Journal Pre-proof

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

Qaisar Abbas, Rizwan Raza, Imarn Shabbir, A.G. Olabi

PII: S2468-2179(19)30214-X

DOI: https://doi.org/10.1016/j.jsamd.2019.07.007

Reference: JSAMD 245

To appear in: *Journal of Science: Advanced Materials and Devices*

Received Date: 24 April 2019

Revised Date: 23 July 2019

Accepted Date: 26 July 2019

Please cite this article as: Q. Abbas, R. Raza, I. Shabbir, A.G Olabi, Heteroatom Doped High Porosity Carbon Nanomaterials as Electrodes for Energy Storage in Electrochemical Capacitors: A Review, *Journal of Science: Advanced Materials and Devices*, https://doi.org/10.1016/j.jsamd.2019.07.007.

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

Qaisar Abbas [a], Rizwan Raza b, Imarn Shabbir[c] and A.G.Olabi, [d,e]*

a School of Engineering, Computing and Physical Sciences, University of the West of Scotland, Paisley PA1 2BE, United Kingdom.

b Department of Physics, COMSATS Institute of Information Technology, Lahore, Pakistan

c Energy Optimisation-Energy Department Tata Steel, Port Talbot U.k

d Department of Sustainable and Renewable Energy Engineering, University of Sharjah, Sharjah, United Arab Emirates

e Mechanical Engineering and Design, School of Engineering and Applied Science, Aston University, Aston Triangle, Birmingham B4 7ET, UK

Corresponding author e-mail address: qaisar.abbas@uws.ac.uk

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.

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

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.

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.

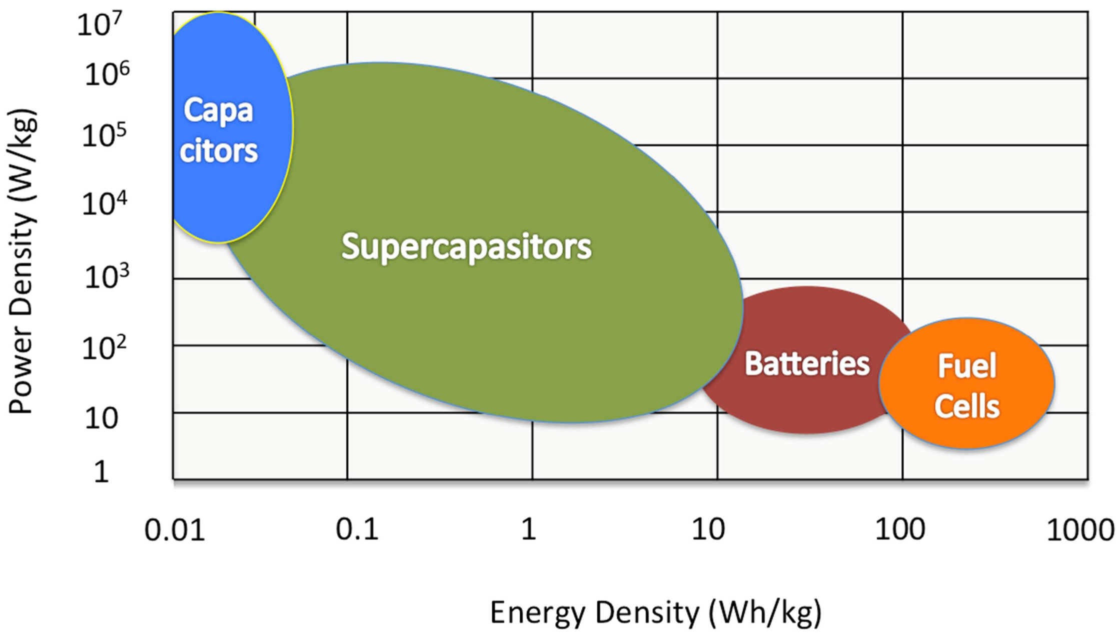

Figure 1:- Ragone plot of energy density vs power density for various electrical energy storage and conversion devices [1].

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.

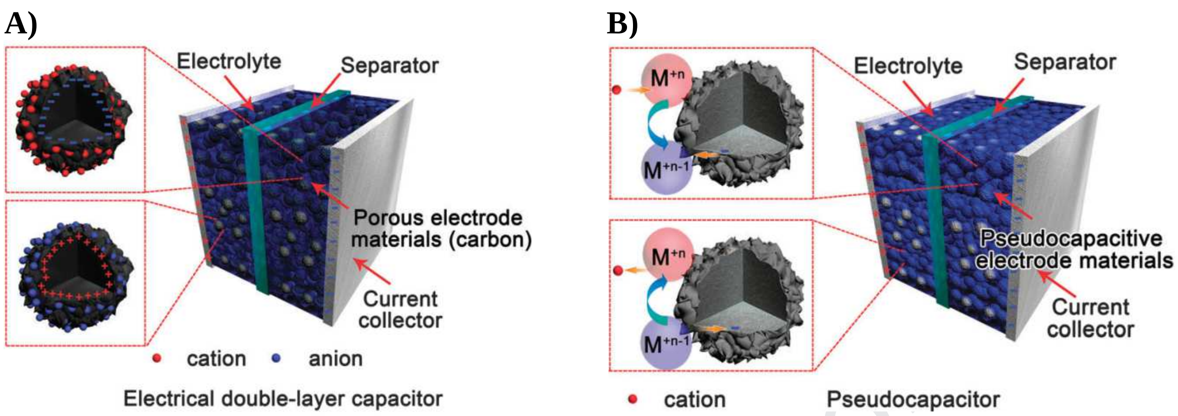

Figure 2:- Schematic diagram of A) an electric double layer capacitor [EDLC] B) a pseudo-capacitor [PC] [6].

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.

$$C = \varepsilon_0 \varepsilon_r \frac{A}{d} \quad (1)$$

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^2g^{-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].

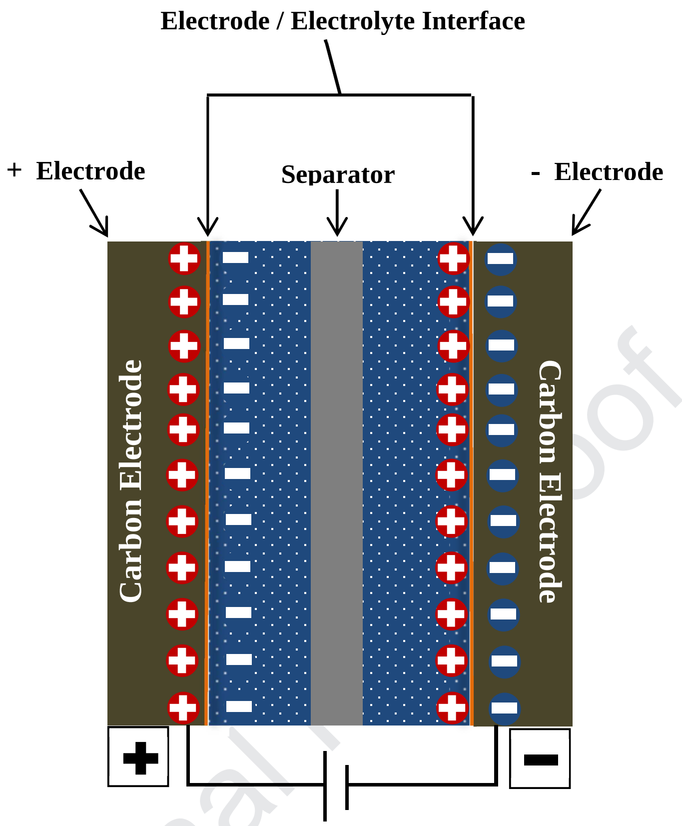

Figure 3: Schematic of charge storage mechanism of electrical double layer capacitor

