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Review Article

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 electrodes 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 the present era, as a result of the rapid developments 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 researchers to evaluate the performance of new heteroatoms functionalised materials such as sulphur, phosphorus and boron lately. Literature is widely available on nitrogen doped materials research for energy storage applications; however, there has been a limited number of review works on other functional materials beyond nitrogen. This review article thus aims to provide important insights and an up-to-date analysis of the most recent developments, the directions of future research, and the techniques used for the synthesis of these functional materials. A critical review of the electrochemical performance including specific capacitance and energy/power densities is made, when these single doped or co-doped active materials are used as electrodes in electrochemical capacitors.

1. 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 signify 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 Fig. 1.

Electrochemical capacitors, 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. 5 $kWkg^{-1}$) [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

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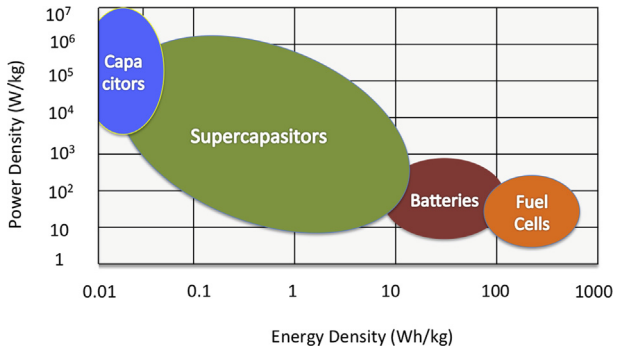

Fig. 1. Ragone plot of energy density vs power density for various electrical energy storage and conversion devices [1].

electronic transfer at the electrode/electrolyte interface [5], a schematic diagram of the charge storage mechanism of both electric double layer capacitor and pseudo-capacitor is shown in Fig. 2, followed by a detailed discussion on the charge storage mechanism in the electric double layer capacitors (EDLCs) and pseudocapacitors (PCs).

1.1. Energy storage mechanism of electrochemical capacitors

As discussed in the 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. EDLCs store electrical charge on the same principle as in electrostatic capacitors, however, in case of the 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 Fig. 3. Specific capacitance of a capacitor can be calculated using equation (1).

$$C = \varepsilon_0 \varepsilon_r \frac{A}{d} \tag{1}$$

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 an electric double layer, and the specific surface area 'A' of an active material is much higher (up to 3000 m^2g^{-1}) [16–19] when compared with electrostatic capacitors. Charge storage in EDLCs is

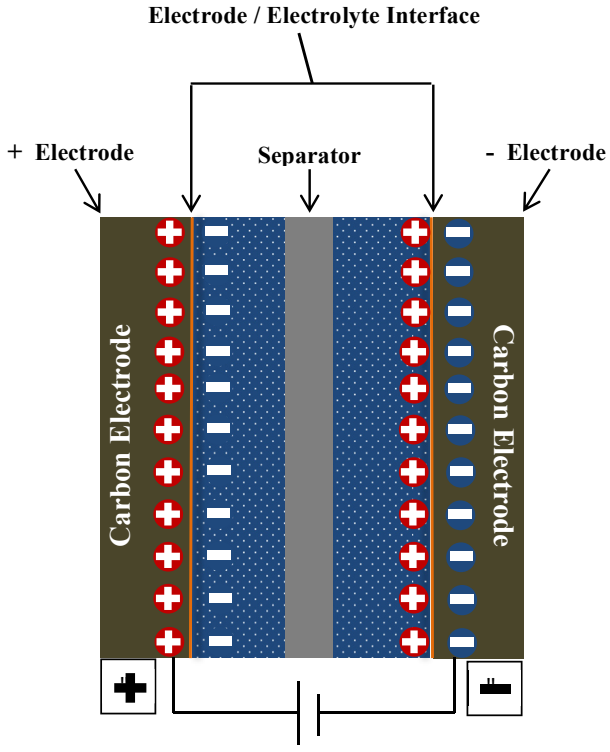

Fig. 3. Schematic of the charge storage mechanism of an electrical double layer capacitor.

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 a very short span of time [20,21] and retains an exceptionally long cycle life [22,23].

