NOVEL NANOSTRUCTURED CARBON SUPPORTS FOR PLATINUM AND NON-PLATINUM PEMFC CATHODE CATALYSTS

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Introduction

At present, platinum and its alloys supported on carbon black are used as oxygen reduction catalysts in proton exchange membrane fuel cells (PEMFC) due to their high catalytic activity and stability in fuel cell environment (Costamagna, 2001; Gasteiger, 2005). However, platinum is expensive metal of low abundance, and challenge facing PEMFC is to reduce platinum loading without sacrifice of fuel cell performance. Platinum utilization in catalyst layer and performances of the cathode catalysts depend substantially on characteristics of carbon support, such as porous structure, surface area, electrical conductivity, etc. (Thompson, 2001; Ralph, 2002).

Recently, carbon nanostructured materials, like carbon nanofibers (CNF), have attracted great interest as promising catalyst support materials (Bessel, 2001; Gangeri, 2005; Ismagilov, 2005) due to their exceptional structural and textural properties, electrophysical characteristics and chemical stability as well as progress in controlled large-scale CVD synthesis of such materials with predetermined characteristics. It is well-known (De Jong, 2000; Reshetenko, 2003) that CNF properties can be easily tailored by regulating growth conditions, primarily, catalyst used for the groth, carbon precursor, and temperature. CNF are mesoporous materials with surface area of 100–300 m^2/g and definite arrangement of graphite layers forming 'herringbone', 'platelet' or nanotubular structure depending on synthesis parameters. It has been shown (Bessel, 2001; Matsumoto, 2004; Gangeri, 2005; Ismagilov, 2005) that application of CNF can lead to increase of efficiency of platinum supported catalysts as compared with commercial carbon black. Furthermore, our previous studies demonstrated that nanostructured carbon materials of another type – amorphous microporous carbons (AMC) with very high surface area up to 3300 m^2/g and large microporous volume up to 2 cm^3/g (Barnakov, 2003) are promising supports for platinum, and Pt/AMC catalysts exhibit better performance in membrane/electrode assembly (MEA) tests as compared with Pt/Vulcan XC-72R (Ismagilov, 2005; Sakashita, 2005).

For preparation of high-dispersed carbon supported platinum catalysts, presence of surface functional groups is desirable. They improve adhesion of nanoparticles, leading to high dispersion of active component, more uniform distribution over the support and higher stability resulting in high performance of such electrocatalysts (Matsumoto, 2004; Maiyalagan, 2005). Moreover, enhanced electroconductivity of nitrogen-doped carbons in comparison with non-modified counterparts (Miyamoto, 1997; Golberg, 2003) favours high electrocatalytic activity.

On the other hand, nitrogen-containing nanocarbons are promising supports for non-noble metal catalysts. Oxygen reduction catalysts based on transition metals like Fe or Co can be produced by pyrolysis of Fe (or Co) salts adsorbed onto nitrogen-containing carbon support (Jasinski, 1964; Lefèvre, 2002; Jaouen, 2003). During the heat treatment at high temperature (600 – 1000°C) Met-N_4 or Met-N_2 species (where Met = Fe or Co) are formed. From the results of XPS and secondary ion mass spectroscopy (Lefèvre, 2002; Jaouen, 2003) it was established that, in order to obtain an active catalyst, nitrogen atoms have to be of pyridinic type in phenanthroline-like structure (Met-N_2 site) or pyrrole type (Met-N_4 site) similar to phthalocyanine. Activity of these non-noble catalysts increases with nitrogen content on the support surface. Thus, nitrogen content and its electronic state are important for the preparation of active electrocatalysts, and ability to finely tune these parameters at the stage of support synthesis is very desirable.

