

Role of Polymers in Enhancing the Performance of Electrochemical Supercapacitors: A Review

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In this modern era, there is an increasing significance in the usage of supercapacitor devices in power applications due to their outstanding power density, ultrafast charging/discharging capability, and prolonged cycling ability. Extensive efforts are being made to improve their capacitive performance by engineering high-performing polymeric materials as electrode and electrolyte materials. Predominantly, the employment of conducting polymer (CP)-based composite materials as electrode materials has led to practical and theoretical benefits such as the outstanding surface area that facilitates quick access of dispersed electrolyte ions. The insertion of carbon materials such as graphene, carbon nanotubes, and porous carbon within the CPs matrix has an imperative role in refining the overall system's specific capacitance. The electrodes' specific capaci-

tance proficiency and cycling constancy are improved synergistically by integrating both materials for efficient energy-storage applications. This Minireview encompasses the storage mechanism in different gel polymer-based electrolytes and their role in enhancing the pseudocapacitance of redox-active materials for supercapacitor applications. Further, the Minireview focuses on the influence of conducting polymers in promoting the device performance with a view on the synthesis methodology and pseudocapacitive nature. The different types of supercapacitors designed with polymer gel electrolyte, solid polymer electrolyte, and biodegradable polymer-based electrolytes for improved supercapacitive performance are critically reviewed.

1. Introduction

The demand for alternative energy storage and conversion technology with high power and energy densities has been increasing exponentially over the last three decades toward meeting the raising demands of electronic and transport sectors.^[1–5] The most efficient and practically applicable electrochemical energy conversion and storage systems include batteries, fuel cells, and electrochemical supercapacitors.^[2,6] Among the three systems, the fuel cell is considered an energy conversion device while batteries and supercapacitors are conversion and storage systems. Fundamentally, electric energy may be stored in two distinct ways: Indirectly via the faradaic redox process involving chemical reactions and directly through the non-faradaic storage process.^[7] The possibility of later process *viz.*, storing charges on surfaces, was discovered in ancient times by rubbing amber. Later in the eighteenth century, this effect was explained by the theory of "static electricity". With subsequent experiments carried out by Michal Faraday and Millikan, the science of charge separation and storage became popular. The discovery of the Leyden jar, also

known as "condenser", was a significant milestone. The other modified form of this device were referred to as "capacitor" and the property that determines its capacity to store charge is called "Capacitance (given in Farads)".^[8] Eventually, capacitors were developed by replacing the glass jar with a flat glass plate and observed the same charge storage. This led to the development of "flat plate capacitors". In a few years, Faraday proposed the idea of dielectrics. The concept of storing energy was claimed and patented by Becker in 1957.^[9] The author invented a capacitor made from porous high surface area carbon electrode. In recent years, "supercapacitors" or "ultracapacitors" that have the potential to provide very large Farads of capacitance are in the limelight. They were originally built from carbons of high surface area and have gained increasing attention. This is essentially because of their merits such as long cyclability and appreciable power density.^[10] Supercapacitors are estimated to offer higher power density compared to traditional dielectric capacitors with a specific energy that is similar with batteries, and thus perform the role of bridging the gap in terms of both specific energy and power densities between capacitors and fuel cells/batteries as illustrated in the Ragone plot.^[11,12] Numerous attempts have been made by researchers across the world to develop efficient supercapacitors.^[13–22] In particular, as seen in Figure 1, supercapacitors have seen incredible growth in the past few years due to the energy crisis and also because of the rapid strides seen in the synthesis of advanced materials with various functionalities.

Capacitors are categorized as electrochemical double-layer capacitors (EDLC) and pseudocapacitors, based on the mecha-

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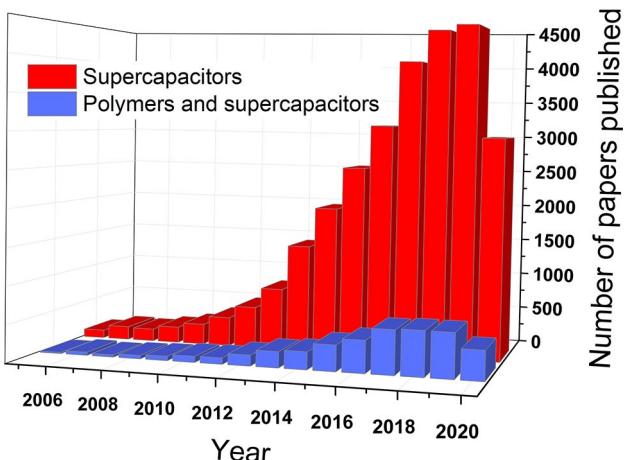


Figure 1. Histogram of Web of Science publication report for search results with topic "supercapacitor" and topic refined by "polymer".

nism of charge storage, as shown in Figure 2. The accumulation of charge in the electric double layer formed at the electrode/electrolyte interface drives EDLCs. Materials that possess low resistivity and high surface area, such as carbon, are typical electrode materials for these systems. Contrarily, reversible, and fast redox reactions or Faradic reactions drive the pseudocapacitors. Oxides of transition metals and conducting polymers are

best suited as electrodes for these capacitors. Interestingly, these two mechanisms can operate at the same time dependent on the nature of the electrode materials. However, the capacitance in pseudocapacitors is much higher than the EDLC's with carbon electrodes.

1.1. Electrochemical Double-Layer Capacitor (EDLC) Models

In the 19th century, Von Helmholtz proposed and detailed the model when he studied the charge distribution at colloidal particle's interface.^[23] Two layers of oppositely charged species generated at the electrolyte/electrode interface atomically separated are represented in the Helmholtz double-layer model. It is very much like that of typical capacitors with two plates, which were discussed earlier. However, this model had a few drawbacks. The Helmholtz model was then altered by Gouy and Chapman, taking into consideration the diffuse layer, which has a continuous distribution of ions driven by thermal motion in the electrolyte.^[24,25] Accordingly, an enormous capacitance value would arise in point charge ions close to the electrode surface since the capacitance of two separated arrays of charges increases inversely with their separation distance. This concept leads to an overestimation of the EDL capacitance. Stern integrated the Helmholtz model with the Gouy-Chapman model in 1924 to differentiate and classify two regions of ion



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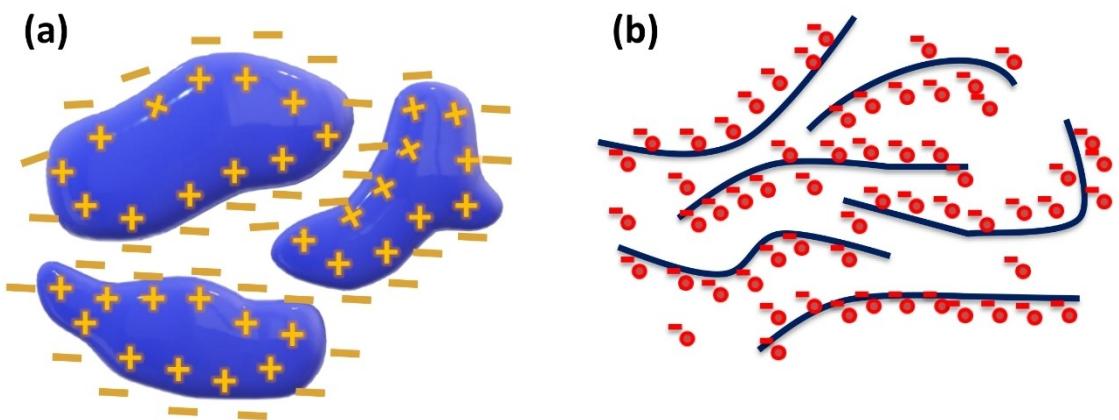


Figure 2. Illustration of the charging mechanism of a) double-layer capacitor (carbon) and b) pseudocapacitor (conducting polymer).

distribution. Therefore, the combination of the Stern type of compact double layer capacitance (C_H) and the diffusion region capacitance (C_{diff}) contributes to the overall capacitance.