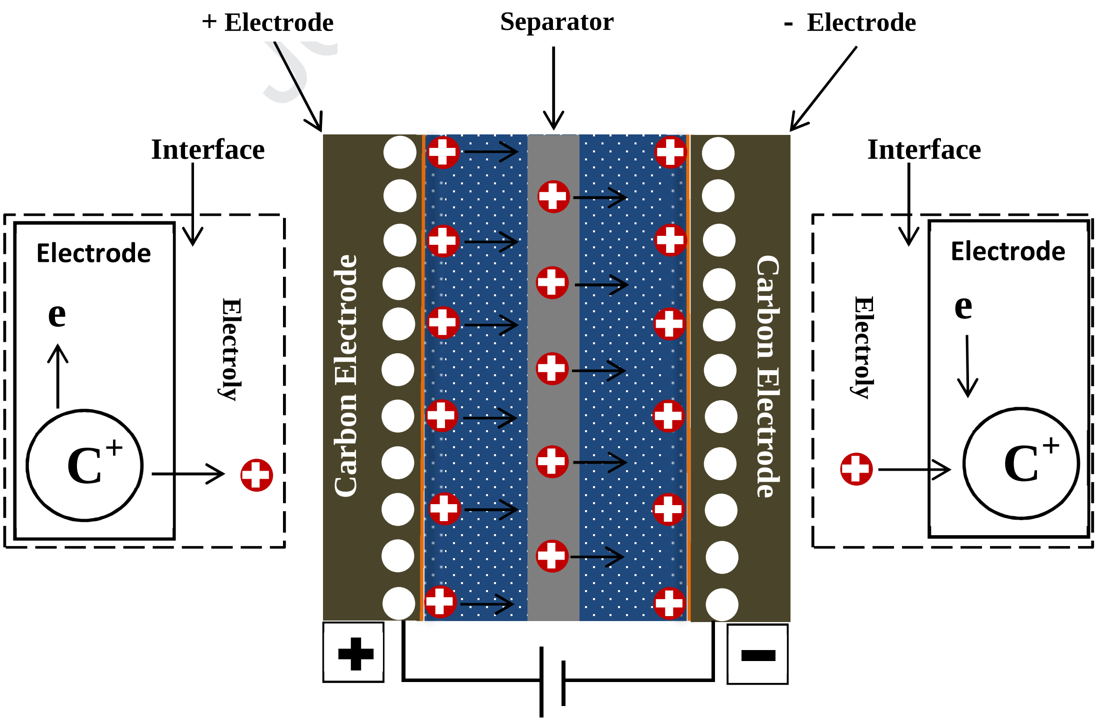

Figure 4: Schematic of charge storage mechanism of pseudocapacitor

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.

$$E = \frac{1}{2} CV^2 \qquad \text{Equation 2}$$

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.

$$P = \frac{1}{2}\frac{(\Delta V)^2}{R} \qquad \text{Equation 3}$$

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 synthesise nitrogen doped carbon is through heat-treatment of un-doped (crude) carbons with nitrogen containing material such as, urea [CH_4N_2O] [45], nitric acid [HNO_3] [46] and ammonia [NH_3] [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 [$C_3H_6N_6$], polyacrylonitrile [C_3H_3N] and polyvinylpyridine, [C_6H_9NO]$_n$ 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 [$C_6H_{13}NO_5$] [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.

$$-\mathrm{C} = \mathrm{NH} + 2\mathrm{e}^- \leftrightarrow -\mathrm{CH} - \mathrm{NH}_2 \qquad \text{Equation 4}$$

$$-\mathrm{C} - \mathrm{NHOH} + 2\mathrm{e}^- + 2\mathrm{H}^+ \leftrightarrow -\mathrm{C} - \mathrm{NH}_2 + \mathrm{H}_2\mathrm{O} \qquad \text{Equation 5}$$

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 ($683\,\mathrm{mF\,cm^{-2}}$ at $2\,\mathrm{mA\,cm^{-2}}$) after nitrogen doping as compared to$330\,\mathrm{mF\,cm^{-2}}$ 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 6.7$Whkg^{-1}$ as compare to 5.9$Whkg^{-1}$ 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° 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.

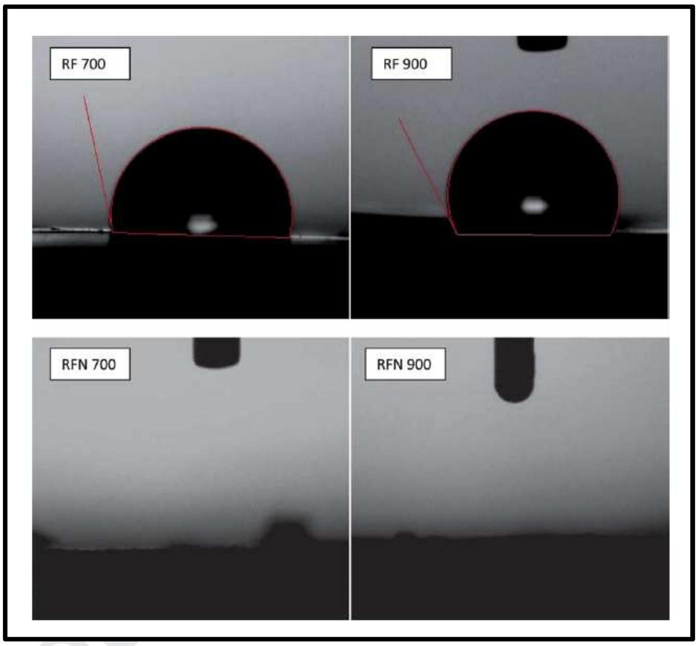

Figure 5:- Images showing the wettability of un-doped (RF) and nitrogen doped (NRF) carbons samples [55]

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 nano-sheets	380	480	83	426	[58]
Activated Carbon	2905	351	39	1.0	[45]
Activated Carbon	1459	451	11	125	[59]

Activated carbon	2255	258	5	10	[60]
Graphene	203	390	55	1800	[54]
Activated biomass	2650	200	6	8	[61]
Activated carbon	2723	221	5	2500	[62]
Graphene aerogels	446	318	60	900	[63]
Activated carbon	1848	261	4	10	[64]
Template derived carbon	2506	337	10	14.4	[65]

It can be established form 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 .

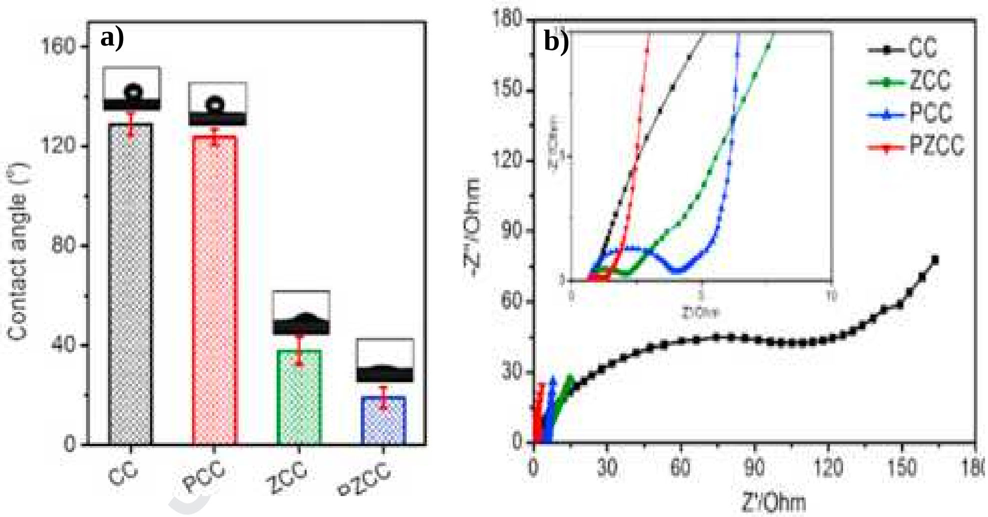

Figure 6:- a) contact angle of 6M KOH on the surface **b)** Nyquist plots of doped and un-doped carbons [66].

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_2SO_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_4NBF_4/PC) [68]. Wide range of phosphorus doped carbon based electrode materials with their physical and electrochemical properties are given in Table2

Table 2 –– Physical and electrochemical characteristics of various phosphorus 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
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 nano-fibre	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 m^2g^{-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 un-doped 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 Table3.

