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### ► To cite this version:

Oscar Pinto-Burgos, Jimena Castro-Gutiérrez, Po Shan Poon, Maria Izquierdo, Alain Celzard, et al.. Enhancing electrochemical capacitor performance of N-doped tannin-derived carbons by hydrothermal treatment in ammonia. *Journal of Power Sources*, 2024, 602, pp.234332. 10.1016/j.jpowsour.2024.234332 . hal-04559743

HAL Id: hal-04559743

<https://hal.univ-lorraine.fr/hal-04559743v1>

Submitted on 25 Apr 2024

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1 **Enhancing electrochemical capacitor performance of N-doped tannin-derived**  
2 **carbons by hydrothermal treatment in ammonia**

3  
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23 **Abstract**

24 This study demonstrates that ammonia concentration when doping carbons using hydrothermal  
25 treatment has crucial impact on textural properties. The latter translates into an improvement of the  
26 electrochemical performance of carbon materials, when used into electrochemical capacitors,  
27 especially at high-rate performance. Nitrogen-doped carbons were synthesized by subjecting tannin to  
28 hydrothermal carbonization in ammonia solutions of varying concentrations. After carbonization and  
29 CO<sub>2</sub> activation, the as-produced activated carbons (ACs) were tested as electrodes for electrochemical  
30 capacitors in symmetric configuration using 1 M H<sub>2</sub>SO<sub>4</sub> as aqueous electrolyte. Interestingly, ammonia  
31 concentration during the hydrothermal synthesis step did not significantly affect the final N content  
32 (ca. 3 and 4 at. %) nor the nitrogen and oxygen functionalities on the surface. However, the use of  
33 ammonia had crucial impact on the textural properties developed by CO<sub>2</sub> activation, and therefore on  
34 the electrochemical performance of the ACs. The best-performing N-doped AC showed specific  
35 electrode capacitance values, based on carbon material, of 212 F·g<sup>-1</sup> at 0.5 A·g<sup>-1</sup> and outstanding  
36 capacitance retention of ca. 71 % at 40 A·g<sup>-1</sup>. It also showed high cycling stability, with capacitance  
37 retention of ca. 96 % after 30,000 cycles. Furthermore, this AC outperformed similar reported  
38 materials, achieving a specific energy of 4.6 W·h·kg<sup>-1</sup> at 12.1 kW·kg<sup>-1</sup>.

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40

41

42 **Keywords:** Tannin; Capacitance; Nitrogen doping; Carbon materials; Sustainable energy

43

## 44 **1. Introduction**

45 The increasing use of renewable energy sources, the rise of electromobility, and the advances in the  
46 development of wireless devices used in our daily lives have significantly contributed to the growing  
47 demand for efficient energy storage systems. Among these, electrochemical energy systems, such as  
48 batteries and electrochemical capacitors (ECs) have emerged as key components [1–3]. While batteries  
49 store energy by means of chemical reactions involving the transformation of chemical bonds through  
50 electrochemical redox reactions, ECs store charge by a physical process, namely the accumulation of  
51 electrostatic charge at the electrode/electrolyte interface [4,5]. As a result, the EC storage process is  
52 rapid and highly reversible, as it involves no chemical or phase change. Consequently, the  
53 charge/discharge cycle can be repeated over a long period with minimal impact on the performance of  
54 the electric device. Therefore, a major advantage of ECs is their extended lifespan, as they can  
55 withstand up to 20,000 charge-discharge cycles with a minor drop of less than 10 % in terms of  
56 performance retention. In contrast, batteries have a lifespan ranging from 500 to 3,000 cycles [6].  
57 However, ECs suffer from a notable drawback: their low specific energy, which prevents them from  
58 storing large quantities of electrochemical energy when compared with batteries.

59 Since the early 2000s, the scientific community has devoted increasing efforts to improve the  
60 specific energy and power of ECs [1,7]. The forefront of research and development in this field has  
61 witnessed the adoption of several key approaches, namely: (i) tailoring the structure of electrode  
62 materials to optimize ion transport and adsorption according to electrolyte properties [8,9]; (ii)  
63 widening the potential window of the working cell using novel electrolytes [10,11]; and (iii)  
64 incorporating specific electroactive molecules to introduce redox contributions [12,13].

65 In this context, activated carbons (ACs) have been widely used as the main material for EC  
66 electrodes due to their ability to be tailored in terms of porosity and surface chemistry to meet specific

67 requirements [14]. In addition, ACs can be synthesized from a variety of raw materials, including, but  
68 not limiting to, coals, petroleum coke, polymeric materials, and various forms of raw or waste biomass  
69 [15–18]. In particular, tannins, based on polyphenolic compounds often extracted from tree bark, have  
70 proven to be excellent precursors for the development of carbon-based electrodes for ECs [9,19–23].  
71 Tannins indeed possess an excellent carbon yield, about 45 %, and an inherent ability for auto-  
72 condensation reactions, making them an attractive option for the production of high value-added  
73 materials [23,24]. Furthermore, the presence of -OH groups enables high reactivity, allowing the  
74 incorporation of other atoms or functionalities [22,25]. In this context, the amination of tannins using  
75 ammonia by hydrothermal carbonization (HTC) has been explored to achieve *in situ* N-doping [26].

76 Considering the amination of a single hydroxyl group in the flavonoid unit, the N content of tannin-  
77 derived materials should be 4.8 wt.% [25,26]. It is expected that tannin amination can proceed beyond  
78 the usual stoichiometry by subjecting it to an HTC process using concentrated ammonia solutions.  
79 However, most research using ammonia during the HTC step does not vary the ammonia  
80 concentration. On the other hand, to obtain optimal performance in ECs [27], the obtained materials  
81 need to be activated either by chemical activation (e.g. using KOH) or by physical activation (e.g.  
82 using CO<sub>2</sub>). While the former results in ACs with higher surface areas [28], the latter enhances  
83 wettability and pore connectivity, leading to ECs with superior performance, particularly for high-  
84 power applications [29].

85 In this study, we focused on the synthesis of N-doped ACs derived from pine bark tannins, using  
86 ammonia solutions as hydrothermal medium. The resulting hydrochars were then carbonized and were  
87 physically activated using CO<sub>2</sub>. This study is mainly concerned with the influence of N content on the  
88 textural and chemical surface properties after CO<sub>2</sub> activation and, ultimately, on their performance as  
89 electrodes for ECs.

## 90 2. Materials and methods

### 91 2.1 Synthesis of carbon materials

92 Ammonia solution (NH<sub>4</sub>OH, 26.2 wt. % in water, Merck), sulfuric acid (H<sub>2</sub>SO<sub>4</sub> 1M aqueous  
93 solution, Sigma Aldrich), polytetrafluoroethylene (PTFE, 60 wt. % suspension in water, Aldrich),  
94 carbon black powder (Sigma Aldrich), and glass fiber separator were used as received.

95 Tannins were obtained by water-ethanol extraction of *Pinus Radiata* bark from Chile [30]. They  
96 were dried, ground and sieved to obtain a roughly unimodal particle size distribution. In a first step,  
97 the tannins were subjected to HTC. In a typical synthesis, 1 g of tannin was added to 9 mL of ammonia  
98 solution with concentrations of ca. 1.6 wt. % or 3.2 wt. %. These values correspond to 4 and 8 mmol  
99 of nitrogen per gram of tannin, respectively. The solution was stirred for at least 15 min at room  
100 temperature, then subjected to HTC at 190 °C for 18 h. For comparison purposes, tannins-derived  
101 hydrochars were also prepared in distilled water. These materials were labelled as N4THC, N8THC  
102 and THC, respectively. The resulting hydrochars were washed with distilled water, dried under vacuum  
103 (80 °C, overnight), and pyrolyzed under N<sub>2</sub> flow (800 °C, 1 h, 10 °C min<sup>-1</sup>). Finally, the pyrolyzed  
104 materials underwent CO<sub>2</sub> activation at 800 °C for 1, 2, and 4 h, and at 900 °C for 1, 1.5, and 2 h to  
105 obtain a wide range of burn-offs (BO). The temperature and time parameters used during the physical  
106 activation step were thus added to the aforementioned labels. For instance, N8THC900-1.5 is the AC  
107 obtained from N8THC after pyrolysis at 800 °C and additional CO<sub>2</sub> activation at 900 °C for 1.5 h.

