



Short communication

## Poly(ethylene terephthalate)-based carbons as electrode material in supercapacitors

M. Domingo-García<sup>a</sup>, J.A. Fernández<sup>b</sup>, M.C. Almazán-Almazán<sup>a</sup>, F.J. López-Garzón<sup>a</sup>,  
F. Stoeckli<sup>c</sup>, T.A. Centeno<sup>b,\*</sup>

<sup>a</sup> Dpto de Química Inorgánica, Facultad de Ciencias, 18071 Granada, Spain

<sup>b</sup> Instituto Nacional del Carbón-CSIC, Apartado 73, 33080 Oviedo, Spain

<sup>c</sup> Physics Department, University of Neuchâtel, Rue Emile Argand 11, CH-2009 Neuchâtel, Switzerland

### ARTICLE INFO

#### Article history:

Received 4 May 2009

Received in revised form

11 December 2009

Accepted 20 December 2009

Available online 13 January 2010

#### Keywords:

Supercapacitor

Double layer

Activated carbon

PET

### ABSTRACT

A systematic study by complementary techniques shows that PET-waste from plastic vessels is a competitive precursor of carbon electrodes for supercapacitors. PET derived-activated carbons follow the general trends observed for highly porous carbons and display specific capacitances at low current density as high as  $197 \text{ F g}^{-1}$  in  $2 \text{ M H}_2\text{SO}_4$  aqueous electrolyte and  $98 \text{ F g}^{-1}$  in the aprotic medium  $1 \text{ M (C}_2\text{H}_5)_4\text{NBF}_4/\text{acetonitrile}$ . Additionally, high performance has also been achieved at high current densities, which confirms the potential of this type of materials for electrical energy storage.

A new method based on the basic solvolysis of PET-waste and the subsequent carbonization seems to be an interesting alternative to obtain porous carbons with enhanced properties for supercapacitors.

© 2010 Elsevier B.V. All rights reserved.

## 1. Introduction

The increasing demand for electrical systems that provide high power in short-term pulses, has focused the efforts to the development of supercapacitors (SCs) based on porous carbons [1–3]. Recent studies have emphasized the advantages of microporous carbons as far as those with pores below 1 nm achieve higher specific capacitances (in  $\text{F m}^{-2}$ ) than materials with wider porosity [3–6]. This capacitance increase has been explained by the distortion of the ion solvation shell, leading to a closer approach of the ions to the carbon surface. Moreover, microporous carbons are more competitive than mesoporous materials in terms of volumetric capacitance (in  $\text{F cm}^{-3}$ ) [4,7].

Another priority for the large-scale implementation of SC systems is actually focused on the development of low-cost carbons [8]. In this context, the utilization of residues as precursors of carbons with a high surface area and a porosity centered in the micropores range is an interesting strategy. The current plastic vessels consumption rate generates a huge amount of poly(ethylene terephthalate) (PET) waste. This solid presents a low bio- and photodegradability which leads to an environmental concern. Previous studies have suggested the production of activated carbons with

suitable features to be used as adsorbents for processing PET-waste [9–12].

This work presents the potentiality of PET as a low-cost precursor of microporous carbons with promising properties for electrodes in both aqueous ( $\text{H}_2\text{SO}_4$ ) and organic (tetraethyl ammonium tetrafluoroborate in acetonitrile) supercapacitors.

## 2. Experimental

The present study is based on eight activated carbons derived from PET as raw material. Their synthesis has been reported elsewhere [10,11]. Basically, it was performed by two procedures. The first one is that frequently used, which consists of the carbonization of PET at  $950^\circ\text{C}$  and the further activation of the char with  $\text{CO}_2$  at the same temperature for 4 and 8 h (A-series in Table 1). The preparation of sample AN900-4 includes the treatment of the char with concentrated  $\text{HNO}_3$  for 4 h and the pyrolysis and the activation of the product at  $900^\circ\text{C}$ . The second procedure consists of the basic solvolysis of the precursor with KOH in ethylene glycol (sample GK650-8) or in water (HK-series). The numbers 650 and 800 in the names of these samples refer to the temperature of pyrolysis ( $650\text{--}950^\circ\text{C}$ ), whereas the last number is the soaking time (1–8 h).

