

# Morphological and microstructural characterization of some petroleum cokes as potential anode materials in lithium ion batteries

I. CARAZEANU POPOVICI<sup>\*</sup>, S. BIRGHILA, G. VOICU<sup>a</sup>, V. IONESCU<sup>b</sup>, V. CIUPINA<sup>b</sup>, G. PRODAN<sup>b</sup>

*Ovidius University, Chemistry Department, Constanța, 900527, Romania*

*<sup>a</sup>Politehnica University of Bucharest, Faculty of Applied Chemistry and Materials Science, PO-Box 12-134, Bucharest, Romania*

*<sup>b</sup>Ovidius University, Physics Department, Constanța, 900527, Romania*

We report here experimental studies performed on petroleum cokes to be used as anode materials for Li-ion secondary batteries. Our study is also relevant for other uses of petroleum coke include making carbon anodes for the aluminum industry, graphite electrodes for arc furnaces, polycarbonate plastics, steel, carbon refractory bricks for blast furnaces, packing media for anode baking furnaces. Three calcinated petroleum cokes were chosen to perform this study focused on the structural and morphological characterization by X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques, including energy dispersive X-ray (EDAX) analysis and high-resolution electron microscopy (HRTEM). X-ray diffraction study reveal interlayer spacing and microcrystalline parameters of petroleum cokes. The SEM – EDAX analysis of petroleum cokes confirmed the presence of large particles “chained” together forming agglomerates. The SAED and HRTEM analysis reveal that lattice fringe which can be ascribed to 2.85 nm diffraction plane of graphite. Also intercalated amorphous layers generate distortions crystals were observed.

(Received August 2, 2010; accepted September 15, 2010)

*Keywords:* Petroleum coke, XRD, Microstructure, SEM, TEM

## 1. Introduction

The petroleum coke belongs to a group of materials with high carbon content. Coke is a by-product of the petroleum refining process, which has mainly been used as supplementary and primary fuel for power generation [1-3]. Petroleum coke is nowadays as a good precursor for preparing high surface area activated carbon because of its high carbon content, low volatility and ash content [4,5].

The primary use of calcined coke is in making carbon anodes for the aluminum industry. Other uses include making graphite electrodes for arc furnaces, polycarbonate plastics, steel, carbon refractory bricks for blast furnaces, packing media for anode baking furnaces, and material for cathodic protection of pipelines.

The quality and availability of petroleum coke used in the manufacture of carbon anodes for aluminium production is a growing concern to the industry. Coke quality and yields have progressively declined as changes in refinery practice and the move towards processing an increasing proportion of heavier sour crudes have affected coke properties, resulting in an increase in the metal impurities and sulfur content of the coke [6]. An alternative supply of anode coke is required to supplement or eventually replace calcined petroleum coke. The significant domestic reserves of coal could represent a viable carbon resource for anode production, provided defined coke specifications can be met and at a cost that is economically viable.

In the last years, with the petroleum coke use as anode

materials in lithium ion batteries, a high added value can be obtained [7]. For this reason, coke producers, such the petroleum industry, are highly interested in improving the electrode performance of these materials.

Carbon materials are the most actively used as anode materials for Li-ion secondary batteries due to their small surface change, stable structure, and favorable price. Generally, carbon materials can be differentiated by three kinds of standards. First of all, they can be divided into graphitizable carbons and non-graphitizable carbons according to their differences in graphitization process. Secondly, there are low-temperature heat treated carbons and high-temperature heat treated carbons with various heat treatment temperatures, and lastly, they can be distinguished as graphitic carbons and non-graphitic carbons with different graphitization degrees.

Although the discharge capacity of Li-ion secondary batteries could change a little bit with the structure of carbon materials, the layered structure of graphitic carbon electrode has well developed and the Li-ions could insert between the adjacent parallel graphene sheets to give high theoretical capacity of 372mAh/g forming LiC<sub>6</sub>. However, it is difficult to make full use of energy as much as the theoretical capacity due to the decrease of capacity along with the charge–discharge progress. Since non-crystalline carbon materials are amorphous carbons, most of them have disordered structure and the adjacent carbon layers are arranged irregularly. Basically, their layers near the crystalline edges of parallel carbon are shifted irregularly or distorted and the Li-ions can also insert between the

crystalline edges of irregularly arranged carbon layers. As for cokes, besides that higher capacity than the theoretical capacity of graphite can be obtained, the rapid charge–discharge is also possible due to the fast diffusion of Li-ions caused by the small crystalline size and wide layer distance of cokes [8]. Therefore, the development of carbonaceous anode materials having high capacity, high power, and long lifetime has been studied progressively to investigate the appropriate combination method of crystalline carbon materials and amorphous carbon materials to supplement disadvantages of these two kinds of carbon materials [9].