108

## 109 2.2 Physicochemical characterization

110 The textural properties of the ACs were obtained from nitrogen and hydrogen adsorption-desorption  
111 isotherms at -196 °C acquired using a 3Flex equipment (Micromeritics). First, the Brunauer-Emmet-  
112 Teller area ( $A_{\text{BET}}$ ) was obtained from nitrogen adsorption isotherms following the IUPAC  
113 recommendations [31]. The Gurvich volume ( $V_{0.97}$ ) was determined at a relative pressure ( $P/P^\circ$ ) of  
114 0.97. The non-local density functional theory kernel for heterogeneous surface (NLDFT-HS) with the  
115 parameter  $\lambda = 3.2$  was also applied to  $\text{N}_2$  and  $\text{H}_2$  adsorption isotherms to estimate the pore size  
116 distribution (PSD). From the latter, specific surface area (SSA), total pore volume ( $V_{\text{T}}$ ), ultra-  
117 micropore volume ( $V_{\text{u}\mu}$ , pore diameter below 0.7 nm), supermicropore volume ( $V_{\text{s}\mu}$ , pore diameter  
118 between 0.7 and 2 nm), micropore volume ( $V_{\mu} = V_{\text{u}\mu} + V_{\text{s}\mu}$ ) and mesopore volume ( $V_{\text{meso}} = V_{\text{T}} - V_{\mu}$ )  
119 were calculated. The choice of the  $\text{N}_2+\text{H}_2$  adsorption isotherm combination instead of  $\text{N}_2+\text{CO}_2$  was  
120 made to extend the lower limit value of the PSD and to prevent potential specific interactions between  
121  $\text{CO}_2$  and N-functional groups that that could lead to misleading textural characterization [32,33]. The  
122 average pore width ( $\langle w \rangle$ ) for each range was calculated by Eq. (1):

$$123 \quad \langle w \rangle = \frac{\sum_i \frac{dV}{dw_i} w_i \Delta w_i}{\sum_i \frac{dV}{dw_i} \Delta w_i} \quad (1)$$

124 Surface chemistry and the nature of oxygen and nitrogen functional groups were analyzed by X-ray  
125 photoelectron spectroscopy (XPS) using an OMICRON ESCAPlus system equipped with a non-  
126 monochromatized Mg  $K\alpha$  X-ray source (1253.6 eV). The C 1s, O 1s, and N 1s spectral regions were  
127 deconvoluted by assigning peaks based on Smith et al. [34] and Ayiania et al. [35] and fitting them  
128 with Gaussian-Lorentzian curves. Elemental analysis (C, N, H, and O) was carried out using a Vario  
129 EL Cube analyzer (Elementar). TEM images were acquired using TEM JEOL 1200 EXII equipment

### 130 2.3 Electrochemical characterization

131 Electrochemical characterization of the ACs as electrodes for ECs was conducted using a BioLogic  
132 VMP3 workstation with a symmetrical two-electrode configuration in a Swagelok cell. The electrode  
133 preparation involved an 85:10:5 weight ratio of carbon material, PTFE as binder, and carbon black as  
134 conductive additive, respectively. Ethanol was added to ensure homogeneity, and the resulting paste  
135 was dried overnight. Disc-shaped electrodes with a 5 mm diameter and a mass load close to  $10 \text{ mg cm}^{-2}$   
136 were cut from the paste. Prior to analysis, the electrodes were soaked in 1 M  $\text{H}_2\text{SO}_4$  electrolyte for at  
137 least two days for impregnation. The electrochemical cell assembly consisted of gold current  
138 collectors, carbon electrodes and a porous quartz fiber separator, arranged from the outermost  
139 component towards the cell center. All components were immersed in the aqueous electrolyte.

140 Electrochemical impedance spectroscopy (EIS) measurements were performed by applying an  
141 alternating current at open circuit potential (OCP) over a frequency range from 100 kHz to 1 mHz with  
142 a sinusoidal amplitude of 10 mV. The data obtained were used to generate Nyquist and Bode plots.  
143 The bulk electrolyte resistance ( $R_s$ ) and charge transfer resistance ( $R_{CT}$ ) were calculated applying Eq.  
144 (1) in the high-frequency region [36], and the equivalent series resistance (ESR) was estimated using  
145 a linear line fit in the low-frequency region of the Nyquist plot [37].

$$146 \quad \left( Z_r - R_s - \frac{R_{CT}}{2} \right)^2 + Z_i^2 = \left( \frac{R_{CT}}{2} \right)^2 \quad (1)$$

147 Cyclic voltammetry (CV) experiments were conducted using a 0 – 1 V potential window, with scan  
148 rates ranging from 5 to 1000  $\text{mV s}^{-1}$ . The specific cell capacitance ( $C_{CV,cell}$ ) was calculated using Eq.  
149 (2) where  $I$  is the current,  $v$  is the scan rate,  $\Delta V$  is the potential window, and  $m$  is the total mass of  
150 carbon used in both electrodes:

$$151 \quad C_{CV,cell} = \frac{\int I dV}{v \Delta V m} \quad (2)$$



152 The collected CV data, obtained at different scan rates, were used to estimate electric double-layer  
153 capacitance ( $C_{EDL}$ ) and pseudo-capacitance ( $C_{PSC}$ ) contributions using Trasatti's method [38]. A brief  
154 description of this method is included in the supplementary material (SM).

155 Galvanostatic charge/discharge (GCD) cycling was also performed within the same 0 – 1 V  
156 potential window, applying a specific current from 0.5 to 40 A g<sup>-1</sup>, based on the total mass of an  
157 electrode. The specific cell capacitance ( $C_{GCD,cell}$ ) was also determined from the GCD discharge curves  
158 using Eq. (3):

$$159 \quad C_{GCD,cell} = \frac{I}{\left(\frac{dV}{dt}\right)_m} \quad (3)$$

160 where  $I$  is the applied current,  $m$  is again the total mass of carbon in the electrodes, and  $dV/dt$  is the  
161 slope of the discharge curve in V s<sup>-1</sup>. The  $dV/dt$  slope was calculated in the range 0.4 – 1 V after  
162 subtraction of the corresponding potential drop ( $iR$ ) [39,40]. The specific cell capacitances obtained  
163 from CV ( $C_{CV,cell}$ ) and GCD ( $C_{GCD,cell}$ ) are based on the carbon material. Additionally, to provide a  
164 basis for comparison, the specific capacitance of a single electrode ( $C_{el}$ ) is calculated according to Eq.  
165 (4) [10]:

$$166 \quad C_{el} = 4 \cdot C_{cell} \quad (4)$$

167 which is valid for a symmetrical electrode configuration, where both electrodes are equal in terms of  
168 mass, thickness, size and material. The specific cell capacitances obtained from the GCD curves were  
169 used to calculate specific energy ( $E$ , in W·h kg<sup>-1</sup>) and power ( $P$ , in W kg<sup>-1</sup>) using Eq. (5) and (6),  
170 respectively:

$$171 \quad E = \frac{1}{2 \times 3.6} C_{GCD,cell} V^2 \quad (5)$$

$$172 \quad P = 3600 \frac{E}{t_D} \quad (6)$$

173 In these equations, the potential window is corrected by the corresponding  $iR$  drop, and  $t_D$  is the time  
174 required for complete discharge of the electrochemical cell.

### 175 3. Results and discussion

#### 176 3.1 Chemical composition

177 The chemical composition of the ACs in the bulk and on the surface of the materials was obtained  
178 by elemental analysis and XPS, respectively. **Table S1** in supplementary material (SM) shows a  
179 summary of these results as a function of the burn-off (BO) used to obtain each AC. Elemental analysis  
180 of the materials revealed some notable features with increasing BO. For instance, the use of ammonia  
181 during the HTC step resulted in the incorporation of a very similar N content, 4.6 and 4.8 wt.% in  
182 N4THC and N8THC, respectively. The N content decreased after CO<sub>2</sub> activation to values of 3.0 – 3.7  
183 wt.% for the N4THC-derived ACs, and 3.3 – 4.2 wt.% for the N8THC-derived ACs. An increase in O  
184 content was observed as well, with the undoped material exhibiting approximately 4.5 wt. %, while  
185 N4THC800 and N8THC800 had O contents close to 6.7 and 6.2 wt.%, respectively.

186 The C content in the bulk decreased after 4 h of activation with CO<sub>2</sub> at 800 °C. This decrease was  
187 more pronounced for N-doped samples, suggesting a catalytic effect during the activation process,  
188 which corresponds to the observed increase in BO for the samples subjected to 4 h CO<sub>2</sub> activation. In  
189 addition, these N-doped series exhibited a remarkable increase in O content, 13.2 and 13.1 wt.% for  
190 N4THC800-4 and N8THC800-4, respectively. Similarly, the series of carbons activated at 900 °C  
191 followed a similar trend, with a slight decrease in C content and increase in O content. In contrast, the  
192 non-activated N-doped samples (N4THC800 and N8THC800) showed a lower C content than the non-  
193 doped THC800 sample. Simultaneously, the O content increased both in the bulk material, according  
194 to elemental analysis, and at the surface, according to XPS analysis. As expected, the N content was  
195 noticeably higher in N-doped samples than in non-doped samples. However, the N content showed no  
196 significant differences between N4THC800 and N8THC800, either in bulk or in surface composition.

197 Due to the highly oxygen content in tannins, their carbonization results in a non-graphitizable  
198 carbon material [41]. Previous studies on tannin-derived carbon materials [19,20,42] have verified,  
199 through Raman spectra, the disordered nature of the carbon network in these materials, where the  
200 intensity of the D1 band is comparable to, or even greater than, that of the G band. A slight increase in  
201 the intensity ratio of the D and G bands is expected with CO<sub>2</sub> activation, along with a narrower D band  
202 [42], indicating that CO<sub>2</sub> tends to react with the most disordered or defective regions of the carbon  
203 network.