The resulting PET-based carbons are of high purity, with ash content below 0.01% for A- and AN-series and between 0.3 and 0.8% for the GK- and HK-series.

\* Corresponding author. Tel.: +34 985119090; fax: +34 985297662.

E-mail address: [teresa@incar.csic.es](mailto:teresa@incar.csic.es) (T.A. Centeno).

**Table 1**  
Preparation conditions and textural properties of PET derived-activated carbons.

Carbon	Burn-off (%)	$W_0$ (cm <sup>3</sup> g <sup>-1</sup> )	$L_0$ (nm)	$S_{mi}$ (m <sup>2</sup> g <sup>-1</sup> )	$S_e$ (m <sup>2</sup> g <sup>-1</sup> )	$S_{total} = S_{mi} + S_e$ (m <sup>2</sup> g <sup>-1</sup> )	$S_{comp}$ (m <sup>2</sup> g <sup>-1</sup> )	$S_{av}$ (m <sup>2</sup> g <sup>-1</sup> )
A950-4	87	0.41	0.84	976	6	982	977	980
A950-8	93	0.46	1.16	793	12	805	739	772
AN900-4	94	0.53	1.14	930	6	936	1063	1000
GK650-8	93	0.32	0.91	703	104	836	885	861
HK650-8	78	0.30	0.66	909	65	974	948	961
HK800-1	80	0.41	0.90	911	85	996	1022	1009
HK800-4	83	0.42	1.03	815	93	908	888	898
HK800-8	84	0.53	1.23	862	91	953	924	939
SC-10	–	0.65	1.31	992	21	1013	990	1001
Super DLC-30	–	0.60	1.24	968	11	979	965	972

The porous structure of the carbons was analysed by N<sub>2</sub> adsorption at –195 °C (*Micromeritics ASAP 2010*). The microporosity characterization was based on Dubinin's theory which leads to reliable values of the micropore volume  $W_0$ , the average micropore width  $L_0$  and the microporous surface area  $S_{mi}$ . Additionally, the analysis of the adsorption isotherm by a classical comparison plot based on the reference N<sub>2</sub> adsorption for a non-porous carbon (*Vulcan 3G*) provided information on the external (non-microporous) area  $S_e$  and the total surface area  $S_{total}$  of the carbons [7,13,14]. The N<sub>2</sub>-based specific surface area of the carbons has been estimated from the average of  $S_{total} = S_{mi} + S_e$  and  $S_{comp}$ , i.e.  $S_{av} = (S_{total} + S_{comp})/2$ . The corresponding values are given in Table 1. For comparison purposes, the table also includes two typical carbons of standard quality, used industrially.

The electrochemical performance of carbons was analyzed in two-electrode capacitors by galvanostatic charge–discharge voltage cycles at current densities in the range 1–100 mA cm<sup>-2</sup> and cyclic voltammetry experiments at scan rates between 2 and 50 mV s<sup>-1</sup> (potentiostat–galvanostat *Autolab-Ecochimie PGSTAT 30*). The electrodes (8 mm in diameter) were made of a mixture of carbon (70 wt.%), polyvinylidene fluoride (25 wt.%) binder and carbon black (Super P, 5 wt.%). They were separated by glassy fibrous paper and placed inside a Swagelok-cell. The electrolytes were aqueous solution 2 M H<sub>2</sub>SO<sub>4</sub> and 1 M tetraethyl ammonium tetrafluoroborate in acetonitrile, (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NBF<sub>4</sub>/AN. The cell voltage ranged from 0 to 0.8 V for aqueous medium and between 0 and 2 V for the aprotic electrolyte.

The accuracy in the Ragone plots obtained with our laboratory-scale device has been estimated to be around ±8%.

