Heteroatom Doped High Porosity Carbon Nanomaterials as Electrodes for Energy Storage in Electrochemical Capacitors: A Review

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Abstract

At present it is indispensable to develop and implement new/state-of-the-art carbon nanomaterials as electrode in electrochemical capacitors, since conventional activated carbon based supercapacitor cells cannot fulfil the growing demand of high energy and power densities of electronic devices of present era, as a result of rapid development in this field. Functionalized carbon nanomaterials symbolize the type of materials with huge potential for their use in energy related applications in general and as an electrode active material for electrochemical capacitors in particular. Nitrogen doping of carbons has shown promising results in the field of energy storage in electrochemical capacitors gaining attention of researcher to evaluate the performance of new heteroatoms functionalised materials such as sulphur, phosphorus and boron lately. Literature is widely available on nitrogen doped materials for energy storage application however; there has been very limited reviewed published work on other functional materials beyond nitrogen. This review article provides insight and up to date analysis of the most recent development, direction of future research and preparation techniques used for the synthesis of these functional materials. This will also review the electrochemical performance including specific capacitance and energy/power densities when these single doped or co-doped active materials are used as electrode in electrochemical capacitors.


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Key Words

Environmental concerns, Energy crisis, Electrical energy storage, Heteroatom doped carbon nanomaterials, Electrochemical energy storage systems

1.0 Introduction

Energy landscape is expected to go through significant transformation attributed to the crisis instigated by the imbalance in world’s energy supply and demand. Environmental concerns and expanding gap between supply and demand of energy, signifies the implementation of renewable energy technologies such as solar, wind and tidal towards diversification of energy generation in order to maintain un-interrupted supply of energy at relatively lower cost combined with numerous environmental benefits. Due to the intermittent nature of these
renewable sources of energy, appropriate electrical energy storage systems are required for ensuring security and continuity in the supply of energy from a more distributed and intermittent supply base to the consumer. Among different electrical energy storage systems, electrochemical batteries and electrochemical capacitors (ECs) play a key role in this respect. ECs are devices that can fill the gaps between electrochemical batteries and electrostatic capacitors in terms of energy and power densities as shown in Figure 1.

**Figure 1:** Ragone plot of energy density vs power density for various electrical energy storage and conversion devices [1].

Electrochemical capacitors (ECs) also known as supercapacitors or ultra-capacitors (UCs) are high power electrical energy storage devices retaining inimitable properties such as exceptionally high power densities (approx. 5kWkg\(^{-1}\)) [2], rapid charge discharge (millisecond), excellent cycle-ability (> half a million cycles) [3] and high charge retention (> 90% capacitive retention) [4]. Depending on their charge storage mechanism, ECs can be classified into two categories; electric double layer capacitors (EDLCs) and pseudo-capacitors (PCs). In EDLCs, capacitance arises from purely physical phenomenon involving separation of charge at polarized electrode/electrolyte interface where as in PCs electrical energy is stored through fast and fully reversible faradic reaction coupled with the electronic transfer at the electrode/electrolyte interface [5], a schematic diagram of charge storage mechanism of both electric double layer capacitor and pseudo-capacitor is shown in Figure 2.
followed by detail discussion on charge storage mechanism in both electric double layer capacitors (EDLCs) and pseudocapacitors (PCs) in the following section.

Figure 2:- Schematic diagram of A) an electric double layer capacitor [EDLC] B) a pseudocapacitor [PC] [6].

1.1 Energy storage mechanism of electrochemical capacitors

As discussed in previous section there are two types of charge storage phenomenon i.e. surface charge storage (physical storage of charge) and bulk charge storage (electrochemical storage of charge) also known as electric double layer capacitance and pseudocapacitance respectively. Carbon based materials such as activated carbons [7], graphene [8], carbon nano-tubes [9, 10], carbide derived carbons [11] and carbon fibres [12] are the key electrode materials used as electrodes in electric double layer capacitors. Electric double layer capacitors (EDLCs) store electrical charge on the same principle as in electrostatic capacitors however, in case of electric double layer capacitor two separate layers of electrical charges are formed between positively/negatively charged carbon electrodes and electrolyte ions respectively [13, 14] as illustrated in Figure 3. Specific capacitance of a capacitor can be calculated using equation 1.

$$C = \varepsilon_0 \varepsilon_r \frac{A}{d}$$

EDLCs maintains specific capacitance six to nine orders of magnitude higher when compared with conventional capacitors [15] since charge separation ‘d’ is much smaller during the formation of electric double layer and specific surface area ‘A’ of active material is much higher (up to 3000 m$^2$g$^{-1}$) [16-19] when compared with electrostatic capacitors. Charge storage in EDLCs is purely a physical phenomenon without any electronic transfer which makes EDLCs an ideal candidate for high power application since it can be fully charged or
discharged in very short span of time [20, 21] and retains exceptionally long cycle life [22, 23].

