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Review Article

Carbon Soot for Electrochemical Energy Storage Applications

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New forms of carbon nanomaterials for energy storage application are always at a focal point. This review is envisaged the soot derived-carbon nanoparticles (SCNs), which are relatively newer candidates for energy storage applications. These carbon nanoparticles are interlinked and highly ordered with the particle size of nearly 10-50 nm. Due to their nano size, high electrochemically accessible surface area, and excellent electrical conductivity they are used for energy storage applications. From the electrochemical aspect, SCNs offers fast charge-discharge electrode kinetics with desirable specific power in supercapacitor and high capacity at high current densities in the lithium ion battery. In addition, they can be utilized as conductive additives for activated carbon, nucleation and conductive support for redox additives. This review provides an elaborate account of the potential of SCNs as electrode materials with emphasis on physical and electrochemical properties which are important for energy storage systems, in particular, lithium ion batteries and supercapacitors.

Keywords: Carbon Soot; Carbon; Energy Storage; Lithium-ion Battery; Supercapacitor

Introduction

Today, there is a surge in global demand of the energy due to competitive industrial development and growth in the manufacturing sector (Pleßmann *et al.,* 2014). Persistent efforts are under way for the production and conservation of energy and utilization of conventional energy resources to meet the energy demand. In this review, the main emphasis is on the potential of environmentally benign, easily available and low-cost carbon soot based energy storage systems such as lithium ion battery and supercapacitor.

Carbon materials deserve significant attention in energy storage sector due to their outstanding properties like high surface area, porous structure, excellent electrical conductivity, extraordinary chemical and mechanical stabilities, lower cost, and availability in various forms (Simon *et al.,* 2013). So far, widely used carbons are activated carbon derived from various sources such as organic deposits of coal, oil, flammable solvents, wax and peat (biomass). (Zhao *et al.,* 2011). Owing to their high surface area and wide ranges of porosity, activated carbons are extensively used as active electrode material in the energy storage devices such as batteries and supercapacitors. Ease of synthesis and simple fabrication of electrodes make them viable candidates for commercial devices in the energy storage sector. Extensive research is still taking place on carbon-based materials to enhance electrochemical properties in order to achieve the maximal capacity. Carbon nanotubes and graphene-based energy storage systems are potential candidates, but their commercialization has hurdles mainly due to complex synthesis method and the overall cost. In order to fabricate the cost-effective electrochemical energy storage (EES) device, newer carbon materials can be explored with high surface area and well-optimized pore structures available at a lower cost without compromising on electrochemical properties.

The energy from green resources can be stored and utilized effectively by means of carbon nanostructures or their hybrids with redox active materials (Bandaru *et al.* 2015). The detailed discussion on individual energy storage device

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*Author for Correspondence: E-mail: cssharma@iith.ac.in pertaining to electrochemical aspect of carbon electrodes is as follows: A supercapacitor is an electrochemical energy storage device with major advantages of fast charge-discharge capacity, high power density, excellent cycle life, sharp response time, low cost of fabrication, microfabrication, and less hazardous electrode materials over conventional batteries (Simon *et al.,* 2013). Supercapacitors can deliver supplementary power very efficiently in shorter duration than that by batteries but they lack in specific energy (Conway *et al.*, 1999). The construction of supercapacitor is similar to batteries consisting of two electrodes, porous separator, and an electrolyte. The electrodes are generally made up of high surface area, conductive, and porous active materials and are the most accountable factors for EES in supercapacitors (Potphode *et al.,* 2015). Supercapacitors are basically divided into three types depending on the mechanism of charge storage and the active electrode materials such as electric double layer capacitors (EDLCs), pseudocapacitors, and hybrid capacitors. First type is the supercapacitor with high surface area carbon comprising non-faradaic charge storage, on the other hand, capacitors with faradaic (fast redox reversible reactions at the electrode/electrolyte interface) charge storage comprising metal oxide and polymers are classified as hybrid supercapacitors. However, capacitors with faradaic charge storage (redox reactions at electrode surface) in neutral electrolytes are named as pseudocapacitors. Nanostructured carbon-based EDLCs have received momentous attention due to various features such as electrostatic charge storage, high surface area, pores structure, excellent conductivity, outstanding electrochemical stability, easy bulk production and lower cost (Zhu *et al.,* 2017). Carbon based supercapacitors are also called as ultra-capacitors, due to their ultra-high power density and high energy density (Conway *et al.,* 1999). Most of the commercially available electrode materials are based on mesoporous carbon such as activated carbons, biomass derived carbons, graphene and its derivatives (Wang *et al.,* 2017). Moreover, the recent trend is on developing newer carbonaceous materials with novel nanostructures, high surface area and optimal pore size to achieve energy storage efficiency up to their theoretical limit which is still an imminent prospect (Tang *et al.,* 2013).

Methodically, various charge storage mechanisms are classified on the basis of electrode materials used as cathode or anode: electrosorption with non-faradaic charge storage, interfacial redox reactions with faradaic charge storage, and combination of both non faradaic and faradaic to achieve synergistic effect to bring high energy density in EES devices (Bandaru *et al.* 2015). The most noticeable contribution in electrochemical energy storage, more particularly in supercapacitor is from EDLCs. In EDLCs, the energy is stored at the electrode/electrolyte interface by accumulation of electric charges on the electrode surfaces and thereby forming an electric double layer with the help of counter ions of opposite sign from the electrolyte. The high electrosorption rate is due to the absence of electrochemical reactions at the electrode (non-faradaic charge storage). This enables EDLCs to deliver high specific power (Lahe„„r *et al.,* 2015). There are several attempts to further enhance the power density by activation of carbons. The activated carbon can be synthesized by incorporating functional groups and creating porous structures (Yang *et al.,* 2011).

Even though some enhancement was achieved, the specific energy of EDLCs is limited due to non-faradaic charge storage in carbon materials. In order to overcome this, a combination of carbon materials and redox active materials resulting in synergistic effect are being used. Accordingly, redox active polymers, metal oxides, metal hydroxides, metal hydroxyl carbonates, and metal chalcogenides were used in combination with the carbon materials to improve the energy density (Simon *et al.,* 2014). Depending on the electrochemical reaction between the electrode material and electrolyte, the electrochemical response changes from electric double layer formation to redox reaction (faradaic) and the energy storage classified to pseudocapacitors or battery type hybrid supercapacitors. In contrast to EDLCs, hybrid supercapacitor involves the slower charge transfer between active material at electrode and electrolyte. For instance, when Co(II)/CoO reacts with OH^- ion in KOH electrolyte, it forms Co(III)/CoOOH by transferring an electron (Yang *et al.,* 2014). This chemical conversion lowers the rate of electrochemical reaction at electrode/electrolyte interface and hence the energy density improves due to oxidation and reduction of active material (Simon *et al.*, 2014). When these redox active electrode materials are combined with nano size carbon it actively utilizes the highly accessible electrochemical surface area to contribute EDLC charge storage in addition to the redox reactions, thereby enhancing electrochemical stability and specific energy of the composite material (Sahu *et al.*, 2017). SCNs topographies the high electrochemical surface area due to their interconnected nano size and are favorable materials for preparing nanocomposites. Due to nano size, the electrolyte can easily penetrate into the innermost part of the electrode hence total active material at the electrode can be utilized at utmost. Further, interconnected nano-network allows easy charge transportation and helps to minimize the internal resistance at electrode (Plonska-Brzezinska *et al.*, 2013). In this way, the electrochemical performance of SCNs can be improved in terms of specific energy and hybrid supercapacitor can be developed.

