

Nitrogen-Enriched Carbons for ‘Asymmetric’ Electrochemical Capacitors

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1. Introduction

Electrochemical capacitors (ECs), commonly referred to as supercapacitors, are electrical energy storage devices that complement the application of batteries in electrical systems. ECs have been commercially available for many years and are an increasingly important group of energy storage devices [1]. The use of ECs has not become widespread due to their inadequate cost/performance ratio. New materials developments are necessary for ECs to achieve their full commercial potential.

ECs exhibit high cycling efficiency [2] and long lifetimes, typically over 100,000 cycles [3], under charge/discharge. The superior rate capability of ECs in comparison with batteries renders their use beneficial in applications where pulses of power are required. Batteries exhibit reduced efficiency and experience a deleterious effect on cycle-life when supplying power in short bursts. Battery lifetime, as well as power output, can be significantly improved through judicious use of ECs in combination with batteries in electrical supply systems. As with batteries, fuel cells operate best under a constant load; therefore, their dynamic response can also be improved by utilising ECs for short-term energy storage. The incorporation of ECs into electrical supply systems results in a reduction in the total size of the energy storage devices required.

ECs can be used in electric (and hybrid electric) vehicles to provide added acceleration when required, for example during an overtaking manoeuvre, or when climbing a gradient. They are especially useful when dealing with the typical urban drive cycle involving many stop-start segments. ECs have the ability to accept greater charging currents than batteries, making them useful in regenerative braking systems. However, ECs provide an inadequate quantity of energy for stand-alone use EVs, and are best employed in a supplementary role to a combustion engine, fuel cell or battery (or combination thereof).

ECs can also be used to protect grids from energy spikes and “brown-outs”, and to increase energy efficiency through load-leveiling. Short-term energy storage using ECs can rectify instabilities in grids. As more renewable energy sources are connected to grids, controlling the supply of energy becomes more problematic, owing to the fact that the majority of renewable energy sources generate energy intermittently *e.g.* wind, wave *etc.* An energy storage system employing ECs can support the production of renewable energy by allowing surplus energy to be stored until it is required.

Electrochemical capacitor is a generic term to describe devices that display a potential which varies according to the quantity of stored energy. ECs can be distinguished by the predominant charge storage mechanism used in the device. Conventional dielectric capacitors behave according to a parallel plate model where the quantity of energy stored varies directly with the surface area of the plates and inversely with the separation between the plates. Electrical double-layer capacitors (EDLCs) differ from dielectric capacitors as they employ electrodes with a high specific surface area and contain an electrolyte rather than a dielectric between the electrodes. Typically, an activated carbon (surface area *ca.* 1500m²/g) is used in EDLCs and the use of an electrolyte exploits the phenomena of double-layer capacitance. This reduces the effective separation between the plates to approximately half the diameter of the electrolyte ions and results in EDLCs possessing a capacitance several orders of magnitude greater than that of dielectric capacitors.

Pseudocapacitors exhibit a different charge storage mechanism, similar to that observed in Li ion batteries, as charge is not only stored at the surface of the electrode but propagates into the electrode material. Faradaic reactions between the electrode and electrolyte result in charge transfer; changes in the rate of charge acceptance with changes in potential result in a ‘pseudo’-capacitance being observed. High specific capacitances are observed in pseudocapacitive materials with hydrous ruthenium dioxide displaying the highest reported values of 850F/g [4]. However, the relative abundance of Ruthenium renders it impractical for commercial purposes.

EDLCs can be seen as two capacitors in series, where the total capacitance of the cell (C_T) is governed by the relation between the absolute capacitances of the positive (C_P) and negative (C_N) electrodes given below:

$$\frac{1}{C_T} = \frac{1}{C_P} + \frac{1}{C_N}$$

For a symmetric capacitor using identical masses of the same material, cell capacitance is roughly half of the capacitance measured for an individual electrode. Asymmetry is inherently present in EC cells due to variations in the strength of chemisorption between electrolyte ions and the electrode surface [5]. By incorporating one electrode of appreciably larger capacitance, the total capacitance approaches that of the smaller capacitance electrode; potentially increasing cell capacitance by a factor of two [6]. These cells are known as asymmetric ECs and are especially useful in transport applications. However, asymmetry is usually accomplished by using expensive electrode materials which limits their commercial viability.

