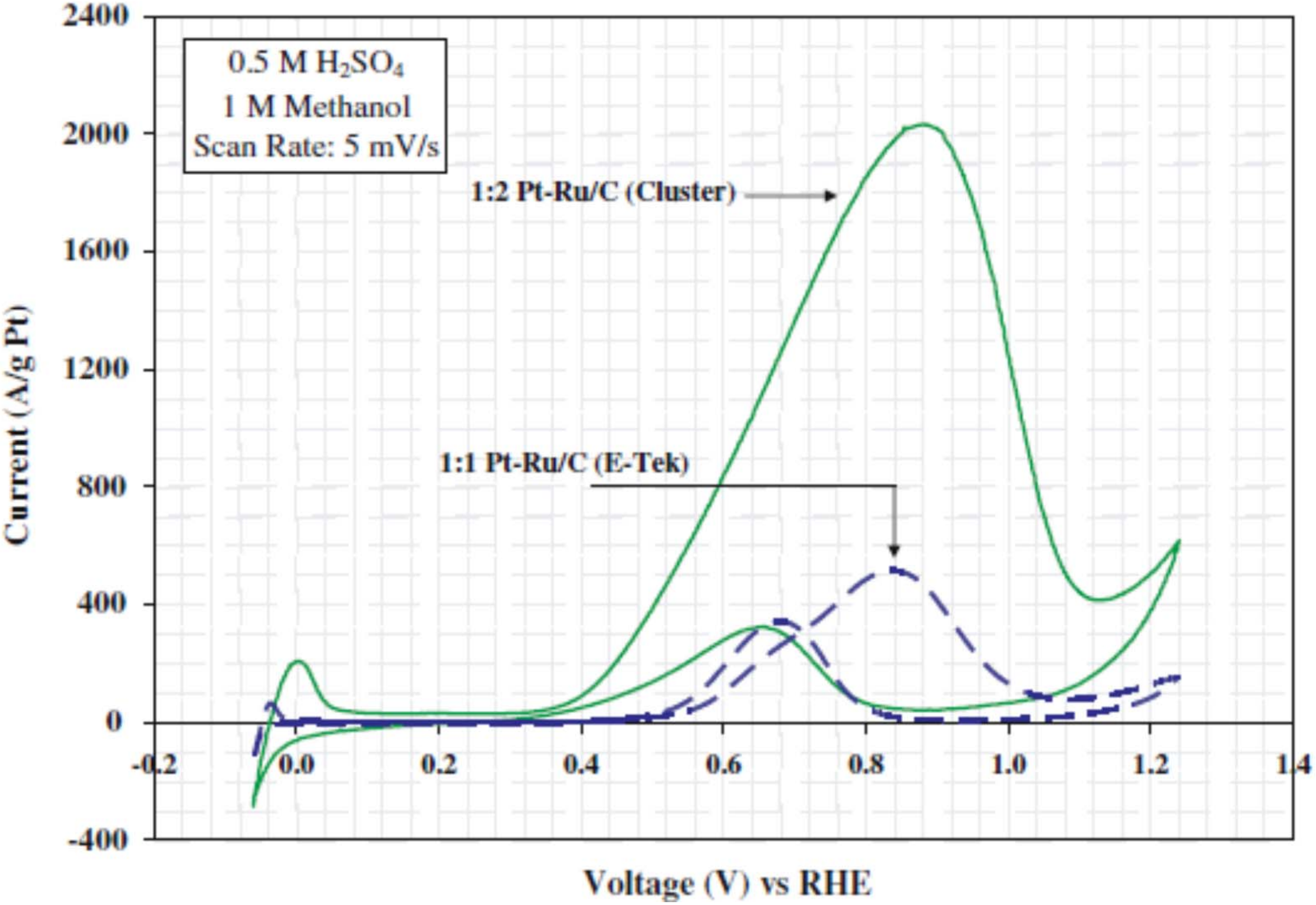
TEM sample of catalyst 44 ww% 1:2 PtRu/C as a precursor of catalyst was used cluster $Pt_2Ru_4(CO)_{18}$



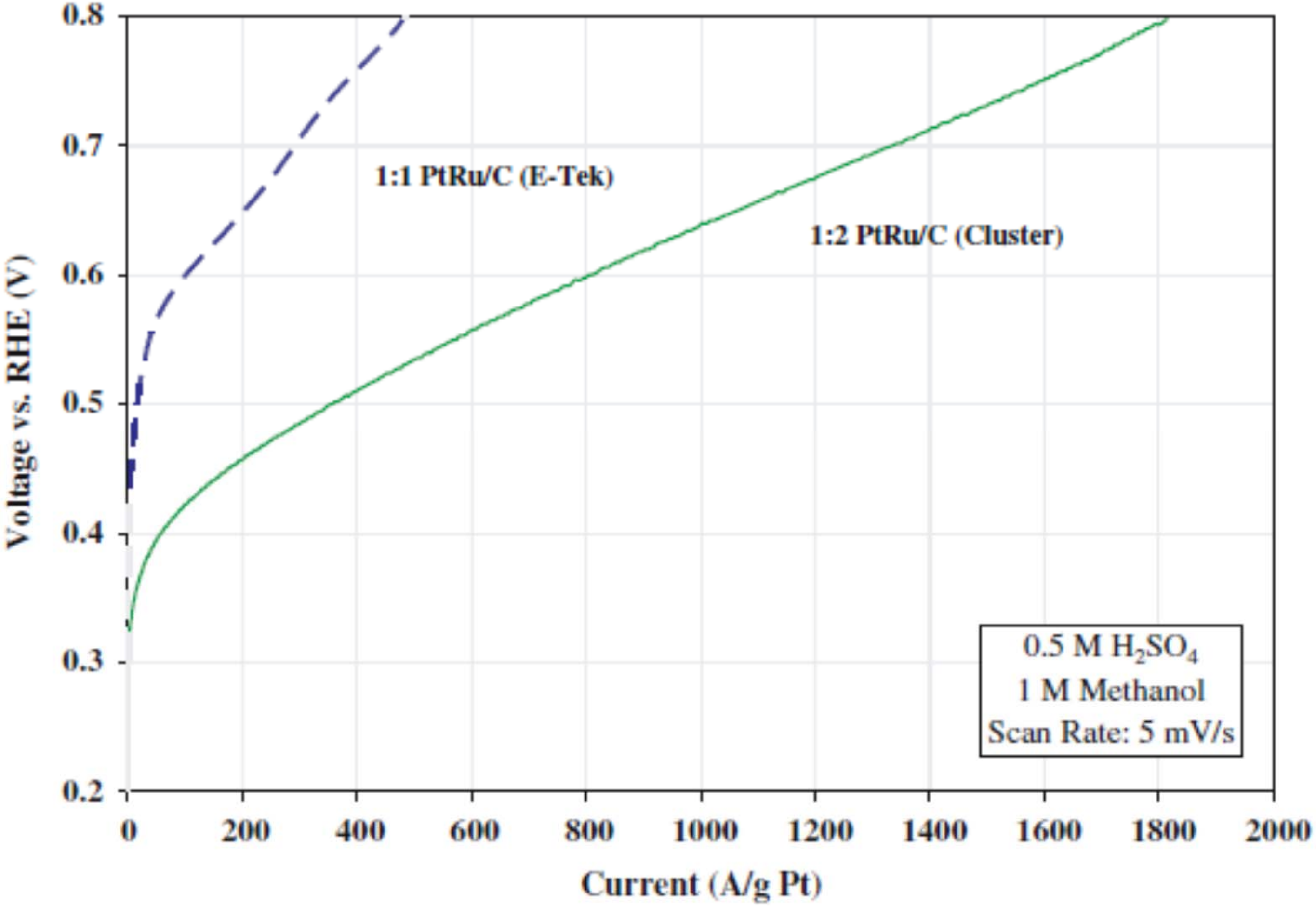
TEM sample commercial catalyst E-TEK 52 ww. % 1:1 PtRu/C.



Cyclic voltammograms of commercial catalyst E-TEК and catalyst from cluster $Pt_2Ru_4(CO)_{18}$ deposited on GC in 0.5 M H_2SO_4 in the presence of 1M CH_3OH. Scan rate 5 mV/s. Ammout of Pt ~ 40.0 nmol.



Polarisation curves oxidation 1 M CH_3OH in 0.5 M H_2SO_4 obtained from cyclic voltammogram commercial catalyst E-TEK and the catalyst from cluster $Pt_2Ru_4(CO)_{18}$. Scan rate 5 mV/s



Catalyst on the basis cluster for EtOH electrooxidation

Adsorption of ethanol on Pt

$$Pt + CH_3CH_2OH \rightarrow Pt - OCH_2CH_3 + H^+ + e^-$$

$$Pt + CH_3CH_2OH \rightarrow Pt - CHOHCH_3 + H^+ + e-$$

The products of oxidation:

CH_3CHO; CH_3COOH; CO_2; CH_4

Increase of electrocatalitic activity modification of Pt

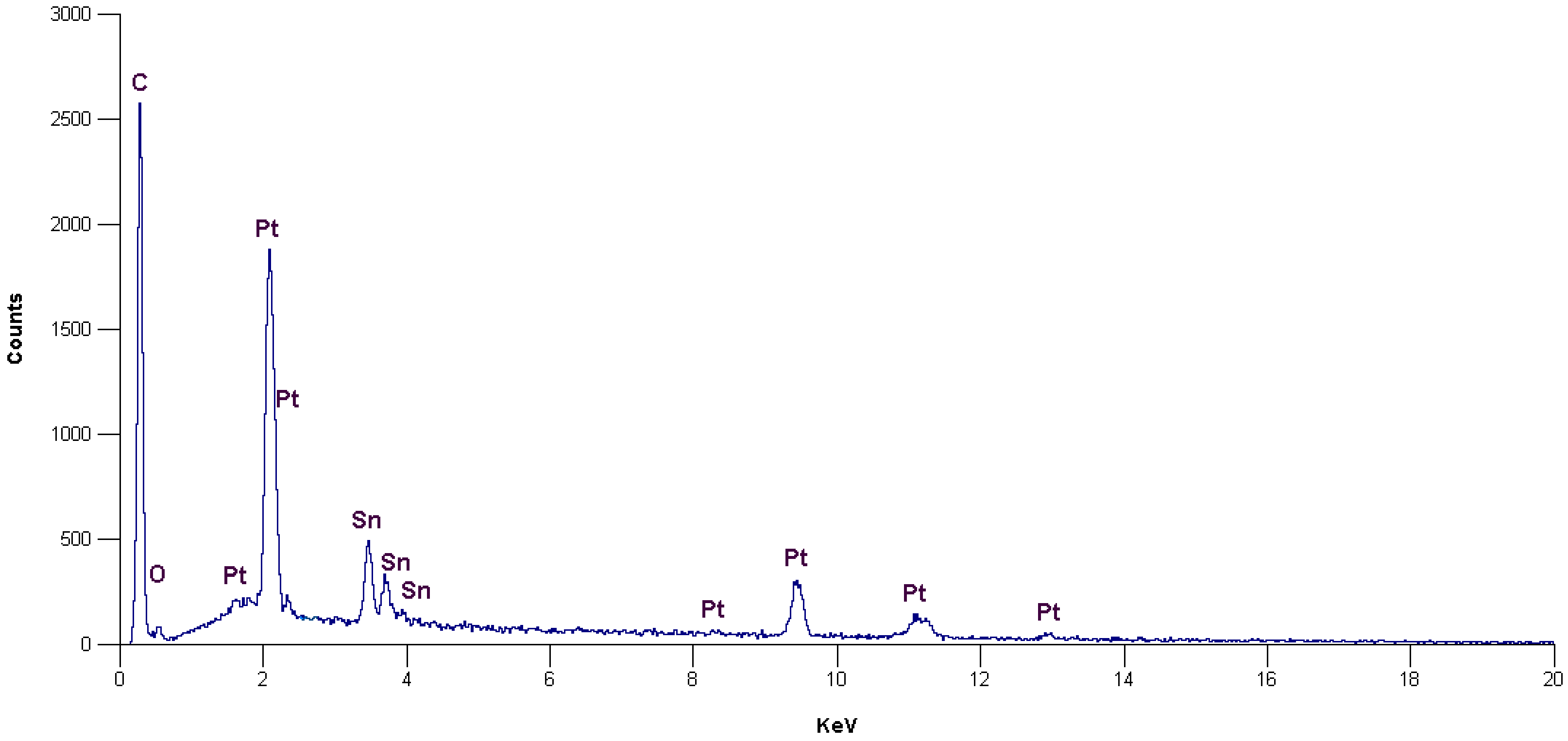
by metalls Ru, Pb, Sn.

Preparation of Pt-Sn cluster

- $(C_{10}H_{12}OC_2H_5)2Pt_3(OC_2H_5)_4$
- Anhydrous $SnCl_2$
- $Ph_2PCH_2PPh_2$ (dppm)
- ionic cluster $[diglimSnCl]^+$ $[dppmPt(SnCl_3)_3]^-$
- according to the data of X-ray diffraction (XRD) analysis, it contained three

direct platinum–tin bonds in the anion.

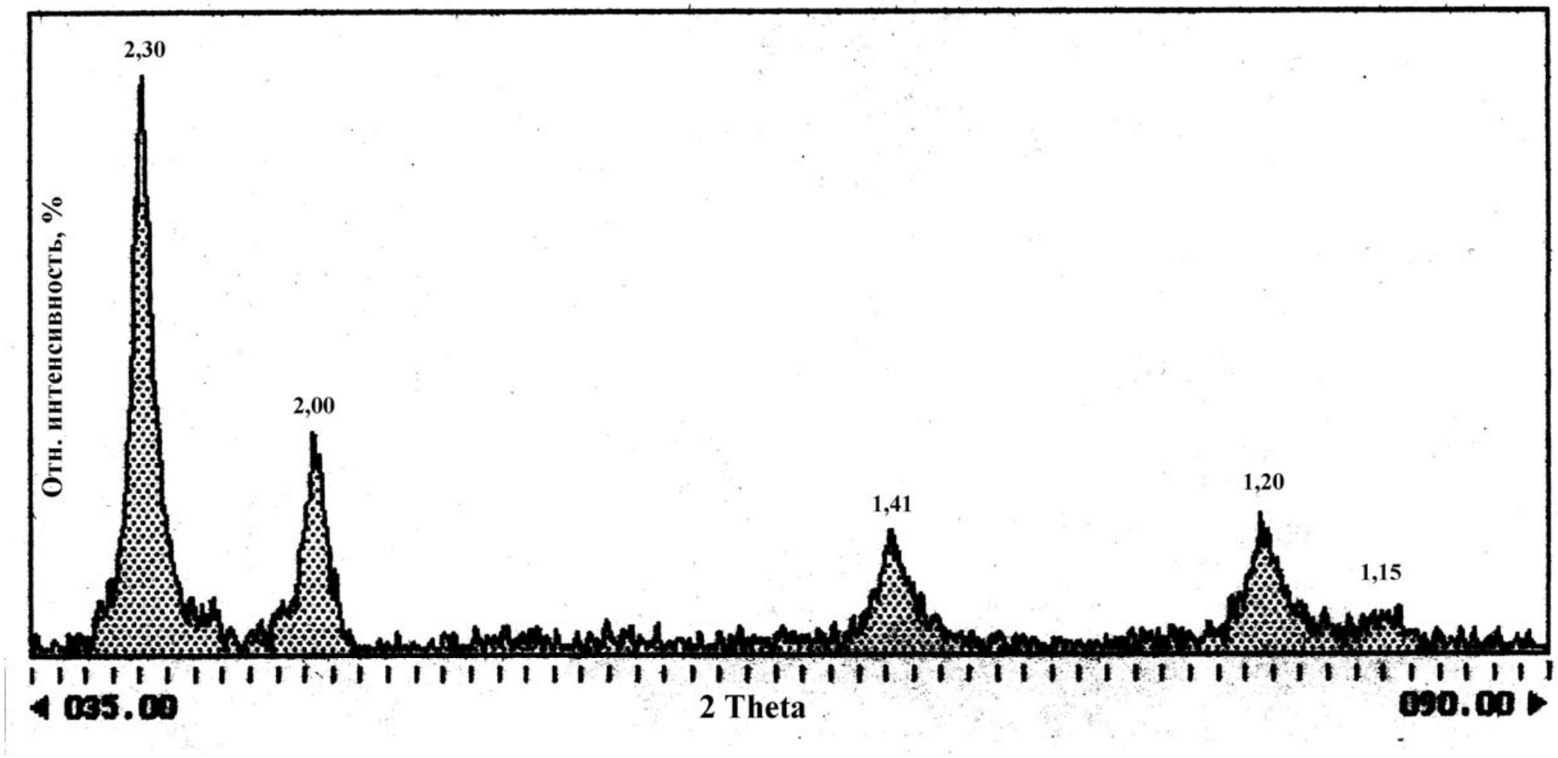
EDAX spectrum nanoelectrocatalyst Pt-Sn/C



Title: Obr AP-237 Pt-Sn Time: 1:24:58 PM Date: Mon, Sep 03 2007 Accelerating Voltage: 25 KV Take Off Angle: 35 Degrees

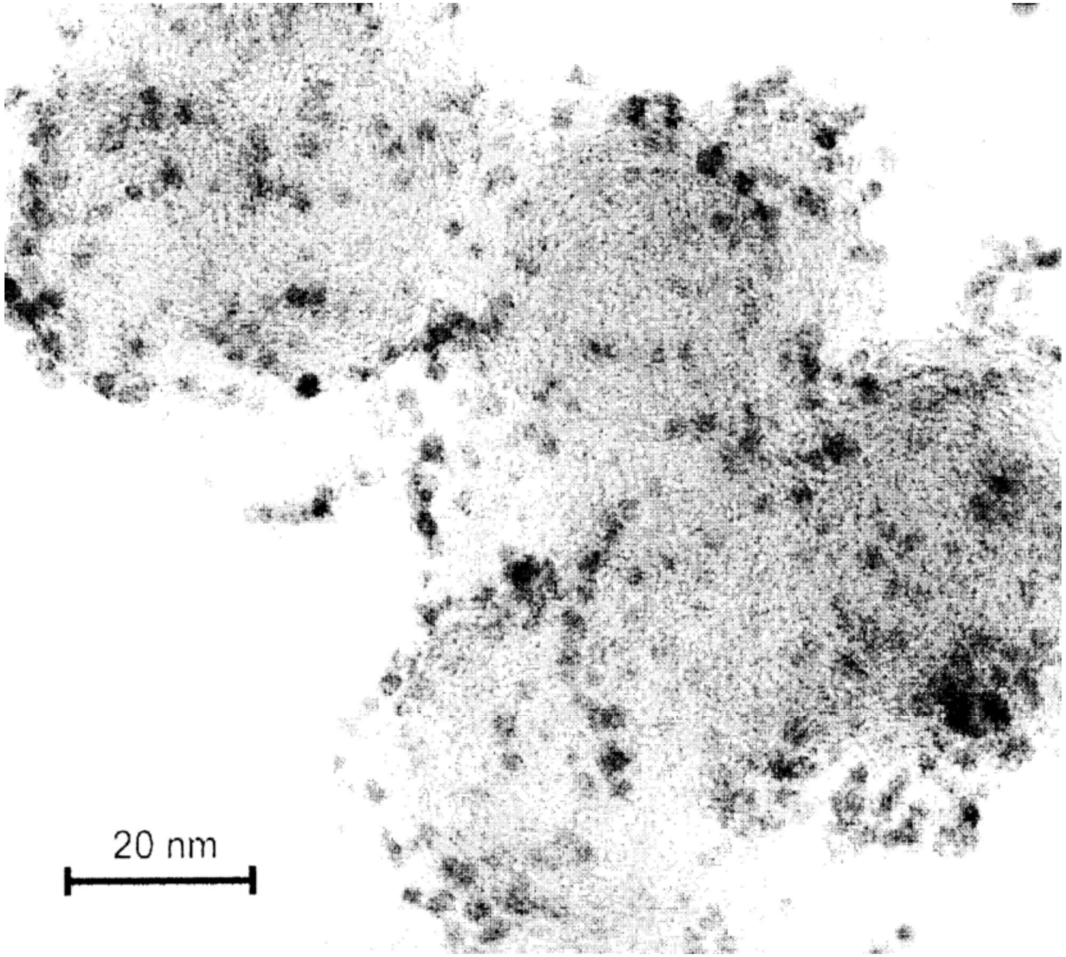
- Quantitative Analysis Results - Standardless Analysis :
- Spectrum8 Obr AP-2037 Pt-Sn Mon, Sep 03 2007
- EDS Parameters - 25KV, Takeoff Angle: 35.0°, Fit Index: 65.63
- Correction: ZAF, Cycles: 3
-
- Element, Atoms%, Compound, Weight%, Error(±), Norm%,
-
- Sn , 1.19, Sn, 8.04, 0.31, 8.04,
- Pt , 2.26, Pt, 25.16, 1.79, 25.16,
- C , 96.55, C, 66.80, 0.54, 66.80,
-
- <Total>, 100.00, , 100.00, , 100.00,

XRD spectrum of bimetallic cluster catalyst (30 mass. % Pt–Sn on carbon carrier).

