ADVANTAGEOUS USE OF CARBON NANOFIBERS IN FUEL CELLS AS CATALYST SUPPORT

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1. Introduction

Fuel cells present unique and favourable advantages over conventional energy converting devices. However, some aspects regarding cost and durability have to be addressed before their widespread commercialization. Great efforts are being carried out to achieve a higher Pt-specific power density, mainly: the reduction of the platinum loading while maintaining high power densities; and the reduction of mass-transport induced voltage losses at high current densities [1]. In this sense, nanotechnology can provide new materials with a great potential to improve currently used electrocatalysts. Carbon nanofibers have attracted interest because of their unique structural, electrical and textural properties, which are expected to offer a great potential in their application as catalyst supports [2]. In this work, carbon nanofibers with different properties have been obtained by methane catalytic decomposition and have been functionalized with acid aqueous solutions under conditions of different severity.

2. Experimental

A co-precipitation method has been used to obtain a $Ni:Cu:Al_2O_3$ catalyst. Then, a methane flow passes through the catalyst in a fixed bed reactor and decomposes into hydrogen and carbon nanofibers. Reaction conditions such as temperature or gas composition have been varied to study the influence on the carbonaceous material properties. Carbon characterization has been carried out by scanning electron microscopy (SEM), nitrogen physisorption and X-Ray diffraction (XRD). The electrical conductivity has been determined by a two-probe method applying pressure over the powder. Functionalization of carbon nanofibers has been carried out by treatment with nitric acid or a mixture of nitric and sulphuric acid at room or boiling temperature, according to the best results obtained previously [3]. The amount and nature of oxygen surface groups have been determined by temperature programmed desorption (TPD), analyzing CO and CO_2 desorbed by gas chromatography.

3. Results

One of the advantages that carbon nanofibers present as catalyst support for fuel cells is their negligible content in micropores in contrast with commonly used carbon blacks (Vulcan XC-72R). This is due to the morphology of carbon particles, formed by entangled nanofilaments constituted in turn by carbon layers disposed at a determined angle with respect to the growth axis. A SEM micrograph can be observed in Figure 1 as an example. Table 1 shows surface area and pore volume values, determined from nitrogen physisorption isotherms, for Vulcan XC-72R and three selected CNFs obtained at 750ºC (CNF-HT), 600ºC (CNF-MT) and 550ºC (CNF-LT). As can be observed from the table, the highest values of mesoporous surface area (166.4 m^2/g) and pore volume (0.712 cm^3/g) correspond with CNFs obtained at low temperature (CNF-LT), with a negligible quantity of micropores. However, the highest values of electrical conductivity were observed at CNFs obtained at higher temperatures, showing even higher conductivity than Vulcan XC-72R (sample CNF-HT) as can be observed in Figure 2. This corresponds with a high graphitization degree confirmed by XRD analyses (not shown).

Oxygen surface groups are created by oxidizing treatment. These functional groups decompose into CO_2 and CO at temperatures from 200ºC to 1000ºC, depending mainly on

their nature. Figures 3 and 4 show the profiles obtained in TPD experiments for three oxidation conditions: a mixture of nitric and sulphuric acids (1:1 v/v) at boiling temperature (F-NS110), nitric acid at boiling temperature (F-N110) and again a mixture of nitric and sulphuric acids (1:1 v/v) at room temperature (F-NS025). On one hand, boiling temperature favors the creation of carboxylic and phenol groups, by the comparison of the peak at 300ºC in CO_2 profile and the shoulder at 600ºC in CO profile, respectively, in samples F-NS025 and F-NS110. On the other hand, the use of sulphuric acid increases the amount of groups created, by comparison of F-N110 and F-NS110.

Acknowledgments

References:
[1] H.A. Gasteiger, S.S. Kocha, B. Sompalli, F.T. Wagner, Applied Catalysis B: Environmental, **56** (2005) 9-35.
[2] K. Lee, J. Zhang, H. Wang, D.P. Wilkinson, Journal of Applied Electrochemistry, **36** (2006) 507-522.
[3] L. Calvillo, M. Gangeri, S. Perathoner, G. Centi, R. Moliner, M.J. Lázaro, Journal of Power Sources, (2008), doi:10.1016/j.jpowsour.2009.01.005.