Figure 3: Schematic of charge storage mechanism of electrical double layer capacitor
Energy storage in pseudocapacitors is realized through fast and fully reversible Faradic charge transfer, which is an electrochemical phenomenon where an electronic transfer occurs at the electrode/electrolyte interface [24-26] as shown in Figure 4. Ruthenium oxide [27], manganese oxide [10], iron oxide [28] and nickel oxide [29] are the most commonly used metal oxides whereas polyacetylene [30], polypyrrole [31], poly(3,4-ethylenedioxythiophene) [32] and polyaniline [33] are frequently used conducting polymers as electrode materials in pseudocapacitors.

PCs have much higher energy densities as compared to EDLCs since specific capacitance of pseudocapacitive devices are also much higher which can have a positive impact on energy density of the device according to Equation 2. However pseudocapacitive devices have lower cycle life [34] and cyclic efficiency [35] in comparison to EDLCs since charge is stored within bulk of the active materials where long term cycle-ability can have adverse effect on the integrity of the active material.

1.2 Energy and power merits of electrochemical capacitors

Despite maintaining high power densities, ECs suffer from inferior energy densities as compare to other electrochemical energy storage and conversion devices such as electrochemical batteries and fuel cell respectively, limiting their engineering applications requiring high power/energy capabilities. To overcome this challenge, extensive research has been undertaken to improve the energy densities of ECs, in order to broaden their scope of applications [36, 37]. Since the energy density (E) of an electrochemical capacitor is directly proportional to its capacitance (C) and square of the operating voltage (V) and is defined by Equation 2.

\[ E = \frac{1}{2} CV^2 \]  

Equation 2

Where the operation voltage V is limited by the type of electrolyte used.

Either by increasing the specific capacitance or the operating voltage is considered the effective way to enhance the energy density of the EC cell. However by using electrolytes with higher working voltages such as organic or ionic liquids results in higher equivalent series resistance (ESR) which results in poor power densities, power density of EC is given by Equation 3.
Alternative approach to enhance energy densities of electrochemical capacitor cell is by increasing the specific capacitance of ECs. Improved specific capacitance is attainable by introducing the pseudo-capacitive entities such metal oxides/conducting polymers [38] or heteroatoms (nitrogen, sulphur, boron and phosphorous) on the surface or within structure of carbon based active material where the total capacitance is the sum of both electric double layer capacitance (EDLC) and pseudo-capacitance (PC). EDLC is exhibited by carbon based active material and PC is due to the dopant such as metal oxides/conducting polymers or heteroatoms. However, use of metal oxides based dopants in practical application is limited due to, higher cost, low conductivity (with the exception of ruthenium oxide) and limited cycle stability [39]. Heteroatoms doped carbons have displayed improved capacitive performance due to the pseudo-capacitive contribution through fast and fully reversible Faradic reaction without forfeiting the excellent power density and long cycle life [40].

Numerous research studies have been performed to evaluate the contribution made by nitrogen [41], boron [42], phosphorus [43] and sulphur [44] based functional groups in the field of energy storage especially when incorporated in carbon based electrode active material for supercapacitor applications. Nitrogen is by far the most extensively investigated heteroatom whereas other heteroatoms are considered for investigation more recently.

2.0 Functionalized Nano-carbons

2.1 Nitrogen [N] functionalized carbons

Diverse range of synthesis techniques has been adopted to produce N-doped carbons however; some of the most frequently used techniques are deliberated below. One of the most frequently used method to synthesize nitrogen doped carbon is through heat-treatment of undoped (crude) carbons with nitrogen containing material such as, urea \( \text{[CH}_4\text{N}_2\text{O]} \) [45], nitric acid \( \text{[HNO}_3\text{]} \) [46] and ammonia \( \text{[NH}_3\text{]} \) [47] where nitrogen is introduced on the surface of active material. Another, simple approach of producing N-doped carbons is through carbonization of nitrogen containing precursors such as melamine \( \text{[C}_3\text{H}_6\text{N}_6\text{]} \), polyacrylonitrile \( \text{[C}_3\text{H}_3\text{N]} \) and polyvinylpyridine, \( \text{[C}_6\text{H}_9\text{NO]} \text{n} \) where nitrogen can be introduced inside carbon structure. Finally, alternative technique which is comparatively cost-effective way of producing N-doped carbons is through thermal treatment of nitrogen containing biomass such as glucosamine \( \text{[C}_6\text{H}_{13}\text{NO}_5\text{]} \) [48, 49]. These nitrogen doped carbons produced through variety
of synthesis techniques are widely used for electrical energy storage in supercapacitors since N-doping results in superior performance of the electrochemical capacitor cell where specific capacitance of nitrogen doped active material is the sum of both electric double layer capacitance (EDLC) due to the physical phenomenon occurring at the electrode/electrolyte interface and the pseudo capacitance (PC) due to the fast and fully revisable Faradic reaction coupled with electronic transfer owing to the electron donor properties of nitrogen [50] as represented by Equation 4 and 5.

