X Encontro Brasileiro sobre Adsorção
27 a 30 de Abril de 2014
Guarujá - SP

MICROPOROUS ACTIVATED CARBON FIBER FELT PRODUCED FROM BRASILIAN TEXTILE PAN FIBER

J.S. Marcuzzo[1,2]; A. Cuña[3]; N. Tancredi[3]; H.A. Polidoro[1]; S. Otani[1]; C. Otani[1]

1 - Divisão de Materiais Carbonosos - Multivácuo Aeroespacial Ltda
Rua Pedro Rachid, 846 - Santana - CEP 12 211-180 - São José dos Campos - SP
Telephone : (12) 988408446 - Email: jossano@gmail.com
2- Faculdade de Tecnologia do Estado de São Paulo - FATEC - Campus São José dos Campos
Av. Cesare Mansueto Giulio Lattes, S/Nº - CEP: 12247-014 - São José dos Campos - SP
Telephones: (12) 3905-2423, (12) 3905-4979 e (12) 3905-4699 - Email: jossano@gmail.com
3- Cátedra de Fisicoquímica, Laboratorio de Fisicoquímica de Superficies, DETEMA- Facultad de Química - Universidad de la República, General Flores 2124 - CP: 11800 – Montevideo – Uruguay.
Telephone : (598) 29248352 – Fax: (598) 29241906 – Email: acuna@fq.edu.uy, nestor@fq.edu.uy

ABSTRACT: Activated carbon fibers (ACFs) are known as excellent adsorbent materials due to their fast adsorption rate and easy handling characteristic. The ACFs can be manufactured from the poliacrilonitrile fiber, based on a usual carbon fibers (CFs) production process accomplished by an additional activation process. The aim of the present work is to describe the production and characterization results of activated carbon fiber felt (ACFF) produced from textile PAN fiber, using a set of homemade equipment by Multivácuo Aerospacial Ltda and FAPESP PIPE. The 5.0 dtex PAN fiber tow with 200 thousand filaments was oxidized and used as raw material for felt production. The oxidized PAN fiber felt (OPFF) was displaced in a special sample holder, and carbonized (900 °C) and then activated in CO_2 atmosphere at 1000 °C in an electric tubular furnace. All steps of the process were performed as fast as possible, and characterization was done by 77 K N_2 isotherms, adsorption isotherms in liquid fases, SEM and DRX. The results confirmed the production of essentially microporous (pore < 3.2 nm, centered on 1.2 nm), 1,300 m^2/g activated carbon fiber felt.

KEYWORDS: micropores; nanopores; activated carbon fiber; activated felt.

1. INTRUDUTION

Activated Carbons (AC) is one of the most widely used adsorbent materials around the world. Normally, ACs is used for drinking and waste water treatment and in many other applications where the removal of generally dispersed contaminant molecules is desired (Marsh, 2006). ACs also have important applications in energy storage such as electrode material of supercapacitors and Lithium-ion rechargeable Batteries (Inagaki , 2014).

Activated carbon fibers (ACFs) have special characteristics when compared with common activated carbons (granular or powder). It can be transformed into fabric, woven or yarn forms which gives them self-sustainable characteristics. In addition, ACFs show well defined pore structures on their surface which provide a high and fast adsorption capacity for specific components (Solano, 2008; Yoon, 2000). In spite of all advantages of ACFs application, it use has been limited due to it relatively high cost.

One of the most important characteristics, which make ACFs a very special adsorbent material, is their pore size distribution. The architecture and structure of pores on ACF surface are characterized by huge amount of micropores localized directly on the surface, leading to a faster and less energetic adsorption mechanism, especially for gases (Mochida, 2000).

The common methods used to produce ACFs from a carbon fiber (CF) are not far from those used for AC production. The process can be simply described as a thermal treatment oxidant atmosphere at temperatures between 700 and 1000 °C (Solano 2008; Yoon, 2000; Carrot, 2001).