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 Fig. 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 the specific capacitances of pseudocapacitive devices are also much higher which can have a positive impact on energy density of the device according to Equation (2). However, the pseudocapacitive devices have lower cycle life [34] and cyclic efficiency [35] in

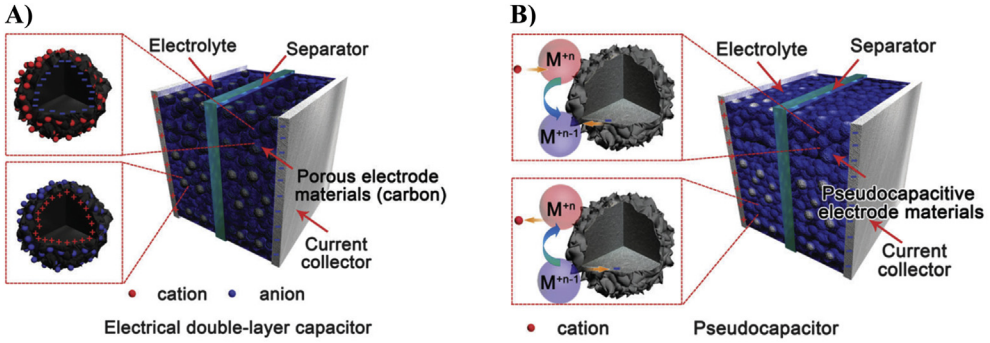

Fig. 2. Schematic diagrams of A) an electric double layer capacitor [EDLC] and B) a pseudo-capacitor [PC] [6].

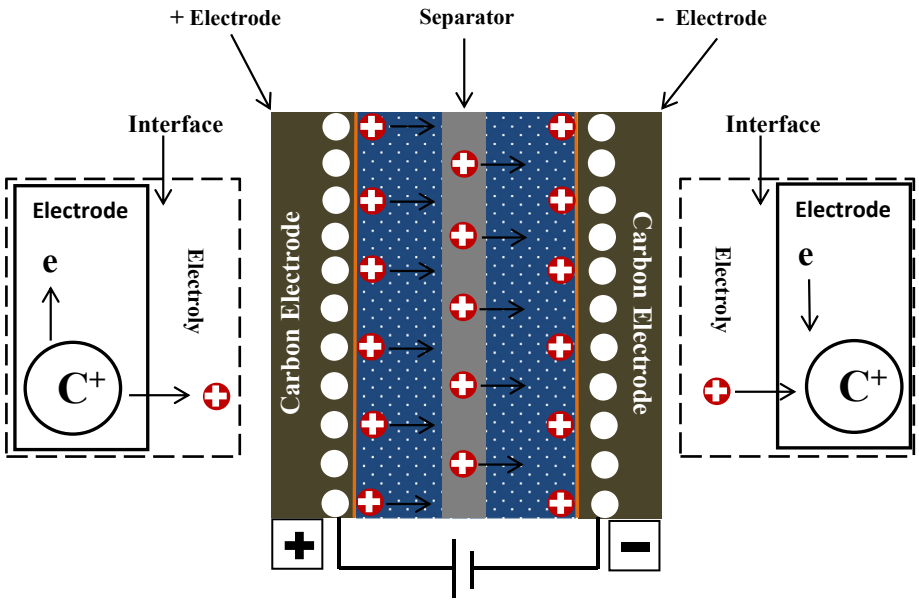

Fig. 4. Schematic of the charge storage mechanism of a pseudocapacitor.

comparison to EDLCs since charge is stored within bulk of the active material where long term cycle-ability can have an 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 compared 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) as defined by Equation (2).

$$E = \frac{1}{2}CV^2 \tag{2}$$

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 an effective way to enhance the energy density of the EC cell. However, using electrolytes with higher working voltages such as organic or ionic liquids results in higher equivalent series resistance (ESR) which results in the poorer power density; the power density of EC is given by Equation (3).

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

Alternative approach to enhance the energy density of an electrochemical capacitor cell is by increasing the specific capacitance of ECs. The improved specific capacitance is attainable by introducing the pseudo-capacitive entities such as metal oxides/conducting polymers [38] or heteroatoms (nitrogen, sulphur, boron and phosphorous) on the surface or within the structure of a carbon based active material where the total capacitance is the sum of both EDLC and PC. EDLC is exhibited by a carbon based active material and PC is due to the dopant such as metal oxides/conducting polymers or heteroatoms. However, the use of metal oxides based dopants in practical applications is limited due to its higher cost, lower conductivity (with the exception of ruthenium oxide) and limited cycle stability [39]. Heteroatoms doped carbons have displayed an improved capacitive performance due to the pseudo-capacitive contribution through a 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 materials for supercapacitor applications. Nitrogen is by far the most extensively investigated heteroatom whereas other heteroatoms are considered for investigation more recently.