$$-C = NH + 2e^- \leftrightarrow -CH - NH_2$$  \hspace{1cm} \text{Equation 4}

$$-C - NHOH + 2e^- + 2H^+ \leftrightarrow -C - NH_2 + H_2O$$  \hspace{1cm} \text{Equation 5}

Specific capacitance of electrochemical capacitor can be improved substantially by the mean of nitrogen doping in one such study, Han et al. prepared the pueraria-based carbon (PC) followed by nitrogen doping achieved by simple thermal treatment of pueraria powder and melamine (NPC). It was observed that nitrogen doped carbon exhibited remarkably superior capacitance of 250 Fg\(^{-1}\) as compared to 44 Fg\(^{-1}\) for un-doped carbon at the current density of 0.5 Ag\(^{-1}\) using 6M KOH as electrolyte with capacitance retention over 92% [51]. Another study by Mao et al. showed that N-doping results in improved electrochemical performance where N-doped carbon displayed excellent areal capacitance with attained specific capacitance of more than twice (683 mF cm\(^{-2}\) at 2 mA cm\(^{-2}\)) after nitrogen doping as compared to 330 mF cm\(^{-2}\) for an un-doped carbon when used as electrode in supercapacitor cell with an excellent long term cyclic stability of more than 96% after 10000 cycles [52]. Inferior energy densities of supercapacitors is one of the key reason for their limited application commercially, nitrogen doping can be adopted as favourable technique to improve their energy densities for their wider adoption in practical applications. Improved energy density of 6.7Whkg\(^{-1}\) as compare to 5.9Whkg\(^{-1}\) was attained after the introduction of nitrogen functionalities which provides the clear evidence that N-doping is an efficient way of improving the energy densities of supercapacitor cell and enhancement in energy densities will lead to their commercial applications [53]. Exceptionally high energy density of 55 Wh kg\(^{-1}\) (one of the highest available in literature for this type of active material) at power density of 1800 W kg\(^{-1}\) with excellent cycling efficiency of over 96% was achieved when S Dai and co-workers used nitrogen doped porous graphene as electrode and n BMIMBF\(_4\) electrolyte to benefit from higher operating potential of around 3.5V [54]. Nitrogen doping also improves the wetting behaviour of electrolyte which improves the electrode/electrolyte
contact at the interface along with reduction in solution resistance. A study by Candelaria et al. showed that the wettability improved after nitrogen doping with the drop in contact angle from $102.3^\circ$ to zero as shown in Figure 5. Nitrogen doped carbon attained capacitive value of twice than that un-doped carbon [55]. Further examples of nitrogen carbons when used as an active material in supercapacitors with comprehensive evaluation of their physical and electrochemical properties presented in the literatures is shown in Table1. Table 1 shows various physical and electrochemical properties of different types of nitrogen doped carbon based materials when used as electroactive materials.

![Figure 5](image_url)

**Figure 5:** Images showing the wettability of un-doped (RF) and nitrogen doped (NRF) carbons samples [55]

Table 1 — Physical and electrochemical characteristics of various nitrogen doped carbons used as active material in supercapacitors.

| Electrode materials                  | Specific surface area (m$^2$ g$^{-1}$) | Capacitance (Fg$^{-1}$) | Energy density (Wh kg$^{-1}$) | Power density (kW kg$^{-1}$) | Reference |
|--------------------------------------|----------------------------------------|--------------------------|-------------------------------|------------------------------|-----------|
| Carbon nano-cages                    | 2407                                   | 313                      | 6                             | 22                           | [56]      |
| Activated carbon                     | 1580                                   | 855                      | 39                            | 23                           | [57]      |
| zeolite-templated carbon             | 3600                                   | 273                      | 8                             | 98000                        | [53]      |
| Graphene nanosheets                  | 380                                    | 480                      | 83                            | 426                          | [58]      |
| Activated Carbon                     | 2905                                   | 351                      | 39                            | 1.0                          | [45]      |
| Activated Carbon                     | 1459                                   | 451                      | 11                            | 125                          | [59]      |
It can be established from the above discussions that nitrogen doping is the most favourable route to synthesise functional electrode-active materials for supercapacitors applications. N-doping is advantageous to improve both physical and electrochemical properties such as wettability, capacitive performance and energy/power densities respectively which can have positive impact on the overall performance of the system.