Supercapacitor energy storage is inadequate in terms of specific energy than that of the batteries, whereas batteries are insufficient for high power application. A combination of these two can be a solution for future energy storage by taking advantage of high power density supercapacitors and high energy density lithium ion batteries (LiBs). Batteries are one of the best renewable energy sources to date. Based on the energy storage mechanism batteries are classified into two, primary batteries and secondary batteries. Primary batteries store charges irreversibly, therefore these are limited to a single usage. Secondary batteries are known as rechargeable batteries because of the reversible charge storage mechanism and can be used many times. LiBs are the commercialized and widely used rechargeable batteries. LiBs are introduces in 1990 into the commercial market by Sony corporation. A typical lithium ion cell consists of anode, cathode and lithium ion conducting electrolyte. Generally, anode (negative terminal of the battery) consists of a carbon material which can intercalate lithium ion reversibly and a cathode (positive terminal of the battery) is made up of lithium metal oxide. To enhance battery performance in terms of capacity and durability the role of anode and cathode materials are equally important. The limited resources of lithium compel researcher to find out newer anodic and cathodic materials with high capacity for efficient usage of lithium. In commercial LiBs, graphite is used as an anode material because of its excellent cyclic stability, flat discharge profile and good electrical conductivity. Nevertheless, the limited specific capacity (372 mAh/g) of graphite is one of the bottlenecks in energy storage (Yang *et al*., 2012). Therefore, it is important to find out new anode material with high lithium ion storage to replace the graphite. In this regard, carbon materials such as graphene oxide, graphene, multi-walled carbon nanotubes, single-walled carbon nanotubes are the promising anode materials, but these are very expensive (Landi *et al.*, 2009; Liu *et al.*, 2012; Goriparti *et al.*, 2014; Zhu *et al.*, 2014; Zhao *et al.*, 2015). Expensive anode materials would obviously increase the cost of the battery, so inexpensive alternatives are highly sought after. Soot is always a waste product after combustion, but making use of this soot in a productive way is a skillful approach. Soot is formed because of the incomplete combustion of hydrocarbons and is amorphous in nature. It mainly contains C-O, O-H, and C-H groups (Singh *et al*., 2018). Soot is produced from various sources such as candle wax, oil lamps, coal, waste incineration, etc. Among these candle soot contains lesser impurities. In addition, its good adhesion to the substrate made it favorable for the binder free electrode fabrication. Vacuum filtration, electrophoretic deposition, chemical vapor deposition, and electrospinning techniques are the main approaches for binder free electrode fabrication till date but these methods are expensive (Ban *et al.*, 2010; Choi *et al.*, 2010; Yang *et al.*, 2015). In this regard, candle soot deposition approach is highly appealing because, the source of carbon is from the inexpensive candle wax and it can be directly deposited on stainless steel substrate and the fabricated anode electrode is free from conventional PVDF binder. Here, the wax in the carbon soot plays the role of a binder. Bhattacharjya *et al.* reported another interesting result, the facile method of preparation of nitrogen doped carbon nanoparticles by flame synthesis and its usage as anode material in lithium ion battery. Nitrogen doped carbon soot particles are prepared from acetonitrile by modified flame synthesis (Bhattacharjya, H.-Y. Park, *et al.*, 2014). The paper also discussed the preparation of carbon nanoparticles from acetone by flame synthesis and the electrochemical performance is compared with the nitrogen doped carbon nanoparticles. A recent report shows that the graphitization of the soot at high temperature will lead to the formation of carbon nano onions. Lee *et al.* reported that lithium ion storage capacity of the graphitized soot which is converted into highly crystalline graphite and was found to form carbon nano onions (Lee *et al.*, 2018). The graphitized soot exhibits a good reversible capacity and cycle stability.

In brief, carbon soot is an effective and inexpensive anode material and has potential to replace the commercial anode. The binder-free electrode fabrication (using SCNs) is advantageous over other binder-free electrode fabrication. The tunability in the crystalline nature of the soot is the other interesting aspect when compared to the other carbon structures, this enhances the reversible lithium storage capacity of the material. However, the direct use of soot as anode material will decrease the reversibility of the electrode because of the agglomeration of carbon nanoparticles. The agglomerated and amorphous carbon nanoparticles show large lithium intake in initial cycles and a drastic decrement in subsequent cycles due to the irreversible lithium ion storage (Kakunuri *et al.*, 2015).

This review is focused on carbon soot as a new material for energy storage, owing to their excellent electrochemical performance in batteries and supercapacitors with respect to their competencies at nano level as compared to expensive carbon nanotubes, graphene derivatives, and fullerenes. Several reports are available on carbonaceous material, carbon nanotubes, carbide derived carbons but the exploration of environmentally benign and cost effective sustainable energy materials need to be focused for new generation energy storage.

Synthesis and Physical Characterization of Carbon Soot

Carbon soot is a forthcoming potential candidate of carbon family consisting of small and ordered nanostructures ranging from 10-50 nm in size and they are available at a lower cost than those other commercially available carbonaceous material (Wang *et al.,* 2016). The production and collection of carbon soot are very facile and low-cost process; (shown in Fig. 1). These impressive features encourage many researchers to use carbon soot in various applications like energy storage (Zhang *et al.,* 2014), microbial fuel cell (Singh *et al.,* 2018), solar cell (Wei *et al.,* 2014), heavy metal detectors (Li *et al.,* 2011), fluorescent detectors (Lui *et al.,* 2007) dye adsorptions and catalysis (Zhang *et al.,* 2015), oil cleanup (Gao *et al.,* 2014), etc. The flame synthesis of carbon soot yields quasi-graphitic structures which are strongly dependent on the flame parameters, collection methodology, and the organic content of the precursor (Wang *et al.,* 2011).