2. Functionalized nano-carbons

2.1. Nitrogen [N] functionalized carbons

A 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 methods 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 an 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, an alternative technique, which is a 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 a 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 the specific capacitance of a nitrogen doped active material is the sum of EDLC due to the physical phenomenon occurring at the electrode/electrolyte interface and 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 Equations (4) and (5).

$$-C=NH+2e^{-}\leftrightarrow -CH-NH_2 \quad (4)$$

$$-C-NHOH+2e^{-}+2H^{+}\leftrightarrow -C-NH_2+H_2O \quad (5)$$

Specific capacitance of an 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 a simple thermal treatment of pueraria powder and melamine (NPC). It was observed that nitrogen doped carbon exhibited a 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 an electrolyte with its capacitance retention over 92% [51]. Another study by Mao et al. showed that N-doping resulted in the improved electrochemical performance where N-doped carbon displayed an excellent areal capacitance with the 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 an electrode in the supercapacitor cell with an excellent long term cyclic stability of more than 96% after 10000 cycles [52]. Inferior energy densities of supercapacitors limit their practical applications, and nitrogen doping can be adopted as a favourable technique to improve their energy densities for their wider adoption in practical use. The improved energy density of 6.7 $Whkg^{-1}$ as compared to 5.9 $Whkg^{-1}$ was attained after the introduction of nitrogen functionalities which provides a clear evidence that N-doping is an efficient way of improving the energy densities of the supercapacitor cells and the enhancement in energy densities will lead to their commercial applications [53]. An exceptionally high energy density of 55 Wh kg^{-1} (one of the highest values ever reported in the literature for this type of active material) at a power density of 1800 W kg^{-1} with an excellent cycling efficiency of over 96% was achieved when Dai and co-workers used the nitrogen doped porous graphene as an electrode and n $BMIMBF_4$ electrolyte to benefit from the higher operating potential of around 3.5 V [54]. Nitrogen doping also improves the wetting behaviour of the 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 Fig. 5. The nitrogen doped carbon attained capacitive value of twice higher than that of an un-doped carbon [55]. Further examples of nitrogen carbons when used as an active material in supercapacitors with a comprehensive evaluation of their physical and electrochemical properties presented in the literature is shown in Table 1. Table 1 shows various physical and electrochemical properties of different types of nitrogen doped carbon based materials when used as electroactive materials.

It can be established from the above discussions that nitrogen doping is the most favourable routes to synthesise functional electrode-active materials for supercapacitor 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 a positive impact on the overall performance of the system.

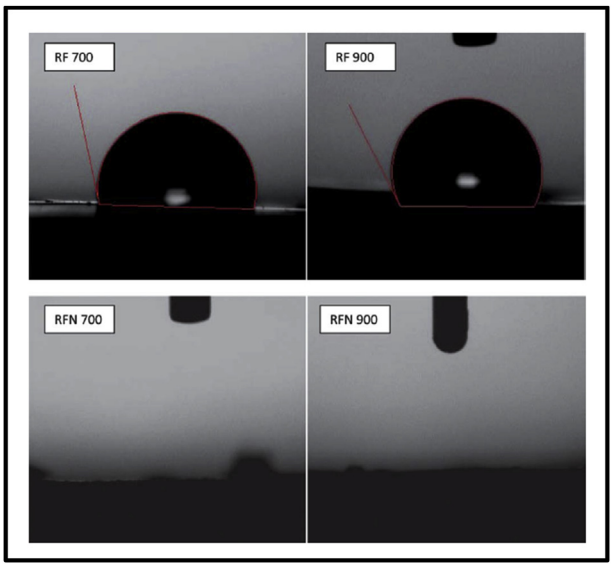

Fig. 5. Images showing the wettability of the un-doped (RF) and nitrogen doped (NRF) carbons samples [55].

2.2. Phosphorus [P] functionalized carbons

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

A 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 the latter process P-doped carbon materials can be synthesised by precisely controlling the P content.

