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Electrode and electrolyte materials for electrochemical capacitors

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Abstract

Among different electric energy storage technologies electrochemical capacitors are used for energy storage applications when high power delivery or uptake is needed. Their energy and power densities, durability and efficiency are influenced by electrode and electrolyte materials however due to a high cost/performance ratio; their widespread use in energy storage systems has not been attained yet.

Thanks to their properties such as high surface area, controllable pore size, low electrical resistance, good polarizability and inertness; activated carbons derived from polymeric precursors are the most used electrode materials in electrochemical capacitors at present. Other electrode materials such as shaped nano-carbons or metal oxides are also investigated as electrode materials in electrochemical capacitors, but only as useful research tools.

Most commercially used electrochemical capacitors employ organic electrolytes when offering concomitant high energy and high power densities. The use of aqueous based electrolytes in electrochemical capacitor applications is mainly limited to research purposes as a result of their narrow operating voltage. Recent studies on room temperature ionic liquids to be employed as electrolyte for electrochemical capacitor applications are focused on fine tuning their physical and transport properties in order to bring the energy density of the device closer to that of batteries without compromising the power densities.

In this paper a performance analysis, recent progress and the direction of future developments of various types of materials used in the fabrication of electrodes for electrochemical capacitors are presented. The influence of different types of electrolytes on the performance of electrochemical capacitors such as their output voltage and energy/power densities is also discussed.

Broader Context

In order to meet the low-carbon energy strategy set for 2050 and as the global energy demand increases, renewable energy sources (wind, wave and solar) will need to be deployed effectively on a large scale. With continuous increase in the contribution of electricity generated from renewables to our growing energy demands, energy storage is becoming more important now than any time in the history. On the other hand the wide variations of energy /power requirements of future devices necessitates the design of adaptable energy storage/power supply systems, offering wide ranges of energy and power densities, to overcome the problems associated with poor power quality and inherent intermittency of renewable resources. In the case of no energy generation, technologies capable of storing large amounts of energy and releasing it over a longer period of time are needed. In contrast, in peak demands when energy surge in short discharge periods is required, technologies delivering high power to flatten power outputs fluctuations become imperative. Since no single energy storage technology can address this wide range of energy/power requirements simultaneously, a variety of storage technologies and systems consisted of their combinations have been developed. As a new technology supercapacitors represent energy densities greater than those of conventional capacitors and power densities greater than those of batteries. They are capable of providing additional peak power demands as and when required, and allow engineers to match the specification of various energy storage technologies (such as internal combustion engines, batteries and fuel cells) closer to that of the average power demand. The evolution of the electrochemical supercapacitor to fulfil the ever-increasing power demands of newly emerging devices is largely dependent on the development of optimised electrode materials (in line with the chosen electrolyte) and electrolytes.

Keywords

Energy storage; Electrochemical capacitors; Electrode materials; Electrolytes; Energy density; Power density

Introduction

The future energy landscape foresees significant concerns associated with energy crisis caused by imbalance between the world's energy demand and supply. The global energy demand is going to be doubled in next 50 years [1] and the world is preparing for an era of massively increased energy costs because of escalating shortage of energy resources. Furthermore, there is increased global warming and its affiliated environmental problems due to carbon emission caused by our overdependence on, and increase in the consumption of fossil fuels [2]. In response to these overlapping worldwide concerns the utilization of energy

in the form of electricity generated from renewable energy sources such as the wind, tidal and solar power, as cheap and clean (low or zero emission) energy supplies, has become a primary focus of the major world powers and scientific community. However, as the contribution of electricity generated from these intermittent energy resources grows, energy storage and power management become increasingly important. The development of storage technologies to improve efficiencies in supply systems at times of high demand, by storing energy when in excess and releasing it over a variety of timescales, becomes imperative. In this regard batteries, electrochemical capacitors (ECs) and fuel cells recognized as three kinds of the most important electrochemical energy storage/conversion devices will play a vital role to unlock the door of renewable energy to our future energy demands. Yet, the inherent intermittency of supply from generating technologies can only be addressed if there is a step-change in energy storage capability of these devices to ensure security and continuity of energy supply to the consumer from a more distributed and intermittent supply base.

As one of the key electrochemical energy storage devices, electrochemical capacitors also known as supercapacitors have, especially, shown great potential in recent years to meet the short-term power needs and energy demands over the timescale of 0.1–100s [3]. Their excellent power handling characteristics when combined with various primary energy sources, allow engineers to utilise them as an attractive power solution for an increasing number of applications in order to match the specification of the primary energy sources closer to that of the average power demand in each particular case. However, to fully exploit the potential of ECs in the field of energy storage, further advances in the engineering of materials used for their manufacturing are required. The recent developments in the synthesis of novel electrode materials such as i) carbon nano fibres [4], carbon xerogels [5], carbon spheres [6] and carbon nano-sheets [7] ii) metal oxides including MnO_2 [8] Ni-Co [9] NiO [10] and iii) carbon-metal oxide composites [11-14] has resulted in a significant increase in the capacitance, energy density and power density of the ECs. However with the emergence of new technologies further advances in materials used in ECs are required to address this increasing power/energy demands. In this review the development and recent trends of ECs concerning their energy storage mechanism, power handling characteristics and their applications are reviewed and discussed. In addition, detailed review of different types of carbons as one of the most used electrode materials together with a brief review of different electrolytes and materials used as binder in electrode fabrication for electrochemical capacitors are provided and discussed through extensive analysis of the literature.

Electrochemical capacitors and their energy storage characteristics

First patented by Becker at General Electric Corporation in 1957 [15] and later commercialised by SOHIO in 1978 [16] electrochemical capacitors have developed significantly over the past decades to become an attractive power solution for an increasing number of applications. Unlike the battery in which energy is available as chemical energy through faradaic (oxidation and reduction process) reactions of the electrochemical active materials which facilitates the release of charges between two electrodes with different potentials, an electrochemical capacitor stores energy in a reversible manner in which charges are distributed on electrodes surfaces by physical processes without involvement of the breaking and formation of chemical bonds. This gives the device fast charge/discharge capability and long cyclic stability ($>10^5$ cycles).

Depending on their mechanism of charge-storage, ECs are mainly classified into two broad categories known as electrical double-layer capacitors (EDLC), and pseudocapacitors (PC). Another class of the technology which benefits from the combination of these two mechanisms of charge storage is also developed. This class is known as hybrid capacitors (HC) and exhibit a much higher capacitance for pulse power [17].

In a double-layer capacitor the capacitance arises from electrostatic charge separation and formation of electrochemical double-layer of charges at the interface between a conductive electrode and an adjacent liquid electrolyte. Following the natural attraction of unlike charges, solvated ions in the electrolyte are attracted into the pores of the electrode with opposite charges equally accumulated on the electrode's surface effectively creating two capacitors in series connected ionically by electrolyte. In this regard the pores of the electrode can be carefully engineered to provide high internal surface area and prevent the recombination of the ions that coupled with the nanometre scale thickness of the double layers allow EDLCs achieving the energy density of several orders of magnitude higher than those of conventional capacitors.

In pseudocapacitors electrical energy is stored through reversible faradaic redox reactions in which the oxidation state of the electro-active material utilized in electrodes changes during electron transfer without breaking and formation of chemical bonds. These reactions occur only at the electrode/electrolyte interface and do not propagate into the electrode's bulk material as seen in batteries. In theory, their capacitive ability is expected to be much higher than that of the double-layer capacitors.

The process of energy storage in batteries and electrochemical capacitors is substantially different from the energy conversion/storage process in a fuel cell which is an open system. In this case both the anode and the cathode act only as charge-transfer media with the active masses undergoing the redox reactions delivered from outside of the cell through continuous supply of fuel which can be hindered by the thermodynamic /Carnot cycle [18].

Table 1 compares the characteristics of electrical energy storage devices which include Li-ion batteries, supercapacitors and fuel cells. As seen, electrochemical batteries and fuel cells are energy storage devices with typical gravimetric energy densities in the range of 100 – 200 Wh/kg and 600 – 1200 Wh/kg, respectively with ability to store large amounts of energy and release it over a longer period of time. On contrary, ECs represent a much lower energy densities typically ranging between 0.05 – 30 Wh/kg [19, 20], however in case of short discharge periods where high energy is required, for example, in overcoming fluctuations in the output of a wind turbine, they can offer periods of pulsed power that would otherwise be difficult to engineer. As none of these technologies by themselves can serve all applications with the capability to fulfil the wide spectrum of our future energy needs, systems compromising a combination of these technologies will be able to respond to peak power demands and fast charge/discharge at short time periods, and high storage capacities for long time energy demands.

Table1 -- Performance characteristics of different electrical energy storage technologies.

Characteristics	Li – ion Batteries	Supercapacitors	Fuel Cells
Gravimetric energy density (Wh/kg)	100-200 [21]	0.05-30 [20]	600-1200 [20]
Volumetric energy density (Wh/L)	200-600 [20]	>100,000 [20]	500-3000 [20]
Power density (W/kg)	150-315 [22]	500-5000 [22]	5-500+ [22]
Cycle efficiency	95% [21]	85-98% [23]	25-58% [24]
Discharge time	0.3-3h [25]	0.3-30s [25]	1s - >24h [20]
Durability (years)	14-16 [26]	>20 [20]	15 [27]
Durability (cyclic)	800-3,000 [28]	500,000 [29]	20,000 [27]
Capital cost (\$/kWh)	600-2500 [30]	300-2000 [30]	6000-20,000[30]
Availability*	97% [20]	99.99%+ [20]	90% [20]

*Availability of technology commercially which is associated with their maturity.

A comparison of the different energy storage technologies in terms of their specific energy, specific power and time scale of their energy delivery is presented in Fig. 1.