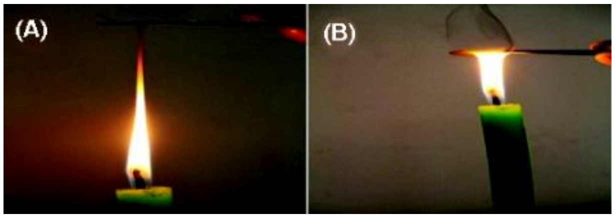

Fig. 1: Candle soot collection on stainless steel substrate (a) at the tip of the flame and (b) middle of the flame. Data adapted from reference (Kakunuri *et al.,* 2015)

Candle soot is one of the members in the carbon soot family which possess hydrophilicity. The soot properties vary depending on the regions of the flame from where the soot is collected as shown in Fig. 1. It exhibits higher electrical conductivity when collected at the tip of the flame and higher hydrophobicity when collected at the inner flame (Zhang *et al.,* 2014). In this aspect, the deposition process of candle soot becomes vital based on the application. In energy-related applications such as batteries, supercapacitors, fuel cells the electrode material should possess high electrical conductivity for the fast transfer of electrons. There are three different regions of the candle flame; the tip, the middle and the inner portion. Based on the temperature zone of the candle flame, the amount of wax in the soot particles and its wettability varies. The soot deposited from the tip of the flame has higher-conductivity and contains less amount of wax and other organic compounds, while the soot collected from the middle of the flame contains more amount of wax, non-conductive elements and other organic compounds indicating the partial oxidation process (Zhang *et al.,* 2014). The difference in the collected soot from different temperature zone has been reported with the help of X-ray diffraction (XRD), Raman spectroscopy, and Fourier-transform infrared spectroscopy (FTIR). The amorphous nature and the degree of disorder are clearly visible from the XRD and Raman spectrum given in Fig. 2(a&b). The

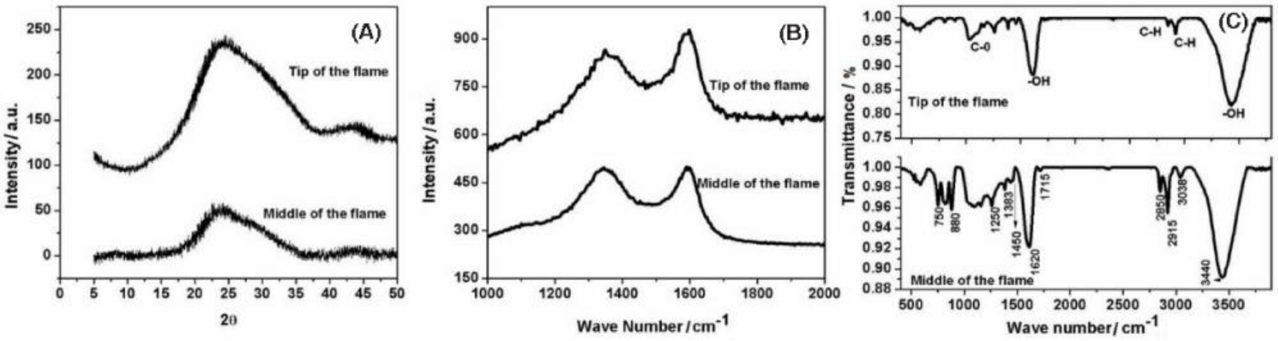

Fig. 2: (A) X-ray diffraction pattern (B) Raman spectrum and (C) FTIR spectrum of candle soot collected from the tip of the flame and middle of the flame. Data adapted from reference (Kakunuri *et al.*, 2015)

broader peak around 25° corresponding to (002) plane emphasizes that the carbon soot particles are amorphous in nature. The broad D band (1350 cm^{-1}) and G band (1580 cm^{-1}) in the Raman spectra also indicated the amorphous nature as well as defects in the structure. FTIR spectrum (Fig. 2(C)) of the soot collected from the tip of the flame and middle of the flame showed similarity in the functional group region (1000-4000 cm^{-1}) but in finger print region in between 750-900 cm^{-1} additional aromatic C-H bonds are present in the soot collected from the middle of the flame. The strong peaks at 3440 cm^{-1} and 1620 cm^{-1} indicate the stretching and bending mode of hydrogen bond in hydroxyl group due to adsorbed water (Kakunuri *et al.*, 2015). The peaks at 2850-3050 cm^{-1} attributed to the C-H stretch and the bonds at 3038 cm^{-1} for the soot collected from the middle of the flame may be assigned to aromatic C-H stretch. In addition to that, the peaks at 1250 cm^{-1}, 1383 cm^{-1}, and 1450 cm^{-1} can be attributed to bending, rock and scissoring of C-H peaks respectively in both spectra. Figure 3 shows the thermogravimetric analysis of the candle soot in the zero air at 10°C/min heating rate. The soot collected from the candle exhibits a good thermal stability up to 450°C, also no weight loss is observed around 100°C. This indicates the absence of physisorbed water and this in turn emphasizes the hydrophobicity of the collected soot (Kandjani *et al*., 2016). The nano size particles of candle soot derived carbon is shown in Fig. 4 (a and b).

Transmission electron microscopy (TEM) image of candle soot shows the fractal like carbon nanoparticles which is amorphous in nature. Lee *et al*. reports show that after graphitization of the soot collected from ship at high temperature around 2700°C, carbon nano onions were formed with average (Fig. 4) diameter of 70 nm (Lee *et al*., 2018). Another report shows the possibility of nitrogen-doped carbon soot by flame synthesis and the presence of nitrogen is confirmed by X-Ray photoelectron spectroscopy and the results are compared with undoped carbon prepared from acetone by flame synthesis (Fig. 5) (Bhattacharjya *et al.,* 2014). In C 1s spectrum, the peak at 284.5 eV is related to the sp^2 carbon and the peak at 285.2 eV is related to the combination of sp^3 carbon and C–N bonding. An additional peak is observed at 288.8 eV assignable to N–C=O bond, in nitrogen doped carbon where as it is absent in C 1s spectra of undoped carbon. In N 1s spectrum the peaks at 398.2, 399.2 and 400.7 eV are assigned to pyridinic, pyrrolic, and graphitic nitrogen, and the peak at 404 eV is related to terminal N–O bond (Fig. 5a).

