Influence of the Activation Parameters on the Electrochemical Performance of Chemically Activated Graphene Materials

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In this work, activated graphene-like materials were obtained by varying both, the ratio of activated agent/graphene precursor and the activation temperature. The resulting materials were then characterized, resulting in higher values of specific surface area (SSA) when increasing the impregnation ratio at each temperature, reaching values up to $1325 \text{ m}^2 \text{ g}^{-1}$. Gravimetric capacitances ranging between 11.0 and 49.0 F g^{-1} when charging/discharging at 0.5 A g^{-1} were obtained. The highest capacitance value was achieved not for samples with the highest SSA but with a micropore volume up to $\sim 63 \%$ of total pore volume. Overall, the capacitance values decreased significantly at activation temperatures of 600 and $700 \text{ }^\circ\text{C}$ at $2:1$ and $4:1$ impregnation ratios, regardless of an enhanced SSA, which could be explained considering the release of surface oxygenated functional groups during the thermal treatment. These results present the activated graphene materials as promising electrodes in energy storage devices.

Supercapacitors (SCs), also known as electrochemical capacitors, are energy storage devices mainly characterized by their great power and suitability to supplement, for they eventually replace, traditional batteries in applications such as wearable electrical devices, electric and hybrid vehicles, airplanes, and smart grids, among others (1). SCs are classified according to their energy storage mechanism as electrostatic double-layer capacitors (EDLC), and pseudocapacitors which also store electricity by means of faradaic reactions. In both cases, the characteristics of the active electrode materials in terms of morphology, texture and chemical composition, are key parameters to achieve devices with appropriate electrochemical performance. In addition to commonly used activated carbons, a wide variety of nanocarbon materials such as carbon nanofibers (CNFs), carbon nanotubes (CNTs) and graphene-based materials, have been explored. Graphene, an atom-thick bi-dimensional (2D) carbon nanostructure is attractive for SCs applications because it shows moderate specific surface area (SSA) ($\sim 500 \text{ m}^2 \text{ g}^{-1}$), excellent electrical conductivity, good chemical stability and outstanding mechanical behavior (1–4). However, single-layer graphene has large-scale-production issues, which include high production costs. Furthermore, when graphene is used as active material for the fabrication of electrodes, it is necessary to prevent the restacking of its layers into a graphitic structure,

to provide connections between individual sheets which ensure suitable size of the pores formed as a result of single layers assembly (5). In that sense, different graphene-like materials such as graphene oxide (GO) and thermally-reduced graphene oxide (TRGO), have been proposed as suitable alternatives, showing an interconnected network of pores accessible for electrolyte ions, high SSA values, and proper electrical conductivity, as well as their possibilities of production in bulk amounts (6).

One of the commonly used methodologies to obtain GO is the chemical oxidation of graphite (7), which results in graphite oxide (GrO) as intermediate product, followed by its exfoliation and reduction, which can be carried out by different procedures (1), (2), (8), (9). Thermal exfoliation/reduction of GrO has been reported as a single-step, eco-friendly alternative for the scalable synthesis of TRGOs, a type of graphene-like materials with promising physicochemical and electrochemical properties (2). By applying temperatures above 550 °C, a significant removal of oxygenated functional groups (carboxyl and epoxy) from GO is observed. This contributes to the restoration of the Csp^2 aromatic network, which also implies a restacking of the graphene-like sheets and therefore a decrease in SSA (10–13). In addition, the removal of these functional groups directly affects the graphene material hydrophilicity (6), (8), (14). Chemical activation of GO with potassium hydroxide (KOH) consists of a series of redox reactions where carbon is oxidized to CO, CO₂ and carbonate, while KOH is reduced into K₂CO₃ or metallic potassium (15). This procedure is considered a promising option to prevent graphene sheets agglomeration, thus obtaining a rigid three-dimensional (3D) structure with well-defined pore size distribution, developed from the gasification and separation of graphene layers from the graphitic structure (16–18). Thus, KOH-activation can provide a significant increase of SSA compared to precursor TRGO, reaching values close to the theoretical one (2630 m² g⁻¹) (3), (17).

