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Characterization of platinum deposited on carbon hollow fibers / carbon cryogel composites

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Platinum supported on high surface area carbon material is one of the most intensively studied catalysts. However, physico-chemical characteristics and surface chemistry of carbon influence properties of the support itself as well as of a catalyst. In our studies we deposited platinum on hollow fibers with or without carbon cryogel. Carbon materials were characterized by nitrogen adsorption/desorption isotherms measurements, X-ray fluorescence spectrometry and scanning electron microscope. Deposition of platinum was performed chemically and electrochemically. The electrochemical deposition was performed on the grinded samples at the same conditions for all substrates with the aim to study the activity of the catalyst. It was noticed that the nature of carbon support affected structure of platinum deposits and thus their activity.

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1. Introduction

Interest in applications of nanostructure catalysts results from their unique electronic and morphological structure and developed surface area. During last several decades platinum catalyst supported on high surface area carbon material has been intensively studied. The importance of the carbon supporting material properties for the functioning of the catalysts is well recognized (1). It was noticed that the nature of carbon support affected structure of platinum deposits and thus their activity. This results in the further developed of new types of carbon materials techniques and technologies. Most industrial carbon materials consist of "blends" of carbons with different structures, textures and properties.

The increase in specific surface area of the support increases the specific surface area of platinum and decreases Pt particle size (2,3). The decrease in Pt particle size leads to the increase in the activity eg. on the electrocatalytic oxidation of small organic molecules.

Carbon cryogels retain the mesoscopic structure of their organic precursor to a large extent. Two pore size regimes occur in this material: mesopores (diameter 2-50 nm) and micropores (diameter < 2 nm). The evolution of the pore size distribution in the nanopore range (larger micropores and small mesopores) should be further improved for activated carbon. This property, together with the high surface area and their electrical conductivity makes carbon cryogel promising materials for applications as electrodes in supercapacitors or in the fuel cells.

In this study we examined new type of carbon porous material –carbon hollow fibers/carbon cryogel composite as a catalyst support. Also, we examined the influence of different methods used for Pt deposition (chemically and electrochemically) on the electrochemical properties of carbon material support. Prior to electrochemical Pt deposition material was grinded.

2. Experimental

2.1 Sample preparation

Carbon hollow fibers/carbon cryogel composite (HF+RF) were prepared with regenerated cellulose hollow fibers and resorcinol-formaldehyde solution (RF) as precursors, respectively. RF solution with sodium carbonate as a catalyst was added to the hollow fibers (HF). Mole ratio of resorcinol to formaldehyde was 0.5, mole ratio of resorcinol to catalyst was 100 and mass percentage ratio of resorcinol to distilled and deionized water was 10. Carbon cryogel were synthesized by polycondensation and freeze-drying and subsequent carbonization which was previously described in detailed (4).

Chemically deposition of Pt was performed by HF embedding in the chloroplatinic acid solution (0.5 M H_2SO_4 + 6 mM H_2PtCl_6) for 15 minutes and subsequent drying at 120 ^{o}C. The composites prepared with these hollow fibers were denoted as HF+RF + Pt.

2.2 Sample characterization

Adsorption and desorption isotherms of N_2 were measured on solid (HF+RF, HF+RF + Pt and HF) and grinded (HF+RF and HF+RF + Pt) samples at -196 ^{o}C using the gravimetric McBain method. From the isotherms, the specific surface area, S_{BET} was calculated using BET method and pore size distribution using BJH method. The micropore volume V_{MIC} and the external surface area S_{EXT} for the samples were calculated using the high resolution α_s plot using the standard nitrogen isotherm proposed by Kruk M., et al (5).

Chemically deposited Pt was examined by X-Ray fluorescence spectrometry (XRF) with ^{109}Cd as the excitation source. The x-ray energy determines the elements present in the sample. Surface of incorporated Pt and carbon support was examined with scanning electron microscopy (SEM).

2.3 Electrochemical measurements

All electrochemical measurements were conducted at room temperature in a standard electrochemical cell. The counter electrode was a Pt wire while a bridged saturated calomel electrode (SCE) was used as a reference one. All the potentials are expressed on the SCE scale.

The solutions were prepared with triply pyrodistilled water and p.a. grade chemicals (Merck). The electrolyte was deaerated with the bubbling of nitrogen.