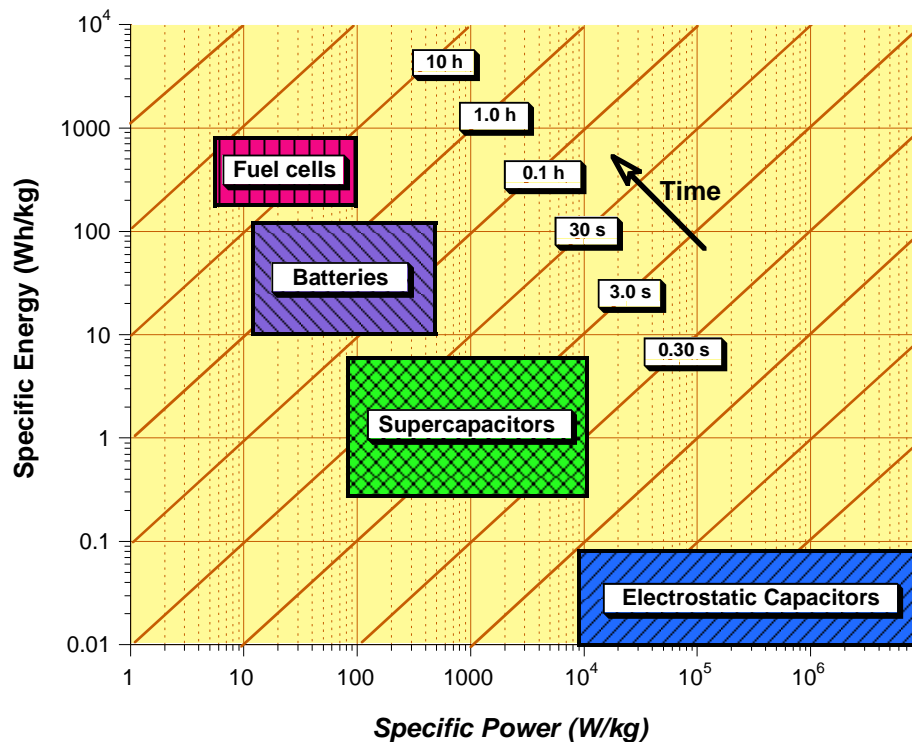


Fig.1 — Specific energy, specific power and delivery time of different energy storage technologies.

In terms of the energy delivery times, the graph exhibits an extreme end with very high power and very low energy densities happening in short time spans of fraction of seconds for conventional electrostatic capacitors to another end of high energy and low power densities with longer period of energy delivery in time spans of hours for fuel cells. Batteries and electrochemical capacitors as two main technologies at the forefront of electrical energy storage devices, located between these two energy characteristic ends, store energy in different ways. The mode of energy storage in batteries involves the interconversion of the chemical electrode reagents with high energy storage within the bulk of electroactive materials. Their charge/discharge rates and power capability are restricted by mass transport and reaction kinetics and their cycle life is limited to thousands of charge/discharge cycles as a result of limitations in mechanical stability and chemical reversibility of the redox reactions in electrode materials. In electrochemical capacitors, where there is no chemical reaction of

electroactive materials involved and therefore no excess and deficiencies of electron charges in the bulk of the electroactive materials utilised in electrodes occur, a system with high reversibility capable of hundreds of thousands of charge/discharge cycles without appreciable loss of energy-storage capacity is possible. However as the mode of energy storage in ECs is physical charge storage restricted on the surface of the electrode only, energy density of the device is low and the power densities are also limited by the electrolyte operating potential.

As shown in Fig. 1, electrochemical capacitors are capacitive storage devices that bridge the gap in energy density between batteries and the conventional electrostatic capacitors and provide continuity in the energy supply/delivery spectrum. When used in hybrid energy-storage systems they complement batteries by providing pulsed power that would otherwise be difficult to engineer to meet the challenges of contemporary energy-storage/ power-delivery systems. This hybrid combination then has an overall power/energy density specification better than either components alone [31].

In electrochemical capacitors energy is stored on the same principle as electrostatic capacitors where electric charge in the form of electric field between the capacitor plates accompanied by ion separation at electrode/electrolyte interface results in ten-fold higher specific capacitance due to a large specific surface area of electrodes (e.g. in the order of 1000 m²/g). The capacitance is proportional to the surface area ‘S’ of the material and to the relative permittivity of the solution ‘ε’ and reciprocally dependant on the thickness ‘d’ of the double layer in accordance to equation (1) [32, 33].

$$C = \frac{S\varepsilon}{d} \quad (1)$$

The amount of energy that theoretically can be stored and delivered by an electrochemical capacitor (E) is proportional to its capacitance (C) and its operating voltage (V) which is limited by the electrochemical window of the electrolyte:

$$E = \frac{1}{2} CV^2 \quad (2)$$

The power density defined as the energy expanded per unit time is given by:

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

Where R is the equivalent series resistance (ESR) which includes the resistance of electrode, electrolyte, current collector and resistance of dielectric material [3]. Fig. 2 shows a graphical representation of the mechanism of charge storage in different capacitive devices. Depending on the mechanism of charge storage, the energy and power densities of a capacitor vary

fundamentally. In a typical electrostatic capacitor, no movement of ions (charge carriers) is involved and no electron is transferred across the electrodes interfaces. The storage of electric charge and energy is purely due to the redistribution of electronic charges and mainly valence electrons [16] followed by the change in the atomic positions of bond length of molecules referred to as atomic polarization. This substantial intermolecular dipole to dipole interaction between the dielectric materials gives rise to much higher polarization values resulting in high dielectric constant and subsequently high capacitance values in a significantly short time scale with limited movements of non-conduction electrons. It results in very high discharge rates in the range of milliseconds or microseconds in a device with low energy density and extremely high power density of up to 10^8 W/kg [34]. On the contrary, the electrons involved in the double layer charging are the delocalized conduction-band electrons of the electroactive materials used in the electrode with the degree of electron transfer in the range of 0.17 to 0.20 e^- /atom of accessible surface [16]. There are intermediate situations in which Faradaic charge transfer due to reversible redox reactions give rise to a pseudocapacitance. Although the Faradaic mode is the essential process that takes place in battery cells where electrons are transferred across the double layer paving the way for change in the oxidation state within the bulk of the electroactive materials, however as shown in Fig. 2 in a pseudocapacitor a similar reversible process with the degree of electron transfer in the range of 1.0 to 2.50 e^- /atom of accessible surface in addition to the capacitive double layer charging results in a much higher energy density with a high degree of reversibility for the device. Ultimately continuum of the charge storage continues in battery chemistries where huge quantity of Faradaic charge (as much as 3 e^- /atom within the molecule of bulk phase) can be transferred which is not restricted by the available surface area and can propagate into the bulk of the electrode material. Based on these significant differences between the level of electron transfer and charge storage mechanisms in capacitive and Faradaic storage devices, ECs can be seen as transitional states between conventional capacitor technology and intercalation batteries [35]. Nevertheless this emphasises the fact that ECs should not be seen as a replacement for batteries but as a complementary technology that can assist in the design of new energy storage systems.

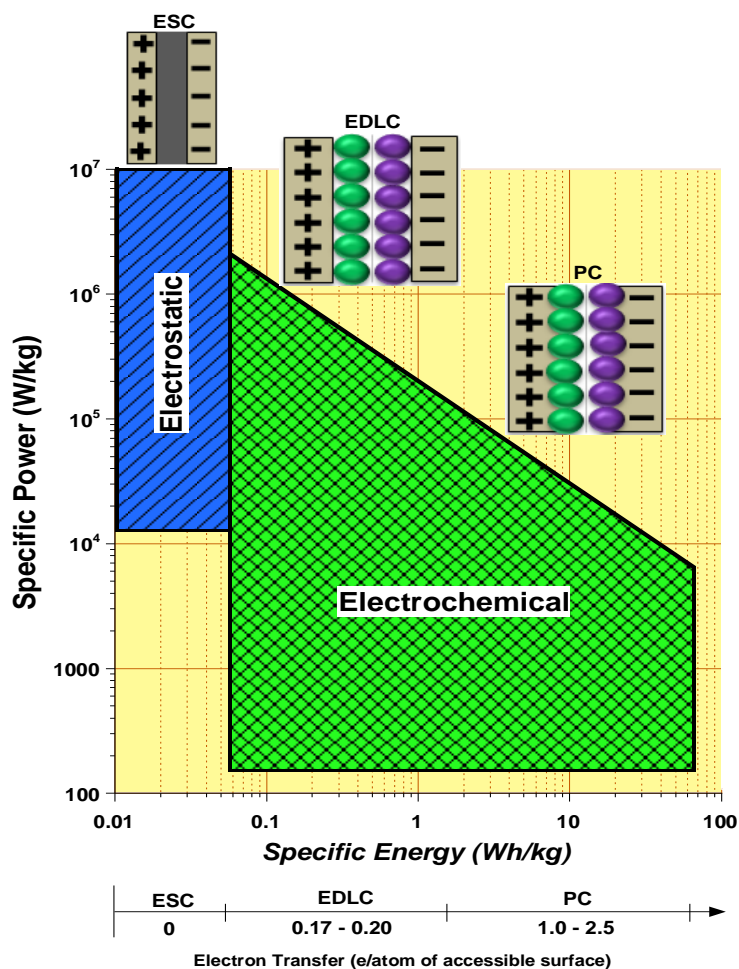


Fig.2 -- Mechanism of charge storage and electron transfer in different capacitive devices (ESC: Electrostatic Capacitor; EDLC: Electric Double Layer Capacitor; PC: Pseudo- Capacitor).

The evolution of these technologies is largely dependent on the development of electrode materials and electrolytes with optimised characteristics aimed at delivering high power and energy densities considering safety and operability.

Electrode materials for electrochemical capacitors

Electrodes are the fundamental constituents of ECs and therefore different properties of electroactive materials used in the fabrication of electrodes play a remarkable role impacting the energy and power densities and the capacitive performance of the final device. Because of lower specific energy of ECs compared to that of electrochemical batteries enormous amount of research has been done to produce new and innovative electrode materials to reduce the

gap between the specific energy of these technologies and retain continuity in energy storage/delivery continuum.

Electroactive materials used in the fabrication of electrodes for electrochemical capacitors can be generally grouped into two categories known as carbon-based active materials mainly used in electric double layer capacitors and pseudo-capacitive active materials including transition metal oxides and conducting polymers predominantly employed in redox capacitors or pseudo-capacitors. Though another category which benefits from the incorporation of heteroatoms/or metal oxides into the structure of carbon is also developed. Electrochemical capacitors using materials in this category as electroactive materials in their electrodes have shown a significant increase in specific energy of the device as a result of the addition of pseudocapacitive properties to the electric double layer capacitance of carbon based electrodes. The performance of this group of materials in electrochemical capacitors will be discussed later in this review.