At this moment, it is generally understood that the coke graphitization process occurs during calcinations of coke and is related not only to the calcinations temperature, but also to other parameters (composition, process conditions). As coke graphitization affects electrolytic cell performance, it should be monitored and quantified. It is known that above approximately 1100°C coke graphitizes with increasing temperature and that this graphitization is irreversible [10-14].

This study is focuses on the structural and morphological characterization of three petroleum cokes done by X-ray diffraction (XRD) and electron microscopy (SEM, EDAX and TEM) studies.

## 2. Experimental

Three petroleum coke samples, which were calcinated at the temperature of 950°C referred to as P<sub>1</sub>, P<sub>2</sub> and P<sub>3</sub>, with different origin, have been investigated.

The compositional analysis was performed in conformity with ASTM D 622-08 standard [15], using a Philips Venus 200 Wavelength Dispersive X-ray Fluorescence Spectrometer, equipped with X-ray detection in the wavelength from about 0.52nm to about 0.55nm (specifically at 0.537 nm).

Several complementary methods were used to characterize the structure of the petroleum coke samples. X-ray powder diffraction patterns of the samples were collected on a Shimadzu XRD 6000 diffractometer with CuK<sub>α</sub> radiation ( $\lambda = 1.5418\text{\AA}$ ). The  $2\theta$  range was 15° - 50° with a step size of 0.05° and a resolution of 0.01.

Scanning electron microscopy (SEM) Hitachi S 2600 N and energy dispersive X-ray analysis (EDAX) were utilized to study morphology and microstructures of petroleum cokes. For keep out of ionization, the samples were coated with silver and examined in the as-fired condition, i.e., without polishing.

TEM images were recorded with a Philips CM 120 ST microscope, which at 100 kV provides a resolution of 2Å. TEM specimens were prepared by dispersing fine powder grinded from bulk sample in ethanol, followed by ultrasonic agitation, and then deposition onto a carbon-enhanced copper.

## 3. Results and Discussion

The WDXRF spectroscopy analysis showed for P<sub>1</sub> coke sample a value for sulfur content of 40.95 ppm, for P<sub>2</sub> sample a value of 52.16 ppm and for P<sub>3</sub> sample 64.95 ppm.

The micro-structural properties of petroleum cokes are related to the prearrangement of carbon atoms into three dimensional crystalline structures, witch determine graphitization character of cokes. A calcined coke is considered as a two-dimensional, random-layered structure. On a diffraction pattern such a structure is revealed by the presence of only (*hk0*) and (*00l*) reflections. In the case of graphite-type materials, crystallites are stacks of graphitic carbon platelets located parallel to one another.

Crystallinity of petroleum coke is in general measure of quality affecting suitability for end use and is a function of the heat treatment. The crystallinity thickness is used to determine the extended of such heat treatment for example during calcinations. The value of intensity determined is not affected by coke microporosity or the presence of foreign noncrystalline material such is dedust oil. X-ray powder diffraction is a fast method for determining the average size of crystallites.

The X-Ray diffraction technique is used here to determine the degree of crystalline alignment in cokes. For calcinated cokes, the average stacking height of graphene layers L<sub>c</sub> is a good indication of their graphitizability upon graphitization heat treatment [16]. The crystallite size L<sub>c</sub> in calcinated cokes can increase from 5 nm, which is a typical size for turbostratic crystallites, to approximately 100 nm or more with increasing graphitization temperature [17].

The feature of the diffraction peaks (002) and (100) for the probe of petroleum cokes in Figure 1 is evidence that the samples have a turbostratic structure. This turbostratic model assumes that the samples is made of graphite-like microcrystallites, bounded by cross linking network, consisting of several graphite-like layers, stacked nearly parallel and equidistant, with each layer having a random orientation [16].

