

SYNTHESIS OF FUEL CELL CATALYSTS IN SUPERCRITICAL CARBON DIOXIDE AND THEIR STRUCTURE INVESTIGATION

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It is possible to propose some versions of supercritical technology applications in Fuel Cell production. These are: 1 - cleaning of polymer membranes of new population (polybenzimidazoles, polybenzimidides, polyaryleneesterketones and others) from high boiling organic solvents (DMF, phenol, N-methylpyrrolidone) rests, 2 - a making of catalytic layer in membrane surface by diffusion into it of catalysts precursors namely of noble metal organic complexes (Pt, Pd, Ru) from SC CO₂ – solutions and following reduction of a metal, 3 - adsorption of catalysts precursors on carbon supports (carbons black) from SC CO₂ - solutions and following thermal metal reduction, 4 - a dilution of hydrogen at its transportation to anode with carbon dioxide for decrease of its explosiveness in manufacture (by way of discussion).

An application of critical technology for creation of fuel cell catalysts is positioned now in study of laboratory developments. Preliminary results show availability of the course. For the first time using of supercritical fluids (SCF) for creation of fuel cell catalysts was reported by Erkey^{1,2}. In view of the problem actuality peculiarities of synthesis, structure and properties of the catalysts obtained in SC CO₂ have to investigate thoroughly. We studied these peculiarities on two kinds of carbon black. The structure and morphology of the catalysts were investigated by elemental analysis, RFA, TEM, SAXS, WAXD and electrochemical method.

EXPERIMENTAL PART:

Material: two sorts of carbon black were used as a carbon support: domestically produced AC-1 (Institute of graphite) obtained by acetylene polymerization under influence of an air-blast with specific surface about 120 m²/g and Vulcan (XC-72R) purchased from "Chimmed" Ltd. Corp. (~ 130 m²/g) with more polar oxidized surface. COD Pt (CH₃)₂ was obtained from "Aldrich" and was used without additional purification. A selection of the complex was determined its solubility in SCCO₂ and known decomposition temperature. Carbon dioxide with purity 99,997 v.% was purchased at "Moscow plant of pure gases".

EQUIPMENT:

A standard set of high pressure for making a liquid CO₂ on a base of syringe press ("High Pressure Equipment", USA). Reactor from stainless steel has cylinder form and insight volume about 35 cm³. The reactor was immersed into silicone bath which was placed on heating magnetic stirrer "RCT basic" of "IK Werke" plant. The temperature was controlled to within ± 0.5° C.

METHODICS:

Carbon black 0.1 -0.3 g and metal precursor 0.01-0.03 g were loaded into reactor which was pressurized and washed out with argon for 5 min. Then it was immersed into silicone bath on magnetic stirrer and was heated up to 120°C. Then pressure of 25 MPa was given with a help of syringe press. A stir-bar was used in some experiments. The pressure was controlled on manometer to within ± 1 bar. After ending of the first experimental step (impregnation) the reactor was cooled and depressurized. The second step (metal reduction) was carried out at temperature 150-180°C in inert medium (argon or CO₂) in static or flow mode of operation (20-30 cm³ / min) or in static mode with double gas medium exchange for moving off ligand decomposition products. After ending of the experiment carbon black with Pt particles was pumped out in vacuum for 1 hour at the temperature of 100°C for total moving

away of ligand decomposition products.

ANALYTICAL TECHNIQS:

SAXS-measurements were carried out by traditional method on improved laboratory diffractometer AMUR-K (elaboration of Institute of Crystallography RAS, Moscow) at fast irradiation wave-length $\lambda = 0.1542$ nm. WAXD analysis was carried out on "Rigaku D/max-RC" provided with powerful 12kWt source of radiation with rotated anode (graphite crystal-analyzer, CuK_α -radiation). Dispersive particles of carbon substrate with deposited metal was placed for TEM analysis on film-substrate according to standard procedure of investigated samples preparation. Microphotos were made on LEO912AB (Carl Zeiss, Germany) and were analyzed with a help of Femtoscan software (Russia). The analysis included measurement of Pt particles sizes, particles size distribution bar charts construction, determination of particle diameter average value and its standard deviation, calculation of polydispersion coefficient and partial surface.