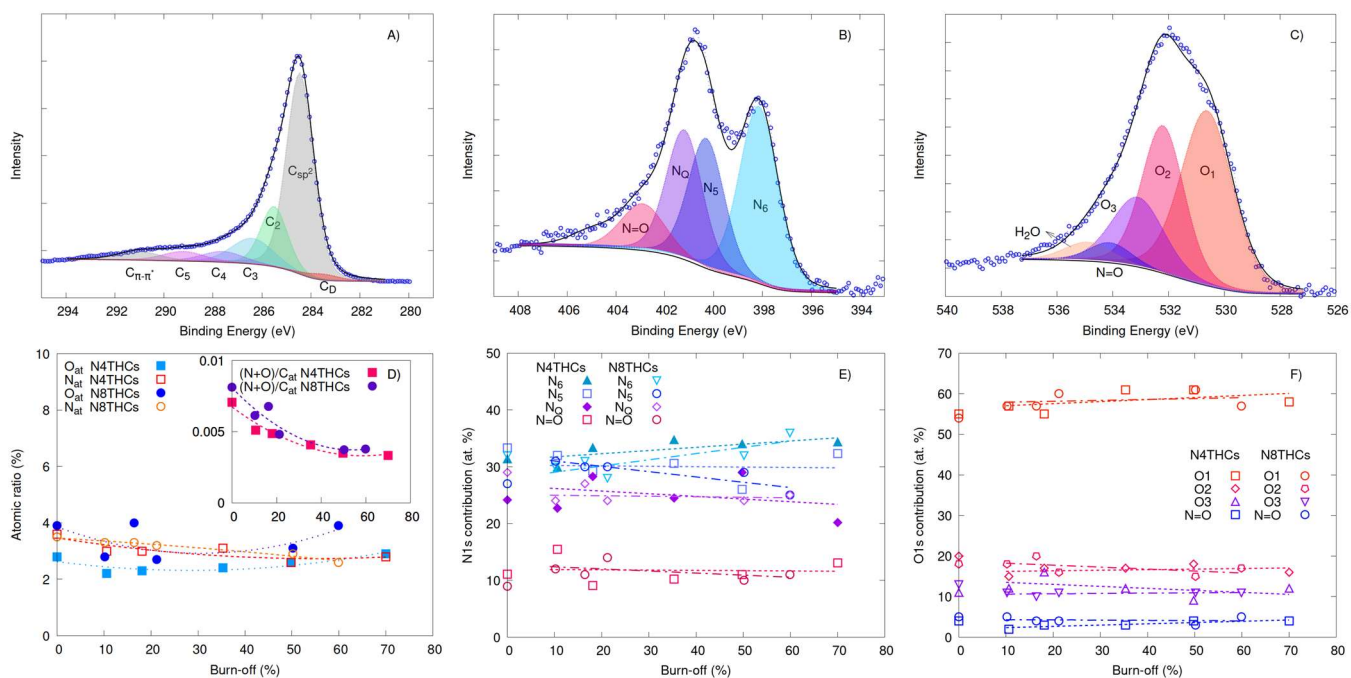
204 The XPS results presented in **Table S1** (SM) suggest that in the absence of N, the non-doped  
205 carbons (THC800 series) exhibited a similar surface chemical composition, i.e., C and O contents  
206 remained nearly the same, regardless of the BO, which increased from approximately 10 to 25 %. It is  
207 evident that the C content at the surface of the doped materials decreased compared to that of the  
208 THC800 materials due to the introduction of N functionalities by the amination process. The O content  
209 at the surface showed minimal variation between the non-doped and the two N-doped series, being  
210 slightly higher for materials derived from N8THC.

211 **Figure S1** in the supplementary material (SM) shows the XPS spectra of non-activated carbon  
212 materials, namely THC800, N4THC800, and N8THC800. The interpretation of the XPS spectra is  
213 based on previous studies [34,35,43], which provide valuable insights into this matter. For a detailed  
214 analysis of the relative atomic composition of the deconvoluted peaks in the C 1s, O 1s, and N 1s  
215 regions for tannin-derived carbons and N-doped tannin-derived carbons, please refer to **Table S2** and  
216 **Table S3** in the SM. These tables provide an overall understanding of the atomic composition of the  
217 materials. As an illustrative example, **Figure 1** shows the XPS spectra and peak deconvolution for C  
218 1s, N 1s and O 1s regions of the sample N8THC900-2. **Figure 1A** shows the C 1s spectrum and the  
219 corresponding peak deconvolution. The main peak observed at 284.4 eV, Csp<sup>2</sup>, corresponds to

220 graphitic carbon, indicating the presence of carbon atoms arranged in a planar hexagonal lattice  
221 structure. Additionally, a series of peaks associated with N or O bonding can be identified. These  
222 include the C<sub>D</sub> peak at 283.5 eV, which is associated with defects in five-atom rings and/or to the  
223 formation of graphitic carbon nitrides. The C<sub>2</sub> peak at 285.5 eV is assigned to carbon atoms outside  
224 the basal planes, exhibiting sp<sup>3</sup> hybridization. The C<sub>3</sub> peak at 286.4 eV is assigned to ether- or  
225 hydroxyl-bonded C, or to C-bonded nitrogen oxides. The C<sub>4</sub> peak at 287.6 eV indicates the presence  
226 of lactones or pyridines. The C<sub>5</sub> peak at 289.2 eV is assigned to carboxylic acids, while the Cπ-π\*  
227 peak at 291 eV is assigned to HUMO-LUMO transitions associated with the Csp<sup>2</sup> peak.

228 On the other hand, **Figure 1B** shows the XPS spectra in the N 1s region with the corresponding  
229 peak deconvolution. In the case of the non-doped carbons, the signals of the N 1s spectrum were too  
230 faint for reliable deconvolution and related analysis. Both N-doped series showed pyridinic species  
231 with the N<sub>6</sub> peak at 398.3 eV as the main contribution, followed by the N<sub>5</sub> peak at 400.2 eV, associated  
232 with pyrroles and/or pyridones. These two nitrogen functionalities are located on the edge of the carbon  
233 layers and are generally associated with an increase in the capacitance of N-doped carbon materials  
234 due to redox reactions, particularly in acidic electrolytes [44,45]. The N8THC series exhibited an  
235 increase in N<sub>6</sub> species over N<sub>5</sub> species for higher BOs, which is consistent with data reported in the  
236 literature [46,47]. However, it is important to note that this trend is also somewhat observed for the  
237 N4THC series. The presence of graphitic N, with the N<sub>Q</sub> peak at 401.2 eV, accounts for approximately  
238 26 – 34 % in the N4THC series and 26 – 32 % in the N8THC series. The presence of this nitrogen  
239 functionality is highly desired, as it improves the electronic structure of the carbon material by reducing  
240 the band gap [45]. Finally, a peak at 402.9 eV corresponding to oxygen-bound nitrogen, N=O,  
241 represents approximately 9 – 15 % in both cases, without significant variations as the BO increases.

242 **Figure 1C** shows the deconvolution of the O 1s spectrum, revealing five distinct peaks. Among  
 243 these, the quinone groups, with peak O1 at 530.9 eV, are the main ones, accounting for around 60 %.  
 244 This observation corresponds to the characteristic catechol B-ring on the pine tannin precursor [48,49].  
 245 A smaller proportion of phenol/ether groups, with peak O2 at 532.3 eV, representing around 20 %, can  
 246 be observed. Carboxylic acid groups, with peak O3 at 533.1 eV, accounting around 10 %, are also  
 247 present. Additionally, a minor percentage of nitrogen-bound oxides, with peak O=N at 534.1 eV, and  
 248 a small peak at 534.9 eV associated with chemisorbed water, can be observed. The main difference  
 249 between the materials series is a slight increase in carboxylic acid groups (O3) at the expense of  
 250 quinone-like groups (O1) for both N4THCs and N8THCs compared with THCs. This change is  
 251 attributed to the tannin amination [20,26]. However, as depicted in **Figures 1E** and **1F**, the atomic  
 252 contributions of specific N- and O-containing functional groups between the two N-doped series do  
 253 not exhibit significant variations with BO.



254  
 255 **Figure 1.** XPS spectra and deconvolution of the C 1s, N 1s and O 1s regions for sample N8THC900-  
 256 2: A) C 1s; B) N 1s; C) O 1s. D) N and O atomic ratios estimated by XPS (inset: N+O/C ratios); E)

257 contribution of N functionalities according to N 1s region deconvolution; and F) contribution of O  
258 functionalities according to O 1s region deconvolution for N4THC (dashed trend line) and N8THC  
259 series (dotted-dashed trend line).

