

NITROGEN DOPED SUPERACTIVATED CARBONS PREPARED AT MILD CONDITIONS AS ELECTRODES FOR SUPERCAPACITORS IN ORGANIC ELECTROLYTE

María José Mostazo-López¹, Ramiro Ruiz-Rosas¹, Tomomi Tagaya², Yoshikiyo Hatakeyama², Soshi Shiraishi², Emilia Morallón³, Diego Cazorla-Amorós^{1*}

¹*Departamento de Química Inorgánica and Instituto Universitario de Materiales, Universidad de Alicante, Apartado 99, 03080-Alicante, Spain*

²*Division of Molecular Science, Graduate School of Science and Technology, Gunma University, 376-8515, Gunma, Japan*

³*Departamento de Química Física and Instituto Universitario de Materiales, Universidad de Alicante, Apartado 99, 03080-Alicante, Spain*

SUPPLEMENTARY DATA

SD-I. Pore Size Distribution.

Figure S1 shows the pore size distribution (PSD) obtained for all activated carbons. The pore size distributions for the materials have been calculated from the N_2 adsorption isotherms using NL-DFT method as proposed by Jagiello and Olivier [1] using SAIEUS© software.

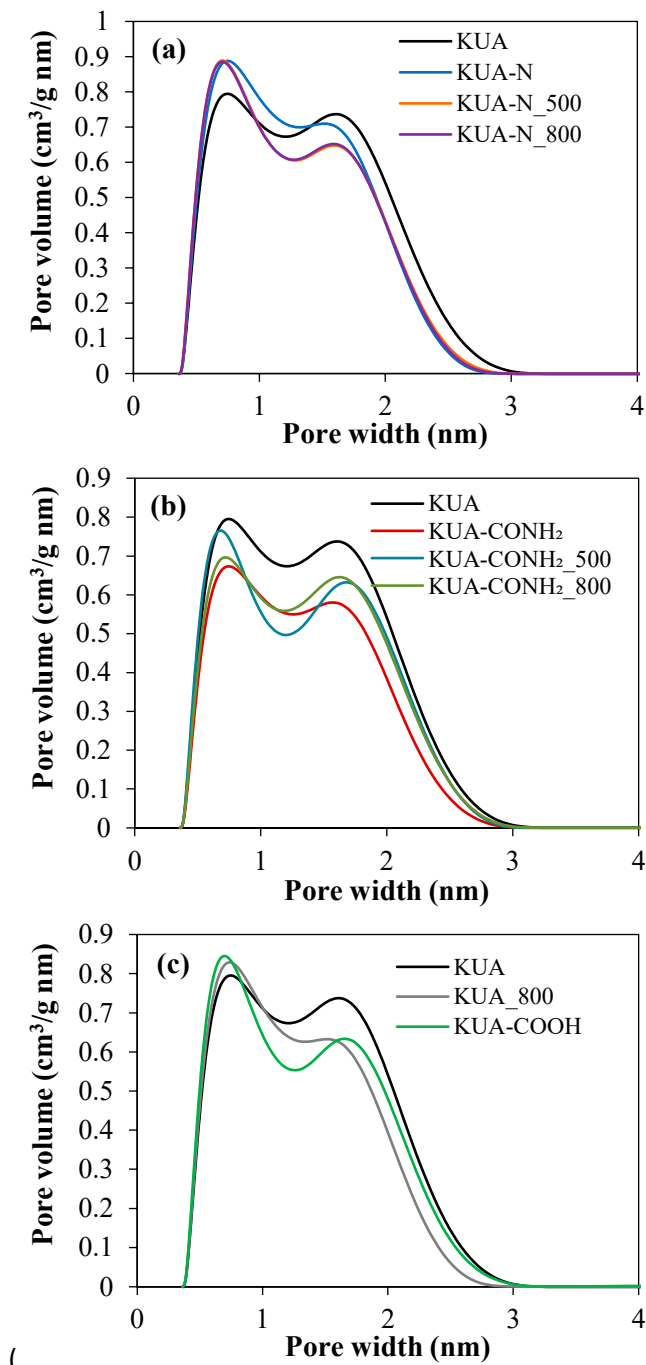


Figure S1. Differential pore size distributions obtained by NL-DFT calculations for all activated carbons.