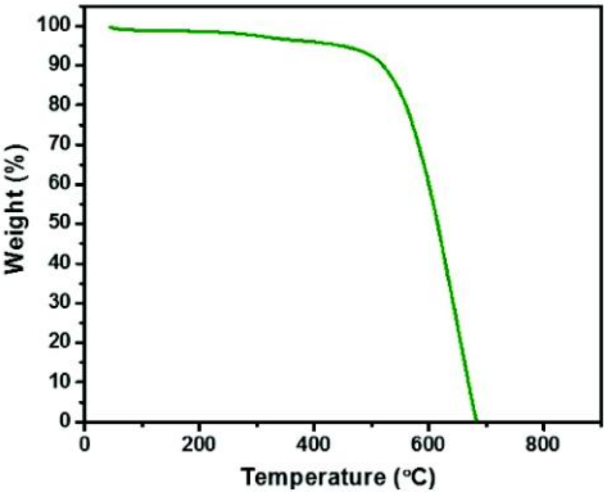

Fig. 3: Thermogravimetric analysis of as prepared candle soot in zero air atmosphere

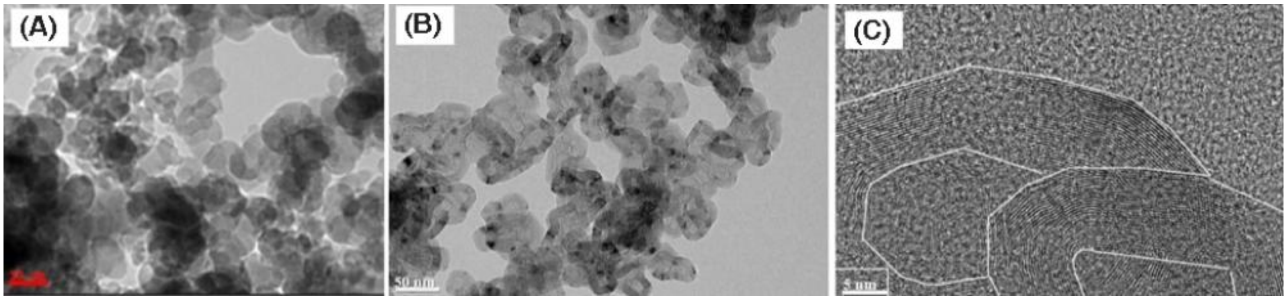

Fig. 4: High resolution TEM images of the candle soot (b&c) Low and high resolution TEM images of annealed soot (soot collected from the ship exhaust). Data adapted from references (a)-(Kakunuri *et al.*, 2015), (b & c)-(Lee *et al.*, 2018)

The tunability of various properties such as particle size, morphology, and surface area is possible by optimizing the flame synthesis (Falco *et al.*, 2017). The precise control of physico-chemical properties of carbon nanoparticles has always shown a good impact on application point of view, in particular energy storage systems such as lithium ion batteries and supercapacitor. As-prepared candle soot consist of nano size spherical carbon structures with 3-4% unburned wax content, which maintains the hydrophobicity in the as prepared materials mainly due to organic carbon fractions (Zhang *et al.*, 2014) reported that hydrophobicity can be removed by heating this candle soot at 450^{o}C in open air for 2 h, the resulting high purity candle soot derived carbon showed promising supercapacitive performance with the highest specific capacitance of 106 F/g at the current density of 1 A/g. (See section 4 for further discussion). Further, activation or functionalization of the candle soot with nitric acid is reported by (Raj *et al.*, 2016) they claim functionalization improves the crystallinity of the carbon nanoparticles with the increase in surface area from 87.5 m^2/g to 137.9 m^2/g. Retention of excellent surface morphology of carbon and extra functionalities leads to enhanced specific capacitance up to 187 F/g. (See section 4 for further discussion)

Carbon Soot as an Anode in Lithium Ion Battery

Carbon soot is a recent candidate in the energy storage systems.It constitutes more than 80% of carbon materials with a small amount of hydrogen, oxygen, nitrogen and other insoluble hydrophobic material. Manohar *et al.*, 2015 reported the inexpensive preparation of integrated fractal-like network of carbon nanoparticles from the combustion of candle wax and its direct usage as anode material in lithium ion battery. The schematic representation of the electrode fabrication is shown in Fig. 1A, where soot has been collected from the tip of the flame to minimize the wax content in the electrode. The assembled cell using candle soot derived carbon nanoparticles as anode material and lithium foil as counter and reference electrode exhibited an initial capacity of 4037.3 mAh/g and charge capacity of 637.0 mAh/g at 0.1C rate (shown in Fig. 6(A)). Further at 10C

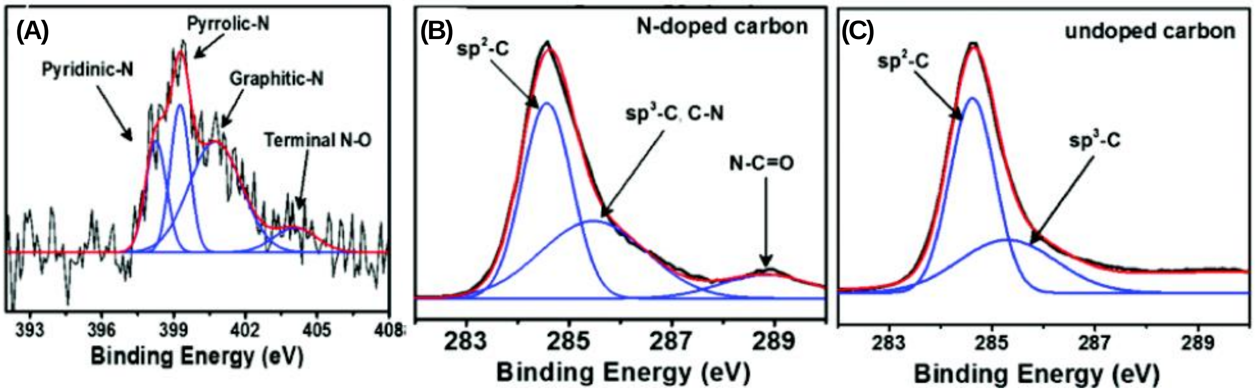

Fig. 5: High-resolution XPS spectra with Gaussian fitting for (a) N1s peak (b) C 1s peak of nitrogen-doped carbon (c) C 1s peak of undoped carbon Data adapted from reference (Bhattacharjya *et al.*, 2014)

rate, the cell exhibited an initial discharge capacity of 988.4 mAh/g and charge capacity of 383.4 with an initial coulombic efficiency of 38.8% and 93.4% after 10 cycles. Fig. 6(B) represents the stability of the cell, the cell showed a stabilized capacity of 220 and 170 mAh/g for 1000 cycles at 5C and 10C rate respectively. The electrochemical performance of the cell is superior over other carbon structures including graphene and nanocarbon structured material (Yoo *et al.*, 2008; Abouimrane *et al.*, 2010; Wu *et al.*, 2011; Zhao *et al.*, 2011; Hassoun *et al.*, 2014; Kakunuri *et al.*, 2015). This paper clearly described the ability of the candle soot to work in high current densities rather than lower current densities.