Experimental

CNF synthesis

CNF were synthesized by catalytic decomposition of CH_4 at 550-700°C and 1 bar pressure over metal catalysts. The catalysts with high (70 – 90 wt. %) loading of iron-subgroup metals were prepared by coprecipitation of active component and alumina from nitrate solution as described elsewhere (Reshetenko, 2003). The catalysts used were 65Ni-25Cu-Al_2O_3 and 62Fe-8Co-Al_2O_3 Herein and after in the catalyst code, the number before the element symbol indicates the metal content in initial catalyst, wt %. Alumina content equals to the rest and ranges between 10 – 30 wt. %.

Nitrogen-containing CNF were synthesized by catalytic decomposition of C_2H_4/NH_3 mixture at 450 – 675°C over 65Ni-25Cu-Al_2O_3 catalyst. The initial C_2H_4/NH_3 mixture contained 25, 50 and 75 vol. % of ammonia. Carbon yield G (g_C/g_{cat}) was calculated as a ratio of the mass of produced carbon to that of initial catalyst.

N-AMC synthesis

Microporous N-AMC materials were prepared by chemical and subsequent thermal treatment of various nitrogen-containing organic compounds, like 8-oxyquinoline, o-nitroaniline, 1,2,3-benzotriazole (Fig. 1), or their mixtures. The typical synthetic procedure was based on chemical treatment of an organic precursor with concentrated aqueous solution of sodium hydroxide in mass ratio of (NaOH)/(precursor) = 1 ÷ 3. The mixture was heated to evaporate water and form a melt. Then the melt was subjected to carbonization at 700 – 900°C for 20 – 80 min under reductive medium of carbonization gases or in inert atmosphere. The obtained material was cooled in air, thoroughly washed with hydrochloric acid and, next, with water until neutral medium. The washed product was dried at 105 – 115°C up to constant weight.
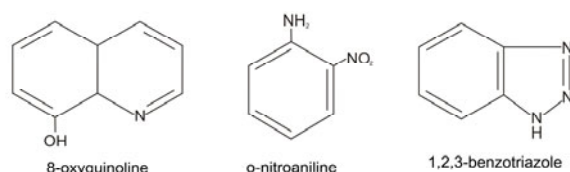
Figure 1. Nitrogen-Containing Organic Precursors of N-AMC.

Preparation of platinum catalysts

For preparation of Pt catalysts a method of adsorption of a Pt precursor on carbon supports suspended in water via alkaline hydrolysis and Pt reduction was used. H_2PtCl_6 was used as the starting Pt compound. The method is described elsewhere (Ismagilov, 2005).

Preparation of cobalt catalyst

Cobalt catalysts were prepared by adsorption of cobalt acetate (CoAc) on carbon followed by pyrolysis of the resulting powder at 600 or 900°C in Ar or $NH_3/H_2/Ar$ similar to described elsewhere (Lefevre, 2002).

The preparation procedure was performed as follows. A calculated quantity of CoAc was added to suspension of N-CNF or N-AMC in water (1 – 2 g of carbon) to provide 1.5 wt. % of cobalt on carbon support. The CoAc/carbon suspension was stirred for 2 h, and then water was completely evaporated, first by gentle heating and finally by heating at 75°C. The resulting dry powder (0.5 – 1 g) was placed in a quartz boat and inserted into quartz tube. The tube was first purged with Ar at ambient temperature for 30 min. Then sample was heated to 400°C and maintain at this temperature for 1 h in Ar flow. The final pyrolysis stage was performed in Ar at 600 or 900°C or in $NH_3/H_2/Ar$ (2:2:1) mixture at 600°C for 1 h. Then the samples were cooled in the argon flow to ambient temperature.

After the calcination, the catalysts were treated under stirring with 0.5 M H_2SO_4 to wash acid-soluble forms of cobalt. Then the samples were subjected to multiple washing with water till neutral medium.

Results and Discussion

## *Characterization of platinum catalysts*

Samples of carbon supports were investigated by XRD, TEM and adsorption methods. The catalysts were investigated by XRD and TEM, Pt dispersion was measured by XRD and CO adsorption method.