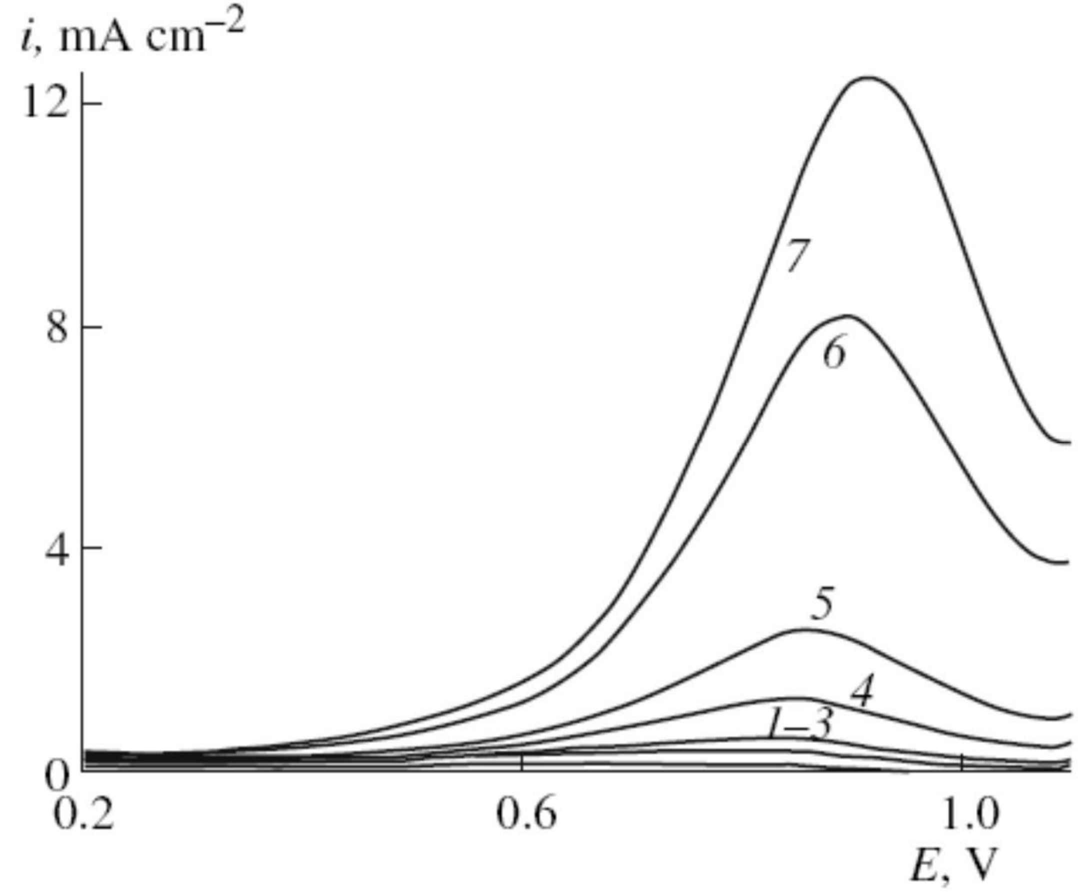


XRD analysis deposited catalyst indicated on the presence the intermetalllide composition Pt_3Sn with cubic structure

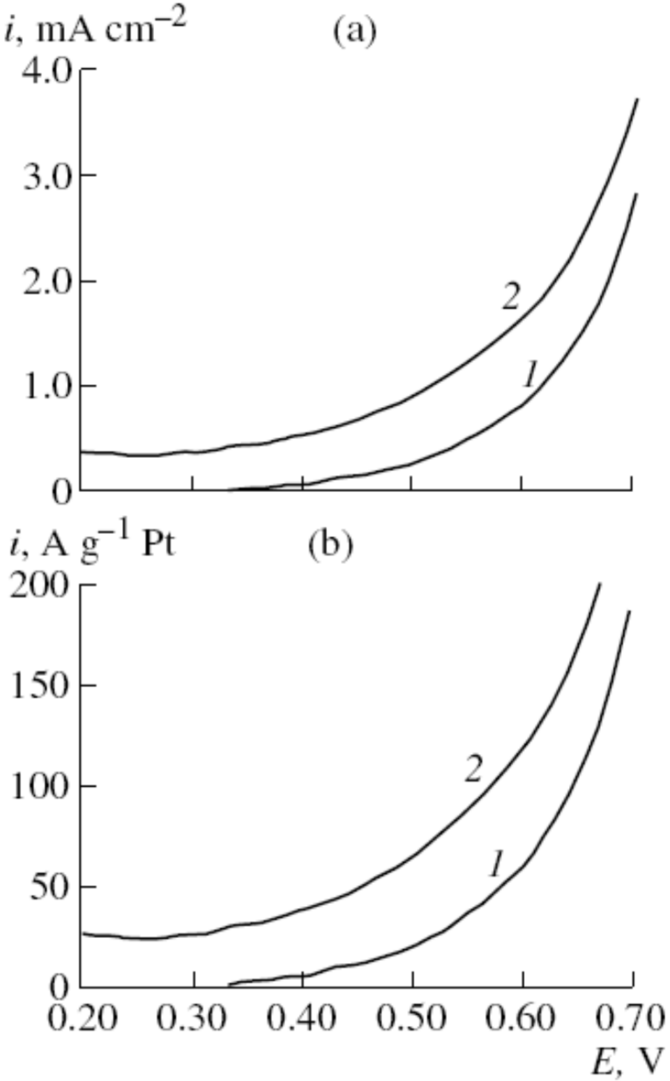
TEM morphology bimetallic nanoelectrocatalyst Pt-Sn/C



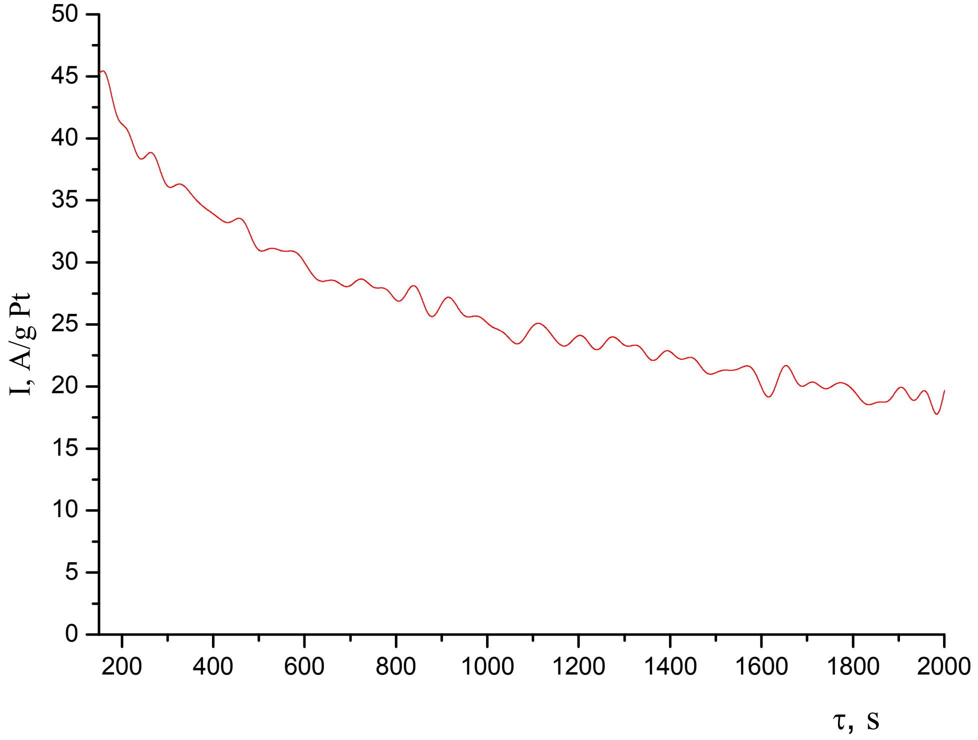
Polarisation curves electrooxidation of ethanol in 0.5 M H_2SO_4 at nanoelectrocatalyst Pt-Sn. Electrode rotation velocity 2200 rpm. The concentration of ethanol in solution: 1- 10^{-3}; 2- 5 10^{-3}; 3-10^{-2}; 4- 5 10^{-2}; 5-10^{-1}; 6- 5$10^{-1}$; 7-1 M



Polarisation curves electrooxidation of ethanol in 0.5 M H_2SO_4 at commercial platinum catalyst E-TEК (1) and nanoelectrocatalyst Pt-Sn (2)



The dependence of the current oxidation of ethanol (1 M) in 0.5 M H_2SO_4 at nanoelectrocatalyst Pt_3Sn upon time hold the potential under potential 0,5 V