Practically capacitors do not exhibit ideal pure capacitive behavior wherein there is a phase shift of 90° between the real and imaginary parts of the impedance. A resistive component in series is also present, called the equivalent series resistance (ESR). A high ESR drastically contributes to power loss and energy dissipation, and therefore its minimization is important while fabricating a supercapacitor. In general, the parameters, namely, energy density (E , Wh kg^{-1}), equivalent series resistance (ESR, Ω), and power density (P , kW kg^{-1}) of the supercapacitor, shed light on the efficiency of any supercapacitor. It can be obtained from the equations given below [Eqs. (1)–(3)].^[26]

$$E = \frac{C \times \Delta V^2}{2} \times \frac{1000}{3600} \quad (1)$$

$$\text{ESR} = \frac{iR_{\text{drop}}}{2 \times I} \quad (2)$$

$$P = \frac{I \times \Delta V}{2 \times m_{\text{ac}}} \times 1000 \quad (3)$$

where 'I' represents the discharge current in amperes, ΔV in volts is the change in potential after a complete charge or discharge, m_{ac} is the weight of the electrode material (including the binder and the graphite) in grams, and iR_{drop} (V) is defined as the electrical potential difference between the two ends of a conducting phase during charging-discharging. Researchers are extensively showing interest towards electronically conducting polymers (ECPs) for application in supercapacitor devices comprised of ionically conducting membranes and electrolytes. Investigations based on a combination of all-solid-state redox-active electrodes materials for flexible supercapacitors is also gaining attention.^[27] Initial studies reveal that the response of polymer-based redox capacitors is significantly influenced by the internal resistance linked to the electrode process's kinetics and ion conduction in the polymer electrolyte membrane.^[21,28]

1.2. Conducting Polymers, Pseudocapacitive Electrode Model

In early 1984, the potential contribution of capacitive current in conducting polymers was pointed out by Feldberg in the early 1980s.^[29] Without much delay, voltammetric and impedance spectroscopic studies were employed to shed light on this capacitive nature.^[30–32] Newly discovered electronically conducting polymers (ECPs) enclose significant attention and extensive concern from educational and engineering researchers to investigate their prospective in energy storage applications. ECPs are basically organic compounds or polymers that exhibit both metallic and semi-metallic characteristics, also known as synthetic metals, discovered in 2000. In general, ECPs are widely explored as electrode materials for supercapacitor devices due to their low cost and high charge density compared with metal oxides.^[33,34] Owing to their pseudocapacitive nature, a fast redox reaction happens in bulk, contributing to the capacitive behavior. Also, ECPs deliver high specific energies compared to the double layer carbon-based supercapacitors. Conductive polymers with various nanostructures of different dimensions, including nanoparticles, nanofibers, and nanosheets of 0, 1 and 2 dimensions respectively, developed by researchers worldwide have been applied in electronics, sensors, and energy storage and conversion devices, and many other technologies.^[35–39] A few other potential applications of conducting polymer gels include temperature/humidity conditioner, solar power harnessing, and artificial skin. However, a major bottleneck is that these nanostructured conductive polymers' electrical properties could be lowered by inhomogeneous aggregation caused by structural defects, restacking upon prolonged cycling, and poor contacts while assembly. In terms of productivity, nanostructured conductive polymers with tunable microstructures and controllable chemical / physical properties remain a significant challenge.^[40] As shown in Figure 3, probing the possibility of utilizing conducting polymers in supercapacitors as pseudocapacitive materials by taking advantage of fast and reversible exchange reactions at or near the electrode surface is in progress.^[28] The conjugated polymers exhibit high pseudocapacitance and mechanical flexibility but, on the downside, suffer

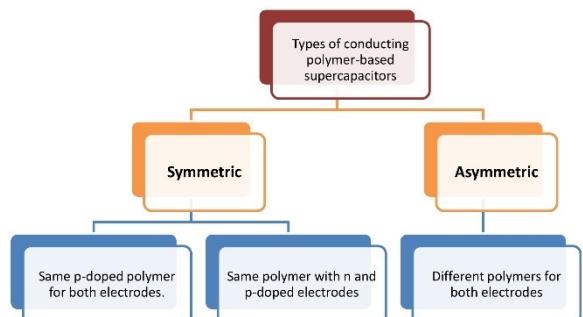
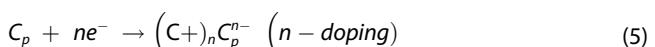


Figure 3. Classification of supercapacitors based on the type of conducting polymer.

from poor cycle ability and rapid capacitance decay. This phenomenon could be attributed to the high-volume change and the electrochemical reaction driven change in doping states. The conductivity of conducting polymers is achieved by forming a conjugated bond along the backbone of polymer with π electron system in their structure. Such intrinsically conducting polymers have a low energy optical transition, low ionization potential, and a high electron affinity.^[41] They are formed through electrochemical or chemical oxidation of the monomer. With the coincident insertion of a dopant/counter ion like Cl^- , these two oxidation reactions occur simultaneously.^[26] The controlled doping level below one dopant per polymer unit: approximately 0.3–0.5, *i.e.*, 2–3 monomer units per dopant limits the degree of closeness of the positive charges (so-called polarons) along the polymer chain. In general, conducting polymers with appreciable intrinsic conductivity ranging from a few Scm^{-1} to 500 Scm^{-1} in the doped state and low bandgap are of interest.^[26] It is possible to p-dope polymers with anions when oxidized and n-dope with cations when reduced. These two charging processes are expressed by simplified equations as follows [Eqs. (4) and (5)]:



The polymers most widely explored for supercapacitor systems are polypyrrole, polyaniline, and polythiophene derivatives.^[21,26,42–47] Their structures are shown in Figure 4. In numerous non-aqueous electrolytes, these polymers have been reported to have high gravimetric and volumetric pseudocapacitance at operating voltages of about 3 V.^[48,49] A specific capacitance of 775 Fg^{-1} for PANI,^[50] 480 Fg^{-1} for PPy,^[51] and 210 Fg^{-1} for PEDOT^[52] have been reported. Their merits, demerits, and performance in supercapacitors are discussed by thorough literature study. Further, new trends in material processing are critically reviewed.