The coke samples subjected to XRD analysis produced two fundamental peaks, associated with (002) and (110) reflections, at Bragg angles  $2\theta$  corresponding to interplanar distances *d* presented in Table 1.

The original XRD patterns were analysed using OriginPro8 software (from OriginLab Corporation). Peak Analyzer for profile fitting was applied to find the full width at half maximum *B* (corrected for instrument broadening) in the case of the peaks (002) and (100), from each diffraction pattern.

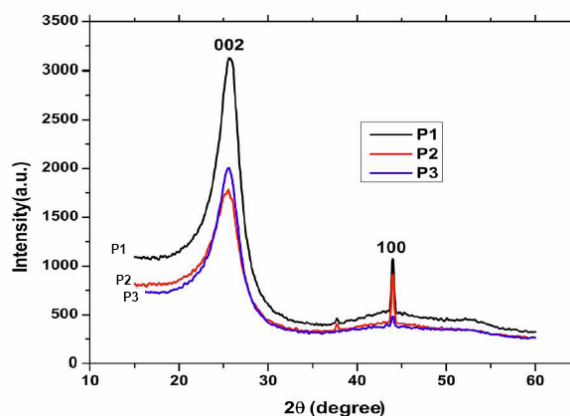


Fig.1. Diffraction patterns for samples P<sub>1</sub>, P<sub>2</sub> and P<sub>3</sub> of calcinated petroleum cokes.

Ignoring lattice strain which may have an effect on the line broadening, the crystallite diameter, dimension  $L_a$  in the plane of the layers (parallel to the basal plane), may be calculated using the broadening  $B(110)$  of the  $d(110)$  linewidth [19]:

$$L_a = 1.84\lambda / [B(110) / \cos \Theta] \quad (1)$$

The crystallite thickness, or layer dimension perpendicular to the basal plan of graphite  $L_c$ , may be estimated from the broadening  $B(002)$  of the  $d(001)$  linewidth, using the equation [19]:

$$L_c = 0.89\lambda / [B(200) / \cos \Theta] \quad (2)$$

where  $\lambda$  is the X-ray wavelength ( $\lambda = 0.15406$  nm in our case) and  $2$  is the Bragg's angle.

The effective dimension  $L$  of the graphitic microcrystallites can be written as [20]:

$$L = \left[ \frac{\pi}{4} L_a^2 L_c \right]^{1/3} \quad (3)$$

The values of  $2\theta$ , interlayer spacing  $d$  and the values of microcrystalline parameters  $L_a$ ,  $L_c$  and  $L$  are presented in Table 1.

SEM, equipped with energy dispersive X-ray spectroscopy, can be used to determine the particle size and their composition [21-24].

The chemical composition of the calcinated coke samples was evaluated using wide energy range EDAX spectra. The figure 2 shows that all the samples contain Si, S and like impurity Ag (for investigation the samples were coated with silver). No carbon peaks were located in those spectra, the EDAX analysis being performed from energy of about 0.5 keV.

Table 1. Interlayer spacing and microcrystalline parameters of petroleum cokes.

Sample	X-ray data				Microcrystallite parameter		Effective dimension
	$d_{002}$ (nm)	$d_{110}$ (nm)	$2\theta_{002}$ (deg.)	$2\theta_{100}$ (deg.)	$L_c$ (nm)	$L_a$ (nm)	$L$ (nm)
P <sub>1</sub>	3.468	2.056	25.66	43.99	2.7584	56.6785	19.0892
P <sub>2</sub>	3.497	2.056	25.44	43.99	4.7295	57.4946	23.0663
P <sub>3</sub>	3.484	2.057	25.54	43.98	5.0124	57.3607	23.4809

