Tailoring the Surface Chemistry of Zeolite Templated Carbon by Electrochemical Methods

R. Berenguer[1,*], E. Morallón[2], D. Cazorla-Amorós[2], H. Nishihara[3], H. Itoi[3], T. Ishii[3], T. Kyotani[3]

[1]*Department of Chemical Engineering, School of Industrial Engineering, University of Malaga, Campus de Teatinos s/n, 29071 Malaga, Spain.*

[2]*Instituto Universitario de Materiales de Alicante. Universidad de Alicante. Apdo. 99. E-03080 Alicante, Spain.*

[3]*Institute of Multidisciplinary Research for Advanced Materials. Tohoku University, Sendai 980-8577, Japan.*

Abstract

One option to optimize carbon materials for supercapacitor applications is the generation of surface functional groups that contribute to the pseudocapacitance without losing the designed physical properties. This requires suitable functionalization techniques able to selectively introduce a given amount of electroactive oxygen groups. In this work, the influence of the chemical and electrochemical oxidation methods, on the chemical and physical properties of a zeolite templated carbon (ZTC), as a model carbon material, have been studied and compared. Although both oxidation methods generally produce a loss of the original ZTC physical properties with increasing amount of oxidation, the electrochemical method shows much better controllability and, unlike chemical treatments, enables the generation of a large number of oxygen groups (O = 11000- 3300 µmol/g), with a higher proportion of active functionalities, while retaining a high surface area (ranging between 1900-3500 m^2/g), a high microporosity and an ordered 3-D structure.

Resumen

Una posibilidad para optimizar los materiales carbonosos para su aplicación en supercondensadores es la generación de grupos funcionales que contribuyan a la pseudocapacidad sin perder las propiedades físicas iniciales. Esto requiere de técnicas de funcionalización adecuadas, capaces de introducir selectivamente una determinada cantidad de grupos oxigenados electroactivos. En este trabajo, se han estudiado y comparado los efectos de los métodos de oxidación química y electroquímica en las propiedades químicas y físicas de un material carbonoso preparado mediante el uso de una zeolita Y como plantilla (en inglés, zeolite templated carbon (ZTC)). Aunque de forma general ambos métodos dañan las propiedades originales del ZTC, el método electroquímico muestra un mayor control que, a diferencia de los tratamientos químicos, permite la generación de una gran cantidad de grupos oxigenados (O = 11000- 3300 µmol/g), con una mayor proporción de grupos activos, manteniendo al mismo tiempo una elevada área superficial (entre 1900-3500 m^2/g), una elevada microporosidad y una estructura 3-D ordenada.

1. Introduction

Supercapacitors are already a sufficiently developed technology, with growing range of applications, that in a few more years will become a mainstream technology alongside batteries [1,2]. However, in order to compete with or assist batteries in some applications, the energy density of supercapacitors needs to be increased. In principle, this can be done by widening the stability potential window of the electrolyte and/or the electrode material, or by increasing the capacitance of this last one. One of the most promising approaches to reach high capacitances is to combine high-surface area carbon materials, the so called electrochemical double-layer (DL) capacitors, with highly-dispersed electroactive materials, like metal oxides and/or conductive polymers, which can exhibit a large pseudocapacitance contribution [1-3]. Another alternative is to increase the pseudocapacitance contribution of carbon materials by increasing the amount of oxygen functional groups.

Regarding this approach, the design of the carbon material as well as the employment of a suitable technique for their functionalization are considered of utmost importance to achieve an optimum supercapacitor performance. First, the combination of an accessible high surface area with both a tailored and ordered pore network may result in a high double-layer capacitance contribution and an excellent rate performance, respectively [1,2]. Second, among the different surface groups, the phenol, carbonyl/quinone and/or anhydride oxygen-based functionalities have been found to actively participate in pseudocapacitive reactions [1,2,4]. Consequently, the modification technique may play a key role, since it is required to show a high efficiency and selectivity to introduce homogeneously the maximum amount of active groups, but at the same time, it must minimize any possible damage of the designed structural properties.