Despite chemical activation accompanied by an important environmental impact, the obtained materials are commercially available as electrodes for SCs due to their large SSA, reasonably good electric conductivity, and low cost. Different authors have synthesized activated graphene materials by KOH-activation: Wu *et al.* (14)] and Murali *et al.* (16) used microwave-exfoliated graphene oxides (MEGOs) as the starting materials which were subsequently activated by means of KOH:GO ratios up to 60:1 at temperatures between 400 and 1000 °C. In both studies, samples with clear trends in the relationship between capacity and SSA were obtained. Zheng *et al.* (17) prepared activated graphene materials from TRGOs by a post-oxidation treatment with HNO₃ resulting in materials with high SSA values. On the other hand, Ma *et al.* (18), carried out the activation of ultrasound-exfoliated GOs. Likewise, Zhang *et al.* (19) prepared a highly conductive, flexible graphene film where mesopores were incorporated into the material. Nevertheless, their complicated preparation procedures and high cost manipulations largely restricted their practical uses in large scale. Therefore, an easy methodology resulting in activated graphene materials with suitable properties to be used as electrodes in SCs is still needed.

This article presents the microstructural and textural characteristics of chemically activated graphene materials obtained by a single-step thermal treatment at low KOH:GO ratios. The influence of the activation parameters on the porosity, and surface chemical composition of activated graphene materials, are also discussed. Finally, a study about the influence of the activation on the electrochemical performance of the resulting materials as electrodes in SCs was carried out. According to the results, the performance of the KOH-activated

graphene materials markedly depends on different characteristics such as SSA, hydrophilicity and micropore volume.

Experimental

Synthesis of activated graphene materials. -GrO was synthesized from synthetic graphite powder ($< 20\ \mu\text{m}$, Aldrich), by using the modified Hummers method previously described in detail by Botas *et al.*, 2012 (20). Subsequently, GrO was exfoliated at $150\ ^\circ\text{C}$, heating rate of $5\ ^\circ\text{C}\ \text{min}^{-1}$ in a vertical quartz reactor (under N_2 flow, $100\ \text{mL}\ \text{min}^{-1}$). From the exfoliation, GO was obtained. Then, it was mixed with deionized water ($5\ \text{mg}\ \text{mL}^{-1}$) with the aid of an ultrasonicator for 10 minutes at room temperature. The as-obtained GO suspension was impregnated with $6.0\ \text{M}\ \text{KOH}$, as activating agent, at three KOH:GO mass ratios of 2:1, 4:1 and 10:1 (C2, C4 and C10, henceforth) for 2 h, with constant stirring at room temperature. Impregnated GO was oven-dried at $100\ ^\circ\text{C}$ for 12 hours, and afterwards, it was heated up to 600 , 700 and $800\ ^\circ\text{C}$ at $10\ ^\circ\text{C}\ \text{min}^{-1}$ for 1 h under N_2 flow ($180\ \text{mL}\ \text{min}^{-1}$). After the activation/reduction step, the activated TRGOs obtained were soaked with $1.0\ \text{M}\ \text{HCl}$, followed by sequential washing with distilled water, and they were centrifuged at $4000\ \text{rpm}$ until neutral pH was obtained. Last, the materials were dried at $100\ ^\circ\text{C}$ for 12 hours. They were labeled considering both the impregnation ratio used and the activation temperature. For example, the C10-700 sample was obtained with an impregnation ratio of 10:1 at $700\ ^\circ\text{C}$.

Materials characterization. - Adsorption-desorption isotherms of N_2 at $-196\ ^\circ\text{C}$ ($77\ \text{K}$) were obtained from an ASAP2020 Plus (Micromeritics). GO was previously degassed at constant vacuum (P/P_0 of $10\ \mu\text{m}\ \text{Hg}$) and $150\ ^\circ\text{C}$, while activated TRGOs were degassed at $350\ ^\circ\text{C}$ for 6 hours. SSA values were calculated by applying the B.E.T model. Micropore volume was calculated with Dubinin-Radushkevich model (V_{micro}). Mesopore volume (V_{meso}) was obtained with Gurvitch rule (V_{meso}) by the difference between the total pores volume (V_t) and micropores volume (V_{micro}). Mesopore size was calculated from the Barrett-Joyner-Halenda (BJH) method based on Kelvin equation from nitrogen desorption data at $-196\ ^\circ\text{C}$ (D_{BJH}). Micropore size (D_{micro}) and pore size distributions were estimated by non-local density functional theory (NLDFT). Samples morphology was characterized by scanning electron microscopy (SEM) in JEOL JSM-6490LV. On the other hand, the oxygen content was quantified with the arrangement of the sample in an LECO-TF-900 oven coupled to the LECO-CHNS-932. The surface chemical analysis was performed by X-Ray Photoelectron Spectroscopy (NAP-XPS) in a Specs device with a PHOIBOS 150 1D-DLD analyzer and with a monochromatic source of $\text{Al-K}\alpha$ ($1486.7\ \text{eV}$, $13\ \text{kV}$, $100\ \text{W}$) with step energy of $90\ \text{eV}$ for general spectra and $20\ \text{eV}$ for high resolution spectra. The low yield of the activated sample C10-800 did not generate a complete characterization of the material.