Carbon based electrode materials

Because of its unique chemical and physical properties such as: high conductivity, good corrosion resistance, high temperature stability, low cost (as compared to metal oxides) and excellent chemical inertness and also its wide availability and established industrial processes for its production in large scale, carbon is the most commonly electrode material used in a wide range of energy storage technologies [36]. Its existence in several allotropic forms such as fullerenes, graphite and nanotubes with different dimensionality from 0 to 3D [3] and also possibility of its production with different degrees of hardness and porous structure depending on the type of precursor used, have made carbon as the most suited electrode material that satisfies major requirements such as: high surface area; low electrical resistance; good polarizability; controllable porous structure and pore size for EC application.

In these section details of various carbonaceous materials from the most widespread types to the newest developments including the source of materials; the method of their production; and also enhancement of their capacitive properties through incorporation of functionalized groups and heteroatoms into their structure from both research and application perspectives are reviewed and discussed. Brief details of the properties of the materials such as their porous parameters, specific surface area, their chemical composition and correlation between their properties with their capacitive values when used as electroactive material in the fabrication of electrode for ECs are also presented.

Activated carbon (AC)

Activated carbon is a form of carbon with a network of micro-pores produced from carbonaceous source materials through a mild oxidation process known as the activation process in which surface area, pore size and pore size distribution of the carbon can be controlled by altering various parameters such as temperature, burn off time and activation agents used during the treatment of carbon. This can be achieved by heat treatment of the carbon at high temperatures by physical or chemical activation and results in a material with small, low-volume pores with high degree of microporosity and a surface area in excess of 1000 m²/g as determined by gas adsorption/desorption techniques that increase the surface area available for charge storage.

In physical activation (also known as thermal activation) carbon is activated at a temperature between 400 - 1200 °C under the constant flow of CO₂ whereas in chemical activation carbon is activated at lower temperatures in the range 400 - 700 °C in the presence of a dehydrating agent such as H₂SO₄, ZnCl or KOH. Activated carbons are different because of the starting material and manufacturing methods. The base raw material and pre-treatment steps prior to the activation process can affect many of the physical and activity characteristics of activated carbons. Depending on different parameters during the activation stage such as the type of the agent, degree of burn off and activation temperature the internal surface area of carbons can be increased. The activation process results in exceptionally high surface area finished porous product.

Polymer based activated carbon (AC)

Polymer based carbons are the type of synthetic carbon materials produced through the carbonisation of polymeric gels by heat treatment at high temperatures of up to 800 °C under inert environment such as argon or nitrogen. One of the main advantages of these carbons is improved control of their porous structure during the synthesis of the polymeric gel precursors prior to the carbonization process. Because of the cross-linked structure of the initial gel which can be adjusted during the polycondensation step of the gelation process, these type of carbons possess a three dimensional structure with very high conductivity which is vital for carbon based electrodes used in any electrical devices such as electrochemical capacitors. A further control on the porosity of these carbons can be achieved by producing activated carbons through the activation process. Structural control, ease of processability and cost effectiveness makes polymeric based activated carbons as the most investigated and commercialized materials used for different engineering applications. One of the applications

of these carbons is for electrodes in EC's. Several studies have been conducted to control the porosity of activated carbons and find out the relationship between their various structural properties and capacitive performance of EC's which will be discussed in detail in porosity subsection of this paper [37-39].

Naturally occurring activated carbon

Naturally occurring materials such as cotton [40], rice husk [41], bamboo [42], wood [43] and peanut shells [44] have also been investigated to produce activated carbons adopted as the active materials in the fabrication of electrode for ECs [40]. These carbons have shown extremely high specific surface area (SSA) and specific capacitance when used as electrode materials for EC applications. Yang et al., have synthesised activated carbons with exceptionally high SSA of 3000 m²/g from bamboo recently [42]. Specific capacitance of 120 F/g, 200 F/g and 210 F/g have been achieved when using these high surface area carbons as electroactive materials in conjunction with organic, aqueous and ionic liquid electrolytes in an electrochemical cell, respectively [37, 45]. Alonso et al., also prepared activated carbons with SSA of around 3204 m²/g through chemical activation of Sasol-Lurgi gasifier pitch by KOH. The carbons exhibited specific capacitance of up to 400 F/g in an electrochemical cell using aqueous solution of sulphuric acid (2 M) as electrolyte [46].

Activated carbon fibres (ACF)

Activated carbon fibres are a class of activated carbons mostly obtained by electro-spinning of natural materials such as pitch or through the use of polymeric solutions. Processes involving the fabrication of activated carbon fibres from electro-spun precursors are oxidative stabilization in oxygen containing environment in the temperatures range of 180 - 300 °C; carbonization in inert atmosphere; graphitization with further heating of the fibre up-to 3000 °C; and finally activation in oxidizing environment in temperatures range of 700 -1200 °C. The first activated carbon fibre utilized as the electroactive material in ECs was patented by Nishino et al., in 1988 [47, 48]. Recently Su et al., used the same method to produce activated carbon fibre with specific surface area of 2332 m²/g showing high specific capacitance of 430 F/g in 1.0 M H₂SO₄ as electrolyte with capacitance retention of 60% [49]. Efforts have been made to produce ACFs at reduced cost by direct activation of stabilized fibre to avoid the carbonization stage and save both energy and time. ACF produced by direct activation of stabilized fibres have shown high specific capacitance of 100 F/g in 1.0 M of H₂SO₄ [50]. Jin et al., have also reported a very high specific surface area of 3223 m²/g and specific capacitance of 280 F/g for activated carbon fibres in 1.0 M of H₂SO₄ [51]. Although

these materials exhibit high capacitance when used as electrode materials in electrochemical capacitors, however the cost and extremely complex processes used for their production, has so far hindered their inclusive use as electrode materials in ECs.

Carbon materials with heteroatoms

Capacitive properties of carbon materials can be enhanced by introducing pseudocapacitance properties alongside their electric double layer through fast faradic reactions in ECs. Higher capacitances can be attained by doping the porous carbon with pseudo-capacitive materials such as metals oxides or by the introduction of oxygen, nitrogen or boron's heteroatoms into the carbon network or on their surface. These improve the specific capacitance of the electrode and its wettability with the electrolyte. Oxygen and nitrogen are the most frequently introduced functionalities. Oxygen heteroatoms are often acidic in nature and induce electron acceptor characteristics into carbon material whereas nitrogen functional groups with five valance electrons exhibit electron donor characteristics and basic nature [52].

Nitrogen containing carbons

Nitrogen can be introduced on the surface /or within the structure of carbon by either treating the porous carbon with nitrogen containing regents like urea [53], nitric acid [54], pyrrole [55], potassium hydroxide [56] , and ammonia [57] or by carbonization of various nitrogen containing precursors such as urea polymer [58], melamine and melamine based organic gels [59-61] and nitrogen containing biomass [62-64] . Treatment of a porous carbon with regents such as ammonia introduces nitrogen containing functional groups on its surface whereas carbonization of nitrogenous precursors where materials such as melamine or urea are used results in the inclusion of nitrogen into the carbon structure [65]. Compared to carbon with heteroatoms of oxygen, nitrogen containing carbons have been investigated for supercapacitor applications intensively since they can be used with both aqueous and organic based electrolytes [66].

Zhou et al., synthesized KOH activated nitrogen rich carbon by pyrolysis of the polymerized ethylenediamine and carbon tetrachloride. It was shown that a specific capacitance of 363 F/g and excellent cycling stability (97% capacitance retention over 5000 cycles) can be achieved when using this carbon as electroactive material in an electrochemical capacitor [56]. A study by Candelaria et al., also showed that the wettability of the carbon surface increases significantly after doping the carbon with nitrogen. The nitrogen modified carbon exhibited a capacitance nearly double the capacity of EDLC [67]. Nitrogen doped porous carbon produced by urea formaldehyde resins and calcium acetate monohydrate as hard templates

have shown a specific capacitance of 335 F/g with capacitance fading of only 1% after 5000 cycles [53]. High specific capacitances of 293 F/g and 47 F/g with very high energy and power densities of 47.5 Wh/kg and 10.5 kWh/kg were also achieved when using nitrogen doped porous graphitic carbon material (NPGC) with surface area of 1027 m²/g and nitrogen content of 7.72% synthesized by pyrolysis of tetraethyl, nickel nitrate, glucose and melamine as the electrode material using aqueous and organic electrolytes, respectively. Electrodes fabricated from this porous carbon exhibited a high columbic efficiency of 99.9% over 5000 cycles [68].

Oxygen containing carbons

Introduction of oxygen containing functional groups in carbon framework is another attractive way of improving the specific capacitance of ECs. Oxygen rich carbons can be synthesized by either carbonization of oxygen rich precursors or by treating carbon in strongly oxidative environment. Due to the irreversible reaction of oxygen containing functional groups with organic electrolytes, the use of carbons with oxygen functional groups is limited to the aqueous based electrochemical capacitors only [66, 69].

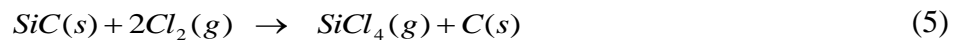
Both acidic and basic oxygen functionalities can exist in carbon, where former can be introduced by the activation of carbon at elevated temperatures and latter is present in carbon network when carbon is treated at high temperatures under inert conditions followed by cooling down and exposure to the atmospheric oxygen [3]. It is shown that introduction of both oxygen and nitrogen functional groups, improves the specific capacitance of the carbon electrodes significantly. Fan et al., synthesized ordered porous carbons by using SiO₂ colloidal crystals as template and phenol resin as precursor followed by etching with 98% HNO₃. It was shown that the introduction of both oxygen and nitrogen heteroatoms on the surface of carbon improves the wettability and specific capacitance in both acidic and basic electrolytes. The specific capacitance was increased from 127.5 F/g for untreated carbon to a value of 178 F/g in acidic electrolyte. The results also showed a considerable increase in specific capacitance from 115.4 F/g for untreated carbon to 160 F/g for heteroatoms doped carbon in basic electrolyte. This increase in the capacitance was achieved despite of a decrease in the specific surface area of the carbon from 711 m²/g to 381.5 m²/g with treatment in 98% HNO₃. Wettability of the carbon was also significantly enhanced with a considerable decrease in the contact angle from 136° to 40° before and after the treatment, respectively due to the introduction of hydrophilic oxygen and nitrogen based functional group [54]. In another study Oh et al., investigated the effect of oxygen functional groups on

capacitance of ECs using reduced graphene oxide (RGO) as electroactive material in a electrochemical cell using an alkaline electrolyte. The cell exhibited a capacitance of 215 F/g and 226 F/g for RGO only when using 6 M KOH and 1 M H₂SO₄ as the electrolyte, respectively. It was shown that the contribution of carboxyl and phenol groups to these total capacitances are 67 F/g and 55 F/g for KOH electrolyte and 66 F/g and 65 F/g for H₂SO₄ electrolyte, respectively as a result of the pseudocapacitive contribution of functional groups. The pseudocapacitive contribution of carbonyl and quinone groups in acidic electrolyte were also determined as 42.67 F/g and 36.33 F/g, respectively [70].