Considering the unique structure of zeolite template carbon (ZTC) [5-7] for fundamental research (as a model material) (Fig. 1a) and/or for potential application as electrode for electrochemical capacitors [8,9], in this work the chemical and electrochemical [10,11] oxidations of ZTC have been studied in order to compare their suitability and advantages for the control of chemical and physical properties of carbon materials that remarkably influence their capacitance performance.

2. ZTC oxidation experiments

ZTC was prepared using zeolite Y as a hard template by the method reported elsewhere [5,7]. A squared-molded ZTC paste (0.1 g and 3 cm^2 geometric area) was prepared, without binder, by vacuum filtration of an aqueous ZTC suspension through a 0.5 µm pore-size hydrophilic membrane filter. Next, the ZTC paste on the membrane filter was pressed against a Ti/RuO$_2$ mesh anode and then sandwiched with another membrane filter by thermal sealing (“membrane basket”) (Fig. 1b). The thickness of the carbon material was ca. 1.5 mm.

The ZTC electroxidation was performed anodically by galvanostatic polarization (current = 2-50 mA) at 25 ºC, in a conventional three-electrode electrochemical cell, for different times (1-36 h) in three electrolytes:

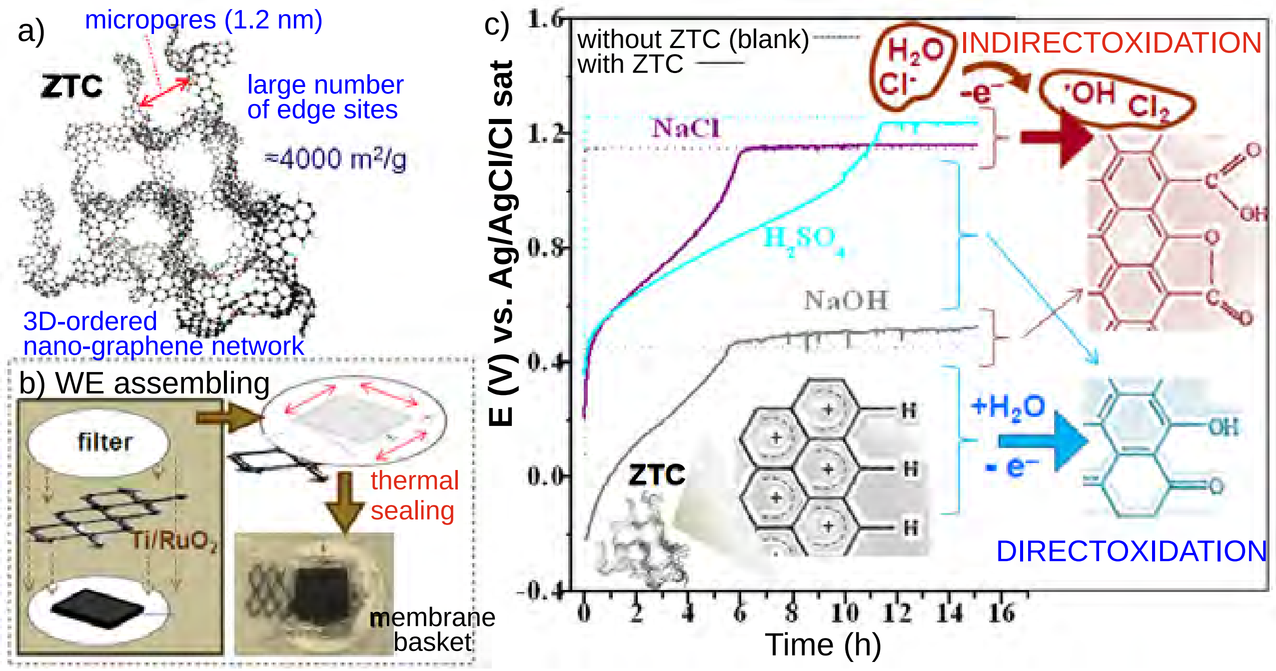

Figure 1. (**a**) ZTC molecular structure, (**b**) scheme of the electrode/ZTC paste (WE) assembling and (**c**) polarization curves of ZTC in different electrolytes (5 mA, 15 h) together with the proposed electroxidation mechanism of carbon materials.