The ACF is highly quoted for adsorbent use, but it is very brittle and does not have enough mechanical resistance to be applied in normally used textile process. Consequently, it is very difficult to transform ACF in textile form. To solve this problem, oxidized textile PAN fiber was produced and then transformed in oxidized PAN fiber felt (OPF). The OPF was carbonized and activated to produce activated carbon fiber felt (ACFF).

Textile PAN fiber, oxidation set up, carbonization furnace and all process and technique needed to make the ACFF, was developed by Multivácuo Aerospacial Ltda by FAPESP PIPE financial support.

2. EXPERIMENTAL

The commercial 200 k tow of 5.0 dtex textile PAN fibers was oxidized in a laboratory scale oven set built by Multivácuo Aeroespacial Ltda/PIPE FAPESP Nº 07/51606-5, aiming an experimental production of flame resistant fibers. About 200 kg of oxidized PAN was produced and transformed in felt (OPFF) with 200g/m^2.

During the carbonization process, the oxidized PAN loses about 50% in mass and linearly shrinks 10%. The shrinkage is an important parameter and must be controlled (Marcuzzo, 2012), and for this purpose, the OPFF sample was cut with about 0.7X0.25m and displaced in a special sample holder that can control the sample shrinkage in two dimensions.

The set of such sample holder with felt was introduced in an electrical furnace (Figure 1). Both ends of the furnace tube were closed by flanges, which allow the insertion and the purge of argon gas to provide an inert atmosphere condition necessary for carbonization.

The carbonization was performed in argon atmosphere at final temperature of 900 °C, applying the maximum heating rate attainable (30 °C/mim). The processing time for maximum temperature was set in 20 min for carbonization. The activation process was preformed immediately after the carbonization by changing the argon to carbon dioxide and rising up the temperature to 1000 °C, which was maintained during 50 min. The activation time was defined by a previous essay where the mechanical evaluation was done, and 50 min activation was fixed to guarantee the minimal mechanical characteristic for handling the activated fiber samples.

After finishing the carbonization and activation process, the gas was shifted again from CO_2 to Ar and the furnace was turned off. This condition of inert atmosphere was maintained until the room temperature was achieved inside reactor.

The sample characterization was performed by N_2 adsorption aiming the measurements of surface area and pores sizes distribution function. The nitrogen isotherm was performed at 77 K by Beckman Coulter SA 3100 equipment. The BET method was applied to determine the total surface area and the pore size distribution was estimated by applying the NLDFT method (Tarazona, 1995) over adsorption isotherm, and the micropore volume was also determined by same method. The burn off was estimated weighing the sample before and after the activation process.

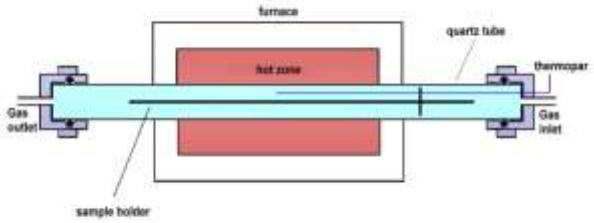

Figure 1. Carbonization and activation set up

The methylene blue and iodine adsorption capacities were also determined in liquid media, due to the fact that these characteristics are normally used as reference in the adsorbate industry. High resolution SEM was used to check surface fiber integrity. The structure of activated carbon fiber was analyzed by X-ray diffraction technique (Rigaku Ultima IV) operated with monochromatic incident CuKα (λ= 1.5418A˚) ray and an automatic data acquisition system.

3. RESULTS AND DISCUTION

3.1. N_2 Isotherm

Figures 2 and 3 show, respectively, the nitrogen gas adsorption isotherm at 77 K and pore size distribution functions.

The isotherm of Figure 2 is typically a type I curve, with no hysteresis, and it shows that the gas saturation occurs at 0.2 P/Po, indicating that this activated material is predominantly populated with

micropores. The pore sizes distribution curve is showed in Figure 3, and it clearly shows that the maximum pore width presented is around 3.2 nm and the predominant pores are sized at around 1.2 nm. This technique does not give information about pores less than 1.0 nm diameter, due to the N_2 penetration limit, but it can be clearly observed in this curve that the distribution in the region for a size width less than 1 nm is ascendant in the direction of origin. This fact infers that the actual micropores volume and surface area of this material may be larger than those calculated by using these isotherms.

