Components of Supercapacitors

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The enormous demand for energy due to rapid technological developments pushes mankind to the limits in the exploration of high-performance energy devices. Among the two major energy storage devices (capacitors and batteries), electrochemical capacitors (known as 'Supercapacitors') play a crucial role in the storage and supply of conserved energy from various sustainable sources. The high power density and the ultra-high cyclic stability are the attractive characteristics of supercapacitors. However, the low energy density is a major downside of them, which is also responsible for the extensive research in this field to help the charge storage capabilities thrive to their limits. Discoveries of electrical double-layer formation, pseudocapacitive and intercalation-type (battery-type) behaviors drastically improved the electrochemical performances of supercapacitors. The introduction of nanostructured active materials (carbon-/metal-/redox-active-polymer/metal-organic/covalent-organic framework-based electrode materials), electrolytes (conventional aqueous and unconventional systems) with superior electrochemical stability and unprecedented device architectures further boosted their charge storage charage characteristics.

energy storagesupercapacitorselectrodeselectrolytesBindersSeparatorsCurrent collectors

1. Introduction

Energy storage devices are inevitable candidates in the field of energy preservation and its utilization. In general, the four types of energy storage through mechanical, electrical, chemical, and electrochemical systems have been employed for various applications, including large-scale energy conservation ^[1]. Among them, electrochemical energy storage with the help of capacitors and batteries plays a significant role, especially in electric vehicles and portable electronics. Electrochemical capacitors (supercapacitors) have grasped more attention due to their higher power density and ultra-cyclic stability ^[2]. In the middle of the 18th century, the concept of electrical double layer (EDL) structure and the formation of electrical potential at the solid–electrolyte interface were put forward by H. von Helmholtz, which seeded the fundamentals of the charge storage mechanism and the electrical double layer capacitance (EDLC) ^[3]. After hardly a century, the EDLC and the charge–discharge processes were demonstrated in an experimental electrochemical cell constructed by H. I. Becker for the 'General Electrical Company' ^[4]. It led to the first commercial supercapacitor based on EDLC by Ohio state's Standard Oil Company, and it was subsequently licensed to the Nippon Electrical Corporation (NEC) in 1971 for computer technology ^[5]. The term 'Supercapacitor' was first coined by the NEC, and the corporation also marketed the device in the name as well. Afterward, the term 'Supercapacitor' became familiar in Asia. Shortly, in 1982, the 'Pinnacle Research Institute'

(PRI) developed a high-power electrochemical cell based on ruthenium oxide and commercialized it under the name of 'PRI ultracapacitor' that popularized the alternate term 'ultracapacitor' in North America ^[6]. In the past several decades, electrochemical energy storage systems have evolved with enormous growth by introducing new concepts of pseudocapacitance ^[Z], battery-type behavior ^[8], and asymmetric and hybrid device ^{[9][10]} architectures towards high-performance and next-generation energy storage devices.

Vast efforts have been invested to improve the performances of the supercapacitors by the proper materials design and device configurations ^[11]. The development of high-performing electrode and electrolyte materials is crucial to achieving improved electrochemical energy storage. The introduction of multi-role nanostructured materials has enormously boosted the electrochemical performances of supercapacitors ^[12]. Furthermore, the energy density/specific energy (the amount of energy stored by a unit volume/mass of the electrode material) of the supercapacitor (<30 Wh L⁻¹), which is usually inferior to that of batteries (~500 Wh L⁻¹), is often increased by utilizing the electrolytes that can operate in wider potential window ^[1]. The ionic liquids and the unconventional electrolytes (water-in-salt (WIS) and deep-eutectic solvents (DES)) are examples of higher-performing electrolyte systems for supercapacitors ^[13]. The growth of sophisticated electrochemical characterization techniques resulted in an in-depth understanding of various aspects of the charge storage mechanism and electrode–electrolyte kinetics ^[14].

2. Electrode Materials

The electrode materials constitute the major role among the different components of the supercapacitor device. An ideal electrode material should possess high electrical conductivity, larger electrochemically active surface area, higher electrochemical and thermal stability, and greater surface wettability. Furthermore, it must be cost-effective and recyclable. In general, several factors including morphology, porosity, and accessibility to electrolytes decide the electrochemical performances of the electrode materials. Notably, the incorporation of nanomaterials in the supercapacitors has enormously improved the device's performance.

2.1. Carbon-Based Materials

Several carbon-based materials are known as active electrode materials for supercapacitors, including activated and mesoporous carbons ^{[15][16][17]}. The zero, one-, two-, and three-dimensional (0D, 1D, 2D, and 3D, respectively) carbon nanomaterials such as fullerenes, carbon nanotubes, carbon nanofibers, graphene/reduced graphene oxide, and 3D graphene derivatives are also well studied for this purpose ^[18]. In general, carbon-based materials have high porosity and electrical conductivity when compared to metal-based compounds as well as conducting organic polymers. For instance, activated carbon has a maximum surface area of >3000 m² g⁻¹, and a very high electrical conductivity of ~10⁸ S m⁻¹ could be achieved for graphene. In addition to desirable physical properties, they have excellent chemical stability and can operate in a wide range of electrolyte systems. Among various carbon-based materials, activated carbon is broadly employed electrode material for supercapacitors, including in commercial device production. To obtain the activated carbon with high porosity and electrical conductivity, the adopted synthetic methods are crucial and should be appropriate. To be precise, the optimum synthetic technique