260 The role of oxygen functionalities on the capacitive performance of carbon materials has been  
261 extensively studied [50–52]. These functionalities play a crucial role as they improve the wettability  
262 of the materials and induce Faradaic contributions through electron transfer. However, it should be  
263 noted that the presence of oxygen functionalities leads to a decrease in surface electrical conductivity  
264 [51]. Existing literature suggests that quinone groups (referred to as O1) could be of crucial importance  
265 in high-energy density capacitors. Quinones are electrochemically active thanks to reversible two-  
266 electron and proton-coupled electron transfers with hydronium ions, especially in acidic solutions,  
267 which increase Faradaic contributions [22,50,53]. Besides, quinones allow the potential window to be  
268 widened, exhibit good chemical stability, and have no negative impact on electrode cycling stability  
269 [53]. Furthermore, as suggested by previous studies [21,27], it is anticipated that there will be a change  
270 in the surface chemistry of carbon materials due to the incorporation of nitrogen into the carbon matrix  
271 during the HTC step involving ammonia. It is worth noting that no significant differences in nitrogen  
272 to carbon (N/C) and oxygen to carbon (O/C) atomic ratios were observed with ammonia concentration  
273 or physical activation conditions as the BO increased (**Figure 1D**). However, the inset in **Figure 1D**  
274 shows that the  $[(N+O)/C_{at}]$  ratio decreased slightly with increasing BO.

275

### 276 **3.2. Textural properties and morphology**

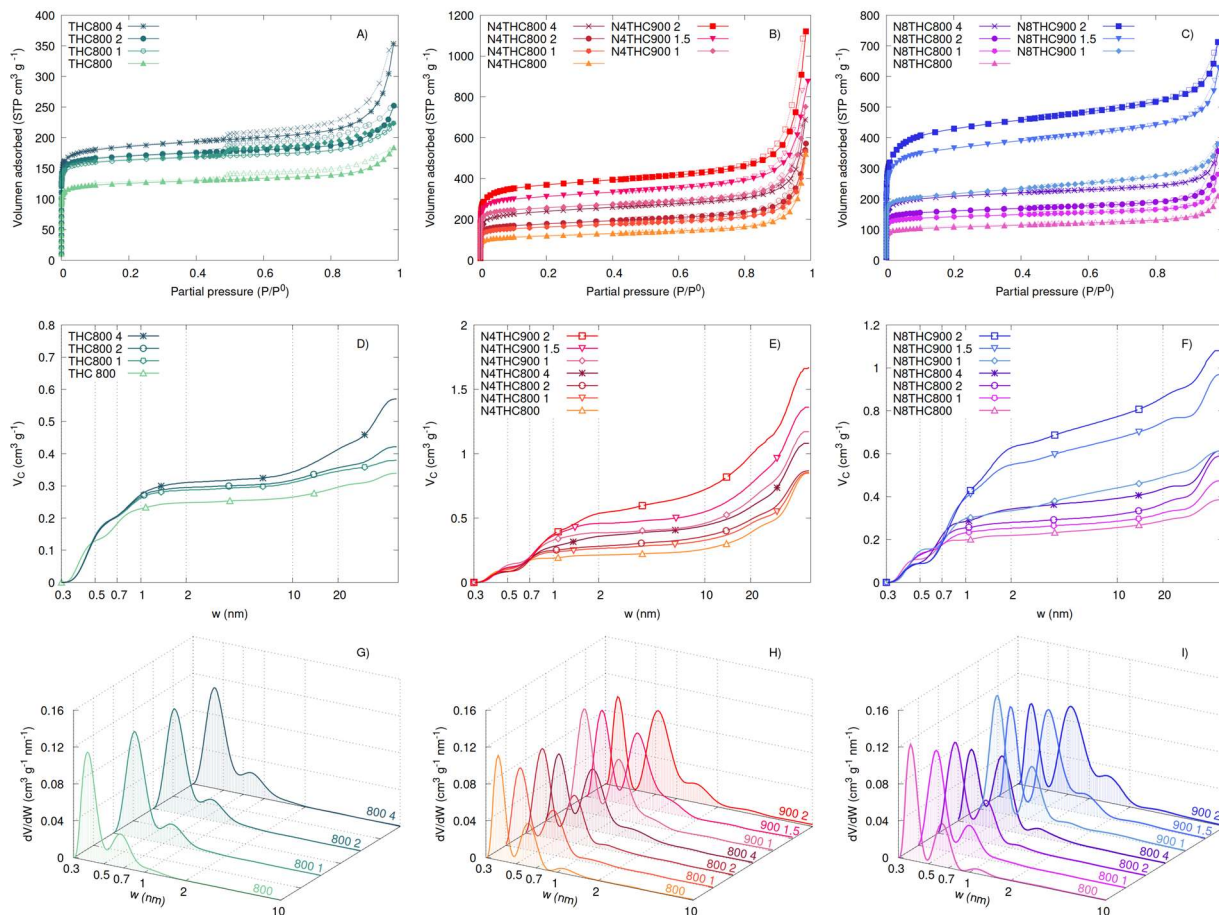
277 The TEM images in **Figure S2** (SM) provide a visual insight into the morphological changes in-  
278 duced by the use of aqueous ammonia in HTC. The composition of images includes the non-doped  
279 carbon material, called THC, alongside the two N-doped carbon materials, designated N4THC and

280 N8THC, presented in the previous section. THC consists of spherical particles of approximately 500  
281 nm in diameter. These findings are consistent with those from hydrothermal carbonization, particularly  
282 for tannins, as reported by Braghiroli et al. [54], where spherical particles ranging from 200 nm to 5  
283  $\mu\text{m}$  were observed. In contrast, both N4THC and N8THC exhibit smaller and more cohesive spherical  
284 particles, approximately 50 nm in diameter. The TEM images in the section below illustrate materials  
285 subjected to carbonization at 800 °C under  $\text{N}_2$  flow. A comparison reveals that carbonization induces  
286 the development of porosity without significantly altering the overall morphology of any of the mate-  
287 rials studied. This can be seen by comparing TEM images from **Figure S2 A** and **Figure S2 D** (SM).  
288 Despite the carbonization process, the original spherical shape and structural integrity of the materials  
289 persist, highlighting the increase in porosity without compromising the fundamental morphological  
290 features [55,56].

291  $\text{N}_2$  adsorption-desorption isotherms are shown in **Figure 2**. All materials showed a combination of  
292 type I and type II isotherms. High  $\text{N}_2$  uptake at very low  $P/P^\circ$  indicates the presence of significant  
293 microporosity [31], and as the activation time increased,  $\text{N}_2$  adsorption also increased and the knee of  
294 the isotherms gradually broadened, indicating a widening of the micropores [31,57]. Additionally, a  
295 sharp increase in  $\text{N}_2$  uptake near  $P/P^\circ = 0.97$  is observed, indicating the presence of large mesopores  
296 or condensation in interparticle voids [57]. However, significant differences can be observed in the  $\text{N}_2$   
297 isotherms across the various materials. In particular, those for non-doped carbons (**Figure S3A**, SM)  
298 showed a type H4 hysteresis loop, which closes near  $P/P^\circ = 0.5$ . In contrast, those for carbons derived  
299 from N4THC (**Figure S3B**, SM) displayed an H3-type loop, which is often associated with capillary  
300 condensation [57]. Interestingly, the  $\text{N}_2$  isotherms of the N8THC series (**Figure S3C**, SM) showed no  
301 noticeable loop. The  $\text{H}_2$  adsorption isotherms of non-activated and  $\text{CO}_2$ -activated carbons can be found



302 in **Figure S4** (SM), and for further details, the textural parameters estimated from the N<sub>2</sub> and H<sub>2</sub> iso-  
 303 therms at -196 °C are reported in **Table S4** in SM. The  $A_{\text{BET}}$  is presented solely for comparison with  
 304 other studies in the literature, given the well-known limitations of the BET method [58].



305  
 306 **Figure 2.** A, B, C) N<sub>2</sub> adsorption (solid symbols) – desorption (empty symbols) isotherms at -196 °C;  
 307 D, E, F) cumulative; and G, H, I) differential volume pore size distributions (PSDs) estimated by 2D-  
 308 NLDFIT-HS: THC series (A, D, G), N4THC series (B, E, H), and N8THC series (C, F, and I).