### 3. Results and discussion

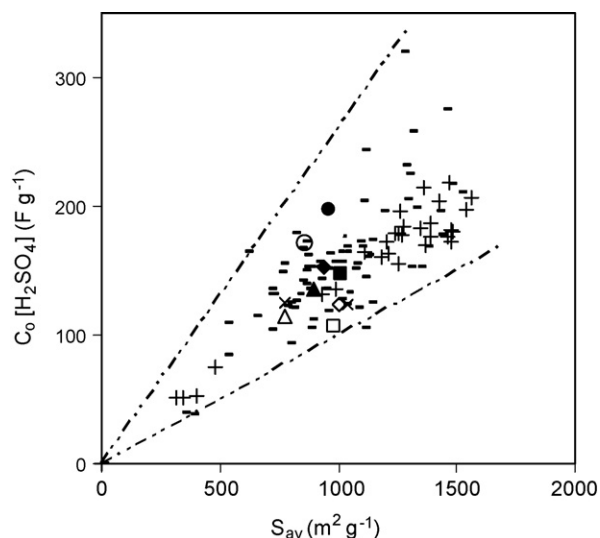
Table 1 shows that the activation of PET-waste by different methods leads to carbons with total specific surface areas between 772 and 1000 m<sup>2</sup> g<sup>-1</sup>, which fit the values for typical activated carbons [13]. It appears that the porosity of the PET-carbons consists mainly of micropores (width <2 nm) with volumes  $W_0$  in the range 0.30–0.53 cm<sup>3</sup> g<sup>-1</sup> and average micropore widths  $L_0$  between 0.66 and 1.23 nm. The surface of mesopores accounts for less than 12% of the overall surface area.

Regarding the electrochemical performance, the comparison with data for a large variety of carbons determined under similar experimental conditions indicates that PET-activated carbons follow the general trends observed in the specific capacitance of materials derived from different precursors and manufacture conditions in aqueous (H<sub>2</sub>SO<sub>4</sub>) and aprotic ((C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NBF<sub>4</sub>/acetonitrile) electrolytes [7,13–16].

As illustrated by Fig. 1, PET derived-carbons are capable of high limiting gravimetric capacitances (expressed per carbon mass of one electrode at 1 mA cm<sup>-2</sup>),  $C_0$  [H<sub>2</sub>SO<sub>4</sub>], which range between 106 and 197 F g<sup>-1</sup> in the acidic electrolyte. As pointed out earlier [1,13], these values depend on the specific surface extension of carbons (purely double layer capacitance) and on the certain oxygen surface functionalities which contribute in the form of quick redox reactions (pseudo-capacitance). In the present case, carbons GK650-8 and HK650-8 with oxygen contents of respectively 25.3 and 18.4%, achieve surface-related capacitances around 0.20 F m<sup>-2</sup>, which are close to the upper bounds found for highly activated carbons [7,13].

As an example, the cyclic voltammograms displayed in Fig. 2 evidence redox peaks connected with pseudofaradaic reactions for carbon HK800-1 (8.3% oxygen) in the aqueous electrolyte. On the other hand, the clear rectangular shaped-voltammograms in (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NBF<sub>4</sub>/acetonitrile suggest that Faradaic-type processes involving surface species are less significant in the aprotic medium.

Since the contribution in the non-aqueous electrolyte does practically not depend on the carbon surface chemistry [15],

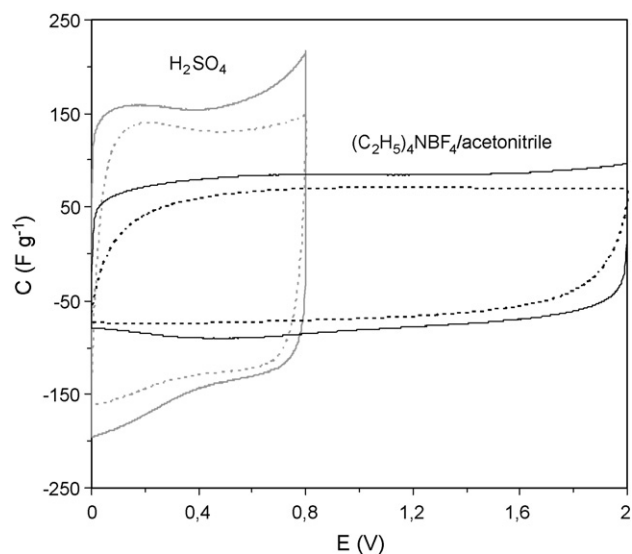


**Fig. 1.** Variation of the specific capacitance at 1 mA cm<sup>-2</sup> in H<sub>2</sub>SO<sub>4</sub> with the total surface area of carbons of Table 1 (A950-4 (□), A950-8 (△), AN900-4 (◇), GK650-8 (○), HK650-8 (●), HK800-1 (■), HK800-4 (▲) and HK800-8 (◆) and other microporous (-) and mesoporous carbons (+) [8–13].