Electrochemical measurements. -Electrochemical behavior of the activated graphene materials was evaluated by using two-electrode electrochemical cells, in a symmetric configuration, with $1\ \text{M}\ \text{H}_2\text{SO}_4$ as electrolyte, and a potentiostat/galvanostat (Metrohm AUTOLAB, PGSTAT204). The different electrodes were prepared by mixing the active material under evaluation with carbon black (as conductive agent) and polytetrafluoroethylene (PTFE, as binder), with a mass ratio of 80:10:10, respectively. The mixture ($4\ \text{mg}$) was deposited onto a graphite paper ($0.785\ \text{cm}^2$), applying $0.44\ \text{MPa}$ using a pneumatic press. Cyclic voltammetry (CV) measurements were carried out at a scan rate

of 2 mV s^{-1} in a voltage window between 0.0 and 0.8 V. The gravimetric capacitance from this technique (C_{cv}) was calculated in accordance with (21).

Results and discussion

Textural characteristics of starting GO were evaluated by using the adsorption-desorption isotherm of N_2 at -196°C (see **Figure 1a**). The isotherm obtained is classified as type IV according to the International Union of Pure and Applied Chemistry (IUPAC) classification, with an hysteresis loop type H3, which could be explained considering the presence of GO slit-shaped aggregates (22), (23). It is noticed that GO pore size distribution shows a wide range of mesopores with sizes below 60 nm (**Figure 1b**).

Regarding the chemically-activated graphene materials, the activation procedure resulted in a remarkable change in pore size distribution, essentially obtaining mesoporous materials. **Figure 2** shows the N_2 isotherms corresponding to samples obtained at different KOH:GO ratio and activation temperatures (**Figures 2a, 2b, and 2c**). The materials showed isotherms type IV with H3 hysteresis loops, according to IUPAC. This type of isotherm is associated to the presence of slit-shaped narrow micropores (which are essentially important, because the pre-adsorbed molecules near the pore entrance often contribute to the subsequent intrapore diffusion) and with a high presence of mesopores (22), (23). In addition, it stands out that as KOH:GO ratio increases, the hysteresis loop gets narrower, which could be explained considering the decrease in the number of pores higher than 4 nm, which is more evident at 600 and 700°C . Then, it can be inferred that C2 ratio promotes a carbonaceous structure with a high mesopore volume percentage, while at C10 ratio a microporous structure was mainly obtained. This behavior was observed at three activation temperatures (**Figures 2a, 2b and 2c**). The pore size distributions of the activated materials are given in **Figures 2d, 2e, and 2f**. Therein, all samples showed greater homogenization in pore distribution below 4 nm than the starting GO. Within this range, the pore size distribution is more heterogeneous. As described above, GO activation with the C10 entails micropores formation ranging from 0.5 and 2 nm, without temperature dependence. In general, with KOH activation, the frameworks of macropores should be broken into smaller and randomly arranged pieces, leading to the increase of mesoporosity.

Table I shows the textural and physicochemical properties of activated samples. SSA values ranged between 164 and $1325 \text{ m}^2 \text{ g}^{-1}$, micropore size between 0.53 and 0.98 nm, and mesopores size between 5.55 and 14.42 nm. The lowest SSA value corresponds, as expected, to the C2-600 sample and the highest value to C10-800. These values were lower than those reported by Murali *et al.* (16), and Ma *et al.* (18), possibly due to differences in the exfoliation conditions of graphene precursor prior GO activation with KOH.

