

NANOSTRUCTURED CARBON MATERIALS BASED ON IR-PYROLYZED POLYACRYLONITRILE

Karpacheva G.P.^{*}, Zemtsov L.M., Bagdasarova K.A., Muratov D.G.¹, Ermilova M.M., Orekhova N.V.

A.V. Topchiev Institute of Petrochemical Synthesis RAS,
Leninsky prospect 29, Moscow GSP-1, 119991 Russia

⁽¹⁾ Moscow State Institute of Steel and Alloys, Leninsky prospect 4, Moscow, 119049 Russia

^{*} Fax: +7 (095) 230 22 24; E-mail: gpk@ips.ac.ru

Introduction

Over the past 10 years increasing scientific and technologic interest in nanostructured carbon materials is due to wide area of their potential applications, especially in nanoelectronics, fuel cells, for hydrogen storage, as a membrane materials, thermoinsulators, carriers for heterogeneous catalysts and others.

The main objective for present work is the developing stable carbon materials based on IR-pyrolized polyacrylonitrile (PAN), which could play the role of carriers for heterogeneous and electrocatalysis providing high specific surface and dispersivity for active catalytic centers.

Results and discussion

An original method and experimental set for preparation carbon powders and films through the pyrolysis of PAN under noncoherent infrared (IR) irradiation was developed. The method includes next steps: preliminary irradiation in air with low intensity IR-light during ten minutes, high intensity IR-irradiation in inert atmosphere for 2–20 s and rapid hardening ($v = 20$ °/s).

Consecutive stages of carbon material formation in the conditions of IR-pyrolysis of PAN were investigated with the use of IR-, Auger-, X-ray photoelectron and Raman spectroscopy as well as X-ray phase analysis and. It was found that chemical transformations occurring under low intensity IR-irradiation in air include reactions of nitrile groups cyclization and dehydrogenation of main PAN polymer chain. As a result band-like cyclic structure containing systems of conjugated C=C and C=N double bonds are developed. The exposure of preliminary structured PAN films to intensive IR-irradiation in inert atmosphere leads to developing carbonization process with the formation of ordered carbon structures.

The kinetics of chemical composition change as a function of IR-pyrolysis intensity and time treatment was investigated. The increase of IR-light intensity was shown to lead to decrease nitrogen and hydrogen content. In so doing

nitrogen content does not reduce up to $T=400^{\circ}\text{C}$ and after this quick loss thereof takes place. For example, nitrogen content in samples irradiated during 6 s with intensive IR-light, providing the film heating up to $T=800^{\circ}\text{C}$, account for no more than 1% mas. As for hydrogen content it is absent throughout at $T=600^{\circ}\text{C}$.

X-ray phase analysis evidenced several amorphous phases in the structure of IR-irradiated PAN. The basic amorphous carbon phase are: intermediate phase, corresponding to a wide halo with a halfwidth of $\sim 15^{\circ}2\theta$ and $d_{\text{max}}=3$ Å; graphite-like phase is identified from $d_{002}=3,35-3,80$ Å; the polynaphthene phase ($d=4,7$ Å). Graphite-like phase is amorphous due to irregular shifting graphite network one relatively to another and small dimensions of crystallite coherent scattering regions. The content of graphite-like phase is increased with the growth of IR-light intensity and it composes 100% at $T=800^{\circ}\text{C}$. The PAN films carbonized during the IR-annealing are characterized by a high degree of perfection of the graphite networks as indicated by the line frequency 1584 cm^{-1} in Raman spectrum. The increase of degree of ordering of graphite-like structures with the growth of IR-light intensity is borne out by the decrease of parameter d_{002} from $3,74$ Å to $3,43$ Å and the growth of crystallites. On the basis of analysis of X-ray diffraction, electron microscopy and Auger-spectroscopy results was shown that structure of amorphous carbon materials is inhomogeneous. There are nanocrystal incorporations which dimensions are no more than 100 nm.

Some electrophysical properties of carbon materials obtained were studied. It was shown that conductivity level is defined by degree of ordering of polyconjugated systems obtained that is defined in turn by IR-irradiation intensity and treatment duration. The growth of electroconductivity with the irradiation time under constant IR-light intensity was established. While investigating temperature dependence of electroconductivity of samples obtained under the IR-light intensity, corresponding to $T=800^{\circ}\text{C}$, was shown to become

quite good linearized in coordinates $\lg \sigma - 1/T$. It notes semiconductive character of conductivity. The intensity rise up to $T=1030^\circ\text{C}$ ($t=8$ c) allows one to prepare carbon films with metallic conductivity (surface resistance $\rho=21 \text{ Ohm/cm}^2$, $\sigma=6,3 \cdot 10^3 \text{ S/cm}$, resistance temperature coefficient $R<10^{-4} \text{ K}^{-1}$). In such a way, the conductivity level may be controlled through varying the IR-pyrolysis intensity and duration.

Method of preparation of carbon-carbon nanocomposite materials containing carbon nanotubes was developed. Nanotubes inserting in composite structure is put into practice through their dispersing in PAN solution in DMF with subsequent intensive IR-annealing. As a result nanocomposite carbon-carbon material in which carbon nanotubes exist in matrix of the main carbon material making up in PAN IR-pyrolysis conditions.

The possibility of obtaining carbon networks and carbon nanotubes in specially developed conditions of PAN IR-pyrolysis was shown. Some considerations was applied to the mechanism of nanotubes growth during IR-treatment of PAN.

All carbon materials obtained are hydrophobic. They are stable at high temperatures over a long period of time as well as in humid and corrosive media (acid and alkaline), in hyperbaric conditions.

Thus, stable carbon materials based on IR-pyrolized PAN were developed. They represent thin porous hydrophobic conductive films and powders with controlled level of conductivity to the extent of metallic one. Carbon materials obtained may be applied as a carrier for heterogeneous catalysts.

The developed by us method of preparation carbon materials was applied firstly for inserting nanosized particles of catalitically

active metals in structure of carbon matrix "in situ" while the IR-pyrolysis of precursor composition based on PAN and metal compounds occurs. In this case, in parallel with the formation of ordered carbon structures the effective metal reduction with the participation of hydrogen evolving in dehydrogenation of the main PAN chain. With the use of developed method metal-carbon nanocomposites based on IR-irradiated PAN and nanosized particles of Pt, Pd, Re and others. Metal-carbon composite materials including nanosized bimetallic particles Pt-Re and Pt-Ru were obtained. On the basis of X-ray diffraction data bimetallic nanoparticles are the Pt-Re or Pt-Ru alloys. They have simple cubic lattice with the parameter $a=3,888 \text{ \AA}$ for Pt-Re alloy and $a=3,899 \text{ \AA}$ for Pt-Ru one. Decrease of crystal lattice parameters in compare with value of parameter a for Pt evidences the obtaining the solid solution of substitution. On the basis of X-ray diffraction data bimetallic nanoparticles was shown to be finely dispersed in carbon matrix. Histograms for nanoparticles sizes distribution were done, $3<d<18 \text{ nm}$.

Conclusions

Thus, developed by us method of PAN IR-pyrolysis on the one hand allows to obtain stable nanostructured carbon materials which may be applied as a carrier for the immobilization of active components of electrocatalysts. And on the another hand it allows to insert catalitically active metals in carbon matrix "in situ" in the course of it formation.

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