provides the sp²-hybridized carbon structure with three-dimensional morphology consisting of micro/macro pores. In a typical procedure, the carbon precursor, which could be synthetic organic molecules or derived from natural sources, is deposited over soft or hard templates. The usually employed synthetic carbon precursors are phenol, resorcinol, thiourea, formaldehyde, benzoxazine, and melamine. Similarly, a variety of biomaterials derived from natural sources, namely, cellulose, starch, lignin, and chitin, are used after carbonization and activation processes [19][20][21][22][23][24][25][26]. These natural biomaterials are obtained from the abundant plant- (rice rusk, coconut shell, and seeds), coal-, and animal waste-based resources $\frac{[27][28][29]}{2}$. Porous zeolites and silicates (SiO₂) are employed as hard templates, and surfactant-based micelles as soft counterparts. The templates have inherently porous structures, which help to construct the frameworks of carbon precursors in a three-dimensional fashion. After that, the thermal pyrolysis converts the precursors into sp²-carbon-rich structures, and the process is called 'carbonization'. Subsequently, the removal of the template from the above structure leads to voids from the space covered by them. The amount of porosity is further improved by treating the prepared carbonized structures with strong acidic (H₃PO₄/ZnCl₂) or basic (KOH/K₂CO₃) medium, known as 'activation'. The main reason for the activation process is to create additional porosity upon itching the labile functional groups together with the sp³carbon-rich domains. The activation process could also be carried out by treating the carbonized structures with a mixture of CO₂ and H₂O under higher temperatures. The latter method is considered efficient and less hazardous when compared to harsh activation conditions with acids and bases.

Fullerenes are 0D carbon nanomaterials that have cage-like structures and sizes in the range of <1 nm $\frac{[30]}{2}$. The fullerene with sixty carbon atoms (C₆₀, also known as Buckminsterfullerene) has fused five-membered (12 numbers) as well as six-membered (20 numbers) carbon rings, which form the nano soccer ball-like structure. Due to their excellent electron transport properties, they have extensively been in solar cell devices. Similarly, the nano/microstructures derived from fullerene-based materials are highly suitable for the fabrication of electrode materials for supercapacitors [31]. In addition, the one-dimensional carbon nanomaterial, namely carbon nanotubes, have highly conjugated hexagonal lattices of sp²-carbons $\frac{[18]}{2}$. They have a higher surface area (1500 m² g⁻¹) and excellent electrical conductivity ($\sim 10^6 - 10^7$ S m⁻¹), which establish them as important electrode materials for supercapacitors. In general, carbon nanotubes are synthesized via chemical vapor deposition, arc discharge method, and laser ablation process. The chemical vapor deposition technique is more suitable and widely utilized to grow vertically aligned carbon nanotube-based electrode materials. The mixture of carbon-containing gases such as CH₄, acetylene, or ethylene and the carrier gases, namely NH₃, N₂, or H₂, are used as sources for the syntheses of carbon nanotubes with the help of metal catalysts (NiO, MgO, or Alumina) at higher temperatures in the range of 700 °C. In addition to one-dimensional carbon nanotubes, their two-dimensional counterpart, namely, graphene and graphene-based materials are also employed as electrode materials for supercapacitors [32][33][34]. Exfoliation of bulk graphite into individual graphene layers in the solution phase is a cheap method; however, it usually provides low yields. Due to very strong intertubular/interlayer π -stacking interactions, the carbon nanomaterials exist as bundled tubular/restacked layered structures that subsequently reduce the active surface area. The covalent/noncovalent functionalization of carbon nanotube/graphene is the best option to address this issue. For example, the surface functionalization of graphene oxide, an oxidized form of graphene obtained from bulk graphite, is carried out with various inorganic/organic materials. After that, a chemical or thermal reduction in functionalized graphene oxide partially restores the hexagonal sp² carbon-rich π -conjugated structures that have better electrical conductivity than fully oxidized graphene oxide. The above synthetic technique is proven as an efficient and scalable method to prepare a variety of graphene-based materials for supercapacitors. Apart from the 0D, 1D, and 2D carbon nanomaterials, the 3D porous architectures (self-assembled hierarchical flowerlike/crumbled sheet-like/aligned array-like structures) are also employed to develop high-performance electrode materials ^[35]. The 3D porous structures are usually composed of self-assembled fullerene, carbon nanotubes, or graphene derivatives ^[36]. In general, the controlled self-assembly (templated/non-templated) in the solution state followed by the lyophilization would lead to nano as well as microporous structures with larger surface area.