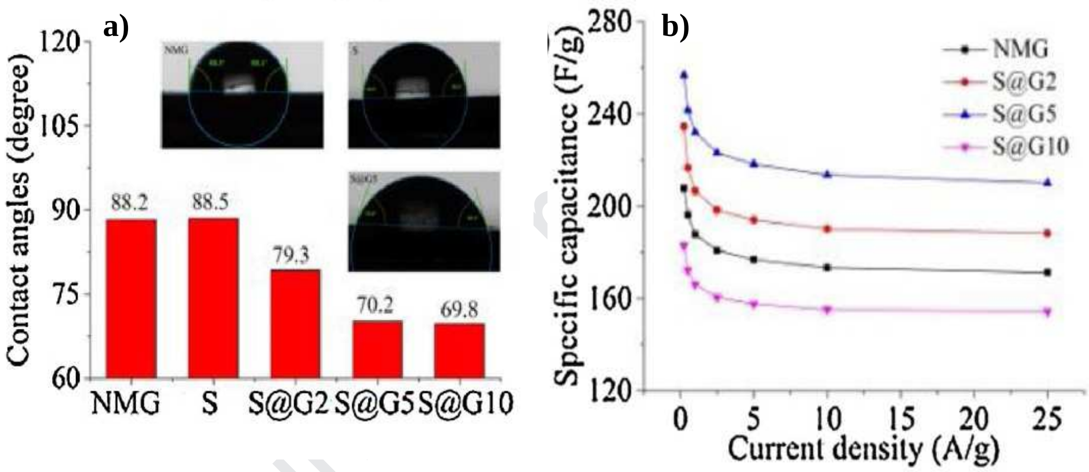

Figure 7:- a**)** Contact angle of a water droplet on doped and un-doped samples. **b)** Specific capacitances of electrodes at different current densities

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 nano-sheets	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]

Graphene	288	270	…..	…..	[98]
Activated carbon	1730	283	…..	…..	[99]
Activated carbon	1057	332	…..	….	[100]
Bio-carbon	660	225	…..	….	[101]
Graphene	497	21	20	624	[102]
Graphene oxide	1500	65	…..	…..	[103]
Activated carbons	…..	325	22	7393	[96]

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 (B_2O_3) [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 W h 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 Fg^{-1} was attained after boron doping which is considerably higher than 221 Fg^{-1} for an un-doped carbon at $5mVs^{-1}$. Exceptionally low solution resistance R_S of 1.05Ω 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_2O_3 as shown in Figure 8. Exceptionally high specific capacitance of 448 Fg^{-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].

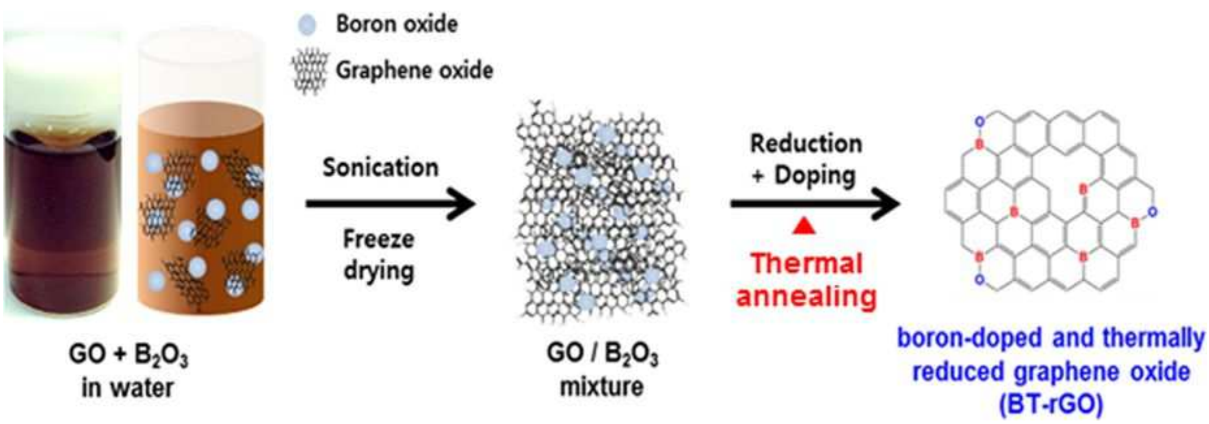

Figure 8:- Schematic presentation of the preparation of BT-rGO

More examples of boron doped carbon when used as active material in supercapacitors are presented in Table 4 below.

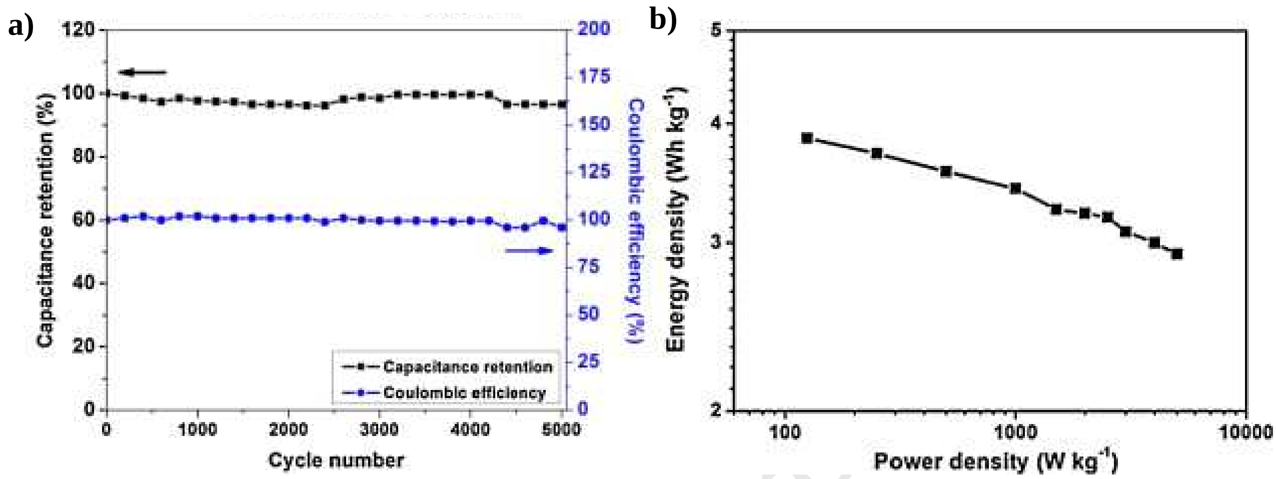

Figure 9:- a) Cycling stability and coulombic efficiency of Boron doped electrode **b)** Ragone plot of symmetric cell [117]

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

Electrode materials	Specific surface area (m^2 g^{-1})	Capacitance (Fg^{-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]

Graphene	170	268	21	5	[129]
Carbon nanofiber	641	180	22	400	[130]

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 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, EMIMBF4) 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 Fg^{-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 (Fg^{-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]

Carbon nano-sheets	N&S	1147	280	7	487	[152]
Hierarchical carbon	N&P	1431	337	23	14	[141]
Graphene aerogels	N&S	217	203	100	0.94	[140]
Activated carbon	O,N &S	2650	576	107	900	[146]
Carbon sphere	P,N&O	890	157	10	750	[153]
Hierarchical carbon	O,N&S	1307	245	9	100	[154]

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.

References

[1] M. Aslani, "Electrochemical double layer capacitors (supercapacitors)," *Standford University,* 2012.

[2] X. Luo, J. Wang, M. Dooner, and J. Clarke, "Overview of current development in electrical energy storage technologies and the application potential in power system operation," *Applied energy,* vol. 137, pp. 511-536, 2015.

[3] M. Mirzaeian, Q. Abbas, A. Ogwu, P. Hall, M. Goldin, M. Mirzaeian*, et al.*, "Electrode and electrolyte materials for electrochemical capacitors," *international journal of hydrogen energy,* vol. 42, pp. 25565-25587, 2017.

[4] I. Hadjipaschalis, A. Poullikkas, and V. Efthimiou, "Overview of current and future energy storage technologies for electric power applications," *Renewable and sustainable energy reviews,* vol. 13, pp. 1513-1522, 2009.

[5] M. Mirzaeian, Q. Abbas, A. Ogwu, P. Hall, M. Goldin, M. Mirzaeian*, et al.*, "Electrode and electrolyte materials for electrochemical capacitors," *International Journal of Hydrogen Energy,* 2017.

[6] C. Zhong, Y. Deng, W. Hu, J. Qiao, L. Zhang, and J. Zhang, "A review of electrolyte materials and compositions for electrochemical supercapacitors," *Chemical Society Reviews,* vol. 44, pp. 7484-7539, 2015.

[7] X.-L. Su, J.-R. Chen, G.-P. Zheng, J.-H. Yang, X.-X. Guan, P. Liu*, et al.*, "Three-dimensional porous activated carbon derived from loofah sponge biomass for supercapacitor applications," *Applied Surface Science,* vol. 436, pp. 327-336, 2018.