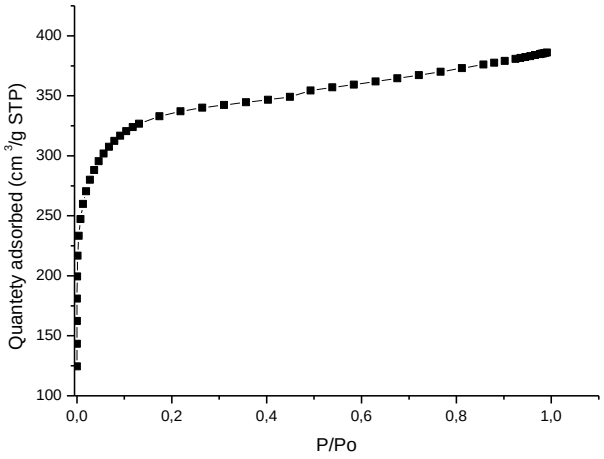

Figure 2. Nitrogen isotherm at 77 K.

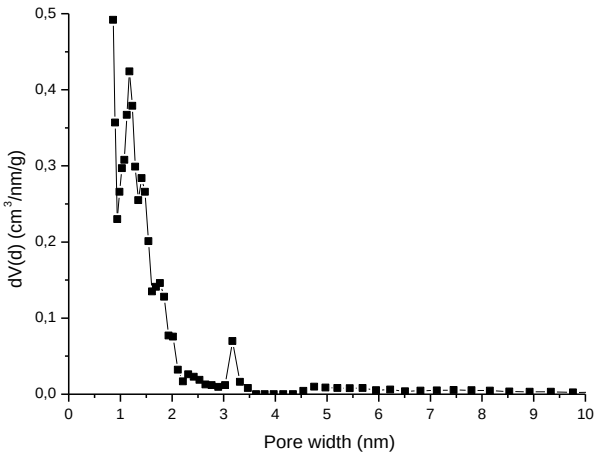

Figure 3. Pore size distribution by NLDFT

Table 1 presents the surface characteristics of activated carbon fiber felt obtained from textile PAN fiber, and the burn off value of activation process.

Table 1. Surface characteristics of ACFF

Sample	Burn off (w %)	S_{BET} (m^2/g)	$V_{micropore}$ (cm^3/g)	V_{Total} (cm^3/g)
ACFF	35	1260	0,53	0,59

3.2. Iodine and methylene blue Isotherm

Iodine and methylene blue adsorption capacity of activated materials are parameters normally used to classify them as water pollutants organic compounds removing materials. Moreover, the adsorption capacity of iodine is associated to the presence of micropores sized between 0,5 and 1,5 nm (Fernandez, 1991), while the methylene blue adsorption capacity is related to small mesopores (Baçaoui, 2001)

For common activated carbon, the typical value of Iodine adsorption is around 1000 mg/g and methylene blue is between 100 and 350 mg/g.

Figure 4 and 5 show, respectively, adsorption isotherms of iodine and methylene blue, and they show that the saturation values for both chemical compounds are about double of typical values presented by activated carbon. These results allow us to infer that the ACFF may be used as adsorbent for organic compounds.

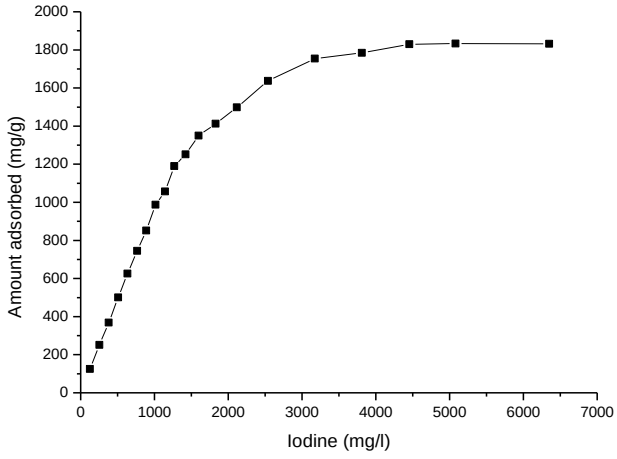

Figure 4. ACFF iodine isotherm

3.2. SEM

The carbonization heating rate used in this work is a rate not usually applied in the production of material essentially containing micropores. The usual activation process parameter of heating described is in the range of 1 to 10 °C/min (Ronaldo, 2007). Against that, it was used the maximum heating rate allowed for the furnace which was 30 °C/min. The choice of such process