2.2. Transition Metal-Based Compounds

A variety of transition metal-based compounds, namely, oxides, sulfides, nitrides, and phosphides, are usually employed as active materials for supercapacitors due to their reversible redox reactions, which increase the overall energy density of the device [37][38]. In particular, the transition metal oxides are preferable because of higher electrochemical stability and multiple redox states with faster charge transport of oxide lattice. For example, ruthenium oxide (RuO₂) is a well-known transition metal oxide that has been utilized extensively for supercapacitors as it has higher electrical conductivity and chemical stability [39]. However, the high cost and toxicity restrict its use towards sustainable supercapacitor devices. As cheap alternatives to RuO2, the oxides of vanadium (V₂O₅), manganese (MnO₂ and Mn₃O₄), cobalt (CoO and Co₃O₄), nickel (NiO and Ni₂O₃), copper (Cu₂O and CuO), and zinc (ZnO) are used as active electrode materials. The electrochemical characteristics of the transition metal oxides could further be improved by adopting binary (CoMn₂O₄ and NiCo₂O₄) and ternary (CoNiFeO₄) metal oxides, as they introduce additional redox states and enhances electrical conductivity. Furthermore, the incorporation of oxygen vacancies in the oxide lattice improves the charge storage behavior due to the increased electrode kinetics. Another counterpart of oxides, namely transition metal sulfides are also familiar electrode materials for supercapacitors. For instance, the sulfides of first-row transition metals such as manganese (MnS), cobalt (CoS, Co₃S₄, and Co₉S₈), nickel (NiS and Ni₃S₂), and copper (CuS) demonstrate better electrochemical characteristics due to their superior structural integrity and electrode kinetics. Like transition metal oxides, the binary transition metal sulfides (NiCoS₄, CoMnS, and CuMnS) also serve as better electrode materials than their mono-transition metal sulfides. When the oxygen and sulfur are replaced with low electronegative nitrogen, the resultant transition metal nitrides exhibit comparable electrochemical properties. Several transition metal nitrides such as VN, CrN, FeN, Co₃N, Mo₂N, and Mo₃N₂ are utilized for this purpose. Most of these transition metal compounds are synthesized by wet chemical methods from their precursor metal salts of chlorides and nitrates under hydro/solvothermal conditions. These reaction conditions provide the transition metal compounds with three-dimensionally oriented morphological features with higher porosity and electrical conductivity, which mainly determine the electrochemical performances. In addition, the charge storage characteristics of the transition metal-based compounds are further improved by preparing the composite materials with a variety of components including carbon nanomaterials and other types of transition metal compounds, which enhance electrical conductivity, porosity, and electrode kinetics [40].

2.3. 2D Layered Materials

The two-dimensional layered materials beyond graphene, namely, MXenes [41], layered double hydroxides (LDHs), transition metal dichalcogenides (TMDs) $\frac{[42]}{2}$, boron nitride, and graphitic C₃N₄ have attracted interest due to their fascinating properties ^[43]. Among them, the MXenes ^[44], LDHs ^[45], and TMDs ^[46] are widely utilized as active materials towards supercapacitors. In general, the exfoliated few/monolayers of these materials have superior physical and chemical properties than their bulk structures due to the higher surface area and electrical conductivity. So, the exfoliated 2D layers are preferred to prepare the active electrode materials for supercapacitors. For example, the individual layers of MXenes ($M_n X_{n-1}$) are extracted from a metal-ceramic phase (MAX) consisting of a transition metal (M), element (A) of IIIA/IVA group, and C/N (X). The bonding (M-X) of 'M' with 'X' is very strong because of the combined covalent, ionic, and metallic characteristics, whereas the M-A interaction is a weaker metallic bond, which makes it easier to extract the $M_n X_{n-1}$ layers from the MAX phase. The extracted $M_n X_{n-1}$ layers, after the removal of 'A' atoms, possess several surface vacancies and defects in the 'M' coordination positions that can accept other elements to undergo surface modifications. In general, the etching method is employed to extract the $M_n X_{n-1}$ layers from the MAX phase with the help of hydrofluoric acid. Furthermore, the less harsh etching techniques are also utilized for this purpose by replacing the HF with a mixture of metal fluorides (LiF and FeF₃) and HCI. In addition, the intercalation of neutral molecules (hydrazine, dimethylformamide and dimethylsulfoxide) also results in the delamination of $M_n X_{n-1}$ layers from the bulk phase.

Another example of a 2D layered material, namely LDH, has a chemical formula of $[M^{2+}_{1-x} M^{3+}_{x} (OH)_2]^{x+} [A^{n-}]_{x/n}$. zH₂O with bivalent (magnesium, nickel, cobalt, and zinc), trivalent (aluminum, manganese, iron, and cobalt), and anionic (chloride, nitrate, and carbonate) species [45]. The mole ratio of bivalent and trivalent metal ions varies in the range of 0.2–0.33. The basal plane of LDH is made up of M(OH)₆ units having a brucite-like structure, and it is electrostatically balanced by the counter anions to form the stacked bulk material. Most of the LDHs are synthesized by the chemical bath deposition method in the presence of divalent/trivalent metal salts and precipitating agents (ammonia or organic amines such as hexamethylenetetramine). Furthermore, electrodeposition, solvent evaporation, spin coating, and ion exchange methods are also employed to synthesize various LDH-based 2D materials. Like the MXenes, the exfoliated LDH layers show better electrochemical properties than the bulk phase. Similarly, TMDs are considered promising electrode materials for supercapacitor applications, due to their highly reversible redox processes and faster electrode kinetics [42]. The TMDs have a chemical formula of MX₂ with the transition metal (Ti, Zr, Hf, V, Nb, Ta, Mo, W, Tc, or Re) and chalcogen (S, Se, or Te). The electronic property of TMD depends on the transition metal and the chalcogen; for example, pristine MoS₂ is a semiconductor, whereas NbS₂ has a metallic character, and HfS₂ is an insulator. Similarly, the polymorphs of the same TMD show different chemical stability and electrical conductivity. The more stable 2H phase of MoS₂ is semiconducting, and its metastable 1T phase has metallic behavior. It is mainly due to the variations in the coordination types of the 'Mo' atom with the 'S' atoms. In the 2H phase, the 'Mo' atom has a trigonal prismatic geometry, whereas in the 1T phase, it has a distorted octahedral geometry [47]. The hydro/solvothermal methods are employed to synthesize the bulk TMDs from the precursor salts. On the other hand, the chemical vapor deposition technique is utilized to grow the individual layers over the substrate, and the chemical/electrochemical intercalation of alkali metal (Li, Na, or K) in between the layers of bulk TMDs also leads to the formation of exfoliated individual layers in solution ^[48]. The chemical stability and electrochemical characteristics of these exfoliated TMDs are further tuned by surface modifications.