[8] X. Li and L. Zhi, "Graphene hybridization for energy storage applications," *Chemical Society Reviews,* vol. 47, pp. 3189-3216, 2018.

[9] N. Rey-Raap, M. Enterría, J. I. c. Martins, M. F. R. Pereira, and J. L. s. Figueiredo, "Influence of multiwalled carbon nanotubes as additives in biomass-derived carbons for

supercapacitor applications," *ACS applied materials & interfaces,* vol. 11, pp. 6066-6077, 2019.

[10] W. Shi, X. Zhou, J. Li, E. R. Meshot, A. D. Taylor, S. Hu*, et al.*, "High-performance capacitive deionization via manganese oxide-coated, vertically aligned carbon nanotubes," *Environmental Science & Technology Letters,* vol. 5, pp. 692-700, 2018.

[11] P. Yan, X. Zhang, M. Hou, Y. Liu, T. Liu, K. Liu*, et al.*, "Ultrahigh-power supercapacitors based on highly conductive graphene nanosheet/nanometer-sized carbide-derived carbon frameworks," *Nanotechnology,* vol. 29, p. 255403, 2018.

[12] M. Vijayakumar, R. Santhosh, J. Adduru, T. N. Rao, and M. Karthik, "Activated carbon fibres as high performance supercapacitor electrodes with commercial level mass loading," *Carbon,* vol. 140, pp. 465-476, 2018.

[13] K. Sharma, A. Arora, and S. Tripathi, "Review of supercapacitors: Materials and devices," *Journal of Energy Storage,* vol. 21, pp. 801-825, 2019.

[14] X. Zhao, H. Chen, F. Kong, Y. Zhang, S. Wang, S. Liu*, et al.*, "Fabrication, characteristics and applications of carbon materials with different morphologies and porous structures produced from wood liquefaction: A review," *Chemical Engineering Journal,* 2019.

[15] M. Jayalakshmi and K. Balasubramanian, "Simple capacitors to supercapacitors-an overview," *Int. J. Electrochem. Sci,* vol. 3, pp. 1196-1217, 2008.

[16] D. Yu, Y. Ma, M. Chen, and X. Dong, "KOH activation of wax gourd-derived carbon materials with high porosity and heteroatom content for aqueous or all-solid-state supercapacitors," *Journal of colloid and interface science,* vol. 537, pp. 569-578, 2019.

[17] X. Chen, M. Chi, L. Xing, X. Xie, S. Liu, Y. Liang*, et al.*, "Natural Plant Template-Derived Cellular Framework Porous Carbon as a High-Rate and Long-Life Electrode Material for Energy Storage," *ACS Sustainable Chemistry & Engineering,* vol. 7, pp. 5845-5855, 2019.

[18] L. Zhang, Y. Guo, K. Shen, J. Huo, Y. Liu, and S. Guo, "Ion-matching porous carbons with ultra-high surface area and superior energy storage performance for supercapacitors," *Journal of Materials Chemistry A,* vol. 7, pp. 9163-9172, 2019.

[19] N. Wang, C. Wang, L. He, Y. Wang, W. Hu, and S. Komarneni, "Incomplete phase separation strategy to synthesize P/N co-doped porous carbon with interconnected structure for asymmetric supercapacitors with ultra-high power density," *Electrochimica Acta,* vol. 298, pp. 717-725, 2019.

[20] A. Sobhani-Nasab, M. Rahimi-Nasrabadi, H. R. Naderi, V. Pourmohamadian, F. Ahmadi, M. R. Ganjali*, et al.*, "Sonochemical synthesis of terbium tungstate for developing high power supercapacitors with enhanced energy densities," *Ultrasonics sonochemistry,* vol. 45, pp. 189-196, 2018.

[21] X. Liu, W. Zang, C. Guan, L. Zhang, Y. Qian, A. M. Elshahawy*, et al.*, "Ni-Doped Cobalt–Cobalt Nitride Heterostructure Arrays for High-Power Supercapacitors," *ACS Energy Letters,* vol. 3, pp. 2462-2469, 2018.

[22] Z. Y. Jin, A. H. Lu, Y. Y. Xu, J. T. Zhang, and W. C. Li, "Ionic Liquid-Assisted Synthesis of Microporous Carbon Nanosheets for Use in High Rate and Long Cycle Life Supercapacitors," *Advanced Materials,* vol. 26, pp. 3700-3705, 2014.

[23] T. Huang, X. Chu, S. Cai, Q. Yang, H. Chen, Y. Liu*, et al.*, "Tri-high designed graphene electrodes for long cycle-life supercapacitors with high mass loading," *Energy Storage Materials,* vol. 17, pp. 349-357, 2019.

[24] G. Wang, S. Oswald, M. Löffler, K. Müllen, and X. Feng, "Beyond Activated Carbon: Graphite-Cathode-Derived Li-Ion Pseudocapacitors with High Energy and High Power Densities," *Advanced Materials,* vol. 31, p. 1807712, 2019.

[25] X. Zang, C. Shen, E. Kao, R. Warren, R. Zhang, K. S. Teh*, et al.*, "Titanium disulfide coated carbon nanotube hybrid electrodes enable high energy density symmetric pseudocapacitors," *Advanced Materials,* vol. 30, p. 1704754, 2018.

[26] Y. Jiang and J. Liu, "Definitions of pseudocapacitive materials: a brief review," *Energy & Environmental Materials,* vol. 2, pp. 30-37, 2019.

[27] R. V. Prataap, R. Arunachalam, R. P. Raj, S. Mohan, and L. Peter, "Effect of electrodeposition modes on ruthenium oxide electrodes for supercapacitors," *Current Applied Physics,* vol. 18, pp. 1143-1148, 2018.

[28] Y. Zeng, M. Yu, Y. Meng, P. Fang, X. Lu, and Y. Tong, "Iron-based supercapacitor electrodes: advances and challenges," *Advanced Energy Materials,* vol. 6, p. 1601053, 2016.

[29] Y.-z. Zheng, H.-y. Ding, and M.-l. Zhang, "Preparation and electrochemical properties of nickel oxide as a supercapacitor electrode material," *Materials Research Bulletin,* vol. 44, pp. 403-407, 2009.

[30] G. A. Snook, P. Kao, and A. S. Best, "Conducting-polymer-based supercapacitor devices and electrodes," *Journal of power sources,* vol. 196, pp. 1-12, 2011.

[31] L.-Z. Fan and J. Maier, "High-performance polypyrrole electrode materials for redox supercapacitors," *Electrochemistry communications,* vol. 8, pp. 937-940, 2006.

[32] J. Carlberg and O. Inganäs, "Poly (3, 4-ethylenedioxythiophene) as electrode material in electrochemical capacitors," *Journal of the Electrochemical Society,* vol. 144, pp. L61-L64, 1997.

[33] V. Gupta and N. Miura, "High performance electrochemical supercapacitor from electrochemically synthesized nanostructured polyaniline," *Materials Letters,* vol. 60, pp. 1466-1469, 2006.

[34] Y. Wang, A. Du Pasquier, D. Li, P. Atanassova, S. Sawrey, and M. Oljaca, "Electrochemical double layer capacitors containing carbon black additives for improved capacitance and cycle life," *Carbon,* vol. 133, pp. 1-5, 2018.

[35] D. Wang, Z. Geng, B. Li, and C. Zhang, "High performance electrode materials for electric double-layer capacitors based on biomass-derived activated carbons," *Electrochimica Acta,* vol. 173, pp. 377-384, 2015.

[36] M. Lu, *Supercapacitors: materials, systems, and applications*: John Wiley & Sons, 2013.

[37] K. Naoi, S. Ishimoto, J.-i. Miyamoto, and W. Naoi, "Second generation 'nanohybrid supercapacitor': evolution of capacitive energy storage devices," *Energy & Environmental Science,* vol. 5, pp. 9363-9373, 2012.

[38] Q. Abbas, A. G. Olabi, R. Raza, and D. Gibson, "Carbon/Metal Oxide Composites as Electrode Materials for Supercapacitors Applications," 2018.

[39] Q. Abbas, M. Mirzaeian, and A. A. Ogwu, "Electrochemical performance of controlled porosity resorcinol/formaldehyde based carbons as electrode materials for supercapacitor applications," *International Journal of Hydrogen Energy,* 2017.