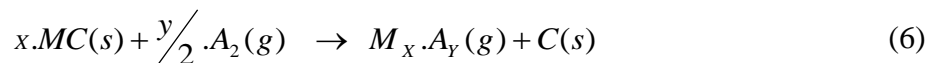
Carbide-derived carbons (CDC)

Carbide derived carbons are class of carbons obtained by the removal of metal or metalloid atoms from ceramic precursors like SiC, TiC, Mo₂C and VC using either physical processes such as thermal decomposition or by chemical processes such as halogenation. Unique properties including exceptionally high surface area, controlled pore size and very narrow pore size distribution attained by the selection of the precursor used and the synthesis parameters applied make carbide derived carbons as one of the most investigated electrode materials for electrochemical applications in recent years.

Chlorination of silicon carbide first patented by Otis Hutchins in 1918 is one of the frequently used methods for the preparation of CDC represented by simple reaction between silicon carbide and chlorine gas at elevated temperatures as shown by the following equation.



The reaction can be expressed in more general form when other halogen containing gases and their mixtures are used as follow:



Where A is a gaseous halogen such as Cl₂, Br₂, I₂, and F₂ or mixture of them or halogen containing enchain agent (e.g. HCl, HF) and M_xA_y is the gaseous reaction product [71].

In hydrothermal treatment method, metals or metalloid atoms are removed by using supercritical water at very high pressure in the order of hundreds of MPa to produce high surface area carbide derived carbons [72].

Korenblit et al., used ordered mesoporous silicon carbide derived carbon with the maximum specific surface area of 2430 m²/g as electrode material for electrochemical capacitors. The

cell exhibited a high specific capacitance of 170 F/g and only a small decrease (i.e. 2.5%) in capacitance was witnessed when the current density was increased by tenfold from 1750 mA/g to 17500 mA/g indicating an improved ion transportation due to the ordered mesoporous structure of the electrode [73]. It has been observed that ordered mesoporous CDCs can be useful for better response on much higher frequencies and capacitance retention at high current densities due to their fast ion transportation whereas microporous CDCs lack these properties. It is also shown that microporous CDC with higher specific surface area also result in high energy storage capabilities in electrochemical capacitors. The recent study by Tee and his co-workers shows a 40% increase in specific capacitance with cyclic efficiency of 98% when doubling the microporous specific surface area of CDC synthesised from SiC powder (SiC-CDC) from 1100 to 2270 m²/g by CO₂ activation [74].

Wu et al., also reported very high specific capacitance of 242.7 F/g with excellent columbic efficiency of 100% after 10000 cycles using a combination of ordered microporous and mesoporous carbide derived carbon material originated from chromium carbide [75]. The carbon material possessed a specific surface area of 1236 m²/g and pore size of 3.43 nm. It is discussed that the improved specific capacitance and cycleability are mainly benefited from both higher SSA and larger pore size which result in improved electrolyte accessibility and ion transportation.

Perez et al., have reported a microporous carbon with very narrow pore size distribution in the range of 0.5-2.0 nm and very high SSA of up to 2167 m²/g prepared from titanium carbide [76]. The carbon exhibited a high specific capacitance of 132 F/g with capacitance retention of 75%.

Although CDCs have been investigated as potential electrode material for electrochemical capacitors' applications in the recent years however high production cost and environmental concerns because of the use of halogen gases for their production has limited their commercial use in many engineering applications.

Template derived carbons (TDCs)

Template derived carbons (TDCs) are class of carbons synthesised using an inorganic sacrificial scaffold such as ordered silica or zeolite and a carbon precursor such as sucrose solution, polyfurfuryl alcohol, propylene or pitch. The preparation of TDCs involve three steps including the synthesis of template itself, infiltration of carbon precursor, and removal of the skeletal template as shown in Fig. 3 [77].

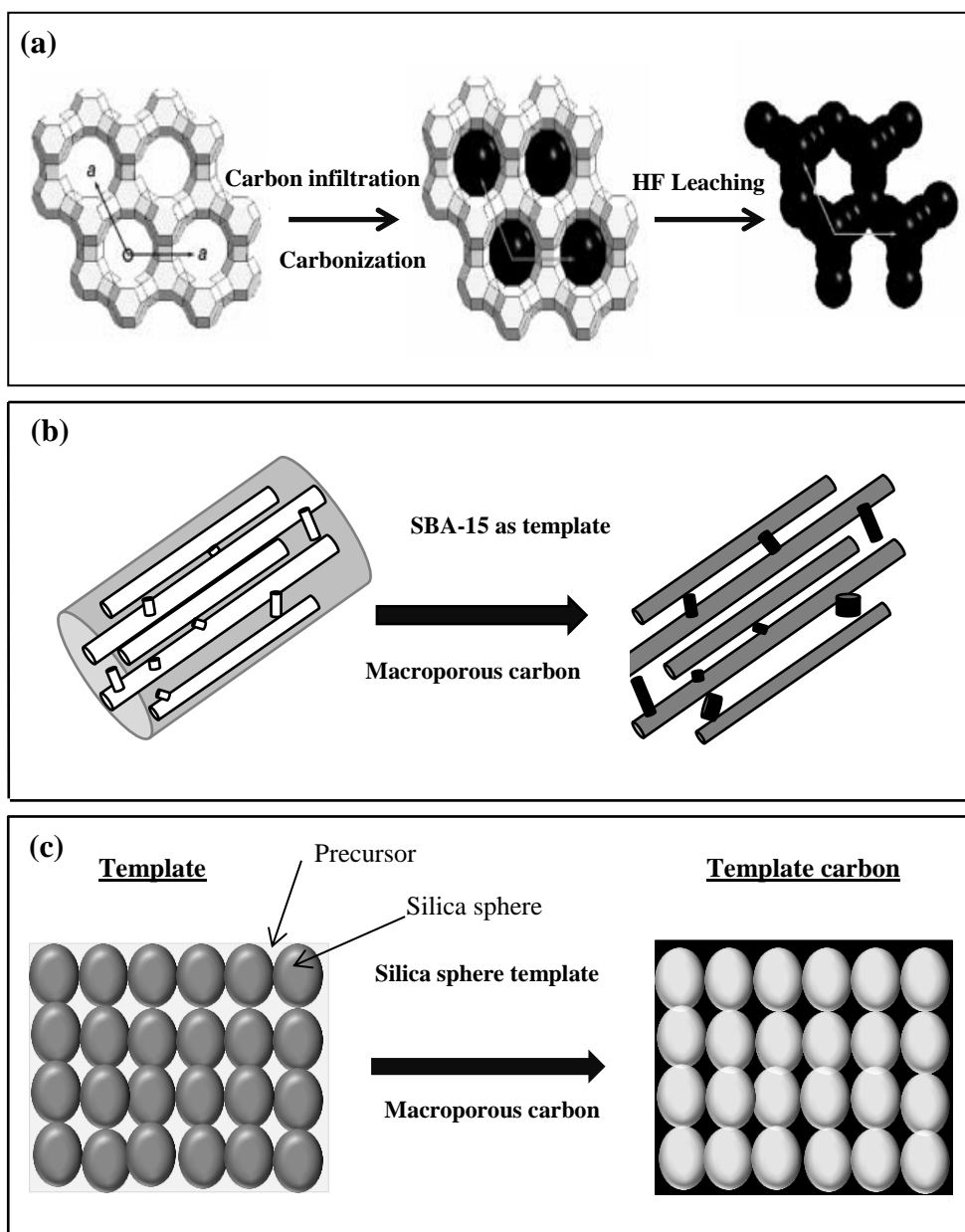


Fig.3 — (a) Microporous carbon fabricated using Zeolite Y as template. Reproduced with permission from ref. [78] (b) mesoporous carbons using SBA-15 as template (c) macroporous carbons using silica spheres as template.

Carbons with controlled pore structure and very high specific surface area can be prepared by template carbonization method. Matsuoka et al., have prepared ordered microporous carbons with remarkably high specific surface area of $3360 \text{ m}^2/\text{g}$ with a narrow pore size distribution where most of the pores are in the range of 1-2 nm by template method using Zeolite Y as a template and furfuryl alcohol as the precursor [79]. In a case study by Chen et al., zinc benzoate complex was prepared by mixing $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and sodium benzoate in aqueous solution which produced nano carbon and also acted as metal organic frameworks [80]. The carbon material exhibited a high SSA of $1466.4 \text{ m}^2/\text{g}$. An enormous specific capacitance of

314.1 F/g and high energy density of 67.2 Wh/kg was achieved due to orderly interconnected internal structure of the carbon used as electroactive material in an electrochemical capacitor using 6 mol/L KOH as electrolyte.

Despite the ease of fine-tuning their pore size and controlling their -microporous /mesoporous structure with narrow pore size distribution, TDCs are mainly important from research point of view and have limited commercial potentials due to high cost, safety and environmental concerns associated with their production.

Composites carbons

Activated carbons, CNTs and graphene have been used extensively as substrate to make composite structures as electrode materials for electrochemical capacitor applications [81]. Composite carbons obtained by doping these carbonaceous substrates with a variety of transition metal oxides such as MnO_2 , RuO_2 and V_2O_5 , and oxides of other metals such as Fe, Ag, Cu, and Zn at different oxidation states have been widely investigated [32]. Some transition metal oxides with pseudo-capacitive properties possess promising characteristics such as battery-level energy density, superior cycle life, improved efficiency, and high power density when used for electrical energy storage in EC's [82]. Many studies have shown that the incorporation of these materials within the highly porous carbon structures increases the capacitance and power density of the composite electrodes significantly due to the contribution of both electric double layer and pseudocapacitive charge storage processes. Liu et al., used a composite of RuO_2 and poly (3, 4-ethylenedioxythiophene) based carbon nanotube as electroactive material for energy storage in an electrochemical cell. The cell showed power and energy densities of 20 kW/kg and 28 Wh/kg, respectively with a specific capacitance of 1217 F/g when the composite material was used. This capacitance is almost one order of magnitude higher than the capacitance of 150 F/g for carbon based substrate [83] and the capacitance of 644 F g^{-1} for RuO_2 coated onto carbon nano tubes when used as the electroactive materials [84]. Exceptionally high energy and power densities of 39.28 Wh/kg and 128.01 kW/kg, respectively have also been reported for ruthenium oxide (RuO_2) anchored graphene and CNT hybrid foam composites [85].