2.4. Redox-Active Polymers

The redox-active polymers are better alternative electrode materials to heavy, scarce, and toxic metal-based compounds [49]. The supercapacitors with these polymers are flexible, environmentally friendly, and easily recyclable when compared to their metal counterparts. For example, redox-active polymers can easily be transformed into small organic molecules via chemical treatments, and the derived resultant molecules are used as resources for the synthesis of other organic materials. In general, redox-active polymers are classified based on their chemical structures. In certain polymers, the redox-active groups act as the backbone, and they are interconnected through the π -conjugated units [50][51][52][53]. These polymers are also categorized as 'conducting polymers' due to their intrinsic electrical conductivity resulting from the alternating single and double bond structure, which includes poly(p-phenylene), poly(p-phenylenevinylene), polyacetylene, polyaniline, polythiophene, polypyrrole, polyimides (perylenetetracarboxyldiimide), and poly(3,4-ethylenedioxy thiophene). They undergo reversible redox reactions upon binding/unbinding with the electrolyte ions, which impart charge storage characteristics. Some polymers have redox-active groups as pendants, mostly in a non-conjugated polymeric backbone. The commonly employed redox-active pendants are carbonyl (quinone), nitroxyl, ferrocene, triphenylamine, and organosulfur compounds. The electrochemical performances of the redox-active polymers mainly depend on the molecular weight, polydispersity, and chemical stability of oxidized/reduced species. Fine control over the molecular weight and the solution processibility is crucial to achieving high-performance redoxactive polymeric electrode materials. However, the inferior charge storage characteristics of these polymers, when compared to their metal counterparts, are overcome by compositing with the other materials having higher conductivity and redox behaviors [54].

2.5. Metal-Organic and Covalent Organic Frameworks

Among various inorganic and organic electrode materials, the metal-organic framework (MOF) and covalent organic framework (COF)-based materials have attracted significant interest due to their inherent porosity, electrical conductivity, and electroactive properties ^[55]. The MOFs are porous coordination polymers with one-dimensional to three-dimensional framework architectures created via metal coordination bonding with the organic ligands. Based on the types of metal ions and linker units, the pore size, surface area, and electrical conductivity of the resultant MOF structures are determined. The electronic properties, ionic radii, and coordination geometry of the metal ions further control the morphology and electrochemical properties. The organic linker units with different donor sites, charges, and lengths are utilized to construct the multi-dimensional framework structures. In addition, the counter ions and the nature of the solvent medium used also affect the resultant properties of the MOF architectures. Various synthetic methods are employed to prepare the MOF structures with desired properties, which include electrodeposition, chemical vapor deposition, the sol-gel method, in situ polymerization, and solvothermal/hydrothermal and co-precipitation methods. The MOF materials based on transition metals such as cobalt, nickel, iron, copper, and zinc are commonly used for supercapacitor devices. For example, the MOF

structure synthesized from the cobalt ions and the fluoro-substituted terephthalic acid and hexamethylenetetramine show a layered structure with a surface area of >12 m² g⁻¹ and a pore diameter of ~4 nm ^[56]. When the linear linkers are replaced with a '*C3*'-symmetric linker such as a triazine molecule substituted with the *p*-aminobenzoic acid groups, the higher surface area of 28 m² g⁻¹ and the pore diameter of 44 nm are observed for the Co-based MOF structures ^[57]. Similarly, Ni-based two-dimensional MOF structures having the '*C3*'-symmetric hexaminotriphenylene linker units are synthesized with a higher surface area of >600 m² g⁻¹ and the one-dimensional channel size of 1.5 nm ^[58]. Furthermore, the metal and heteroatoms (nitrogen and boron)-doped carbon materials derived from these MOF structures by the carbonization process at higher temperatures also demonstrate better electrochemical performance for supercapacitors ^[59].

Covalent organic frameworks are better alternatives to MOF-based electrode materials due to their light weight, less toxic, tunable redox activity and higher structural stability over MOFs towards the supercapacitor devices ^[60]. In the COF materials, the multi-dimensional porous frameworks are attained through the strong covalent bonds among the complementary linker units. For instance, the 2D COF structures comprising aminopyridine units and substituted-phloroglucinol linkers are obtained via the solvothermal method with a higher surface area of ~690 m² g⁻¹ and a pore width of >1 nm ^[61]. Similarly, a 2D COF structure consisting of a diaminoanthraquinone unit and the triformylphloroglucinol linker is prepared as surface-oriented thin films with a thickness of ~200 nm. It shows the few-layered 2D nanosheets with a surface area of >1000 m² g⁻¹ ^[62]. The redox activity of these 2D COF nanosheets is further improved by incorporating a radical pendent group such as (tetramethyl piperidinyl)oxidanyl moiety (TEMPO) ^[63].