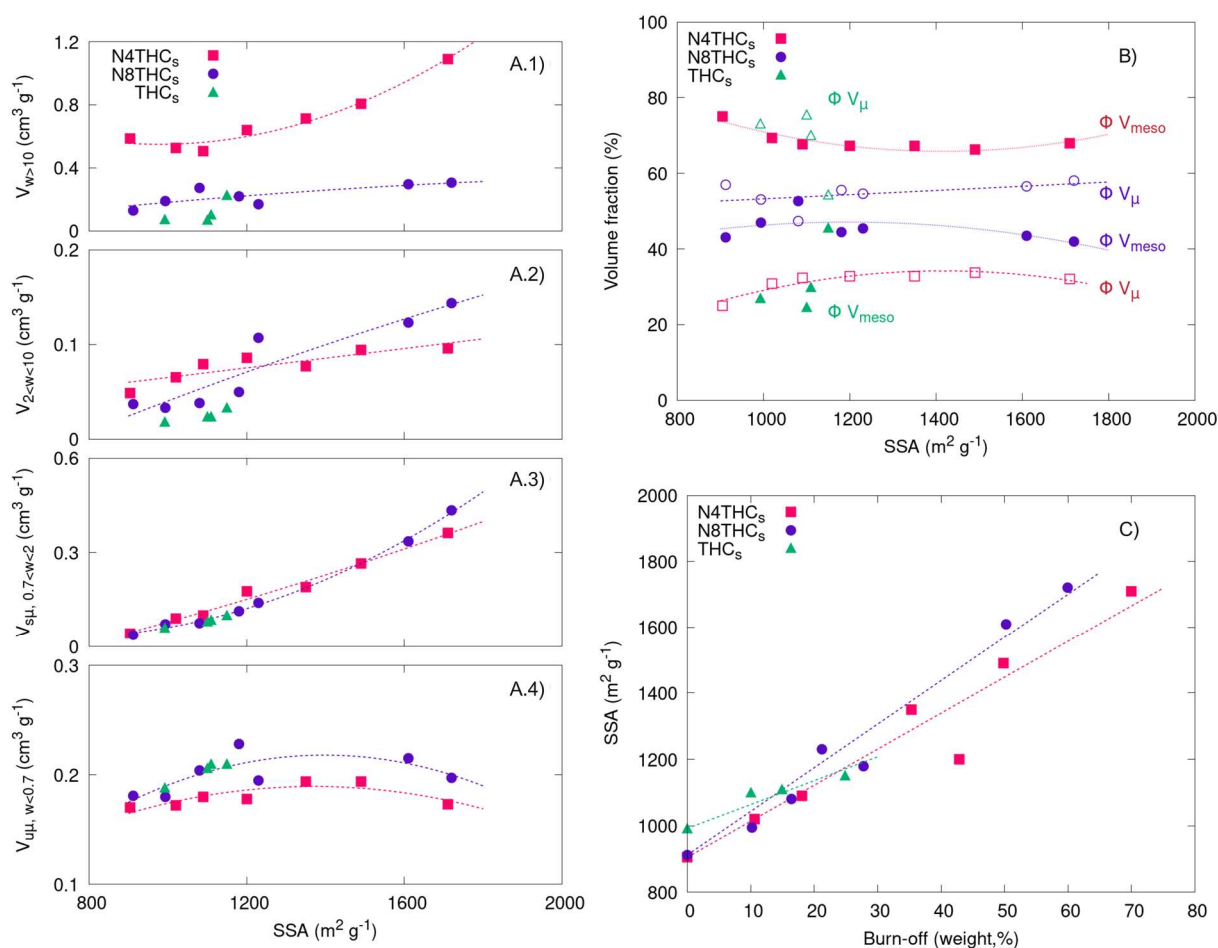
309  
 310 As can be observed in **Figure 2G, 2H** and **2I**, all carbon materials have a similar pore size distribu-  
 311 tion (PSD) with peaks centered on ultra-micropores, which is a characteristic feature of tannin-derived  
 312 carbon materials [19,20,42]. For instance, two main peaks are observed on all the materials, one at ca.

313 0.4 nm and another of much less intensity at ca. 0.7 nm. For both N4THC and N8THC series, as  
314 activation conditions become more severe, a broadening of the ultra-micropores occurs, leading to a  
315 widening of the aforementioned peaks. The appearance of a third broad peak between 1 and 2 nm is  
316 observed under the most severe activation conditions (**Figure 2H** and **2I**). It should be noted that,  
317 although slightly, this third peak between 1 and 2 nm is also observed for non-activated N-doped sam-  
318 ples (N4THC800 and N8THC800), suggesting that N could be responsible for promoting the formation  
319 of larger micropores.

320 The ultra-micropore volume followed a negative parabolic curve as the BO increase, as can be  
321 observed in **Figure 3A.4**, which is a well-documented behavior for ultra-micropores [29,59]. In  
322 addition, **Figure 3A.3** shows the monotonic increase of the supermicropore volume ( $V_{\text{su}}$ ) as a function  
323 of SSA for both N-doped series, with  $V_{\text{su}}$  increasing to  $0.36 \text{ cm}^3 \text{ g}^{-1}$  for N4THC900-2 and  $0.43 \text{ cm}^3 \text{ g}^{-1}$   
324 <sup>1</sup> for N8THC900-2. Mesopores are widely distributed throughout their range of pore sizes, without  
325 significant peaks, but they represent a significant fraction of the total pore volume on both N-doped  
326 carbon materials series, as is observed in **Figure 3B**. To clarify the differences between the N4THC  
327 and N8THC series, the mesopores region was divided into two zones, namely the range of wide  
328 mesopores,  $10 < w < 50 \text{ nm}$ , and the range of narrow mesopores,  $2 < w < 10 \text{ nm}$ , as observed in **Figure**  
329 **3A.1** and **A.2**, respectively. The samples from the N4THC series have a substantial volume increase  
330 in the range of wide mesopores, increasing with SSA from ca.  $0.64 \text{ cm}^3 \text{ g}^{-1}$  (N4THC800) to a maximum  
331 of  $1.19 \text{ cm}^3 \text{ g}^{-1}$  (N4THC900-2). However, in the range of narrow mesopores (**Figure 3A.2**), the  
332 increase in volume is slightly noticeable. In contrast, the mesopore volume for the N8THC series  
333 changes significantly in the range of narrow mesopores, from  $0.04$  to  $0.14 \text{ cm}^3 \text{ g}^{-1}$ , while for wider  
334 mesopores it increases from  $0.13$  to  $0.31 \text{ cm}^3 \text{ g}^{-1}$ . Although the reasons for these differences in porosity

335 development are not evident, they are crucial in explaining the contrasting electrochemical behavior  
 336 of the two series, as discussed in the next section.

337 Finally, **Figure 3C** shows the influence of BO on specific surface area (SSA), revealing a linear  
 338 relationship between BO and SSA. The non-activated materials exhibited relatively low SSA values,  
 339 with 990, 905, and 910  $\text{m}^2 \text{g}^{-1}$  for THC800, N4THC800 and N8THC800, respectively. As the BO  
 340 increased due to the intensification of activation conditions, the SSA followed the same trend. For  
 341 instance, N4THC900-2 and N8THC900-2, activated at 900 °C for 2 hours, reached values of 1710 and  
 342 1720  $\text{m}^2 \text{g}^{-1}$ , respectively, corresponding to a BO of ca. 70 % and 60 %, respectively.



343  
 344 **Figure 3.** Volumes of: A.1) wide mesopores ( $10 < w < 50$  nm); A.2) narrow mesopores ( $2 < w < 10$   
 345 nm); A.3) supermicropores ( $V_{s\mu}$ ,  $0.7 < w < 2$  nm); and A.4) ultramicropores ( $V_{u\mu}$ ,  $w < 0.7$  nm) as a

346 function of SSA. B) Volume fractions of micropores and mesopores ( $\Phi V_{\mu}$  and  $\Phi V_{\text{meso}}$ , respectively)  
347 as a function of SSA. C) SSA as a function of burn-off (BO).

348

### 349 3.3. Electrochemical performance

350 Electrochemical impedance spectroscopy (EIS) was used as a technique to evaluate the kinetic and  
351 mass transport performance of the carbon materials as electrodes for ECs using 1 M H<sub>2</sub>SO<sub>4</sub> as electro-  
352 lyte. **Figure 4A** and **4B** show the Nyquist plot obtained in the two-electrode cell system for representa-  
353 tive samples, while the Nyquist and Bode plots for all the materials are shown in **Figure S5** (SM). It  
354 can be seen that the graph did not start at the origin, but with a shift close to 1.8  $\Omega \text{ cm}^2$  along the  $Z_r$   
355 axis, associated with the bulk electrolyte resistance ( $R_s$ ) [60]. Notable differences can be observed  
356 between samples, with the behavior of non-doped carbon materials being particularly evident. Taking  
357 THC800-4 as example for undoped materials, it is characterized by a significant charge transfer re-  
358 sistance ( $R_{CT}$ ) indicated by a distinct semicircular area. In addition, the sample presented a semi-infi-  
359 nite Warburg impedance behavior in the region of mass transfer control, evidenced by the slope close  
360 to 45° at high values of  $Z_r$  (**Figure 4B**), which indicates a high resistance to ion diffusion from the bulk  
361 to the surface of this material, with a non-capacitance behavior. The subpar electrochemical perfor-  
362 mance of undoped materials can be attributed to their surface chemistry, characterized by a significant  
363 presence of carboxylic acid species, as revealed by the XPS results in **Table S3** (SM). These carboxylic  
364 acid species have been demonstrated to hinder the formation of the electric double layer, thereby lim-  
365 iting electrical storage [61,62].