The XRD studies were performed in a HZG-4 diffractometer using Cu K_α radiation. Crystallite sizes were calculated from the line width following the Scherrer equation, TEM pictures were obtained in a JEM-100 CX. The adsorption measurements were carried out using an ASAP-2400 to provide adsorption of N_2 at 77 K.

Metal dispersion was probed by express method with CO chemisorption in a conventional flow system with a thermal conductivity detector and hydrogen as a support gas. Assuming CO adsorption on surface Pt in proportion 1 molecule per atom, the Pt dispersion was calculated by the formula: $D = CO_{ads}$ (moles)/Pt (moles). The average particle size was estimated using the formula: d (nm) = 1.08/D (Anderson. 1975).

The properties of the CNF samples used for Pt catalysts preparation are given in Table 1. TEM pictures of the catalysts prepared on CNF samples are shown in Figures 2 and 3.

Table 1. Properties of CNF.

Sample	Catalyst used for CNF growth	CNF structure	S_{BET}, m^2/g	V_{pore}, cm^3/g	Pore diameter D^{BET}, nm
CNF-1	62Fe8Ni	Multiwall nanotube	150	0.66	17.5
CNF-2	65Ni25Cu	Platelet	263	0.39	5.9
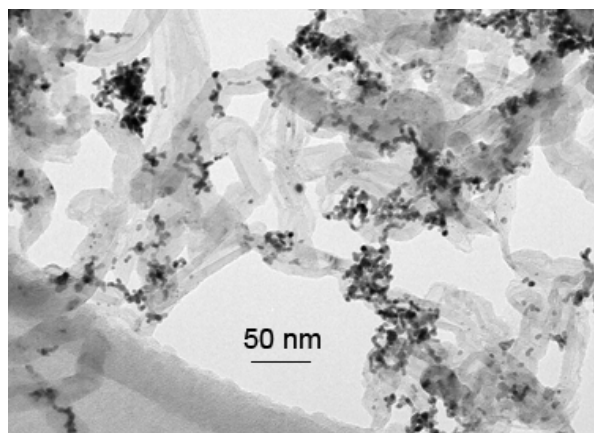
Figure 2. TEM Image of 30% Pt/CNF-1.
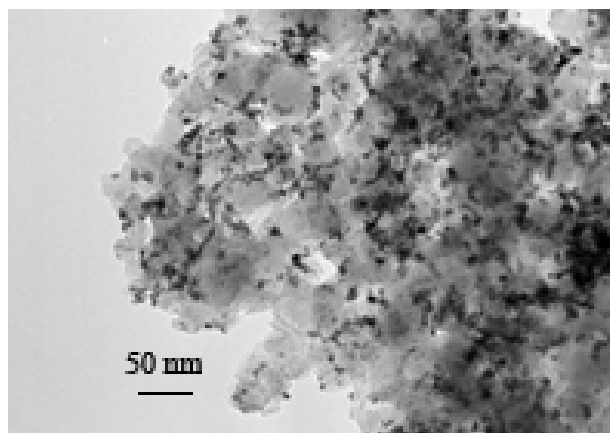
Figure 3. TEM image of 30% Pt/CNF-2.

The prepared CNF are mesoporous carbon supports with regular structure. It was supposed that this feature may favor good electrochemical activity in oxygen reduction on Pt catalysts prepared on these supports.

The electrochemical activity of the catalysts was measured with rotating disk electrode in 0.5 M H_2SO_4. The results are given in Table 1. For comparison, a catalyst containing 30% Pt on standard support Vulcan XC-72R was synthesized by the same method. The results of the measurement of the activity in oxygen reduction reaction show that the catalysts prepared on CNF, especially on CNF with nanotube structure exhibit substantially higher specific activity than the catalyst prepared on the support XC-72R. These results show good prospects for application of these nanocarbon supports in PEMFC.

Table 2. Kinetic Parameters of the Oxygen Reduction Reaction in 0.5 M H_2SO_4 at 20°C on the Prepared Platinum Catalysts.

