

# Nitrogen modification of highly porous carbon for improved supercapacitor performance

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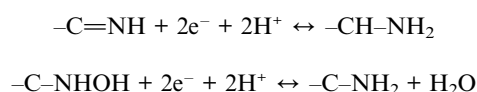
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Nitrogen is added to porous carbon, in both the bulk network as heteroatoms and coated on the surface of the pores, to increase the capacitance of electrodes for supercapacitor applications. Surface modification increases the amount of nitrogen by four times when compared to unmodified carbon that only contains nitrogen in the bulk. Pyrolysis of the modified carbon at a lower temperature also retains up to three times more nitrogen than high temperature pyrolysis. The surface modification dramatically improves the wetting behavior of the porous carbon and produces a capacitance that is nearly twice that of the unmodified carbon through a combination of double-layer formation and pseudocapacitive reactions.

## Introduction

Pseudocapacitance can be induced through the introduction of foreign elements in highly porous carbon used for electric double-layer supercapacitors.<sup>1</sup> These elements modify the electron donor–acceptor properties of the carbon, which in turn provide pseudocapacitive Faradaic reactions.<sup>2,3</sup> Some recent research has focused on substituting heteroatoms into the graphene layers of the carbon network, frequently concentrating on oxygen because it closely associates with the carbon surface.<sup>3</sup> Often the oxygen functionalities are acidic in nature, inducing electron acceptor characteristics into the carbon material.<sup>4</sup> While the use of oxygen heteroatoms has proven to be beneficial in aqueous electrolytes, they would be detrimental in organic electrolytes due to irreversible reactions between oxygen and the electrolyte ions.

Recently, there has also been research into introducing nitrogen heteroatoms into the carbon network. Nitrogen is known for its alkaline character, providing electron donor characteristics to the carbon.<sup>4</sup> A number of studies have reported improved capacitance by using carbon enriched with nitrogen in aqueous electrolytes.<sup>5–10</sup> It is believed that nitrogen heteroatoms contribute pseudocapacitance through Faradaic reactions, such as the following proposed by Frackowiak<sup>3</sup> in acidic medium:



Adding nitrogen to the porous carbon network can be done in a number of different ways. One is to use nitrogen-containing

precursors to obtain a carbon with nitrogen heteroatoms. Carbon prepared from melamine, an inexpensive polymer with 45 wt% nitrogen, was found to produce pseudocapacitance when tested in sulfuric acid.<sup>5</sup> Other precursors include pyridine, quinoline, and polyaniline.<sup>8–12</sup> Ammoxidation, which involves heating samples in a mixture of ammonia and air, is another technique used to introduce nitrogen heteroatoms at different stages in the synthesis of activated carbon.<sup>4,13</sup> An improvement in capacitance of up to *ca.* 10% was noticed for carbons that were subjected to ammoxidation after pyrolysis but before activation. It was observed, however, that all samples that underwent ammoxidation have less developed porous structure and total surface area than unmodified carbon. It is concluded that nitrogen somewhat blocks the out-gassing of carbon during activation. This is most prominent when ammoxidation was performed on the precursor, resulting in a sample with the most nitrogen heteroatoms retained after activation.<sup>4</sup>

There is also ongoing research investigating the modification of the carbon surface with nitrogen-containing groups. In this way, nitrogen is on the surface of the carbon rather than in the bulk as heteroatoms. Recently, researchers have been looking at the deposition of nitrogen-containing conductive polymers, such as polyaniline and polypyrrole,<sup>14–17</sup> on high surface area carbon. These polymers create Faradaic pseudocapacitance by reversibly oxidizing and reducing over a potential range. Polyaniline is perhaps the most researched because it has several oxidation states. Adding this nitrogen-containing polymer to carbon has been found to increase the capacitance significantly due to the combined effects from double-layer capacitance and pseudocapacitance. However, special care must be taken to avoid blocking the carbon pores with the polymer during deposition. Additionally, swelling and shrinking of the polymers may lead to decreased cyclic stability.<sup>14</sup>

The research performed here utilizes porous carbon both containing nitrogen heteroatoms in the bulk and with nitrogen