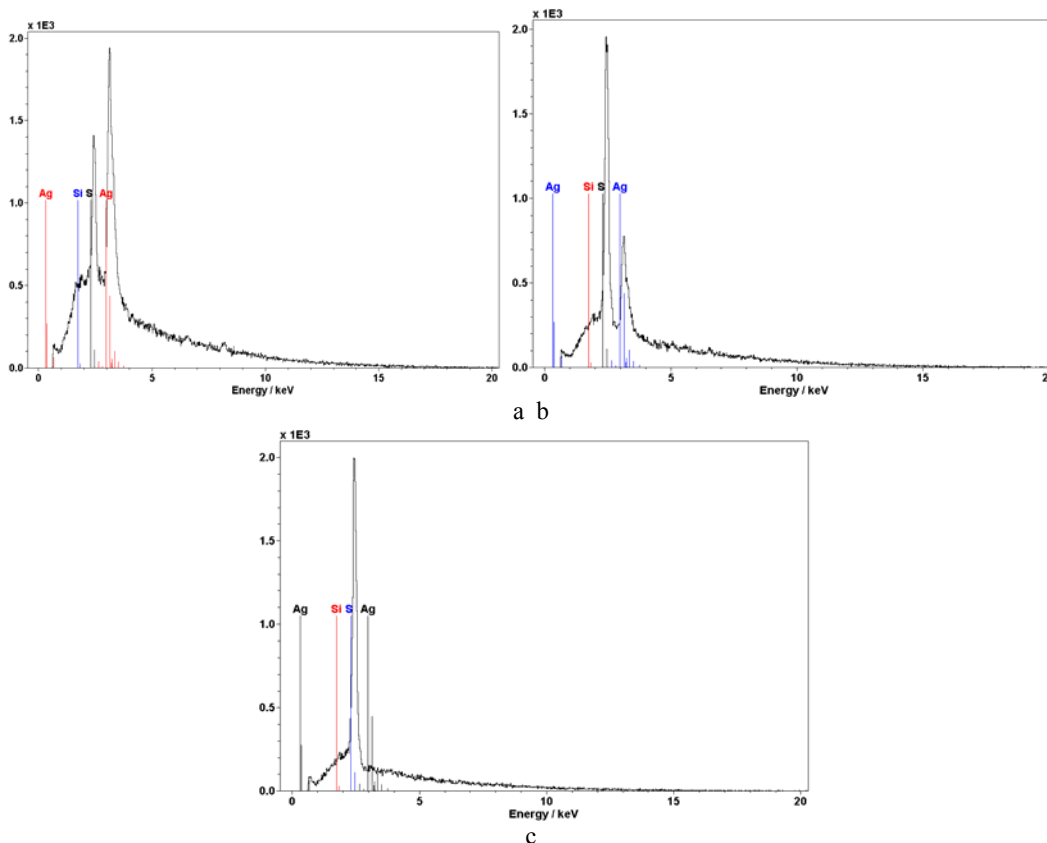
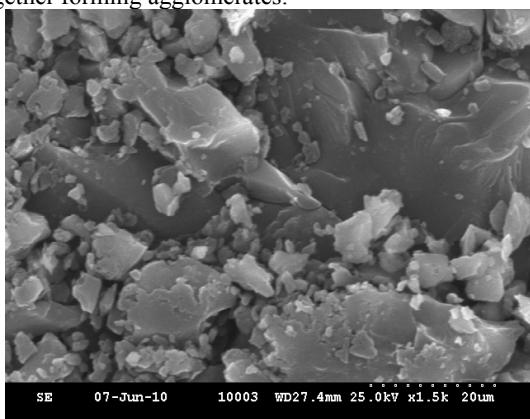


Fig 2. EDAX spectra for investigated petroleum cokes samples: a) P<sub>1</sub>, b) P<sub>2</sub>, c) P<sub>3</sub>.

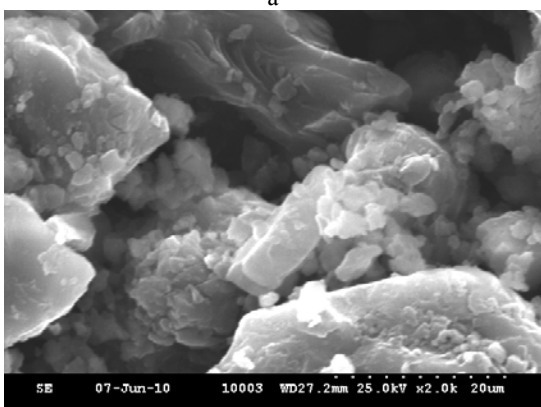
Fig. 3 a-c are the SEM images of the structures developed in all investigated samples.

From fig. 3.a. it can be observed that the microstructure morphology of sample  $P_1$  include some crystalline formations, with the diameter in the range of a few dozens of  $\mu\text{m}$ , irregular dispersed on a continuous surface (dark area) with some peaks and valleys. The samples  $P_2$  and  $P_3$  present some evident crystalline aggregates, a few of them with the diameter over  $100 \mu\text{m}$ , as we can see in fig. 3. b-c.