Catalyst	Size of Pt particles, nm, by XRD	i at E=0.85 V, mA/mg catalyst	i at E=0.85 V, mA/mg Pt
30%Pt/CNF-1	4.3.	6.0	22.0
30%Pt/CNF-2	4.4	4.4	14.4
30%Pt/XC-72	4.4	2.2	7.3

Characterization of cobalt catalysts

Characteristics of carbon supports used for the preparation of cobalt catalysts as well as heat treatment conditions are given in Table 3. For all the catalysts the initial cobalt content was equal 1.5 wt. %. However, the actual cobalt concentration in the samples washed with 0.5 M H_2SO_4 was always smaller. According to the chemical analysis data reported in Table 3 and Fig. 4, quantity of strongly bound acid-insoluble cobalt in the samples after acid washing increases with the nitrogen content in carbon support independent on the support nature or its textural properties. The highest amount of cobalt retained in the catalyst, viz. 1.4 wt. %, was found for the catalyst prepared on N-AMC#8 support containing 8 wt. % of nitrogen. Comparison of the results obtained for the samples heat treated under different conditions showed that content of cobalt retained decreases in series Ar 900°C > Ar 600°C ≥ $NH_3/H_2/Ar$ 600°C.

In the series of Co/N-AMC catalysts treated at 600°C in Ar the amount of adsorbed CO (mol) related to the cobalt amount (mol) increases with nitrogen content in the support, indicating the fraction of Co atoms capable of binding CO increases. Furthermore, the sorption capacity of cobalt depends on the heat treatment procedure. Catalysts treated at 600°C both in Ar and $NH_3/H_2/Ar$ mixture have rather close values of CO specific capacity. However, the CO sorption capacity decreases for the samples calcined in Ar at 900°C (Table 5). Probably, increasing of the pyrolysis temperature up to 900°C causes sintering of cobalt particles and/or produces cobalt carbide coating that is inactive in CO chemisorption.

Table 3. Effect of Carbon Support and Heat Treatment Conditions on Concentration and CO Sorption Capacity of Strongly Bound Acid-Insoluble Cobalt in Co/C Catalyst after Acid Washing in 0.5 M H_2SO_4.

Support	N, wt. %	S_{BET}, m^2/g	Co [a], wt. %	HT [b]	CO_{ads}/Co, (mol/mol)·100%
N-CNF#3	0.9	244	0.14	Ar, 600°C	8.07
			0.01	$NH_3/H_2/Ar$, 600°C	11.00
			0.15	Ar, 900°C	n.d. [c]
N-CNF#4	3.1	286	0.31	Ar, 600°C	n.d. [c]
N-CNF#5	6.8	191	0.74	Ar, 600°C	n.d. [c]
N-AMC#1	0.9	3117	0.04	Ar, 600°C	3.00
N-AMC#2	1.9	2352	0.16	Ar, 600°C	1.56
N-AMC#4	4.3	1643	0.16	Ar, 600°C	4.46
			0.11	$NH_3/H_2/Ar$, 600°C	4.00
			0.41	Ar, 900°C	0
N-AMC#5	5.3	840	0.76	Ar, 600°C	9.15
N-AMC#8	8.0	472	1.40	Ar, 600°C	n.d. [c]