[40] Q. Abbas, M. Mirzaeian, A. A. Ogwu, M. Mazur, and D. Gibson, "Effect of physical activation/surface functional groups on wettability and electrochemical performance of carbon/activated carbon aerogels based electrode materials for electrochemical capacitors," *International Journal of Hydrogen Energy,* 2018.

[41] J. Zhou, L. Hou, J. Lian, W. Cheng, D. Wang, H. Gou*, et al.*, "Nitrogen-doped highly dense but porous carbon microspheres with ultrahigh volumetric capacitance and rate capability for supercapacitors," *Journal of Materials Chemistry A,* 2019.

[42] D. Wang, Z. Wang, Y. Li, K. Dong, J. Shao, S. Luo*, et al.*, "In situ double-template fabrication of boron-doped 3d hierarchical porous carbon network as anode materials for li-and na-ion batteries," *Applied Surface Science,* vol. 464, pp. 422-428, 2019.

[43] J. Patiño, N. López-Salas, M. C. Gutiérrez, D. Carriazo, M. L. Ferrer, and F. del Monte, "Phosphorus-doped carbon–carbon nanotube hierarchical monoliths as true three-dimensional electrodes in supercapacitor cells," *Journal of Materials Chemistry A,* vol. 4, pp. 1251-1263, 2016.

[44] Z.-S. Wu, Y.-Z. Tan, S. Zheng, S. Wang, K. Parvez, J. Qin*, et al.*, "Bottom-up fabrication of sulfur-doped graphene films derived from sulfur-annulated nanographene for ultrahigh

volumetric capacitance micro-supercapacitors," *Journal of the American Chemical Society,* vol. 139, pp. 4506-4512, 2017.
[45] K. Zou, Y. Deng, J. Chen, Y. Qian, Y. Yang, Y. Li*, et al.*, "Hierarchically porous nitrogen-doped carbon derived from the activation of agriculture waste by potassium hydroxide and urea for high-performance supercapacitors," *Journal of Power Sources,* vol. 378, pp. 579-588, 2018.
[46] D. I. Arango, Z. Zapata-Benabithe, E. C. Arenas, and J. C. Perez-Osorno, "Influence of surface modification with nitric acid on electrochemical performance of agroindustrial waste-based activated carbon," *Journal of Materials Science: Materials in Electronics,* pp. 1-13, 2018.
[47] S. Li and Z. Fan, "Nitrogen-doped carbon mesh from pyrolysis of cotton in ammonia as binder-free electrodes of supercapacitors," *Microporous and Mesoporous Materials,* vol. 274, pp. 313-317, 2019.
[48] L. Zhao, N. Baccile, S. Gross, Y. Zhang, W. Wei, Y. Sun*, et al.*, "Sustainable nitrogen-doped carbonaceous materials from biomass derivatives," *Carbon,* vol. 48, pp. 3778-3787, 2010.
[49] J. Sun, J. Niu, M. Liu, J. Ji, M. Dou, and F. Wang, "Biomass-derived nitrogen-doped porous carbons with tailored hierarchical porosity and high specific surface area for high energy and power density supercapacitors," *Applied Surface Science,* vol. 427, pp. 807-813, 2018.
[50] E. Frackowiak and F. Beguin, "Carbon materials for the electrochemical storage of energy in capacitors," *Carbon,* vol. 39, pp. 937-950, 2001.
[51] X. Han, H. Jiang, Y. Zhou, W. Hong, Y. Zhou, P. Gao*, et al.*, "A high performance nitrogen-doped porous activated carbon for supercapacitor derived from pueraria," *Journal of Alloys and Compounds,* vol. 744, pp. 544-551, 2018.
[52] Z. Mao, S. Zhao, J. Wang, Y. Zeng, X. Lu, and Y. Tong, "Facile synthesis of nitrogen-doped porous carbon as robust electrode for supercapacitors," *Materials Research Bulletin,* vol. 101, pp. 140-145, 2018.
[53] M. J. Mostazo-López, R. Ruiz-Rosas, A. Castro-Muñiz, H. Nishihara, T. Kyotani, E. Morallon*, et al.*, "Ultraporous nitrogen-doped zeolite-templated carbon for high power density aqueous-based supercapacitors," *Carbon,* vol. 129, pp. 510-519, 2018.
[54] S. Dai, Z. Liu, B. Zhao, J. Zeng, H. Hu, Q. Zhang*, et al.*, "A high-performance supercapacitor electrode based on N-doped porous graphene," *Journal of Power Sources,* vol. 387, pp. 43-48, 2018.
[55] S. L. Candelaria, B. B. Garcia, D. Liu, and G. Cao, "Nitrogen modification of highly porous carbon for improved supercapacitor performance," *Journal of Materials Chemistry,* vol. 22, pp. 9884-9889, 2012.
[56] J. Zhao, H. Lai, Z. Lyu, Y. Jiang, K. Xie, X. Wang*, et al.*, "Hydrophilic Hierarchical Nitrogen-Doped Carbon Nanocages for Ultrahigh Supercapacitive Performance," *Advanced materials,* vol. 27, pp. 3541-3545, 2015.
[57] T. Lin, I.-W. Chen, F. Liu, C. Yang, H. Bi, F. Xu*, et al.*, "Nitrogen-doped mesoporous carbon of extraordinary capacitance for electrochemical energy storage," *Science,* vol. 350, pp. 1508-1513, 2015.
[58] M. S. Javed, S. S. A. Shah, T. Najam, M. K. Aslam, J. Li, S. Hussain*, et al.*, "Synthesis of mesoporous defective graphene-nanosheets in a space-confined self-assembled nanoreactor: Highly efficient capacitive energy storage," *Electrochimica Acta,* vol. 305, pp. 517-527, 2019.
[59] C. Wang, D. Wu, H. Wang, Z. Gao, F. Xu, and K. Jiang, "Biomass derived nitrogen-doped hierarchical porous carbon sheets for supercapacitors with high performance," *Journal of colloid and interface science,* vol. 523, pp. 133-143, 2018.
[60] G. Wang, J. Zhang, S. Kuang, J. Zhou, W. Xing, and S. Zhuo, "Nitrogen-doped hierarchical porous carbon as an efficient electrode material for supercapacitors," *Electrochimica Acta,* vol. 153, pp. 273-279, 2015.

[61] M. Sevilla, N. Diez, G. A. Ferrero, and A. B. Fuertes, "Sustainable supercapacitor electrodes produced by the activation of biomass with sodium thiosulfate," *Energy Storage Materials,* vol. 18, pp. 356-365, 2019.

[62] P. Song, X. Shen, W. He, L. Kong, X. He, Z. Ji*, et al.*, "Protein-derived nitrogen-doped hierarchically porous carbon as electrode material for supercapacitors," *Journal of Materials Science: Materials in Electronics,* vol. 29, pp. 12206-12215, 2018.

[63] P. Xu, Q. Gao, L. Ma, Z. Li, H. Zhang, H. Xiao*, et al.*, "A high surface area N-doped holey graphene aerogel with low charge transfer resistance as high performance electrode of non-flammable thermostable supercapacitor," *Carbon,* vol. 149, pp. 452-461, 2019.

[64] J. Zhou, Z. Zhang, W. Xing, J. Yu, G. Han, W. Si*, et al.*, "Nitrogen-doped hierarchical porous carbon materials prepared from meta-aminophenol formaldehyde resin for supercapacitor with high rate performance," *Electrochimica Acta,* vol. 153, pp. 68-75, 2015.

[65] M. Chen, H. Xuan, X. Zheng, J. Liu, X. Dong, and F. Xi, "N-doped mesoporous carbon by a hard-template strategy associated with chemical activation and its enhanced supercapacitance performance," *Electrochimica Acta,* vol. 238, pp. 269-277, 2017.

[66] J. Yi, Y. Qing, C. Wu, Y. Zeng, Y. Wu, X. Lu*, et al.*, "Lignocellulose-derived porous phosphorus-doped carbon as advanced electrode for supercapacitors," *Journal of Power Sources,* vol. 351, pp. 130-137, 2017.

[67] M.-q. Guo, J.-q. Huang, X.-y. Kong, H.-j. Peng, H. Shui, F.-y. Qian*, et al.*, "Hydrothermal synthesis of porous phosphorus-doped carbon nanotubes and their use in the oxygen reduction reaction and lithium-sulfur batteries," *New Carbon Materials,* vol. 31, pp. 352-362, 2016.