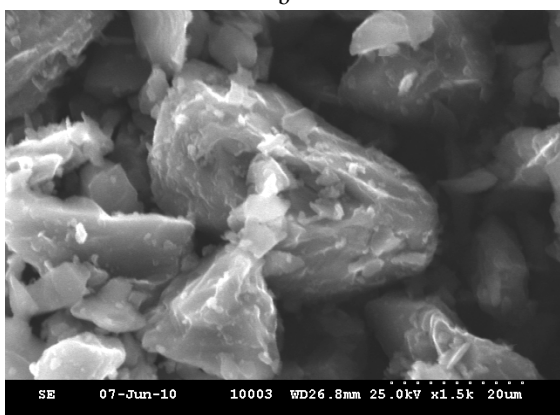
The SEM – EDAX analysis of calcined petroleum cokes confirmed the presence of large particles “chained” together forming agglomerates.



a

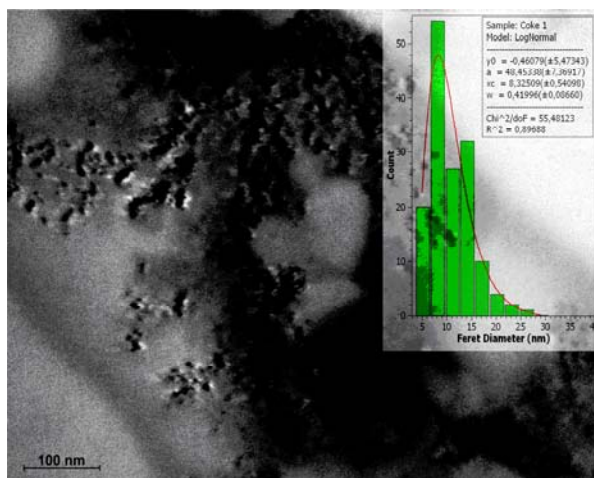


b

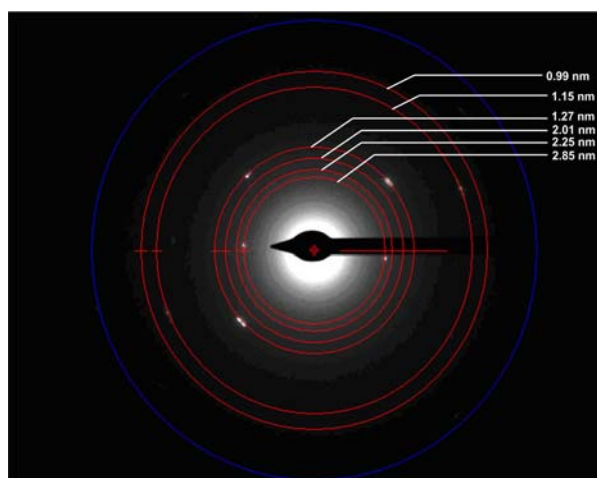


c

Fig. 3. Morphological SEM images of coke samples: a)  $P_1$ ; b)  $P_2$ ; c)  $P_3$ .



a



b

Fig. 4. (a) TEM image of coke sample  $P_1$  and SAED pattern of the same probe (b).

The diffraction rings shown in the SAED pattern from fig.4.b. are corresponding to the interplanar distances of 2.85 nm, 2.25 nm, 2.01 nm, and 1.27 nm, 1.15 nm and 0.99 nm which fits well with the distances reported by Aust and Drickamer [25] or by Shterenberg and Bogdanova [26] for graphite crystalline structure.

In sample  $P_1$  small precipitate are identified by TEM analysis and mean size of those particles, determined from experimental data histogram assumed a lognormal distribution, is about 8.3 nm (see fig. 4.a).

HRTEM image for  $P_1$  sample presented in fig.5 show lattice fringe ascribed to 2.85 nm diffraction plane of graphite.

From sample  $P_2$  only amorphous phase was identified by a cross sectional TEM image (see Fig.6).

A nice structure with well arranged atomic planes oriented in different directions can be seen from HRTEM image for  $P_3$  sample, showed in Fig.7.