parameters has been assigned to the production of macropores, cracks and other surface damages, however the SEM analysis of fiber surface showed the surface integrity of activated samples.

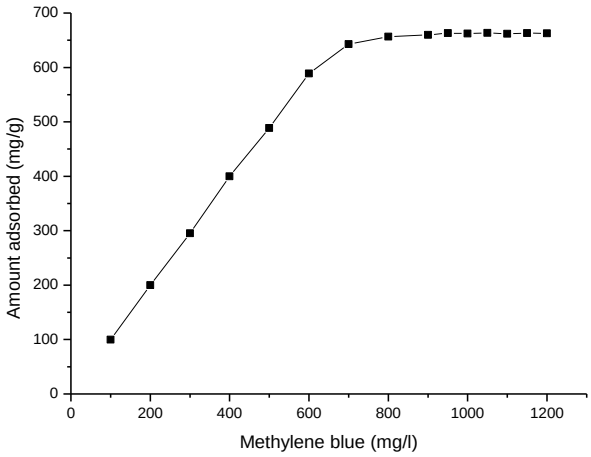

Figure 5. ACFF methylene blue isotherm

Figure 6 shows the felt fibers distribution over view. It shows that the fibers are not broken towards a small length. This is associated to their handle felt mechanical characteristic.

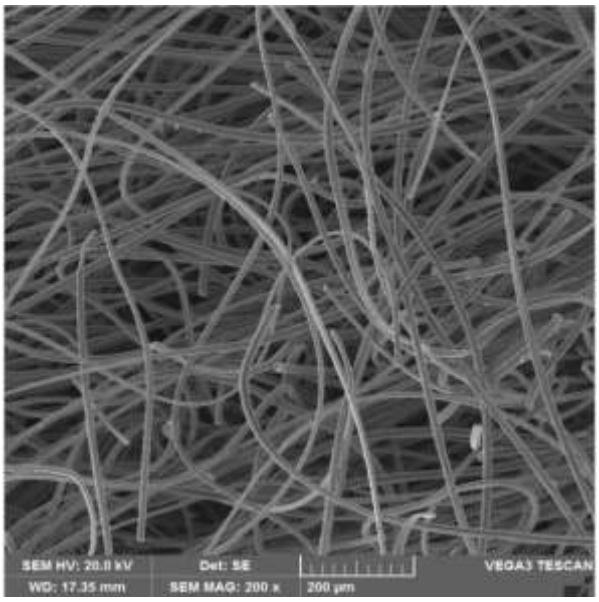

Figure 6. Filament structure ACFF over view.

Figure 7 shows details of the carbon fiber filament. It can be observed that macropores, cracks, collapsed filaments and any other macroscopic surface impairment are absent. In addition it can be said that the surface of activated fibers is clear and smooth.

As the ultimate surface damages analysis, the high resolution SEM image, with 150 k magnification, is also provided and presented in Figure 8. This micrograph shows that the activated carbon fiber surface is exempted of macro-damages, which in turn indicates that the high heating rate doesn`t have any relation with macropores or damages production on the activated carbon fiber surface.