Research in the field of ECs has favoured the development of nanoporosity in carbon materials, aiming to increase electrode gravimetric capacitance. It was recently reported that the presence of ultramicropores (<7Å in diameter) has a significant effect on specific capacitance of carbons [7,8] and a new heuristic model has been proposed [9] that allows for the influence of pore curvature.

The carbonisation of organic xerogels allows for control of the porous structure of the electrode on a nanometre scale [10-13]. Carbonised resorcinol-formaldehyde (RF) gels have been widely investigated as an electrode material in ECs [14-18]. Carbon electrodes with a larger specific capacitance can be obtained by incorporating heteroatoms into the carbon structure. Carbons used in EDLCs contain markedly variable amounts of other elements; retained through incomplete precursor carbonisation, or added during preparation. Typically, heteroatoms present in appreciable quantities (up to 10% wt.) include oxygen, hydrogen and nitrogen [19]. These different atoms alter the electronic properties and surface functionality of the carbon. Heteroatoms can affect the capacitive behaviour of the carbon materials via participation in Faradaic reactions, changing the electronic conductivity of the bulk material [20], or by influencing the wettability of the carbon surface. The addition of hydrophilic surface groups increases the area of electrode in contact with aqueous electrolyte resulting in an increased quantity of stored energy. However, increases in specific capacitance due to the incorporation of heteroatoms can be accompanied by increases in ESR and self-discharge rate [21].

The presence of oxygen-containing functional groups on carbons is almost unavoidable, as empty valencies remaining from high-temperature treatment react on exposure to air yielding surface functionalities such as phenol, carbonyl, carboxyl, quinone and lactone groups [19]. Nanoporous carbons are typically produced using activation, an oxidative thermal treatment, which results in a significant amount of hydrophobic moieties present on the carbon surface. These groups reduce the wettability of the carbon surface, which in turn decreases the electrochemically active area and hence, electrode capacitance.

Nitrogen-enriched carbons have been investigated as electrode materials for ECs, with increased capacitance values being observed in carbons containing nitrogen. Ammoxidation of carbonaceous materials, (a process similar to gas-phase activation using a fraction of ammonia in the feed stream) has been studied as a way of adding nitrogen to electrode carbons. [22, 23] The addition of nitrogen in this manner caused a decrease in surface area, but resulted in an increase in specific capacitance. A comparison between carbons with comparable surface areas revealed that an increase in nitrogen content from 9.3% wt. to 13.2% wt. resulted in a threefold increase in capacitance. Carbonised melamine-formaldehyde resins (and their composites) [24-27], polyacrylonitrile (PAN) composites [28,29], urea and melamine impregnated activated carbon precursors [30,31], carbonised nitrogenous fibres [32] and carbonised organic liquids in mica templates [33] have also been explored as nitrogen-enriched materials for EC electrodes. It has been proposed that the presence of nitrogen-containing functional groups on the electrode surface increases specific capacitance via participation in pseudocapacitive reactions [34,35].

Nitrogen content and pore structure of carbons can be tailored through the co-pyrolysis of a polymer gel impregnated with a nitrogenous compound [36]. Nitrogen-enriched carbons for the sequestration of CO₂ were recently studied, where co-pyrolysis mechanisms, as well as amine 'catalysed' polymerisation were explored. Controlled addition of nitrogen to RF xerogel derived carbons was achieved through co-pyrolysis with *m*-phenylenediamine (*m*PDA), while retaining a significant degree of porosity and surface area. [37] *m*PDA contains roughly 26% wt. nitrogen and possesses an aromatic ring that is reactive during co-pyrolysis. Addition of up to 40% of the original xerogel mass as *m*PDA resulted in a fairly linear increase in nitrogen content of the resultant carbon.