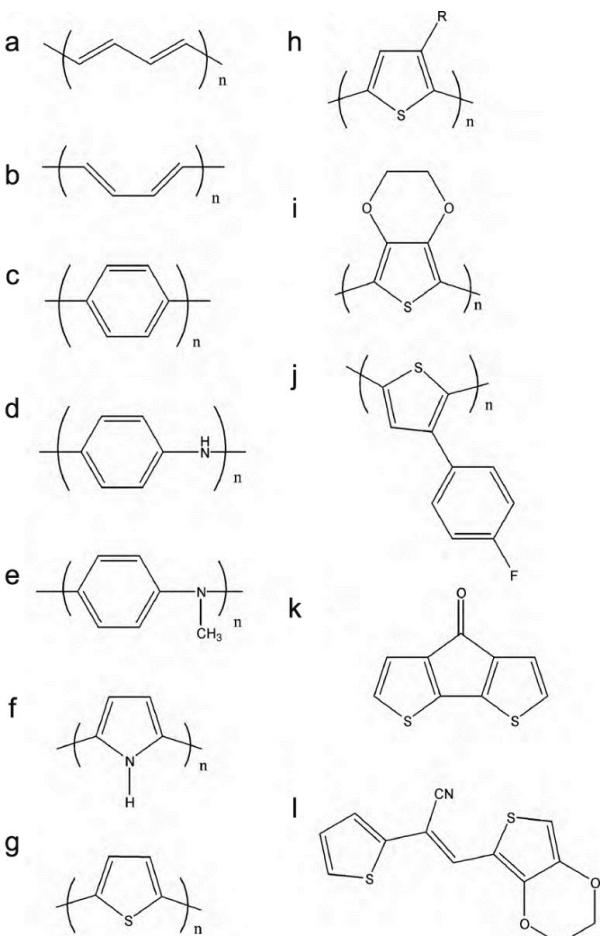


Figure 4. Various conducting polymer structures. a) Trans-poly(acetylene), b) cis-poly(acetylene), c) poly(p-phenylene), d) polyaniline (PANI), e) poly(n-methyl aniline) (PNMA), f) polypyrrole (PPy), g) polythiophene (PTh), h) 3-substituted polythiophene, i) poly(3,4-ethylenedioxythiophene) (PEDOT), j) poly(3-(4-fluorophenyl)thiophene) (PFPT), k) poly(cyclopenta[2,1-b;3,4-b-dithiophen-4-one]) (PcDT), l) 1-cyano-2-(2-[3,4-ethylenedioxythienyl])-1-(2-thienyl)vinylene (PThCNVEDT). Reproduced with permission from Ref. [53]. Copyright 2011, Elsevier.

1.2.1. Polyaniline

Polyaniline (PANI) is found to stand out in terms of its applicability due to the simplicity of synthesis, low-cost monomer, tunable properties, and greater stability than other conducting polymers. Chemical, electrochemical, template, enzymatic, plasma, photo, and several other special methods have been used to synthesize polyaniline. It is worth noting that heterophase, solution, interfacial, seeding, metathesis, self-assembling, and sonochemical polymerizations are again branched into chemical polymerization.^[54–57] It finds applications as a membrane for gas separation, pH switching actuator, and neutral solute separation.^[58–61] Interestingly, it is also used to shield electromagnetic interference because of its change in dielectric constant irradiation with electromagnetic radiation.^[62]

As far as its role in electrochemistry is concerned, the redox peaks embedded in a high background current of cyclic voltammogram reflect the pseudocapacitive nature of PANI. Typically, the CV curve consists of three redox pair reactions

over a large spectrum of potential, including the redox transition between the isolating leucoemeraldine and the conducting emeraldine, pbenzoquinone, hydroquinone, emeraldine, and pernigraniline protonate. Most reports on PANI-based supercapacitors suggest that the PANI-based electrodes can function efficiently at a potential window of 0.8–0 V.^[63–66] A charge density of 140 mAh g⁻¹ is achieved, which is smaller than that of costly metal oxides like LiCoO₂, but much higher than 15 mAh g⁻¹ carbon-based electrodes. (perhaps ~40 mAh g⁻¹ for the distinct electrode). 3–4 kW kg⁻¹ specific power and 3–5 Wh kg⁻¹ specific energy can be achieved by carbon-carbon symmetric supercapacitor devices when fully packaged. In contrast, at 2 kW kg⁻¹, a PANI-based conducting polymer supercapacitor can attain a marginally lower power but twice the specific energy. (10 Wh kg⁻¹).^[67–69] Numerous research works have been carried out to employ polyaniline as electrode material.^[70–74] Self-doped PANI nanofibers prepared by reverse pulse voltammetry method and PANI/Nafion/hydrous RuO₂ composite prepared by chemical process respectively delivered a specific capacitance value of about 480 and 475 Fg⁻¹.^{[75][76]} The mixture of PANI, carbon nanomaterials, and metal oxides is very desirable, since each of these components synergistically contributes to the overall efficiency of the supercapacitor. The carbon nanomaterials are provided with a spacious scaffold for the polymer to expand, but their capacitive contribution is not as much as pseudocapacitive materials such as low surface metal oxides. The electrochemical efficiency of PANI/metal oxide is therefore dependent significantly on the slow diffusion of the solid-state. The effects of these compositing elements are also acceptable to achieve collectively.^[30–32,77–80] Among the conducting polymers, PANI exhibits the lowest self-discharge, which is one of the critical aspects of PANI supercapacitors.^[81]

1.2.2. Polypyrrole

Polypyrrole (PPy) is a conducting polymer formed from many associated structures of the pyrrole ring. It is synthesized through various methods viz, chemical synthesis, electro-polymerization (EP) of pyrrole through potentiostatic,^[82] galvanostatic,^[83] potentiodynamic,^[84] and pulsed one.^[85] It includes numerous applications such as protective electromagnetic shields, electrical contacts in the structure of an electroluminescent diode, antistatic coatings on synthetic polymer fibers vehicle for drug delivery, etc.^[86] PPy exhibits a high capacitance per unit volume (400–500 F cm⁻³) due to its greater density.^[87,88] However, the dense growth also results in limited access for dopant ions to the interior of the polymer. The thick electrode coating onto the current collector contributes to a reduction in capacitance per gram.^[89] It is worth noting that among the other conducting polymers, PPy provides a greater degree of versatility in electrochemical processing.^[90] The material has, therefore, been the subject of research as a supercapacitor or battery electrode.^[89,91,100–105,92–99] Furthermore, Bhardwaj *et al.* reported the highest capacitance of 1086 Fg⁻¹ by preparing anionic surfactant sodium dodecylbenzene sulphonate decorated polypyrrole grafted with hybrid carbon array composite via emulsion polymerization.^[106]

The increased capacitance is due to the mechanism as shown in Figure 5, a) hybrid carbon array is the combination of nanotubes of carbon and graphene lead to the formation of the 3D network, which provides a high surface area to the settlement of polymeric layer, b) this 3D network offers a conductive platform and provides a contact among conducting polymer layer to current collector graphite sheet, c) carbon nanotubes act as obstructers to the restacking of graphene sheets and this combination provide improved mechanical strength to the overall system and d) engagement of surfactant doped polypyrrole with hybrid carbon array leads to easy immigration of KOH electrolytic ions due to shrinking diffusion

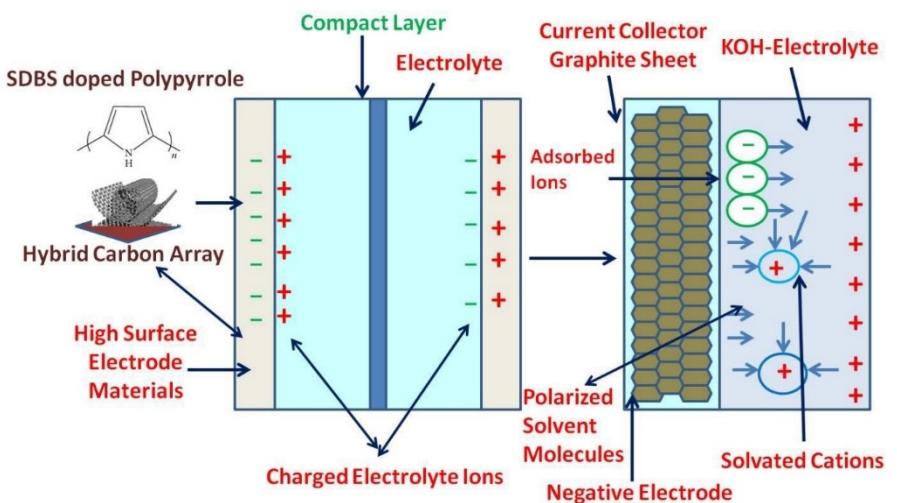


Figure 5. A schematic illustration of storage mechanism in SDBS surfactant decorated Polypyrrole-grafted hybrid carbon array composite. Reproduced with permission from Ref. [106]. Copyright 2020, Elsevier.

path and overall boost the pseudocapacitance values of conducting polymer.