[a] Co content after acid-washing;
[b] Heat-treatment conditions;
[c] Not determined.
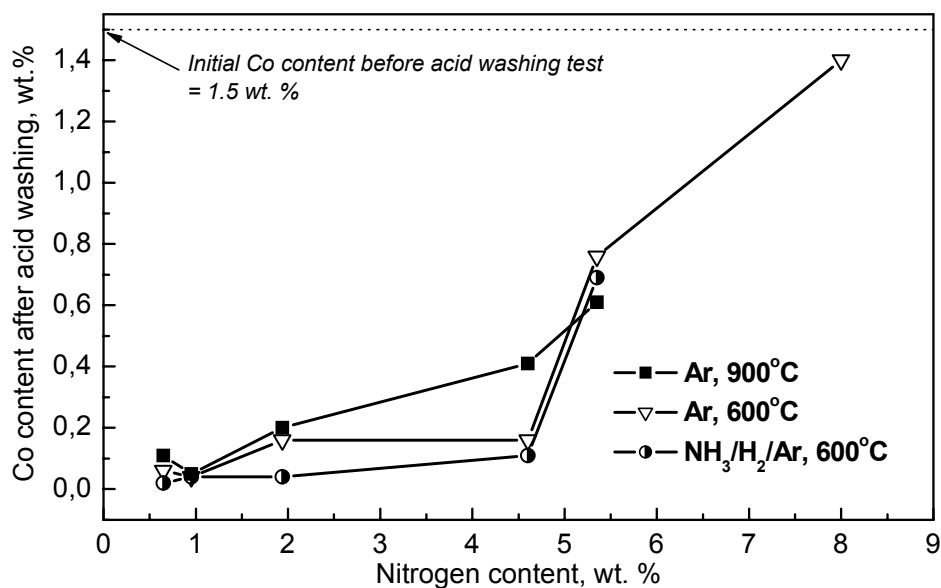
Figure 4. Stability of Co/N-AMC Catalysts to Acid Washing.

Figures 5 shows cobalt particles in the N-AMC#5 supported catalysts after heat treatment in Ar flow at 600°C before acid washing. The sample contains 1.42 wt. % Co. Obviously, the cobalt particles are of different sizes. TEM images show the particles with a size of 10 – 50 nm as well as the large particles up to 300 nm in size. Small particles are encapsulated into amorphous carbon structure forming bended hollow caverns (Fig. 9, right). These particles are nanosized aggregates constituted by cobalt disoriented crystallites.

The micrographs of the acid washed Co/N-AMC#5 sample are presented in Figure 6. It can be seen that after acid washing only small particles of 10 – 50 nm in size remain on the support surface. The cobalt particles are also built from disoriented cobalt crystallites (Fig. 10, right) as in unwashed sample.
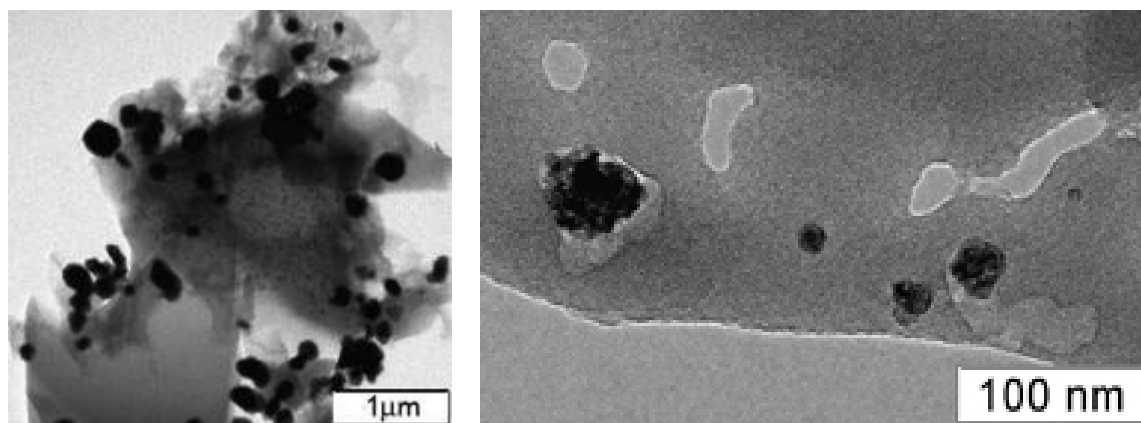