Due to its superior electrochemical performance, natural abundance and low cost, MnO_2 has been also considered as one of the most investigated metal oxides used in supercapacitor applications. Recent study by Lee and his co-workers shows a specific capacitance of 168 F/g is achieved for MnO_2 -doped activated carbon aerogels which is significantly higher than the capacitance of 98 F/g when the activated carbon substrate is used by its own [86]. In another

study by Yu et al., a specific capacitance of 315F/g for nanoparticles of MnO₂ electrodeposited onto graphene coated textiles has been reported which is 5 times higher than the specific capacitance of graphene coated textiles nano-sheets [87]. In a very recent study Wei et al., have also reported exceptionally high specific capacitance of 709.8 F/g with capacitive retention of 97.6%, after 1000 cycles for manganese oxide (MnO₂)/three-dimensional (3D) reduced graphene oxide (RGO) composites [88].

Graphene

Graphene is a two dimensional (2D) carbon structure composed of monolayers of carbon atoms arranged in a honeycomb network with six-membered rings. Due to its unique structure it exhibits many unexplored properties for different applications. It has been used in different forms and shapes such as graphene, activated graphene, doped graphene, graphene metal oxide composites and fullerene, nanotubes, and graphite as electrode material in EC's [89]. Following its discovery by Geim and co-workers in 2004 [90], variety of methods including, mechanical exfoliation of bulk graphite [91], sublimation of silicon from silicon carbide (SiC) wafers [92], arc-discharge synthesis of multi-layered graphene [93] and epitaxial growth by chemical vapour deposition (CVD) of hydrocarbons on metal substrates [94] have been used for its production. Oxidation of graphite to graphite oxide, thermal or mechanochemical exfoliation of graphite oxide to graphene oxide (GO) sheets followed by reduction the GO sheets to graphene are the most adopted methods which result in the production of graphene with higher yields [95, 96].

Three dimensional (3D) mesoporous graphene has been used as the electrode material in a supercapacitor. It showed the specific capacitance and energy density of 341 F/g, 16.2 Wh/kg and 166 F/g, 52.5 Wh/kg with 96% and 86% capacitance retention after 1000 cycles in alkaline and organic electrolytes, respectively [97]. A specific capacitance of 306 F/g with 93% capacity retention after 10000 cycles have also been achieved for a composite of microwave exfoliated graphene oxide and single wall carbon nano tube [98]. Despite its superior characteristics including high specific surface area, good electrical conductivity and rich surface chemistry, utilization of graphene as electrode material in ECs is currently limited to research works and commercial preparation of good quality graphene based material in a cost effective way is a challenge yet.

Shaped carbon nano structures

These materials are carbons with a special designed structures mainly obtained through complex synthesis routes which improves the functionality and configuration of the carbonaceous materials for different applications. Carbon nanotubes, carbon nanofibers, carbon nano-horns, carbon nano onions and carbon nano foams are types of carbons in this category. A brief introduction of different shaped carbon nano structures and their application as electroactive material for ECs is given as follow:

Carbon nano tubes (CNTs)

Carbon nano tubes are rolled up graphitic sheets creating tube like shape with both ends usually capped with fullerene-like structure first prepared by S Iijima in 1991 [99]. CNT's can be synthesised by arc discharge, laser ablation and catalyst chemical vapour deposition (CCVD) methods whereas CCVD is the most frequently used technique for their large scale production. Addition of extra graphitic sheets around the core of single wall carbon nanotubes (SWCNT) results in the formation of double wall carbon nanotubes (DWCNTs) or multiwall carbon nanotubes (MWCNTs). Specific surface area of these carbons varies from 200-2000 m²/g. SWCNTs exhibit much higher surface area with more expensive production cost when compared with DWCNTs and MWCNTs. Hiraoka et al., synthesized SWCNT with very high SSA of 2240 m²/g and used it as electroactive material for energy storage in a supercapacitor where high energy and power densities of 24.7wh/k and 98.9 kwh/kg were achieved, respectively [100]. Recent study conducted by Inagaki shows that electrodes prepared by commercially available single-walled carbon (SWCNTs) nano tubes possess twice the gravimetric capacitance per BET surface area as compared to the electrodes made from ACs [101].

The overall capacitance of ECs when using CNTs as the electroactive material can be increased by introducing pseudocapacitance material into CNTs structure or synthesizing the composites of CNTs and materials such as conducting polymers. Enhanced specific capacitance of 373.5 F/g for Polyaniline/ tailored carbon nanotubes composites (PANI/TCNTs) has been achieved which is higher than the specific capacitance of pure PANI (324 F/g) [102]. Another study by Sun et al., also showed that a specific capacitance of up to 475 F/g for sulfonated CNTs and PANI composites can be achieved when compared to a specific capacitance of 271 F/g for PANI nanorods [103].

A cost comparison between the use of carbon nanotubes with activated carbons as electrode materials for ECs applications has shown that the cost of electricity storage when using AC

as the electrode material in ECs is around 2-3 \$/Wh whereas this cost increases considerably to 5200- 8300 \$/Wh when using SWCNT as the electrode material [104]. Therefore due to their very high production cost and more complex synthesis routes, the use of CNTs as the electroactive material has been limited in commercial EC applications and more than 80% of ECs commercially available today use ACs as active material.

However, despite these limitations, CNTs are still be used to enhance the power capability of ECs by decreasing the internal resistance of the electrode when mixing them with cheaper electrode materials like ACs. A study by Markoulidis et al., has shown that addition of only 0.15% MWCTs to produce a MWCNT - AC composite as electroactive material used in an electrochemical capacitor , increases the specific capacitance of the cell from 50 to 135 F/g, its energy density from 17 Wh/kg to 28 Wh/kg and its power density from 18 kW/kg 38 kWh/kg compared to when AC was only used as the electroactive material in the electrode [105]. Similarly, it has been shown that the addition of MWCNTs between the graphene layers increases power and energy densities of the graphene electrodes by 39% and 31%, respectively [106].

Although one drawback of CNT's is their high production costs in larger scale at present stage however enormous research is under way to make them commercially viable since these materials have a great potential for the development of ECs with high power capabilities.

Carbon nano fibres (CNF's)

Carbon nano fibres have cylindrical nano structures fabricated through the synthetic approaches similar to those used for the preparation of CNT's in which carbon precursor is heated in the presence of a catalyst. Change in experimental conditions such as the type of precursor or the type of catalyst used determines whether CNT's or CNF's are to be produced [107]. Electrospinning is one of the most commonly adopted methods for the synthesis of CNF's with controlled fibre diameter [108]. Ma et al., synthesized microporous CNF's by electrospinning and improved their porous texture through KOH activation. They produced CNF's with diameters in the range of 252-666 nm and used them as the electroactive materials in ECs. Maximal specific capacitance of up to 256 F/g were obtained for these materials and excellent capacitance retention of 67% (170F/g) was kept when increasing the current density by 100 times [109].

The capacitive performance of EC's using CNF's as electrode material can be improved by introducing the functional groups such as nitrogen into their structure and also by utilising

them with carbon nano tubes and transition metal oxides as dopants. For example Chen et al., used nitrogen doped CNF's as electroactive material for energy storage in ECs. The carbons showed high specific capacitance of 202 F/g at a high current density of 1 A/g in 6 mol/L KOH aqueous electrolyte with excellent capacitance retention capability of 81.7% [110]. In another recent study Xu at al., used nitrogen doped hallow activated CNF's as free standing electrode material without using any binding and conductive additives. These CNFs showed superior capacitance of 197 F/g when compared to solid activated CNF's with the capacitance value of 143 F/g under the similar conditions [111].

Enhanced specific capacitance of 213.6 F/g for hierarchical three-dimensional carbon nanostructure of vertically aligned carbon nanotubes on carbon nanofibers was achieved as compared to specific capacitance of 128 F/g for CNF's only [112]. Abouali et al., has also prepared CNF's doped with a metal oxide to increase their capacitance and power capability when used as electroactive materials in ECs. They synthesized CNF's containing uniformly dispersed cobalt oxide (Co_3O_4) nanoparticles and used them for the fabrication of electrodes delivering exceptionally high specific capacitance of 586 F/g at a high current density of 1 A/g [113].

Fig. 4 shows schematic structure of carbon nano fibres and carbon nanotubes. As seen CNT's consist of graphene layers parallel to the cylindrical axis with diameters in the range of 1-30 nm whereas CNF's consist of carbon nano chips with diameters in the range of 50-200 nm stalked up on top of each other to form a fibre shape [114]. Despite having very analogous structure, there is clear difference in their shapes and they exhibit considerably different performances when used as the electrode material in ECs.

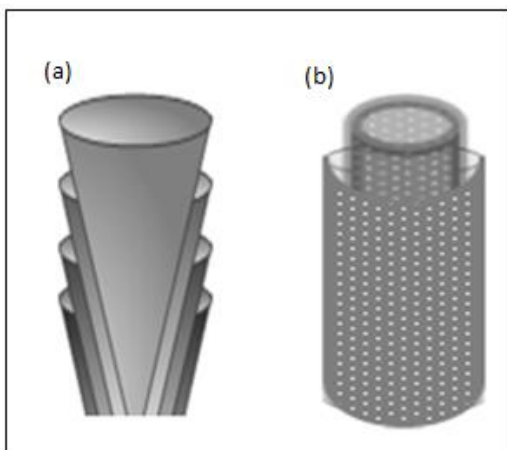


Fig.4 – Schematic structure of carbon nano fibres and carbon nanotubes: (a) Carbon nano fibre (CNF) (b) MWCNT.

Carbon nano horns (CNH's)

As one of the least explored nano carbons, carbon nano horns (CNH's) were first produced by the CO₂ laser ablation without using any catalyst [115]. The structure of carbon nano horns are closely related to CNT's, consisted of single tubular structure with cone shape ending of diameter of 2-5 nm bundled up in dahlia flower-like structured aggregate with an average diameter of about 80 nm [116, 117]. Izadi and Najafabadi used a nanocomposite of single walled nanohorn (SWNH) with single wall nanotube (SWNT) as electrode material in an EC. The nanocomposite exhibited very high power rating of 990 kW/kg with capacitance decline of only 6.5% after 10000 cycles [118]. ECs electrodes composed of SWNH and Fe₃O₄ composite also have displayed a high capacitance of 377F/g [119].

