Chemical functionalization of carbon materials for energy storage and generation

Funcionalización química de materiales carbonosos para almacentamiento y generación de energía

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Objectives and Novelty

The research on the field of energy storage and conversion systems have attracted considerable attention in the last decades due to the increasing demand of energy. One of the main challenges of the scientific community is focused on the development of more efficient and sustainable technologies. In this context, the use of electrochemical devices (such as supercapacitors and fuel cells) is a promising alternative to reach a sustainable energy production.

Supercapacitors are energy storage devices of great interest due to their high-power density and long cycle life. However, their energy needs to be increased to expand their use to different applications. For this, it is necessary to use electrodes and electrolytes able to provide high capacitance and operation voltage. Carbon materials have been extensively used as electrodes for electric double layer capacitors (EDLC) due to their well-developed porosity, tunable surface chemistry and high electrochemical stability. Moreover, the presence of nitrogen functionalities can improve the performance by increasing the electrochemical stability, wettability, conductivity or pseudocapacitance. However, the role of the different nitrogen groups is still not well understood, since the performance is strongly affected by other properties, such as the porous texture and the co-existence with other heteroatoms (such as oxygen).

Fuel cells are electrochemical devices that convert the chemical energy of a fuel into electricity. However, the slow kinetics of the oxygen reduction reaction (ORR), that takes places in the cathode, make necessary the development of new electrocatalysts to improve the performance. Platinum-based catalysts show the highest activity, but their high cost, low availability and poor durability compromises their large-scale implementation. Heteroatom-doped carbons are one of the most promising candidates to replace electrocatalysts based on noble metals, mainly due to their high surface area, electrical and mechanical properties, and low cost. Specifically, N-doped carbon electrodes show remarkable performance. However, the heterogeneity of carbon surface makes difficult to elucidate the nature of the active sites. Moreover, several works pointed out that the enhancement of surface area increases the electrocatalytic performance.

For these reasons, this thesis focused on the development of new functionalization strategies with nitrogen functional groups of highly microporous carbon materials and the study of its effect on their performance as electrodes for supercapacitors and electrocatalysts for the ORR. The specific objectives of this work were: (i) N-functionalization of activated carbons (ACs) through organic chemistry protocols at mild conditions and thermal treatments; (ii) evaluation of the effect of nitrogen groups on the performance of different carbon materials as electrodes for supercapacitors in aqueous, organic and ionic liquid electrolytes; (iii) study of the effect of nitrogen groups on the performance of highly microporous ACs as electrocatalysts for the ORR.

Results

N-doped activated carbons prepared at mild conditions as electrodes for supercapacitors

N-functionalization of highly microporous AC (>3000 m^2/g) was carried out using post-modification methods based on organic chemistry reactions at low temperature (chemical oxidation, amidation and amination reactions) [1,2]. The functionalization protocol produced the incorporation of large content of nitrogen (up to 4.1 at. % N XPS) in form of different surface groups (amines, amides, pyrroles, etc.). The attachment of nitrogen moieties did not produce significant modifications in the porous texture of the carbon materials, preserving most part of the microporosity of the pristine material (70-100 %). Thus, the evaluation of the electrochemical properties of these materials makes possible to elucidate the role of surface heteroatoms in their performance as electrodes for supercapacitors. Their electrochemical properties were assessed by using different configurations (symmetric and asymmetric in mass) and electrolytes (aqueous [2], organic [3] and ionic liquids [4]). The capacitors based on these materials provided large capacitance and energy values in all tested electrolytes: 41-72 F/g and 8-14 Wh/kg in aqueous electrolyte (1M H_2SO_4, 1.4 V); 36-41 F/g and 31-37 Wh/kg in organic medium (1M $TEMABF_4$/PC, 2.5 V); and 37-40 F/g and 44-48 Wh/kg in ionic liquid-based electrolyte (1M Pyr_{14}TFSI/PC, 3V). The large values were associated to their high microporosity development and tailored porous texture, which was mostly preserved after the incorporation of nitrogen moieties. Moreover, the devices based on N-doped carbon materials evidenced larger stability, improved rate performance and efficiency when working