The synthesis of nitrogen-doped carbon nanoparticles by flame synthesis was the other development in the era of soot and its application in lithium ion battery. N-doped carbon nanoparticles are prepared by burning the acetonitrile in the air atmosphere, and the soot has been collected over the cold surface of the conical flask (Bhattacharjya *et al.*, 2014). The obtained soot was used for the preparation of the electrode using PVDF as a binder and NMP as a solvent. The same group reported the preparation of carbon nanoparticles from acetone and the physical and electrochemical performances are compared with the nitrogen doped carbon nanoparticles. N-doped nanoparticles exhibited a first charge and discharge capacity of 1190 and 594 mAh/g respectively with the coulombic efficiency of 50% (Fig. 7(A)). The irreversible reduction of dioxygen molecules or oxygenated functional groups present in the turbostratic carbon and the formation of the solid electrolyte interphase (SEI) layer due to the decomposition of electrolyte are pointed as the reason for the initial capacity loss and the low coulombic efficiency. In the comparative study authors projected the capacity enhancement of N-doped nanoparticles and compared that to graphite and undoped carbon nanoparticles as shown in Fig. 7(B). The rate capability and the stability test presented in Fig. 7(C&D) further confirms the potential of the material.

The graphitization of the soot and its usage as anode material in lithium ion battery is the latest development in the energy storage system. Lee *et al.* reported that the graphitized soot (the soot collected from a ship) at high temperature 2700 °C converted into highly crystalline graphite and was found to form carbon nano onions with an average diameter of 70nm (Lee *et al.*, 2018). TEM image clearly depicted the difference between the raw soot and the heat treated soot (Fig.4(b & c)). After heat treatment and annealing, the graphene layers grew significantly and changed to almost graphite crystalline structure. The electrochemical performance of the cell using graphitized soot as an anode is evaluated in the half cell mode at different C rates C/5, C/2 and 1C and the cell exhibited a reversible capacity of 282, 273, and 261 mAh/g respectively with minimum fading (Fig. 8(a)). The lithium ion insertion and exertion became more easy with increasing specific surface area via the graphitic edges exposed to outside through the graphitization process and was considered as the reason for the minimum capacity fade of the cell.

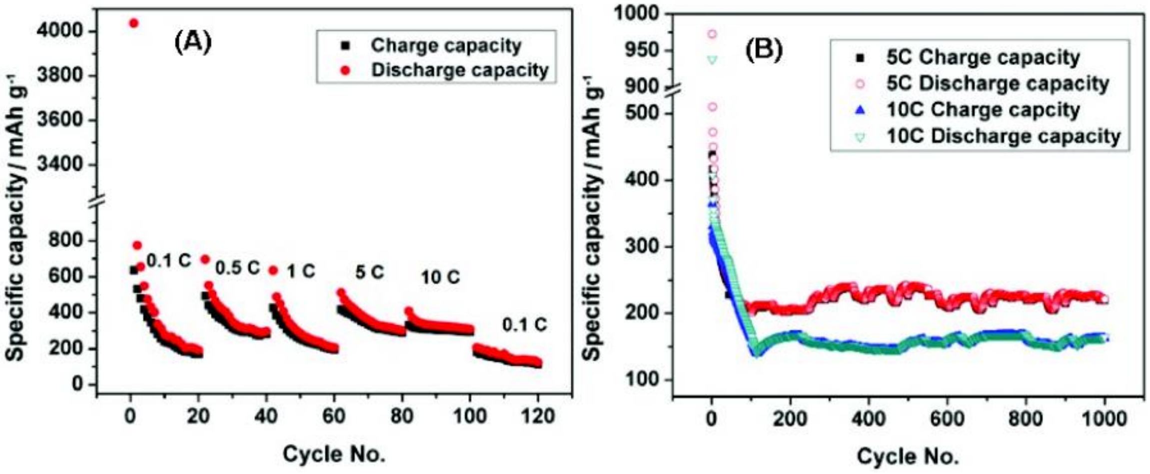

Fig. 6: Rate capability test of candle soot derived carbon nanoparticles (a) at different C rates (b) cycling performance of candle soot derived carbon nanoparticles at 5C and 10C rates. Data adapted from reference (Kakunuri *et al.*, 2015)

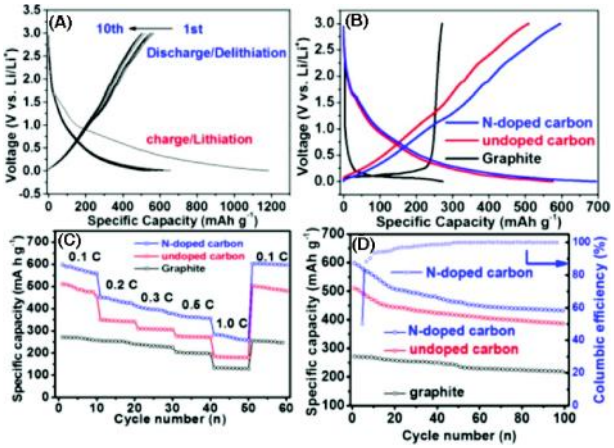

Fig. 7: **Charge-discharge profiles of (A) N-doped carbon in the voltage range of 0.02-3.0 V (vs Li+/Li) at 0.1 C current rate. Comparison of (B) charge-discharge profiles at 0.1 C rate, (C) discharge capacity at different current rate ranging from 0.1 to 1 C, and (D) discharge capacity for 100 cycles for N-doped carbon, undoped carbon, and graphite. Data adapted from reference (Bhattacharjya *et al.*, 2014)**

Furthermore, the cell exhibited a good cycle life and reversibility after cycling over 150 at 1C rate and exhibited a capacity of 260 mAh/g (Fig. 8(b). The high reversible capacity and good cycling performance of the material emphasize the characteristics of the ideal electrode material. The results of these three materials are summarized in the Table 1.