Carbon nano onions (CNO's)

Carbon nano onions (CNO's) also called carbon onions (CO's) or onion like carbons (OLC's) are comprised of concentric layers of spherical closed carbon shells which create the onion like structure. They were first discovered by S Iijima in 1980 and were first used along with nano diamond, carbon black and MWCNTs as electrode material in EC's in 2007 by C Ported and co-workers [120, 121]. Various techniques have been employed to synthesize the CNO's but the most commonly method used for the preparation of CNO's is annealing at very high temperature ranging from 1400 °C to 2000 °C under vacuum or under inert gases. CNO's can be synthesised in larger quantities at atmospheric temperature and pressure with reduced complexity and cost by arc discharge method [122]. However this process results in the production of other nanostructured carbons like carbon nano tubes, polyaromatic and amorphous carbon as impurities. Other techniques including laser excitation, ion implantation and chemical vapour depositions (CVD) are also employed for the fabrication of CNO's [123].

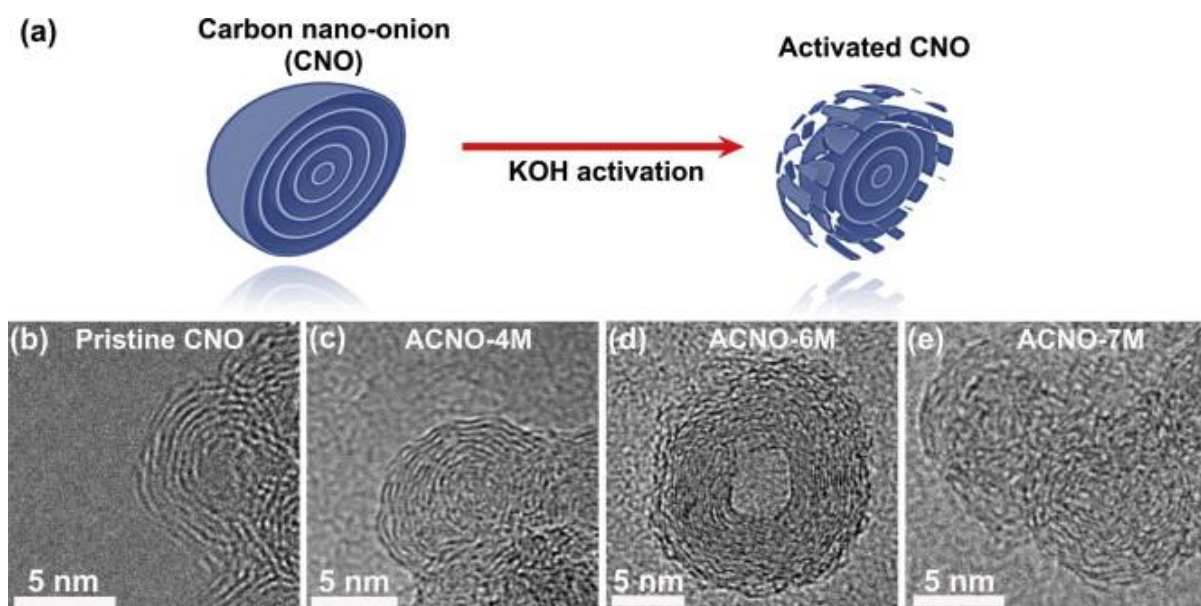


Fig.5 – a) A schematic showing the chemical activation of CNOs in KOH electrolyte with different concentrations. TEM images of pristine CNO (b), ACNO-4M (c), ACNO-6M (d), and ACNO-7M (e). Reproduced with permission from ref. [124].

BET surface area of CNO's ranges from 400 to 600 m²/g where the non-porous outer shell contributes to very high power capability. Due to their inaccessible inner surface area these materials exhibit low energy densities when used the electrode material for ECs. Gao et al., increased the BET surface area of a CNO synthesised through a laser-assisted combustion process in open air using ethylene (C₂H₄) and oxygen (O₂) as precursors increased from 440 to 804 m²/g by introducing the porosity into its nonporous outer shell as shown in Fig. 5. The material showed a fivefold increase in specific capacitance from 24 F/g to 115 F/g with power and energy densities of 153 kW/kg and 8.5 Wh/kg when used as the electrode material in an EC cell [124]. Composites of RuO₂ and CNO's with 67.5 wt. % of RuO₂ have also been prepared and exhibited promising performance for EC applications with very high specific capacitance of 334 F/g at scan rate of 20 mV/s and excellent power and energy densities of 242.8 kW/kg and 11.6 Wh/kg, respectively [125]. Despite their potential as electrode materials for energy storage in electrochemical capacitors for high power applications, CNO's are still between the least studied carbon nano structures due to the difficulties and cost involved in their production on commercial scale.

Carbon foams (CF's)

Carbon foams are extremely porous macroporous structure carbons with low density, high electrical conductivity and excellent hydrophobic surface characteristic. They can be

synthesised by variety of methods but the most common techniques used for their synthesis include template carbonization, blowing of carbon precursors, and compression of exfoliated graphite and graphene foams by assembly of graphene nano sheets. Template carbonization method is useful for controlling the porous structure of the carbon foam while graphene nano sheets method reduces energy consumption for the carbonization process and blowing of carbon precursor method is useful for improving the electrical and thermal conductivity of the carbon foam. High electrical and thermal conductivity foams are prepared by blowing of carbon precursor technique [126].

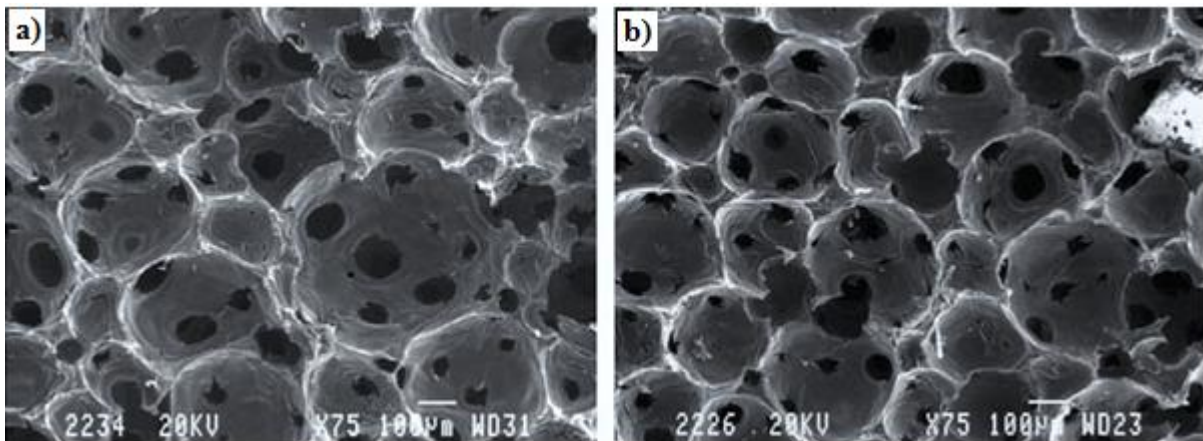


Fig.6 – SEM images of carbon foams prepared under a pressure of 6.8 MPa with pressure release time of 5 sec a) 293°C and b) 300°C . Reproduced with permission from ref. [127].

Due to their macroporous structure, carbons foams are mainly used as the substrate for the synthesis of carbon foam/active material composites by integrating the active materials onto the foam skeleton. He and Chen produced a composite of MnO_2/CF with 3.4 % weight ratio of MnO_2 by carbonizing commercially available melamine resin foam as substrate for the growth of MnO_2 nano sheets onto the foam skeleton. They used the composite as electrode material in an electrochemical capacitor where very high specific capacitance and specific energy of 1270.5 F/g and 86.2 Wh/kg, respectively was achieved [128].

In a study by Yang et al., graphene foam was adopted as supporting template to prepare graphene-pyrrole /carbon nanotube-polyaniline composite. The composite material exhibited a specific capacitance of 350 F/g which is five times the capacitance of graphene-pyrrole aerogels and 2.2 times that of carbon nanotube /polyaniline composite [129].

Table 2 – Specific surface area and performance characteristics of various carbons used as electrode material in EC's.

Carbon materials	Specific surface area (m ² /g)	Capacitance (F/g)	Energy density (Wh/kg)	Power density (kW/kg)
Activated carbons (AC)	3000 [42]	400 [46]	35 [130]	13.9 [131]
Activated carbon fibre (ACF)	3223 [51]	430 [49]	8.1 [132]	2.98[132]
Carbon with heteroatoms	2690 [55]	363 [56]	47.5 [68]	10.5 [68]
Carbide derived carbons (CDC)	2430 [73]	713.4 [133]	42 [134]	133 [134]
Template derived carbons (TDC)	3360 [79]	314.1 [80]	67.2 [80]	1.5 [135]
Transition metal oxide composites	2106 [136]	1217 [83]	39.28 [85]	20 [83]
Graphene	1230 [137]	341 [97]	74 [138]	338 [138]
Carbon nano tubes (CNT's)	2240 [100]	475 [103]	168 [106]	987 [139]
Carbon nano fibres (CNF's)	800 [140]	256 [109]	27.9 [141]	89.57 [110]
Carbon nano onions (CNO's)	840 [124]	334 [125]	11.6 [125]	242.8 [125]
Carbon foam (Composites) (CF)	1313 [142]	1207.5 [128]	86.2 [128]	133.4 [143]

Table 2 shows comprehensive comparison of different type of carbons used as electrode materials in EC's based on their specific surface area, specific capacitance, energy densities and power densities in the literatures. It is shown that carbon nano tubes with ordered internal structure result in higher power densities due to the ease of electrolyte ion's movements. Activated or shaped nano carbons obtained from organic/polymeric precursors where their porous structure can be tuned during the preparation of the organic/polymeric frameworks provide the highest specific surface area or path ways for transfer of electrolyte and ions, respectively. Due to their three dimensional cross linked structure, these carbons are highly conductive [25], however due to their wide pore size distributions and inaccessibility of their internal surface area for charge storage they show lower power and

energy densities [37, 144]. The highest capacitance and energy density can be achieved when using composite carbons in which materials such as activated carbon or carbon nanotube as substrate and metal oxides as the dopant are combined [145]. The capacitance obtained by the use of the composite materials represents the sum of both electric double layer capacitance as well as pseudocapacitance.

