Investigation of catalytic vacuum black in the electrodes low-temperature electrochemical devices

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ABSTRACT
Research of catalytic compositions based on noble metal black, received by magnetron deposition of metal in vacuum thickness-control, disclosed. Such blacks have unique bush-like structure formed by thin filaments of platinum with diameter near 10 nm and 200-300 nm long. This structure compared with structure of platinized platinum, received by electrochemical deposition from solution. On basis of electrochemical research disclosed that vacuum platinum blacks (VPB) based on titan, nickel and carbon, provide high activity in anode hydrogen oxidation reaction and cathode hydrogen restoration in low temperature electrochemical devices.

1. INTRODUCTION
Amount of platinum for commercial use of power modules based on hydrogen-air proton exchange membrane fuel cells (PEFC) must be lowered to 0.2 mg/cm² and specific power value should be no less than 0.6 W/cm² [1]. Similar objectives for minimization of noble metals in electrode stand in catalyst development for other low temperature electrochemical devices that uses platinum group metals. This applies to polymer electrolyte electrolysis units, alkaline hydrogen-air fuel cells. Also using of platinum catalysts in alkaline hydrogen generator electrodes could be reasonable for noticeable lowering of power inputs in water electrolysis.

In connection with this, scientific centers provide large number of researches devoted to development of active electrode with low noble metal content. Different methods are used for catalytic layer formation. Among them such methods as rolling, screen printing, aerosol catalyst deposition, platinum restoration from saline, etc. could be separated. Some publications contain alternative methods such as using of ion beam for deposition of platinum particles on E-TEK paper [2-4]. Using of thin film deposition vacuum technology allows effective preparation of electrode surface, application of intermediate layer and receiving of catalytic compositions that could be controlled by constitution, structure and thickness of noble metal particle layer. It’s been showed that aerosolizing method provides effective usage and high platinum activity [5-8]. Method of cathode aerosolizing provides significant lowering of platinum in hydrogen-air PEFC and keeps platinum and iridium catalytic activity at the same level [9-10]. Such iridium deposition technology on anode of polymer membrane electrolyzer allows reaching 10-fold catalyst lowering [11-12].

Described method allows to receive unique nanodispersed structure of vacuum catalytic black (VCB) received by aerosolizing of Pt and PtIr cell. This work assigned task for detailed research of such dispersed structures by methods of structural, elemental, electrochemical analysis and catalysis activity research.

2. RESEARCH METHODS
2.1. Electrodes and catalyst preparation
Application of catalyst on substrate front surface was provided by using of magnetron. Pt cell
was sputtered in vacuum. Developed technology allows controlling structure of deposited layers from quasiamorphous condition to high grade texture. Using of preliminary surface ionic cleaning and deposition of intermediate layers allows receiving adhesion coating durability much higher than film putted by vacuum evaporation or chemical deposition. In addition, method of magnetron deposition has high productivity. Sputtering speed was $(1-3) \times 10^{-4}$ g/min·cm$^2$. Coating adhesion durability was provided by high condensing particles energy (5-10 eV). In this research was used specially developed method that allows receiving dispersed catalytic compositions with controlled by constitution and thickness of noble metal blacks. Black matted surface of dispersed structure is characteristic of this method.

For structure and activity of catalytic composition based on plain substrate research, titan foil (100 µm thickness), preliminary treated in 50% solution of H$_2$SO$_4$ and temperature 100ºC was used. For development of PEFC anode catalyst deposited on the microporous layer of carbon paper Sigracet 10bb (0.42 mm thickness, 84% porosity). Also for expansion of electrochemical reaction area on fuel cell anode, emulsion of Nafion ionomer was sprayed (in air environment). Scheme of gas diffusing electrode is showed on Fig.1.

![Figure 1](image)

**Figure 1.** (A) - Gas diffusing electrode; 1 - gas diffusion layer (GDL); 2 - microporous layer (MPL, carbon-black); 3 –catalytic layer ((VPB) Pt black); (B) - Gas diffusing electrode Sigracet 10bb [14]

Catalyst for alkaline electrolysis based on VCB was formed on the front surface of porous nickel electrode (porosity 65%, thickness 1 mm) with biporous structure (large pores with diameter 20-30 µm and small pores with diameter 1-5 µm).