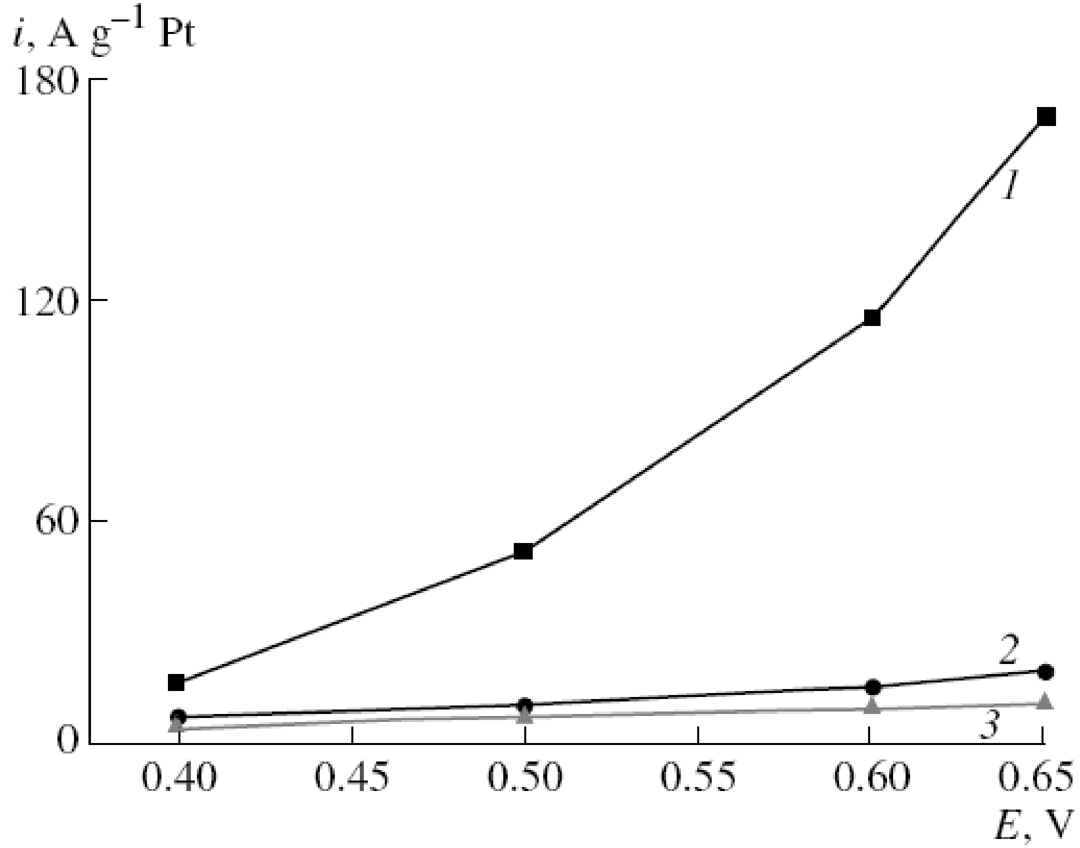


V.A.Grinberg, N.A.Mayorova, A.A.Pasynskii // Russ. J. Electrochem. 2009. V.45. N 12. P. 1321.

Polarisation curves oxidation 1 M ethanol on cluster catalyst Pt-Sn/C (*1*) and more active catalysts of system Pt–Sn (*2- Pt/Sn= 5:1, 3- Pt/Sn=10:1*) in 0.5 M H_2SO_4. Scan rate potential – 5 mVs–1.

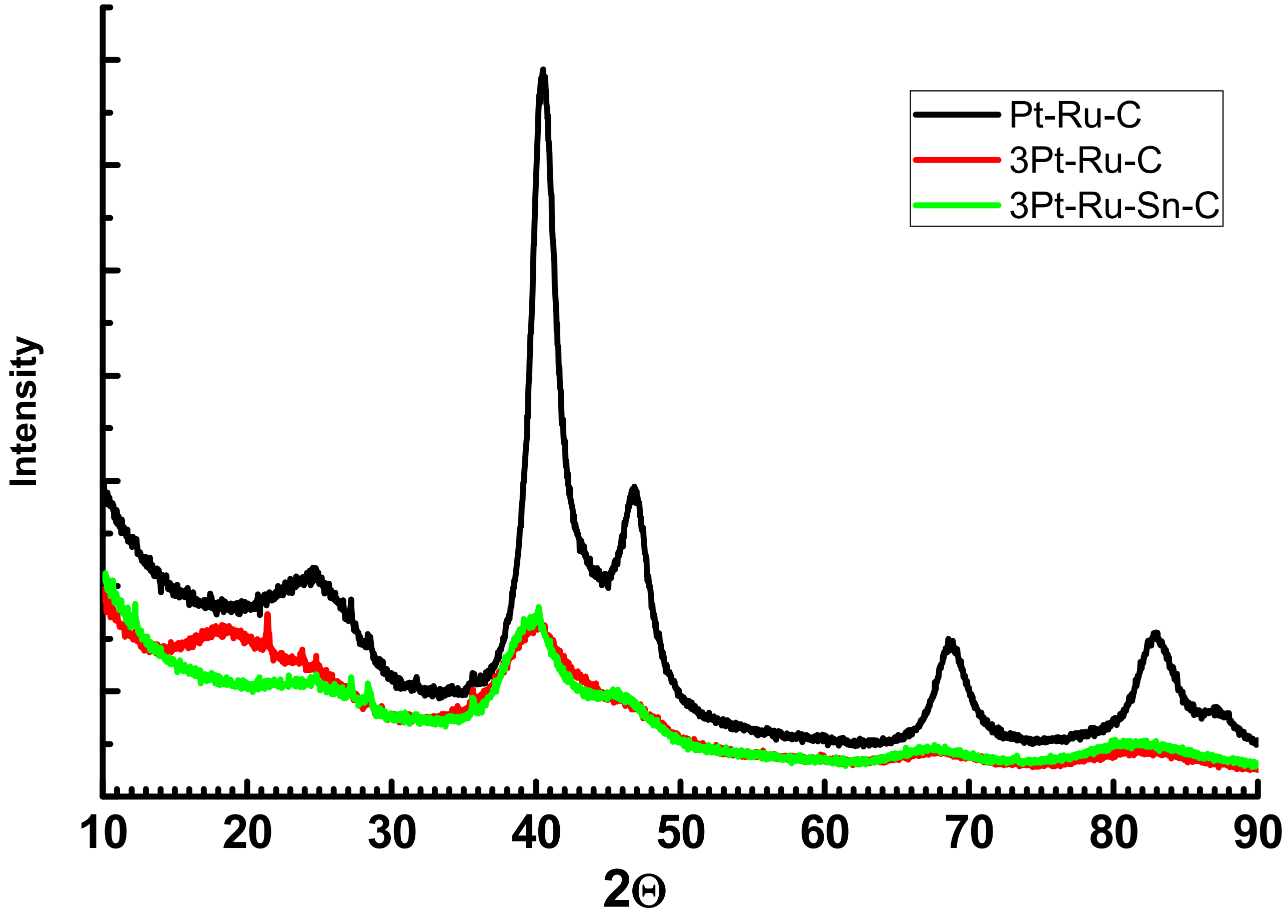
(***Vigier F., Coutanceau C., Perrard A., Belgsir E.M.,***