2.2 Phosphorus [P] functionalized carbons

Phosphorus displays analogous chemical properties as nitrogen since it has same number of valence electrons; however, due to higher electron-donating capability and larger atomic radius makes it the preferred choice for its adoptions as a dopant in carbon materials.

Commonly used method to produce phosphorus doped carbons is through thermal treatment of carbon with phosphorus containing regents both at carbonization and activation stages [66-68] which results in introducing phosphorous on to the carbon surface whereas phosphorous species can be doped inside the carbon matrix when phosphorous containing precursor is carbonized at elevated temperatures [69, 70]. It is more convenient to prepare P-doped carbons through the first procedure however by adopting latter process P-doped carbon material can be synthesised by precisely controlling the P content.

Adoption of phosphorus-doped carbons for their application in broad field of energy storage such as electrochemistry generally and as an electrode material in electrochemical capacitors particularly is a highly promising concept however; the use of phosphorous doped carbon as an electrode in electrochemical capacitors has been limited, resulting in lacking in understanding its effect on physio-chemical properties ultimately restricting its potential to be used as an active material and understanding its effects on the overall performance of
supercapacitor cell [71]. Phosphorous doping results in improved charge storage due to the additional pseudo-capacitive component alongside electric double layer since phosphorus also possess electron-donor characteristics and also enhanced transport capability due to exceptionally high electrical conductivity when used as active material [72]. J Yi et al. synthesised cellulose-derived both un-doped carbon (CC) and phosphorous doped carbon (P-CC) resulting in an excellent capacitive performance along with improved conductivity. Specific capacitance of 133 Fg\(^{-1}\) at high current density of 10 Ag\(^{-1}\) and excellent capacitance retention of nearly 98% after 10000 cycles was achieved. A momentous drop from 128.1 to 0.6 Ω in charge transfer resistance alongside drop in contact angle from 128.3º to 19.2º after phosphorus doping was witnessed [66] as shown in Figure 6 where 4a) shows the drop in contact angle with improved wetting behaviour and 4b) represents the Nyquist plots of various carbons characterizes the resistive behaviour of various carbon samples.

**Figure 6:** a) contact angle of 6M KOH on the surface b) Nyquist plots of doped and undoped carbons [66].

In another study, phosphorus doped graphene was synthesised by activation of graphene with sulphuric acid which resulted in P-doping of 1.30%. It was established that P-doping not only improves the capacitive performance it also widens operating voltage window of the cell which results in enhanced energy density as given by Equation 1. Exceptionally high energy density of 1.64 Whkg\(^{-1}\) at high power density of 831 Wkg\(^{-1}\) was realised due to higher operating potential of 1.7 V rather than 1.2V for aqueous electrolyte (1M H\(_2\)SO\(_4\)) [73]. It has also been reported in literature that oxygen surface functionalities such as chemisorbed oxygen (carboxylic groups) and quinones of active material are electrochemically active and
can contribute towards the overall performance of the cell [40] however; these surface functional groups are unstable in nature and can cause deterioration in capacitive performance [74]. Phosphorous can also be used as oxidation protector when introduced within the carbon structure preventing the combustion of oxygen species which contributes toward the enhancement in cell performance accompanied by the obstruction in formation of electrophilic oxygen species [75, 76]. A recent study by W Ma et al. has shown that phosphorous doping not only enhances the capacitive performance due to additional capacitance arising from the reversible redox reaction it also prevents the formation of unstable quinone and carboxylic groups resulting in higher operating voltage of 3.0V much higher when used in conjunction with pure carbon (around 2.5V) resulting in the delivery of exceptionally high energy density of 38.65 Wh kg$^{-1}$ at power density of 1500 W kg$^{-1}$ when used with the organic electrolyte (1 M Et$_4$NBF$_4$/PC) [68]. Wide range of phosphorus doped carbon based electrode materials with their physical and electrochemical properties are given in Table 2