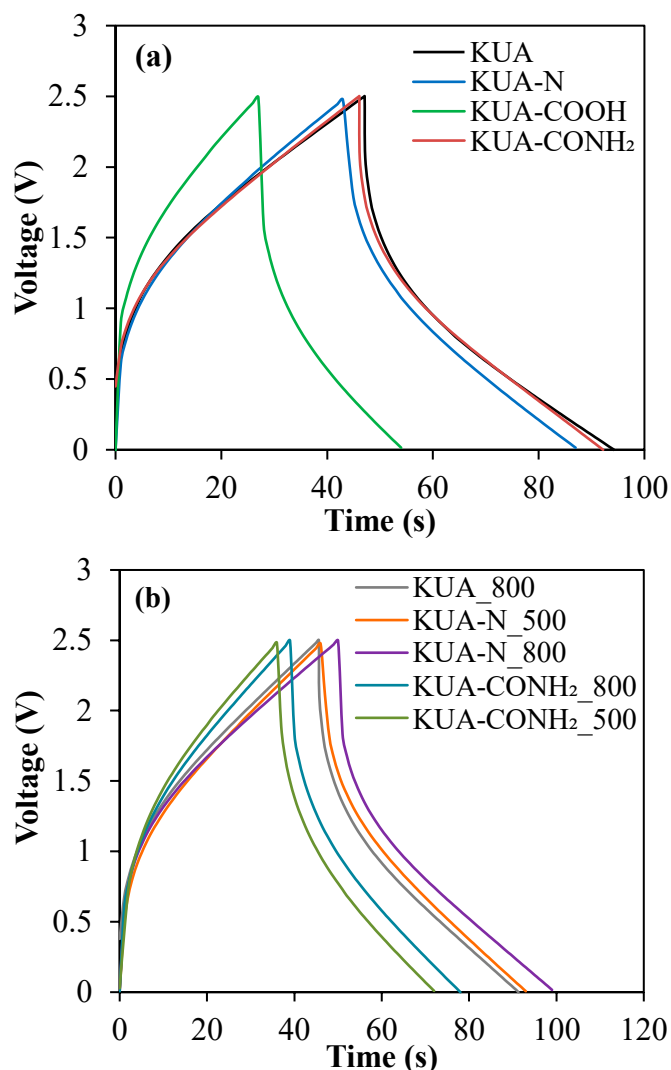


Figure S2. GCD curves obtained for EDLCs (activated carbons-based symmetric capacitors). 1M TEMABF₄/PC. $j = 1000$ mA/g. $V = 2.5$ V.

SD-II. Electrochemical performance of N-doped commercial activated carbon obtained by chemical functionalization at mild conditions.

The nitrogen doping strategy developed is used to functionalize a commercial activated carbon (YP50F, Kuraray, Japan) that is used as electrode in supercapacitors. The nitrogen doping method described in section 2.1.2 (second approach) was applied to YP50F and the obtained sample was named as YP50F-N.

Table S1. Textural properties and elemental surface composition (XPS and TPD) for YP50F and YP50F-N.

| Sample | N _{XPS} (at.%) | O _{XPS} (at.%) | CO ₂ TPD ($\mu\text{mol/g}$) | CO TPD ($\mu\text{mol/g}$) | S _{BET} (m ² /g) | V _{DR} ^{N₂} (cm ³ /g) |
|---------|----------------------------|----------------------------|--|---------------------------------|---|--|
| YP50F | - | 7.0 | 160 | 520 | 1790 | 0.71 |
| YP50F-N | 2.3 | 5.8 | 100 | 560 | 1740 | 0.69 |

Table S1 summarizes the textural properties and surface composition of the pristine and modified carbons. The nitrogen functionalization protocol (avoiding the oxidation process) over YP50F produces the attachment of nitrogen functional groups (2.3 at. % XPS, Table S1) as well as a decrease of oxygen of 1.2 at. % XPS, evidencing that nitrogen is anchored to the surface by substitution of oxygen moieties. Figure S3 shows the N1s XPS spectrum recorded for YP50F-N, that evidences that nitrogen is attached to the surface in form of pyridines, amines/amides and pyrroles/pyridones [2–5].

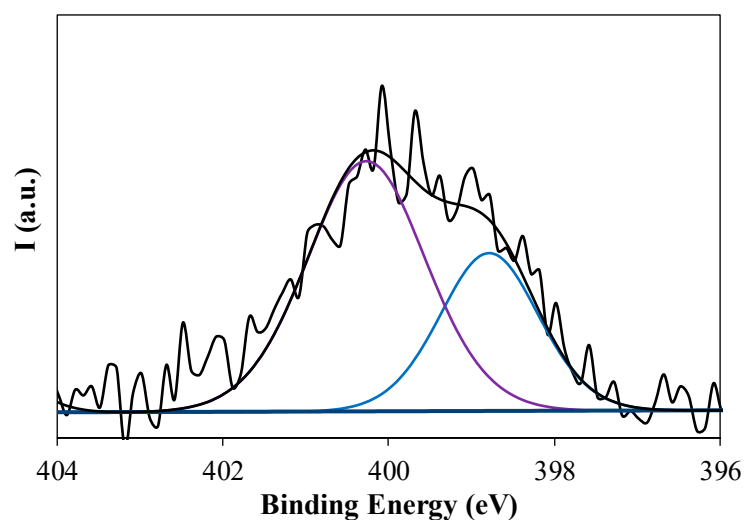


Figure S3. N1s XPS spectrum obtained for YP50F-N activated carbon.