The other advantage of the soot material that it can be obtained from byproduct of the combustion reaction. Moreover, soot can be deposited on the current collector and use as anode material in LiBs. This simplistic method binder-free electrode fabrication makes it preferable over another binder-free electrode fabrication such as electrophoretic deposition, vacuum filtration, electrospinning, morphosynthesis, chemical vapor deposition. In addition, it also provides an opportunity to tune the material structure and properties according to the demand of application (or in particular the LiBs)

Table 1: Capacity and number of cycles achieved for various carbon soot based anodes

Electrode material	C rates	Discharge capacity (mAh/g) (Cycle number)
Candle soot	10 C	170 (1000)
Nitrogen doped soot	0.1 C	400 (100)
Graphitized soot	1 C	260 (150)

Carbon soot in Supercapacitors

Carbon materials such as activated carbon with high surface area has been productive contributor in supercapacitors research. Candle soot derived carbon materials are rather new in energy storage (Zhang *et al.*, 2014) demonstrated the flame synthesis of candle soot derived mesoporous carbon with the pore size 2-10 nm for supercapacitor application. The ease of synthesis and their potential EES makes it attractive to the researcher in the field of energy storage. The direct deposition of candle soot over the current collector allows the binder-free approach that enhances the electrochemical performances by minimizing internal resistance at electrode. The mesoporous carbon nanoparticles (candle soot derived carbon) tested as electrode material in a two-

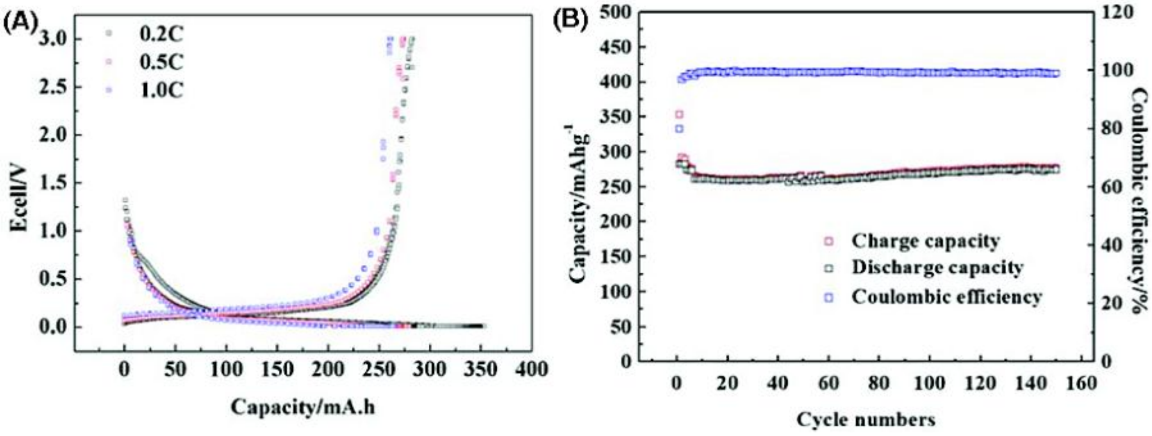

Fig. 8: **(A) Galvanostatic discharge/charge curves (B) cycling performance and coulombic efficiency of the annealed soot cycled at a rate of 1C. Data adapted from reference (Lee *et al.*, 2018)**

electrode system with 6M KOH electrolyte showed an ideal capacitive behavior like EDLC. The electrochemical performance of the candle soot can be seen in Fig. 9. The highest specific capacitance they reported is 106 F/g, with remarkable electrochemical stability up to 98.5% after 10,000 charge-discharge cycles at a current density of 1 A/g. The absence of semicircle at higher frequency end in Nyquist plot (Fig. 9 (c)) indicates lower internal resistance of the candle soot derived carbon materials.

Furthermore, to enhance energy storage competence of the candle soot derived carbon, they prepared nanostructured MnO_2 composites by coating candle soot derived carbon nanoparticles with MnO_2 by hydrothermal method. The carbon particles obtained from candle soot were fully covered by pompon like MnO_2. When tested as supercapacitor electrode material in an aqueous 1M Li_2SO_4 solution, the composite electrode MnO_2@CS exhibited highest specific capacitance of 309 F/g at a current density of 1 A/g and capacitance retention of 58% after 10000 charge-discharge cycles. This was far superior compared to the bare MnO_2 electrodes (62% after 1000 charge-discharge cycles). The synergistic effect was observed between MnO_2 and candle soot as a nanocomposite electrode material with combined effect of electrical double layer capacitance due to candle soot particles and pseudocapacitance due to the reversible redox transitions from MnO_2. Concisely, candle soot performance can be enhanced by incorporating redox active materials and can be utilized as active material in energy storage.

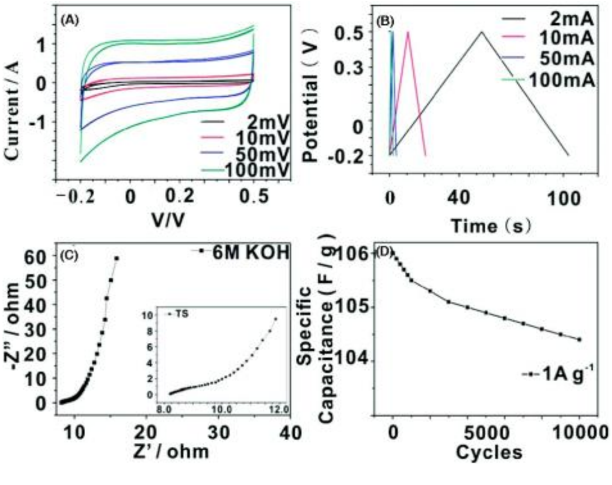

Fig. 9: Electrochemical performance of candle soot with a two-electrode system in 6 M KOH electrolyte (a) Cyclic voltammetry at the scan rates of 2, 10, 50, and 100 mV/s; (b) Charge-discharge test at a current of 2, 10, 50 and 100 mA/g; (c) impedance plots, the inset is the high frequency regions; (d) cycling performance at a current density of 1 A/g. Data adapted from reference (Zhang *et al.*, 2014)

In another study, (Raj *et al.*, 2016) compared bare, washed and nitric acid functionalized candle soot derived carbon particles. The nitric acid treatment on candle soot has shown the enhanced electrochemical performance of the candle soot. This acid treatment not only improves the surface functionalities of the carbon nanomaterial but also increases its surface area and pore volume; therefore double layer capacitance of the candle soot derived carbon increases. The surface area of functionalized candle soot was improved from 87.49 m^2/g to 137.93 m^2/g after acid treatment. When it is tested as an electrode material for supercapacitor in a three electrode system using an aqueous 1M H_2SO_4 electrolyte at various scan rates, the quasi-rectangular CV curves were observed for functionalized candle soot due to pseudocapacitive behavior induced by oxygen functionalities (Fig. 10). The functionalized candle soot exhibited an enhanced specific capacitance value of 156 F/g compared to bare (16 F/g) and washed candle soot (48 F/g) at 5 mV/s scan rate. Further, galvanostatic charge/discharge measurements on functionalized candle soot supported a high capacitance of 187 F/g at 0.15 A/g. Besides, the study also showed low internal resistance for functionalized candle soot based electrode than the bare and washed candle soot electrodes. This indicates that electrical conductivity can be improved by functionalization (Raj *et al.*, 2016). Moreover, oxygen functionalization of the carbon derived from candle soot can enhance the specific capacitance by inducing pseudocapacitance.