RESULTS AND DISCUSSIONS:

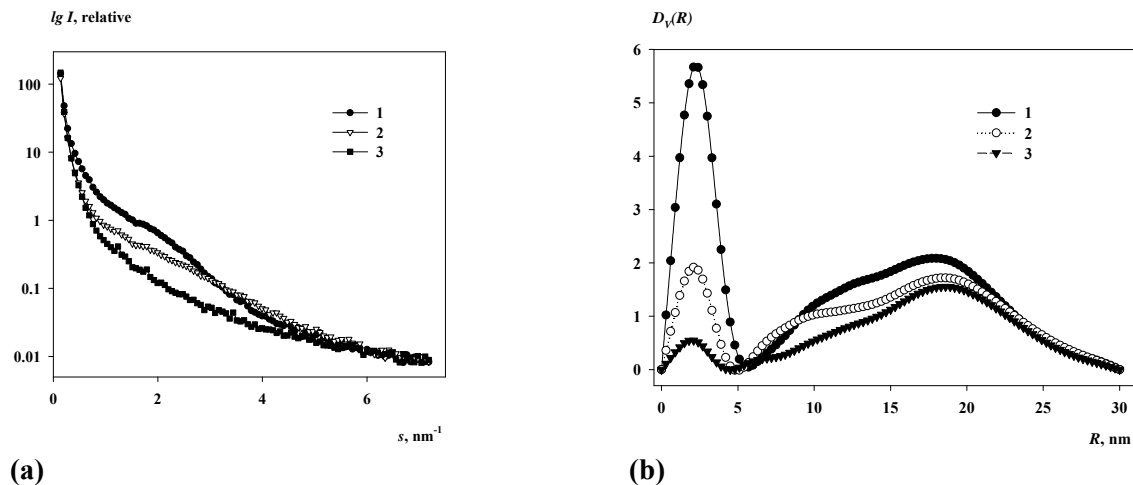
The main results are given in Table 1, including TEM, RDA data and measurements of electrochemically active surface.

Code	Car bonic sup port	Pt, calcul ated, %	Pt, foun ded, %	Pt particles size, nm (TEM)	Crystal lites size (PDA)	Poly dispe rsity coeff icien t (TE M)	Specific surface m^2/g (TEM)	Specific surface m^2/g (H)*	Specific surface m^2/g CO)*
Hi SPEC3000	Vulcan XC72R	20	18.9	1.9 ± 0.5	2.9 ± 0.3	2.0	130	52	85
Hi SPEC4000	Vulcan XC72R	40	36.1	2.9 ± 1.0	3.8 ± 0.4	1.7	80	36	47
N1 CAPtXC72R	Vulcan XC72R	20	~10	2.0 ± 0.5	$1.76 \pm$ 0.13	1.6	120	36	58
N2 CAPtXC72R	Vulcan XC72R	20	~19	1.7 ± 0.6	$2.67 \pm$ 0.15	3	130		
N3 CAPtAC1	AC1	20	~18	1.8 ± 0.5	$2.2 \pm$ 0.14	1.7	130	40	64
N4CAPtAC1	AC1	40	~38	2.1 ± 0.6	3.5 ± 0.4	1.9	110	12	29
N5CCPtAC1	AC1	40	~36	2.3 ± 0.8	3.5 ± 0.5	3	100	22	41
Z1 CAPtXC72R	Vulcan XC72R	20	~12	1.7 ± 0.6	$2.08 \pm$ 0.04	2	130	68	81
Z2 CAPtXC72R	Vulcan XC72R	23	~24	2.3 ± 0.4	$1.88 \pm$ 0.04	1.2	120	29	49
N7CCPtAC1	AC-1	31.14	30.5		$2.24 \pm$ 0.14		100		
N8CAPtAC1	AC-1	38.86	38.4				100		
N9a CAPtAC1/5	AC-1		30				100		
N9b CAPtAC1/5	AC-1		31				130		
N13 CAPtAC1/5	AC-1/5	40	33.4				50	25	44

It is possible to draw a conclusion from the table data about weak dependence of catalyst particles size on metal load. The SC CO₂ method independently from experiment conditions gives

stable Pt particle with small dimensions (1-3 nm). A size distribution is narrow enough (not more than 3). It is possible to note weak dependence of partial catalyst surface on metal load.