366

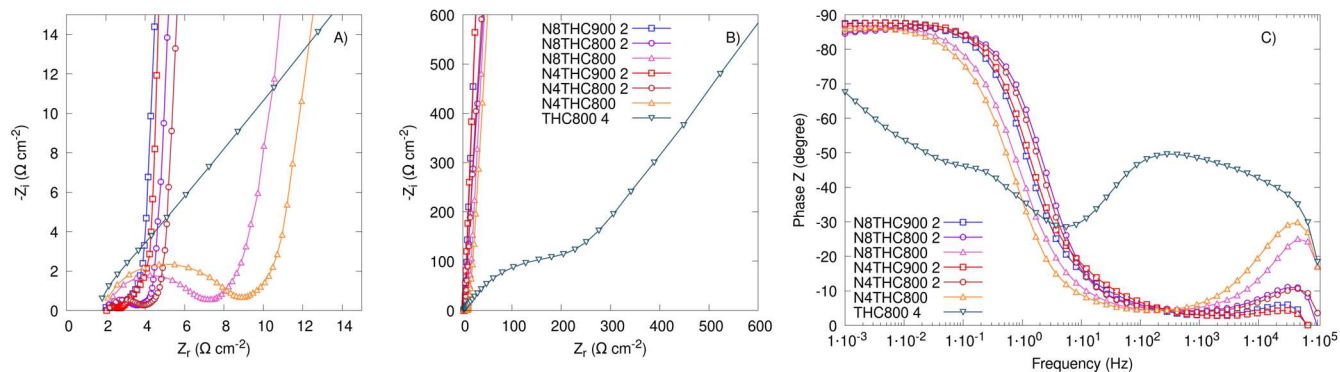
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368

369

370 In contrast, the N-doped carbon materials exhibited a finite-space Warburg impedance, characterized  
371 by a straight line at high frequencies and a phase angle close to  $90^\circ$ , as shown the Bode plot in **Figure**  
372 **4C**, which is typical of capacitive systems. Furthermore, the equivalent series resistance (ESR) can  
373 serve as a global parameter for comparing materials. For instance, THC800-4 had an ESR value of  
374 approximately  $251.5 \Omega \text{ cm}^{-2}$ , which is almost two orders of magnitude higher than values estimated  
375 for N-doped carbon materials. The materials not submitted to physical activation, N4THC800 and  
376 N8THC800, had similar ESR values of ca. 11.4 and ca.  $10.0 \Omega \text{ cm}^{-2}$ . It is worth noting that, in both  
377 cases, around 68 % and 63 % of the ESR values could be attributed to the  $R_{CT}$ , after subtracting the  
378 electrolyte resistance value ( $R_s$ ) to calculate the respective percentages. In this context, the physical  
379 activation process resulted in a decrease in materials electrical resistivity by improving charge transfer,  
380 as evidenced by the significant reduction in the arc size shown in **Figure 4A**. For instance, N4THC900-  
381 2 and N8THC900-2, which underwent the most severe activation conditions in their respective series,  
382 had an ESR of ca. 4.2 and  $3.8 \Omega \text{ cm}^{-2}$ , respectively, with  $R_{CT}$  accounting for only 37 % and 45 % of  
383 the total ESR. The overall reduction in ESR of N-doped carbon materials can be attributed to carbon  
384 surface modifications resulting from tannin amination, which improves water affinity, as discussed  
385 above. In addition, pore widening and improved pore connectivity, attributed to the higher degree of  
386 activation [29], contributed to a better charge transfer process but also to better mass transfer (ion  
387 diffusion), as evidenced by the absence of Warburg impedance for N-doped and activated samples.

388



389

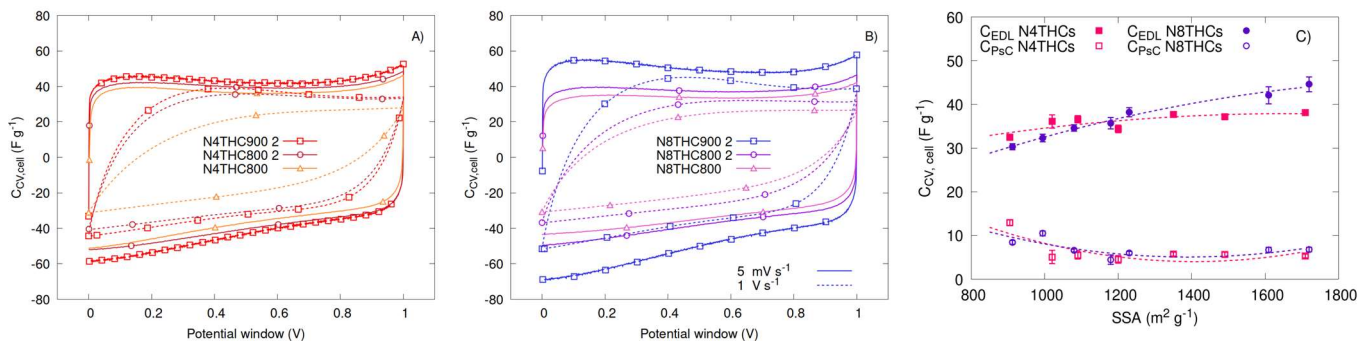
390 **Figure 4.** EIS results for representative N-doped and non-doped samples. For comparison purposes,  
 391 THC800-4 is selected as the reference: A) Nyquist plot; B) large-scale Nyquist plot; C) Bode plot.

392

393 Cyclic voltammetry (CV) was conducted at scan rates from  $5 \text{ mV s}^{-1}$  to  $1 \text{ V s}^{-1}$ , using a potential  
 394 window of  $0 - 1 \text{ V}$ , which was chosen because of the use of an aqueous electrolyte. The results are  
 395 presented in **Figure 5**, and further information is provided in **Figure S6** (SM). The non-doped carbon  
 396 materials, as observed in the voltammograms of THC800-4 shown in **Figure S6A** (SM), did not exhibit  
 397 capacitive behavior, even at low scan rates. However, the amination process improved the electro-  
 398 chemical performance of the tannin-derived carbon materials (**Figures S6B** and **S6C**), in line with the  
 399 EIS results discussed above. **Figure 5A** and **5B** show CV curves for representative carbon materials  
 400 from the N4THC and N8THC series, respectively. A quasi-rectangular shape at a scan rate of  $5 \text{ mV} \cdot \text{s}^{-1}$   
 401  $^1$  is observed on both cases, indicating near-ideal capacitive behavior. As the scan rate increased, the  
 402 curves changed shape due to the gradual decrease in Faradaic contributions, so that the current aroused  
 403 mainly from the formation of the electric double layer. In fact, at  $5 \text{ mV} \cdot \text{s}^{-1}$  the specific cell capacitance  
 404 based on carbon material ( $C_{CV,cell}$ ), for N4THC800 and N8THC800 was approximately  $37 \text{ F} \cdot \text{g}^{-1}$  and  
 405  $34 \text{ F} \cdot \text{g}^{-1}$  (the electrode capacitance, also based on carbon material,  $C_{CV,el}$  is  $148 \text{ F} \cdot \text{g}^{-1}$  and  $136 \text{ F} \cdot \text{g}^{-1}$ ),  
 406 respectively, with 43 % and 50 % retention, respectively, when tested at  $1 \text{ V} \cdot \text{s}^{-1}$ . The activation process  
 407 improved  $C_{CV,cell}$  values at low scan rates, with N4THC900-2 and N8THC900-2 exhibiting capacitance

408 values of  $43 \text{ F}\cdot\text{g}^{-1}$  ( $C_{CV,el} = 172 \text{ F}\cdot\text{g}^{-1}$ ) and  $51 \text{ F}\cdot\text{g}^{-1}$  ( $C_{CV,el} = 204 \text{ F}\cdot\text{g}^{-1}$ ), respectively, at  $5 \text{ mV}\cdot\text{s}^{-1}$ . Ad-  
 409 ditionally, the capacitance retention reached remarkable values close to 65 % for both series when  
 410 tested at a high scan rate of  $1 \text{ V}\cdot\text{s}^{-1}$ .

411



412

413 **Figure 5.** Cell capacitance ( $C_{CV,cell}$ ) obtained by cyclic voltammetry at scan rates of  $5 \text{ mV}\cdot\text{s}^{-1}$  (solid  
 414 line) and  $1 \text{ V}\cdot\text{s}^{-1}$  (dashed line) for: A) N4THC-; and B) N8THC-derived carbons. C) Electric double  
 415 layer capacitance ( $C_{EDL}$ ) and pseudocapacitance ( $C_{PSC}$ ) estimated by Trassatti's method for the two  
 416 series of N-doped carbon materials.