The objective of this work is to produce nitrogen-enriched electrode carbons for EC cells using aqueous electrolytes. It is proposed that asymmetric cells using one nitrogen-functionalised electrode will result in a device that can store an increased amount of energy in comparison with non-functionalised electrodes in symmetric cells.

2. Experimental

Organic hydrogels were synthesised in a manner similar to the method employed by Pekala and co-workers [38]. The polycondensation of an aqueous solution of resorcinol (R) with formaldehyde (F) was catalysed by the addition of sodium carbonate (C). A typical synthesis procedure involved the dissolution of 0.10 moles of resorcinol in 110cm³ of distilled water (W). The desired mass of sodium carbonate was added to the solution under stirring to increase the pH, a crucial factor determining the structure of the resultant gel [#]. 0.20 moles of formaldehyde (37% wt, stabilised by methanol) were added under stirring to obtain a homogenous solution. The molar ratio R/F was kept constant at 0.50 and R/W was kept constant at 0.10 g/cm³. R/C molar ratios between 100 and 500 were investigated. The solution was transferred to a sealed bottle (to prevent solvent evaporation) and maintained at 90°C for 3 days. The resultant hydrogels then underwent solvent exchange with acetone over a period of 3 days. Solvent exchange was performed to minimise shrinkage of the gel due to capillary forces evolved during drying [39].

The required mass of *m*PDPA was solvated in roughly 100 cm³ acetone and added to the wet gel, which was then sonicated for 15mins to ensure a thorough impregnation of *m*PDPA into the gel. The impregnated gels were then agitated for a further 3 days. *m*PDPA was added as a fraction of xerogel mass. Gels were then heated to 60°C in a water bath, to evaporate the majority of acetone present, before being dried at 80°C under vacuum. Xerogels were prepared for carbonisation by milling for 5 mins in a bench-top ball mill. Carbonisation was carried out according to the heating schedule used by Mirzaeian and Hall [13], with a final carbonisation temperature of 850°C maintained for 120mins. Activated samples underwent the same procedure with a further 60 mins at 850°C under CO₂ flowing at 200cm³/min. The furnace was allowed to cool slowly under flowing argon.

Materials Characterisation and Electrochemical Testing

The surface area and pore structure of the carbonised RF xerogels were investigated using nitrogen adsorption/desorption at 77K (Micromeritics, ASAP 2040). Surface areas were calculated using the BET method, total pore volume obtained at a relative pressure of 0.998, micropore volume using the t-plot method, and pore size distribution/ average pore diameter in the mesopore range by applying the BJH method to the adsorption branch of the isotherm. Combustive analysis of the carbonised RF xerogels was carried out at 950°C in oxygen to determine the relative amounts of carbon, nitrogen and hydrogen. (Perkin Elmer 2400 Analyser) The amount of oxygen present in the samples was calculated by difference.

Carbons were milled for 60 mins to obtain a fine powder suitable for electrode manufacture. Electrodes were prepared by pasting a suspension of the obtained carbons with binder and carbon black as a conductivity enhancer (80:10:10 ratio by mass) using an adjustable print applicator to give a wet film thickness of 200µm. Punched disc electrodes (13mm diameter) of near identical mass were then tested in two-electrode cells using 28.5% wt. potassium hydroxide solution electrolyte, nickel foil current collectors and glass fibre separator. Electrodes soaked in electrolyte were treated in an ultrasonic bath to encourage pore filling and were left to soak overnight.

Cells were maintained at 25°C throughout electrochemical testing which was carried out using a Solartron Analytical 1470E Multistat and Frequency Response Analyzer. Specific capacitance values are reported based on the mass of active material in one electrode.