Figura 1. (**a**) Estructura molecular del ZTC, (**b**) esquema del ensamblaje electrodo/ZTC (WE) y (**c**) curvas de polarización del ZTC en diferentes electrolitos (5 mA, 15 h) junto con el mecanismo de electroxidación de materiales carbonosos propuesto en este trabajo.

Table 1. CO and CO_2 evolved from TPD experiments; the total amount of oxygen (O); the introduced oxygen amount (ΔO) and the CO/CO_2 ratio deduced from these values; and the textural characterization of the original and the oxidize ZTC samples.

Tabla 1. CO y CO_2 desorbidos en los experimentos DTP; la cantidad total de oxígeno (O); la cantidad de oxígeno introducido (ΔO); el cociente CO/CO_2; y la caracterización textural de las muestras de ZTC original y oxidadas.

		TPD					**N_2 adsorption**			
	Sample	**CO μmol/g**	**CO_2 μmol/g**	**O μmol/g**	**ΔO μmol/g**	**$\frac{CO}{CO_2}$**	**S_{BET} (m^2/g)**	**$V_T(N_2)$ (cm^3/g)**	**$V_{DR}(N_2)$ (cm^3/g)**	**%S_{BET}**
	ZTC	2644	286	3216	0	9.24	3650	1.63	1.54	100
Chemical	H-R-15h	3937	1363	6663	3447	2.89	2200	1.06	0.93	60
	N-R-1h	4909	1702	8313	5097	2.88	2150	1.02	0.90	59
	N-45-15min	4181	1506	7193	3977	2.78	2230	1.07	0.93	61
	N-80-15min	4327	1923	8173	4957	2.25	1870	0.88	0.72	51
	N-80-2h	4708	2864	10436	7220	1.64	1140	0.52	0.46	31
Electrochemical	10Cl⁻ 1h	3260	365	3990	774	8.93	3140	1.42	1.34	86
	50Cl⁻ 1h	5083	709	6501	3285	7.17	2680	1.25	1.16	73
	50Cl⁻ 3h	5880	1760	9400	6184	3.34	1210	0.54	0.50	33
	5Cl⁻ 15h	4669	1146	6961	3745	4.07	2430	1.15	1.01	67
	5OH⁻ 15h	3372	2033	7438	4222	1.66	1610	0.72	0.67	44
	5H⁺ 15h	6095	1090	8275	5059	5.59	2290	1.07	0.89	63
	2H⁺ 36 h	7159	1966	11091	7875	3.64	1860	0.87	0.77	51

2 wt. % NaCl (Cl^-), 0.5 M H_2SO_4 (H^+) and 0.5 M NaOH (OH^-). The membrane basket (Ti/RuO_2 + ZTC) was used as a working electrode (WE), where the Ti/RuO_2 anode is used as both collector and ZTC modifying electrode [11]. A Pt wire was used as counter electrode, and Ag/AgCl/Cl^- sat. as reference electrode. For conventional chemical treatments, 70 mg of ZTC and 140 ml of a 30 wt% HNO_3 (N) or H_2O_2 (H) solution were magnetically stirred in ground glass stoppered flasks at different temperatures (R= room, 45 and 80 ºC) for different times (15 min-15 h).

After filtration, washing and vacuum drying (110 ºC overnight), all samples were characterized by physisorption of N_2 at -196 ºC, X-ray diffraction, and temperature-programmed desorption (TPD) experiments.