Adoption of phosphorus-doped carbons for their application in the 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 the limited understanding of its effect on physiochemical properties ultimately restricting its potential to be used as an active material and hence on the overall performance of a supercapacitor cell [71]. Phosphorous doping results in an improved charge storage due to the additional pseudo-capacitive component alongside electric double layer since phosphorus also possesses electron-donor characteristics and also an enhanced transport capability due to its exceptionally high electrical conductivity when used as an active material [72]. Yi et al. synthesised the cellulose-derived both un-doped carbon (CC) and phosphorous doped carbon (P-CC) showing an excellent capacitive performance along with the improved conductivity. A specific capacitance of 133 Fg^{-1} at a high current density of 10 Ag^{-1} and the excellent capacitance retention of nearly 98% after 10000 cycles were achieved. A momentous drop from 128.1 to 0.6 Ω in charge transfer resistance alongside drop in contact angle from 128.3° to 19.2° after phosphorus doping was witnessed [66] as shown in Fig. 6, where Fig. 6a) shows the drop in contact angle with an improved wetting behaviour

Table 1
Physical and electrochemical characteristics of various nitrogen doped carbons used as active materials 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]

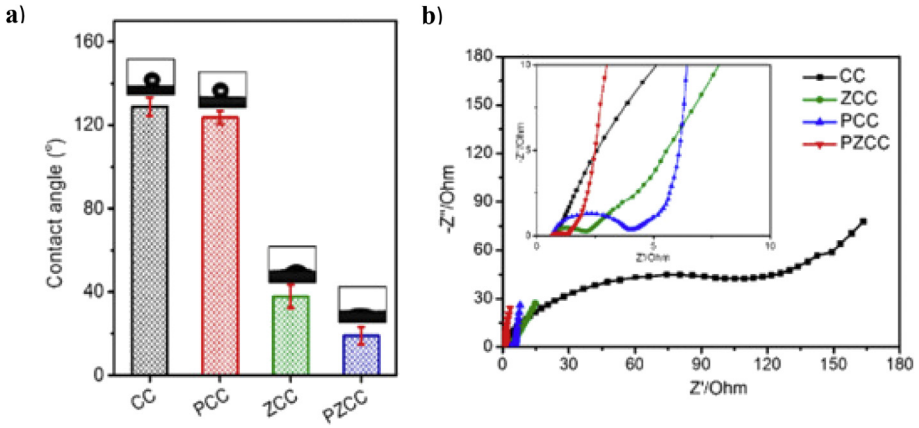

Fig. 6. a) Contact angle of 6M KOH on the surface; **b)** Nyquist plots of the doped and un-doped carbons [66].

and Fig. 6b) represents the Nyquist plots of various carbons characterizing the resistive behaviour of various carbon samples.

In another study, phosphorus doped graphene was synthesised by the activation of graphene with sulphuric acid, which resulted in P-doping of 1.30%. It was established that P-doping not only improved the capacitive performance it also widened an operating voltage window of the cell which resulted in the enhanced energy density as given by Equation (1). An exceptionally high energy density of 1.64 $Whkg^{-1}$ at a high power density of 831 Wkg^{-1} was realised due to the higher operating potential of 1.7 V rather than 1.2 V for an aqueous electrolyte (1M H_2SO_4) [73]. It has also been reported that oxygen surface functionalities such as chemisorbed oxygen (carboxylic groups) and quinones of an 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 an oxidation protector when introduced within the carbon structure preventing the combustion of oxygen species which contributes toward the enhancement in the cell performance accompanied by the obstruction in formation of electrophilic oxygen species [75,76]. A recent study by Ma et al. has shown that phosphorous doping not only enhances the capacitive performance due to the additional capacitance arising from the reversible redox reaction, but also prevents the formation of unstable quinone and carboxylic groups, resulting in a higher operating voltage of 3.0 V much when used in conjunction with pure carbon (around 2.5 V) leading to the delivery of an exceptionally high energy density of 38.65 $Wh\ kg^{-1}$at a power density of 1500 $W\ kg^{-1}$ when used with the organic electrolyte (1 M Et_4NBF_4/PC) [68]. A wide range of phosphorus doped carbon based electrode materials with their physical and electrochemical properties is given in Table 2.

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

Table 2
Physical and electrochemical characteristics of various phosphorus doped carbons used as active materials 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]

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 155 °C. Specific capacitance of 257 Fg^{-1} was attained which was 23.5% higher than un-doped graphene for the doping level 5 wt% of sulphur alongside drop in contact angle from 88.2° to 69.8° after doping as shown in Fig. 7 [92]. Some further explaes of sulphur doped active materials are provided in Table 3.