1.2.3. Poly(3,4-ethylenedioxothiophene)

Poly(ethylene dioxythiophene) (PEDOT) has been of great interest among conductive polymers because of its stability, high electrical conductivity, and its wide variety of applications.^[107,108] For supercapacitor systems, several researchers have investigated PEDOT as an electrode. PEDOT is synthesized commonly by three processes, namely oxidative chemical polymerization and electrochemical polymerization of the EDT-based monomers, and transition metal-mediated coupling of di-halo derivatives of EDT. The highly stable films prepared from the aqueous PEDOT/PSS solution have a high degree of mechanical integrity with conductivities ranging between 1 and 10 S cm^{-1} and can be subjected to heat treatment at 100°C for 1000 h with no change in conductivity.^[109–111] One of the most prevalent applications of these PEDOT systems is the applicability of these in polymer and organic LEDs as a buffer between ITO and the materials that are light-emitting or hole transporting.^[112–119]

PEDOT has also been used as a redox couple in photoelectrochemical cells to enhance the charge transfer rates between the electrodes.^[120] This review focuses on the use of PEDOT derivatives and their use as electrodes for capacitors. A process using PEDOT and a simple impregnation step as opposed to pyrolysis or electrochemistry was developed.^[46,121,122] A type I supercapacitor based on PEDOT nanotube electrodes (two symmetric electrodes) was developed by Liu et al. The device exhibited high power, owing to the fast charging and discharging evidenced upon using the nanotubular structures. To elaborate, these hollow nanotubes permitted counter-ions to easily penetrate the polymer and access their internal surfaces. At the same time, a short diffusion distance to facilitate the ion transport was provided by the thin walls. Compared to pure PEDOT or pure PPy electrodes, composite electrodes made of PEDOT/PPy presented higher specific capacitance, which is attributed to PPy and PEDOT's synergistic effect that provides an effective energy extraction.^[103] On the other hand, poly(3,4-propylenedioxothiophene) and PEDOT has also been studied as electrodes in conjugation with various ionic electrolytes.^[123]

With respect to supercapacitor applications, attempts to replace manganese dioxide with organic materials with higher conductivities and good high-frequency properties have been probed. In this regard, an efficient way to improve performance is by fabricating asymmetric supercapacitors with MnO_2 and poly(3,4-ethylene dioxythiophene) (PEDOT) as the positive and negative electrodes, respectively.^[124] Owing to the different operating potentials of both electrodes, the device showed an operating voltage of 1.8 V. The energy density of the asymmetric capacitor was found to be 13.5 Wh kg^{-1} at a current density of 250 mA g^{-1} , which is larger when compared to symmetric capacitor based on PEDOT in an aqueous medium. The cell also offered good electrochemical stability in neutral

aqueous electrolyte. Similarly, on comparing the electrochemical performance of redox type supercapacitor with two PEDOT electrodes and the hybrid type supercapacitor with PEDOT and activated carbon, it was found that specific discharge capacitance is $\sim 56\text{ F g}^{-1}$ by using LiPF_6 in EC/DMC after 1000th cycle in the range 0–3 V.^[124]

1.2.4. Bottlenecks

Conducting polymers witness a few bottlenecks when used in supercapacitors. The first drawback is the low capacitance owing to the restricted access to the inner layer of the electrode compared to the theoretically calculated capacitance. The poor cyclic stability in long term charge-discharge processes is another issue that needs to be carefully worked on. It is understood that three main reasons contribute to this poor cycling stability in conducting polymer electrodes^[125]

- (1) Poor mechanical stability resulting in swelling, shrinkage, cracks, or breaking of the electrode surface. This is caused by undesirable volumetric changes occurring during charge-discharge due to repeated insertion and de-insertion of ions.
- (2) The conducting polymers that peel off or dissolve into the electrolyte from the current collector result in loss of active material and subsequent decrease in capacitance.
- (3) The reduced working potential range is limited by the over oxidative degradation of the polymer.

Nevertheless, composites of conducting polymers and carbon nanotubes were experimentally found to exhibit improved electrical, mechanical, and electrochemical properties in comparison to their unmodified counterpart. The electronically conducting polymer–carbon nanotube composites are very capable as novel supercapacitors with ultra-high capacitance and power density due to the synergistic blend of large pseudocapacitance of the polymers and improved properties of the carbon nanotubes. There are three different approaches to synthesize ECP–CNT composites viz: (i) an inexpensive and simple chemical oxidation method suitable for mass production. (ii) The electrochemical deposition of ECPs on CNT to form an inhomogeneous structure which reduces the synergistic effect of the two components (iii) Electrochemically co-deposited composites with homogeneous network structure to facilitate ion and electron transport.^[126]

1.2.5. Electrodes as Carbon Precursors from Polymers for EDLC

A crucial consideration for achieving high energy density is high-capacitance materials (a high surface area or pseudoactive species). In contrast, the high electrical conductivity of the electrode materials and the electrolyte solution is mandatory for increased charge transport and high-rate capability. Since the energy storage in EDLC is based on the adsorption of electrolyte ions on the large specific surface area, porous electrically conductive electrodes such as porous carbons, conducting polymers, and both noble^[20,127] and transition metal

oxides^[50,109,134–138,110,111,128–133] are used. Conway^[8] has reported that the carbons used as the electrode materials in EDLCs must possess high specific surface areas of more than 1000 m² g⁻¹, good intra- and inter-particle conductivity, and high wettability to allow the electrolyte to access the pores of the electrode. Numerous strategies have been opted for industrial applications.^[139–143] Using synthetic polymer precursors is one efficient way to synthesize porous carbons for use in advanced EDLC systems. The preparation of ACs from synthetic polymers by a one-step chemical activation process with KOH was carried first carried out by Yushin and his group.^[144]

Synthetic carbon materials produced through the carbonization of polymeric gels by heat treatment at high temperatures of up to 800 °C under an inert environment such as argon or nitrogen fall under the category of polymer-based carbon materials. An interesting benefit of these carbons is the improved control of their porous structure during the synthesis of the polymeric gel precursors before the carbonization process. The cross-linked structure of the initial gel can be adjusted during the polycondensation step of the gelation process, which enables the building of three-dimensional structures with a controlled pore size distribution for use as electrode materials. Using conductive three-dimensional conductive materials as prototypes and depositing on these 3D structures, materials which possess pseudocapacitive nature such as conductive polymers and metal oxide is another amazing technique to design better-performing electrodes for supercapacitors. It has also been studied to regulate the porosity of activated carbons and figure out the relationship between their structural properties and their electrochemical activity when used as active material in ECs.^[145,146] For instance, PANI was grown over hollow carbon spheres as supercapacitor electrode materials.^[147] Superior performance was also documented in the design of nanostructured PANI-RuO₂ core-shell arrays as electrodes for highly stable pseudocapacitors.^[148]

A one-step route by designing a novel hybrid conducting polymers cores shell nanoparticles in a triple-phase interface system is constructed by Lei et al. This is achieved by partitioning the reaction system into three phases, PPy and PANI in individual non-interference interfaces in the presence of oxidation agent in the middle aqueous phase. The superior capacitive behavior was attributed to strong interactions in the nano/micro-hierarchical super-structure. This significantly improved the charge-transfer kinetics process between electrode and electrolyte that is comprised of PPy and PANI.^[149] As stated previously, due to their high conductivity and rapid redox activity, conducting polymers have been seen as promising electrode materials.^[150,151] Conversely, the degradation issues of the polymer, such as swelling and shrinkage, can be overcome by employing a carbon-based material to support the conducting polymer.^[152,153] An exciting approach was conceptualized based on the electrostatic interactions between negatively charged graphene oxide sheets and positively charged surfactant micelles by Zhang et al.^[154]

Zhang and his co-workers designed and developed PPy spheres grafted with graphene oxide pillar structures via the simplest emulsion polymerization method using cationic surfactant dodecyl trimethylammonium bromide (DTAB) and 1-decanol as solvent as shown in Figure 6. The enhanced specific capacitance is due to the a) presence of GO sheets that offer an enlarged accessible surface area to the PPy on both sides and adsorption of electrolytic ions, b) combination of graphene oxide and conducting polymer creates a three-dimensional assembly that improves mechanical strength and restrains the polymeric layer degradation during charge-discharge cycles, c) reduction in dynamic resistance of electrolyte ions by the existence of GO nanostructures with PPy and d) PPy contribute an excellent pseudocapacitance element to the overall energy storage by providing access of electrolyte ions voluntarily.