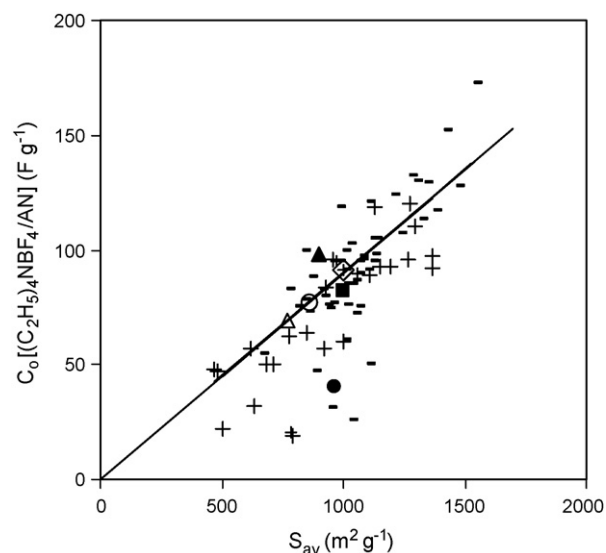
the PET-based carbons deliver significantly lower limiting capacitances. At 1 mA cm<sup>-2</sup>,  $C_0$  [(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NBF<sub>4</sub>/AN] ranges from 69 to 98 F g<sup>-1</sup> (Fig. 3) and it compares favourably with standard activated carbons [1,15,16]. The only exception is carbon HK650-8 which has an average micropore size of 0.66 nm and a capacitance of 40 F g<sup>-1</sup>. This drop reflects the presence of a significant fraction of pores below 0.7 nm, inaccessible to the aprotic cation (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N<sup>+</sup> (0.68 nm) [16]. As a consequence, by comparison with HK800-1 (1009 m<sup>2</sup> g<sup>-1</sup>) only 50% of the specific capacitance expected from the total surface area of HK650-8 (961 m<sup>2</sup> g<sup>-1</sup>) is observed.

As a first approximation, dynamic aspects of the performance of SC based on PET-carbons were provided by cyclic voltammetry. The preservation of the rectangular shape of cyclic voltammograms, with steep current change at the switching potentials, over a wide range of scan rates reveals quick charge propagation in the corresponding electrodes (Fig. 2).

Ragone-type plots relating power density to achievable energy density of capacitors allowed further evaluation to confirm the rel-



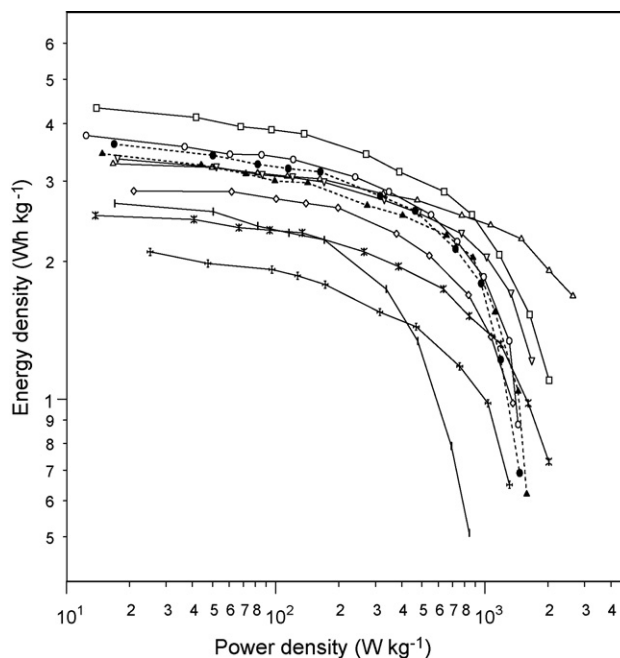
**Fig. 2.** Voltammograms of supercapacitor based on HK800-1 at 2 mV s<sup>-1</sup> (—) and 50 mV s<sup>-1</sup> (---) in aqueous 2 M H<sub>2</sub>SO<sub>4</sub> and 1 M (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NBF<sub>4</sub>/acetonitrile.