***Lamy C.* // J. Appl. Electrochem. 2004. V. 34. P. 439**■

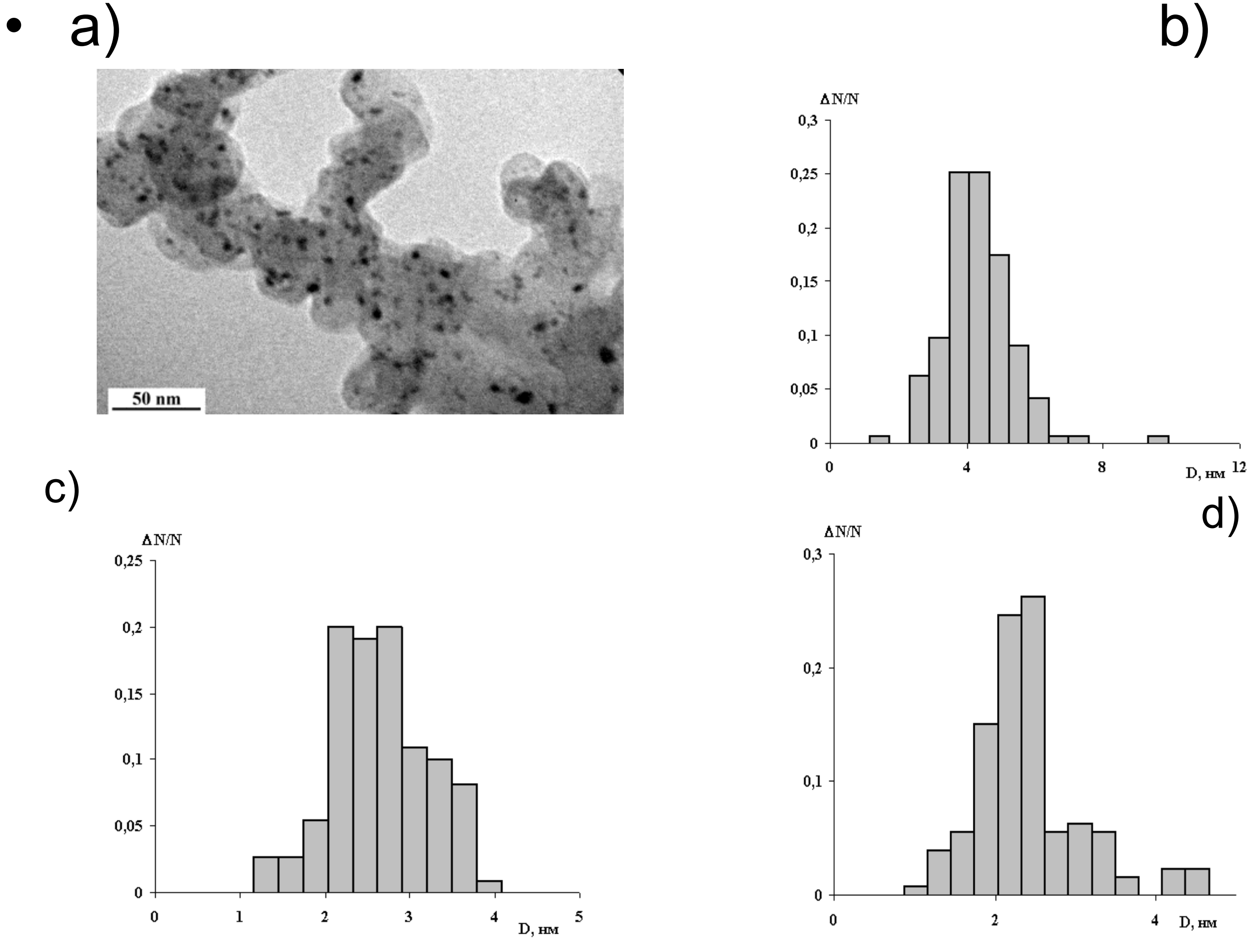


Catalysts on the basis coordination compounds for MeOH electrooxidation

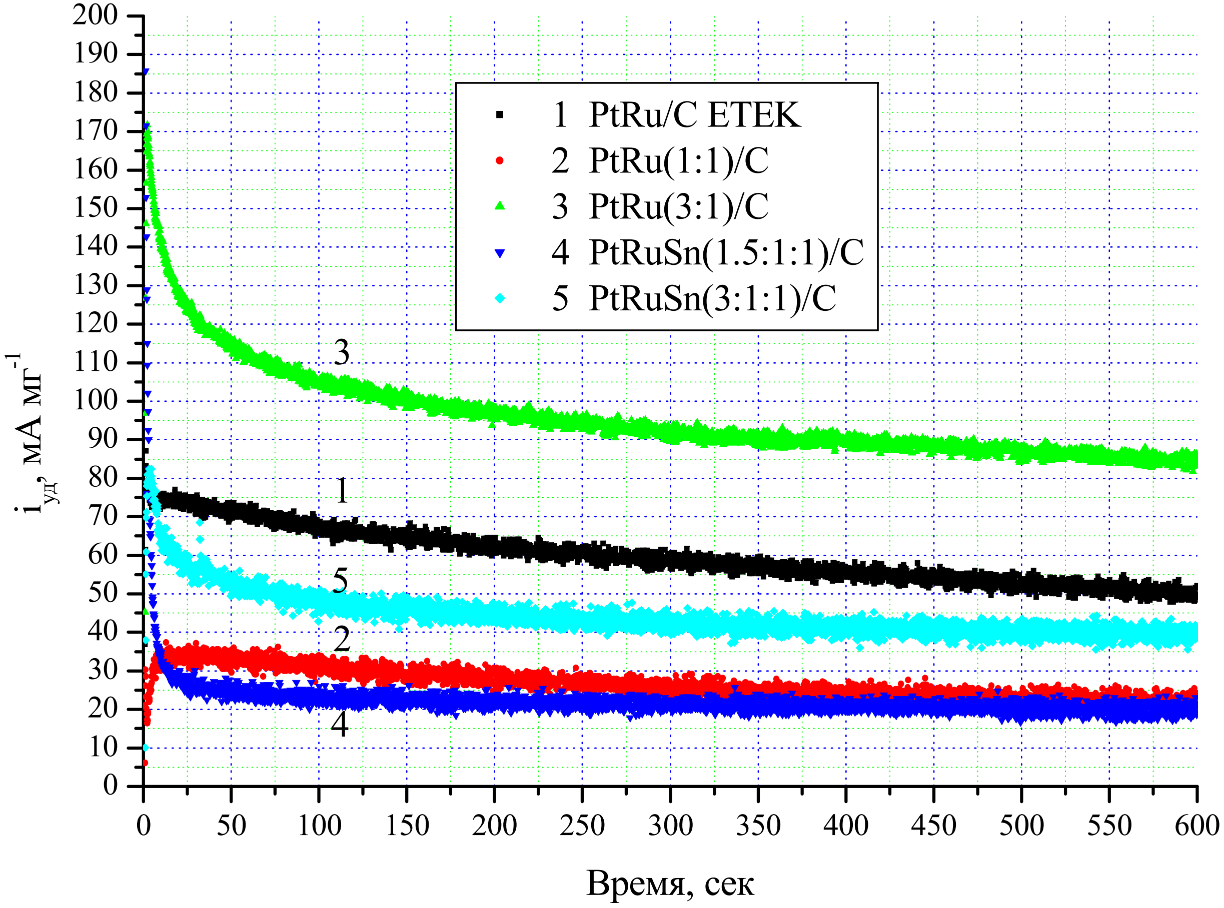
X-ray diffraction patterns



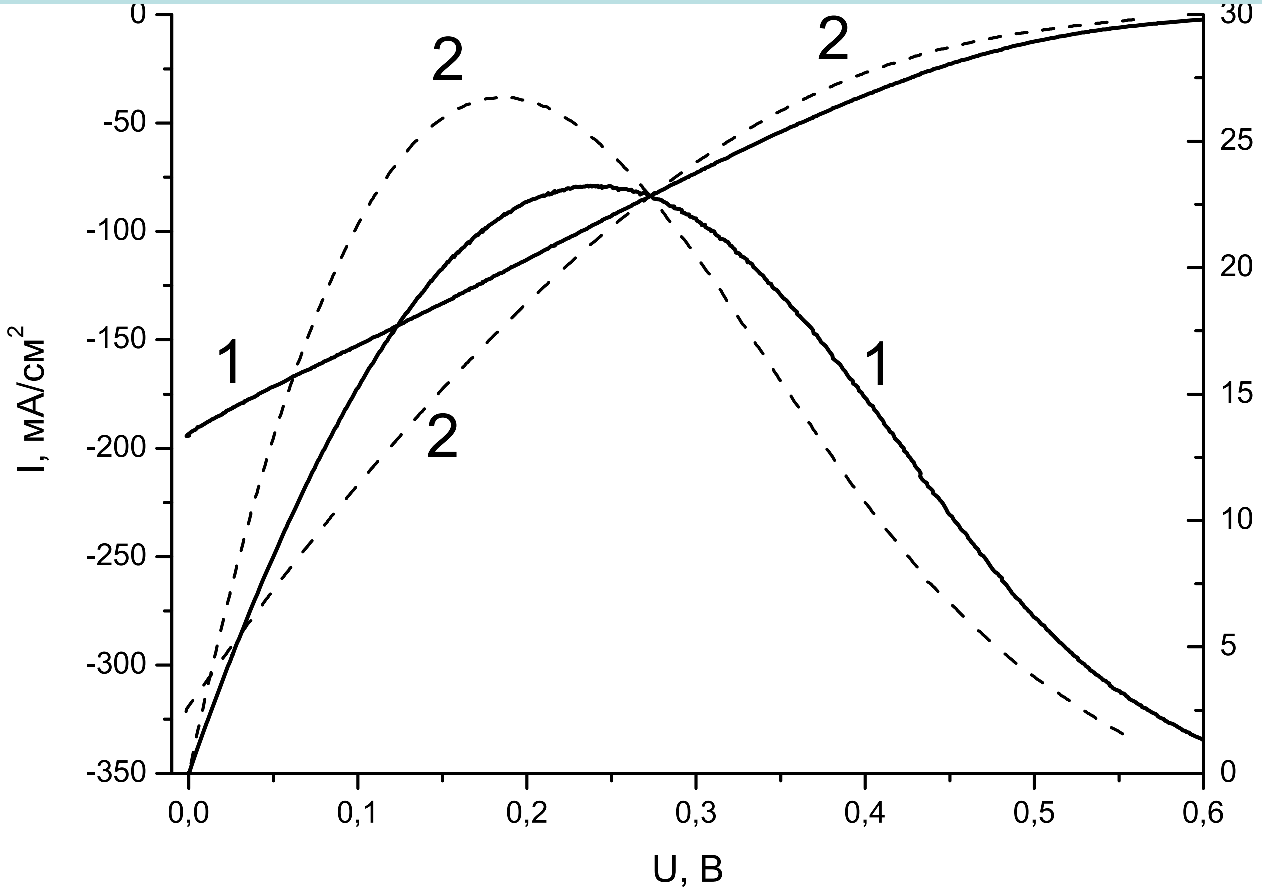
(a) Microphotograph of PtRu/C sample and histograms of particle size distribution for the catalysts (b) PtRu/C, (c) 3Pt-Ru/C, (d) 3Pt-Ru-Sn



Транзиенты тока окисления метанола на дисперсных катализаторах PtRu/C E-TEK -коммерческий (1), PtRu(1:1)/C (2), PtRu(3:1)/C (3), PtRuSn(1.5:1:1)/C (4) и PtRuSn(3:1:1)/C (5) в перемешиваемом аргоном 1 М растворе CH_3OH при температуре 50°C. Фоновый электролит - 0.5 М H_2SO_4. Потенциал электрода - 0.5 В.



Разрядные характеристики МВТЭ с мембраной Nafion 117 с анодами на основе коммерческого Pt-Ru/C (1:1) 2 мгсм-2 производства Cabot США (кривые 1) и синтезированным 3Pt-Ru/C (3:1) 2мгсм-2 (кривые 2 -пунктир). В обоих случаях 1.5 M MeOH и катод 20% Pt (E-TEK 2.5 мгсм-2).