The capacitive behaviour and resistance of these cells was determined using electrochemical impedance spectroscopy (EIS). An ac amplitude of 10mV over the frequency range 10mHz to 10kHz was applied to the cells at +0.5V vs the open circuit potential (OCP). Equivalent series resistance (ESR) was determined at 1kHz and cell capacitance was calculated from the impedance at 10mHz. Cyclic voltammetry was performed at various sweep rates 2-50mV/s over a potential window of +1V vs OCP. Charge dynamics were evaluated using Galvanostatic charge-discharge cycling (GC) over a range of current densities (2mA-100mA) between 0 and +1V (vs OCP). Average capacitance values were calculated on the discharge curve of 20 cycles using the relationship below;

$$C = (I\Delta t)/\Delta V$$

3. Results and Discussion

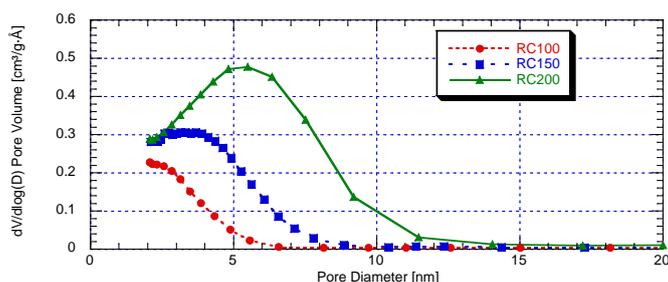


Fig. 1 Mesopore size distribution of carbons produced using different R/C ratios

Figure 1 shows the mesopore size distribution curves for carbonised RF xerogels produced using different R/C ratios. RF R/C 100 carbon exhibits a peak at a pore diameter of 2nm; this peak shifts to wider pore diameters with increasing R/C ratio. From analysis of the nitrogen adsorption/desorption isotherms (not shown) the porous characteristics of RF xerogel derived carbons, given in Table 1, were calculated. It is seen that with the increase in R/C ratio from 100 to 500 the total pore volume and average pore diameter increase from 0.2764 to 1.0972 cm³/g and 3.01 to 12.85nm, respectively. These results corroborate the reported findings that careful alteration of the R/C ratio in RF gels allows the porous structure (particularly, pore volumes and pore size distributions) of the derived carbons to be controlled on the nanometre scale.

R/C ratio	<i>m</i> PDA [%]	Activated	S _{BET} [m ² /g]	V _{total} [cm ³ /g]	V _{micro} [cm ³ /g]	V _{meso} [cm ³ /g]	D _{av} [nm]
100	-	N	515	0.2764	0.1832	0.0658	3.01
150	-	N	560	0.3424	0.1861	0.1369	3.40
200	-	N	624	0.4333	0.1780	0.2450	4.06
500	-	N	610	1.0972	0.1806	0.8239	12.85
500	10	N	525	0.8018	0.1667	0.6303	13.36
500	20	N	440	0.6987	0.1320	0.5496	12.59
500	30	N	335	0.6113	0.0917	0.5010	13.78
500	40	N	245	0.4752	0.0661	0.3909	14.76
100	-	Y	965	0.5194	0.3664	0.1027	3.42
100	10	Y	490	0.2694	0.1867	0.0630	3.61
100	30	Y	410	0.2130	0.1763	0.0231	3.44

Table 1. Porous characteristics determined by nitrogen adsorption/desorption of RF carbons and nitrogen-enriched RF carbons

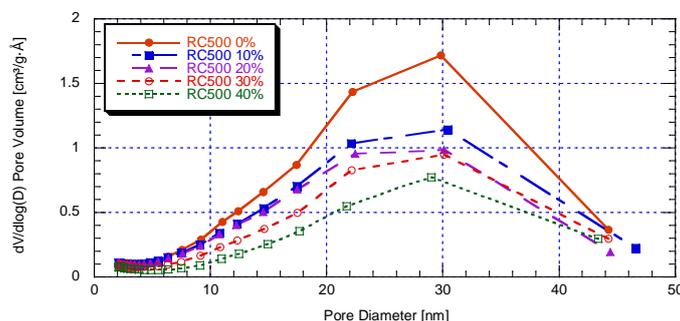


Fig. 2 Mesopore size distribution of RF R/C 500 carbons co-pyrolysed with different fractions of *m*PDA

Figure 2 shows the mesopore size distribution curves for RF R/C 500 xerogels co-pyrolysed with varying mass fractions of *m*PDA. Similar curves, with a peak at roughly 30nm, are retained upon addition of up to 40% *m*PDA although the magnitude of this peak decreases with increasing *m*PDA addition. Table 1 indicates that this effect is accompanied by reductions in surface area and pore volumes, and is in accordance with reported findings. The co-pyrolysis mechanism is expected to affect the pore size distribution curves in such a manner as nitrogenous moieties are added to the surface of the RF xerogel during carbonisation.