[68] W. Ma, L. Xie, L. Dai, G. Sun, J. Chen, F. Su*, et al.*, "Influence of phosphorus doping on surface chemistry and capacitive behaviors of porous carbon electrode," *Electrochimica Acta,* vol. 266, pp. 420-430, 2018.

[69] W. Yang, W. Yang, L. Kong, A. Song, X. Qin, and G. Shao, "Phosphorus-doped 3D hierarchical porous carbon for high-performance supercapacitors: A balanced strategy for pore structure and chemical composition," *Carbon,* vol. 127, pp. 557-567, 2018.

[70] R. Yang, J. Wu, and W. Yan, "Phosphorus-doped hierarchical porous carbon as efficient metal-free electrocatalysts for oxygen reduction reaction," *International Journal of Hydrogen Energy,* 2019.

[71] L. Zu, X. Gao, H. Lian, X. Cai, C. Li, Y. Zhong*, et al.*, "High Electrochemical Performance Phosphorus-Oxide Modified Graphene Electrode for Redox Supercapacitors Prepared by One-Step Electrochemical Exfoliation," *Nanomaterials,* vol. 8, p. 417, 2018.

[72] L. Zhang, T. You, T. Zhou, X. Zhou, and F. Xu, "Interconnected hierarchical porous carbon from lignin-derived byproducts of bioethanol production for ultra-high performance supercapacitors," *ACS applied materials & interfaces,* vol. 8, pp. 13918-13925, 2016.

[73] Y. Wen, B. Wang, C. Huang, L. Wang, and D. Hulicova-Jurcakova, "Synthesis of Phosphorus-Doped Graphene and its Wide Potential Window in Aqueous Supercapacitors," *Chemistry–A European Journal,* vol. 21, pp. 80-85, 2015.

[74] H. A. Andreas and B. E. Conway, "Examination of the double-layer capacitance of an high specific-area C-cloth electrode as titrated from acidic to alkaline pHs," *Electrochimica Acta,* vol. 51, pp. 6510-6520, 2006.

[75] J. Zhang, X. Liu, R. Blume, A. Zhang, R. Schlögl, and D. S. Su, "Surface-modified carbon nanotubes catalyze oxidative dehydrogenation of n-butane," *science,* vol. 322, pp. 73-77, 2008.

[76] A. Puziy, O. Poddubnaya, and A. Ziatdinov, "On the chemical structure of phosphorus compounds in phosphoric acid-activated carbon," *Applied surface science,* vol. 252, pp. 8036-8038, 2006.

[77] J. Guo, D. Wu, T. Wang, and Y. Ma, "P-doped hierarchical porous carbon aerogels derived from phenolic resins for high performance supercapacitor," *Applied Surface Science,* vol. 475, pp. 56-66, 2019.

[78] Y. Li, D. Zhang, M. Han, J. He, Y. Wang, K. Wang*, et al.*, "Fabrication of the phosphorus doped mesoporous carbon with superior capacitive performance by microwave irradiation under ambient atmosphere: An ultra-facile and energy-efficient method," *Applied Surface Science,* vol. 458, pp. 119-128, 2018.

[79] G.-l. Zhuang, J.-q. Bai, X.-y. Tao, J.-m. Luo, X. Zhou, W.-x. Chen*, et al.*, "Trace phosphorus− doping significantly improving S-content of binary− doped mesoporous carbon network with enhancing electrochemical performance," *Microporous and Mesoporous Materials,* vol. 256, pp. 75-83, 2018.

[80] F. Li, A. Ahmad, L. Xie, G. Sun, Q. Kong, F. Su*, et al.*, "Phosphorus-modified porous carbon aerogel microspheres as high volumetric energy density electrode for supercapacitor," *Electrochimica Acta,* 2019.

[81] P. Karthika, N. Rajalakshmi, and K. Dhathathreyan, "Phosphorus-doped exfoliated graphene for supercapacitor electrodes," *Journal of nanoscience and nanotechnology,* vol. 13, pp. 1746-1751, 2013.

[82] J. Lin, Y. Wang, X. Zheng, H. Liang, H. Jia, J. Qi*, et al.*, "P-Doped NiCo 2 S 4 nanotubes as battery-type electrodes for high-performance asymmetric supercapacitors," *Dalton Transactions,* vol. 47, pp. 8771-8778, 2018.

[83] Y. Li, Y. Liu, M. Wang, X. Xu, T. Lu, C. Q. Sun*, et al.*, "Phosphorus-doped 3D carbon nanofiber aerogels derived from bacterial-cellulose for highly-efficient capacitive deionization," *carbon,* vol. 130, pp. 377-383, 2018.

[84] W. Kiciński, M. Szala, and M. Bystrzejewski, "Sulfur-doped porous carbons: synthesis and applications," *Carbon,* vol. 68, pp. 1-32, 2014.

[85] Y. Yang, L. Liu, Y. Tang, Y. Zhang, D. Jia, and L. Kong, "Bamboo-like carbon nanotubes containing sulfur for high performance supercapacitors," *Electrochimica Acta,* vol. 191, pp. 846-853, 2016.

[86] Z. Yang, Z. Yao, G. Li, G. Fang, H. Nie, Z. Liu*, et al.*, "Sulfur-doped graphene as an efficient metal-free cathode catalyst for oxygen reduction," *ACS nano,* vol. 6, pp. 205-211, 2011.

[87] Z. Yang, H. Nie, X. a. Chen, X. Chen, and S. Huang, "Recent progress in doped carbon nanomaterials as effective cathode catalysts for fuel cell oxygen reduction reaction," *Journal of Power Sources,* vol. 236, pp. 238-249, 2013.

[88] Y. S. Yun, V.-D. Le, H. Kim, S.-J. Chang, S. J. Baek, S. Park*, et al.*, "Effects of sulfur doping on graphene-based nanosheets for use as anode materials in lithium-ion batteries," *Journal of Power Sources,* vol. 262, pp. 79-85, 2014.

[89] J. Wang, S. Chew, Z. Zhao, S. Ashraf, D. Wexler, J. Chen*, et al.*, "Sulfur–mesoporous carbon composites in conjunction with a novel ionic liquid electrolyte for lithium rechargeable batteries," *Carbon,* vol. 46, pp. 229-235, 2008.

[90] X. Ma, G. Ning, Y. Kan, Y. Ma, C. Qi, B. Chen*, et al.*, "Synthesis of S-doped mesoporous carbon fibres with ultrahigh S concentration and their application as high performance electrodes in supercapacitors," *Electrochimica Acta,* vol. 150, pp. 108-113, 2014.

[91] J. Tian, H. Zhang, Z. Liu, G. Qin, and Z. Li, "One-step synthesis of 3D sulfur-doped porous carbon with multilevel pore structure for high-rate supercapacitors," *International Journal of Hydrogen Energy,* vol. 43, pp. 1596-1605, 2018.

[92] Y. Kan, G. Ning, and X. Ma, "Sulfur-decorated nanomesh graphene for high-performance supercapacitors," *Chinese Chemical Letters,* vol. 28, pp. 2277-2280, 2017.

[93] W. Deng, Y. Zhang, L. Yang, Y. Tan, M. Ma, and Q. Xie, "Sulfur-doped porous carbon nanosheets as an advanced electrode material for supercapacitors," *RSC Advances,* vol. 5, pp. 13046-13051, 2015.

[94] S. Liu, Y. Cai, X. Zhao, Y. Liang, M. Zheng, H. Hu*, et al.*, "Sulfur-doped nanoporous carbon spheres with ultrahigh specific surface area and high electrochemical activity for supercapacitor," *Journal of Power Sources,* vol. 360, pp. 373-382, 2017.

[95] J. S. Shaikh, N. S. Shaikh, R. Kharade, S. A. Beknalkar, J. V. Patil, M. P. Suryawanshi*, et al.*, "Symmetric supercapacitor: Sulphurized graphene and ionic liquid," *Journal of colloid and interface science,* vol. 527, pp. 40-48, 2018.

[96] A. Elmouwahidi, J. Castelo-Quibén, J. F. Vivo-Vilches, A. F. Pérez-Cadenas, F. J. Maldonado-Hódar, and F. Carrasco-Marín, "Activated carbons from agricultural waste solvothermally doped with sulphur as electrodes for supercapacitors," *Chemical Engineering Journal,* vol. 334, pp. 1835-1841, 2018.