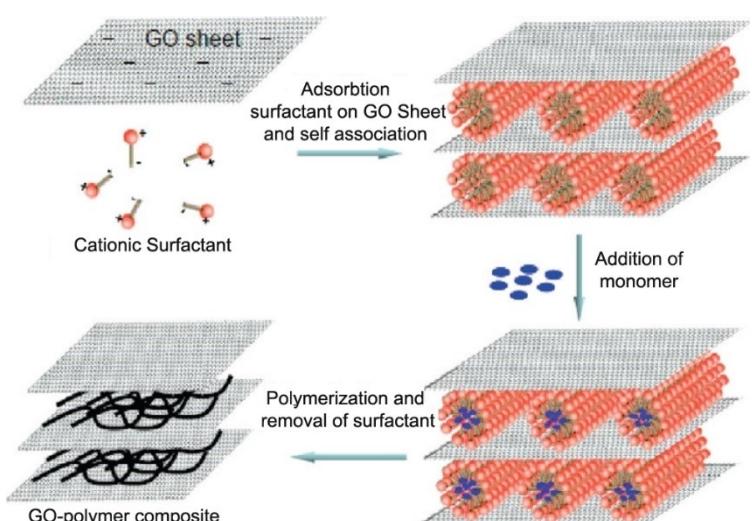


Figure 6. A schematic of formation of polypyrrole spheres grafted with graphene oxide pillar structures via simplest emulsion polymerization method. Reproduced with permission from Ref. [154]. Copyright 2010, American Chemical Society.

2. Electrolytes

2.1. Conduction Mechanism in Polymer Electrolytes

The dynamics of proton migration must be understood to build and configure suitable electrolyte proton conductors for solid supercapacitors. In order to better explain proton transfer in polymer electrolytes, three mechanisms were proposed as illustrated in Figure 7; (a) proton hopping or Grotthuss mechanism; (b) diffusion or vehicle mechanism; and (c) direct transport by segmental polymer chain motions. The mobility of the proton is measured by the creation or cleavage rate of the hydrogen bond in the Grotthuss process between a hydronium ion and a water molecule or other hydrogen-bonded liquids.^[155] Strong hydrogen bonded systems usually exhibit this type of high proton site to the site hoping. One proton combines with solvents species such as water, resulting in a complex and further diffuses in accordance with the diffusion mechanism. This process is sluggish compared to the proton hopping mechanism. Segmental motions of the polymer chains can also contribute to the mobility, in which case the proton transportation is restricted to the amorphous phase of the solvating polymers, where the polymer molecules are free to move.^[156–158]

2.2. Solid Polymer Electrolyte

It is well-known that a majority of the works in the energy-storage device configuration that is two electrodes separated by a separator sealed in liquid or aqueous electrolyte suffer two

major issues that hinder their use in practical wearable applications. The two major concerns with aqueous electrolytes that limit their uses in practical wearable applications that are the high-standard safety encapsulation materials and technology required for liquid or aqueous electrolyte while making supercapacitor device, leakage of electrolytes and that leaked harmful materials will badly impact our environment and also has safety issues. Secondly, segments of the configuration are not incorporated well and, under strong versatility, can shift relative to each other. This would reduce the device's electrochemical efficiency and cycle life.

Replacing the conventional liquid electrolytes with solid polymer electrolytes is, therefore, a very crucial aspect of enhancing the performance of the supercapacitor device. Solid polymer electrolytes (SPEs) will exhibit liquid-like ionic conductivity and preserve the dimensional stability of a solid structure. Solid polymer electrolytes (SPEs) are described as a solvent-free salt solution in a polymer congregation substance that demeanor ions throughout the polymeric chains. Nonetheless, the ionic conductivity of solvent-free polymer electrolytes is generally low for room temperature application.^[160,161] Conductivity is commonly improved upon plasticization by interpenetrating the polymer network (hybrid electrolytes) or using the 'gel electrolytes'. In both cases, the polymer matrix acts as a host for a salt-containing solution which interpenetrates or swells the polymer. Several attempts to replace the liquid electrolyte with a polymer electrolyte in capacitors and batteries have been published.^[20,68,162–164] Using alkaline polymer electrolytes and activated carbon electrodes, an all-solid-state electrical double-layer capacitor was manufactured

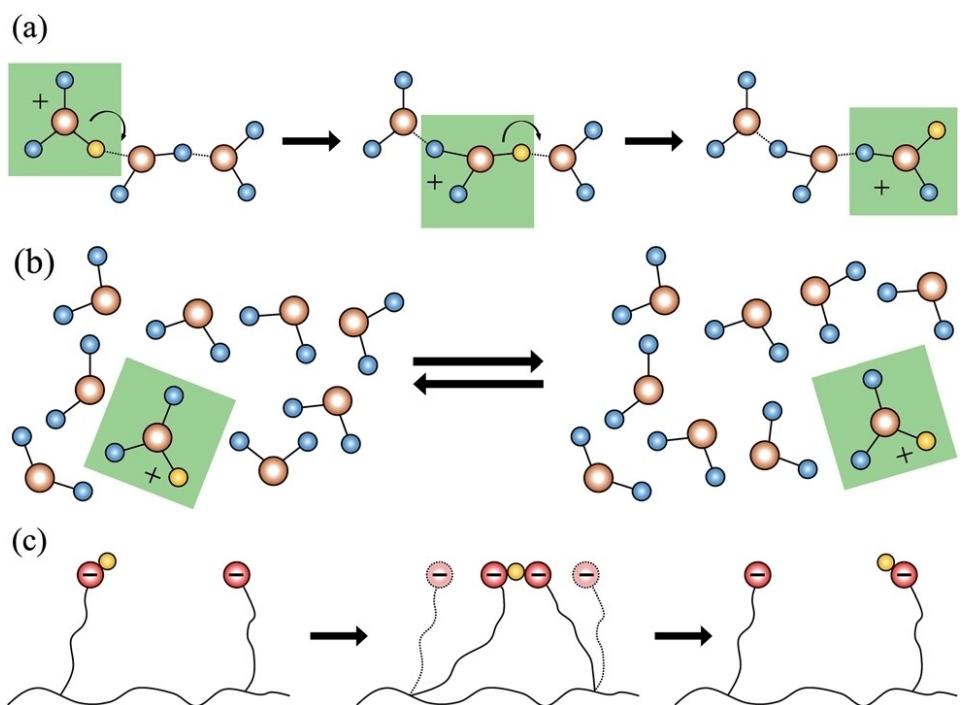


Figure 7. A schematic of low-temperature proton transport mechanisms: a) hopping or Grotthuss mechanism in a system with strong hydrogen bonding; b) diffusion or vehicle mechanism in a system with weak hydrogen bonding; and c) direct transport via polymer chain segmental motions. Reproduced with permission from Ref. [159]. Copyright 2014, Royal Society of Chemistry.

for the first time. As separator and binder, these polymer electrolyte carries out dual roles. The specific carbon capacity per grams was well similar to that of a counterpart dependent on liquid electrolytes.^[165] Also, the specific capacitance of all-solid-state EDLC based on alkaline polyvinyl alcohol (PVA) solid polymer electrolytes (SPEs) is reported in the range of 100–112 Fg⁻¹.^[166]