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

The electronic structure of a carbon based active material can be modified by introducing boron into the carbon framework. It is easier to dope carbon based nanomaterials either with nitrogen or boron since nitrogen and boron possess analogous electronic configuration and sizes 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 an electron acceptor which results in the uneven distribution of charges. This charge transfer results in an improved electrochemical performance due to the pseudo-capacitive contribution originated from this electronic transfer (Faradic reaction) [106]. Boron functionalizing can be accomplished using a 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 the most commonly used technique to produce boron doped active materials, and the

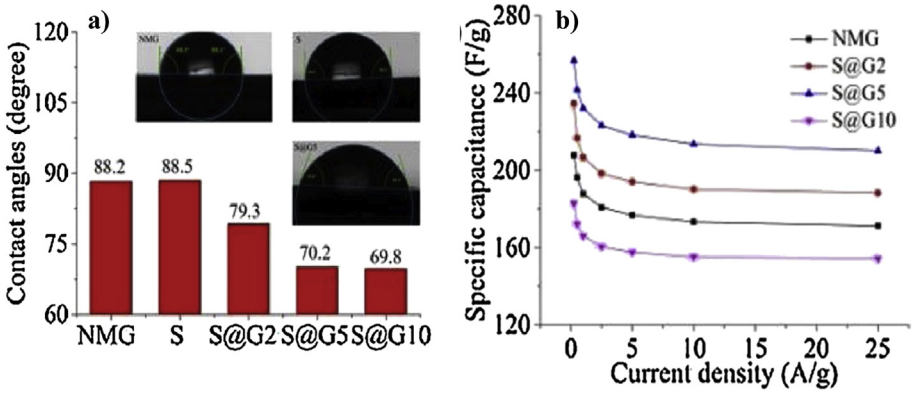

Fig. 7. a) Contact angle of a water droplet on doped and un-doped samples. **b)** Specific capacitances of electrodes at different current densities.

Table 3
Physical and electrochemical characteristics of various sulphur doped carbons used as active materials 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]

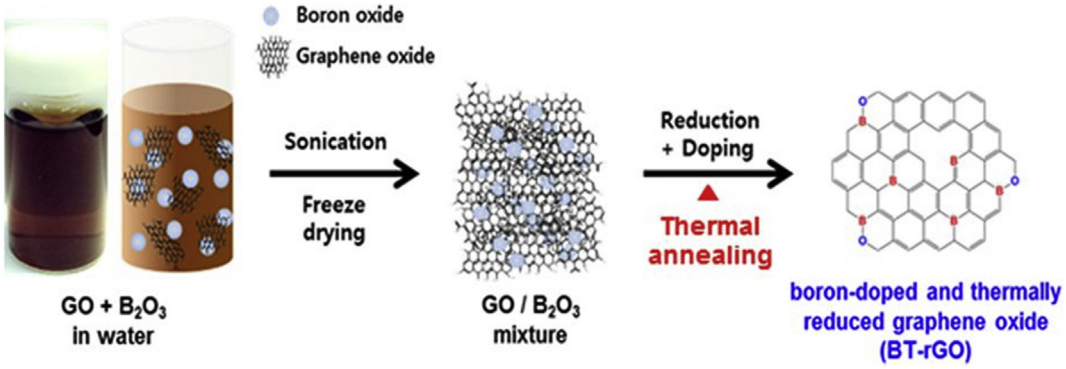

Fig. 8. Schematic presentation of the preparation of BT-rGO.

improved specific capacitance of 173 Fg^{-1} was achieved when boron doped graphene was synthesised through a thermal reaction. An 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 the achieved capacitance of nearly 80% higher than that of an un-doped active material. The electrochemical capacitor cell delivered a superior energy density of 3.86 Wh kg^{-1} at a power density of 125 W kg^{-1}, and managed to retain the energy density of 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 Fig. 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 Gao and co-workers, where boron doped controlled porosity meso-porous carbon was prepared using a hard template approach, showed that the 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 5 mVs^{-1}. The exceptionally low solution resistance R_S of 1.05Ω was also obtained due to the improved wettability after the incorporation of boron functional groups [118,119]. Improving the surface chemistry of an electrode active material after boron doping can have other benefits such as superior conductivity. Boron doped graphene oxide was synthesised through a simple thermal annealing of GO/B_2O_3 as shown in Fig. 8. The exceptionally high specific capacitance of 448 Fg^{-1} was