Platinum was electrochemically deposited on grinded samples HF+RF, HF+RF+Pt and HF. Before the deposition, both solid and grinded samples were characterized by cyclic voltammetry in 0.5 M H_2SO_4 solution. The same amounts of the grinded samples, used as the supports for Pt catalysts, were ultrasonically re-dispersed in the same volume of triply pyrodistilled water and the same volumes of the prepared suspensions were attached onto the polished surface of glassy carbon and dried at 60°C. After drying, each support layer was covered with the same volume of diluted aqueous Nafion solution and dried again.

Platinum was electrodeposited by potential step method in deoxygenated 0.5 M H_2SO_4 + 6 mM H_2PtCl_6. The potential perturbation from – 0.2 V to 0.1 V was applied after 0.5 s at the initial potential. Pt was deposited under the same conditions with loading of 50 wt%. The same procedure in preparation and platinum deposition was used also in the case of Carbon black Vulcan XC-72R used for comparison of the catalysts activity. The amount of platinum was estimated from integrated charge measured from the *I*-t transient response corrected for charging of the support. After deposition, the electrode was thoroughly rinsed with triply pyrodistilled water and transferred to the cell containing 0.5 M H_2SO_4 as supporting electrolyte. The activity of the prepared Pt catalysts was studied in 0.5 M H_2SO_4 + 0.5 M HCOOH solutions. After the immersion of the electrode in the supporting electrolyte, the potential was cycled between hydrogen and oxygen evolution regions at 50 mV s^{-1} until a steady-state voltammogram was obtained. Then formic acid was added while the potential was held at –0.2 V for 3 min and the positive-going scan was initiated with the rate of 50 mV s^{-1} (potentiodynamic polarization curves) or 1 mV/s (quasi-steady-state polarization curves).

3. Results and discussion

Nitrogen adsorption isotherms, as the amount of N_2 adsorbed (n) as function of relative pressure (P/P_0), are shown in Figure 1 for solid samples (HF+RF, HF+RF+Pt and HF) and in Figure 2 for grinded samples (HF+RF and HF+RF+Pt).

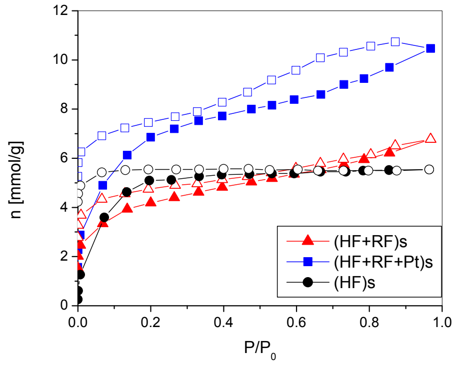

Fig. 1. Nitrogen adsorption desorption isotherms for solid carbon samples (s). Solid symbols-adsorption, open symbols-desorption.

Isotherm for hollow fibers with plateau belongs to the type –I (according to the IUPAC classification). the Type of isotherms were changed by adding RF with or without Pt. Embedding hollow fibers in the chloroplatinic acid solution increase adsorption characteristics of composite that is confirmed by analysis of calculated values (see Table 1).

Isotherms for composite samples are very similar to the type –IV but with a more or less expressed hysteresis loop which is associated with mesoporous materials. There is no overlapping of adsorption-desorption isotherms for both solid and grinded carbon hollow fibers/carbon cryogel composites (HF+RF). This indicates that the adsorbate retains in the pores.

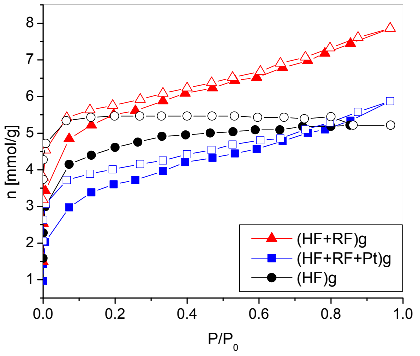

Fig. 2. Nitrogen adsorption desorption isotherms for grinded carbon samples (g). Solid symbols-adsorption, open symbols-desorption.

After materials grinding, the adsorption characteristics are change, which is confirmed by comparing calculated values shown in Table 1.