### 2.2. Structural changes

For research of porous structure of gas diffusing electrode, method of standard porosimetry was used (MSP) [13-15]. Its main advantage over method of mercury intrusion is ability to differentiate hydrophobic and hydrophilic pores [13]. Pore distribution by radius could be received by using of octane as wetting liquid. All pores are hydrophilic relatively octane. Using of water as wetting liquid allows defining hydrophilic pores. Research with MSP method was provided by automotive porosimeter «Porotech» that allows to receive porograms of dispersed samples with pores at range 2 nm - 30 µm [13-14]. Octane ACS (99.99%) and deionized water (>10 Mom) were used as working liquids. Also, scanning electron microscopy was used for receiving pictures of catalytic compositions (SEM TM-1000, Hitachi and SEM JSM-6390LA, Jeol).

### 2.3. Electrochemical measuring
For catalyst electrochemical research, potentiostat Solartron 1287 was applied. As auxiliary electrode platinized titan foil was used, Hg/HgSO₄ used as reference electrode. For measuring in alkaline 6M KOH solutions Hg/HgO was used as reference electrode. Potentials were reduced to reversible hydrogen electrode. Platinum catalytic black active surface was defined by adsorptive hydrogen oxidation currents. For anode activity definition «floating» gas diffusing electrode was used in electrochemical cell, represented on Fig.2.

**Figure 2.** Scheme of electrochemical cell for GDE activity research by «floating electrode» method.: 1 – gas diffusing electrode; 2 – reference electrode; 3 – auxiliary electrode; 4 – hydrogen intake channel; 5 – hydrogen output channel; 6 – hydroseal; 7 – leakproof cover; 8 – valves.

Electrode (Fig 2, position 1) look like 1 cm² round matrix with titan shunt, stuck with carbon-graphite glue from the back side of gas diffusion layer (GDL). At time of experiment electrode was touching electrolyte solution - 0.5 M H₂SO₄. For solution cleaning purposes hydrogen (99.99%) blowing was used. Hydrogen was feeding into cell under solution during measurement. Anode scanning speed (50 mV/s) was using to obtain polarization curves.

### 2.4. Elemental analysis

For research of catalyst elemental composition, energodispersed analyzer of electron scanning microscope Jeol JSM 6380LA was using.

### 3. RESEARCH RESULTS AND DISCUSSION

#### 3.1. Structural measurement

Fig.3. shows scaled-up images of vacuum catalytic black based on smooth titan substrate. Visually, catalytic covering has black color. Structure of covering consists of fiber like branches with thickness near 10 nm, length from 100 to 400 nm. With increasing amount of platinum on the surface of substrate, length of branches also increase.

Fig.4. shows scaled-up SEM images of initial porous electrode based on carbonyl nickel particles (Fig.4.a) and the same electrode after platinum black deposition (Fig.4.b,c).

Apparently, smooth round (diameter 5-6 μm) carbonyl nickel particles covered with platinum dispersed catalytic coating with structure of thin branches with diameter 10-14 nm and length 200-300 nm. Such formations form the surface like bushes with size of a few hundred nm.
Figure 3. Scaled-up images of vacuum catalytic black (VCB) based on smooth titan substrate: 
\[ a) \text{ - } m_s = 0.594 \text{ mg/cm}^2, f=336; \quad b) \text{ - } m_s = 1.26 \text{ mg/cm}^2, f=602; \quad c) \text{ - } m_s = 2.0 \text{ mg/cm}^2, f=1152 \]

Figure 4. Scaled-up images of catalytic platinum black (a, c) on the surface of carbonyl nickel particles (0.36 mg/cm²), (b) – initial sample.
Fig. 5. shows differential porograms of initial porous nickel electrode sample (curve 1) received by MSP method with octane as working liquid and after deposition of 0.36 mg/cm$^2$ PtIr(20%) black on front surface (curve 2). As seen, there is new nanosized structure with pore size of 10 nm, which forms between densely spaced platinum braches with diameter 10-12 nm (Fig. 5, curve 2).

**Figure 5.** Biporous nickel electrode differential porograms before (1) and after (2) deposition of vacuum platinum black (VPB) on the front surface.

3.2. **Electrochemical research.**

Method of cyclic voltammetry (CV) was used in this research for definition of electrode active surface with vacuum catalytic black based on smooth titan substrate. Fig. 6. Shows CV-curves for dense thin covering on titan (1) and for platinum black-based electrodes with different amount of platinum (2-4). Apparently, CV-curves look like platinum curves.