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modification on the surface of the pores. The carbon was first prepared using resorcinol and furfural as the precursors and hexamethylenetetramine (hexamine) as the catalyst. Historically, a metal ion catalyst such as NaOH has been used. However, this can leave impurities in carbon that can reduce the cyclic stability of the device. Hexamine, on the other hand, contains no metal ions and participates in the polycondensation reaction, adding nitrogen to the bulk. Resorcinol–furfuraldehyde gels catalyzed with hexamine have been studied previously and the pore structure has been optimized for supercapacitor and energy storage applications.<sup>18</sup>

The resorcinol–furfuraldehyde derived porous carbon is modified with nitrogen on the pore surfaces using hexamine. This nitrogen-containing molecule was selected for modification for multiple reasons. First, it is a small, cage-like molecule that can easily penetrate into the porous structure. Also, hexamine does not contain oxygen. While oxygen heteroatoms have proven to induce pseudocapacitance in aqueous electrolytes,<sup>4</sup> oxygen can deteriorate an organic electrolyte, decreasing device lifetime. An organic electrolyte is used in this study because of the larger voltage window than aqueous electrolytes, allowing for increased energy and power density.

A previous study investigated the sublimation of hexamine into the pores of activated resorcinol–furfural carbon.<sup>1</sup> The nitrogenated carbon exhibited pseudocapacitive behavior and an increase in capacitance that was almost twice that of unmodified carbon. The cyclic stability was also improved. However, one drawback is that the carbon was heated to 900 °C during pyrolysis. When carbon is heated above 850 °C, the amount of nitrogen that can be found within the bulk dramatically decreases.<sup>3,5</sup> As such, any nitrogen present in the carbon network from the precursor catalyst hexamine might be removed during pyrolysis. Another limitation was the large decrease in surface area that occurred when the nitrogen groups were deposited on the surface. This can be an artifact of the nitrogen groups blocking pores, decreasing the amount of surface area that is accessible to the electrolyte ions. In another study that deposited ammonia borane into porous carbon using a wet chemical process,<sup>19</sup> the surface area actually increases with modification.

In this study, nitrogen-modified carbon is prepared and tested for supercapacitor applications. Nitrogen is added to highly porous carbon both in the bulk network as heteroatoms and coated on the surface of the pores in order to induce pseudocapacitance. The effects of both the bulk nitrogen and surface-coated nitrogen are investigated using multiple techniques, including X-ray spectroscopy, nitrogen adsorption analysis, cyclic voltammetry, galvanic cycling, and electrochemical impedance spectroscopy.

## Experimental

### Synthesis

The procedure for synthesizing highly porous carbon from resorcinol–furfuraldehyde gels is similar to that reported elsewhere.<sup>20</sup> The furfuraldehyde to resorcinol molar ratio is set to 2.5 and the resorcinol to hexamine molar ratio is 50. The resorcinol and furfuraldehyde are mixed together first, followed by the addition of the solvent *tert*-butanol. Hexamine is added last as the

catalyst. If the hexamine does not dissolve quickly, a small amount of deionized water can also be added. The mixture is sealed and cured in an oven at 80 °C for 7 days to allow for gelation and aging to strengthen the newly formed three-dimensional gel network.

Nitrogen modification of the organic gel takes place during solvent exchange. This procedure has been used previously to dope porous carbon with ammonia borane for hydrogen storage applications.<sup>19</sup> Solvent exchange is performed by placing the gel in 10 times its volume of *tert*-butanol for 24 hours, then repeating the process two more times with fresh *tert*-butanol. For modification, 2 wt% of hexamine is dissolved in *tert*-butanol during the first solvent exchange step. The subsequent two steps are performed in pure *tert*-butanol to avoid precipitation of hexamine in the pores. After modification, the gels are dried under vacuum at –50 °C in a Labconco FreeZone 1 L freeze dryer. The dried samples are then pyrolyzed in nitrogen at high temperature to remove unwanted organic functional groups and increase the internal surface area.