The mesopore size distribution curves of activated RF R/C 100 xerogel derived carbons curves (not shown) have a similar shape to those in figures 1 and 2 with a peak centred in the micropore region (<2nm diameter). Increased mass fractions of *mPDA* again result in a decrease in surface area and pore volumes. Samples were activated for 60 mins in CO₂ to increase porosity which facilitates electrode manufacture. Activation has the disadvantages of reducing nitrogen content and introducing oxygen functional groups onto the surface of the carbon, but still allows for comparisons of capacitive behaviour based on nitrogen content to be made. Table 2 gives results obtained from the electrochemical testing of cells using these activated carbons.

<i>mPDA</i> [%]	ESR [Ω]	C _{EIS} [F/g]	C _{EIS} [μF/cm ²]	C _{GC 2mA} [F/g]	C _{GC 2mA} [μF/cm ²]	C _{GC 64mA} [F/g]	C _{GC 64mA} [μF/cm ²]
0	0.34	52.10	5.41	65.80	6.83	55.64	5.77
10	0.27	42.75	8.69	62.72	12.76	42.58	8.66
30	0.18	42.94	10.47	50.14	12.22	41.25	10.06

Table 2. Electrochemical testing results of activated RF R/C 100 carbons co-pyrolysed with different fractions of *mPDA*

Equivalent series resistance from EIS measurements is seen to decrease with the mass fraction of *mPDA* added. Rather than being a result of added nitrogen this can be attributed to the reduced porosity of the carbons. Increases in porosity are accompanied by decreases in material density which reduces electrical conductivity due to the reduced number of electron percolation pathways. Nyquist plots (not shown) display a fairly vertical imaginary impedance component indicating that ionic diffusion does not limit the capacitance of these cells.

EIS measurements show a decrease in specific capacitance values, which is anticipated due to the relationship between double layer capacitance and specific surface area. However, when the values of specific capacitance are normalised on the basis of surface area, an increase in capacitance/surface area with nitrogen content is observed. Cells using carbon with no added nitrogen produce a value of 5.41 μF/cm² whereas the carbon produced by the co-pyrolysis of 30% *mPDA* with RF R/C 100 shows an increased capacitance of 10.47 μF/cm². Galvanostatic cycling at high rate (*ca* 4A/g) gives capacitance values that agree with the EIS measurements and follow a similar trend.

Galvanostatic cycling at a significantly lower rate (*ca* 125mA/g) shows a similar trend in specific capacitance but not in surface area normalised specific capacitance. For the gel impregnated with 10% *mPDA*, a peak value of surface area normalised specific capacitance 12.76 μF/cm² is observed. It is reasonable to assume that the slower rate of charge results in a longer period for ions to diffuse and form complete double layers at the electrode surface.

4. Conclusions

Careful alteration of the R/C molar ratio in resorcinol-formaldehyde gels allows the porous structure of derived carbons to be tailored on the nanometre scale. Reductions in surface area and pore volumes accompany increased impregnation of *m*-phenylenediamine in co-pyrolysed RF xerogels.

Nitrogen-enriched carbons suitable for use in EC electrodes were produced by co-pyrolysis of RF xerogels with *mPDA* and an increase in surface area normalised capacitance with increased nitrogen content was observed, but it is evident that a great deal of further work is required.

5. Further Work

To validate and expand on the results presented many possible investigations are proposed (some are currently in progress). These include: the manufacture of asymmetric cells employing one nitrogen-enriched carbon electrode and studies using a three-electrode cell, conductivity testing, exploring different electrolytes (such as H₂SO₄ to identify protonic reactions), thorough pore size characterisation, systematic studies on the effects of synthesis conditions on capacitance as well as an extended activation period to study the effects of nitrogen with increased porosity, and FTIR studies to identify and quantify the surface groups present.

6. References

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