| Electrode materials      | Specific surface area (m$^2$ g$^{-1}$) | Capacitance (F g$^{-1}$) | Energy density (Wh kg$^{-1}$) | Power density (kW kg$^{-1}$) | Reference |
|--------------------------|----------------------------------------|--------------------------|-------------------------------|-------------------------------|-----------|
| Activated carbon         | 940                                    | 367                      | 8.5                           | 10                            | [69]      |
| Activated carbon         | 1535                                   | 133                      | 4.7                           | 0.83                          | [66]      |
| Activated carbon         | 2133                                   | 121                      | 39                            | 1500                          | [68]      |
| Carbon aerogels          | 1618                                   | 406                      | 17                            | 200                           | [77]      |
| Activated carbon         | 2055                                   | 210                      | ......                         | ......                         | [78]      |
| Mesoporous carbon        | 1122                                   | 228                      | ......                         | ......                         | [79]      |
| Activated carbon         | 2133                                   | 121                      | 39                            | 1500                          | [68]      |
| Carbon aerogel           | 1450                                   | 110                      | 17                            | 170                           | [80]      |
| Graphene                 | 221                                    | 115                      | 11.6                          | 0.83                          | [73]      |
| Graphene                 | ......                                  | 367                      | 59                            | 9                             | [81]      |
| Nano-tubes               | ......                                  | 2080                     | 42                            | 750                           | [82]      |
| Carbon nanofibre         | 586                                    | 336                      | ......                         | ......                         | [83]      |
Phosphorus-doping can assist in achieving higher capacitive performance alongside other supplementary benefits such as improved conductivity and reduced charge transfer resistance (owing to improve wettability). However, immense research is mandatory in order to understand the underlying reasons for these improvements to adopt phosphorus doped active materials for use as electrode for electrochemical capacitors commercially.

2.3 Sulphur [S] functionalized carbons

When compared with nitrogen, oxygen or boron, sulphur doping of carbon materials is still very rare which signifies an excellent research opportunity in the field of carbon materials for energy storage applications in general and electrochemical capacitors in particular. Very little has been known until very recently about the effect sulphur functional groups on the performance of these materials when adopted in applications related to field of energy storage. Electronic reactivity of active material can be improved by incorporating sulphur functional groups within the carbon scaffold or on the surface, since sulphur modifies the charge distribution within the carbon structure or on the surface respectively due to its electron donor properties which results in an increased electrode polarization and specific capacitance via fast and fully reversible faradaic process [84, 85]. Sulphur functionalized active carbon nanomaterials have been prepared using various methods which include the direct thermal treatment of sulphur containing compounds or by co-carbonization of carbon with elemental sulphur [86-89]. Improved conductive performance and electrode/electrolyte wettability can be achieved by doping the carbon based electrode material with both nitrogen and sulphur functional groups however, recent work by X Ma and co-workers has shown that sulphur functionalities results in superior conductive performance as compared to nitrogen doping [90]. Since sulphur doping improves electronic conductivity, so higher specific capacitance achieved due to pseudo-capacitive contribution along with electric double layer capacitance (EDCL) coming from sulphur functionalities and the porous parameters respectively of the active material. Sulphur functionalizing improves the energy density of the cell without any drop in its excellent power density due to its superior conductivity. Highly porous Sulphur doped carbon with specific surface area of 1592 m²g⁻¹ and pore structure ranging from micro to macro was synthesised by carbonizing sodium lignosulfonate. Sample with high sulphur weight percentage of up to 5.2 wt% was prepared which exhibited the highest specific capacitance of 320 Fg⁻¹ with high energy density of up to 8.2 Wh kg⁻¹ at power density of 50 W kg⁻¹ [91]. In another study capacitive performance
Improvement from 145 Fg\(^{-1}\) to 160 Fg\(^{-1}\) was attained at the scan rate of 10 mVs\(^{-1}\) for undoped and sulphur doped graphene respectively. High energy density of 160 Whkg\(^{-1}\) at a power density of 5161 Wkg\(^{-1}\) was reached using 6M KOH electrolyte for doped carbon. Improved wetting behaviour and capacitive performance was realized when sulphur-decorated nano-mesh graphene was used as an electro-active material. Sulphur decorated nano-mesh graphene was synthesised by thermal treatment of elemental sulphur with nano-mesh at 155ºC. Specific capacitance of 257 Fg\(^{-1}\) was attained which was 23.5% higher than un-doped graphene for the doping level 5wt% of sulphur alongside drop in contact angle from 88.2º to 69.8º after doping as shown in Figure 7 [92]. Some further explaes of sulphur doped active materials are provided in Table 3.