Moreover, complexes of poly(ethylene oxide)-grafted poly (methyl)-methacrylate (PEO-PMMA) and tetraalkylammonium salts [tetrabutylammonium perchlorate, tetraethylammonium perchlorate, and tetraethylammonium tetrafluoroborate (TEABF₄)] have been investigated as solid polymer electrolyte for EDLC with activated carbon fiber cloth electrodes.^[167] Owing to the concentration and size of each ion, the PEO-PMMA and tetraalkylammonium composites exhibited high ionic conductivity $>10^{-4}$ S cm⁻¹ at 298 K. The composites were also stable over a wide potential range (ca. 5.0 V). The above-said capacitors showed charge/discharge behavior with large values of capacitance and high Coulombic efficiency. Moreover, very wide range voltage retention was observed in the self-discharge test of the capacitor with TEABF₄. It is worth stating at this juncture that apart from the electrolyte, the electrodes also play a vital role in influencing the performance of quasi-solid and gel type supercapacitors. Unconventionally, very recently, carbon nanotubes (CNTs) pastes that are screen-printed on carbon cloth were calcined using a dc-pulse nitrogen atmospheric-pressure plasma jet (APPJ). The procedure resulted in porous structures by efficiently oxidizing and vaporizing the organic binders. After a cycling stability test for 1000 cycles, the fabricated quasi-solid state supercapacitors showed a capacitance retention rate of 94.70% for H₂SO₄/PVA gel electrolyte supercapacitors.^[168]

2.2.1. Gel Polymer Electrolytes

Gel polymer electrolytes (GPEs) comprise a polymer membrane onto which a small amount of standard “salt–solvent” mixture is inserted. The organic solvent should be selected from the catalogue of ordinary sodium or lithium salts and carbonate solvents utilize in aqueous electrolytes. The gel processing of the membrane assists the interfacial adjoining with the electrode as a contrast with SPEs. Stephan has extensively reviewed the state-of-art polymer electrolytes in view of their electrochemical and physical properties for lithium batteries’ applications.^[161] To build supercapacitors of high performance to satisfy the high safety criteria for realistic use at room temperature, gel polymer electrolytes,^[169] such as polyvinyl alcohol (PVA)–KOH,^[170] PVA–H₂SO₄,^[170] polymethyl methacrylate (PMMA)–EC–PC–TEAClO₄,^[171] PVA–phosphomolybdic acid (PMA)^[172] and polyacrylate (PAA)–KCl,^[35] PVA–PEO–KOH are being developed. Such polymer electrolytes can be used to form leakage-free thin, and flexible devices with high reliability.

EIS measurement is an excellent tool to identify the capacitive nature of a material. In particular, gel electrolytes have ideal electrochemical capacitance behavior, i.e., imaginary parts of impedance show a nearly linear at the low-frequency

domain, which is characteristic of Warburg impedance, “W”.^[173] The impedance spectra of a gel polymer electrolyte, which is redox-mediated and prepared by adding PB to PVA–H₂SO₄ gel polymer electrolyte, and activated carbon electrodes rendered near-ideal capacitive behavior.^[174]

The gel membranes were prepared by immobilizing an ethylene carbonate-propylene carbonate (EC-PC) solution of lithium perchlorate (LiClO₄) in a poly (methyl methacrylate), PMMA matrix, reported by Clemente was proposed for use as electrolyte separators in low-resistance, thin-film redox capacitors in terms of electrochemical characteristics. The infiltration of the liquid into the membranes provides appreciable interfacial contact between the electrodes and electrolyte.^[27] A supercapacitor with activated carbon electrode and p-benzenediol-mediated PVA–H₂SO₄ gel polymer electrolyte was developed by Yu et al.,^[174] wherein the author employed the redox reaction of p-benzenediol/p-benzoquinone and its quick electron relay at the electrode/electrolyte interface. The device showed outstanding electrochemical performance. GO, as an ionic conducting promoter for ion gel (PVDF-HFP)-1-ethyl-3-methylimidazolium tetrafluoroborate -EMIMBF₄-GO gels), has been demonstrated for the first time to dramatically improve the ionic conductivity of GO-doped ion gel compared with that of pure ion gel. Interconnected and continuous transport channel was built to allow ion transport and resulted in a substantial increase in ion conductivity and lower internal resistance due to GO’s homogeneous distribution as a 3D network in GO-doped ion gels.^[175] Gel polymer electrolyte made up of IL 1-ethyl-3-methylimidazolium hydrogen-sulfate added with redox-additive hydroquinone and immobilized in PVA/PVP exhibited appreciable flexibility, thermal and electrochemical stability with ideal ionic conductivity of ~ 9.3 mS cm⁻¹ at room temperature. The addition of redox-active HQ in the electrolyte improved the energy density of supercapacitors fabricated with carbon electrodes from 9 to 24.3 Wh kg⁻¹.^[176] In contrast with solid polymer electrolytes, gel polymer electrolytes demonstrate benefits of better ionic conductivities, nearly to the estimated values experiential for aqueous electrolytes. The accumulation of a minute quantity of solvent makes possible the detachment of the salt within the polymer matrix that produces the superior polarity, which offers a more prominent effect in the enhancement of capacitance values. GPEs provide excellent ionic conductivity; their processing into thin films is more complex than for SPEs. Conversely, when the GPE polymer membrane is utilized in the electrode preparation, than GPE polymer membrane act as a binder, it will auxiliary diminish the contact resistance among electrodes and electrolyte, in scrupulous if the gel process step is executed later than cell or device congregation, this process can escort to “fusion” of the diverse layers within the device or cell.

Polyzwitterions are a class of charged polymer with appreciable water retention ability. This property is due to the presence of a zwitterionic group in a repeat unit that makes these materials work as potential gel electrolyte scattering for highly efficient solid-state supercapacitors. Unlike the polyelectrolytes that are conventionally used, polyzwitterions are a different class of material. They exhibit the so-called ‘anti-

polyelectrolyte' effect, resulting in good solubility in aqueous solutions having a high concentration of salt.^[177,178]

The zwitterionic nature of poly (propyl sulfonate dimethylammonium propylmethacrylamide) (PPDP) led to its application in graphene-based solid-state supercapacitor as gel electrolyte.^[179] Their physical properties are depicted in Figure 8. The zwitterionic nature of PPDP as gel electrolyte offers robust water retention ability. It brings ion migration channels to the ions in the electrolyte, leading to enhanced cyclability with 103% capacitance retention after cycling for 10,000 cycles. Very recently, natural zwitterionic polymer hydrogel with exceptional mechanical strength and flexibility was prepared and employed as an electrolyte for all-solid-state zinc-ion hybrid supercapacitor with Zn foil and activated carbon electrode.^[180]

2.3. Biodegradable Polymer Electrolytes

Sudhakar *et al.* reported, for the first time, a biodegradable polymer, cellulose acetate, with different concentrations of LiClO₄ as an ionic system. An optimized blend of chitosan and starch plasticized with glycerol as host polymer and lithium perchlorate (LiClO₄) as salt was prepared using solution casting technique and employed as biodegradable polymer electrolyte.^[181] For optimization, the variation of conductivity as a function of polymer blend ratio, plasticizer content, and LiClO₄ concentration at a temperature range of 298–343 K has been investigated using EIS by the same group. The maximum conductivity of $3.7 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature for 60:40 (CS/starch) concentrations. The authors concluded that the salt incorporation was responsible for the conductivity of the CS/starch blend films in the plasticizer medium. The plasticizer helps to dissociate the salt into ions that accumulate at the electrode-electrolyte interface at low frequencies.^[182]