Table 1. Porous properties of solid and grinded carbon materials.

Sample	HF+RF solid	HF+RF+Pt solid	HF solid	HF+RF grinded	HF+RF+Pt grinded	HF grinded
S_{BET} $\left[\frac{m^2}{g}\right]$	335	531	393	276	436	376
S_{EXT} $\left[\frac{m^2}{g}\right]$	39	57	7	22	21	12
V_{MIC} $\left[\frac{cm^3 STP}{g}\right]$	109	171	119	103	149	108

Carbon cryogel matrix induce decrease of specific surface area (S_{BET}) but contents of mesopores (S_{EXT}) represented through the external surface area (S_{EXT}) increases. The specific surface area (S_{BET}) as well as contents of mesopores and micropores (V_{MIC}) increases after embedded the HF into chloroplatinic acid solution before the sample preparation. The acid produces activation of the material. Deposited Pt mostly blocked microporous surface of hollow fibers and induce the decreasing of the V_{MIC} and increasing of the S_{EXT}. After grinding porous properties of the carbon composites decrease especially content of mesopores for the HF+RF+Pt. Chemically deposited Pt has poor connection with carbon support and grinding induce less decrease of micropore volume than the external surface area.

Presence of chemically deposited Pt is confirmed by XRF studies (see Figure 3).

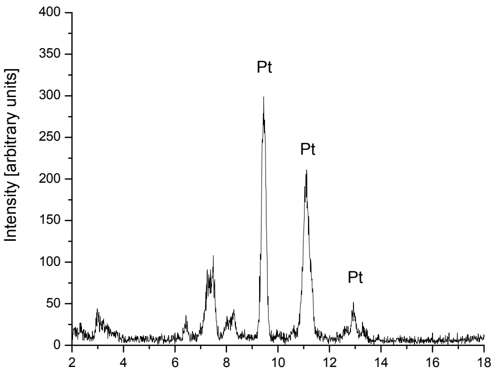

Fig. 3 XRF spectra of HF+RF+Pt grinded sample: three peaks are related to Pt, the others are phons.

The HF embedding in the chloroplatinic acid solution could provoke the splitting of the HF after carbonization process (see Figure 4).

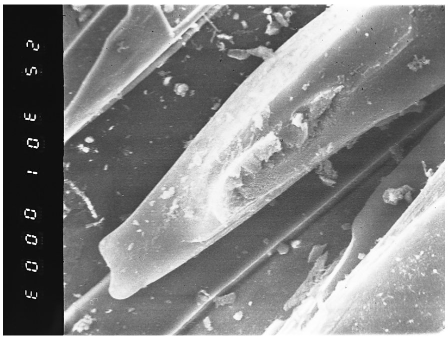

Fig. 4. SEM micrograph of split hollow fiber after carbonization process.

Chemically deposited Pt on inner and outer surface of carbonized hollow fibers could be seen on the SEM micrograph of the carbon composite HF+RF+Pt (see Figure 5). Cross section of carbon composite HF+RF is shown in Figure 6.

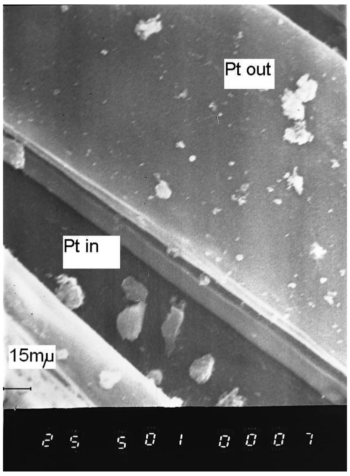

Fig. 5. SEM micrograph of chemically deposited Pt on the inner (Pt in) and on the outer (Pt out) surface of carbonized hollow fibers

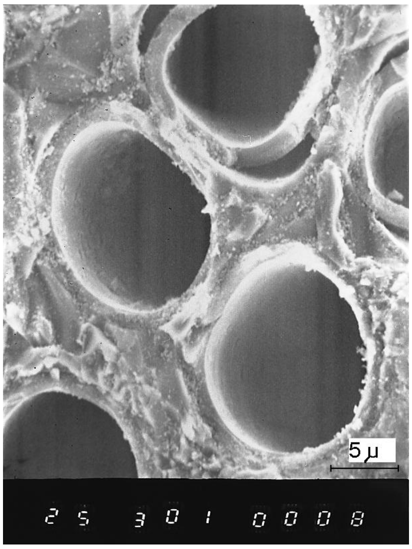

Fig. 6. SEM micrograph of Cross section of carbon composite HF+RF.