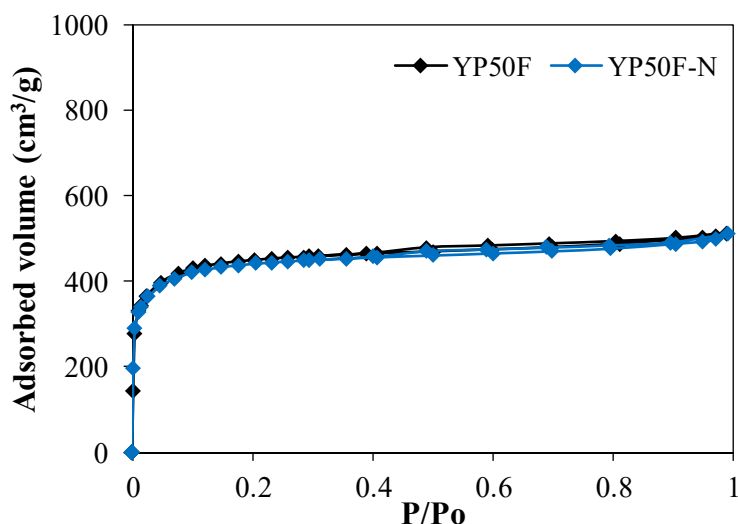


Figure S4. N₂ adsorption-desorption isotherms of the activated carbons YP50F and YP50F-N.

The activated carbon YP50F provides large apparent surface area with well-developed microporosity (Figure S4). As happened when using the activated carbon KUA, the chemical functionalization does not reduce or block the microporosity of the pristine carbon material and allows the preservation of the whole apparent surface area. Thus, these carbons have identical porous texture but different surface chemistry.

The carbon materials were electrochemically characterized in a three-electrode cell in aqueous electrolyte. Figure S5 shows the CVs obtained in a potential window where the materials are stable. Both of them **curves** show a rectangular shape characteristic of porous carbons and provide large capacitance values (156 and 131 F/g for non-doped and N-doped activated carbons, respectively). However, the CVs display some differences in the electrochemical performance of the materials. YP50F exhibits the characteristic redox pair associated with the quinone-hydroquinone redox process [6], while this response is not observed in the case of the N-functionalized carbon. These electroactive oxygen groups can be responsible of degradation processes under oxidation conditions, and consequently, the lower occurrence of this process may lead to an improvement of the durability of supercapacitors based on this N-doped carbon [7]. To deepen into the performance of this material, the durability of the corresponding capacitors was evaluated in organic medium under severe conditions of temperature and voltage. Figure S6 shows the evolution of capacitance and coulombic efficiency during the durability test performed for YP50F and

YP50F-N. As happened with N-doped KUA, the nitrogen doping does not affect the capacitance in organic electrolyte due to preservation of the microporosity. Also, the nitrogen functionalities do not increase the capacitance. However, there is an improvement of retention of capacitance upon durability of 7 % that is related to the generation of nitrogen groups with high electrochemical stability produced by the nitrogen doping at mild conditions.

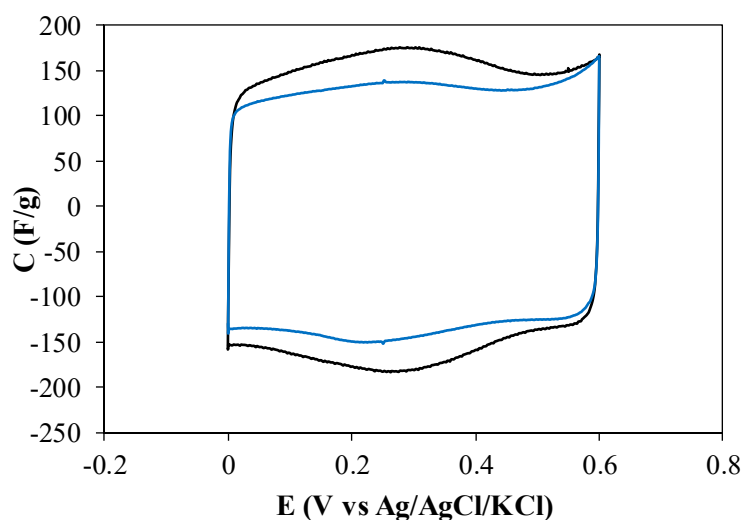


Figure S5. Cyclic voltammograms in the potential range between 0V and 0.6V for YP50F and YP50F-N electrodes. 1M H₂SO₄. V=1 mV/s.