**Figure 7:**- a) Contact angle of a water droplet on doped and un-doped samples. b) Specific capacitances of electrodes at different current densities

**Table 3** — Physical and electrochemical characteristics of various sulphur doped carbons used as active material in supercapacitors.

| Electrode materials | Specific surface area (m\(^2\)g\(^{-1}\)) | Capacitance (Fg\(^{-1}\)) | Energy density (Wh kg\(^{-1}\)) | Power density (kW kg\(^{-1}\)) | Reference |
|---------------------|----------------------------------------|----------------------------|-------------------------------|-------------------------------|-----------|
| Carbon nanosheets   | 2005                                   | 312                        | 7                            | 21.6                          | [93]      |
| Carbon sphere       | 3357                                   | 405                        | 54                            | 0.074                         | [94]      |
| Graphene            | 187                                    | 150                        | 124                           | 2                             | [95]      |
| Activated carbon    | 1952                                   | 325                        | 37                            | 274                           | [96]      |
| Activated carbon    | 1592                                   | 320                        | 8                             | 0.05                          | [91]      |
| Activated carbon    | 2225                                   | 162                        | .....                         | .....                         | [97]      |
Sulphur doping can be considered as an efficient way to improve the active material performance including enhanced specific capacitance, conductivity and wettability whereas drop in charge transfer resistance and solution resistance of the active material can also be achieved. By Improving these performance parameters, energy density can be improved without scarifying their superior power densities which is the major hurdle towards the commercialisation of electrochemical capacitor technology. However, still very little research work has been performed to study the effect of sulphur doping and under lying reasons for these improvements.

2.4 Boron [B] functionalized carbons

Electronic structure of carbon based active material can be modified by introducing boron into carbon framework. It is easier to dope carbon based nanomaterials either with nitrogen or boron since nitrogen and boron possess analogous electronic configuration and size when compared with carbon atom [104, 105]. Charge transfer between neighbouring carbon atoms can be facilitated by introducing boron into carbon lattice since it has three valence electrons and act as electron acceptor which results in uneven distribution of charges. This charge transfer results in improved electrochemical performance due to the pseudo-capacitive contribution origination from this electronic transfer (Faradic reaction) [106]. Boron functionalizing can be accomplished using diverse range of synthesis techniques such as laser ablation [107], arc discharge method [108, 109], by means of hydrothermal reaction [110] , by substitutional reaction of boron oxide (B₂O₃) [111-113] or by adopting chemical vapour deposition technique [114-116]. Hydrothermal reaction is most commonly used technique to produce boron doped active material, improved specific capacitance of 173 Fg⁻¹ was achieved when boron doped graphene was synthesised through thermal reaction. Atomic percentage of
4.7% of boron was found to be the optimum level of boron doping when introduced into the bulk of graphene, with achieved capacitance of nearly 80% higher than un-doped active material. Electrochemical capacitor cell delivered superior energy density of 3.86 Wh kg\(^{-1}\) at a power density of 125 W kg\(^{-1}\), and managed to retained energy density 2.92 Wh kg\(^{-1}\) at a much higher power density of 5006 kW kg\(^{-1}\) with an excellent cycling stability of nearly 97% after 5000 charge/discharge cycles as shown in Figure 9 (a & b) [117]. Among other synthesis techniques template or nanocasting method (hard or soft template) is also considered as a useful procedure which assists in controlling the porous structure (specific surface area, pore size and pore shape) in a precise manner resulting in a positive effect on the performance of the electrochemical cell. Boron doping not only improves capacitive performance it also enhances electrode/electrolyte wettability resulting in reduction in solution resistance. A study by J Gao and co-workers, where boron doped controlled porosity meso-porous carbon was prepared using hard template approach; specific capacitance of 268 F g\(^{-1}\) was attained after boron doping which is considerably higher than 221 F g\(^{-1}\) for an undoped carbon at 5 mVs\(^{-1}\). Exceptionally low solution resistance \(R_S\) of 1.05 \(\Omega\) was also obtained due to improved wettability after the incorporation of boron functional groups [118, 119]. Properties such as improving the surface chemistry of electrode active material after boron doping can have other benefits such superior conductivity. Boron doped graphene oxide was synthesised through simple thermal annealing of GO/B\(_2\)O\(_3\) as shown in Figure 8. Exceptionally high specific capacitance of 448 F g\(^{-1}\) was reached after boron doping without using any conductivity enhancer such as carbon black since boron doping resulted in improved conductivity of active material [120].

Figure 8: Schematic presentation of the preparation of BT-rGO
More examples of boron doped carbon when used as active material in supercapacitors are presented in Table 4 below.