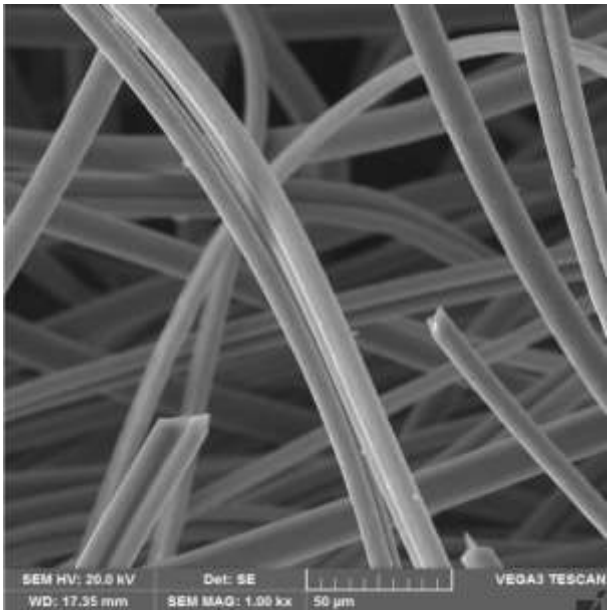

Figure 7. Detail of activated carbon fiber in the **f**ilament structure of activated carbon fiber felt.

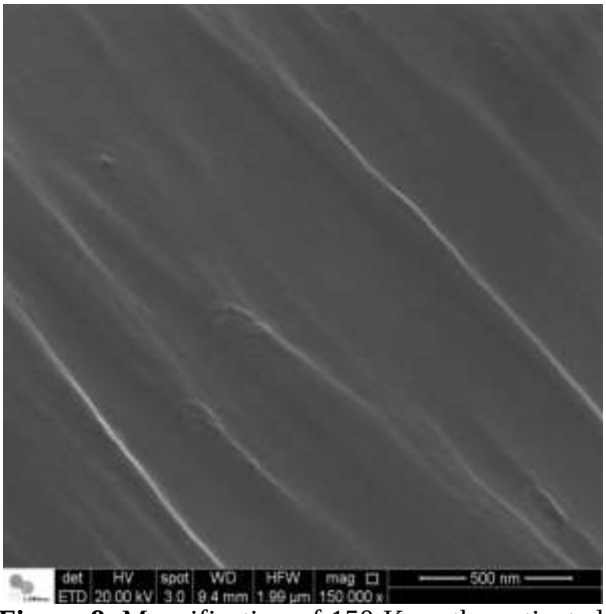

Figure 8. Magnification of 150 K on the activated carbon fiber.

3.3. DRX

The X-ray diffractogram of the activated carbon fiber felt is shown in Figure 9. The amorphous character of this fiber was confirmed. Two broad peaks appear at approximately 2θ = 25º and 44 º. The first peak is associated with *(002)* line, while the second at 2θ = 44 º is *(10)* line. The presence and the shapes of these two bands indicate that the activated carbon fiber (prepared by carbonization at 900 °C) has a more organized aromatic structure with marked sp^2 bonding character than other amorphous ~~-like~~ carbon, reported in the literature. These materials when prepared at lower temperature, such as the one used in this work, presents higher sp^3 bonding character (Cuña, 2013; Celorrio, 2011; Kennedy, 2004; Mochidzuki, 2003).

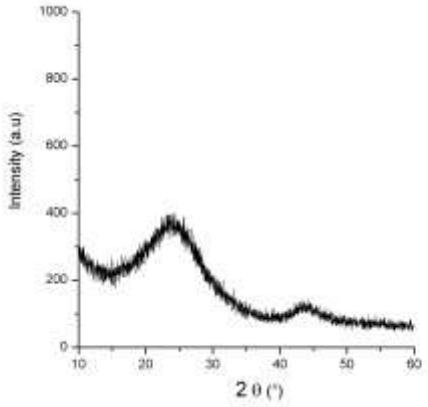

Figure 9. X-ray diffractogram of ACFF.

Based on these results, it is expected that this fiber presents a relatively good electrical conductivity, what is an important characteristic for applications such as in supercapacitor electrode manufacture (Cuña, 2013).

5. CONCLUSION

It was proved that Oxidized PAN fiber felt can be transformed in relatively high surface specific area activated material, with 1,300 m^2/g. Moreover, the heat treatment and the activation treatment parameters can be adjusted in a way that they drastically reduce the time and energy consumption for the manufacturing process.