Active catalyst surface based on platinum black significantly higher than smooth Pt/Ti electrode (1).

Definition of active surface ($S_a$), rough factor (f) and specific surface ($m_s$) based on CV-curves.

Platinum black active surface ($S_a$) calculated from electric charge value, spent for adsorbed hydrogen oxidation in the region of potentials between $E_1 = 0$, $E_2 = -0.4$ V relatively hydrogen electrode [15].

$$Q_a = \frac{1}{w} \int_{E_1}^{E_2} I \cdot dE$$  \hspace{1cm} (1)

where:

I - current instantaneous value, mA; w- electrode potential changing speed, mV/s
Figure 6. Cyclic I-E curves for Pt based on smooth titan substrate in 0.5 M H₂SO₄ solution, speed w=0.05 V/s and t=25°C: 1 - Pt dense coating \( m_s = 0.12 \text{ mg/cm}^2, f=8.3 \); 2 - Pt black \( m_s = 0.594 \text{ mg/cm}^2, f=336 \); 3 - Pt black \( m_s = 1.26 \text{ mg/cm}^2, f=602 \); 4 - Pt black \( m_s = 2.0 \text{ mg/cm}^2, f=1152 \).

Active electrode area evaluated with equation:

\[ S_0 = \frac{Q_s}{Q_S} \quad (2) \]

where \( Q_s \) - electricity amount during hydrogen monolayer oxidation on smooth platinum electrode with area 1 cm². Value \( Q_s = 210 \mu \text{C cm}^{-2} \) for platinum could be evaluated by equation (3) with assumption that any atom in crystal grid adsorbs one atom of hydrogen, which then oxidized with transfer of one electron:

\[ Q_s = n_{\text{Pt}} \cdot e \quad (3) \]

gде \( e = 1.6 \times 10^{-19} \text{ C} \) - electron charge; \( n_{\text{Pt}} = 1.31 \times 10^{15} \times 1.6 \times 10^{-19} \) - amount of Pt atoms on 1 cm² smooth Pt area.

Value of catalyst active area defined as:

\[ S_m = \frac{S_s}{m_s} \quad (4) \]

Electrode rough factor was found by equation:

\[ R_f = \frac{S_s}{S} \quad (5) \]

where
S - electrode geometrical surface

For dispersed vacuum catalytic black particles based on titan, dependence of $R_f$ on time of catalyst deposition (or $m_s$ value) is close to linear.

Table 1 shows parameters for dispersed sediments of vacuum catalytic Pt black on titan with different thickness.

| $m_s$, mg/cm$^2$ | 0.594 | 1.26 | 2.0 |
|------------------|-------|------|-----|
| $R_f$, sm$^2$/cm$^2$ | 336   | 602  | 1152|
| $S_m$, m$^2$/g   | 56.5  | 47.7 | 57.6|

Comparison of vacuum catalytic black (on smooth titan substrate) with parameters of catalytic particles of platinized Pt [16] and Pt nanoparticles on carbon-black [17] is of big interest.

Besides $S_e$ and $m_s$, there are other parameters for comparison: form of catalyst particles, relation $h_2/h_1$ which characterize texture of catalyst surface. Here:

$h_1$, $h_2$ - height of current desorption peak, solidly and weakly bound hydrogen respectively (Fig.7).

**Figure 7.** Hydrogen desorption peaks on cyclic volt-ampere characteristics of catalytic Pt black on titan substrate in 0.5 M $\text{H}_2\text{SO}_4$, $V=0.05$ V/s and $T=25^\circ\text{C}$:
As shown on Fig.7, specific hydrogen desorption currents $i_m$ and its relation to potential in minimal degree depend on thickness of catalytic Pt black layer. It tells about equally accessible surface of Pt. Parameter $h_2/h_1$ in this case equals $0.8 \pm 0.02$, and this is characteristic of samples with developed active surface.