Figure 3a shows a relationship between SSA and KOH:GO mass ratio at different temperatures. As the KOH:GO ratio increases, the SSA raises at the three temperatures assayed. At C2, there is no linear trend between temperature and SSA values, being these values smaller than the obtained for GO. For C4, the SSA and V_{micro} are higher than the starting GO, mainly at 600 and 700°C . However, both values decreased as the temperature increased. This behavior shown at C2 and C4 could be associated with restacking of graphene-like sheets, due to the removal of oxygenated functional groups (as a consequence of the thermal treatment), which decreased the SSA. The most significant

changes in microporosity, in comparison with GO, have been observed at C10-800. However, at this temperature a significant loss weight of activated material was observed, resulting in lower yields.

As previously mentioned, SSA increased as KOH:GO ratio increases for each activation temperature. KOH activation provides oxygen functional groups and porous networks ranging from 0.5 to 4 nm. At temperatures above 400 °C, the surface was weakened by the presence of redox reactions, $2C+6KOH\rightarrow 2K+2CO_3+3H_2$ (carbon etching). Moreover, at temperatures equal and above 700 °C, CO_2 (g) and H_2O (g) were released and associated with the decomposition of the K_2CO_3 over GO surface (24), (25). **Figure 3b** shows the relationship between micropore and mesopore volume ratio (V_R) with SSA for all activated samples. In this figure, a maximum value was determined at $730\text{ m}^2\text{ g}^{-1}$, $V_R = 2.55$ was calculated. The rise of mesoporous structure at higher activation temperature was due to the widening of micropores, which occurs during the release of CO_2 and H_2O during the activation process (26).

Chemical composition of the resulting materials was analyzed by XPS. **Table I** shows the C/O_{XPS} ratios, whose values range between 8.20 – 21.00. These results are typical of carbon-based materials, due to oxygen chemisorption on the outer side of the exposed carbon surface (27). The C/O ratio decreases as the KOH:GO ratio increases for each temperature, for XPS. In accordance with the XPS analysis, the presence of nitrogen and sulfur functional groups was also measured, even though in markedly low percentages, 0.19 – 0.91 wt.% and 0.15 – 0.58 wt.%, respectively. The high resolution XPS results for C_{1s} and O_{1s} are presented as supplementary information. The O_{1s} spectra deconvolution presented five peaks that correspond to the binding energies around 530.2 eV (quinones), 531.3 eV (C=O) corresponding to carbonyl and carboxylic groups, 532.4 eV (hydroxyl/epoxy), 533.4 eV (C-O, C-OH and C-O-C) corresponding to phenol and ether groups, and 534.5 eV (physisorbed and chemisorbed water) (28), (29).

Figure 4 shows the surface oxygen content and oxygen functional groups percentages determined by XPS as a function of KOH:GO ratio for each activation temperature. From these figures, hydroxyl/epoxy-type oxygen functional groups (C–O–H) predominate over the surface of activated samples. Moreover, at 600 and 700 °C their contribution is enhanced as KOH:GO ratio increases until reaching a value around 45 %, followed in greater proportion by the functionalities with a single C–O bond (20 – 30 %), a double bond and, in smaller proportions, quinones and hydroquinones. At these two temperatures, the O_{XPS} reaches its maximum value at C4, although the hydroxyl/epoxy-type oxygen functional groups continue having a greater presence on the surface at 800 °C.

Figure 5 presents the morphology of the materials activated at C2 and C10 ratios, by applying 600, 700 and 800 °C, respectively. As it can be seen, all the materials are conformed by several crumpled sheets, which are detached from each other. These flake-like sheets are configured in a noticeably distorted 3D arrangement, typical of the thermal expansion that the starting material undergoes in the exfoliation and reduction steps. At C2 ratio (**Figures 5a** to **5c**) no significant differences in the size and integrity of the graphene-like layers are observed. **Figure 5c** (C2-800) shows a larger structural order, with shorter distances between the different sheets as a consequence of the thermal treatment applied. (18). The structures obtained at C10 show surface etching developed by KOH. The loss of structural order is evidenced as the activation temperature increases and is greater for the

C10-800 sample (**Figure 5f**). It is evident that the surface of this material becomes more crumpled after KOH activation. According to Wu *et al.* (14), surface etching caused by redox reactions between carbon and KOH leads to higher SSA, which implies that KOH activation was efficient even at concentrations lower than the already reported.

