

CHARACTERIZATION OF PLATINUM DEPOSITED ON NANOPOROUS CARBON MATERIALS

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Abstract

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 different types of carbon nanoporous materials such as 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.

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 (Leon y Leon C.A., Radovic L.R.,). 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 (Attwood P.A., et al; Jovanović V.M et al.). 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.

Experimental

Sample preparation

Carbon hollow fibers/carbon cryogel composite (HF+RF) were prepared with polysulphone 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 (Babić et al).

Chemically deposition of Pt was performed by HF embedding in the chloroplatinic acid solution (0.5 M H₂SO₄ + 6 mM H₂PtCl₆) for 15 minutes and subsequent drying at 120 °C. The composites prepared with these hollow fibers were denoted as HF+RF + Pt.

Sample characterization

Adsorption and desorption isotherms of N₂ were measured on solid (HF+RF, HF+RF + Pt and HF) and grinded (HF+RF and HF+RF + Pt) samples at -196 °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. Micropore volume V_{MIC} and external surface area S_{EXT} which includes mesopores were calculated using α_s method using the standard nitrogen isotherm proposed by Carrot P.J.M., et al.

Chemically deposited Pt was examined by X-Ray fluorescence spectrometry (XRF) with ¹⁰⁹Cd 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).

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 H₂SO₄ 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 H₂SO₄ + 6 mM H₂PtCl₆. 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 H₂SO₄ as supporting electrolyte. The activity of the prepared Pt catalysts was studied in 0.5 M H₂SO₄ + 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).

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).

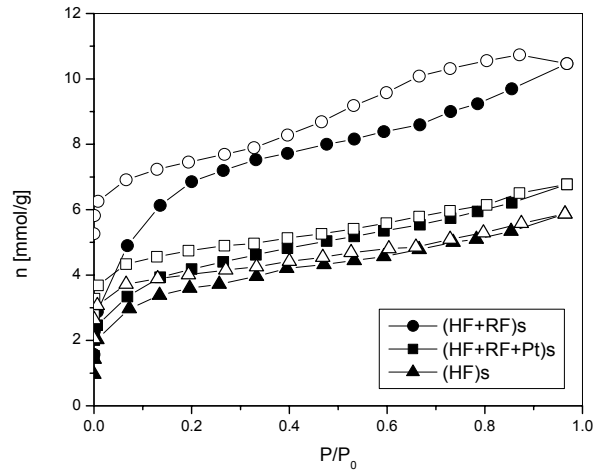


Figure 1. Nitrogen adsorption-desorption isotherms for solid carbon samples (s). Solid symbols-adsorption, open symbols-desorption.

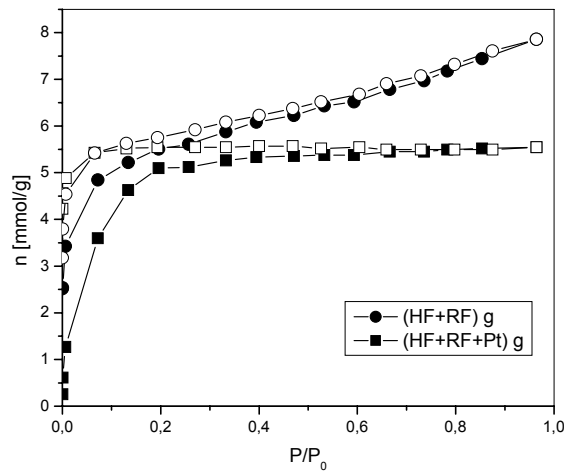


Figure 2. Nitrogen adsorption-desorption isotherms for grinded carbon samples (g). Solid symbols-adsorption, open symbols-desorption.

Isotherms for most samples are very similar to the type –IV (according to the IUPAC classification) 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. 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
S_{BET} [m ² /g]	531	335	276	436	393
S_{EXT} [m ² /g]	8.5	7.8	1.6	1.8	1.2
V_{MIC} [cm ³ /g]	0.189	0.100	0.088	0.146	0.173

Chemical deposition of Pt on the carbon composite HF+RF induce decrease of specific surface area (S_{BET}) as well as contents of mesopores (S_{EXT}) and micropores (V_{MIC}). Deposited Pt mostly blocked microporous surface of hollow fibers. After grinding porous properties of the carbon composite HF+RF decreases especially content of mesopores. But chemically deposited Pt has poor connection with carbon support and grinding induce increase of micropore volume.