V.A. Grinberg, V.V. Emets, N.A. Mayorova, A.A. Pasynskii et al., Coordination compounds as the precursors for preparation of platinum-containing mixed-metal catalysts of methanol electrooxidation reaction // Coordination chemistry 2015 (in press)

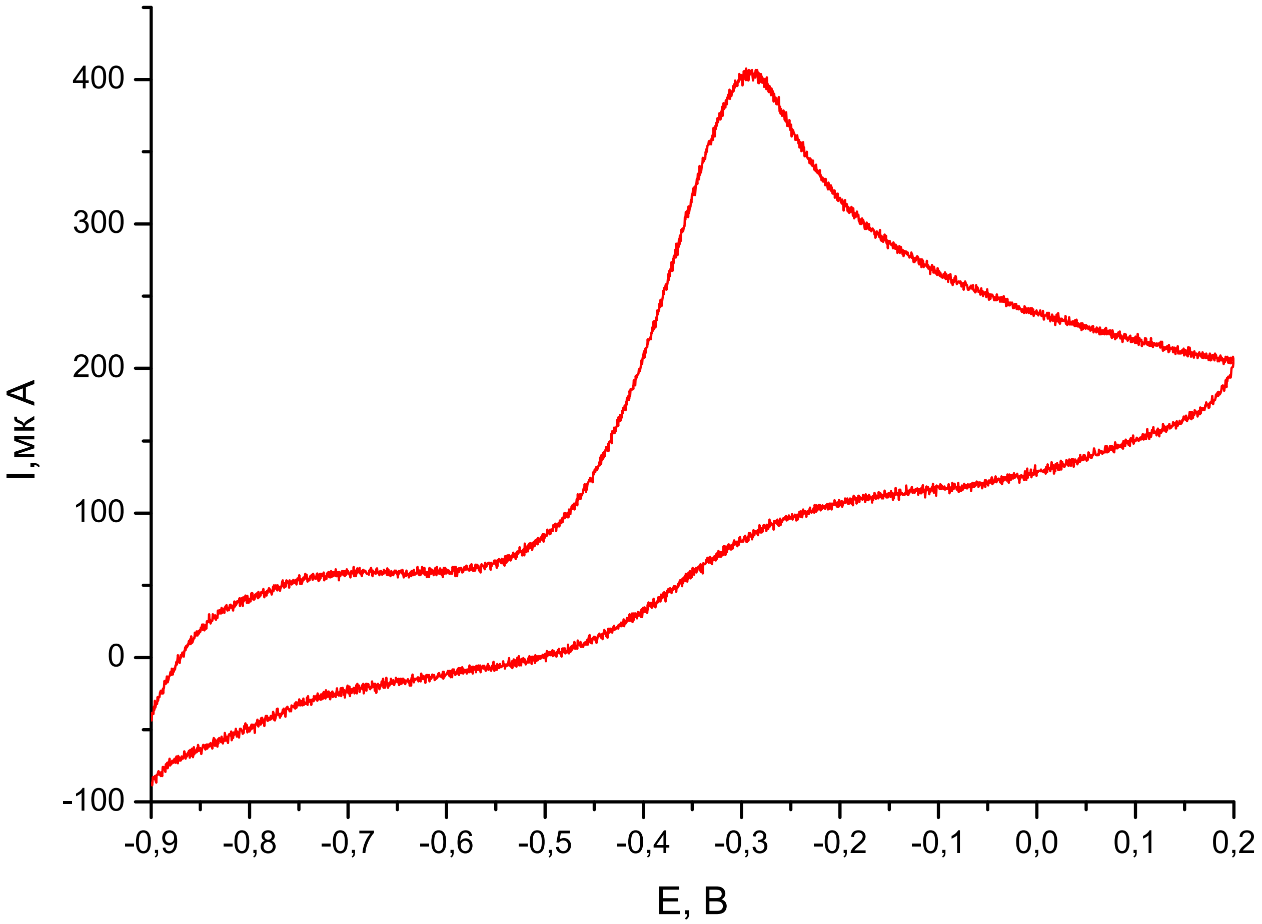
CONCLUSIONS

- **A bimetallic platinum–tin and platinum–ruthenium nanoelectrocatalysts are synthesized by depositing on highly dispersed carbon black from coordination compounds corresponding metals.**
- **Ethanol and methanol electrooxidation at this catalysts were studied.**
- **It was shown that the specific catalytic activity of the synthesized catalysts exceeds that of platinum containing bimetallic systems prepared from simple salts by impregnating carbon black.**
- **The catalysts may be perspective as anodic material for applications in ethanol- and methanol–air fuel cells.**

ELECTROCATALYSTS ON THE BASIS Ni–Ru/ C AND Ni–Ru–F/C ALLOYS FOR DIRECT BOROHYDRIDES ELECTROOXIDATION

- Anodic reaction - electrooxidation of borohydride in alkaline electrolyte :
- $BH_4^- + 80H^- \rightarrow BO_2^- + 6H_2O + 8e$, $E_1^0 = –1.24$ В. (1)
- Cathode reaction - the oxygen reduction:
- $20_2 + 4H_20 + 8e \rightarrow 80H^-$, $E_2^0 = 0.40$ В. (2)
- Overall cell reaction:
- $BH_4^- + 2O_2 \rightarrow BO_2^- + 2H_2O$, $E_3^0 = 1.64$ В, (3)
- where E_1^0 и E_2^0 – standard potential reactions (1) и (2), E_3^0 – the open circuit potential of the cell (EMF).
- Теоретическая удельная энергия боргидрида составляет около 9,3 кВтч/кг

Electrooxidation of borohydride in alkaline electrolyte on gold electrode



Preparation of Binary Catalysts on the basis coordination compounds

Ni:Ru = 10:1; ratio metals:carbon black30:70

Ni−Ru/C

$(C_2H_5)_3NNi(OOCCMe_3)_2$

$Ru_3(CO)_{12}$.