To be concise, among the various types of electrode materials discussed in this section, carbon-based materials (activated carbon, bio-derived carbon, carbon quantum dots, carbon nanotubes, and graphene derivatives) are environmentally friendly, abundant, and affordable for large-scale applications. Furthermore, they have better tunability of electrochemical performance by controlling the pore size, hydrophilicity, and conductivity via simple chemical and thermal processes. However, the lack of redox-active functionalities of native carbon materials restricts their charge storage mechanism to the electrical double-layer formation, though they often show a certain percentage of pseudocapacitance due to the oxidized carbon domains created during the material processing. To address the issue, composites based on carbon materials are frequently prepared by incorporating metal/conductive polymer-based pseudocapacitive materials. On the other hand, transition metal-based electrode materials became familiar to replace the costly and scarcer noble metal-based compounds as active electrode materials. In particular, the transition metal-based 2D lavered materials are well explored as electrodes due to their intriguing properties such as tunable interlayer spacing, reactivity of induced defects (defect engineering), polymorphism and greater electrical conductivity. Furthermore, the pristine metal-organic framework (MOF) structures as well as the metal-doped interconnected carbon-based materials derived from the thermally treated MOF structures are also employed as better electrode materials due to the combined characteristics of metal domains as well as the porous carbon architectures. As the cheap and environmentally benign alternative to metalbased compounds, the redox-active polymers and covalent organic framework (COF) structures are introduced as pseudocapacitive and battery-type electrode materials because of their intrinsic redox characteristics. Nevertheless, the electrochemical performances of the redox-active polymers and COF structures are

comparatively inferior to that of metal-based electrodes. So, the development of effective synthetic protocols and unprecedented fabrication techniques would probably open up a new pathway to more sustainable as well as highperformance electrode materials.

3. Binder and Conductive Additives

For large-scale or commercial production of supercapacitors, the electrodes are prepared by coating or printing the slurry (a recipe consisting of active materials and additives dispersed in a solvent) of electrode materials over the suitable current collector [64]. The major additives that are employed for the preparation of electrode slurry include polymeric binders and conductive agents. The polymeric binders help the electrode material to adhere firmly over the current collector and increase the mechanical stability of the electrodes throughout the life cycle of the device. Similarly, the conductive agents are added to the electrode slurry for the enhancement of the electrical conductivity of the prepared electrodes, thereby reducing the charge transfer resistance [64]. However, the mass percentage of the additives should not be higher than 5-20% of the total mass of the slurry components. The usage of inappropriate additives partially kills the electrochemical performance of electrode materials. The commonly employed polymeric binders are poly(tetrafluoroethylene) (PTFE), poly(vinylidene fluoride) (PVDF), and poly(tetrafluorosulfonic acid)-co-(tetrafluoroethylene) (known as 'Nafion'). The PTFE binder possesses only perfluoro ethylene units that provide hydrophobicity and insulator behavior to the electrodes, which results in poor electrolyte wettability and higher contact resistance. On the other hand, since the PVDF binder is a partially fluorinated polymer, it has higher electrochemical stability and relatively lower hydrophobicity, and is a more suitable binder additive for the electrode preparation compared to the other two polymers. The copolymer, Nafion, is a proton-conducting polymer and is used mainly for the electrode materials that show proton adsorption during the charge storage process ^[65]. The combination of two different polymers is also used as binder additives to improve mechanical stability and electrolyte wettability. For example, the addition of carboxymethylcellulose to the PTFE polymer considerably reduced the contact resistance and improved the adhesion of electrode materials over the current collector [66]. Poly(vinylidene chloride) and sulfonated poly(ether ether ketone) (SPEEK) polymers have also been used as binder additives for electrode preparation. The conductive additives are added to the electrode slurry to reduce the contact resistance and improve the charge transport properties of the prepared electrodes. Carbon black is a widely utilized conductive additive for electrode preparation, and is a paracrystalline carbon with a high surface-to-volume ratio [67]. It is usually prepared by the partial combustion of various carbon sources, including petroleum byproducts, coal, ethylene/acetylene gas, and so on. The carbon black obtained from the acetylene combustion is known as 'acetylene black' and it is also a commonly used conductive additive for supercapacitors.

4. Current Collectors

The current collectors play a crucial role in the preparation of electrode materials by providing physical support, especially for the powdered active materials ^[68]. Furthermore, they act as a medium to transfer electrons between the electrode materials and the external circuit. The total internal resistance of the fabricated supercapacitor partly