Figure 6a shows the cyclic voltammograms (CVs) recorded on the different activated samples at 2 mV s^{-1} . At 600°C , C2 presents a typical EDCL capacitor behavior, as it can be seen from its symmetric, quasi-rectangular shape and the absence of pseudocapacitive contribution. However, samples C4 and C10 exhibited a deviation from this ideal behavior. CVs are narrower at potential values above 0.3 V due to diffusional limitations of the hydrated bisulfate ions into the micropores, producing an ion-sieving effect (30), (31). Furthermore, materials obtained at higher activation temperatures showed an improved performance, due to an increase of the mesopore volume; except at C10-700 that exhibited a mesopore volume lower than $0.1 \text{ cm}^3 \text{ g}^{-1}$. Charge/discharge curves recorded at an applied current density of 0.5 A g^{-1} on the different materials evaluated, are shown in **Figure 7**. The obtained profiles have a quasi-symmetric and triangular shape typical of ideal supercapacitors. Capacitance values of the whole cells, calculated from cyclic voltammograms (C_{CV}) and charge/discharge profiles (C_{CP}), are summarized in **Table II**. The as-obtained values ranged between 11 and 49.5 F g^{-1} , C2-800 showing the lowest capacitance and C10-600 the highest one. C10-600 charge/discharge profile shows a deviation from the ideal, which could be due to limitations on the diffusion of ions into the micropores.

Figure 8 presents the Nyquist plots recorded on the different devices as a function of frequency. In the high frequency region, all samples showed a well-developed semicircle characteristic of a charge transfer resistance followed by a straight line in the low frequency region related to a capacitive behavior with some diffusion problems. The calculated C_{EIS} values, summarized in **Table II**, ranged between 18.0 and 66.0 F g^{-1} , the highest value corresponding to C4-600 and the lowest to C2-800. Capacitance values calculated from discharge curves are lower than EIS, this difference is more apparent for C4-600. Sample C4-600 showed the highest oxygen content, total and superficial, and this could be allowed that alternating current penetrates into the electrode bulk without some hindrance (32).

Figure 9 shows the influence of the SSA on the C_{EIS} and IC_{EIS} values of the activated samples. There is not a clear relation between C_{EIS} and SSA (**Figure 9a**). An increment of micropores might improve the capacitance value; nevertheless, some micropores may not be suitable for electrolyte accessibility due to the presence of surface functional groups. The lack of correlation between specific surface area and capacitance values could be explained considering the SSA analysis method, which is based on nitrogen adsorption/desorption, whereas the electrochemical performance of electrodes is evaluated in an aqueous electrolyte.

The filling of the pores of the activated graphene materials by the aqueous electrolyte is rather different when compared to N_2 , not only due to different molecule sizes but mainly due to effects of interaction with the carbon surface. Nitrogen distributes in a similar proper way through hydrophilic and hydrophobic pores. In addition, **Figure 9b** shows a decrease of IC_{EIS} as SSA increases, at the three activation temperatures assayed. As SSA increases, the percentage of active sites of the basal planes on the walls of micropores decreases respect to edge sites mainly on the external surface, thus, the EDCL capacitance inside graphitic basal planes is reduced, as well as the interfacial capacitance

(33). IC_{EIS} values varied between 7.2 and 25.6 $\mu F\ cm^{-2}$, and the sample C2-600 was the only one that exceeded the interfacial capacitance value of a clean graphite surface (20 $\mu F\ cm^{-2}$), indicating good accessibility to the microporosity (34).

Figure 10 shows the influence of the surface O content on the C_{EIS} and ESR values of the activated graphene materials. As surface oxygen content increases, gravimetric capacitance increases (**Figure 10a**). This behavior is due to fixing oxygen functions with large polarity on the sample surface. As expected, if the hydrophobicity of the carbon surface decreased, its wettability is improved thus facilitating the electrical double layer formation when applying the voltage to the device (35). In C10-600 there is a high presence of hydroxyl/epoxy functional groups, while over C4-600 and C4-700 their content of such functional groups is similar. The equivalent series resistance values were calculated extrapolating the straight-line intersection of the medium frequency region and impedance axis. This value is the sum of electrolyte resistance, active material resistance and diffusion in the carbonaceous structure. **Figure 10b** shows that ESR decreased as surface oxygen content increases, indicating good electrolyte ions mobility being this behavior consistent with **Figure 10a** results.