![Figure 9](image_url)

**Figure 9:** a) Cycling stability and coulombic efficiency of Boron doped electrode  
b) Ragone plot of symmetric cell [117]

Table 4 — Physical and electrochemical characteristics of various boron doped carbons used as active material in supercapacitors.

| Electrode materials       | Specific surface area (m² g⁻¹) | Capacitance (F g⁻¹) | Energy density (Wh kg⁻¹) | Power density (kW kg⁻¹) | Reference |
|---------------------------|---------------------------------|----------------------|--------------------------|--------------------------|-----------|
| Graphene                  | …..                             | 308                  | 10                       | 2.02                     | [121]     |
| Activated carbon          | 1257                            | 268                  | …..                      | …..                      | [118]     |
| Graphene nano-sheets      | …..                             | 53                   | 5                        | 1                        | [122]     |
| Meso porous carbon        | 1258                            | 222                  | 6.5                      | 5                        | [119]     |
| Graphene nano-platelets   | 466                             | 200                  | …..                      | …..                      | [123]     |
| Graphene oxide            | …..                             | 113                  | 1.25                     | 6                        | [122]     |
| Activated carbon          | 670                             | 197                  | …..                      | …..                      | [124]     |
| Graphene Nano-platelets   | 466                             | 200                  | …..                      | …..                      | [123]     |
| Activated carbon          | 1657                            | 196                  | …..                      | …..                      | [125]     |
| Graphene                  | …..                             | 173                  | 4                        | 125                      | [117]     |
| Graphene                  | …..                             | 491                  | 80                       | 221                      | [126]     |
| Graphene                  | 1102                            | 336                  | …..                      | …..                      | [127]     |
| Graphene                  | …..                             | 270                  | 40                       | …..                      | [128]     |
We have discussed various functional materials including nitrogen, sulphur, phosphorus and boron which have been widely used by researcher to improve the performance of electrochemical capacitors. However, there is still an enormous scope to enhance the capacitive-ability of these electrochemical devices further which is achievable though co-doping of these carbon based electrodes. Co-doping of active material using different combinations such as nitrogen/boron, nitrogen/sulphur or in some cases introducing more than two functional groups on the surface or inside the carbon matrix has been adopted, co-doping and its impact on physical and electrochemical properties will be discussed in detail in the following section.

2.5 Functionalized carbons through co-doping

Efforts have been made to understand the impact of co-doping on the performance of energy storage materials recently [58, 131-133]. Overall performance of energy storage devices can be improved further due to the synergetic effect of co-doping. Introduction of more than a single heteroatom, can results in enhancing the capacitive performance of the carbon when used as an electrode material by tailoring its properties such as by improving wetting behaviour toward the electrolyte, by introducing pseudo-capacitive species and decreasing its charge transfer resistance [134]. Heteroatoms such as nitrogen, boron, phosphorus and sulphur are incorporated in various combinations to tune carbon materials in desired manner for superior performance of energy storage devices when used as electrodes [135-137].

A study by Wang et al [138] showed that the capacitive performance of nitrogen and sulphur co-doped carbon samples outperformed the capacitive performance of carbons using either nitrogen or sulphur as dopant due to the synergetic pseudo-capacitive contribution made by nitrogen and sulphur heteroatoms. Specific capacitance of 371 Fg$^{-1}$, 282 Fg$^{-1}$ and 566 Fg$^{-1}$ was achieved for nitrogen, sulphur and nitrogen/sulphur co-doped samples respectively when used in supercapacitor cell with 6M KOH as an electrolyte [138]. Maximum specific capacitance of 240 Fg$^{-1}$ and 149 Fg$^{-1}$ were achieved for aqueous and ionic liquid electrolytes respectively at a high current density of 10 Ag$^{-1}$ using nitrogen and sulphur co-doped hollow cellular carbon nano-capsules which is much higher capacitive values for this type of electrode material reported in literature [139]. Nitrogen and sulphur co-doped graphene

| Material           | Value 1 | Value 2 | Value 3 | Value 4 | Reference |
|--------------------|---------|---------|---------|---------|-----------|
| Graphene           | 170     | 268     | 21      | 5       | [129]     |
| Carbon nanofiber   | 641     | 180     | 22      | 400     | [130]     |
aerogel offered high energy density of 101 Wh kg\(^{-1}\) when used as electrode active material which is one of the highest presented in literature for this type of material. The electrode materials also offered a large specific capacitance of 203 F g\(^{-1}\) at a current density of 1 A g\(^{-1}\) when used alongside ionic liquid (1-ethyl-3-methylimidazolium tetra-fluoroborate, EMIMBF\(_4\)) as an electrolyte [140]. Similarly a recent study by J Chen et al. showed that nitrogen and phosphorus co-doping results in very high specific capacitance 337 F g\(^{-1}\) at 0.5 A g\(^{-1}\) which can deliver the energy density of 23.1 W h kg\(^{-1}\) to 12.4 W h kg\(^{-1}\) at power densities of 720.4 W kg\(^{-1}\) to 13950 W kg\(^{-1}\), respectively [141]. Boron and nitrogen is considered as an excellent combination of heteroatoms which is used by researchers to elevate the performance of electrode active material through synergistic effects of more than single dopant, nitrogen and boron co-doped materials have demonstrated excellent electrochemical performance recently [142-145]. Very recently researchers have been trying to evaluate the impact of trinary doping where more than two functional groups are introduced and overall electrochemical performance is sum of electric double layer capacitance coming from the porous parameters of the active materials and pseudo-capacitance of heteroatoms. Very recent study by G Zhao and co-workers has shown that excellent electrochemical performance can be attained when more two functional groups are introduced in highly porous carbon. Specific capacitance of 576 F g\(^{-1}\) together with extraordinary energy density of 107 Wh kg\(^{-1}\) at power density 900 W kg\(^{-1}\) was achieved, when active material was co-doped with oxygen, nitrogen and sulphur functional groups [146]. Performance characteristics of various carbon based active materials have been summarised in Table 5 below.