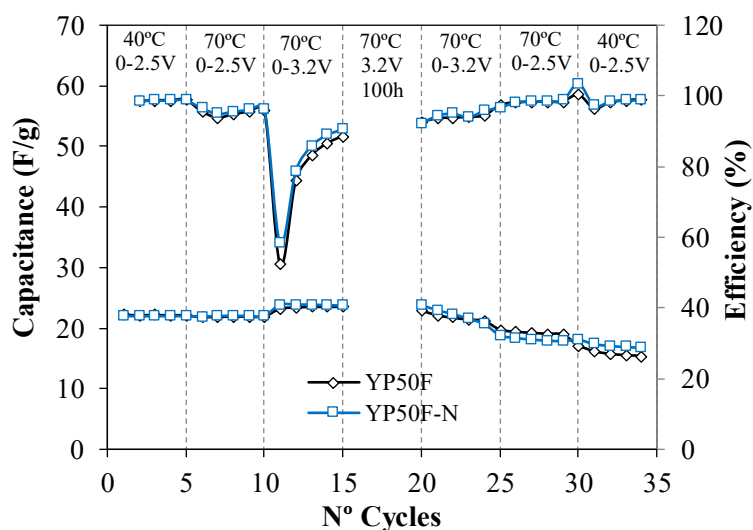


Figure S6. Evolution of capacitance and coulombic efficiency during the durability test for YP50F and YP50F-N based capacitors. 1M TEMABF₄. j = 40 mA/g.

In conclusion, a microporous commercial activated carbon used for supercapacitor application has been functionalized with nitrogen groups by following organic chemistry

protocols. The chemical method allowed the incorporation of 2 N at. % in form of different groups, by consumption of oxygen functionalities. The microporosity of the pristine carbon is fully retained after the chemical treatment. The nitrogen doping affects the electrochemical response of the carbon in acid medium, by removing the electroactivity associated to the quinone-hydroquinone redox pair. Consequently, this leads to an improvement of the electrochemical stability of the N-doped carbon which is demonstrated when tested as electrode for electrochemical capacitor in organic electrolyte.

References

- [1] J. Jagiello, J.P. Olivier, 2D-NLDFT adsorption models for carbon slit-shaped pores with surface energetical heterogeneity and geometrical corrugation, *Carbon*. 55 (2013) 70–80. doi:10.1016/j.carbon.2012.12.011.
- [2] E. Raymundo-Piñero, D. Cazorla-Amorós, A. Linares-Solano, The role of different nitrogen functional groups on the removal of SO₂ from flue gases by N-doped activated carbon powders and fibres, *Carbon*. 41 (2003) 1925–1932. doi:10.1016/S0008-6223(03)00180-5.
- [3] E. Raymundo-Piñero, D. Cazorla-Amorós, A. Linares-Solano, J. Find, U. Wild, R. Schlögl, Structural characterization of N-containing activated carbon fibers prepared from a low softening point petroleum pitch and a melamine resin, *Carbon*. 40 (2002) 597–608. doi:10.1016/S0008-6223(01)00155-5.
- [4] Y. Yamada, J. Kim, S. Matsuo, S. Sato, Nitrogen-containing graphene analyzed by X-ray photoelectron spectroscopy, *Carbon*. 70 (2014) 59–74. doi:10.1016/j.carbon.2013.12.061.
- [5] R.J.J. Jansen, H. van Bekkum, XPS of nitrogen-containing functional groups on activated carbon, *Carbon*. 33 (1995) 1021–1027. doi:10.1016/0008-6223(95)00030-H.
- [6] M.J. Bleda-Martínez, D. Lozano-Castelló, E. Morallón, D. Cazorla-Amorós, A. Linares-Solano, Chemical and electrochemical characterization of porous carbon materials, *Carbon*. 44 (2006) 2642–2651. doi:10.1016/j.carbon.2006.04.017.

- [7] M.J. Mostazo-López, R. Ruiz-rosas, E. Morallón, D. Cazorla-Amorós, Nitrogen doped superporous carbon prepared by a mild method. Enhancement of supercapacitor performance, *Int. J. Hydrogen Energy*. 41 (2016) I9691–I9701. doi:<http://dx.doi.org/10.1016/j.ijhydene.2016.03.091>.