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

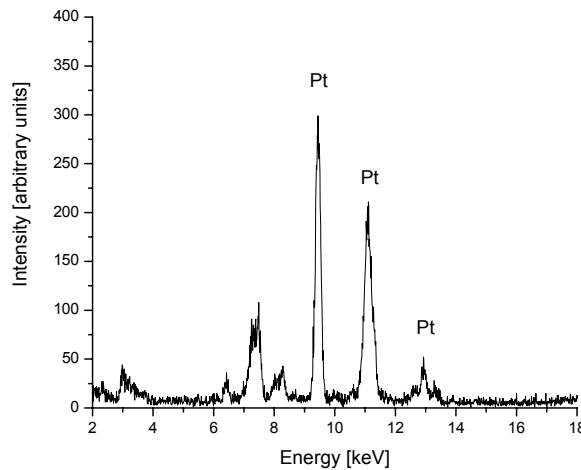


Figure 3 XRF spectra of HF+RF+Pt grinded sample: three peaks are related to Pt, the others are phonons

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 4**). Cross section of carbon composite HF+RF is shown in **Figure 5**.

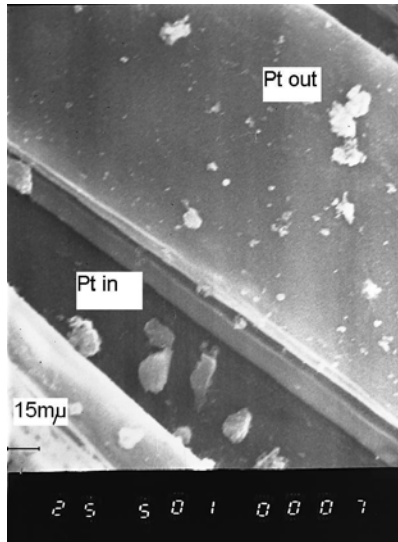


Figure 4. SEM micrograph of chemically deposited Pt on the inner (Pt in) and on the outer (Pt out) surface of carbonized hollow fibers

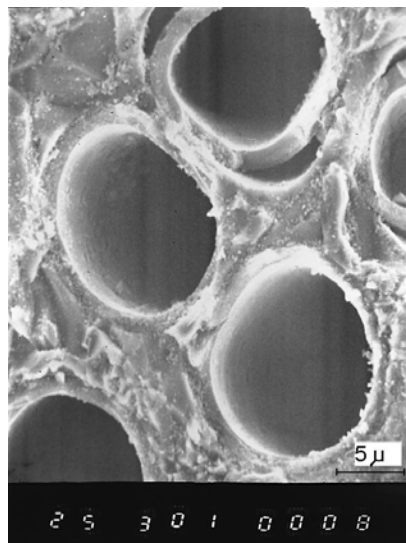


Figure 5. SEM micrograph of Cross section of carbon composite HF+RF

Electrochemical characterization of the solid samples showed large double layer charge, wide applicable potential region (electrochemical window) and no faradaic 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 **Figure 6**). 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.

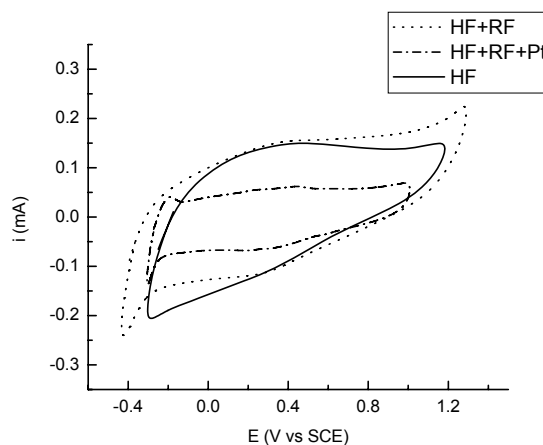


Figure 6. Cyclic voltammograms of grinded samples in 0.5 M H₂SO₄; sweep rate: 50 mV s⁻¹.

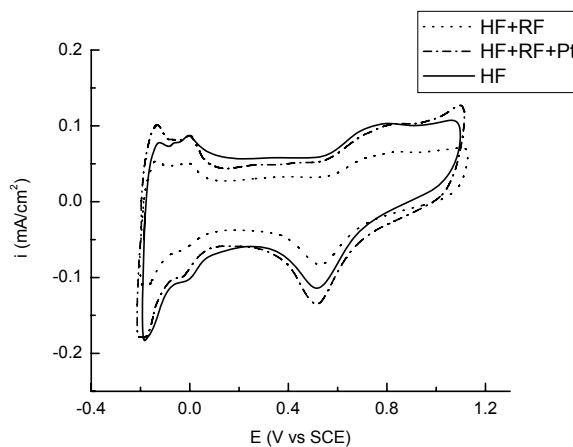


Figure 7 Cyclic voltammograms of Pt deposited on grinded samples in 0.5 M H₂SO₄; sweep rate: 50 mV s⁻¹

Figure 7 shows typical cyclic voltammograms of Pt catalysts on grinded samples. The cyclic voltammograms resemble the voltammogram for polycrystalline Pt electrode [Yahikozawa K., et al.] 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 weakly and strongly bounded hydrogen could be due to some difference in predominant crystallographic structure of the catalysts on different supports [Stoyanova A., et al.].