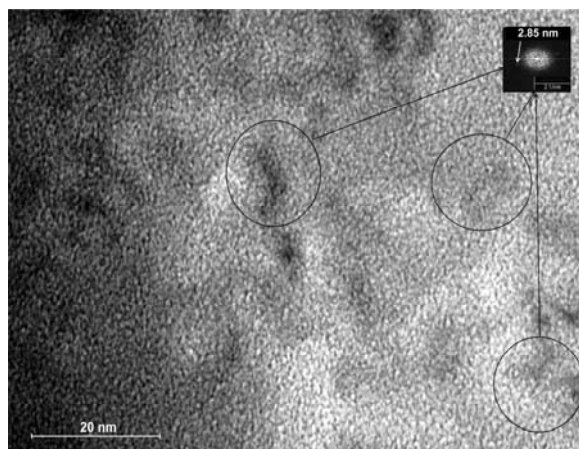


Fig. 5. HRTEM image of sample  $P_1$ .

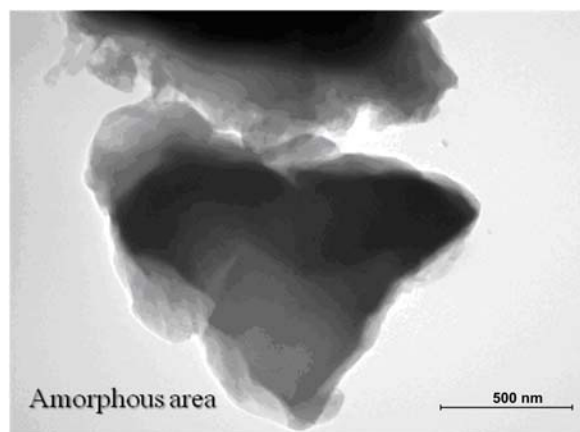


Fig. 6. TEM image of  $P_2$  sample.

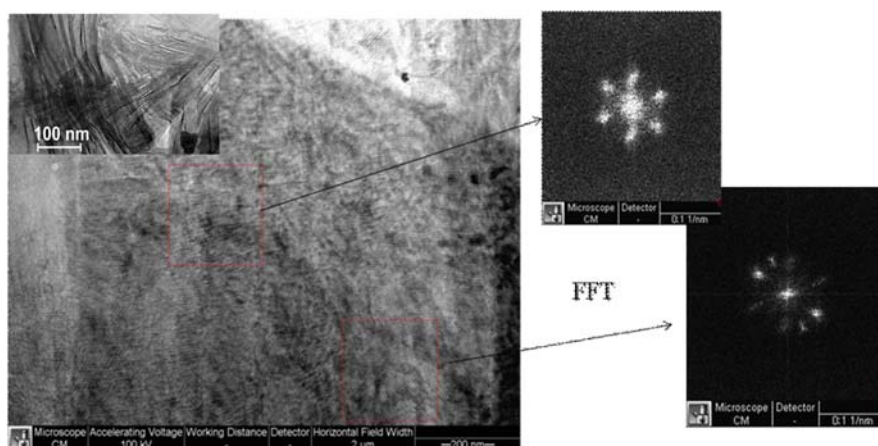


Fig. 7. HRTEM image of  $P_3$  sample, with the identification of silicate structure.

The intercalated amorphous layers generate distortions crystals. For improvement of this HRTEM image, it was applied a blob type filter and recalculated image without noise. The arranged diffraction spots of the Fast Fourier Transform diffractogram (see fig.7), can be associated with silicate ( $\text{SiO}_2$ ) crystalline structure, with intercalated amorphous layers.

## 5. Conclusions

Three calcinated petroleum cokes with different origin were investigated for structural and morphological characterization.

The crystallites diameter, thickness and effective dimension were calculated from XRD data for all the samples investigated.

EDAX patterns indicated the presence of sulfur and silicon in all the calcinated coke samples investigated.

$P_1$  sample, with the lowest sulfur content (showed by WDXRF analysis) present the lowest effective dimension of the crystallites, as we could see from XRD investigations.

Morphological SEM images for  $P_1$  sample presented some crystalline formations (with a few dozen  $\mu\text{m}$  in diameter), irregular dispersed in the matrix.

TEM investigations for the same probe relived the existence of precipitate phase with particles having the diameter of a few nm. Here, the SAED pattern confirmed the existence of graphite-like microstructure, suggested by XRD analysis. A silicate crystalline phase was indicated by HRTEM analysis for  $P_3$  sample.