The phase angles (φ) was obtained at the lowest frequency and relaxation time(τ) was determined from the loss of energy calculated at the maximum frequency (**Table II**). Sample C10-600 showed the highest value of φ (-84.6°), which is close to -90° , corresponding to ideally capacitive devices (36), and favoring energy storage. This decrease in conductivity may be associated with higher densities of basal planes with regard to the edge densities wherein the ESR increases and therefore, the C_{EIS} decreases. Furthermore, τ is a quantitative measurement of the speed at which the device can be loaded and unloaded ($\tau=1/2\pi f$) (35). The lower τ values correspond to the samples at 600 °C, might for the high number of sheets that promotes a higher conductivity.

Conclusions

In summary, this study reports the impact exerted by the relationship between KOH:GO ratio and the activation temperature on the characteristics of the activated graphene materials. In fact, the authors were able to generate KOH:GO with various structures by carefully controlling these experimental parameters. The results of the activation reveal that the synthesis conditions significantly affect the SSA, the development and distribution of the porosity, the structural order, and the oxygenated functional groups content in the samples obtained. By KOH activation of GO as precursor, an activated graphene material (C10-600) with an SSA value of 422 $m^2\ g^{-1}$ and a 63 % volume of micropores was obtained, which allows 49.0 $F\ g^{-1}$ to be stored. The KOH activation mechanism contributes to the enhancement of the SSA of the material by adding micropores and functional groups, thus preventing the graphene-like sheets from re-stacking. Therefore, the activation procedure could be an efficient strategy to improve electrochemical storage in supercapacitors.