[97] H. Chen, Z. Zhao, P. Qi, G. Wang, L. Shi, and F. Yu, "Sulphur-doped banana peel-derived activated carbon as electrode materials for supercapacitors," *International Journal of Nanomanufacturing,* vol. 15, pp. 181-195, 2019.

[98] X. Zhang and R. Zhang, "Outstanding long-term cycling stability of a sulfur-doped graphene electrode for supercapacitors obtained by post-tailoring the chemical states of doped-sulfur," *Applied Surface Science,* vol. 479, pp. 1039-1047, 2019.

[99] L. Sun, J. Liu, Z. Liu, T. Wang, H. Wang, and Y. Li, "Sulfur-doped mesoporous carbon via thermal reduction of CS 2 by Mg for high-performance supercapacitor electrodes and Li-ion battery anodes," *RSC advances,* vol. 8, pp. 19964-19970, 2018.

[100] W. Lei, H. Liu, J. Xiao, Y. Wang, and L. Lin, "Moss-derived mesoporous carbon as bi-functional electrode materials for lithium–sulfur batteries and supercapacitors," *Nanomaterials,* vol. 9, p. 84, 2019.

[101] M. Demir, A. A. Farghaly, M. J. Decuir, M. M. Collinson, and R. B. Gupta, "Supercapacitance and oxygen reduction characteristics of sulfur self-doped micro/mesoporous bio-carbon derived from lignin," *Materials Chemistry and Physics,* vol. 216, pp. 508-516, 2018.

[102] M. Kota, M. Jana, and H. S. Park, "Improving energy density of supercapacitors using heteroatom-incorporated three-dimensional macro-porous graphene electrodes and organic electrolytes," *Journal of Power Sources,* vol. 399, pp. 83-88, 2018.

[103] R. Reece, C. Lekakou, P. A. Smith, R. Grilli, and C. Trapalis, "Sulphur-linked graphitic and graphene oxide platelet-based electrodes for electrochemical double layer capacitors," *Journal of Alloys and Compounds,* vol. 792, pp. 582-593, 2019.

[104] Z. Wen, X. Wang, S. Mao, Z. Bo, H. Kim, S. Cui*, et al.*, "Crumpled nitrogen-doped graphene nanosheets with ultrahigh pore volume for high-performance supercapacitor," *Advanced materials,* vol. 24, pp. 5610-5616, 2012.

[105] H. M. Jeong, J. W. Lee, W. H. Shin, Y. J. Choi, H. J. Shin, J. K. Kang*, et al.*, "Nitrogen-doped graphene for high-performance ultracapacitors and the importance of nitrogen-doped sites at basal planes," *Nano letters,* vol. 11, pp. 2472-2477, 2011.

[106] D.-W. Wang, F. Li, Z.-G. Chen, G. Q. Lu, and H.-M. Cheng, "Synthesis and electrochemical property of boron-doped mesoporous carbon in supercapacitor," *Chemistry of Materials,* vol. 20, pp. 7195-7200, 2008.

[107] P. Ayala, J. Reppert, M. Grobosch, M. Knupfer, T. Pichler, and A. Rao, "Evidence for substitutional boron in doped single-walled carbon nanotubes," *Applied Physics Letters,* vol. 96, p. 183110, 2010.

[108] J. Robin and R. David, "Boron-doping effects in carbon nanotubes," *Journal of Materials Chemistry,* vol. 10, pp. 1425-1429, 2000.

[109] L. Panchakarla, K. Subrahmanyam, S. Saha, A. Govindaraj, H. Krishnamurthy, U. Waghmare*, et al.*, "Synthesis, structure, and properties of boron-and nitrogen-doped graphene," *Advanced Materials,* vol. 21, pp. 4726-4730, 2009.

[110] T. Lin, F. Huang, J. Liang, and Y. Wang, "A facile preparation route for boron-doped graphene, and its CdTe solar cell application," *Energy & Environmental Science,* vol. 4, pp. 862-865, 2011.

[111] Z.-H. Sheng, H.-L. Gao, W.-J. Bao, F.-B. Wang, and X.-H. Xia, "Synthesis of boron doped graphene for oxygen reduction reaction in fuel cells," *Journal of Materials Chemistry,* vol. 22, pp. 390-395, 2012.

[112] W. Han, Y. Bando, K. Kurashima, and T. Sato, "Boron-doped carbon nanotubes prepared through a substitution reaction," *Chemical physics letters,* vol. 299, pp. 368-373, 1999.

[113] S. K. Hwang, J. M. Lee, S. Kim, J. S. Park, H. I. Park, C. W. Ahn*, et al.*, "Flexible multilevel resistive memory with controlled charge trap B-and N-doped carbon nanotubes," *Nano letters,* vol. 12, pp. 2217-2221, 2012.

[114] X. Li, L. Fan, Z. Li, K. Wang, M. Zhong, J. Wei*, et al.*, "Boron doping of graphene for graphene–silicon p–n junction solar cells," *Advanced Energy Materials,* vol. 2, pp. 425-429, 2012.

[115] Y.-B. Tang, L.-C. Yin, Y. Yang, X.-H. Bo, Y.-L. Cao, H.-E. Wang*, et al.*, "Tunable band gaps and p-type transport properties of boron-doped graphenes by controllable ion doping using reactive microwave plasma," *Acs Nano,* vol. 6, pp. 1970-1978, 2012.

[116] T. Wu, H. Shen, L. Sun, B. Cheng, B. Liu, and J. Shen, "Nitrogen and boron doped monolayer graphene by chemical vapor deposition using polystyrene, urea and boric acid," *New Journal of Chemistry,* vol. 36, pp. 1385-1391, 2012.

[117] L. Niu, Z. Li, W. Hong, J. Sun, Z. Wang, L. Ma*, et al.*, "Pyrolytic synthesis of boron-doped graphene and its application as electrode material for supercapacitors," *Electrochimica Acta,* vol. 108, pp. 666-673, 2013.

[118] J. Gao, X. Wang, Y. Zhang, J. Liu, Q. Lu, and M. Liu, "Boron-doped ordered mesoporous carbons for the application of supercapacitors," *Electrochimica Acta,* vol. 207, pp. 266-274, 2016.

[119] J. Gao, X. Wang, Q. Zhao, Y. Zhang, and J. Liu, "Synthesis and supercapacitive performance of three-dimensional cubic-ordered mesoporous carbons," *Electrochimica Acta,* vol. 163, pp. 223-231, 2015.

[120] D.-Y. Yeom, W. Jeon, N. D. K. Tu, S. Y. Yeo, S.-S. Lee, B. J. Sung*, et al.*, "High-concentration boron doping of graphene nanoplatelets by simple thermal annealing and their supercapacitive properties," *Scientific reports,* vol. 5, p. srep09817, 2015.

[121] J. Li, X. Li, D. Xiong, L. Wang, and D. Li, "Enhanced capacitance of boron-doped graphene aerogels for aqueous symmetric supercapacitors," *Applied Surface Science,* vol. 475, pp. 285-293, 2019.

[122] V. Thirumal, A. Pandurangan, R. Jayavel, and R. Ilangovan, "Synthesis and characterization of boron doped graphene nanosheets for supercapacitor applications," *Synthetic Metals,* vol. 220, pp. 524-532, 2016.

[123] J. Han, L. L. Zhang, S. Lee, J. Oh, K.-S. Lee, J. R. Potts*, et al.*, "Generation of B-doped graphene nanoplatelets using a solution process and their supercapacitor applications," *ACS nano,* vol. 7, pp. 19-26, 2012.

[124] M. Enterría, M. F. R. Pereira, J. I. Martins, and J. L. Figueiredo, "Hydrothermal functionalization of ordered mesoporous carbons: The effect of boron on supercapacitor performance," *Carbon,* vol. 95, pp. 72-83, 2015.

[125] X. Zhai, Y. Song, J. Liu, P. Li, M. Zhong, C. Ma*, et al.*, "In-situ preparation of boron-doped carbons with ordered mesopores and enhanced electrochemical properties in supercapacitors," *Journal of the Electrochemical Society,* vol. 159, pp. E177-E182, 2012.