417 However, despite the relatively similar behavior in capacitance resulting from the activation process,  
 418 there are still interesting features worth highlighting. In this context, Trassatti's method [38] was used  
 419 to differentiate the double-layer capacitance ( $C_{EDL}$ ) from the Faradaic contribution commonly referred  
 420 to as pseudocapacitance ( $C_{PSC}$ ). The dependence of the capacitance on the square root of the scan rate  
 421 and its inverse ( $v^{1/2}$  and  $v^{-1/2}$ , respectively) for the whole series is shown in **Figure S7** (SM), and a  
 422 brief explanation of Trassatti's method is given in the SM, with the main results plotted in **Figure 5C**  
 423 as a function of SSA. The pseudocapacitance arises from surface functionalities present in the material,  
 424 which can improve mass or charge transfer [63]. It can be noticed that  $C_{PSC}$  has comparable values for  
 425 both series, displaying a similar downward trend, followed by a stabilization of its contribution. This

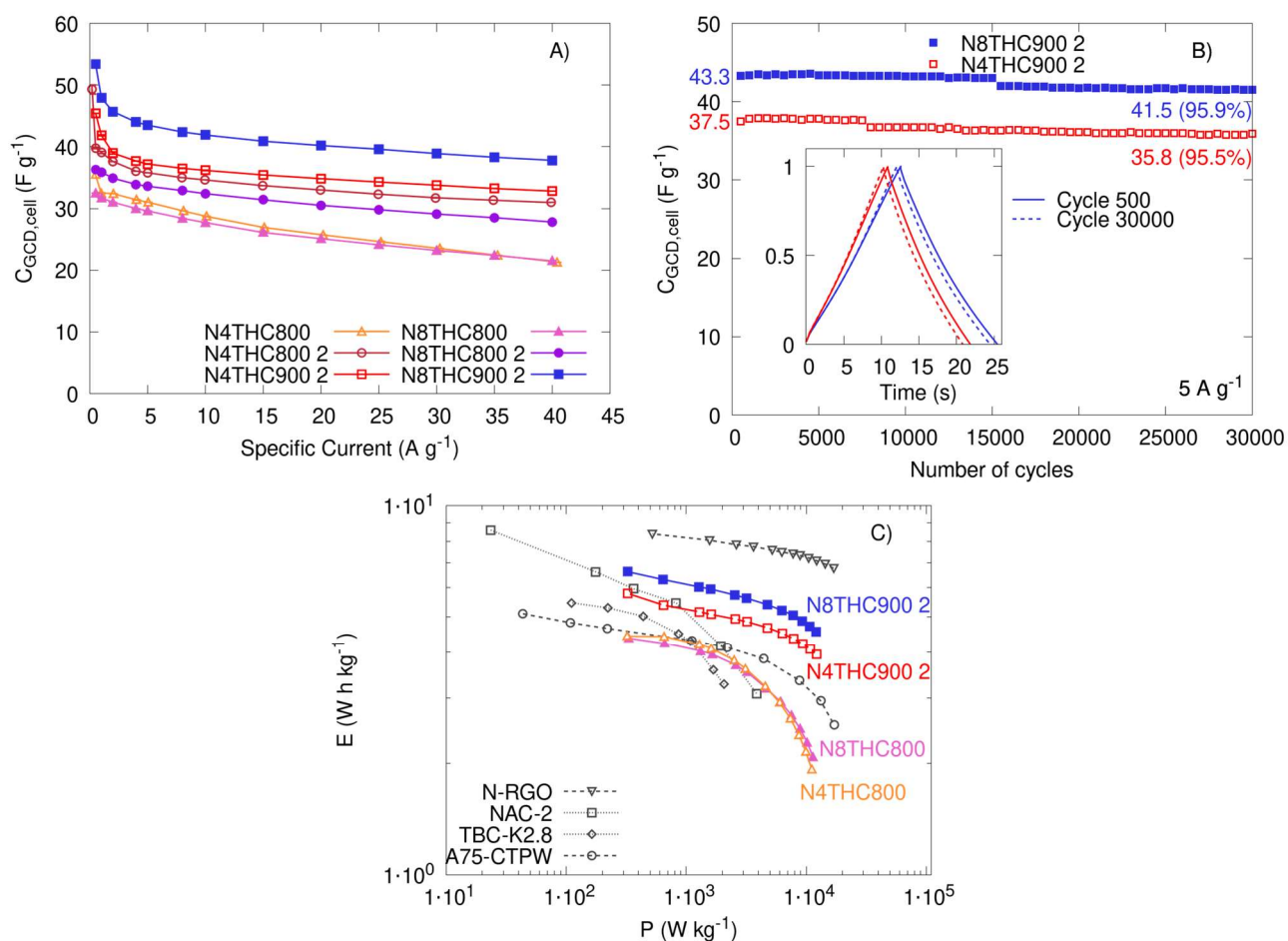
426 behavior is a consequence of the chemical evolution of the carbon surface, as discussed previously  
427 (**Figure 1D**).

428 When considering  $C_{EDL}$ , which originates from the textural properties of the carbon materials [64], it  
429 is essential to analyze the differences between the two series. Despite the noticeable increase in surface  
430 area for the N4THC series, from  $905 \text{ m}^2 \text{ g}^{-1}$  to  $1710 \text{ m}^2 \text{ g}^{-1}$  (see again **Table S4**, SM) for the most  
431 severe activation conditions, only a marginal enhancement in  $C_{EDL}$  was observed. This suggests a sat-  
432 uration of the surface, resulting in a slight increase in  $C_{EDL}$  from 32 to  $38 \text{ F g}^{-1}$ . In contrast, the N8THC  
433 series, although having similar values of surface area, exhibited a significant increase in  $C_{EDL}$  from 30  
434 to  $45 \text{ F g}^{-1}$ . To understand this discrepancy between  $C_{EDL}$  trends for the N4THC and N8THC series, it  
435 is necessary to refer to the results shown in **Figure 2** and **Figure 3**. The PSD for both N-doped series,  
436 as can be seen in **Figures 2H** and **2I**, is similar in the micropore range, which is assumed the key to  
437 ion adsorption and efficient double-layer formation. However, although this has been extensively  
438 demonstrated [8,64–66], the influence of mesopores is often overlooked. Comparing the data in **Figure**  
439 **3A**, it becomes clear that, at least for the electrolyte used in this study, the  $C_{EDL}$  improvement of  
440 N8THCs may be attributed to the development of narrow mesopores. In contrast, the N4THC series  
441 showed no significant development of mesopores in this size range.

442 Similar trends are observed in galvanostatic charge-discharge (GCD) tests performed by varying the  
443 applied specific current from 0.5 to  $40 \text{ A g}^{-1}$ . **Figure S8** (SM) shows the original charge-discharge  
444 curves within the 0 – 1 V potential window and at a specific current of  $5 \text{ A g}^{-1}$ , while **Figure 6A** shows  
445 the calculated specific cell capacitance obtained from the corresponding discharge curves ( $C_{GCD,cell}$ ).  
446 Remarkably, all curves, even at high specific current values, exhibited a triangular shape indicating  
447 capacitive behavior with a low potential drop ( $iR$ ). At a specific current of  $0.5 \text{ A g}^{-1}$ ,  $C_{GCD,cell}$  increased  
448 from  $36 \text{ F g}^{-1}$  ( $C_{GCD,el} = 144 \text{ F g}^{-1}$ ) for N4THC800 to  $45 \text{ F g}^{-1}$  ( $C_{GCD,el} = 180 \text{ F g}^{-1}$ ) for N4THC900-2.



449 As with the CV results, a significant increase in capacitance could be observed for the N8THC series  
450 compared with the N4THC series. Indeed, for the N8THC series,  $C_{\text{GCD,cell}}$  ranged from  $32 \text{ F}\cdot\text{g}^{-1}$   
451 ( $C_{\text{GCD,el}}= 128 \text{ F}\cdot\text{g}^{-1}$ ) to  $53 \text{ F}\cdot\text{g}^{-1}$  ( $C_{\text{GCD,el}}= 212 \text{ F}\cdot\text{g}^{-1}$ ) for the same activation conditions. Interestingly,  
452 as discussed above, there were no notable differences in N or O contents between the two series (**Table**  
453 **S1**, SM) or in the proportions of surface functionalities (**Figure 1E** and **Figure 1F**). Therefore, the  
454 observed increase in  $C_{\text{GCD,cell}}$  could, once again, be attributed to the development of narrow mesopores.  
455 It is worth noting that while the capacitance values obtained by GCD, at low specific current, and CV,  
456 at low scan rate, were comparable, the  $C_{\text{GCD,cell}}$  retention was higher than that obtained from CV tests.  
457 For instance, N4THC900-2 and N8THC900-2, the best performing materials in their respective series,  
458 demonstrated impressive retention rates in GCD tests. At a specific current of  $5 \text{ A g}^{-1}$ , N4THC900-2  
459 retained 82 % of its initial capacitance, while N8THC900-2 retained 81 %. Even at a higher specific  
460 current of  $40 \text{ A g}^{-1}$ , both materials maintained a high level of stability, with N4THC900-2 retaining 72  
461 % of its initial capacitance and N8THC900-2 retaining 71 %. Therefore, to assess their cycling stabil-  
462 ity, N4THC900-2 and N8THC900-2 were subjected to 30,000 continuous GCD cycles at a specific  
463 current of  $5 \text{ A g}^{-1}$ . **Figure 6B** depicts the cycling stability of both carbon materials, demonstrating a  
464 remarkable retention of ca. 96 % for N4THC900-2 and N8THC900-2 relative to their initial capaci-  
465 tance.  
466



467

468 **Figure 6.** A) Specific cell capacitances calculated from GCD curves ( $C_{\text{GCD,cell}}$ ) for N4THC and  
 469 N8THC series; B) cycling stability of N8THC900-2 and N4THC900-2 at  $5 \text{ A g}^{-1}$ , the inset correspond-  
 470 ing to GCD curves for cycle #500 (solid line) and cycle #30,000 (dashed line); C) Ragone plot calcu-  
 471 lated from GCD measurements from 2 to  $40 \text{ A g}^{-1}$  and comparison with the literature (N-RGO [44],  
 472 NAC-2 [67], TBC-K2.8 [19], A75-CTPW [9]).