SAXS analysis data are given on Fig.1. Samples 1 and 2 contain Pt nanoparticles, sample 3 is pure carbonic matrix. Size distribution of dispersive heterogeneities in all samples are shown on Fig.1b.



(a) **(b)**
Fig.1. SAXS curves of studied samples (1 – AC 1-Pt; 2 – Vulcan-Pt; 3 – Vulcan) **(a)** and size distribution of dispersive heterogeneities (1 - AC1-Pt; 2 – Vul-Pt; 3 -Vul) **(b)**.

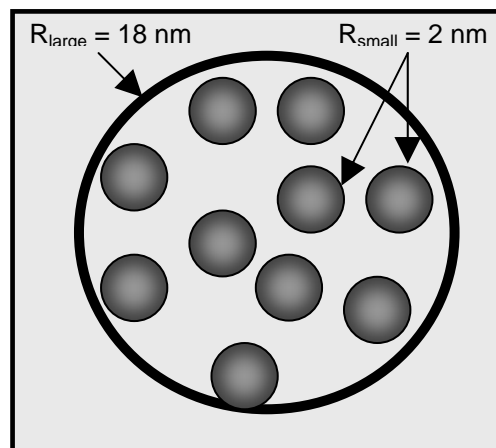
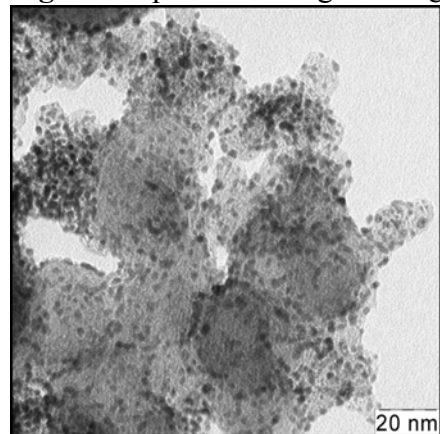


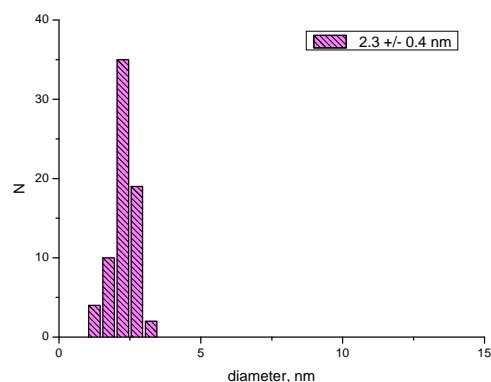
Fig.2. The picture of large heterogeneity.



(a)

All distributions are bimodal and characterize by two maximums with heterogeneities average radiuses of 2 nm and 18 nm. The first value corresponds to characteristic dimension in the system ($2R=4 \text{ nm}$). The second one probably determines the areas size where heterogeneities with the size of 4 nm are fixed (Fig.2).

TEM data for one of investigated samples of PT/carbon black catalyst and calculation data of metal size distribution are given on Fig.3.



(b)

Fig.3. Microphotos of catalytic materials **(a)** and appropriate bar charts of Pt particles size distribution **(b)** for the catalysts synthesized in SC CO_2 (sample Z2CAPtXC72R – 20% Pt on Vulcan XC72R).₂ (sample Z2CAPtXC72R – 20% Pt on commercial substrate Vulcan XC72R

The polydispersion coefficient was determined as relation of weight-average and number-average particles sizes:

$$P \equiv d_w^3/d_n^3 = \frac{\sum_i d_i^3 \times d_i^3}{\sum_i d_i^3} \bigg/ \frac{\sum_i d_i^3}{N} = \frac{N \times \sum_i d_i^6}{\left(\sum_i d_i^3\right)^2}, \quad (1)$$

где d_i – measured value of i -th particle diameter, summation was carried out on all measured values from 1 to $N=70$ (70 measurements were made for everybody sample). The specific surface was calculated by formula:

$$S = \frac{6 \sum_i d_i^2}{\rho \sum_i d_i^3}, \quad (2)$$

where ρ – platinum density (21.45g/cm^3), summation also was carried out on all measured values from 1 to $N = 70$.