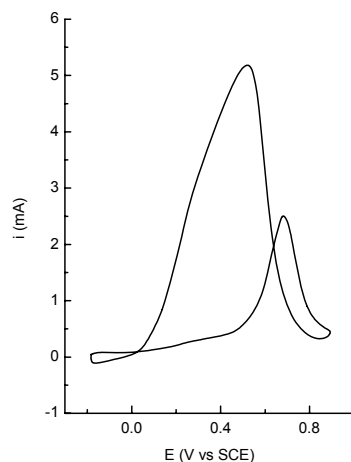


Figure 8. Cyclic voltammograms for oxidation of 0.5 M HCOOH in 0.5 M H₂SO₄ on Pt deposited on grinded sample HF+RF +Pt (sweep rate 50 mV/s).

Voltammograms of formic acid oxidation are similar in shape for all the examined electrodes and the typical one is given in **Figure 8**. 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 9** on mass scale. Analysis of **Figure 9** reveals that the activities of the Pt catalysts differ with the support. The most active one is Pt deposited on sample HF+RF+Pt 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.

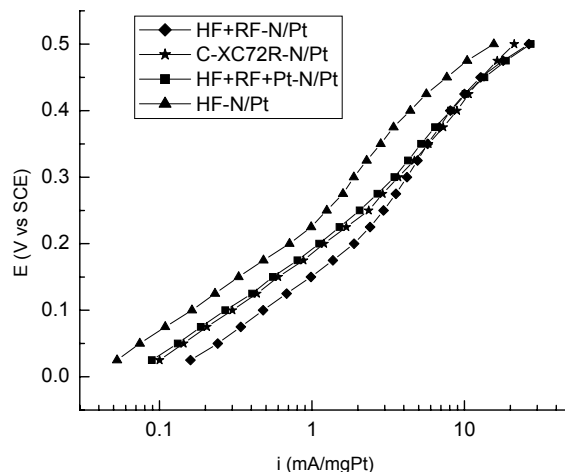


Figure 9. Steady state curves for the oxidation of 0.5 M HCOOH in 0.5 M H₂SO₄ on Pt deposited on grinded samples and Carbon black (sweep rate 1 mV/s).

References

- Attwood P.A., McNicol B.D., Short R.T., 1980. The electrocatalytic oxidation of methanol in acid electrolyte: preparation and characterization of noble metal electrocatalysts supported on pre-treated carbon-fibre papers, *J. Appl. Electrochem.* 10(2):213-222
- Babić B, Kaluđerović, Vračar Lj., Krstajić N., 2004. Characterization of carbon cryogel synthesized by sol-gel polycondensation and freeze-drying, *Carbon* 42 (12-13):2617-2624
- Carrot P.J.M, Roberts R.A., Sing K.S.W., 1987, Standard nitrogen adsorption data for nonporous carbons, *Carbon*, 25(6):769-770
- Jovanović V.M., Terzić S., Tripković A.V., Popović K.Dj., Lović J.D, 2004, The effect of electrochemically treated glassy carbon on the activity of supported Pt catalyst in methanol oxidation. *Electrochim. Comm.*, 6(9):1254-1258
- Leon y Leon C.A., Radovic L.R., 1994, in *Chemistry and Physics of Carbon*, Ed. P.A.Thrower, Marcel Dekker, New York, Vol. 24:213-310.
- Stoyanova A., Naidenov V., Pertov K., Nikolov I., Vitanov T., Budevski E., 1999. Effect of preparation conditions on the structure and catalytic activity of carbon-supported platinum for the electrooxidation of methanol *J. Appl. Electrochem.*, 29(10):1197-1203
- Yahikozawa K., Fujii Y, Matsuda Y., Nishimura K., Takasu Y., 1991. Electrocatalytic properties of ultrafine platinum particles for oxidation of methanol and formic acid in aqueous solutions, *Electrochim Acta*, 36(7):973-978