Tables:

Sample		Vulcan XC-72R	CNF-HT	CNF-MT	CNF-LT
Surface area	Mesoporous	153.2	93.3	130.2	166.4
$(m^2 g^{-1})$	Microporous	65.2	5.8	12.6	18.5
Pore volume	Mesoporous	0.370	0.214	0.568	0.712
$(cm^3 g^{-1})$	Microporous	0.040	0.003	0.007	0.010

Table 1. Textural properties determined from nitrogen physisorption isotherms.
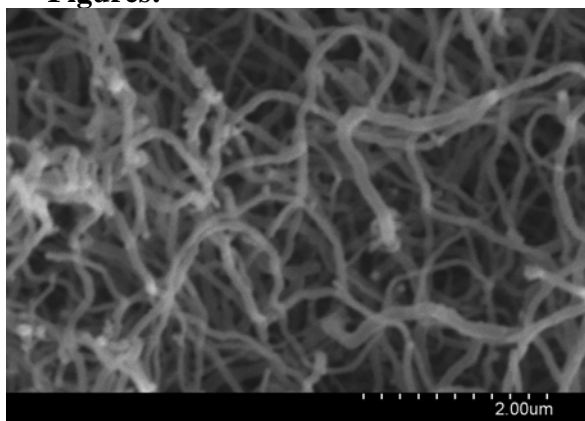
Figures:
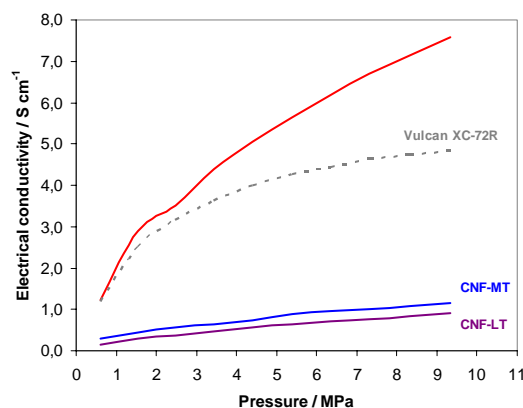

Figure 1. SEM micrograph of carbon nanofibers.

Figure 2. Electrical conductivity of CNFs and Vulcan XC-72R

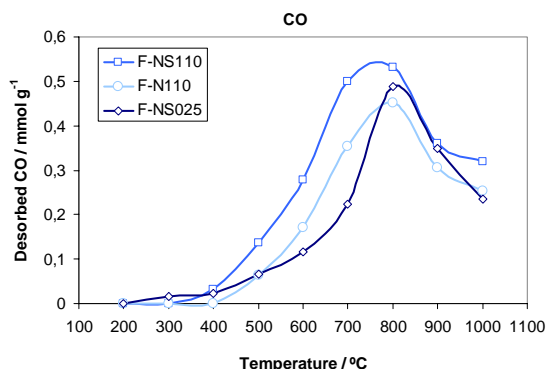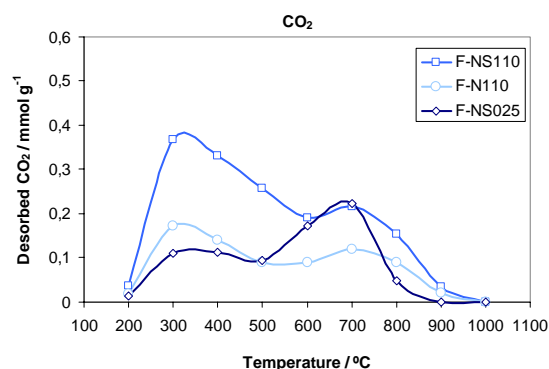Figure 3. CO_2 desorbed in TPD experiments for CNF-MT

Figure 4. CO desorbed in TPD experiments for CNF-MT