Ni−Ru−F/C

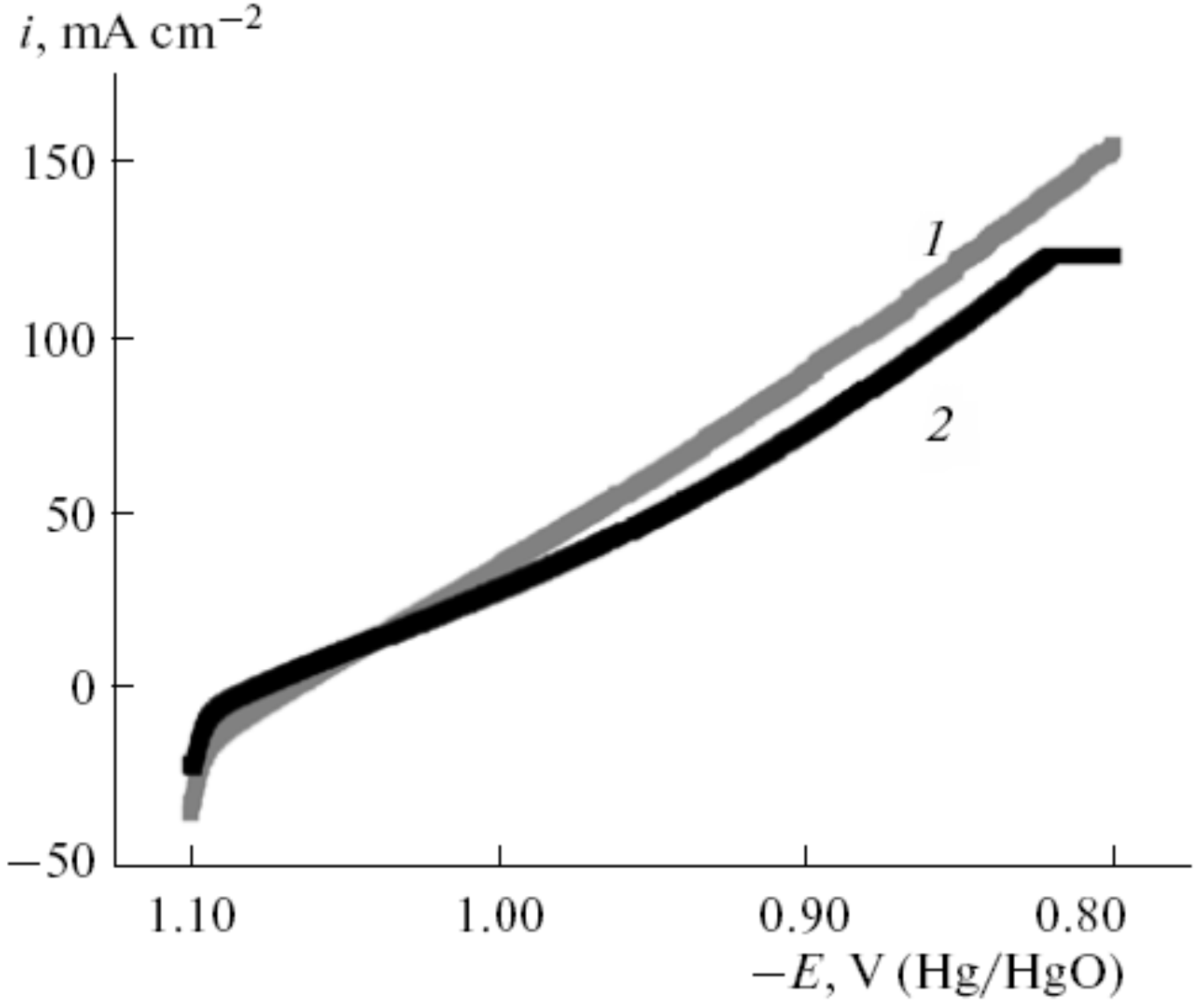
$(C_2H_5)_3NNi(OOCCMe_3)_2$

$Ru_3(CO)_{12}$

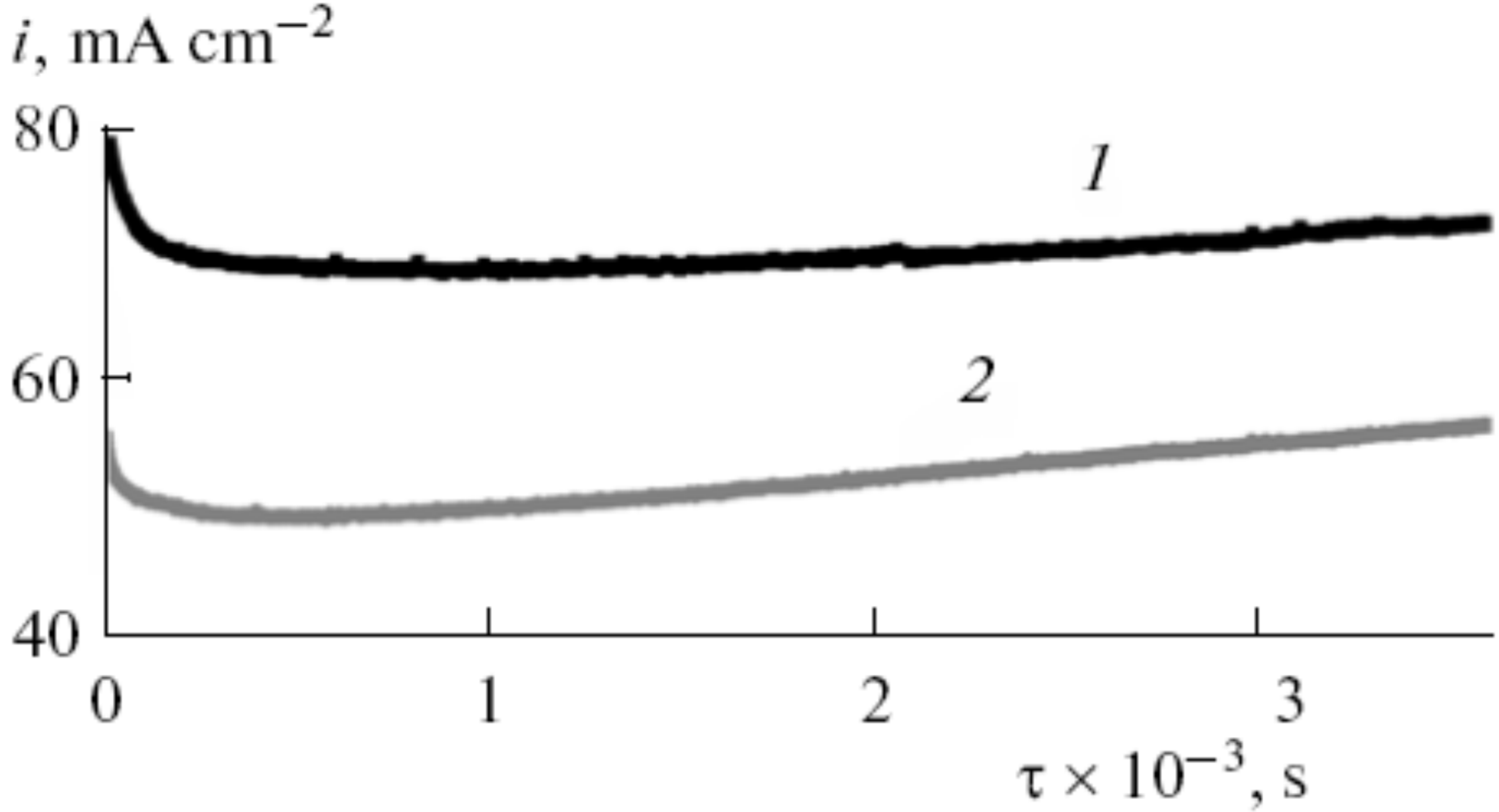
$C_6F_{13}COOH$

- Analysis of difrraction peaks of the sample 30% Ni−Ru−F/C showed that except phases containing in the sample Ni−Ru/C the presence phase of $NiSiF_6(H_2O)_6$ was detected. The magnitudes of the relative intensity of peakes permits make the conclusion that ratio of silicides and alloy of Ni/Ru is due approximately equally in both samples.
- Calculated magnitudes of crystallites of alloy Ni/Ru gives 10.5 и 12.7 nm (calculated in accordance with line 111 Ni).

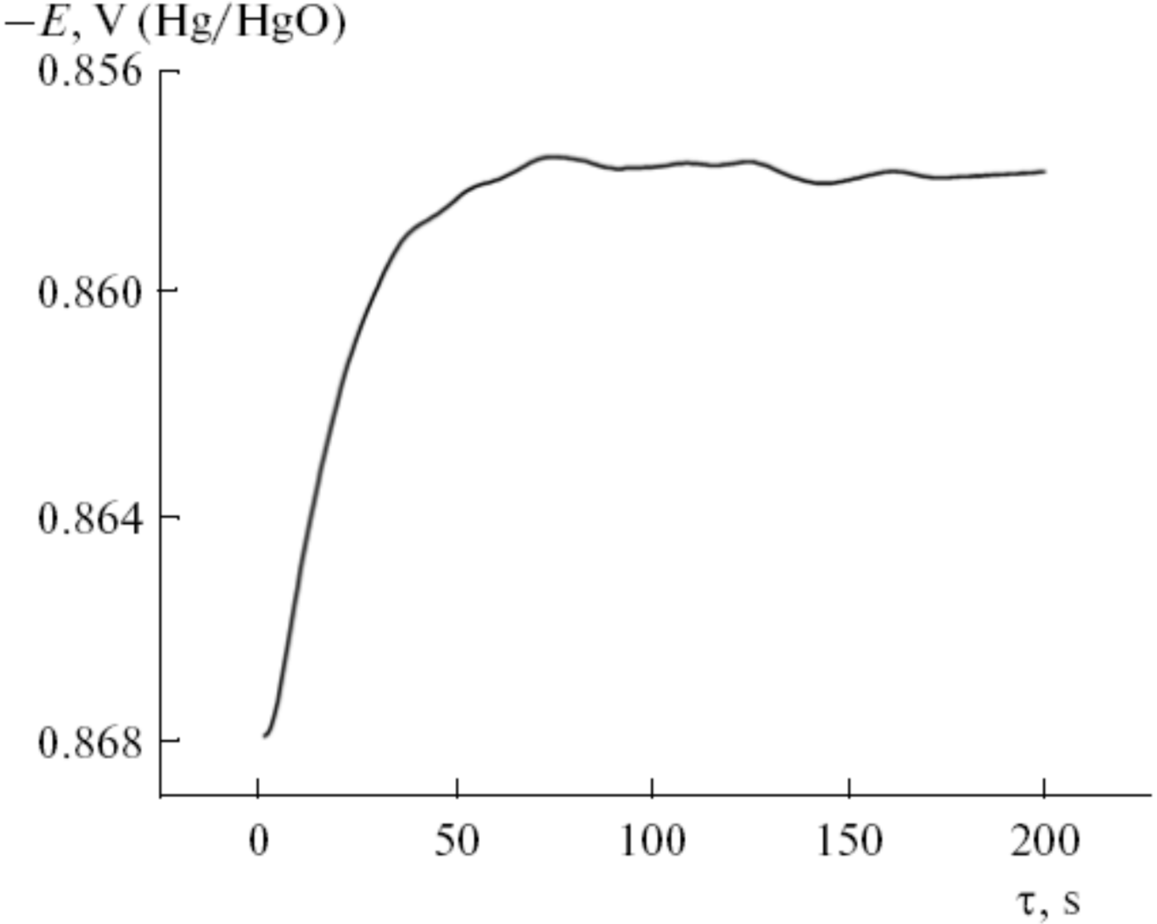
Electrochemical activity of the catalysts 30% Ni–Ru–F/C (1) and 30% Ni–Ru/C (2) in the reaction of NaBH4 (6%) in 6 M КОН electrooxidation.



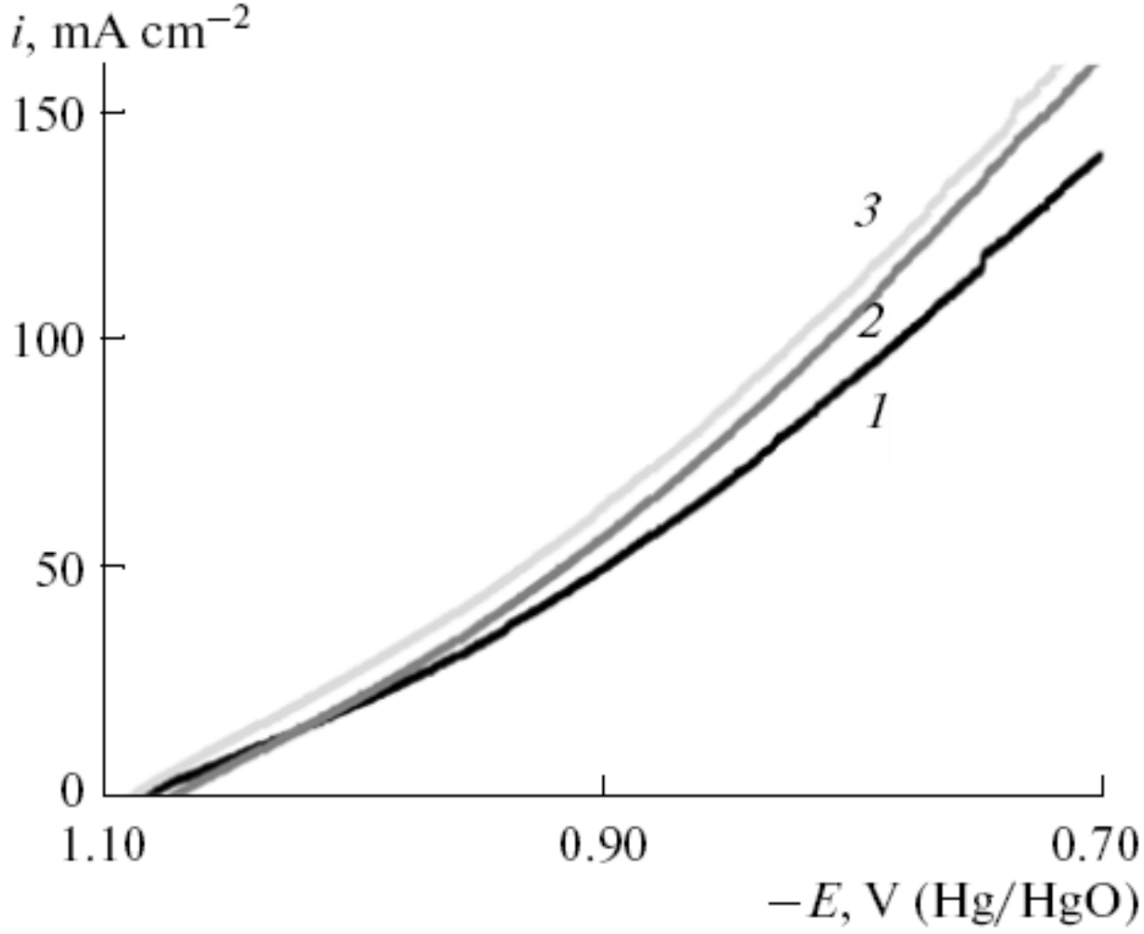
Chronoamperograms electrooxidation NaBH4 (6%) on anodes from the samples of the catalysts 30% Ni-Ru-F/ C, containing of Ru 10% (1) and 30% Ni-Ru / C, containing Ru 10% (2) under potential –0.87 B.