Morphology features by TEM results of synthesized and investigated catalytic materials are summarized on Fig.4.

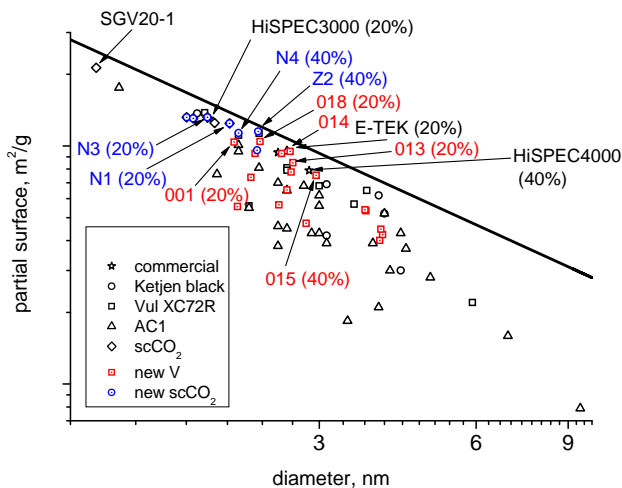


Fig.4. The dependence of specific surface on catalyst particles size.

Really, an intensity of coalescence processes by mechanism of Oswald's ageing (energetically profitable absorbance of smaller particles by larger ones) substantially decreases for ensemble of identical (monodisperse) particles.

It follows from the plot that the catalysts samples Pt / carbon black synthesized in SCCO_2 are nearest to ideal straight line and therefore they have most narrow Pt particles size distribution.

The relation $S = 6/\rho d$ between a specific surface and particle diameter that is correct for ensemble of ideally monodispersed particles is produced by straight line in double logarithmic scale. Experimental points respective to real investigated samples middle diameters for which an average diameter was calculated as simple average and a specific surface was calculated by formula 2 are given in the same place on Fig. 4. The results obtained in SC CO_2 are marked out by blue color. A proximity of experimental points to ideal straight line characterizes a platinum particles polydispersity degree of catalytic material that is important feature determining its resources behavior.

Comparative WAXD spectra of our catalyst samples and commercial catalysts are shown on Fig.5.

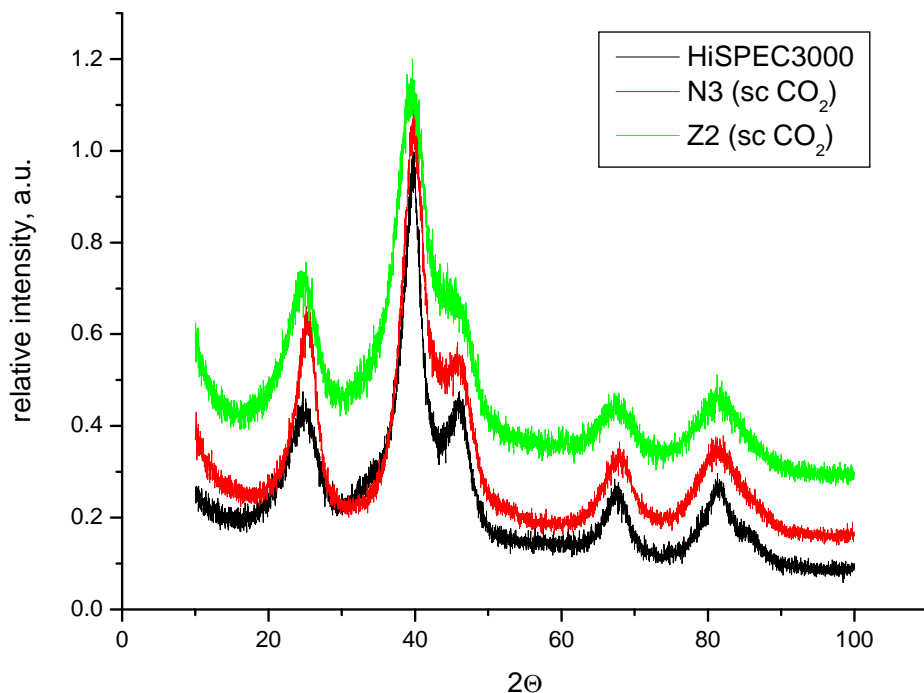


Fig.5. Comparative WAXD spectra of commercial sample HiSPEC3000 (20% Pt/C) and N3 and Z2 synthesized in SC CO₂.