Electrochemical characterization of the solid samples showed large double layer charge, wide applicable potential region (electrochemical window) and no faradeic processes except for the sample HF+RF+Pt when small amount of incorporated platinum was recognized by rapid increase of cathodic current at - 0.25 V for hydrogen evolution. The cyclic voltammogram of this sample also exhibited presence of some other ions, probably from the solution used for Pt incorporation. The cyclic voltammograms of all the grinded samples, on the other hand showed presence of small amounts of carbon functional groups (see Fig. 7). These groups were formed on the defects made by grinding of the solid samples. Platinum in the sample HF+RF+Pt could again be seen by hydrogen evolution, but this sample has the lower double layer charge.

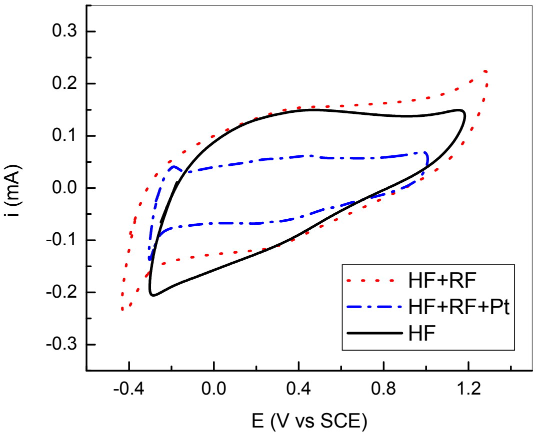

Fig. 7. Cyclic voltammograms of grinded samples in 0.5 M H_2SO_4; sweep rate: 50 mV s^{-1}.

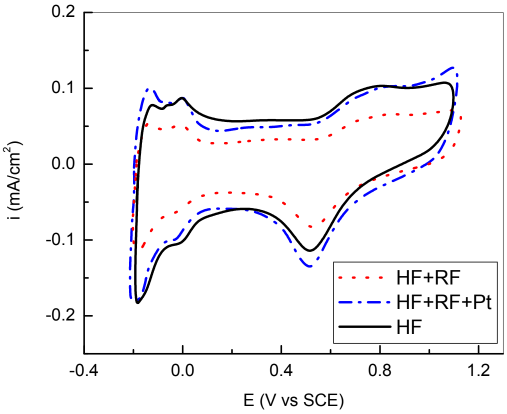

Fig. 8 Cyclic voltammograms of Pt deposited on grinded samples in 0.5 M H_2SO_4; sweep rate: 50 mV s^{-1}.

Fig. 8 shows typical cyclic voltammograms of Pt catalysts on grinded samples. The cyclic voltammograms resemble the voltammogram for polycrystalline Pt electrode (6) with well defined hydrogen adsorption/desorption region (-0.2 V< E < 0.15 V) and region of surface oxidation at higher potentials. The slight shifts of the potential of the peak related to oxide reduction indicates the small differences in particle sizes between the examined Pt catalysts on different supports. Also, different ration between weekly and strongly bounded hydrogen could be due to some difference in predominant crystallographic structure of the catalysts on different supports (7).

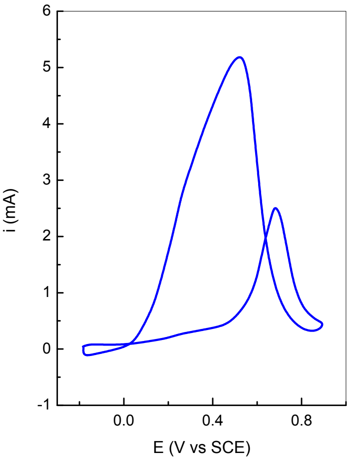

Fig. 9. Cyclic voltammograms for oxidation of 0.5 M HCOOH in 0.5 M H_2SO_4 on Pt deposited on grinded sample HF+RF +Pt (sweep rate 50 mV/s).