Figure. 5. Micrographs of Catalyst Co/N-AMC#5 after Heat Treatment in Ar at 600°C before Acid Washing (1.42 wt. % Co).
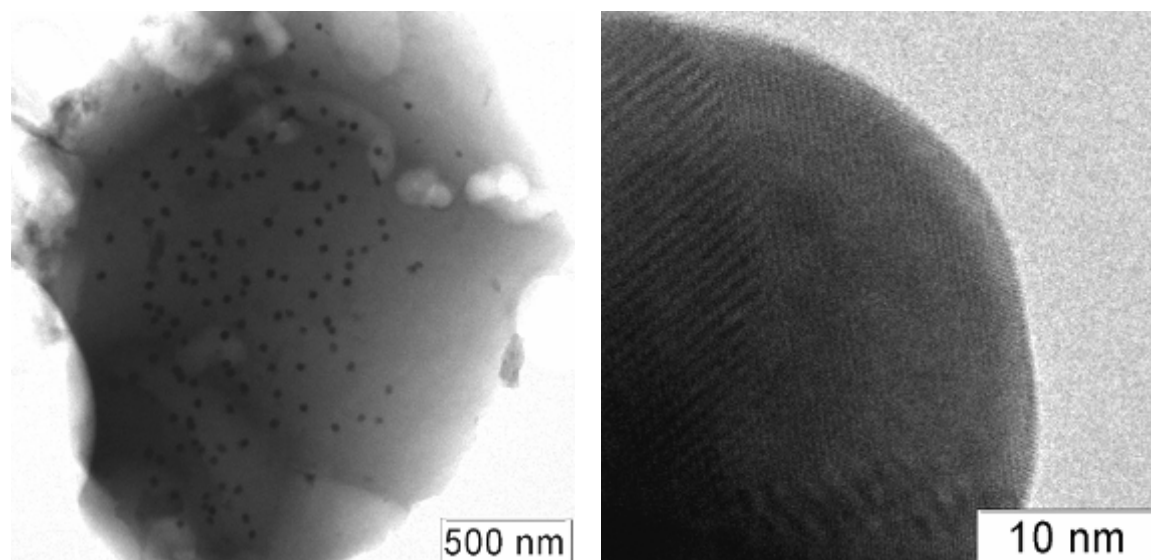
Figure 6. Micrographs of the Catalyst Co/N-AMC#5 after Acid Washing with 0.5 M H_2SO_4 (0.76 wt. % Co).

The Co 2p spectrum XPS spectra of Co/N-AMC#5 catalyst before and after acid washing (Figure 7) show the signals (I) and (IV) at 780.4 eV and 796.2 eV, corresponded to $2p_{3/2,1/2}$ spin-orbital doublet of porphyrinic Co^{2+}, and the signals (II) and (V) at 781.4 eV and 797.4 eV, associated with $2p_{3/2,1/2}$ spin-orbital doublet of cobalt oxides (CoO, Co_3O_4, Co_2O_3). The peaks (III) and (VI) at 785.9 eV and 802.7 eV correspond to the 'shake-up' satellites of two previous signals (II) and (V). The ratio of intensities of the most representative signals (I) and (II) is ca. 0.3.