under high voltage conditions. The enhancement of the supercapacitor characteristics is associated to the effects of the post-modification treatment, that produces the incorporation of stable nitrogen surface groups (pyrroles, lactams, etc.) and avoids the formation of detrimental oxygen groups during the operation of the device. This improvement was demonstrated in all tested media by using different durability conditions: cycling and floating tests under severe conditions of temperature and voltage (3.2 V and 70ºC). Furthermore, the N-functionalization treatment was applied to other carbon materials commonly used in supercapacitors and produced a further improvement of the durability [3,5].

N-doped zeolite templated carbons as electrodes for high power-density supercapacitors

Non-doped and N-doped zeolite templated carbons (ZTC and N-ZTC) were synthesized by chemical vapor deposition using a zeolite Y as template and different carbons sources [6].

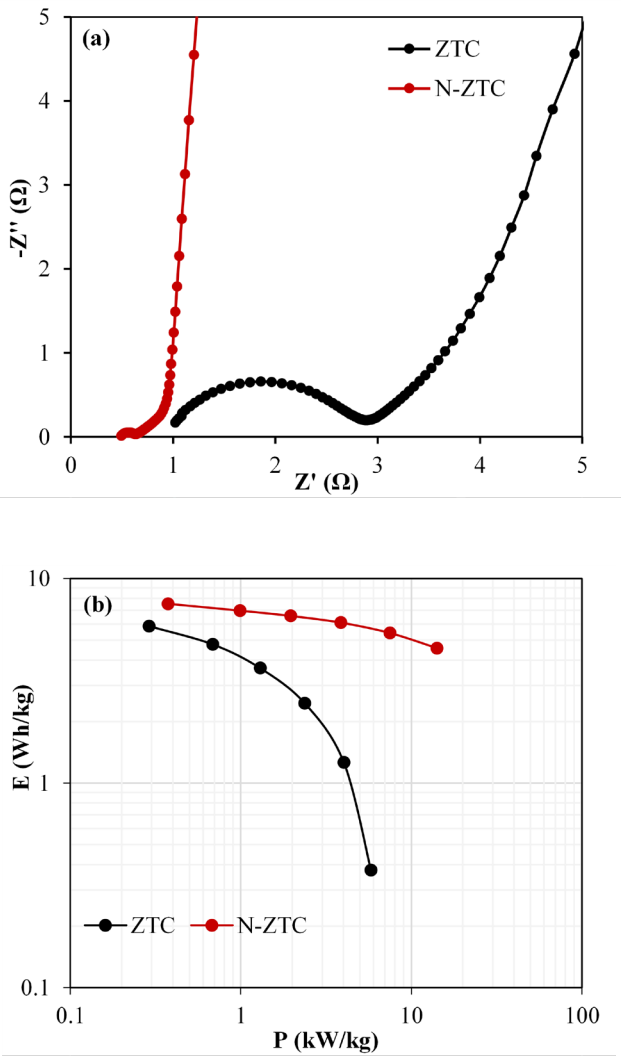

Figure 1. (a) EIS spectra for ZTC and N-ZTC based capacitors. V = 0.05 V. (b) Ragone plot obtained for ZTC and N-ZTC based capacitors. j = 1- 20 A/g. V = 1.2 V. 1M H_2SO_4.

The materials showed high apparent surface area (2760-3600 m^2/g) and different surface groups (3.7 at. % N XPS). The electrochemical characterization of these materials revealed that N-ZTC evidenced higher resistance to electro-oxidation upon positive polarization and, consequently, N-ZTC based capacitor provided larger durability upon cycling. Moreover, N-ZTC showed significant increase of electrical conductivity (EIS spectra, Fig. 1.a) associated to the large content of quaternary nitrogen. Consequently, this device showed outstanding maximum power density (4 times larger than ZTC-based capacitor) (Ragone plot, Fig. 1.b).