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References

1. Q. Ke, J. Wang, *J. Mater.* 2 37–54, (2016).
2. C. Botas, P. Álvarez, C. Blanco, R. Santamaría, M. Granda, M.D. Gutiérrez, F. Rodríguez-Reinoso, R. Menéndez, *Carbon N. Y.* 52 476–485, (2013).
3. Y. Zhu, S. Murali, M.D. Stoller, K.J. Ganesh, W. Cai, P.J. Ferreira, A. Pirkle, R.M. Wallace, K.A. Cychosz, M. Thommes, D. Su, E.A. Stach, R.S. Ruoff, *Science* (80). 332 1537–1542, (2011).
4. B.K. Kim, S. Sy, A. Yu, J. Zhang, *Handb. Clean Energy Syst.* 1–25, (2015).
5. J.H. Lee, N. Park, B.G. Kim, D.S. Jung, K. Im, J. Hur, J.W. Choi, *ACS Nano* 7 9366–9374, (2013).
6. B. Zhao, P. Liu, Y. Jiang, D. Pan, H. Tao, J. Song, T. Fang, W. Xu, *J. Power Sources* 198 423–427, (2012).
7. W.S. Hummers, R.E. Offeman, *J. Am. Chem. Soc.* 80 1339, (1958).
8. P. Álvarez, C. Blanco, R. Santamaría, P. Blanco, Z. González, L. Fernández-García, U. Sierra, M. Granda, A. Páez, R. Menéndez, *Carbon N. Y.* 90 160–163, (2015).
9. R. Muzyka, S. Drewniak, T. Pustelny, M. Chrubasik, G. Gryglewicz, *Materials* (Basel). 11 1050–1065, (2018).
10. R. Larciprete, S. Fabris, T. Sun, P. Lacovig, A. Baraldi, S. Lizzit, *J. Am. Chem. Soc.* 133 17315–17321, (2011).
11. E. Choi, J. Kim, Y. Cui, K. Choi, Y. Gao, S. Han, S.G. Pyo, S. Yoon, *Electron. Mater. Lett.* 13 324–329, (2017).
12. A. V. Dolbin, M. V. Khlistyuck, V.B. Esel'Son, V.G. Gavrilko, N.A. Vinnikov, R.M. Basnukaeva, I. Maluenda, W.K. Maser, A.M. Benito, *Appl. Surf. Sci.* 361 213–220, (2016).
13. Z. Lei, J. Zhang, L.L. Zhang, N.A. Kumar, X.S. Zhao, *Energy Environ. Sci.* 9 1891–1930, (2016).
14. S. Wu, G. Chen, N.Y. Kim, K. Ni, W. Zeng, Y. Zhao, *Small* 12 2376–2384, (2016).
15. W. Deng, T. Kang, H. Liu, J. Zhang, N. Wang, N. Lu, Y. Ma, A. Umar, Z. Guo, *Sci. Adv. Mater.* 10 937–949, (2018).
16. S. Murali, J.R. Potts, S. Stoller, J. Park, M.D. Stoller, L.L. Zhang, Y. Zhu, R.S. Ruoff, *Carbon N. Y.* 50 3482–3485, (2012).
17. C. Zheng, X.F. Zhou, H.L. Cao, G.H. Wang, Z.P. Liu, *J. Mater. Chem. A* 3, 9543–9549, (2015).
18. J. Ma, Y. Sun, F. Yu, *R. Soc. Open Sci.* 4, 1–11, (2017).
19. L.L. Zhang, X. Zhao, M.D. Stoller, Y. Zhu, H. Ji, S. Murali, Y. Wu, S. Perales, B. Clevenger, R.S. Ruoff, *Nano Lett.* 12, 1806–1812, (2012).
20. C. Botas, P. Álvarez, C. Blanco, R. Santamaría, M. Granda, P. Ares, F. Rodríguez-Reinoso, R. Menéndez, *Carbon N. Y.* 50, 275–282, (2012).
21. S. Roldán, D. Barreda, M. Granda, R. Menéndez, R. Santamaría, C. Blanco, *Phys. Chem. Chem. Phys.* 17, 1084–1092, (2015).
22. K.S. W Sing, D.H. Everett, R.A. W Haul, L. Moscou, R.A. Pierotti, J. Rouquerol, *Pure Appl. Chem* 57, 603–619, (1985).
23. M. Thommes, K. Kaneko, A. V Neimark, J.P. Olivier, F. Rodríguez-Reinoso, J. Rouquerol, K.S.W. Sing, *Pure Appl. Chem.* 2015; 87, 1051–1069, (2015).
24. E. Raymundo-Piñero, P. Azaïs, T. Cacciaguerra, D. Cazorla-Amorós, A. Linares-Solano, F. Béguin, *Carbon N. Y.* 43, 786–795, (2005).
25. Y.J. Kim, Y. Horie, Y. Matsuzawa, S. Ozaki, M. Endo, M.S. Dresselhaus, *Carbon N. Y.* 42 (2004) 2423–2432.
26. J. Bin Wu, M.L. Lin, X. Cong, H.N. Liu, P.H. Tan, *Chem. Soc. Rev.* 47 (2018)

- 1822–1873.
27. I. Childres, L.A. Jauregui, W. Park, H. Caoa, Y.P. Chena, in: J.I. Jang (Ed.), *New Dev. Phot. Mater. Res.*, Nova Science Publishers Inc., UK, 2013, pp. 1–20.
 28. Z. Zapata-Benabithé, F. Carrasco-Marín, C. Moreno-Castilla, *J. Power Sources* 219 (2012) 80–8.
 29. C.M. Chen, Q. Zhang, M.G. Yang, C.H. Huang, Y.G. Yang, M.Z. Wang, *Carbon N. Y.* 50 (2012) 3572–3584.
 30. S. Tang, S. Jin, R. Zhang, Y. Liu, J. Wang, Z. Hu, W. Lu, S. Yang, W. Qiao, L. Ling, M. Jin, *Appl. Surf. Sci.* 473 (2019) 222–229.
 31. Z. Zapata-Benabithé, F. Carrasco-Marín, J. De Vicente, C. Moreno-Castilla, *Langmuir* 29 (2013).
 32. G. Salitra, A. Soffer, L. Eliad, Y. Cohen, D. Aurbach, *J. Electrochem. Soc.* 147 (2000) 2486.
 33. K. Kierzek, E. Frackowiak, G. Lota, G. Gryglewicz, J. Machnikowski, *Electrochim. Acta* 49 (2004) 515–23.
 34. A.G. Pandolfo, A.F. Hollenkamp, *J. Power Sources* 157 (2006) 11–27.
 35. Z. Zapata-Benabihe, C. Moreno-Castilla, F. Carrasco-Marín, *Langmuir* 30 (2014) 1716–1722.
 36. H. Cao, X. Peng, M. Zhao, P. Liu, B. Xu, J. Guo, *RSC Adv.* 8 (2018) 2858–2865.
 37. F. Barzegar, J.K. Dangbegnon, A. Bello, D.Y. Momodu, A.T.C. Johnson, N. Manyala, *AIP Adv.* 5 (2015).