accounts for the electrical resistance of the current collector as well as its interfacial resistance with the electrode materials. An ideal current collector should possess a higher mechanical strength, thermal and electrochemical stabilities, electrical conductivity, surface area, lower contact resistance, light weight, and low cost. Metal- and carbon-based materials are commonly employed as current collectors for supercapacitors. Nickel, stainless steel, titanium, copper, and aluminum are used as metal-based current collectors in the form of foil, mesh, and foam. In general, the metal-based current collectors offer higher electrical conductivity ($\sim 6 \times 10^7$ S m⁻¹ for Cu, $\sim 3.8 \times 10^7$ S m^{-1} for AI, and ~1.5 × 10⁶ S m^{-1} for stainless steel) and lower interfacial resistance. However, the usage of these metals as current collectors depends on the type of electrolyte systems and the operational potential window due to the corrosion and dissolution reactions ^[69]. For example, nickel foam is stable for alkaline aqueous electrolytes, whereas it undergoes dissolution in the acidic electrolyte. On the other hand, an alkaline medium, such as sodium and potassium hydroxide aqueous solutions, corrode the aluminum-based current collectors if they are used above the potential of 3 V ^[70]. Furthermore, the copper foil can only be used as a negative electrode in the potential range of 0–2 V and as a positive electrode between 3.5 and 4.5 V in the organic nonaqueous electrolyte for the lithiumion supercapacitors [1]. In order to prevent corrosion/dissolution, the surface of the metal current collector is deposited with protective and non-reactive coatings. For example, a thin layer of carbon coating is formed over the Al/Cu/stainless steel current collector to hamper the corrosion, and it further leads to the better adhesion of electrode materials over it [72][73][74].

Carbon-based current collectors such as carbon cloth, carbon fiber, carbon paper, glassy carbon, and graphite foil are better alternatives to metal-based current collectors due to their high electrochemical and thermal stabilities and light weight ^[75]. Furthermore, they are highly preferable current collectors for large-scale and commercial device fabrications because of their great flexibility and physical strength. For example, the carbon fiber-based current collector shows better electrochemical performance than that of the carbon-coated Al current collector [^{76]}. Furthermore, carbon paper is also used as a current collector for graphene and carbon nanotube-based electrode materials due to their flexibility and non-toxic characteristics ^[77]. Like metal-based current collectors, the surface modification technique is employed to improve the electrochemical performances of the carbon-based current collector. For instance, a thin layer of titanium is coated over the carbon foam to reduce the interfacial resistance with the silicon-based electrode material, which further boosts the charge storage characteristics of silicon electrodes ^[78]. Similarly, the doping of heteroatom, such as nitrogen-doping, is also utilized to improve the electrical conductivity and reduce the charge transfer resistance ^[79].

5. Electrolytes

As stated earlier, the major disadvantage of supercapacitor devices when compared with batteries is lower energy density, which in turn depends on capacitance and operational voltage ^[80]. To achieve it, high-performance electrolytes that operate in a wider potential window are required in addition to the electrode material with higher capacitance. In general, a given electrolyte can work without a considerable decomposition in a particular voltage range, which is called the 'electrochemical stable potential window (ESW)' ^[81]. The electrochemical stability of components such as salt and solvent determines the value of ESW. For the aqueous electrolytes, it usually is in the

range of 1 to 1.2 V due to the water decomposition reaction at 1.23 V vs. NHE, whereas it is in the range of 2.5 to 2.7 V and 3.5 to 4.0 V for non-aqueous (organic solvents-based) and ionic liquid-based electrolytes, respectively. Furthermore, the size of ions, ionic conductivity, viscosity, and freezing point of the electrolytes also affect their performances.

5.1. Conventional Aqueous Electrolytes

In general, the aqueous electrolytes consist of acid ($H_2SO_4/HCI/H_3PO_4$), alkaline (KOH/NaOH/LiOH), or salt ($Li_2SO_4/Na_2SO_4/K_2SO_4$) solutions. The concentration of aqueous electrolyte solution is typically in the range of 0.5 to 6 M. Aqueous electrolytes have higher ionic conductivity than nonaqueous or unconventional electrolytes [82]. For instance, an aqueous solution of 1 M H_2SO_4 has a maximum ionic conductivity of ~0.75–0.8 S cm⁻² at 25 °C. In order to obtain maximum ionic conductivity, the concentration of electrolyte solution should be optimum, and a very low or very high concentration usually leads to lower ionic conductivity. Furthermore, the ionic conductivity of a given aqueous electrolyte depends on the molar ionic conductivity of hydrated cations and anions. The smallest hydronium cation shows a higher value of 350 S cm² mol⁻¹, and the larger perchlorate anion exhibits a lower value of 67 S cm² mol⁻¹. The charge storage capability generally increases with increasing the ionic conductivity of the electrolyte solution. For a given electrode material, it is higher in aqueous electrolytes than non-aqueous electrolytes due to the higher ion mobility and faster interfacial charge transfer kinetics.

In addition to acidic electrolytes, alkaline aqueous electrolytes are also widely used for supercapacitors because of their comparable ionic conductivity with their acidic counterparts. An aqueous electrolyte solution of KOH with a concentration of 6 M possesses a specific conductivity of 0.6 S cm⁻¹ at 25 °C $\frac{183}{100}$. The alkaline electrolyte is more suitable for carbon-based electrode material with a surface functional group that undergoes pH-dependent redox reactions. The transition metal (Mn, Co, and Ni) oxides, sulfides, and nitrides show better electrochemical performances in alkaline electrolytes as their redox reactions are more prominent in these conditions [84]. It further depends on the type of cation of the alkaline electrolyte; for instance, NiO exhibits higher specific capacitance in NaOH solution than in KOH due to the higher intercalating character of the former. Unlike acid and alkaline aqueous electrolytes, neutral electrolytes are extensively used for aqueous supercapacitors because of higher ESW and less corrosiveness. The chlorides, sulfates, and perchlorates of Li, Na, and K metal ions are usually employed for this purpose [85]. Among them, the aqueous solution of Na₂SO₄ is considered an effective electrolyte for transition metal oxides such as MnO₂ and V₂O₅. For example, MnO₂-based electrode materials show higher performance in Na₂SO₄ and NaCl electrolytes when compared to the Li and K salts. It proves that not only the size of metal ion, but also the interactions at the electrode-electrolyte interface affects the electrochemical performances of the electrode materials. Furthermore, the salts of alkaline-earth metal cation (Mg²⁺) show higher performance for transition metal oxide-based electrodes (MnO₂) than alkaline metal salts due to the bivalency of the former, which balances more number of charges during the intercalation reaction.