Pyrolysis takes place at one of two temperatures. Unmodified resorcinol–furfural carbon is pyrolyzed at 900 °C as previously studied<sup>21</sup> and at 700 °C. These samples are referred to as RF 900 and RF 700, respectively. Pyrolysis at 900 °C (or higher) usually results in complete carbonization.<sup>22</sup> However, as mentioned before, the amount of nitrogen found in carbon decreases drastically when heated above 850 °C.<sup>3</sup> According to a recent study of melamine, pyrolysis at 650 °C results in the highest nitrogen to carbon ratio, while pyrolysis at 750 °C shows the highest surface area.<sup>5</sup> Therefore, pyrolysis of nitrogen-containing carbon at 700 °C is expected to provide a favorable combination of both high surface area and high nitrogen content. Carbon samples that are modified with hexamine during solvent exchange are also pyrolyzed at 900 °C and 700 °C and labeled as RFN 900 and RFN 700, respectively.

### Characterization

X-ray photoelectron spectroscopy (XPS) is used to determine the atomic composition of the unmodified and nitrogen-modified carbons. Spectra are taken on a Surface Science Instruments S-probe spectrometer. The X-ray spot size is 800 × 800 μm and the take-off angle is 55°, corresponding to a sampling depth of approximately 50–70 Å. Data analysis is carried out using the Service Physics ESCA 2000-A analysis program (Service Physics, Bend, OR).

Nitrogen sorption isotherms are measured using a Quantachrome NOVA 4200e. Samples are degassed at 250 °C under vacuum for at least 6 hours prior to measurement. The multi-point Brunauer–Emmett–Teller (BET) method is used to determine the total surface area. For the mesopore surface area, pore volume, and pore diameter, the Barrett–Joyner–Halenda (BJH) method is used. Micropore surface area and pore volume are determined using the *t*-method, and the micropore diameter is determined using the Dubinin–Astakhov (DA) method.

Contact angles were measured with the static sessile drop method using a VCA Optima goniometer. Surfaces were wet with approximately 1 μL of DI water and analyzed immediately after the droplet touched the sample. Multiple droplets were placed on each surface at different spots to avoid remeasuring an area that

had already been wet. VCA OptimaXE software was used to measure angles on both the left and right sides of the droplet and the average angle was calculated.

### Electrochemical analysis

Electrodes for electrochemical measurements are prepared from this nitrogenated carbon by first grinding the large pieces into a fine powder. Approximately 3 wt% of polytetrafluoroethylene (PTFE) is added as a binder. The mixture is rolled into sheets with a thickness of 0.07 mm and electrodes are punched out with a diameter of 10 mm. A Celgard® porous film separates the electrodes and specially coated aluminium contacts are used to reduce the interfacial effect. The electrolyte used is tetraethylammonium tetrafluoroborate (TEATFB) in saturated 50–50 propylene carbonate–dimethylcarbonate. The electrode assembly is placed in a flat cell and electrolyte is added in an argon-rich environment. The samples were placed under vacuum to increase the penetration of the electrolyte into the pores. To avoid nitrogen-induced pseudocapacitive reactions in both electrodes, all samples were prepared with RF 900 as the counter and reference electrode.<sup>4</sup>

Cyclic voltammograms (CV) and galvanic cycles (GC) are taken using a Solartron 1287A with a voltage range between 0 and 2 V. The CVs are measured at scan rates of 100, 50, and 10 mV s<sup>-1</sup> and the GCs at 100, 50, 10, 5, 1, and 0.5 mA. Electrochemical impedance spectroscopy is performed using the Solartron 1287A in conjunction with a Solartron 1260FRA/impedance analyzer. The samples are cycled and pretreated for 10 minutes at 2 V before measurements. An AC voltage amplitude of 10 mV and frequency range of 0.1 MHz to 1 MHz is used for this scan. The specific capacitance in F g<sup>-1</sup> is calculated from the discharge slope during galvanic cycling according to the following equation:

$$C = \frac{4I\Delta t}{\Delta Vm} \quad (1)$$

where  $I$  is the discharge current in amps,  $\Delta t$  is the discharge time in seconds,  $\Delta V$  is the discharge voltage in volts, and  $m$  is the total mass of the active materials in both electrodes given in grams.<sup>23</sup>

## Results and discussion

### Composition and structure

Results from XPS are shown in Table 1. RFN 700 has the highest nitrogen content at 2.66 atom%. Pyrolysis of nitrogenated carbon at this lower temperature results in a nitrogen content that is more than three times higher than pyrolysis at 900 °C, as high temperature favors the removal of nitrogen.<sup>3</sup> One

