On the mechanism of pore formation in pyrolyzed polyacrylonitrile

O A Kakorina¹, I V Zaporotskova¹, L V Kozhitov² and A V Popkov²
¹Volgograd State University, Volgograd, Russia
²Moscow Institute of Steel and Alloys, Moscow, Russia

E-mail: olessya.08@mail.ru, irinazaporotskova@gmail.com

Abstract. The paper presents a study of the possibilities and mechanisms of pore formation (based on vacancy defects) in single-layer and two-layer pyrolyzed polyacrylonitrile. The geometrical and electronic-energy characteristics are described, the effect of the number of PPAN layers on the processes under consideration is studied. Theoretical calculations were performed using the molecular cluster model and the quantum chemical method MNDO.

1. Introduction
Nanoporous materials have attracted much attention lately as they are expected to lead a variety of applications that exploit their nanospace structure. They are widely used as membranes for mechanical purification, metering and even spread of liquids or gases, evaporative cooling of high-temperature structures. Due to their excellent porous properties they are exploited as dust collectors and membrane filters. Also they are promising candidates for fabricating and upgrading electrodes in supercapacitors, etc. [1–4].

Graphene sheets [5–7] with artificially created small pores that can discriminate between molecules and ions are expected to find application in separation of isotopes of certain gases (for example, helium), as reported in [8–9]. However, to date, these developments remain only theoretical, since there are technical obstacles that have not been removed so far. Synthesis of large graphene sheets at low costs is still a desirable goal. Besides, using this material as a filter requires low temperatures (about 10 K) [10–11]. However, pyrolyzed polyacrylonitrile a unique polymeric material [12–14], is considered as an effective alternative for graphene. The so-called pyrolyzed polyacrylonitrile (PPAN), which has a graphite-like layer structure, was obtained by exposing the polymer to infrared radiation. The concentration of nitrogen in the system depends on the pyrolysis conditions [15–18].

The purpose of the present study was to explore the possibility and mechanisms of pore formation (based on vacancy defects) on the surface of PPAN. The main method for modelling this process is MNDO [19–20].

2. The pore formation mechanism in PPAN
The object of research was a PPAN monolayer that apart from carbon contained nitrogen atoms that amounted to 20% of the total number of atoms on the surface. The process of defect formation was modelled as follows: an atom of nitrogen or carbon was being removed with an increment of 0.1 Å until it broke loose. Thus, two types of vacancy defect were modelled: 1) the so-called V_N defect,
when a nitrogen atom was removed from the structure; 2) the so-called \( V_c \) defect when a carbon atom was removed from the structure.

The atoms in the nearest environment to the vacancy possessed three degrees of freedom, which allowed them to shift from the equilibrium positions when C or N atom was being removed. At a distance of 0.2 Å, destruction of the layer planarity was observed. At a distance of 0.5 Å, the bonds between the atom being removed and its neighbouring atoms broke, and the monolayer atoms returned to their original positions. Subsequently, the surface atoms exhibited a shift towards the vacancy. A pentagon and a pore surrounded by nine atoms were formed in the defect layer (figure 1).

![Figure 1. The monolayer of pyrolyzed polyacrylonitrile with a vacancy defect on the surface: (a) – without optimization of parameters; (b) – with optimization of parameters.](image)

At a distance of about 2.6 Å from the surface of the monolayer, the effect of the removed atom on the polymer structure was found to be insignificant. As a result, a pore of irregular shape was formed on the monolayer surface. The calculations allowed us to construct the energy curves of the pore formation processes (figure 2) and define the main characteristics of this process (table 1).

![Figure 2. Dependence of the energy on the distance between the removed carbon atom (curve 1) or nitrogen (curve 2) and the pyrolyzed polyacrylonitrile surface: (a) – a PPAN monolayer; (b) – a two-layer structure of PPAN without a shift; (c) – two-layer structure with a shift.](image)

Next, the mechanism of pore formation in two-layer pyrolyzed polyacrylonitrile with the distance of 3.4 Å between the layers was investigated. The following possible two-layer structures were considered: 1) with one layer located exactly above the other (we called it a structure without a shift, option 1); 2) with one layer shifted against the other by 1/2 hexagon (we called it a shift structure, option 2) (figure 3).