Though aqueous electrolytes have many advantages, they have a few drawbacks that prevent them from extensive usage in commercial supercapacitor devices. Among them, the important disadvantage is the water decomposition reaction around the cell potential of 1.23 V vs. NHE ^[84]. Even though the aqueous supercapacitor devices are

intended to operate below the potential window of 1.23 V, the repeated charge–discharge cycles generate hydrogen and oxygen gases at the electrodes due to the minor hydrogen and oxygen evolution reactions. The gradual accumulation of gases leads to the rupture and explosion of the device over time and it is considered a critical performance and safety issue. Furthermore, the aqueous supercapacitor cannot be operated at elevated temperatures other than atmospheric conditions because of the increased rate of water decomposition reaction at higher temperatures. In addition to that, the acid and alkaline electrolytes are highly corrosive, particularly at higher concentrations. This leads to the corrosion of electrode materials after the repeated intercalation/deintercalation processes of metal ions into the electrode materials. It further results in the peeling of active components from the surface of the current collector, which drastically reduces the charge storage capability of supercapacitors [86]. On the other hand, the neutral electrolytes, however, are less corrosive; they exhibit lower electrochemical performance when compared to the acid and alkali electrolytes due to the relatively lower ionic conductivity. In addition, the solubility of neutral salts is comparatively limited to that of acids and alkalis, which further restricts the attainment of higher concentrations resulting in lower ionic conductivity.

5.2. Conventional Nonaqueous Electrolytes

In the nonaqueous electrolytes, the conductive salts are dissolved in the organic solvents. In general, the salts consist of metal cations/organic ammonium ions and perchlorate/fluoride-containing inorganic/organic anions [87]. They include LiClO₄, NaPF₆, tetraethyl tetrafluoroborate (TEA BF₄), and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI). The acetonitrile or carbonate-containing organic solvents, such as ethylene carbonate (EC), propylene carbonate (PC), and dimethyl/diethyl carbonate (DMC/DEC), are used as electrolyte media. The concentration of salts in the nonaqueous electrolytes varies in the range of 0.5 to 1.5 M in a single or a mixture of the abovementioned solvents. Due to the lower solubility of these salts in the organic solvents, the ionic conductivity of the non-aqueous electrolyte is lower than that of its aqueous counterparts. However, the ESW of non-aqueous electrolytes is usually higher in the range of 2.5 to 2.8 V because of the higher electrochemical stability of organic solvents. It subsequently increases the operational potential range of supercapacitors, thereby increasing the energy and power densities. The actual ESW of nonaqueous electrolytes depends on the nature of conductive salt, organic solvent, and the amount of water contamination [81]. Conductive salts play a significant role in determining the electrochemical performances of the nonaqueous electrolyte. An ideal salt for the nonaqueous electrolyte should have higher ionic conductivity, solubility, chemical stability, and lower cost. The organic ammonium salt of TEA BF₄ is a widely used conductive salt for commercial supercapacitors. The common trend of ionic conductivities of organic ammonium cations and fluoro-/chloro-containing anions are as follows: tetramethyl ammonium ion < tetra butyl ammonium ion < tetra propyl ammonium ion < tetraethyl ammonium ion and $CF_3SO_3^- < CIO_4^- < PF_4^- <$ BF₄⁻, respectively. In order to increase the solubility of conductive salts, the organic ammonium salts are asymmetrically substituted with different alkyl groups as well as cyclic aromatic groups. The triethyl methyl ammonium and 1-ethyl-1-methypyrrolidium tetrafluoroborate are a few examples of asymmetrical organic ammonium salts. The symmetrical and asymmetrical organic ammonium ions with bis(oxalate)borate anions also show higher solubility in organic solvents. In addition to ammonium salts, a symmetrically substituted phosphonium salt, namely, tetrakis(diethylamino)-phosphonium hexafluorophosphate exhibits better solubility and higher ESW of 3.2 V in acetonitrile solvent with the concentration of 1 M.