## References

- [1] A. Radenovic, K. Terzic, *Nafta* **61**(3), 136 (2010).
- [2] X. Sun, J.Y. Hwang, X. Huang, B. Li, *Journal of Minerals & Materials Characterization & Engineering*, **8**(4), 249 (2009)
- [3] B. Jiang, Y. Zhang, J. Zhou, K. Zhang, S. Chen, *Fuel* **87**, 1844 (2008)
- [4] E. J. Anthony, A.P. Iribarne, J.V. Iribarne, *Fuel Processing Technology* **88**, 535 (2007).

- [5] C.A. Bizzi, J. Neri, G. Paniz, L.F. Rodrigues, V. L. Dressler, É. Marlon de Moraes Flores, *Microchemical Journal* **96**, 64 (2010)
- [6] J. Andrews, T. Rantell, D. Jacques, J. C. Hower, J. S. Gardner, M. Amick, *Fuel* **89**, 2640 (2010)
- [7] M. Legin-Kolar, D. Ugarković, *Carbon* **31**(2), 383 (1993)
- [8] L. Yu, K.J. Kim, D.Y. Park, M.S. Kim, K.I. Kim, Y.S. Lim, *Carbon Lett.* **9**(3), 210 (2008)
- [9] S. Yang, I. Kim, M. Jeon, K. Kim, S. Moon, H. Kim, K. An, *J. Ind. Eng. Chem.* **14**, 365 (2008)
- [10] A. Concheso, R. Santamaria, R. Menendez, J.M. Jimenez-Mateos, R. Alcantara, P. Lavela, J.L. Tirado, *Electrochimica Acta* **52**, 1281 (2006)
- [11] S. Gupta, V. Sahajwalla, J. Burgo, P. Chaubal, T. Youmans, *Metallurgical and Materials Transactions B* **36**, 385 (2005).
- [12] E. Stach, M. Mackowsky, M. Tichmüller, G.H. Taylor, D. Chandra, R. Techmüller, *Stach's Textbook of Coal Petrology*, Gebrüder Borntraeger, Berlin, Germany (1982) p.54.
- [13] *Stach's Textbook of Coal Petrology*, Gebrüder Borntraeger, Berlin, Germany (1982), p.54.
- [14] ASTM D 2622-08 Standard Test Method for Sulfur in Petroleum Products by Wavelength Dispersive X-ray Fluorescence Spectrometry, *Annual book of ASTM standards*, (2008).
- [15] G. E. Trotten, S. R. Westbrook, R.J. Shah, "Fuel and Lubricants Handbook, Technology, Properties, Performance and Testing, ASTM International (2003), p.777.
- [16] H.O. Pierson, "Handbook of Carbon, Graphite, Diamond and Fullerenes Properties, Processing and Applications", Noyes Publications USA (1993) p.80.
- [17] A.R. Coutinho, J.D. Rocha, C.A. Luengo, *Fuel Processing Technology* **67**, 93 (2000)
- [18] N. J. Cherepy, R. Krueger, K.J. Fiet, A.F. Jankowski, J.F. Cooper, *Journal of Electrochemical Society* **152** (1) A80 (2005)
- [19] F. G. Emmerich, C.A. Luengo, *Carbon* **31**(2) 333 (1993).
- [20] D. Hays, J. W. Patrick, A. Walker, *Fuel*, **9**(62), 1079 (1983)
- [21] L. Liu, Y. Tan, *Modern Applied Science*, **4**(3), 110 (2010)
- [22] J. V. Iribarne, E. J. Anthony, A. Iribarne, *Proceedings of 17<sup>th</sup> International Conference on Fluidized Bed Combustion (FBC2003)*, (2003) p. 387
- [23] D. Hays, J. W. Patrick, A. Walker, *Polymer, Plastics, Technology Engineering*, **33**(6), 713 (1994)
- [24] J. V. Iribarne, E.J. Anthony, A. Iribarne, *Fuel processing technology*, **82**(1), 27 (2003)
- [25] R. B. Aust, H. G. Drickamer, *Science* **140**, 817 (1963)
- [26] L. Shterenberg, S. Bogdanova, *Inorg. Mater.* **15**, 632 (1979)

---

\*Corresponding author: icarazeanu@univ-ovidius.ro