N-doped activated carbons as electrocatalysts for the oxygen reduction reaction

The performance of N-doped ACs as electrocatalysts for the ORR was evaluated in alkaline electrolyte. The materials were synthetised by different post-functionalization treatments of an activated carbon: polymerisation of aniline, organic chemistry reactions and post-thermal treatments under inert atmosphere. These treatments leaded to the generation of materials with different nitrogen groups (amines, pyrroles, etc.) and different content (1-4 % N XPS). The study of their performance towards ORR revealed that N-doped carbon electrodes thermal treated at 800 ºC were more selective towards water formation. The best performance was evidenced by polyaniline-derived activated carbon carbonized at 800 ºC (onset potential of 0.88V and an electron transfer number of 3.4) due to its large concentration of N-C-O sites [7].

Conclusions

Nitrogen doping methods based on organic chemistry reactions were employed to attach a wide variety of N groups in activated carbons while preserving most part of the microporosity. The modification of surface chemistry by this method produced an increase of the electrochemical stability due to the generation of stable nitrogen surface groups (pyrroles, lactams, etc.) and the removal of detrimental oxygen functionalities. Thus, the capacitors based on these materials demonstrated a remarkable enhancement of durability. This improvement was also observed in different carbon materials and electrolytes (aqueous, organic and ionic liquids).

N-doped and non-doped ZTC were employed to evaluate the role of nitrogen in their electrochemical performance as electrodes for supercapacitors. The results revealed an outstanding enhancement of the power density for N-ZTC based capacitor due to its large electrical conductivity (which was associated to the large content of quaternary nitrogen).

The evaluation of the electrocatalytic activity towards ORR of different highly microporous activated carbons showed an enhancement of the performance for the materials thermal treated at high temperature and with large content of N-C-O sites.

Related publications

[1] M.J. Mostazo-López, R. Ruiz-Rosas, E. Morallón, D. Cazorla-Amorós, Generation of nitrogen functionalities on activated carbons by amidation reactions and Hofmann rearrangement: Chemical and electrochemical characterization, Carbon 91 (2015) 252–265.

[2] 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.

[3] M.J. Mostazo-López, R. Ruiz-Rosas, T. Tagaya, Y. Hatakeyama, S. Shiraishi, E. Morallón, D. Cazorla-Amorós, Nitrogen doped activated carbons prepared at mild conditions as electrodes for supercapacitors in organic electrolyte, J. Carbon Res. 6 (2020) 1–19.

[4] M.J. Mostazo-lópez, J. Krummacher, A. Balducci, E. Morallón, D. Cazorla-amorós, Electrochemical performance of N-doped superporous activated carbons in ionic liquid-based electrolytes, Electrochim. Acta 368 (2021) 137590.

[5] T. Tagaya, Y. Hatakeyama, S. Shiraishi, H. Tsukada, M.J. Mostazo-López, E. Morallón, D. Cazorla-Amorós, Nitrogen-doped seamless activated carbon electrode with excellent durability for electric double layer capacitor, J. Electrochem. Soc. 167 (2020) 60523.

[6] M.J. Mostazo-López, R. Ruiz-Rosas, A. Castro-Muñiz, H. Nishihara, T. Kyotani, E. Morallón, D. Cazorla-Amorós, Ultraporous nitrogen-doped zeolite-templated carbon for high power density aqueous-based supercapacitors, Carbon 129 (2018) 510–519.

[7] M.J. Mostazo-López, D. Salinas-Torres, R. Ruiz-Rosas, E. Morallón, D. Cazorla-Amorós, Nitrogen-doped superporous activated carbons as electrocatalysts for the oxygen reduction reaction, Materials 12 (2019).

Full thesis can be downloaded from: *www.rua.ua.es/dspace/*