Electrolytes

Electrolyte is the only media which facilitates the movement of ions between cathode and anode electrodes during charge/discharge process in an electrochemical capacitor. The diffusion of electrolyte into the porous structure of the electrode is an important factor affecting the performance and particularly the power density of the cell. The wettability of the porous electrode by electrolyte also affects the capacitance and high rate chargeability of the cell since incomplete wetting leads to an increase in the electrode-electrolyte contact resistance handicapping high current charging and discharging [146]. The energy density of an EC can also be affected by the nature of its electrolyte, since the operating voltage of the cell is determined by the breakdown potential of the electrolyte adopted [147]. Therefore the type of the electrolyte adopted in line with the surface characteristics of carbon electrode as discussed above is a key factor affecting the cell's overall performance and therefore a better understanding of the combined effect of these parameters is crucial when designing materials for EC applications.

An ideal electrolyte should have properties such as wide potential window, low resistivity, low viscosity, non-flammability, high electrochemical stability and environmental affability. Despite enormous research carried out on the synthesis of electrode materials and improvement of their functionality for electric energy storage in EC's, electrolytes and their effects on the energy and power densities of electrochemical capacitors are not fully investigated. In this section different types of electrolytes including aqueous, organic and ionic liquid based electrolytes and also some newly developed state of art electrolytes used in electrochemical capacitors are reviewed and their impact of the energy and power densities and capacitance of the device are compared.

Aqueous-based electrolytes

Aqueous electrolytes are mainly grouped into acid, alkaline and natural solutions where the most frequently used are H_2SO_4 , KOH and Na_2SO_4 , respectively. Their operating voltage is around 1.23V significantly lower than those of organic or ionic liquid based

electrolytes[148]. Due to their desired properties such as high conductivity, low viscosity (one order of magnitude lower than the viscosity of organic electrolytes), good compatibility, safety, availability and low cost, they are employed as electrolyte in ECs for the applications requiring higher power outputs as shown in Table 3. Additional advantage associated with the use of aqueous-based electrolytes in electrochemical capacitors is their ease of application since they do not require hygroscopic environments such those needed when using organic or ionic liquid electrolytes. Although the most frequently used aqueous-based electrolytes are 1 M H₂SO₄, 6 M KOH and 1M Na₂SO₄ other electrolytes like Li₂SO₄, NaCl and KCl have also been widely used [149-152] and various studies have been conducted to extend their operating voltage up to 2V [153]. According to Zhong et al., investigation of aqueous electrolytes constitute more than 84 % of the research published in the literature on the electrolytes for electrochemical energy storage systems [154].

Table 3 summarizes the operating conditions and performance characteristics of different aqueous electrolytes in conjunction with different electrode materials used in electrochemical capacitors. It can be seen that high power densities up to 500 kW/kg is achievable when using a 1M solution of KOH as electrolyte with reduced graphene oxide (RGO) as the electroactive material for the cell [155]. Despite high values for capacitance and power densities cited in the table, aqueous based electrolytes have shown very low energy densities with the maximum energy density of 73.3 W h/kg as cited for a cell using 1M Na₂SO₄ with graphene composite as the electroactive material [156]. It has been discussed that low viscosity of aqueous based electrolytes allow them to diffuse into the pores of less than 1nm easily [131] and the presence of oxygen/nitrogen functional groups on the surface of the carbon used as the electroactive material in conjunction with the electrolyte enhances the cell performance by improving the electrode/electrolyte contacts significantly [66].

Table 3 -- Aqueous based electrolyte ECs and their performances.

Aqueous electrolyte	Electrode materials	Cell voltage (V)	Specific capacitance (F/g)	Energy density (W h/kg)	Power density (kW/kg)	Ref.
Na ₂ SO ₄ /1M	graphene composite	-1.0 - 0.0	243	73.5	19.8	[156]
Li ₂ SO ₄ / 2M	porous carbon nanosheets (RuO ₂) anchored graphene	0.0 - 1.5	502	32	128	[85]
KOH/6M	Nitrogen-doped carbon nanocages	1.0 - 1.0	313	10.90	22.22	[157]
KOH/6M	1D nanorod-like porous carbon	0.0 - 1.8	306	10	7.53	[158]
KOH/1M	RGO films	0.0 - 1.0	120	25	500	[155]
KOH/1M	Cu/NiO	0.0 - 0.6	296	9.65	1.25	[159]
KOH/6M	Activated carbon fibre	0.0 - 1.0	344	8.1	2.98	[132]
KOH/6M	Graphene	-1.0 - 0.0	341	16.2	---	[97]
KOH/6M	Ag-GF-OMC composite	0.0 - 1.0	213	4.5	5.040	[160]
H ₂ SO ₄ /1M	Ag-GF-OMC composite	0.0 - 1.0	134	4.5	5.040	[160]
H ₂ SO ₄ /.5M	highly graphitized NPCs	0.1 - 0.8	238	19.6	22.90	[161]
H ₂ SO ₄ /1M	Activated nano-carbon	0.0 – 1.0	385	50.5	17.4	[162]
HClO ₄ /1M	PICA nanowires	0.2 - 1.02	350	9.4	1	[163]

Organics-based electrolytes

Organic electrolytes consist of aprotic organic solvents either pure or blended together. Their potential window extends beyond 2.5V much higher than the potential window of aqueous electrolytes [164]. This results in a significant increase in the energy densities when used as the electrolyte in electrochemical capacitors when the energy density is proportional to the squared operating voltage in accordance to equation (2). Acetonitrile (AN) [165] and linear carbonates including ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), diethyl carbonate (DEC), ethylmethylcarbonate (EMC), methyl butyrate (MB) and ethyl butyrate (EB) [166-168] are the most frequently used organic solvents as the electrolyte for electrochemical capacitors. Since the melting points of the organic electrolytes are often

much lower than the melting point of aqueous electrolytes, their use in the device allows its operation at low temperatures below the freezing point of water. For some electrolytes such as ethylene carbonate (EC) where the melting point varies slightly above ambient temperature (35 and 38 °C) DMC, DEC, EMC, MB or EB are added to lower the viscosity and the melting point and improve the temperature stability of the electrolyte. The main disadvantages of organic based electrolytes are their volatility and flammability as safety is more an issue than performance these days. The viscosity of these electrolytes is generally higher than the viscosity of aqueous electrolytes and their ionic conductivity is much lower than that of aqueous and ionic liquid based electrolytes. However low toxicity, high flash point (132 °C) and wide range of liquid state temperature (-48.8 to 242 °C) have made PC based electrolytes as one of the most favourable electrolytes for a range of energy storage technologies particularly in electrochemical capacitors. The operating voltage of the mixed organic electrolytes is significantly higher than the breakdown potential of each individual electrolyte in the mixture. Izadi et al., have reported an extended voltage range of up to 4V using CNT's as electrode materials with 1M Et₄ NBF₄/propylene carbonate as electrolyte in an electrochemical cell [169].

Despite their several advantages, a study by Kang et al., has shown that organic electrolytes are more dependent on temperature variations [170]. It has been also shown that the decomposition of organic electrolytes on the surface of active carbons increases ESR and the aging of EC's due to the blockage of pores with decomposition products[171].

Table 4 summarizes the operating condition and performance characteristics of different organic electrolytes in conjunction with different electrode materials used in electrochemical capacitors. It can be seen that the operating voltage of the cell increases to above 2V and a high energy density of up to 54.7 Wh/kg is achievable when a mixture of TEABF₄/PC as the electrolyte is used with mesoporous carbon nanofiber as the electroactive material in a cell. However due to increase in ESR of the cell and higher viscosity of the electrolyte the power density of the cell is deteriorated [172].

Table 4 -- Organic electrolyte based EC's and their performance.

Organic electrolyte	Electrode materials	Cell voltage (V)	Specific capacitance (F/g)	Energy density (W h/kg)	Power density (kW/kg)	Ref.
NEt ₄ BF ₄ /AN/1.5M	Graphene	2.4	166	52.5	---	[97]
TEABF ₄ /AN/1M	Highly porous graphene	2.5	140	11.7	18.8	[173]
TEABF ₄ /AN /1M	TEA doped graphene-nanocomposite	2.5	211	25.7	---	[174]
TEABF ₄ /AN/1M	Tobacco stem derived AC	2.3	141	---	---	[175]
Et ₄ NBF ₄ /AN/1M	Mesoporous carbon capsules	2.5	162	---	---	[176]
Et ₄ NBF ₄ /PC/1M	Graphene/AC composite	2.5	103	22.3	33.2	[136]
TEABF ₄ /PC/1M	N-doped RGO	2.0	187.8	25	10	[177]
TEABF ₄ /PC	Mesoporous CNFs	1.5	201	54.7	2.8	[172]
TEABF ₄ /PC/1M	NiO hybrid nanoarchitecture	2.0	170	19.4	1.00	[178]
Et ₄ N ⁺ ·BF ₄ /PC/1M	Graphene-wrapped polyaniline NF	2.0	250	19.5	0.74	[179]

Ionic liquids electrolytes

Compared to the other electrochemical energy storage devices like batteries or fuel cells, EC's can deliver much higher power densities, however the energy density of the device has been always a limiting parameter for its use in a wider range of energy requirements. Nowadays emphasis has drawn to develop EC's with higher energy densities by either introducing new electrode materials or by using electrolytes with wider operating potentials. In this case ionic liquid (IL) based electrolytes are used due to their higher electrochemical stability window (ESW) to produce high energy density EC's operating at higher voltages. These electrolytes are mainly composed of asymmetric organic cations and anions, being molten salts and not containing any volatile compound. They normally operate at voltages significantly higher than 3V as the top end voltage of organic based electrolytes and a cell using an IL based electrolyte with operating voltage of 5.5V has been reported [180].

Two most frequently used aprotic ionic liquids are based on either pyrrolidinium or imidazolium cations. Both of these ILs have very distinctive properties. Pyrrolidinium based ILs with larger ESW can operate at higher voltages and ECs using these ILs have considerably higher energy density than the one using imidazolium based ILs. In contrast imidazolium based ILs have lower viscosities and higher ionic conductivities and are useful for higher power applications [181]. Since ILs are thermally stable on a wider temperature range as compared with aqueous and organics electrolytes, the temperature operating range of ECs can be increased and a device with safe operation at higher temperatures can be obtained when using IL as the electrolyte [37, 182, 183].