The spectrum of the acid-washed catalyst 0.76%Co/N-AMC#5 is similar to that of the catalyst 1.42%Co/N-AMC#5, but the intensities of the Co 2p bands are lower. The ratio of intensities of the most representative signals remains the same, meaning that both types of cobalt species are partly removed from the support upon acid washing. The remaining species may be Co^{2+} ions bound to the surface through 2 or 4 nitrogen atoms located at most appropriate distances and metal cobalt particles covered with oxide layer which are resistant to acid-washing because they are embedded (encapsulated) into the support structure, as the TEM studies have shown.
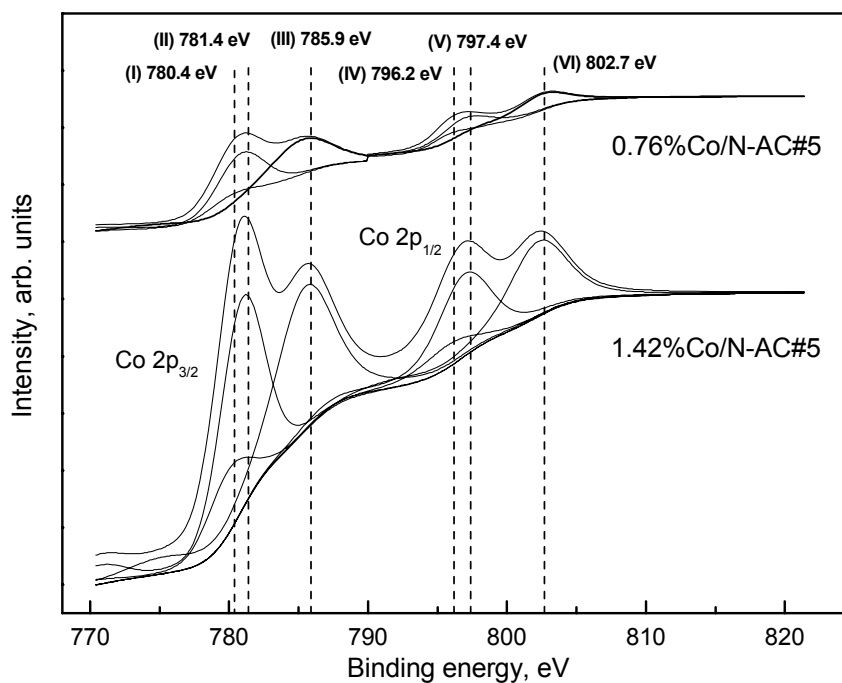
Figure 7. XPS Narrow-Scan Spectra for Co 2p for 1.42%Co/N-AMC#5 Catalyst and the Catalyst after Acid Washing 0.76% Co/N-AMC#5.

Electrochemical activity of the Co catalysts

Figures 8 and 9 show the plots of specific disc current related to the mass of catalyst versus disc potential for the cobalt catalysts supported on N-CNF and N-AMC, respectively. The results show that the catalysts on microporous supports N-AMC#4 and N-AMC#5 with the highest nitrogen content have the highest activity, substantially exceeding the activity of the catalysts on N-AMC#1 and N-AMC#2 with less nitrogen content. Although the Co/N-AMC#5 catalyst have much higher content of cobalt (0.76 wt. %) than the Co/N-AMC#4 catalyst (0.16 wt. %), both these catalysts have comparable activity, probably because they have similar amounts of nitrogen, which favor the formation of ORR active sites based on nitrogen-bound Co^{2+} ions. The same tendency was observed for the cobalt catalyst supported on N-CNF.