In another report by Ghosh *et al.*, they used candle soot derived nanoparticles as conductive support to grow polyaniline by controlled grafting (Ghosh *et al.*, 2018). Addition of the carbon nanoparticles in composite enhances the electrochemical performance compared to bare polyaniline. The maximum specific capacitance they reported is 972 F/g with 90% capacitance retention after 2000 charge-discharge cycles. This covalent approach of grafting candle soot derived carbon nano particles with polyaniline showed excellent electrochemical performance and achieved the

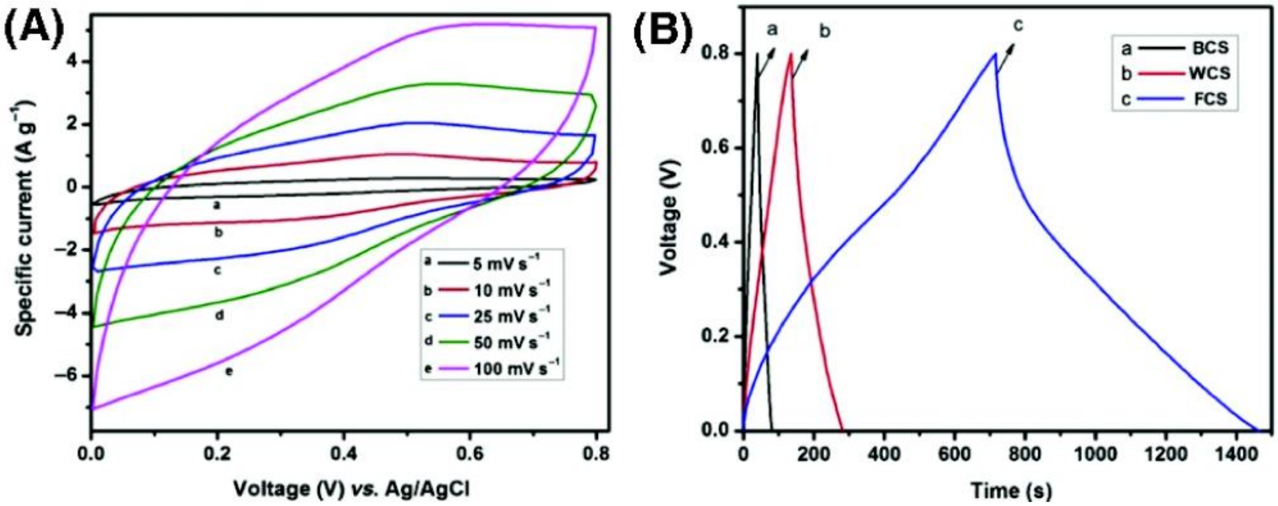

Fig. 10: Electrochemical performance of functionalized candle soot with a three-electrode system in 1M H_2SO_4 electrolyte (A) Cyclic voltammetry at the scan rates of 5, 10, 25, 50, and 100 mV/s; (B) comparison between bare (BCS), washed (WCS), and functionalized candle soot (FCS) by charge-discharge test at a current density of 0.15 A/g. Data adapted from reference (Raj *et al.*, 2016)

highest capacitance than previously reported values for PANI composite. The facile method of incorporating candle soot derived carbon nanoparticles in polyaniline and MnO_2 composite is reported by Wang *et al*. The study emphasized on potential of candle soot as conductive support in composite to enhance the energy storage capacity of individual polyaniline and MnO_2. They reported highly flexible and light weight supercapacitor electrodes with improved electrochemical stability by incorporation of carbon nanoparticles in the composite of polyaniline and MnO_2 (Wang *et al.*, 2016). These studies revealed the scope of incorporating candle soot derived nanoparticles in combination with redox materials for the future high energy density hybrid supercapacitors.

The comparison of carbon soot obtained from different sources can be seen in Table 2. Irrespective of the source, the obtained carbon soot maintained interconnected, nano size carbon particles morphology which is favorable for effective charge storage. Further activation or functionalization of as-prepared carbon soot improved the surface area and porous structure thereby enhancing overall electrochemical performance. The preparation/production is very simple and facile with abundant yield. This is the attractive factor when compared with other forms of carbon like graphene, graphene oxide and multi-walled carbon nanotubes.

The carbon soot derived from clarified butter has been reported by Mohapatra *et al.*, 2016 and named as onion-like carbon has shown encouraging supercapacitive performance. This simple facile, scalable and one-step wick-and-oil flame synthesis of onion-like carbon is a high yield production technique with a pure form of carbon soot. The specific surface area of as-prepared onion-like carbon was found to be 218 m^2/g, which is quite favorable for energy storage application. The as-obtained carbon soot (onion-like carbon) was hydrophilic and tested

Table 2: Electrochemical comparison of carbon soot derived from various sources

Carbon soot source	Electrolyte	Specific capacitance	Analysis method	References
Candle	6M KOH	107 F/g @ 1 A/g	2 electrode setup	(Zhang *et al.*, 2014)
Candle(Functionalized soot)	1M H_2SO_4	187 F/g @ 0.15 A/g	3 electrode setup	(Raj *et al.*, 2016)
Clarified Butter	1M Na_2SO_4	102.16 F/g @20 mV/s	2 electrode setup	(Mohapatra *et al.*, 2016)
Diesel	0.5M Na_2SO_4	194 F/g @5mV/s	3 electrode setup	(Sahu *et al.*, 2017)