![Figure 3. The structure of the two-layer pyrolyzed polyacrylonitrile: (a) – option 1, without a shift; (b) – option 2, with a shift of the layers by \( \frac{1}{2} \) hexagon.](image)
A nitrogen or carbon atom was removed from one of the layers of PPAN. The effect on the other monolayer in the structure was investigated. The process of vacancy pore formation on one of the PPAN layers surface was modelled as described above. It was found that as the atoms were removed from the surface and the interatomic bonds broke, the atoms in the vicinity of the defect (pores) formed began to shift simultaneously towards the pore localization and the bottom layer of the two-layer PPAN (figure 4).

![Figure 4](image-url)

**Figure 4.** The model of two-layer pyrolyzed polyacrylonitrile option 1 (without a shift) with a vacancy defect on the surface: (a) – view from the top; (b) – side view.

In the layer with the defect, a pentagon and pore surrounded by nine atoms were also formed. Figure 2 shows the energy curves of the pore formation process on a PPAN monolayer surface and the energy curves of the pore formation process on the surface of the PPAN layers for options 1 and 2 (with a shift of one layer against the other and without a shift of one layer against the other). The defect formation energy $E_d$:

$$E_d = E_{PPAN} - (E_{def} + E_a),$$

was determined, where $E_{PPAN}$ is the energy of the monolayer or two-layer polymer, $E_{def}$ is the energy of the structure with a vacancy, $E_a$ is the energy of the carbon or nitrogen atom. Analysis of the electron-energy structure of the nanosystems allowed us to construct single-electron spectra of the single-layer and two-layer PPAN with $V_N$ and $V_C$ defects.

The band gap width $\Delta E_g$ in the obtained structures with defects was defined as the difference between the energies of the occupied upper orbital and vacant lower orbital. It turned out that defect formation in the above described cases resulted in an increase in the $\Delta E_g$ of the system. The main electron-energy characteristics of the porous structures based on PPAN are given in table 1.

**Table 1.** The main characteristics of a single-layer and two-layer PPAN with a vacancy (pore): $E_d$ is defect formation energy, $\Delta E_g$ is the band gap width, $E_b$ is binding energy.

|                     | $E_d$, eV | $\Delta E_g$, eV | $E_b$, eV |
|---------------------|-----------|------------------|-----------|
| **The structure of monolayer PPAN option** |           |                  |           |
| Without vacancy     | --        | 3.36             | 7.55      |
| with C atom removed | -11.56    | 4.00             | 7.31      |
| with N atom removed | -11.95    | 4.96             | 7.23      |
| **The structure of PPAN option 1 – without a shift** |           |                  |           |
| Without vacancy     | --        | 3.06             | 7.65      |
| with C atom removed | -9.34     | 3.57             | 6.98      |
| with N atom removed | -9.02     | 3.82             | 6.17      |
| **The structure of PPAN option 2 - with a shift of the layers by 1 \(1/2\) hex** |           |                  |           |
| Without vacancy     | --        | 3.46             | 7.76      |
| with C atom removed | -8.57     | 3.89             | 7.05      |
| with N atom removed | -8.23     | 4.02             | 6.78      |
3. Conclusion
Studies have been performed to define the geometry, electronic structure, and some energy characteristics of single-layer and two-layer pyrolyzed polyacrylonitrile with two types of vacancy defects formed when a carbon atom (V_c defect) or a nitrogen atom (V_N defect) is removed from the layer, resulting in pore formation on the polymer system surface. It is established that a defect formation energy depends on the structure and layer of the polymer. Energetically, pore formation is more advantageous on the two-layer structure of a PPAN, in which one layer shifts with respect to the other by 1/2 hexagon. The presence of a vacancy defect in all the cases under study results in an increase in the width of the band gap of the system. This allows us to predict changes in the conductive properties of the resulting structurally modified polymers, which makes the promising candidates for application in nanoelectronics. Thus, the studies performed suggest that porous pyrolyzed polyacrylonitrile is an effective alternative for difficult-to-synthesize porous graphene to be used as a filter for liquids and mixtures of gases.

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