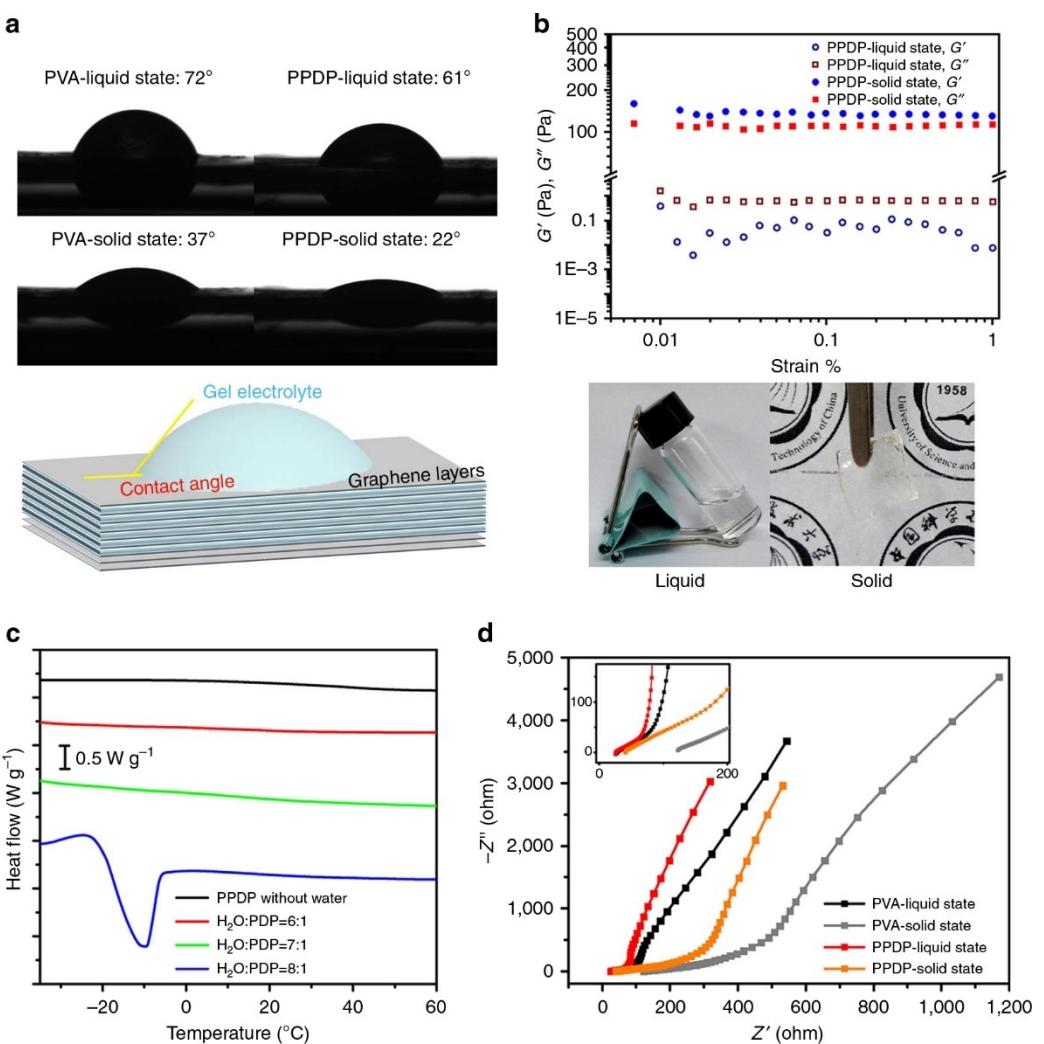


Figure 8. Physical and chemical mechanisms of PPDP gel electrolyte. a) Static contact angles of PVA and PPDP gel electrolytes on the graphene electrode. Inset is the schematic illustration of the penetration of the gel electrolyte into the multilayer graphene electrode. b) Viscoelastic properties of the PPDP gel electrolyte in liquid and solid states. PPDP gel electrolyte is demonstrated at a liquid state in a vial and solid-state with a freestanding solid thin film. c) DSC thermograms of PPDP at different water contents. d) Electrochemical impedance spectroscopy (EIS) of graphene-based solid-state supercapacitors applying PPDP and PVA gel electrolytes at the liquid state and solid-state. Reproduced with permission from Ref. [179]. Copyright 2016, Nature Publishing Group.

In another interesting work, it was found that the electric double-layer capacitance of a highly dense graphite electrode is influenced by the state of the polymer crystallinity and the contact at the interface between the high-density graphite electrode and the solid electrolyte. Further, the effect of the cell temperature and concentration of LiClO_4 also played a major role. It was found that the all-solid-state capacitor with PEO/LiClO₄ polymer electrolyte and PEO/PC/LiClO₄ gel electrolytes showed good charge/discharge behavior with a relatively high capacitance at 80 and 20 °C, respectively.^[183] A number of conducting polymers can be envisioned in electroactive devices, and the use of such organic cations which are electrochemically stable may significantly enhance their switch-

ing lifetimes. These electrolytes may find use in electrochromic displays in which long lifetimes are desired apart from batteries and supercapacitors.^[184–187]

Type I supercapacitors based on dual conducting polymer were assembled by Smith and co-workers using poly(3,4-propylenedioxothiophene) and poly(3,4-ethylene dioxothiophene) as electrodes. Two types of supporting electrolytes have been used to compare the switching speeds and cycle life of these supercapacitors namely lithium bis-trifluoromethanesulfonyle imide and 1-ethyl-3-methyl-1-H-imidazolium bis-trifluoromethanesulfonyle imide. The use of 1-ethyl-3-methyl-1-H-imidazolium bis-trifluoromethanesulfonyle imide as the supporting electrolyte has enabled durable cycle life.

The electrochemistry of composite electrodes prepared from chlorinated poly-(E)-(α)-[(2-thienyl)methylene]-2-thiopheneacetonitrile, poly-(E)-(α)-[(3-methyl-2-thienyl)methylene]-2-thiopheneacetonitrile, and poly-(E)-(α)-[(2-furanyl)methylene]-2-thiopheneacetonitrile, with acetylene black and polytetrafluoroethylene (5 wt%) were tested in 1 M Et_4NBF_4 /acetonitrile using CV, EIS and galvanostatic cycling. The impact of the polymer's structure on their electrochemical properties was found to be in accordance with expected effects for methyl and furan groups. The results indicated p and n-doping levels up to 0.3 electrons per heterocycle for the three polymers make these polymers an ideal choice for use in electrochemical supercapacitors. The best cyclability was demonstrated for poly-(E)-(α)-[(2-thienyl)methylene]-2-thiopheneacetonitrile in its p-doped state with 170 Cg^{-1} after 1000 cycles and for poly-(E)-(α)-[(2-furanyl)methylene]-2-thiopheneacetonitrile in its n-doped state with 130 Cg^{-1} after 1000 cycles.^[20]

When used as an electrode, polyaniline doped lithium salt was found to have larger discharge capacitance and smaller internal resistance than the one doped with protonic acid. It is proven to be suitable as electrode material involving in a redox reaction in a power source.^[188]

In order to rationally design an all-solid-state SC based on PPY-MnO₂ nanoflakes-CF composites, Tao and co-workers recently employed an “in situ growth for conductive wrapping” method, which offered good flexibility and high electrochemical performances. In their work, a thin layer of PPY was wrapped around MnO₂ nanoflakes uniformly by the “in situ growth” method, which was distinct from the conventional “dip-coating” process. In addition to CFs under MnO₂ nanoflakes, this system offered an alternate electron transport path and contributed immensely to the charge storage mechanism of EDLC or pseudocapacitance. The fabrication process and a few noteworthy results are given in Figure 9. The device at a discharge current density of 0.1 A cm^{-2} delivered a high specific capacitance of 69.3 F cm^{-3} .^[189]