It’s known that higher values of $h_2/h_1$ are indirect evidence of texture (111), and shorter textures (100) [16]

Table 2 shows basic characteristics of Pt catalyst.

| Sample                           | $h_2/h_1$ | particle shape | $D$, nm | $R_f$, cm$^2$/cm$^2$ | $Sm$, m$^2$/g |
|----------------------------------|-----------|----------------|--------|--------------------|-------------|
| Pt sheet [16]                    | 0.57      | -              | -      | 5-8                |             |
| Pt /Pt freshly prepared [16]     | 0.82      | sphere         | 9-12   | 400-1400           | 20-35       |
| Pt /Pt aged sample [16]          | 0.7       | sphere         | 15-20  | 100-350            | 10-15       |
| 20 wt.% Pt/C Vulcan XC-72 [17]   | 0.9       | sphere         | 2-3    | -                  | 65-73       |
| Pt vacuum catalyst black (VCB)/Ti(sheet) | 0.80 | branch coral bush | $d=12-14$ | $L=100-300$ | $300-1200$ | $47-58$ |

Petriy O.A. et al. explored structural characteristics of platinized Pt [16]. Particularly, dependence of Pt particles size on deposition potential in H$_2$PtCl$_4$ solution. Shown that linear dependence of rough factor from deposition time exists. Work shows that particles structure of Pt/Pt has normal distribution by size with maximum at 7 nm area for freshly made samples and near 10 nm area for aged samples. If rough factor $R_f$ (defined by hydrogen desorption) for ultra thin freshly made particles was 200 and linearly raised to 1600 (near 10 times) depending on time, then for aged particles grows was only 3 times (from 100 to 300). Comparison of $h_2/h_1$ parameter is thing of interest (relation between current peak height and weekly bound hydrogen). For freshly made samples its value was 0.82 and for aged ones decreased to 0.70, that is became equal to $h_2/h_1$ for smooth Pt. In case of vacuum blacks on GDL (Pt/C) relation $h_2/h_1$ was 0.79 for thick Pt films and 0.78 for thin (precisely calculated).

Pt nanoparticles, formed on carbon-black, have size near 2.6 nm, specific surface near 70 m$^2$/g and have high activity relatively hydrogen anode oxidation reaction [17].

8
1.2. Electrochemical activity research.

Anodic hydrogen oxidation

In contact of «floating» gas diffusing electrode (Sigracet 10bb) with deposited PtIr catalyst (0.36 mg/sm²) with 1 M H₂SO₄ solution in three-electrode electrochemical cell (Fig.2.), three-electrode border appears on which hydrogen oxidation anodic reaction in acid electrolyte solution with hydrogen back feeding appears. This reaction speed defines by electrochemical reaction three-phase areas length, catalyst activity, temperature and transport limitations of reagent supply in reaction area.

Fig.8. shows polarization curves of hydrogen anode oxidation on «floating» gas diffusing electrode (Sigracet 10bb) without catalyst (1) and with PtIr catalyst (2) in different temperatures. Commercial GDL characteristics with 2.1 mgPt/cm² are presented for comparison purpose (4).

Figure 8. Anodic hydrogen oxidation on «floating» electrode curves: 1- GDL with commercial catalyst (Pt-2.1 mg/cm²); 2- GDL (Sigracet 10bb) with Pt-Ir (10%) vacuum catalytic black (0.36 mg/cm²) t=30°C; 3 - ГДС (Sigracet 10bb) with Pt-Ir (10%) vacuum catalytic black (0.36 mg/cm²) t=70°C; Potential scanning speed is 50 mV/s; electrolyte 0.5 M H₂SO₄

Fig.8. shows that specific activity of researched catalyst reduced to Pt mass unit appeared higher than for commercial electrode. At polarization level 0.5 V it has value 1 A/mg Pt.

Hydrogen cathode recovery in alkaline media

High vacuum catalytic black activity on porous electrode found for reaction of hydrogen cathode recovery in alkaline solution. It’s an important thing which lowering energy inputs in Fixed Alkaline Electrolyser (FAE) [18]. Fig.9. shows polarization characteristic for biporous nickel electrode with VPB catalyst (mₙ=0.594 mg/cm²).
Figure 9. Polarization curves of cathode hydrogen recovery on VPB catalyst (0.36 mg/cm²), deposited on front nickel electrode surface (1). Without catalyst (2) t=80 °C; 6M KOH electrolyte.

CONCLUSION

Thus, results of hydrogen-air fuel cell anode characteristic research showed that vacuum technologies allow receiving controlled by thickness catalytic compositions like noble metal blacks on GDL’s microporous layer surface. Electrodes for low temperature electrochemical devices provide high activity. For example, in hydrogen oxidation anode reaction and cathode hydrogen recovery.

ACKNOWLEDGEMENTS

Financial support of this work has been conducted by Government contract with Russian Federal Agency of Science and Innovations from 18 June 2008. № 02.552.12.7046.

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