473 The inset in **Figure 6B** reveals that the triangular-shaped charge-discharge curve remained largely  
 474 unchanged after the cycling test, indicating the excellent stability of the surface functionalities of these  
 475 materials. It is worth noting that although pseudocapacitive contributions represented approximately  
 476 10 % of the total capacitance, as suggested by the CV results discussed earlier (**Figure 5C**), they had  
 477 no significantly impact on the stability of the materials.

478 The Ragone plot in **Figure 6C** shows the electrochemical performance of N4THC900-2 and  
479 N8THC900-2. For comparison purposes, this figure also includes electrochemical characterization  
480 data for other N-doped and tannin-derived carbons reported in the open literature [9,44,67,68]. As  
481 anticipated from the previous results, the material exhibiting the best performance was N8THC900-2,  
482 with a specific energy of approximately  $6.6 \text{ W}\cdot\text{h}\cdot\text{kg}^{-1}$  at a specific power of around  $3240 \text{ W}\cdot\text{kg}^{-1}$ . The  
483 specific energy gradually decreased as the specific power increased, reaching approximately  $4.6$   
484  $\text{W}\cdot\text{h}\cdot\text{kg}^{-1}$  at about  $12100 \text{ W}\cdot\text{kg}^{-1}$ . Although the specific energy of these ACs cannot exceed that ob-  
485 tained with N-doped reduced graphene oxide (N-RGO,  $A_{\text{BET}} = 355 \text{ m}^2 \text{ g}^{-1}$ ,  $\text{O}_{\text{XPS}} = 12.6 \text{ at. \%}$ ,  $\text{N}_{\text{XPS}} =$   
486  $3.0 \text{ at. \%}$ ) [44], it is noteworthy that they outperformed other N-doped ACs [67,68], especially at high  
487 rates. Similarly, an improvement in the electrochemical performance of N8THC900-2 ( $\text{SSA} = 1720$   
488  $\text{m}^2 \text{ g}^{-1}$ ,  $\text{O}_{\text{XPS}} = 2.6 \text{ at. \%}$ ,  $\text{N}_{\text{XPS}} = 3.9 \text{ at. \%}$ ) was observed compared to previously reported non-doped  
489 tannin-derived ACs obtained by  $\text{CO}_2$  activation ( $\text{SSA} = 1614 \text{ m}^2 \text{ g}^{-1}$ ,  $\text{O}_{\text{XPS}} = 5.0 \text{ at. \%}$ ) [9] and by KOH  
490 activation (TBC-K2.8:  $\text{SSA} = 2190 \text{ m}^2 \text{ g}^{-1}$ ,  $\text{O}_{\text{XPS}} = 7.5 \text{ at. \%}$ ) [19], all tested under similar conditions,  
491 confirming the benefits of N-doping in enhancing the electrochemical performance of materials.

492

493 **Conclusion**

494 This study shows that nitrogen doping by hydrothermal carbonization in ammonia not only changed  
495 the surface chemistry of the resulting carbon materials but also improved their textural properties after  
496 CO<sub>2</sub> activation. These changes enhanced the electrochemical performance of the N-doped activated  
497 carbons (ACs) when used as supercapacitor electrodes. The concentration of ammonia used had no  
498 significant impact on the N content nor the nature of the surface chemistry of the carbon materials.  
499 However, it did affect the development of textural properties during CO<sub>2</sub> activation, with a greater  
500 effect observed at higher ammonia concentration. The best-performing material achieved a specific  
501 electrode capacitance value, based on carbon material, of 212 F g<sup>-1</sup> at 0.5 A g<sup>-1</sup> and a capacitance  
502 retention of 71 % at 40 A g<sup>-1</sup>. It also demonstrated outstanding cycling stability with capacitance re-  
503 tention of ca. 96 % after 30,000 cycles. These N-doped ACs outperformed similar carbon materials,  
504 particularly at high output power, demonstrating that N-doped ACs derived from tannins are suitable  
505 electrode materials for electrochemical capacitors, especially when high-rate performance and remark-  
506 able electrochemical stability are required.

507

508 **Acknowledgments**

509 O. Pinto-Burgos thanks ANID - Subdirección de Capital Humano/Doctorado, # 2019/21190633. V.  
510 Fierro, A. Celzard, and J. Castro-Gutiérrez acknowledge the financial support of the European Re-  
511 gional Development Fund (ERDF) through the TALiSMAN and TALiSMAN2 projects. P.S. Poon and  
512 J. Matos thank ANID-FONDEF project 19I10003 and ANID-FONDECYT project 1220228. J. Matos  
513 also thanks ANID-ANILLO project ATE220014.

514

515 **Declaration of competing interest**

516 The authors declare that they have no known competing financial interests or personal relationships  
517 that could have appeared to influence the work reported in this paper.

518

519 **Authors' contributions**

520 **O. Pinto-Burgos** contributed to synthesis, characterization, textural and electrochemical testing,  
521 analysis, writing and revision. **J. Castro-Gutierrez** contributed to characterization, analysis, data  
522 curation and revision. **P.S. Poon** contributed to synthesis and editing. **M.T. Izquierdo** contributed to  
523 XPS characterization. **A. Celzard** contributed to analysis, data curation and editing. **V. Fierro** and **J.**  
524 **Matos** contributed to conceptualization, data curation, analysis, writing and revision.

525

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734 **Captions of Figures**

735 **Figure 1.** XPS spectra and deconvolution of the C 1s, N 1s and O 1s regions for sample N8THC900-  
736 2: A) C 1s; B) N 1s; C) O 1s. D) N and O atomic ratios estimated by XPS (inset: N+O/C ratios); E)  
737 contribution of N functionalities according to N 1s region deconvolution; and F) contribution of O  
738 functionalities according to O 1s region deconvolution for N4THC (dashed trend line) and N8THC  
739 series (dotted-dashed trend line).

740 **Figure 2.** A, B, C) N<sub>2</sub> adsorption (solid symbols) – desorption (empty symbols) isotherms at -196 °C;  
741 D, E, F) cumulative; and G, H, I) differential volume pore size distributions (PSDs) estimated by 2D-  
742 NLDFT-HS: THC series (A, D, G), N4THC series (B, E, H), and N8THC series (C, F, and I).

743 **Figure 3.** Volumes of: A.1) wide mesopores ( $10 < w < 50$  nm); A.2) narrow mesopores ( $2 < w < 10$   
744 nm); A.3) supermicropores ( $V_{\text{sm}}, 0.7 < w < 2$  nm); and A.4) ultramicropores ( $V_{\text{um}}, w < 0.7$  nm) as a  
745 function of SSA. B) Volume fractions of micropores and mesopores ( $\Phi V_{\mu}$  and  $\Phi V_{\text{meso}}$ , respectively)  
746 as a function of SSA. C) SSA as a function of burn-off (BO).

747 **Figure 4.** EIS results for representative N-doped and non-doped samples. For comparison purposes,  
748 THC800-4 is selected as the reference: A) Nyquist plot; B) large-scale Nyquist plot; C) Bode plot.

749 **Figure 5.** Cell capacitance ( $C_{\text{CV,cell}}$ ) obtained by cyclic voltammetry at scan rates of  $5 \text{ mV}\cdot\text{s}^{-1}$  (solid  
750 line) and  $1 \text{ V}\cdot\text{s}^{-1}$  (dashed line) for: A) N4THC-; and B) N8THC-derived carbons. C) Electric double  
751 layer capacitance ( $C_{\text{EDL}}$ ) and pseudocapacitance ( $C_{\text{PSC}}$ ) estimated by Trassatti's method for the two  
752 series of N-doped carbon materials.

753 **Figure 6.** A) Specific cell capacitances calculated from GCD curves ( $C_{\text{GCD,cell}}$ ) for N4THC and  
754 N8THC series; B) cycling stability of N8THC900-2 and N4THC900-2 at  $5 \text{ A g}^{-1}$ , the inset correspond-

755 ing to GCD curves for cycle #500 (solid line) and cycle #30,000 (dashed line); C) Ragone plot calcu-  
756 lated from GCD measurements from 2 to 40 A g<sup>-1</sup> and comparison with the literature (N-RGO [44],  
757 NAC-2 [67], TBC-K2.8 [19], A75-CTPW [9]).

758