Some of the disadvantages of IL based electrolytes include their low ionic conductivity and high viscosity at temperatures lower than ambient temperature which affect the power capability of IL based electrolyte ECs when operating at lower temperatures [184]. It has been shown that the operating temperature range of ECs can be extended in both lower and higher temperatures without decrease in conductivity and increase in viscosity of the electrolyte when an eutectic mixture of ILs is used [185, 186]. In a recent study by Tsai et al., a high capacitance of 180 F/g in a temperature range of -50 to 80 °C with increased cell voltage of 3.5 V is achieved when an eutectic mixture of ionic liquids with molar ratio of 1:1 of N-methyl-N-propylpiperidinium bis (fluorosulfonyl) imide (PIP₁₃-FSI) and N-butyl-N-methylpyrrolidinium bis (fluorosulfonyl) imide (PYR₁₄-FSI) was used as electrolyte with KOH-activated microwave exfoliated graphite oxide as the active material [187].

Due to their hygroscopic nature, ionic liquids based electrolytes require hygroscopic environments and have to be handled in vacuum or under inert conditions [37]. Reducing the production cost and controlling the water content of the electrolyte are the major research challenges for the broader adoption of IL's for EC applications.

Table 5 shows the operating condition and performance characteristics of different IL based electrolytes when used with different electrode materials in electrochemical capacitors. Due to their high breakdown voltage, the operating voltage of the cell using these electrolytes increases and therefore remarkable high energy densities are achievable.

Huang et al., has shown that energy and power densities of 103 W h/kg and 43 kW/kg are achievable, respectively when a cell using a mixture of (N-butyl-N-methylpyrrolidinium/dicyanamide) BMP-DCA IL as electrolyte with Graphene nano-sheets as the electroactive material works with an operating potential of 3.3 V [188].

Table 5 -- Ionic liquids electrolyte based EC's and their performance.

Ionic liquids electrolyte	Electrode materials	Cell voltage (V)	Specific capacitance (F/g)	Energy density (W h/kg)	Power density (kW/kg)	Ref.
EMIMBF ₄	Activated nano-carbons	3.5	140	56.6	17.4	[162]
EMImTFSI/AN	Nitrogen doped activated carbon	3	160	20	42	[189]
BMP-DCA	Graphene nano-sheets	3.3	235	103	43.3	[188]
EMImTFSI/AN	Carbonized citrate salts	3	130	33	14	[190]
EMIMBF ₄	Ordered mesoporous CDC	3.4	203	---	---	[191]
(PIP ₁₃ -FSI) _{0.5} (PYR ₁₄ -FSI) _{0.5}	a-MEGO*	3.5	180	---	---	[187]
EMIMBF ₄	Activated carbon xerogel	3	210	---	---	[37]
[BMIM][TFSI]	Nitrogen doped graphene	3.5	170.1	72.37	---	[192]
[Pyrr][NO ₃] + [Pyrr][TFSI]	Activated carbon	2.5	209	---	---	[186]
EMImTFSI/AN TEABF ₄ /AN	Activated carbon	2.3	162.2	51	0.375	[193]
EMIMBF ₄	Nano tube & graphene aerogels composites	3.5	183	65.6	9.1	[194]

* MEGO: Microwave exfoliated graphene oxide

Non aqueous (gel-polymer) electrolytes

Gel-polymer electrolytes are pioneered solid – or gelified – electrolytes to overcome safety issues of organic electrolytes such as their low flash point and environmental hazards and also the corrosion effect of aqueous electrolytes on metallic electrodes and current collectors. Gel-polymer electrolytes are considered as a combination of a gelator which is a polymeric (or non-polymeric) organic (or inorganic) matrix and an imbedded aqueous or non-aqueous electrolyte providing mobile ions. Non-aqueous gel electrolytes can also be produced by dissolving or immersing silica polymer or block of co-polymer gels in ionic liquids whereas aqueous electrolytes are mainly developed by dissolving poly vinyl alcohol (PVA) matrix in H₂SO₄, KOH or LiCl solutions[195, 196]. The performance characteristics of electrochemical

capacitors using gel-polymer electrolytes in conjunction with different electrode materials reported in the literatures are shown in Table 6.

Despite their high potential window and also improved safety, the main disadvantages of gel-polymer electrolytes are their low ionic conductivity and poor interfacial properties when used as the electrolyte between electrodes in a cell [197].

Table 6: Gel-polymer based EC's and their performance

Gel polymer Electrolyte	Electrode material	Maximum cell voltage (V)	Specific capacitance (F/g)	Energy density (W/kg)	Power density (kW/kg)	Ref.
IL+ PI	MWCNT	4.4	76	17.2	18.9	[198]
IL+PI	AC	3.5	100	42	-----	[199]
IL+PI	AC	----	271	54.3	23.88	[200]
Aq+PI	RGO	3.5	500	44	-----	[201]
IL/SN	AC	2.5	176	36	24.5	[202]
PVA/H ₂ SO ₄	AC	1	543	17.9	[203]

Binders

Binder is the key inactive component of the electrode which holds all the electrode components together and can affect the performance and safety of supercapacitor cell. Choice of the binder will depend upon the electrode active material. Most commonly used binders are fluorinated thermoplastics binders such as polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF). Ideal binder would not have any effects on the porosity, wettability, and conductivity of the electrode however in practice cell performance can be affected by the type and quantity of the binder used. Binder contributes towards equivalent series resistance (ESR) of the cell affecting the power output of the cell. Binders such as PTFE when added to the active material result in reduction in capacitance because of increased ESR and hydrophobicity [204, 205]. In order to reduce the equivalent series resistance in EC's, novel binding materials such as water soluble polymer binders[206] and also exceptionally innovative fabrication techniques for the fabrication of binder free electrodes (monolithic electrodes)[207] have been developed. The wettability of the electrode

material with electrolyte depends mainly on the hydrophilic/hydrophobic nature of the material. A recent study by Paul et al., shows that the addition of small amount of polyvinylpyrrolidone (PVP) into PTFE binder and mixing of two binding materials results in reduction of hydrophobicity of the electrode and increase its wettability toward aqueous electrolytes significantly. It is shown that the contact angle measurements of the electrodes prepared with PTFE binder only without PVP in aqueous electrolyte has an angle of 151° , with superhydrophobicity nature. The addition of 3% PVP drastically decreased the contact angle to 22° indicating the high wettability of the electrode material with the electrolyte [208].

Due to environmental and cost concerns of fluorinated polymeric binders, recent research is mainly focused on more environmentally friendly and cost effective binders, such as sodium carboxymethyl cellulose (CMC). PVDF based binders such as Kynar Flex are commercially in use for electrode preparation for a range of energy storage technologies. They require organic solvents for the electrode fabrication. Binders such (CMC) which are miscible with water at all temperatures has high chemical and thermal stabilities with less environmental concerns. A cost comparison between these types of binders also shows that CMC costs 2 €/kg as compared to 15 €/kg for PTFE or PVDF [209]. Moreover solubility of CMC in water allows the use of aqueous slurries for the electrode preparation, improving the overall safety of the EDLCs manufacturing process. It has been shown that the performance of CMC-based electrodes is comparable with that of electrodes based PVDF binders in several types of electrolytes, both in term of capacitance and cycling stability[210-212].

CMC based binders also can be used with any type of electrolyte excluding aqueous electrolytes due to the solubility of CMC in water. This matter can be addressed by using natural cellulose, the most abundant natural polymer, as the binding material [213]. Considering its abundance and lower costs the introduction of natural cellulose as binder in EDLCs would represent an important contribution for the realization of cheap and environmentally friendly devices. However due to the very low solubility of natural cellulose in both organic and water based solvents alternative processing methods are needed to introduce it in the electrode manufacturing process to replace fluorinated based binders. Natural cellulose is soluble in certain ionic liquids, e.g. 1-ethyl-3-methylimidazolium acetate (EMIM Ac)[214, 215]. Jeong et al., have shown that the use of natural cellulose with ionic liquids as the solvent for electrode preparation can be successfully exploited for the realization of composite electrodes for EDLCs[209]. Recent research has also been dedicated on self-supported binder free electrode materials to eliminate the impact of binding materials

on equivalent series resistance (ESR), specific surface area (SSA) and interfacial properties [11, 216, 217].

Conclusions

Electrochemical capacitors are evolving technology employed in diverse applications requiring reliability (UPS); high power density (hybrid electric transit buses); fast energy capture (regenerative braking system); and long cycle life (stop start system, load levelling and peak shaving/power smoothing). They can be used as a stand-alone or a complementary device along with other electrochemical devices such as batteries for the storage of electric energy. Their success in energy and power handling for a range of commercial applications depends on the development and deployment of new electrode and electrolyte materials and tuning them to enhance specific capacitance.

Carbon is the most commonly electrode material used in commercial ECs. It exists in wide variety of forms such as polymeric and activated carbons to more exotic nano-shaped carbons such as nano-horns, nano-fibres and nano-foams. Due to their high production costs and complex production methods, exotic carbons are mainly important from research point of view.

Owing to their controllable porous structure during their production, polymer-derived activated carbons are of interest and can improve the performance of ECs in a wide range of applications but at higher costs. Since not all the specific surface area is accessible by the electrolyte solution and accessibility of the effective surface area depends on pore size distribution and surface characteristics of the carbon material used, surface modifications and pore size tuning can improve the wettability and capacitive performance of the device.

As one of the key component of ECs, the type of electrolyte used governs the device performance. Electrolytes with higher electrochemical stability window (ESW) increase operating voltage of the device and improve the energy density significantly. Aqueous-based, organic-based and room temperature ionic liquid-based (RTIL) electrolytes can be used in order of increasing their decomposition potential. Since the employment of aqueous electrolytes in ECs offers high power densities at the expense of very low energy handling and limited operating potentials, implementation of organic and RTIL electrolytes make the improvement of the energy densities of the device possible. However enhancing the energy densities without compromising the power densities and cycle life is still the major challenge in ECs development. Increase in ESW usually affects the ionic conductivities and transport of the electrolyte. RTILs with high ESWs offer higher energy densities, but at higher cost and low power capability due to high viscosities. The use of organic liquids shows a good balance

between both energy and power densities in most commercially available devices although enhanced costs related to the manufacture of the device in inert atmospheres is unavoidable. Development of gel-polymer electrolytes is also important where safety is of utmost concern such as transport applications. No single electrolyte meets all the requirements and therefore the choice of electrolyte in a specific EC design depends mainly on the porous characteristics of its electrode and the energy/power output requirements.

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