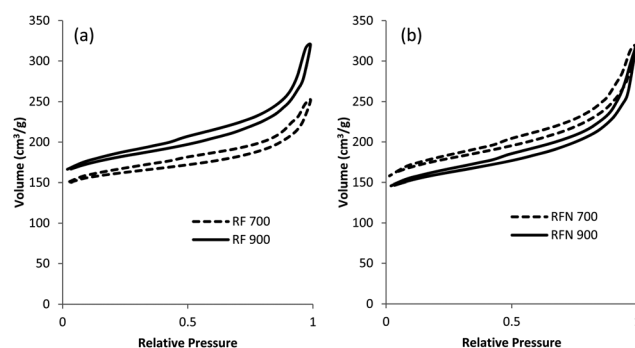
**Table 1** Chemical composition in atom% from XPS

Sample	Composition (atom%)		
	Carbon	Oxygen	Nitrogen
RF 700	96.622	2.723	0.655
RF 900	97.731	1.765	0.505
RFN 700	92.975	4.363	2.662
RFN 900	97.170	2.005	0.825

explanation for why nitrogen is preferentially removed at 900 °C is that the nitrogen may be more loosely bound to carbon than carbon is to other carbon atoms. This is especially possible for nitrogen that is coated on the pore surfaces rather than that surrounded by other atoms in the bulk network. If the carbon–nitrogen bond is weaker, it will break more readily than the carbon–carbon bond, leading to more nitrogen loss at higher pyrolysis temperatures. However, a higher oxygen content is also seen in RFN 700 when compared to the other samples.<sup>8</sup> Further experiments are underway to determine the reason for this. One possibility is that the surface modification blocked the removal of oxygen from the underlying carbon network. Also, because RF 700 has increased oxygen content when compared to RF 900, it is possible that less oxygen is removed at this lower pyrolysis temperature.

Nitrogen sorption was used to determine how the surface area, pore volume, and pore diameter change with nitrogen modification and different pyrolysis temperatures. Isotherms are shown in Fig. 1a and b and the corresponding data are presented in Table 2. For the unmodified samples, the surface area increases when the temperature is raised from 700 °C to 900 °C. The higher temperature is necessary to remove unwanted functional groups more completely and open up the porous structure. However, for the nitrogen-modified carbons, the opposite behavior is noticed. RFN 700 has higher overall surface area than RFN 900, in addition to higher surface area in the mesopore and micropore regions. As shown in a previous study that modified carbon with ammonia borane,<sup>19</sup> chemical modification during the solvent exchange stage results in an increased surface area after pyrolysis. This trend can be seen when comparing RF 700 to RFN 700. However, the surface area is significantly smaller for RFN 900 when compared to RF 900. This surface area decrease is seen in the micropore region. RFN 900 also has a decreased micropore volume, while maintaining a similar micropore diameter to RF 900. This suggests that the total amount of micropores in RFN 900 is decreased. The surface nitrogen is affecting the pyrolysis behavior of the underlying carbon at higher temperatures, particularly in the formation and/or retention of micropores.

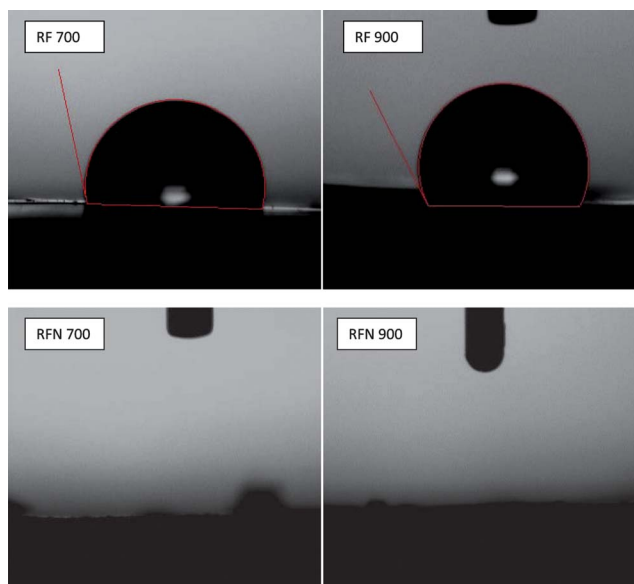
Contact angles were measured to assess how the nitrogen modification affects the surface properties of the carbon. Since the wettability is an indication of how the electrolyte will interact with the material, all measurements were performed with