All samples without exception synthesized in SC CO₂ (as comprising Pt 20% , so comprising Pt 40%) are characterized by minimal size of crystallites at that by size lesser than respective sizes for commercial materials HiSPEC3000 (Pt 20%) and HiSPEC4000 (Pt 40%).

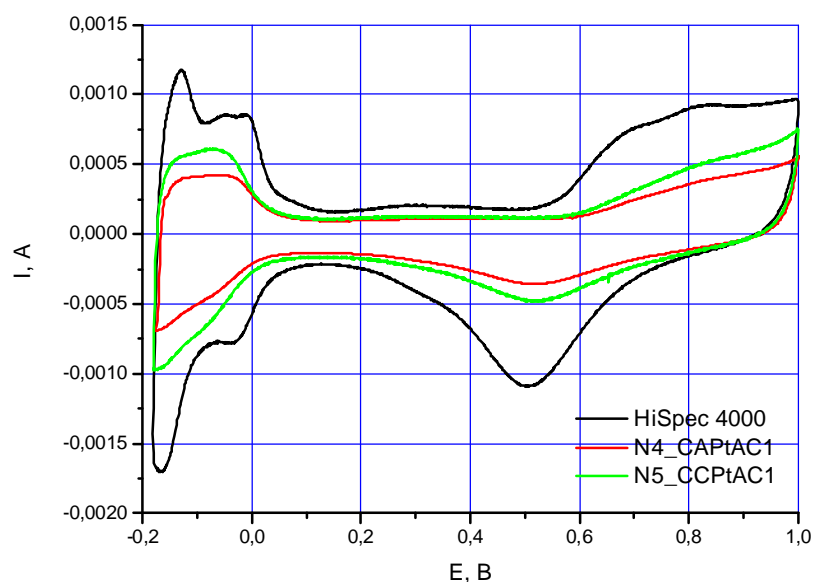


Fig.6. Cyclic voltammograms of HiSPEC 4000, N4CAPtAC 1 and N5CCPtAC 1.

Electrochemical investigations were carried out on methodic of specific surface measurements

(on H₂ and CO desorption), see Fig.6.

A form of lines in H₂ desorption region(-0.2 – 0.0 v) shows that our samples do not reach so far of best industrial catalysts purity.

CONCLUSIONS:

The reproducible laboratory technology of catalysts synthesis for Fuel Cell in SC CO₂ medium. The technology lets a possibility to obtain monodisperse nano size Pt particles independently of hydrophilia degree of carbon substrate surface. The dimensions of obtained particles and partial surface of platinum including electrochemically active surface for synthesized catalysts are identical to the characteristics of better commercial materials HiSPEC3000 и HiSPEC4000 of Johnson-Matthey, Inc.

A peculiarity of the method is practical independence of Pt grain size (1-3 nm) on a metal load (up to 40 w. % counting on a carbon black + metal particles). This has a great importance because gives a possibility to make more thin electrodes at the same current density. The method in any its version is characterized by small and stable Pt particles size and narrow size distribution (1.1-3) independently on synthesis conditions and also a weak dependence of partial surface area of a catalyst on metal concentration in substrate and particles diameter. Ecological purity is also its positive trait.

A main disadvantage of developed approach related with use of SCCO₂ for catalysts synthesis now is high price of technological cycle. Therefore the main task of following development of this approach is decrease of catalysts price. This includes a search of possibilities of price decrease of used materials. In particular, it is necessary to search another Pt complexes that are cheaper than COD Pt (CH₃)₂. It is necessary to check another commercially available materials soluble in SC CO₂ for example Pt (acac)₂ that is 20 % cheaper than COD Pt (CH₃)₂

Besides there are an interesting potential possibility to impregnate CO₂ insoluble metal precursors using liquid carriers insoluble in SC CO₂ but which are able to dissolve a precursor. There is some information in the literature about so processes. If this way will be real then any limitations for selection of Pt comprised initial materials fall away and it will be possible to use the simplest but soluble in water or alcohol compounds of this metal.

ACKNOWLEDGMENTS:

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