3. Conventional chemical oxidation of ZTC

The studied conventional chemical oxidation treatments with HNO_3 are able to introduce a large amount of oxygen functional groups into ZTC (Table 1), which increases with its concentration (data not shown), the temperature and the time of treatment. Under these experimental conditions, the concentration of oxygen groups increases up to 2-3 times in relatively short times (from 15 min to 1 h), indicating that the chemical oxidation of ZTC is remarkably fast. In addition, the marked reduction in the CO/CO_2 ratios points out that these oxidative treatments produce a much higher relative increase in the CO_2-type oxygen groups (Fig. 2a). After these treatments, the characteristic sharp diffraction peak of ZTC, related to the well-defined (111) planes of zeolite Y employed in the ZTC preparation [5,6], completely disappears (Fig. 2b), so that the 3D-dimensionally ordered structure is strongly damaged, and its surface area and volume of micropores remarkably decrease (Table 1). This may cause a decline in the capacitance performance. The oxidation with H_2O_2 solutions (results not shown) involves slower processes and, as a result, the achieved oxidation degrees are lower and limited.

4. Electrochemical oxidation of ZTC

ZTC was subjected to anodic polarization under different conditions of electrolyte, current and time (Table 1). The interpretation of the polarization curves of ZTC (see example in Fig. 1c) provides, for the first time, a clear experimental evidence of the previously proposed [10,11] direct and indirect electroxidation pathways involved in the proposed general electroxidation mechanism. Considering this mechanism, the following four different behaviors have been distinguished: at lower currents (up to 10 mA), the electrode potential slowly increases with time and it remains below the high constant potentials, assigned to the electrogeneration of oxidizing species from electrolyte, for much longer time, so that ZTC may be electroxidized only by direct polarization for longer time (*direct oxidation*). In this case, the oxidation is much slower, and a considerably larger proportion of CO-evolving groups (Fig. 2c) (higher CO/CO_2 ratios) is achieved, despite the high oxidation degrees (Table 1). This kind of groups corresponds to phenol, carbonyl/quinone and/or anhydride functionalities, which have been found electroactive for pseudocapacitive reactions [1,2,4]. In addition, the oxidized carbon materials retain quite good structural and textural properties (Table 1 and Fig. 2c and d), what is highly beneficial for supercapacitor applications. If the low-current treatment is prolonged (for example at 5 mA, Fig. 1c), an intermediate behavior, with a different contribution of both direct and indirect oxidation pathways, is observed (*mixed oxidation*).

On the contrary, **at higher currents** (above 10 mA), the electrode quickly reaches the high constant potentials necessary to generate oxidizing species (figure not shown). During the initial stage of the process (up to 1 h), the still low concentration of oxidizing species results in oxidized materials with still high CO/CO_2 ratios and good physical properties (Table 1) (*soft indirect electroxidation*). If the time of polarization is prolonged under these conditions (Table 1), the introduced oxidation degree and the structural damage are even higher than those observed with the most aggressive chemical treatments (*strong indirect electroxidation*). Under these last conditions, the indirect contribution governs the electroxidation process, approaching it to a chemical one.

5. Influence of the oxidation method

Although the surface area ($\%S_{BET}$) and the structural order ($\%I_{XRD}$) remaining after the oxidation treatments generally decrease with the amount of introduced oxygen (ΔO), a strong influence of the oxidation method can be clearly observed (Fig. 3a). Thus, comparing for similar or higher amounts of introduced oxygen (ΔO), the electrochemically oxidized samples under direct, mixed or soft-indirect conditions exhibit much better structural properties than those produced by chemical treatments, obtaining oxidized-ZTC samples with unique properties: $V_{DR}(N_2)$ = 0.9-1.4 cm^3/g, S_{BET}= 1900-3100 m^2/g, O = 11000-4000 µmol/g, with a large amount of CO-evolving groups and an extraordinary long-range ordered structure; that cannot be prepared from other carbons nor by treating ZTC with conventional chemical methods.