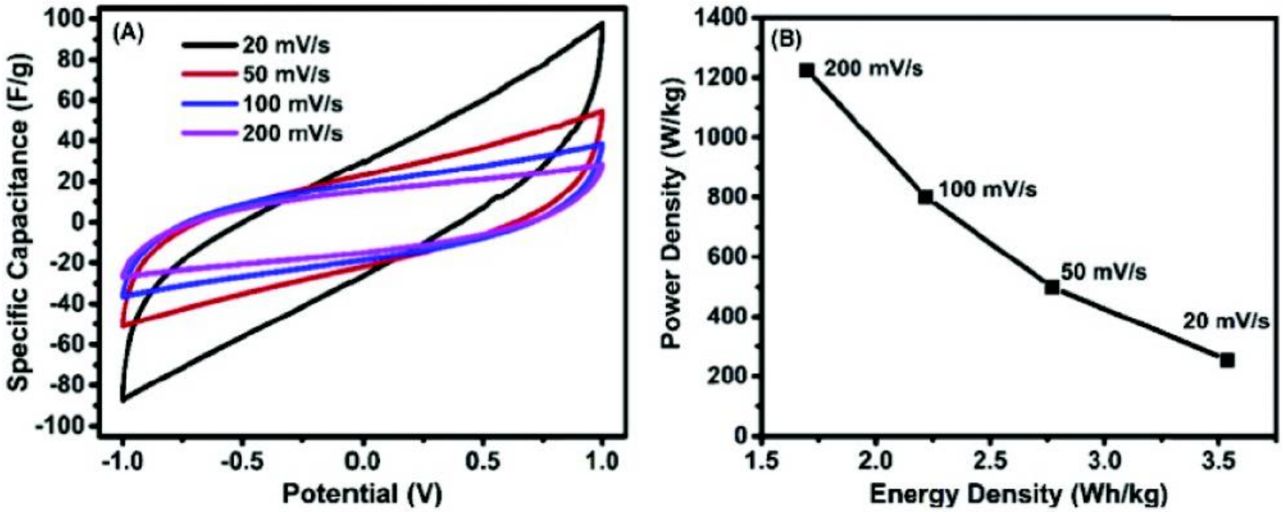

Fig. 11: Electrochemical performance of as-prepared onion-like carbon based symmetric supercapacitor device (A) Cyclic voltammograms at different scan rates (B) Ragone plot. Data adapted from the reference (Mohapatra *et al.*, 2016)

as supercapacitor electrodes in aqueous 1M Na_2SO_4 as the electrolyte. The highest specific capacitance for onion-like carbon was 102 F/g reported with the highest power density and energy density of 1224 W/kg and 3.5 W h/kg, respectively. The electrochemical performance of onion-like carbon is given in Fig. 11.

The recent report on carbon soot derived from diesel has also shown great potential in supercapacitor application. (Sahu *et al.*, 2017). The carbon soot can be produced in bulk by incomplete combustion of fossil fuels or organic matter with interconnected spherical carbon topography. The group reported the collected soot from three different engines and proved that irrespective of source the physical and electrochemical properties of diesel soot is nearly same. The specific capacitance values and surface area of the collected soot from different engines are presented in Table 3.

As the surface area is the key factor in energy storage, carbon soot derived from diesel has the promising surface area and also specific capacitance as compared to other carbon soot obtained from various resources (comparison can be seen in Table 2). Further, the authors have highlighted the recycling of hazardous waste product (diesel soot) from diesel exhaust for high performance supercapacitor electrodes with the combination of redox active MnO_2 (i.e. core–shell α-$MnO_2 \cdot 0.3H_2O$/carbon nanocomposite). A single step approach for functionalized micro/mesoporous carbon and nanocomposite with α-MnO_2 without high-temperature activation resulted in an increase in electrochemical accessible surface area and created intra-particle micro pores carbon structure. The highest specific capacitance measured for bare carbon soot and core-shell α-$MnO_2 \cdot 0.3H_2O$/carbon nanocomposite was 194 and 425 F/g, respectively. The nanocomposite obtained from diesel soot exhibited efficient energy storage performance with a high energy density of 25.5 Wh/kg at power

Table 3: Comparison of carbon soot produced from diesel with three different truck engines. Data adapted from reference (Sahu *et al.*, 2017)

S.No.	Engine/Manufacturer	Surface area (m^2/g)	Specific capacitance (F/g) (CV @5 mV/s; 0.5M Na_2SO_4)
1	96 KW (130 PS) Turbo Charged diesel engine. (TATA 1210 SD Truck)	59.5	194
2	CUMMINS 6BTAA 5.9; Water cooled engine, 5883cc engine displacement. (Tata SE 1613 Truck)	57.8	190
3	Diesel generator (Cummins X1.3 series, 2 cylinder, In-line 4 stroke, radiator cooled engine) JAKSON POWER GENERATION	60.1	195

density of 555.2 W/kg. Furthermore, long term charge-discharge cycling stability study also outperformed with respect to capacitance retention of 97.5% over 5000 cycles whereas bare diesel soot maintained only 82% retention. Therefore, hybridization or nanocomposite preparation with carbon soot is a viable option for developing energy storage devices with high energy density.

Future Prospects of Carbon Soot in Energy Storage System

This review highlighted the merits of carbon soot as an energy storage material in lithium ion batteries and supercapacitors. Soot is the byproduct of the combustion reaction, therefore making use of this abundant soot is environmentally benign and cost-effective. The electrochemical performance of the carbon soot in batteries and supercapacitor shows that soot is a potential candidate for energy storage systems. The nature of the soot usually does not depend on the source of production i.e. candle soot, diesel soot, and ship soot. The purity of the soot material is a question mark toward the direct usage of the soot in different applications. In a future perspective, the production of soot in the commercial scale is possible by the inexpensive way, therefore the usage in energy storage systems is always pertinent. The various approaches of modifying carbon soot in energy storage such as functionalization or chemical activation, tuning in the crystal structure by graphitization, and their hybridization with redox active materials shows the potential of the material in the energy storage system. The electrochemical performance of carbon soot can be further increased by chemical or physical activation such as mild oxidation in air at a lower temperature or acid treatment or by removing inter-particle pore blocking amorphous carbon. The higher order specific surface area enhancement of carbonaceous materials is achieved by KOH activation; this approach can be applied for further enhancement in electrochemical energy storage by the means of enhancing the surface area. Taking advantage of an abundance of carbon soot in the environment as a waste product, this plentiful carbon can be used for the fabrication of micro supercapacitors. The nano size carbon soot can be adopted as a conducting additive in place of the commercial carbon black, furthermore study can be explored to improve the gravimetric and volumetric performance of the batteries and supercapacitors with micro and mesoporous structures in energy storage. In addition, the diffusion study can be explored in order to make carbon soot more viable candidate for energy storage in practical applications. The raw carbon soot and its composite materials can be explored in other storage systems like sodium ion battery, lithium-sulfur battery, etc.

Conclusions

This review shed light on the potential candidature of carbon soot in electrochemical energy storage systems. Various synthesis and fabrication methods with and without binder for aqueous and non-aqueous energy storage systems are overviewed. Based on the mode of synthesis carbon soot properties such as electrochemical surface area, porosity, electrical conductivity, and nanostructured morphology, can be tuned. In electrochemical aspects, carbon soot considered as promising electrode material in supercapacitors and batteries showed superior performance with high specific power and energy densities. The carbon soot can be a futuristic anode material for lithium ion battery because of the low cost of production and scalability. The capacity retention at high current density is an impressive factor for the energy density battery application. The composite of candle soot has not been explored much so there is a long way to go ahead with nano-composites. To further enhance the electrochemical energy storage, composites of carbon soot with redox active materials such as metal oxides, metal chalcogenides, conducting polymers, and redox additives can be explored for high energy density supercapacitors.

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