**Fig. 1** Nitrogen sorption isotherms for (a) unmodified RF 700 and RF 900, and (b) nitrogenated RFN 700 and RFN 900.

**Table 2** Surface areas, pore volumes, and pore diameters of each sample based on nitrogen sorption analysis

Sample	Surface area (m <sup>2</sup> g <sup>-1</sup> )			Pore volume (cm <sup>3</sup> g <sup>-1</sup> )		Pore diameter (nm)	
	Total	Mesopores	Micropores	Mesopores	Micropores	Mesopores	Micropores
RF 700	461.9	60.06	379.8	0.15	0.2128	3.659	1.00
RF 900	525.5	89.38	399.9	0.236	0.224	3.667	1.06
RFN 700	514.3	96.29	375.4	0.2423	0.2125	3.675	1.14
RFN 900	468.7	90.91	340.1	0.2588	0.1906	3.671	1.08



**Fig. 2** Images showing the wettability of unmodified and nitrogen-modified carbons. Each image was taken immediately after the droplet touched the surface. The uneven surfaces in RFN 700 and RFN 900 are from the edges of the sample rolling up and did not affect the measurements.

samples that had been rolled into sheets for making electrodes. As illustrated in Fig. 2, the samples modified with nitrogen had very different wetting behavior than the unmodified carbon. While droplets formed on the RF 700 and RF 900, the surface of the RFN 700 and RFN 900 wet out such that a contact angle was impossible to measure. Since all of the samples have relatively similar pore structure, this drastic change in surface chemistry can be attributed to modifying the carbon with nitrogen. This is further supported when comparing the two unmodified carbon samples. As evidenced in Fig. 2 and Table 3, RF 700 has a slightly smaller contact angle than RF 900. It can be concluded that the better wettability of RF 700 is because of the higher nitrogen content in the bulk carbon network due to the lower pyrolysis temperature of this sample.

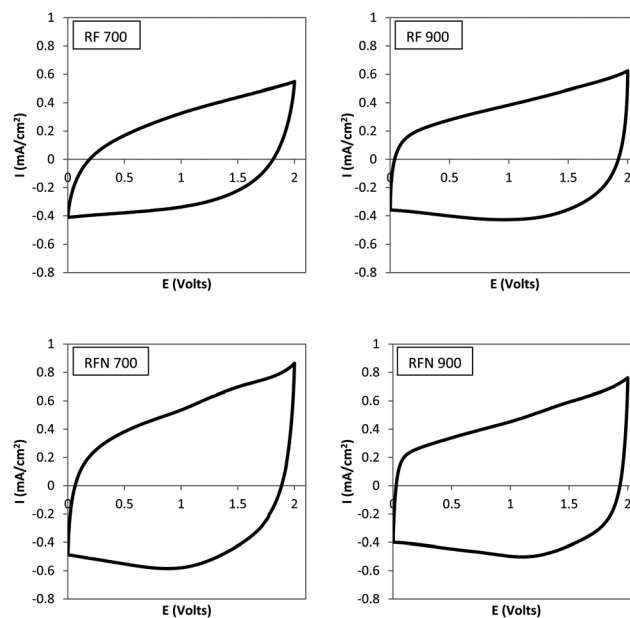
**Table 3** Average contact angles measured immediately after the droplet touched the surface

Sample	RF 700	RF 900	RFN 700	RFN 900
Contact angle	102.3°	118.3°	Complete wetting	Complete wetting

### Electrochemical analysis

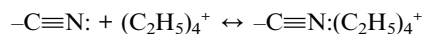
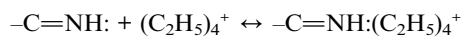
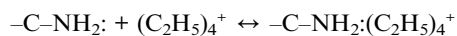
CVs taken at a scan rate of 10 mV s<sup>-1</sup> are shown in Fig. 3. The fairly rectangular shape of RF 900 indicates capacitive behavior from the formation of an electric double layer. RFN 700, on the other hand, exhibits small, broad peaks in addition to the rectangular shape. This indicates pseudocapacitive reactions from nitrogen on the interior surface of the porous carbon. RFN 900 also shows these pseudocapacitive peaks, suggesting that some nitrogen remains on the surface despite the higher pyrolysis temperature. Nitrogen in the bulk of the carbon network does not appear to contribute to pseudocapacitance as much as surface nitrogen, as the RF 700 CV shows no evidence of pseudocapacitive reactions. RF 700 also indicates increased resistance to rapid charging, which is likely due to the smaller surface area of this sample, particularly in the mesopore region.