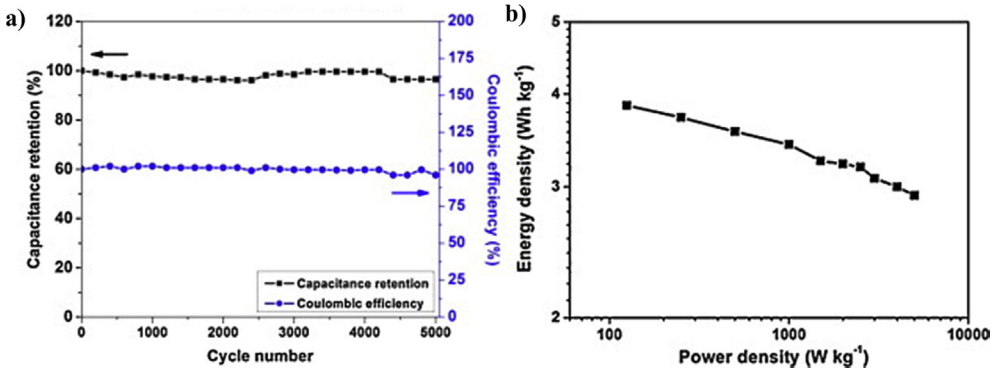

Fig. 9. a) Cycling stability and coulombic efficiency of Boron doped electrode; **b)** Ragone plot of a symmetric cell [117].

Table 4
Physical and electrochemical characteristics of various boron doped carbons used as active materials 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]

reached after boron doping without using any conductivity enhancer such as carbon black since boron doping resulted in the improved conductivity of the active material [120].

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

We have discussed various functional materials including nitrogen, sulphur, phosphorus and boron which have been widely used by researchers 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 an 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, and its impact on the 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 enhance the capacitive performance of the carbon when used as an electrode material by tailoring its properties such as by improving the 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 a 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 values of 371 Fg^{-1}, 282 Fg^{-1} and 566 Fg^{-1} were achieved for nitrogen, sulphur and nitrogen/sulphur co-doped samples respectively when used in supercapacitor cells with 6M KOH as an electrolyte [138]. The maximum specific capacitances 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 are much the higher capacitive values for this type of electrode material reported in the literature [139]. Nitrogen and sulphur co-doped graphene aerogel offered a high energy density of 101 Wh kg^{-1} when used as an electrode, which is one of the highest values ever achieved 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 Chen et al. showed that nitrogen and phosphorus co-doping results in a very high specific capacitance of 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 an electrode active material through the synergistic effects of more than a single dopant; nitrogen and boron co-doped

Table 5
Physical and electrochemical characteristics of various co-doped carbons used as active materials 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]

materials have demonstrated an 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 the overall electrochemical performance is a sum of the electric double layer capacitance coming from the porous parameters of the active materials and the pseudo-capacitance of heteroatoms. A very recent study by Zhao and co-workers has shown that the excellent electrochemical performance can be attained when more than two functional groups are introduced in a highly porous carbon. The specific capacitance of 576 Fg^{-1} together with an extraordinary energy density of 107 $Wh \cdot kg^{-1}$ at power density 900 $W \cdot kg^{-1}$ was achieved, when the active material was co-doped with oxygen, nitrogen and sulphur functional groups [146]. The performance characteristics of various carbon based active materials have been summarised in Table 5.

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. Recent 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 a natural combination for the 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. Conclusion and future outlook

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 another class of functional materials which includes sulphur, phosphorus and boron beyond the nitrogen, possessing physio/chemical properties suitable for superior cell outputs. By adopting these emerging functional materials as electrodes, the performance of an electrochemical cell can be improved substantially. Nitrogen doping results in an improved electrochemical performance (capacitance/energy density) while retaining the high power density of the cell, since the introduction of nitrogen on the surface of the electro-active material results in an improved wetting behaviour which helps to maintain the low equivalent series resistance (ESR) of the cell. Doping carbon based electrode materials with phosphorus results in the superior physio/chemical properties matched with nitrogen doping, and additional benefits of using phosphorus doped active materials include 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 an active material, resulting in a higher pseudo-capacitive contribution when compared with the performance of an active material doped with other heteroatoms. Individual functional materials possess excellent properties which can have a positive impact on both the physical properties and electrochemical performance of the supercapacitor cell when introduced into the matrix or on the surface of the active material independently. However, recent attention has been diverted towards using more than one dopant where synergistic effects of both dopants yield even superior performance. Although nitrogen has been explored extensively and has revealed encouraging results, an immense research drive is till needed to explore other functional materials since this field is still very young with very little deliberation.

Already these functional materials have shown an immense potential however, it will be extremely fascinating for researchers in the field of energy storage to follow further improvements 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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