Solid-state asymmetric supercapacitors were assembled by employing conducting polymers poly(3,4-ethylene dioxothiophene) (PEDOT), and PANI respectively, as the negative and positive electrode, and PVA/H₂SO₄ gel electrolyte as shown in Figure 10.^[190] The asymmetric devices showed a maximum power density of 2.8 W cm^{-3} at an energy density of 9 mWh cm^{-3} . The higher reduction potentials in the PEDOT due to the electron-donating nature of oxygen groups and

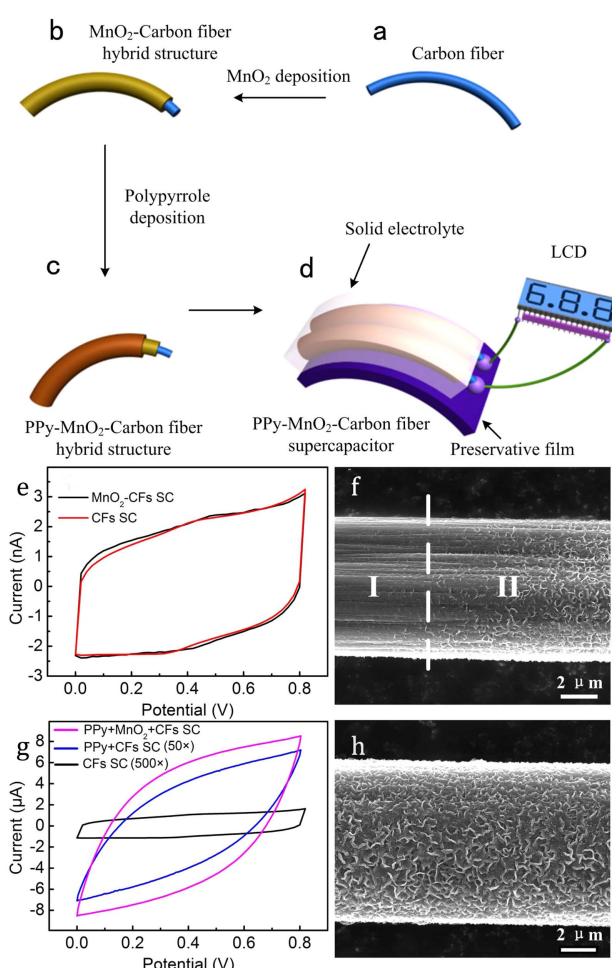


Figure 9. Fabrication process of PPY-MnO₂-CF SCs (top). a, b) A CF was cleaned and cut to a shorter length; then, MnO₂ nanoflakes were coated onto the CF by electrodeposition method; c) PPY was electrodeposited onto the MnO₂-CF; d) two PPY-MnO₂-CFs were assembled on a piece of preservative film to form a PPY-MnO₂-CF SC. Comparison of the different electrode materials (bottom). e) CV curves of MnO₂-CFs SC and CFs SC. f) An SEM image of a MnO₂-CF: region I was immersed into H₃PO₄ solution of 9.1 wt% for 12 h; region II was above the liquid surface. g) CV curves of PPY-MnO₂-CFs, PPY-CFs SC, and CFs SC. For comparison, the current of CFs SC and PPY-CFs SC were magnified 500 and 50 times to their measuring value, respectively. h) An SEM image of a PPY-MnO₂-CF was immersed into H₃PO₄ solution of 9.1 wt% for 24 h. The scan rate of all the CV curves was 100 mV s⁻¹. Reproduced with permission from Ref. [189]. Copyright 2013, Nature Publishing Group.

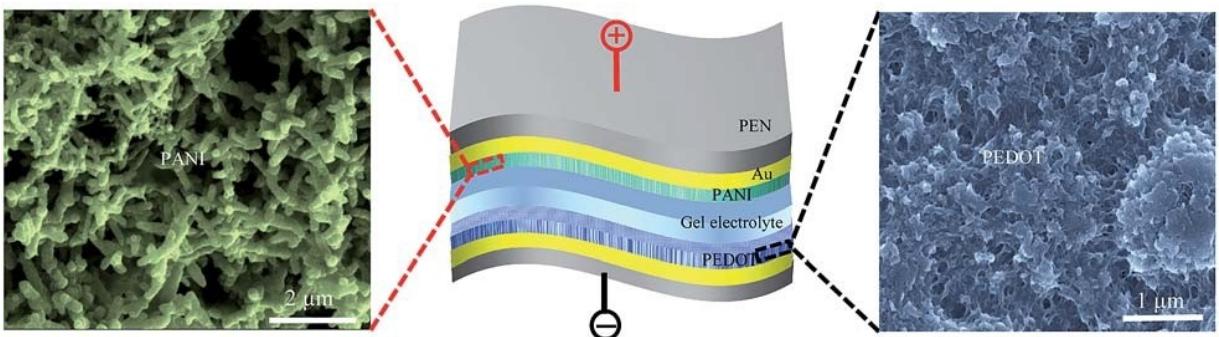


Figure 10. A schematic of the fabrication of asymmetric supercapacitors based on conducting polymer electrodes. PANI//PEDOT ASC device with aqueous gel electrolyte. SEM micrographs of PANI nanofibers and nanostructured PEDOT (false-colored). The thickness of each layer, PEN, 125 μm ; Au, 150 nm; PANI, 2.5 μm ; gel electrolyte, 60 μm ; PEDOT, 4.5 μm . Reproduced with permission from Ref. [190]. Copyright 2015, Royal Society of Chemistry.

increased stability in its oxidized state allow it to be used as a negative electrode material. The polymer can achieve comparable specific capacitance at an appreciably lower cost and with improved mechanical properties and often also enhanced conductivity when compared to metal oxides. Owing to these merits, conducting polymers are considered to play a vital in the development of next-generation supercapacitors.

3. Conclusions and Perspectives

To complete and encounter the necessity of sustainable and ecological power and energy resources for multifarious applications, such as hybrid automobiles, power electronics, high power consumption devices, the supercapacitors are identified as a promising energy storage device. They are ideally acknowledged by experts to accomplish the demand of energy. The conducting polymer-based composite materials contribute appreciably to improving supercapacitors' performance by allowing the diffusion and migration of electrolytic ions rapidly. The ECPs also offer a high specific surface area leading to enhanced capacitance values. Though the strategy and ideal conditions for making outstanding electrode materials statically have become a countless challenge, researchers have extensively studied and tuned the following factors a) pore size b) pore dimensions c) morphology d) surface area e) electrolyte for making ideal electrodes configuration as well as the device. The review article discussed the current development and improvement in ECPs based electrode materials by combining different carbon materials and applications as different electrolytes. Although ECPs materials are suffering from limitations such as poor solubility, swelling, and shrinkage of the layer during the charge-discharge cycling process, and low mechanical strength, it has many pros in supercapacitor devices.

For improving the solubility limit of ECPs, doping of anionic and cationic surfactant has been identified as an effective way during the polymerization process. This doping resulted in an improved surfactant interaction, thereby providing a better yield, conductivity, thermal stability, and intermolecular chain reactions. While addressing the mechanical strength issue, ECPs were incorporated with carbon materials such as porous

carbon, graphene, carbon nanotubes, and hybrid carbon array. Conversely, significant improvements have been carried out by integrating electric double layer materials with pseudocapacitive ingredients to achieve extraordinary capacitance and better rate capability by the synergistic effect of both materials. The different types of supercapacitors device configured by polymer gel electrolyte, solid polymer electrolyte, and biodegradable polymer-based electrolytes for improved supercapacitive performance have also been focused on. The research implication and future advancement would be in developing electrode materials, growth, and innovation route in the fabrication of low cost, economical, non-corrosive, and sustainable materials. Recently discovered nano-scale materials such as 2D MXenes, metal-organic frameworks can also be explored with ECPs to exploit their exceptional electrical conductivity, high porosity, and large surface area to achieve high-performance supercapacitors.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: polymer electrolytes · supercapacitors · conducting polymers · energy storage · specific capacitance

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