Voltammograms of formic acid oxidation are similar in shape for all the examined electrodes and the typical one is given in Figure 9. The reaction commences at the surface partly covered by H_{ad} species, proceeds through double layer region with relatively low currents and the maximum rate is attained at app. 0.7 V. Upon reversing the potential scan a steep increase of the reaction rate appears up to app. 0.5 V followed than by it's gradually decrease. The quasi-steady state curves of formic acid oxidation were recorded by a slow sweep rate of 1 mV/s.

Tafel plots for oxidation of formic acid at all of the examined catalysts together with the one on Carbon black Vulcan XC-72R are presented in Figure 10 on mass scale. Analysis of Figure 10 reveals that the activities of the Pt catalysts differ with the support. The most active one is Pt deposited on sample HF+RF which is about 2 times more active than Pt deposited on Carbon black, used commonly as a support for commercial catalysts. Incorporation of platinum during carbonization did not lead to better properties of the catalyst.

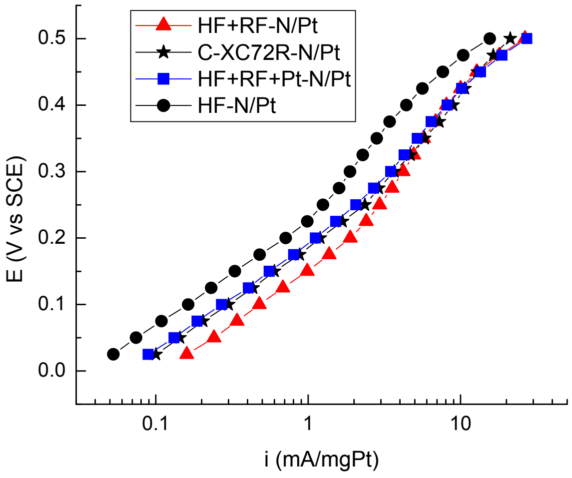

Fig. 10. Steady state curves for the oxidation of 0.5 M HCOOH in 0.5 M H_2SO_4 on Pt deposited on grinded samples and Carbon black (sweep rate 1 mV/s).

4. Conclusions

Carbon composite with porous hollow fibers and porous matrix have been successively prepared. Such composite can be self support and metal ions can be inserted in the carbon hollow fibers. Incorporation of metal ions can improve adsorption characteristics depending on the precursor. Carbon cryogel introduce its mesoscopic structure in the composite that retained after composites grinding.

Electrochemical characterization of the solid samples showed large double layer capacity and recommended this material for further investigation for double layer capacitors.

In the grinded materials there are small differences in particle sizes between the examined Pt catalysts on different supports. Also, amount of carbon surface oxygen groups was low.

Electrocatalytic activity of the Pt catalysts differs with the support. Pt deposited on sample HF+RF+Pt as about 2 times more active than Pt deposited on Carbon black, used commonly as a support for commercial catalysts.

Chemically incorporation of platinum did not lead to better properties of the catalyst. But this could be improved in the future work by increasing amount of functional oxygen groups on the carbon surface.

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References

[1] C. A. Leon, L.R Leon Radovic, 1994, in Chemistry and Physics of Carbon, Ed. P.A.Thrower, Marcel Dekker, New York, Vol. 24:213-310.

[2] P. A. Attwood, B.D. McNicol, R.T. Short, J. Appl. Electrochem. **10**(2), 213 (1980).

[3] V. M. Jovanović, S. Terzić, A. V. Tripković, K. Dj. Popović, J. D. Lović , Electroche.Comm., **6**(9), 1254 (2004).

[4] B. Babić Kaluđerović, Lj. Vračar, N. Krstajić. Characterization of carbon cryogel synthesized by sol-gel polycondensationand freeze-drying, Carbon **42**(12-13), 2617 (2004).

[5] M. Kruk, M. Jaroniec, K. P. Gadkaree, J. Colloid Interface Sci. **192**, 250 (1997).

[6] K. Yahikozawa, Y. Fujii, Y. Matsuda., K. Nishimura., Y. Takasu., Electrochim Acta, **36**(7), 973 (1991).

[7] A. Stoyanova, V. Naidenov, K. Pertov, I. Nikolov, T. Vitanov, E. Budevski, J. Appl. Electrochem., **29**(10), 1197 (1999).

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