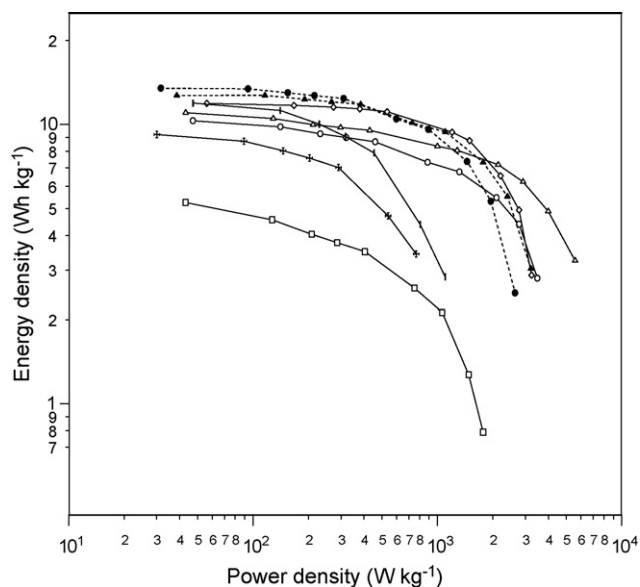
**Fig. 3.** Variation of the specific capacitance at 1 mA cm<sup>-2</sup> in (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NBF<sub>4</sub>/AN with the total surface area of carbons of Table 1 (A950-8 (△), AN900-4 (◇), GK650-8 (○), HK650-8 (●), HK800-1 (■) and HK800-4 (▲) and other microporous (-) and mesoporous carbons (+) [8–13]. The line through the origin corresponds to the linear best fit for activated carbons with average micropore size above 0.8 nm.

evant potential of PET-based carbons in aqueous and organic media.

Fig. 4 shows the excellent performance in H<sub>2</sub>SO<sub>4</sub> of carbons of GK- and HK-series prepared by basic solvolysis of PET-wastes and subsequent carbonization of the products. With these samples, one achieves energy densities around 3–4 Wh kg<sup>-1</sup> at low current loads (20 W kg<sup>-1</sup>). Furthermore, their capacitive behaviour at high current density even appears to be somewhat better than that observed for activated carbons SC-10 (©ARKEMA-CECA) and Super DLC-30 (©NORIT) commercialized for supercapacitor devices. For instance, HK800-1 delivers 2635 W kg<sup>-1</sup> at 1.7 Wh kg<sup>-1</sup>, against 1119 W kg<sup>-1</sup> at 1.5 Wh kg<sup>-1</sup> for Super DLC-30.



**Fig. 4.** Energy density vs. power density for PET-based carbons in 2 M H<sub>2</sub>SO<sub>4</sub> aqueous solution: GK650-8 (○), HK650-8 (□), HK800-1 (△), HK800-4 (◇), HK800-8 (▼), A950-4 (+), A950-8 (\*) and AN900-4 (∩). Commercial activated carbons SC-10 (●) and Super DLC-30 (▲) are included for comparison.



**Fig. 5.** Energy density vs. Power density for PET-based carbons in 1M  $(\text{C}_2\text{H}_5)_4\text{NBF}_4/\text{CH}_3\text{CN}$ : GK650-8 ( $\circ$ ), HK650-8 ( $\square$ ), HK800-1 ( $\triangle$ ), HK800-4 ( $\diamond$ ), A950-8 (+) and AN900-4 ( $\nabla$ ). Commercial activated carbons SC-10 ( $\bullet$ ) and Super DLC-30 ( $\blacktriangle$ ) are included for comparison.

Fig. 5 illustrates the promising performance of these carbons in  $(\text{C}_2\text{H}_5)_4\text{NBF}_4/\text{AN}$  supercapacitors, with the exception of carbon HK650-8. Due to the presence of a significant porosity below 0.7 nm (Table 1), the corresponding surface area is not accessible to the  $(\text{C}_2\text{H}_5)_4\text{N}^+$  ion (0.68 nm) and the power storage is reduced.

The Ragone plots indicate that carbons with similar porosities do not necessarily display the same electrochemical behaviour. This suggests that, although textural parameters play a key role, other factors must be also considered to further maximize the performance of carbon-based supercapacitors.