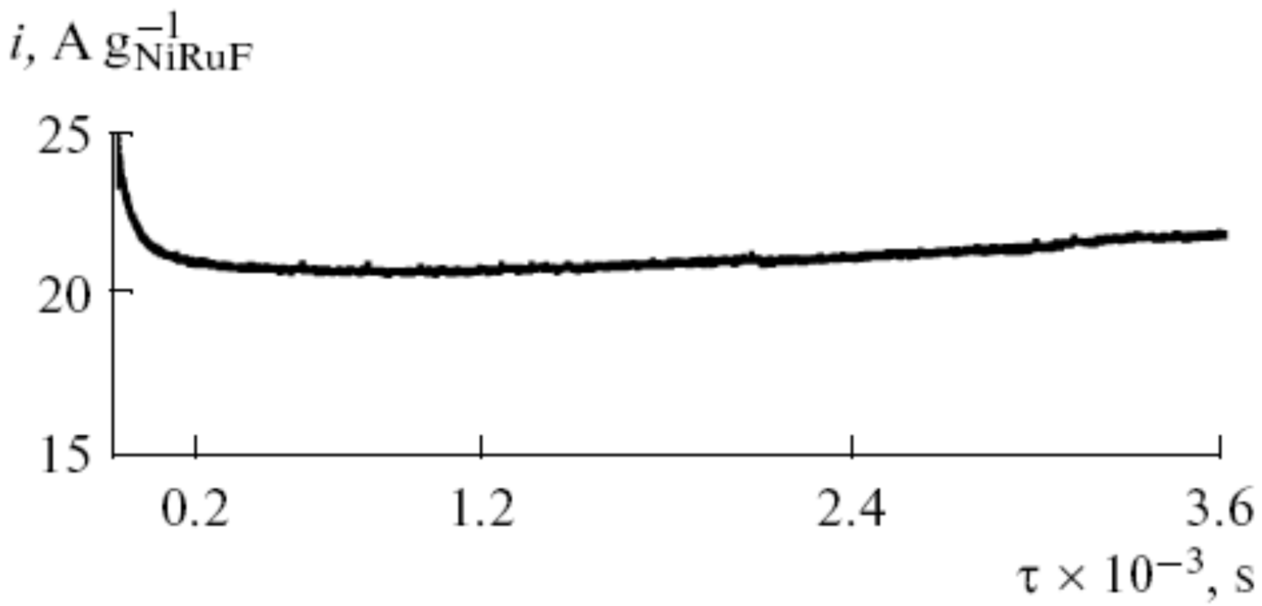
Variation of the anode potential from 30% Ni-Ru-F/C catalyst in time in the reaction of NaBH4 (6%) in 6 M КОН electrooxidation. Current density is 100 mAcm^{-2}



The electrochemical activity of 30% Ni–Ru–F /C catalyst in the reaction of $NaBH_4$ (6%) in 6 M KOH (1) electrooxidation and in the presence of glycerin, %: (1) – 0; (2) – 4; (3) – 10.



Specific activity of electrode on the basis catalysts from fluorinated alloy gross-composition $Ni_{12}RuF_5$ under oxidation of $NaBH_4$ (6%) in 6 M KOH under potential –0.87 V.

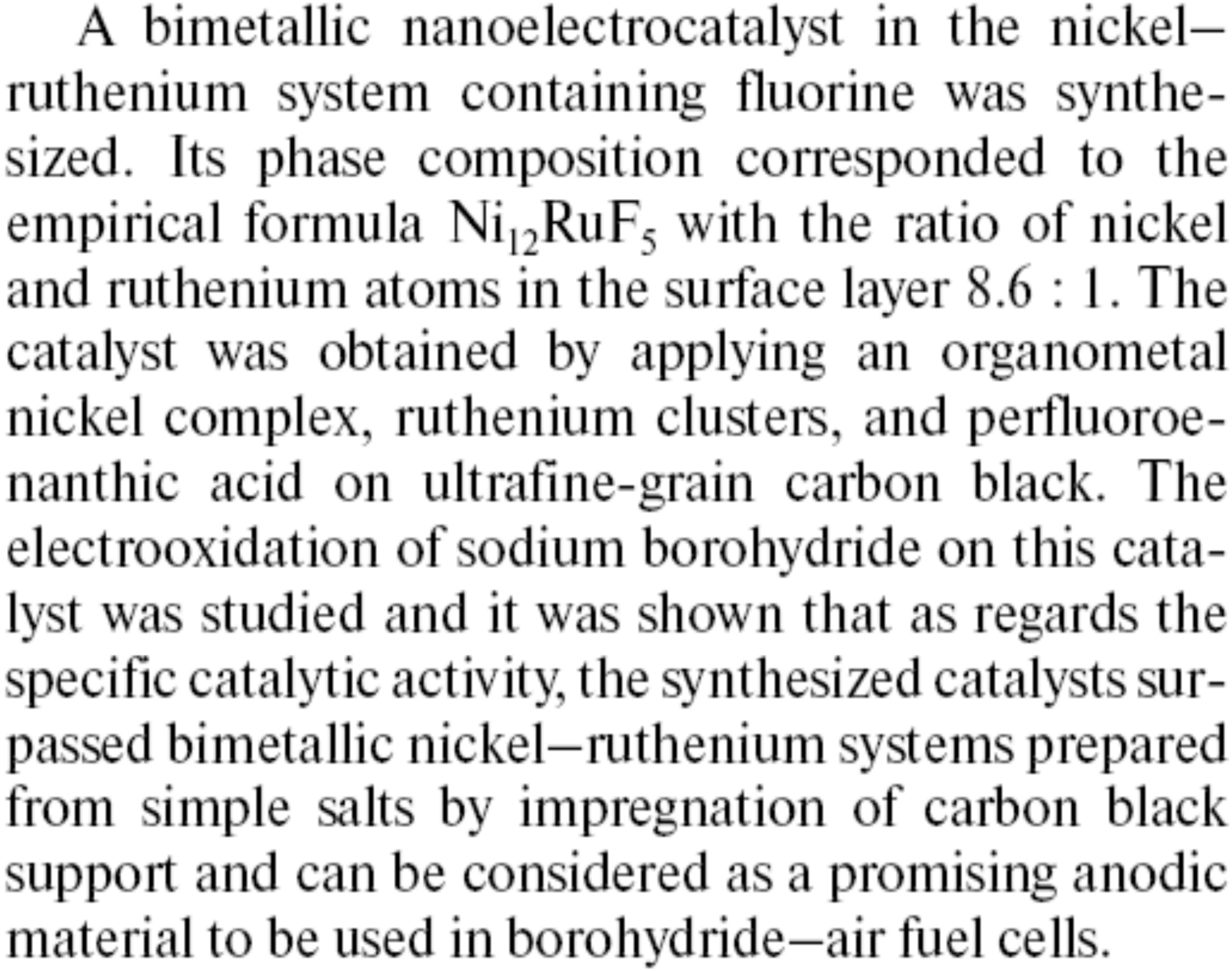


V.A.Grinberg , N.A.Mayorova, A.A. Korlyukov, A.A. Pasynskii // Russ.J. Electrochem.2010. Vol.46. N11. P.1289.

ПАТЕНТЫ ПО ЗАЯВКАМ

- **Наноразмерный катализатор прямого электроокисления боргидридов щелочных металлов Заявка № 2009117276 от 07.05.2009**
- **Анод для прямого электроокисления боргидридов щелочных металлов Заявка № 2009117277 от 07.05.2009**
- **Наноразмерный катализатор электровосстановления кислорода воздуха Заявка № 2009117278 от 07.05.2009**
- **Катод для электровосстановления кислорода воздуха в боргидридных топливных элементах Заявка № 2009117279 от 07.05.2009**
- **Электролит для топливного элемента прямого электроокисления боргидридов щелочных металлов Заявка № 2009117280 от 07.05.2009**
- **Портативный источник тока на основе прямого окисления боргидридов щелочных металлов Заявка № 2009117281 от 07.05.2009**
- **Портативный источник тока Заявка № 2009117282 от 07.05.2009**
- **Источник тока портативный Заявка № 2009117283 от 07.05.2009**
- **Портативный источник тока Заявка № 2009117284 от 07.05.2009**
- **Источник тока портативный Заявка № 2009117285 от 07.05.2009**

CONCLUSIONS



A bimetallic nanoelectrocatalyst in the nickel–ruthenium system containing fluorine was synthesized. Its phase composition corresponded to the empirical formula $Ni_{12}RuF_5$ with the ratio of nickel and ruthenium atoms in the surface layer 8.6 : 1. The catalyst was obtained by applying an organometal nickel complex, ruthenium clusters, and perfluoroenanthic acid on ultrafine-grain carbon black. The electrooxidation of sodium borohydride on this catalyst was studied and it was shown that as regards the specific catalytic activity, the synthesized catalysts surpassed bimetallic nickel–ruthenium systems prepared from simple salts by impregnation of carbon black support and can be considered as a promising anodic material to be used in borohydride–air fuel cells.


4
3
6

- На различных этапах в работе принимали участие:
- Д.х.н. Кулова Т.Л.
- К.х.н. Хазова О.А.
- К.х.н. Модестов А.Д.
- Д.х.н. Емец В.В.

СПАСИБО ЗА ВНИМАНИЕ