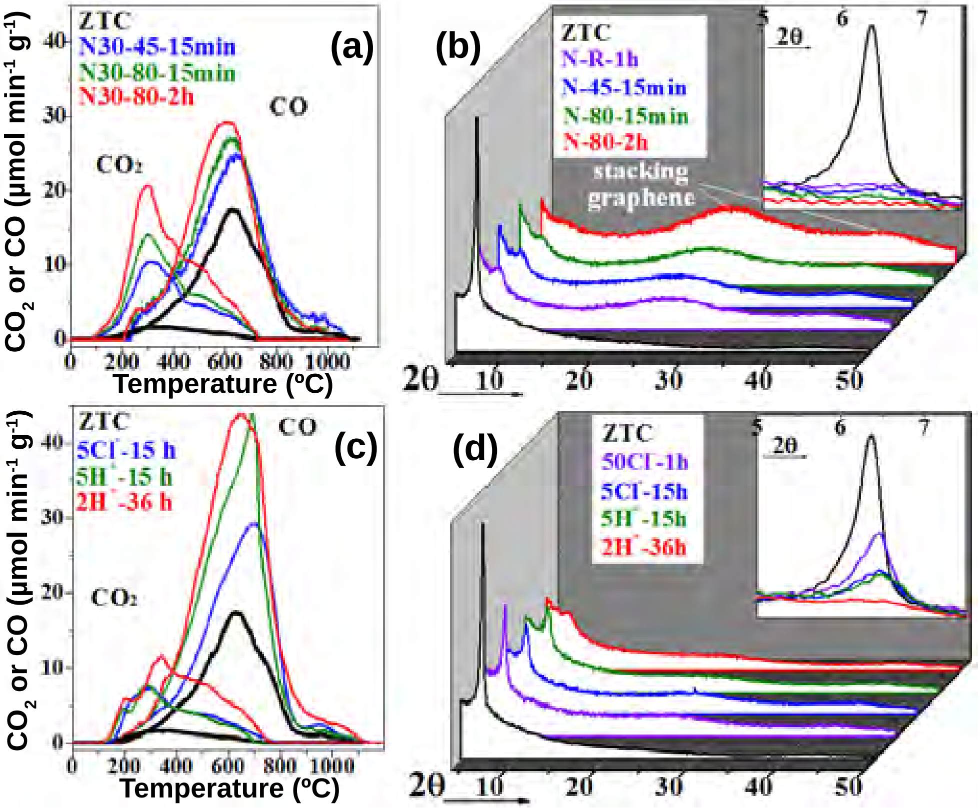

Figure 2. CO_2 and CO evolutions from TPD experiments (a,c) and X-ray diffractogramms (inset: magnified (111)-region) (b,d) for the pristine ZTC and the chemically- (a,b) or electrochemically-treated (c,d) ZTC samples under different conditions.

Figura 2. Desorción de CO_2 y CO en los experimentos DTP (a,c) y los difractogramas de rayos X (recuadro: región (111) magnificada) (b,d) de las muestras de ZTC original y las tratadas químicamente (a,b) o electroquímicamente (c,d) en diferentes condiciones.

As observed in the Fig. 3b, the success of a given oxidation treatment on preserving the original structural properties of ZTC seems to be closely related to the nature of the introduced oxygen groups, i.e. the CO/CO_2 ratios. According to the previously proposed oxidation mechanism for GAC [11], in which CO evolving groups may be formed on free surface sites whereas CO_2-evolving groups would be formed by the oxidation of the existent or fresh CO-evolving groups, the higher CO/CO_2 ratios obtained when the direct oxidation prevails, suggest that it favors oxidation attack to free sites and, therefore, a less aggressive and more controlled oxidation than that produced by oxidizing species in the chemical or the electrochemical indirect one, which must be very fast and less selective to attack any site of the ZTC structure to produce an overall higher proportion of CO_2-evolving groups and a larger number of defects and structural distortions. This must be due to a much greater control of the kinetics of the electroxidation processes, which could permit a gradual generation of the reactants and a preferential oxidative attack to the most reactive sites, preserving the original nanographene structure of the ZTC in a greater extent (Fig. 3b).