Figs. 4 and 5 reveal a similar trend in both electrolytes, the bad performers being mostly the carbons obtained by the more classical method for the manufacture of activated carbons (carbonization of the precursor followed by activation with  $\text{CO}_2$ ). It seems that the new procedure based on the basic solvolysis and the subsequent carbonization is potentially more advantageous to obtain highly porous carbons with enhanced performance in supercapacitors.

#### 4. Conclusions

The present study shows that PET is a competitive precursor of electrode materials for supercapacitors. In this perspective, the use

of PET-wastes to obtain low-cost high-performance carbons is an interesting approach dealing simultaneously with the problems of energy storage and recycling.

PET derived-activated carbons follow the general trends for highly porous carbons and display specific capacitances at low current density between 106 and 197  $\text{F g}^{-1}$  in 2M  $\text{H}_2\text{SO}_4$  and from 69 to 98  $\text{F g}^{-1}$  in 1M  $(\text{C}_2\text{H}_5)_4\text{NBF}_4/\text{acetonitrile}$ . Furthermore, their capacitive behaviour at high current density even appears to be somewhat better than that observed for activated carbons commercialized for supercapacitors.

By comparison with the standard activation protocols, this novel method, based on the basic solvolysis of PET-wastes and the subsequent carbonization, seems to be an interesting alternative pathway to obtain porous carbons with enhanced properties for supercapacitors.

#### Acknowledgements

The support of the Autonomous Regional Government (J. de Andalucía, P. de Excelencia P06-FQM-01585) is acknowledged.

#### References

- [1] A.G. Pandolfo, A.F. Hollenkamp, *J. Power Sources* 157 (2006) 11–27.
- [2] P. Simon, A.F. Burke, *Electrochim. Soc. Interface* 17 (2008) 38–43.
- [3] P. Simon, Y. Gogotsi, *Nat. Mater.* 7 (2008) 845–854.
- [4] J. Chmiola, G. Yushin, Y. Gogotsi, C. Portet, P. Simon, P.L. Taberna, *Science* 313 (2006) 1760–1763.
- [5] J. Chmiola, C. Largeot, P.L. Taberna, P. Simon, Y. Gogotsi, *Angew. Chem. Int. Ed.* 47 (2008) 3392–3395.
- [6] C. Largeot, C. Portet, J. Chmiola, P.L. Taberna, Y. Gogotsi, P. Simon, *J. Am. Chem. Soc.* 130 (2008) 2730–2731.
- [7] J.A. Fernández, M. Arulepp, J. Leis, F. Stoeckli, T.A. Centeno, *Electrochim. Acta* 53 (2008) 7111–7116.
- [8] A. Burke, *Electrochim. Acta* 53 (2007) 1083–1091.
- [9] K. Nakagawa, S.R. Mukai, T. Suzuki, H. Tamon, *Carbon* 41 (2003) 823–831.
- [10] I. Fernández-Morales, M.C. Almazán-Almazán, M. Pérez-Mendoza, M. Domingo-García, F.J. López-Garzón, *Micropor. Mesopor. Mater.* 80 (2005) 107–115.
- [11] M.C. Almazán-Almazán, M. Pérez-Mendoza, F.J. López-Domingo, I. Fernández-Morales, M. Domingo-García, F.J. López-Garzón, *Micropor. Mesopor. Mater.* 106 (2007) 219–228.
- [12] J.B. Parra, C.O. Ania, A. Arenillas, F. Rubiera, J.M. Palacios, J.J. Pis, *J. Alloys Compd.* 379 (2004) 280–289.
- [13] T.A. Centeno, F. Stoeckli, *Electrochim. Acta* 52 (2006) 560–566.
- [14] J.A. Fernández, T. Morishita, M. Toyoda, M. Inagaki, F. Stoeckli, T.A. Centeno, *J. Power Sources* 175 (2008) 675–679.
- [15] T.A. Centeno, M. Hahn, J.A. Fernández, R. Kötz, F. Stoeckli, *Electrochem. Commun.* 9 (2007) 1242–1246.
- [16] T.A. Centeno, J.A. Fernandez, F. Stoeckli, *Carbon* 46 (2008) 1025–1030.