Table 4 — Physical and electrochemical characteristics of various co-doped carbons used as active material in supercapacitors.

| Electrode materials | Dopant | SSA (m\(^2\) g\(^{-1}\)) | Capacitance (F g\(^{-1}\)) | Energy density (Wh kg\(^{-1}\)) | Power density (W kg\(^{-1}\)) | Reference |
|---------------------|--------|--------------------------|-----------------------------|-------------------------------|-------------------------------|-----------|
| Activated carbon    | N & S  | 1047                     | 298                         | 21                            | 180                           | [147]     |
| Activated carbon    | N&S    | 748                      | 362                         | 11                            | 4                             | [148]     |
| Carbon spheres      | N&P    | 232                      | 232                         | 8                             | 601                           | [149]     |
| Carbon nanowires    | B&N    | 1022                     | 504                         | 23                            | 200                           | [144]     |
| Activated carbon    | N&S    | 453                      | 247                         | 34                            | 4220                          | [150]     |
| Activated carbon    | N&S    | 1093                     | 272                         | 12                            | 8                             | [151]     |
Nitrogen is the most explored functional material with promising results however; other functional groups such as sulphur, phosphorus and boron have not been investigated yet in great detail. Lately attention has been focused towards co-doping (binary and trinary doping) with encouraging outcomes as shown in Table 5. Nitrogen and sulphur is considered as the natural combination for maximum cell output whereas still enormous research is required to perfectly tune the combinations of various dopants (functional groups) to maximise the material productivity.

There is still a vast scope of research investigation to analyse the effect of functional groups beyond nitrogen in various combinations while using them alongside non-aqueous electrolytes in order to achieve battery level energy densities.

3.0 Conclusions

Even though nitrogen doped carbon materials have been investigated extensively for their application as electrodes in electrochemical capacitors, it is evident from this review that there is a class of functional materials which includes sulphur, phosphorus and boron beyond the nitrogen, possessing physio/chemical properties suitable for superior cell output. By adopting these emerging functional materials as electrodes, the performance of electrochemical cell can be improved substantially through their advance doping. Nitrogen doping results in an improved electrochemical performance (capacitance/energy density) while retaining high power density of the cell, since introduction of nitrogen on the surface of the electro-active material results in improved wetting behaviour which helps to maintain low equivalent series resistance (ESR) of cell. Doping carbon based electrode materials with phosphorus results in superior physio/chemical properties matched with nitrogen doping, additional benefits of using phosphorus doped active material includes an increase in the operating potential of the supercapacitor cell which can have a positive effect on its energy
density. Whereas, sulphur doping can be beneficial in improving the electronic reactivity of active material which results in higher pseudo-capacitive contribution when compared with the performance of active material doped with other heteroatoms. Individual functional materials possess excellent properties which can have positive impact on both physical properties and electrochemical performance of supercapacitor cell when introduced into the matrix or on the surface of active material independently however; lately attention has been diverted towards using more than one dopant where synergistic effects of both dopants yields even superior performance. Since nitrogen has been explored extensively and has revealed encouraging results, still an immense research drive is needed to explore other function materials since this field is still very young with very little deliberation.

Already these functional materials have shown immense potential however, it will be extremely fascinating for researchers in the field of energy storage to follow further improvement in advanced functionalized carbon materials, and to witness how such materials will start to transform the field of materials for energy applications in general and for their suitability in supercapacitors in particular.

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Highlights

Recent progress in synthesis of functionalized nanostructured carbon materials

Heteroatoms doped carbon nanomaterials improves specific capacitance

Heteroatoms doping results in improving energy density while maintaining the excellent power density