The exact mechanism for how nitrogen is inducing pseudocapacitance in these samples is still unknown at this time. However, following the reactions discussed earlier for nitrogenated carbon in aqueous medium,<sup>3</sup> new reactions can be proposed for nitrogenated carbon in organic electrolytes. It is believed that pseudocapacitance arises from Faradaic reactions induced by lone electron pairs from the nitrogen groups

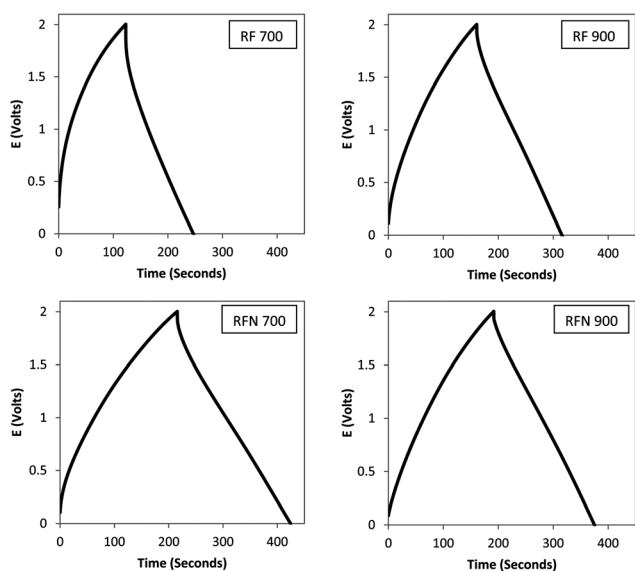


**Fig. 3** CVs of unmodified and nitrogenated carbon samples. Both RFN 700 and RFN 900 show small, broad peaks, indicative of pseudocapacitive reactions.

interacting with the cations in the electrolyte. The following are reactions that could be taking place on the nitrogenated carbon surface:



Galvanic cycling further illustrates pseudocapacitance and resistance in the samples. Fig. 4 shows the GCs measured at 0.5 mA. All samples exhibit non-linear charging behavior characteristic of pseudocapacitive reactions.<sup>21</sup> The specific capacitance is calculated from the discharge slopes of these curves using eqn (1). The results are shown in Table 4. RFN 700 has the most gradual discharge slope, resulting in the highest specific capacitance. The capacitance is almost twice that of either of the unmodified carbon samples. It is also higher than RFN 900, suggesting that it is the nitrogen retained on the surface of the carbon network that is adding to the capacitance through pseudocapacitive reactions.



**Fig. 4** GCs of unmodified and nitrogen-modified carbon. RFN 700 shows the most gradual discharge slope, suggesting the highest specific capacitance.

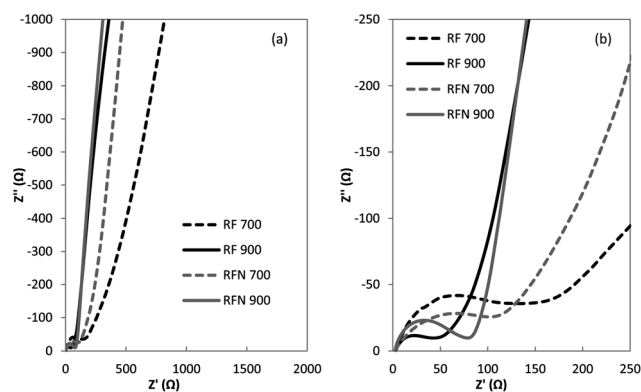
**Table 4** Capacitance based on mass, surface area, and volume. RFN 700 shows the highest capacitance in all three areas. These samples have not been optimized for high capacitance values