It is obvious that the catalytic activity varies from one support to another but the specific surface area of the support is not essential factor in obtaining high activity for ORR. Hence, the most important factor is nitrogen content that can be explained by the fact that nitrogen is known to be part of the two main catalytic sites (Met-N_4/C and Met-N_2/C). The results are in agreement with those obtained for carbon black supported iron presented in [31].
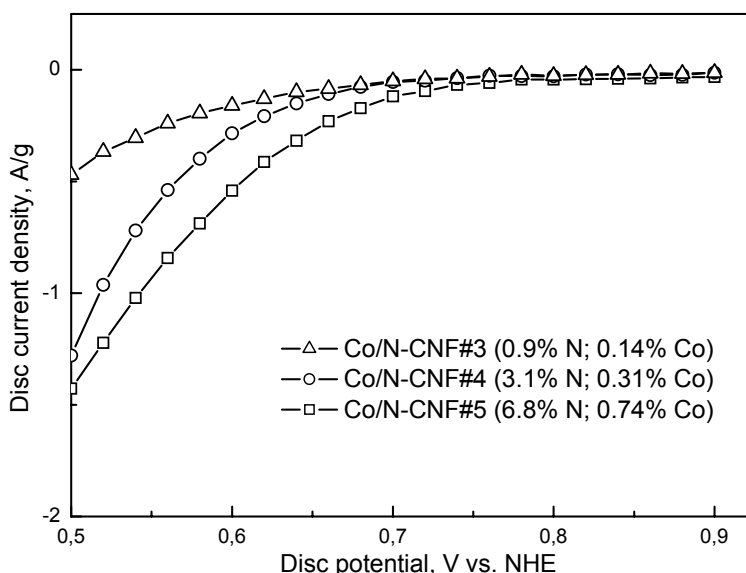
Figure 8. Dependence of the Disc Current Density on the Disc Potential for Cobalt Catalysts Supported on N-CNF.
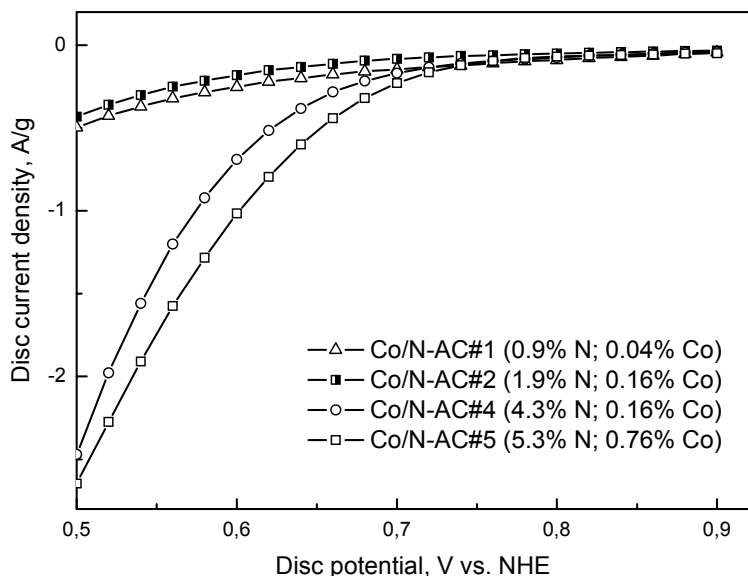
Figure 9. Dependence of the Disc Current Density on the Disc Potential for Cobalt Catalysts supported on N-AMC.

Conclusions

We have shown potential applicability of novel nanocarbon supports – carbon nanofibers (CNF) with nanotube and platelet structure for synthesis of active platinum cathode catalysts for proton exchange membrane fuel cells (PEMFC). The used catalyst preparation technique provides rather high dispersion for the supported platinum at a large Pt loading. The catalysts were further characterized by measurement of specific electrochemical activity with a rotating disk electrode The testing showed that the Pt cathode catalysts on CNF exhibit higher activity in comparison with a catalyst on conventional carbon black support Pt/Vulcan XC-72R. Thus, the application of CNF materials as supports for catalysts for low Pt loading cathodes appears to be promising.

Preparation method for cobalt catalysts on N-doped carbon nanofibers and nitrogen containing microporous amorphous carbons was developed. A series of cobalt catalysts prepared on N-CNF and N-AMC were prepared. It was shown that the fraction of strongly bound acid insoluble cobalt species increases with the nitrogen content in the carbon support used.

TEM study showed that cobalt particles in the initial catalysts are polydisperse. There are two groups of particles: with a size of 10-50 nm and with a size about 300 nm. After catalyst washing with acid, the larger particles are removed and only small particles are observed in the micrographs. These small particles are aggregates containing disoriented cobalt crystallites. The XPS study in the Co 2p region showed the presence of signals belonging to Co^{2+} bound to nitrogen and to Co cations in surface oxides on Co particles.

It was shown that oxygen reduction activities of the catalysts measured by rotating disc method depend on the nitrogen content and enhance with its increase. Further research is now in progress on the development of preparation techniques of nitrogen nanocarbon supports with a higher nitrogen content – up to 20 wt. %, which will be used for development of non-platinum catalysts with sufficiently high activity.

Acknowledgements

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