6. Conclusions

The observed physical fragility of ZTC towards the incorporation of oxygen functionalities highlights the need for the development of more controllable oxidation methods. In this work, the electrochemical modification technique has been proved to be more adequate for tailoring the surface chemistry of ZTC and a promising tool for designing new carbon materials for potential application in supercapacitors. The reasons for the better performance of the electrochemical method can be found on the better controllability of the oxidation kinetics by adjusting the relative participation of the direct and indirect oxidation pathways. The anodic polarization of ZTC in H_2SO_4 at low currents, where the direct oxidation pathway governs the oxidation process, are the better electrochemical conditions to control the surface chemistry of ZTC, i.e. to obtain highly oxidized ZTC samples (higher efficiency) with a larger proportion of pseudocapcitive-active oxygen groups (higher selectivity) and a lower structural damage.

Acknowledgements

Financial support by the MINECO and FEDER for the joint Spanish-Japanese project (PRI-PIBJP-2011-0766) and MAT2010-15273 and CTQ2012-31762 projects, by Generalitat Valenciana (PROMETEO/2009/047), as well as the Japanese Ministry of Education, Science, Sports and Culture, for the Grant-in-Aid for young scientists (A) (23685041)

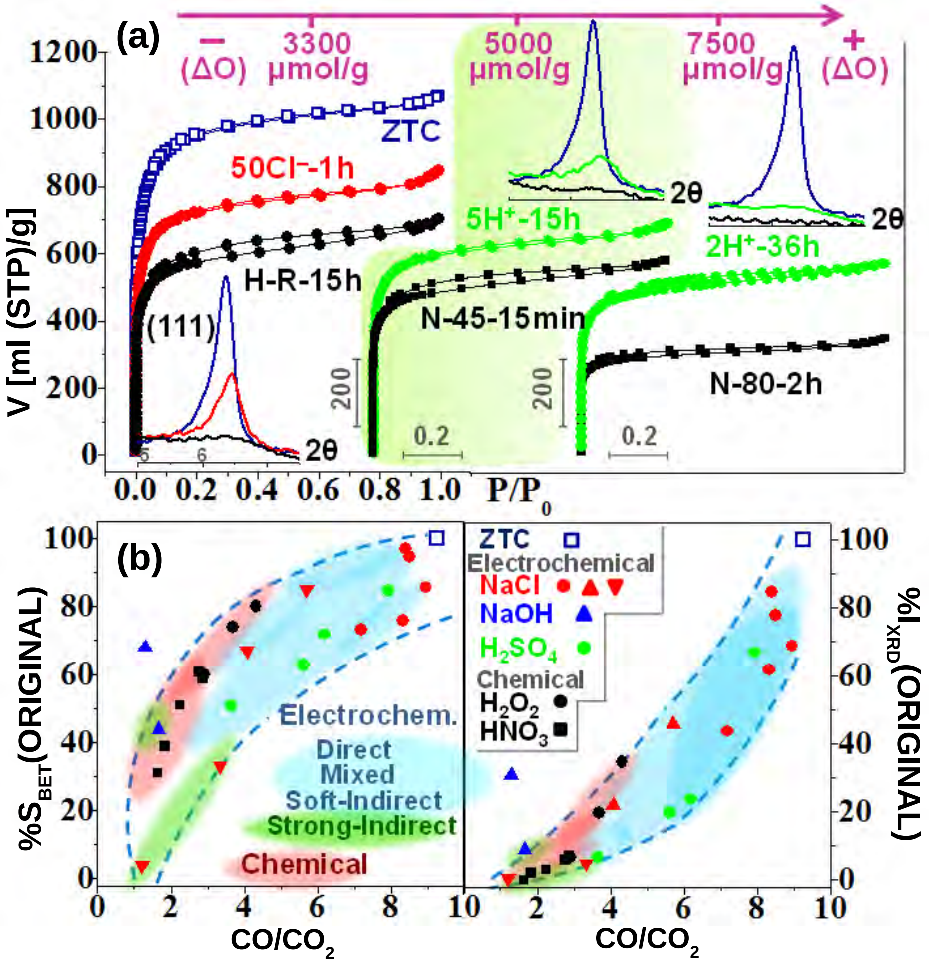

Figure 3. (a) Influence of the oxidation method on the N_2 adsorption isotherms (-196ºC) and the (111) diffraction peaks for similar amounts of introduced oxygen (ΔO); (b) Percentages of the specific surface area (%S_{BET}) or the intensity of the (111) diffraction peak (%I_{XRD}) with respect to the original ZTC remaining after different oxidation treatments as a function of the CO/CO_2 ratios.

Figura 3. (a) Influencia del método de oxidación en las isotermas de adsorción de N_2 (-196ºC) y los picos de difracción (111) para cantidades similares de oxígeno introducido (ΔO); (b) Porcentajes del área superficial específica (%S_{BET}) o de la intensidad del pico de difracción (111) (%I_{XRD}), con respecto a los del ZTC original, que permanecen tras los diferentes tratamientos de oxidación en función de los cocientes CO/CO_2