[126] D. Cui, H. Li, M. Li, C. Li, L. Qian, B. Zhou*, et al.*, "Boron-Doped Graphene Directly Grown on Boron-Doped Diamond for High-Voltage Aqueous Supercapacitors," *ACS Applied Energy Materials,* vol. 2, pp. 1526-1536, 2019.

[127] R. Nankya, J. Lee, D. O. Opar, and H. Jung, "Electrochemical behavior of boron-doped mesoporous graphene depending on its boron configuration," *Applied Surface Science,* 2019.

[128] S. S. Balaji, M. Karnan, J. Kamarsamam, and M. Sathish, "Synthesis of Boron-Doped Graphene by Supercritical Fluid Processing and its Application in Symmetric Supercapacitors using Various Electrolytes," *ChemElectroChem,* vol. 6, pp. 1492-1499, 2019.

[129] S. S. Balaji, M. Karnan, P. Anandhaganesh, S. M. Tauquir, and M. Sathish, "Performance evaluation of B-doped graphene prepared via two different methods in symmetric supercapacitor using various electrolytes," *Applied Surface Science,* 2019.

[130] S. H. Kim and B.-H. Kim, "Influence of boron content on the structure and capacitive properties of electrospun polyacrylonitrile/pitch-based carbon nanofiber composites," *Synthetic Metals,* vol. 242, pp. 1-7, 2018.

[131] B. Liu, Y. Liu, H. Chen, M. Yang, and H. Li, "Oxygen and nitrogen co-doped porous carbon nanosheets derived from Perilla frutescens for high volumetric performance supercapacitors," *Journal of Power Sources,* vol. 341, pp. 309-317, 2017.

[132] C. Peng, T. Zeng, Y. Yu, Z. Li, Z. Kuai, and W. Zhao, "Fluorine and oxygen co-doped porous carbons derived from third-class red dates for high-performance symmetrical supercapacitors," *Journal of Materials Science: Materials in Electronics,* pp. 1-10, 2018.

[133] H. Chen, Y. Xiong, T. Yu, P. Zhu, X. Yan, Z. Wang*, et al.*, "Boron and nitrogen co-doped porous carbon with a high concentration of boron and its superior capacitive behavior," *Carbon,* vol. 113, pp. 266-273, 2017.

[134] P. F. Fulvio, J. S. Lee, R. T. Mayes, X. Wang, S. M. Mahurin, and S. Dai, "Boron and nitrogen-rich carbons from ionic liquid precursors with tailorable surface properties," *Physical Chemistry Chemical Physics,* vol. 13, pp. 13486-13491, 2011.

[135] H. Guo and Q. Gao, "Boron and nitrogen co-doped porous carbon and its enhanced properties as supercapacitor," *Journal of Power Sources,* vol. 186, pp. 551-556, 2009.

[136] D. Sun, R. Ban, P.-H. Zhang, G.-H. Wu, J.-R. Zhang, and J.-J. Zhu, "Hair fiber as a precursor for synthesizing of sulfur-and nitrogen-co-doped carbon dots with tunable luminescence properties," *Carbon,* vol. 64, pp. 424-434, 2013.

[137] C. Wang, Y. Zhou, L. Sun, P. Wan, X. Zhang, and J. Qiu, "Sustainable synthesis of phosphorus-and nitrogen-co-doped porous carbons with tunable surface properties for supercapacitors," *Journal of Power Sources,* vol. 239, pp. 81-88, 2013.

[138] T. Wang, L.-X. Wang, D.-L. Wu, W. Xia, and D.-Z. Jia, "Interaction between nitrogen and sulfur in co-doped graphene and synergetic effect in supercapacitor," *Scientific Reports,* vol. 5, p. 9591, 2015.

[139] Q.-L. Zhu, P. Pachfule, P. Strubel, Z. Li, R. Zou, Z. Liu*, et al.*, "Fabrication of Nitrogen and Sulfur Co-Doped Hollow Cellular Carbon Nanocapsules as Efficient Electrode Materials for Energy Storage," *Energy Storage Materials,* 2017.

[140] Y. Chen, Z. Liu, L. Sun, Z. Lu, and K. Zhuo, "Nitrogen and sulfur co-doped porous graphene aerogel as an efficient electrode material for high performance supercapacitor in ionic liquid electrolyte," *Journal of Power Sources,* vol. 390, pp. 215-223, 2018.

[141] J. Chen, H. Wei, H. Chen, W. Yao, H. Lin, and S. Han, "N/P co-doped hierarchical porous carbon materials for superior performance supercapacitors," *Electrochimica Acta,* vol. 271, pp. 49-57, 2018.

[142] Y. Chang, C. Yuan, C. Liu, J. Mao, Y. Li, H. Wu*, et al.*, "B, N co-doped carbon from cross-linking induced self-organization of boronate polymer for supercapacitor and oxygen reduction reaction," *Journal of Power Sources,* vol. 365, pp. 354-361, 2017.

[143] B. You, F. Kang, P. Yin, and Q. Zhang, "Hydrogel-derived heteroatom-doped porous carbon networks for supercapacitor and electrocatalytic oxygen reduction," *Carbon,* vol. 103, pp. 9-15, 2016.

[144] Z. Zhao and Y. Xie, "Electrochemical supercapacitor performance of boron and nitrogen co-doped porous carbon nanowires," *Journal of Power Sources,* vol. 400, pp. 264-276, 2018.

[145] Q. Geng, G. Huang, Y. Liu, Y. Li, L. Liu, X. Yang, *et al.*, "Facile synthesis of B/N co-doped 2D porous carbon nanosheets derived from ammonium humate for supercapacitor electrodes," *Electrochimica Acta,* vol. 298, pp. 1-13, 2019.

[146] G. Zhao, C. Chen, D. Yu, L. Sun, C. Yang, H. Zhang, *et al.*, "One-step production of ONS co-doped three-dimensional hierarchical porous carbons for high-performance supercapacitors," *Nano Energy,* vol. 47, pp. 547-555, 2018.

[147] Y. Li, G. Wang, T. Wei, Z. Fan, and P. Yan, "Nitrogen and sulfur co-doped porous carbon nanosheets derived from willow catkin for supercapacitors," *Nano Energy,* vol. 19, pp. 165-175, 2016.

[148] L. Wan, W. Wei, M. Xie, Y. Zhang, X. Li, R. Xiao, *et al.*, "Nitrogen, sulfur co-doped hierarchically porous carbon from rape pollen as high-performance supercapacitor electrode," *Electrochimica Acta,* vol. 311, pp. 72-82, 2019.

[149] B. Lv, P. Li, Y. Liu, S. Lin, B. Gao, and B. Lin, "Nitrogen and phosphorus co-doped carbon hollow spheres derived from polypyrrole for high-performance supercapacitor electrodes," *Applied Surface Science,* vol. 437, pp. 169-175, 2018.

[150] M. Karuppannan, Y. Kim, Y.-E. Sung, and O. J. Kwon, "Nitrogen and sulfur co-doped graphene-like carbon sheets derived from coir pith bio-waste for symmetric supercapacitor applications," *Journal of Applied Electrochemistry,* vol. 49, pp. 57-66, 2019.

[151] S. Huo, M. Liu, L. Wu, M. Liu, M. Xu, W. Ni, *et al.*, "Methanesulfonic acid-assisted synthesis of N/S co-doped hierarchically porous carbon for high performance supercapacitors," *Journal of Power Sources,* vol. 387, pp. 81-90, 2018.

[152] L. Miao, D. Zhu, M. Liu, H. Duan, Z. Wang, Y. Lv, *et al.*, "Cooking carbon with protic salt: nitrogen and sulfur self-doped porous carbon nanosheets for supercapacitors," *Chemical Engineering Journal,* vol. 347, pp. 233-242, 2018.

[153] C. Huang, A. M. Puziy, O. I. Poddubnaya, D. Hulicova-Jurcakova, M. Sobiesiak, and B. Gawdzik, "Phosphorus, nitrogen and oxygen co-doped polymer-based core-shell carbon sphere for high-performance hybrid supercapacitors," *Electrochimica Acta,* vol. 270, pp. 339-351, 2018.

[154] F. Liu, Z. Wang, H. Zhang, L. Jin, X. Chu, B. Gu, *et al.*, "Nitrogen, oxygen and sulfur co-doped hierarchical porous carbons toward high-performance supercapacitors by direct pyrolysis of kraft lignin," *Carbon,* vol. 149, pp. 105-116, 2019.

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