Figures

Figure 1. a) N_2 isotherm at -196°C and b) pore size distribution for GO.

Figure 2. N₂ adsorption-desorption isotherms at -196 °C (a, b, and c) and pore size distribution (d, e, and f) for activated graphene materials.

Figure 3. a) Relationship between SSA and KOH:GO mass ratio at different activation temperatures and b) Volume ratio (V_R) vs. SSA for activated graphene materials.

Figure 4. Oxygen content and functional groups obtained by XPS as a function of KOH:GO ratio at a) 600, b) 700 and c) 800 °C for activated graphene materials.

Figure 5. SEM images of the activated graphene materials obtained at a) C2-600, b) C2-700, c) C2-800, d) C10-600, e) C10-700 and f) C10-800.

Figure 6. Cyclic voltammograms recorded at 2 mV s^{-1} on the activated graphene materials obtained at a) 600, b) 700 and c) 800 °C at different KOH:GO ratios.

Figure 7. Charge/discharge profiles recorded at an applied current density of 0.5 A g^{-1} on the activated graphene materials obtained at different KOH:GO ratios and activation temperatures of a) 600, b) 700 and c) 800 °C.

Figure 8. Nyquist plots corresponding to the activated graphene materials obtained at different KOH:GO ratios and activation temperatures of a) 600, b) 700 and c) 800 °C. The inserts display an enlarged view of the high frequency region

Figure 9. Relationship between a) C_{EIS} and b) IC_{EIS} and SSA for KOH:GO samples.

Figure 10. Influence of surface oxygen content (O_{XPS}) on a) C_{EIS} and b) ESR for KOH:GO samples.

Tables

Table I. Textural and physicochemical characteristics of the activated graphene materials

Sample	SSA (m ² g ⁻¹)	V_{micro} (cm ³ g ⁻¹)	V_{meso} (cm ³ g ⁻¹)	D_{micro} (nm)	D_{BJH} (nm)	$\left(\frac{C}{O}\right)_{XPS}$
GO	250	0.091	1.112	0.98	7.58	-
C2-600	164	0.059	0.152	0.80	10.77	9.90
C4-600	357	0.129	0.099	0.61	11.96	8.20
C10-600	422	0.149	0.089	0.64	14.22	9.80
C2-700	260	0.093	0.302	0.53	14.42	11.60
C4-700	309	0.111	0.158	0.77	11.15	8.20
C10-700	730	0.250	0.098	0.59	5.55	9.20
C2-800	184	0.067	0.198	0.84	13.20	14.90
C4-800	277	0.099	0.11	0.58	12.87	21.00
C10-800	1325	0.530	0.248	0.58	6.00	-

Table II. Electrochemical parameters calculated from symmetric two-electrode cells (1.0 M H₂SO₄) for the different activated graphene materials.

Sample	C_{CV} (F g⁻¹)	C_{CP} (F g⁻¹)	C_{EIS} (F g⁻¹)	ESR (Ω)	-φ (°)	τ (s)	I_{C_{EIS}} (μF cm⁻²)
C2-600	37.6	42.0	42.0	3.23	82.7	1.4	25.6
C4-600	43.0	43.0	66.0	3.12	81.9	1.4	18.5
C10-600	49.5	49.0	49.0	3.82	84.6	1.4	11.6
C2-700	29.0	28.0	35.0	2.45	80.8	5.8	13.5
C4-700	28.5	27.0	30.0	2.85	79.6	2.3	9.7
C10-700	43.0	44.5	49.5	3.16	81.1	2.2	6.8
C2-800	14.0	11.0	18.0	4.18	78.7	9.4	9.8
C4-800	14.5	15.0	20.0	4.51	78.0	3.6	7.2