are gratefully acknowledged.

References

[1] Simon P, Gogotsi Y. Materials for electrochemical capacitors. Nat Mater 2008;7(11):845-54.

[2] Inagaki M, Konno H, Tanaike O. Carbon materials for electrochemical capacitors. J Power Sources 2010;195(24):7880-7903.

[3] Zhao X, Mendoza-Sánchez B, Dobson PJ, Grant PS. The role of nanomaterials in redox-based supercapacitors for next generation energy storage devices. Nanoscale 2011;3:839-855.

[4] Bleda-Martínez MJ, Lozano-Castelló D, Morallón E, Cazorla-Amorós D. Linares-Solano A. Chemical and electrochemical characterization of porous carbon materials. Carbon 2006;44(13):2642-51.

[5] Ma ZX, Kyotani T, Tomita A. Preparation of a high surface area microporous carbon having the structural regularity of Y zeolite. Chem Commun 2000;(23);2365–6.

[6] Matsuoka K, Yamagishi Y, Yamazaki T, Setoyama N, Tomita A, Kyotani T. Extremely high microporosity and sharp pore size distribution of a large surface area carbon prepared in the nanochannels of zeolite Y. Carbon 2005;43(4):876-9.

[7] Nishihara H, Yang QH, Hou PX, Unno M, Yamauchi S, Saito R et al. A possible buckybowl-like structure of zeolite templated carbon. Carbon 2009:47(5);1220-30.

[8] Itoi H, Nishihara H, Kogure T, Kyotani T. Three-Dimensionally Arrayed and Mutually Connected 1.2-nm Nanopores for High-Performance Electric Double Layer Capacitor. J Am Chem Soc 2011;133(5):1165-67.

[9] Nishihara H, Kyotani T. Templated Nanocarbons for Energy Storage. Adv Mater 2012;24(33):4473-98.

[10] Berenguer R, Marco-Lozar JP, Quijada C, Cazorla-Amorós D, Morallón E. Effect of electrochemical treatments on the surface chemistry of activation carbon. Carbon 2009;47(4):1018–27.

[11] Berenguer R, Marco-Lozar JP, Quijada C, Cazorla-Amorós D, Morallón E. A comparison between oxidation of activation carbon by electrochemical and chemical treatments. Carbon 2012;50(3):1123–34.