The surface characterizations showed that the produced activated carbon fiber felt is a material populated essentially by micropores sized at 1.2 nm, and with minor component of 3.2 nm mesopores. The investigation analysis must be performed in near future to better describe the pore structure with size below 1 nm, which was not accessed by nitrogen. XRD analysis shows that the activated carbon fiber has not well ordered two dimensional structure.

6. ACKNOWLEDGMENT

The authors want to acknowledge ITA for the conventional SEM images; the CNPEM/ LNNano for the high resolution SEM images; the Multivácuo Aeroespacial Ltda. for the laboratorial infrastructure and FAPESP Process 12/51087-6 for the financial support.

7. REFERENCES

Baçaoui, A.; Yaacoubi, A.; Dahbi, A.; Bennouna, C.; Phan Tan Luu, R.; Maldonado-Hodar, F.J.; Rivera-Utrilla, J.; Moreno-Castilla, C. Optimization of conditions for the preparation of activated carbons from olive-waste cakes. *Carbon*, v. 39, p. 425-432, 2001.

Carrott, P.J.M.; Nabais, J.M.V.; Ribeiro Carrott, M.M.L.; Pajares, J.A. Preparation of activated carbon fibres from acrylic textile fibres, *Carbon*, v.39, p. 1543-1555, 2001.

Celorrio, V.; Calvillo, L.; Pérez-Rodríguez, S.; Lázaro, M.J.; Moliner, R. Modification of the properties of carbon nanocoils by different treatments in liquid phase. *Micropor. Mesopor. Mat.* v. 142, p. 55-61, 2011.

Cuña, A.; Tancredi, N.; Bussi, J.; Deiana, A.C.; Sardella, M.F.; Barranco, V.; Rojo, J.M. E. grandis as a Biocarbons Precursor for Supercapacitor Electrode Application. *Waste and Biomass Valor*. Online Publisher. DOI 10.1007/s12649-013-9257-4, 2013.

Fernandez-Colinas, J.; Denoyel, R.; Rouquerol, J. Characterization of The Porosity of Activated Charcoals by Adsorption from Solution. *Studies in Surface Science and Catalysis*, v. 62, p. 399-408, 1991.

Inagaki, M.; Kang, F.; Toyoda, M.; Konno, H. *Advanced Materials Science and Engineering of Carbon*: USA , Tsinghua University Press Limited, 2014.

Kennedy, L.J.; Vijaya, J.J.; Sekaran, G. Effect of Two-Stage Process on the Preparation and Characterization of Porous Carbon Composite from Rice Husk by Phosphoric Acid Activation. *Ind. Eng. Chem. Res*. v. 43, p. 1832-1838, 2004.

Mochida, I.; Korai, Y.; Shirahama, M.; Kawano, S.; Hada, T.; Seo, Y.; Yoshikawa, M.; Yasutake, A. Renoval of SOx and NOx over activated carbon fiber. *Carbon,* v. 38, p. 227-239, 2000.

Marcuzzo, J.S.; Otani, C.; Polidoro, H.A.; Otani, S. Influence of Thermal Treatment on Porosity Formation on Carbon Fiber from Textile PAN. *Materials Research*. v. 16, p. 136-144, 2012.

Marsh, H.; Reinoso, F.R. *Activited Carbon*, Elsivier, 2006.

Mochidzuki, K.; Soutric, F.; Tadokoro, K.; Antal Jr, M.J.; Toth, M.; Zelei, B.; Varhegyi, G. Electrical and Physical Properties of Carbonized Charcoals. *Ind. Eng. Chem. Res*. v. 42, p. 5140-5151, 2003.

Ronaldo M.A. Roque-Malherbe, *Adsorption and diffusion in nanomaterials*. USA: Taylor and Francis Group, 2007

Solano, A.L.; Amorós, D.C. in*: Adsorption on activated carbon fiber: Adsorption by carbon.* Elsevier, 2008.

Tarazona, P. Solid-fluid transition and interfaces with density functional approaches. *Surface Science,* v. 94, p. 331-333, 1995.

Yoon, S. H.; Koray, Y.; Mochida, I. in: *Carbon fibers and activated carbon fibers: Sciences of carbon materials.* Spain: University of Alicante, 2000.