Sample	Specific capacitance ( $\text{F g}^{-1}$ )	Capacitance based on total surface area ( $\text{F m}^{-2}$ )	Volumetric capacitance ( $\text{F cm}^{-3}$ )
RF 700	9.6	0.021	11.5
RF 900	10.1	0.019	12.1
RFN 700	18.6	0.036	15.3
RFN 900	11.5	0.025	13.8

It is important to note that these samples have in no way been optimized to achieve high capacitance values. The goal is to simply investigate if nitrogen modification can improve capacitance. According to nitrogen sorption, the total surface area of all four of these samples is relatively small, as some studies of activated carbon have achieved surface areas exceeding  $2000 \text{ m}^2 \text{ g}^{-1}$ .<sup>24</sup> As such, Table 4 also shows the capacitance normalized to surface area. These values are relatively lower as well, which is believed to be an artifact of the low mesopore surface area in these samples. Without adequate mesopores in the porous carbon, penetration of the electrolyte is limited by pores that are too small to allow the ions to pass through easily. The total accessible surface area is most likely much lower than the total surface area measured by nitrogen sorption. Additional experiments are underway to further increase the capacitance through optimization of the pore structure and surface area. However, of the four samples, RFN 700 still shows the highest capacitance per unit mass, surface area, and volume, which can be attributed to the nitrogen both in the bulk and on the surface of the carbon.

Electrochemical impedance spectroscopy can provide insight into how the nitrogen modification is affecting the performance of the samples. Nyquist plots are shown in Fig. 5. At low frequencies, RF 700 exhibits the highest diffusivity resistance, as seen in the more gradual slope at higher  $Z'$  values. Nitrogen sorption illustrated that pyrolysis of unmodified carbon at  $700^\circ\text{C}$  results in smaller micropores and lower mesopore surface area, which hinders the diffusion of the electrolyte ions through the pores. When the pyrolysis temperature is raised to  $900^\circ\text{C}$ , the diffusivity resistance decreases because the pores become larger. This increases the capacitance due to improved electrolyte penetration and therefore double-layer formation. RFN 700 also shows evidence of high diffusivity resistance at low frequencies, which can be attributed to the presence of pseudocapacitive reactions.<sup>21</sup> When the nitrogenated carbon is pyrolyzed at  $900^\circ\text{C}$ , the sample loses some of the evidence of Faradaic reactions, behaving very similarly to the unmodified carbon pyrolyzed at the same temperature.

Differences in surface charge resistance are evident at high frequencies, as seen in Fig. 5b. RF 700 has the highest equivalent series resistance (ESR), due to the functional groups that remain



**Fig. 5** Nyquist plots at (a) high and low frequencies and (b) high frequencies only. RFN 700 shows the highest capacitance despite a higher diffusivity resistance and equivalent series resistance.

on the carbon surface from the low pyrolysis temperature. Likewise, RF 900 has the smallest ESR, since the elevated temperature is high enough to remove the unwanted functional groups during pyrolysis. The larger ESR of RFN 700 is an artifact of nitrogen modification on the surface of the carbon. This is further supported by the decrease in ESR for RFN 900, since nitrogen in the sample is lost at this higher pyrolysis temperature. Still, some nitrogen is retained in RFN 900 since the ESR is larger than RF 900. While modifying carbon with nitrogen groups does increase the impedance in the samples, the pseudocapacitance added is significant enough to greatly increase the overall capacitance.

## Conclusion

Modification of porous carbon with nitrogen, both in the bulk carbon network and on the internal pore surface of the carbon, has proved to increase the capacitance of electrodes for supercapacitor applications. The nitrogen induces Faradaic reactions, which contribute to the capacitance that is already present from electric double-layer formation. Pyrolysis at a lower temperature (700 °C vs. 900 °C) was found to retain more nitrogen in the carbon, especially when the nitrogen is coated on the pore surfaces. Lower pyrolysis temperature of nitrogen-modified carbon was also found to result in a carbon with higher surface area in the mesopore and micropore regions. Furthermore, coating carbon with nitrogen was found to significantly increase the wettability, implying a drastic change in surface chemistry. While nitrogen modification does increase impedance in porous carbon electrodes due to diffusivity and surface charge resistance, the contribution of pseudocapacitive reactions is large enough to nearly double the capacitance of a device.

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