Like conductive salts, organic solvents, too, should have better physical and chemical properties to attain highperforming nonaqueous electrolytes. A suitable organic solvent must possess high electrochemical stability, a higher boiling point, lower viscosity, and a lower freezing point. Among various organic solvents available, acetonitrile and propylene carbonate are widely utilized solvents for nonaqueous electrolytes [38]. Acetonitrile has a higher dielectric constant and lower viscosity when compared to propylene carbonate. The acetonitrile-containing nonaqueous electrolytes have better ionic conductivity than that propylene carbonate. However, the higher flash point and lower toxicity are the advantages of propylene carbonate-containing electrolytes. Both the organic solvents can be used in the operational potential window of 2.5 to 2.8 V. The other organic solvents, namely, fluoroacetonitrile, adiponitrile, propionitrile, butylene carbonate, fluoroethylene, and ethyl isopropyl sulfone, are also utilized as they have a higher boiling point and electrochemical stability. The ionic conductivities of nonagueous electrolytes are further increased by employing a mixture of organic solvents. The blending of two or more organic solvents in different ratios considerably lowers the viscosity as well. Mixed organic solvents such as propylene carbonate-trimethylene carbonate, ethylene carbonate-propylene carbonate, and fluoro propylene carbonatepropylene carbonate are commonly used binary organic solvents. The organic additives based on sulfites (diethyl sulfite and 1,3-propylene sulfite), esters (methyl acetate, ethyl acetate, and methyl formate), and aromatic fluorobenzenes (1,3,5-tri fluorobenzene) are often mixed with nonaqueous electrolytes to improve their electrochemical performances. In addition to higher EWS, the nonagueous electrolytes are capable of operating in a wide temperature range of 60 to -40 °C. Since the nonaqueous electrolytes could be operated even at -40 °C, they are highly preferred in commercial device manufacturing, including high-end applications such as spacerelated devices [89].

Though nonaqueous electrolytes have several superior properties, they have a few drawbacks as well. The lower ionic conductivity is a major issue with these electrolytes. The concentration and the degree of dissociation of salts, ionic mobility, size of conductive ions, and the type of organic solvents are the crucial factors that decide the performance of nonaqueous electrolytes [90][91]. In general, the organic salts have a lower degree of dissociation in organic solvents, which in turn affects the ion mobility and ionic conductivity. The degree of dissociation of salts further decreases at a lower temperature (<10 to -30 °C) in the organic solvents, and it reduces the ionic conductivity of the nonaqueous electrolytes, which are intended to work at sub-zero temperatures [92]. The electrochemically induced decomposition of organic groups at electrodes is another drawback with nonaqueous electrolytes. The salts with organic cation (TEA) or anion (TFSI) have the possibility of electrochemical decomposition over time, depending on the chemical potential of the current collector. The carbonate-containing organic solvents (EC, DMC, or DEC) also have more chance of decomposition, followed by the evolution of carbon mono/dioxide gases while going through several charging/discharging cycles [93]. In addition, the presence of impurities, such as water, considerably lowers the performance of these electrolytes. If any trace amount of water is present, it decomposes at the electrode and releases hydrogen and oxygen, as the operational potential window of nonaqueous supercapacitors is larger than that of the water decomposition potential (1.23 V). Therefore, the construction of commercial supercapacitors is usually performed under an inert atmosphere (argon or nitrogen) via a glove box set-up to avoid any moisture contaminations.

5.3. Unconventional Electrolytes

In liquid electrolyte systems, the molten salts (ionic liquids, ILs), superconcentrated salt solutions (water-in-salt, WIS), and deep-eutectic solvents (DES)-based electrolytes have attracted a lot of interest due to their higher operating potential window and lower freezing point, which are essential for the high energy density and superior electrochemical performances at sub-zero temperatures. The ionic liquids are molten salts comprising organic cations and organic/inorganic anions with melting points below 100 °C ^[94]. They have high chemical and thermal stabilities, very low volatility, and non-flammability. Furthermore, based on the type of cations and anions, the properties of the ionic liquids can be tuned easily. The typical cations include ammonium, imidazolium, sulfonium, pyrrolidinium, and phosphonium ions, and the hexafluorophosphate, tetrafluoroborate, bis(trifluoromethane sulfonyl)imide and bis(fluorosulfonyl)imide are the commonly used anions for the ILs [95]. When compared to the conventional organic electrolytes, the ILs have a higher electrochemical stability window, more than 3 V, due to higher resistance towards the decomposition. However, ILs possess many downsides, namely low ionic conductivity and high viscosity. For example, the 1-ethyl-3-methylimidazolium (EMIM)-based ILs show a higher ionic conductivity of ~ 14 mS cm⁻¹ among the other ILs, which is four-fold lower than that of an organic electrolyte at 25 °C (TEABF₄ in acetonitrile) ^[96]. Similarly, the EMIM BF₄ has a viscosity of 41 centipoise, which is very high when compared to the acetonitrile-based electrolytes (0.3 centipoises). The higher viscosity and lower ionic conductivity eventually increase the charge transfer resistance that subsequently reduces the rate performance of the supercapacitor. However, the proper chemical design can overcome these limitations to a considerable extent. For example, a tetracyanoborate (TCB)-based IL, such as EMIM TCB, shows a relatively higher ionic conductivity and low viscosity of 1.3×10^{-2} S cm⁻¹ and 22 cp, respectively [97]. In addition, the other widely used cations and anions for ILs are categorized as N-substituted azepanium-, propylpiperidinium- and 1-methoxymethyl-1methylpyrrolidium- for the former and the dicyanamide, bis(fluoro sulfonyl)imide, and tris(pentafluoroethyl) trifluorophosphate for the latter.

The WIS-based electrolytes are preferable among the various unconventional electrolytes due to their higher electrochemically stable potential window, environmental friendliness, and flame retardancy ^[98]. In general, the WIS electrolytes are highly concentrated salt solutions with the usual concentration range of 17 molal (m) to 33 m. The commonly used salts for the WIS electrolytes are LiTFSI (21 m), $ZnCl_2$ (30 m), $LiNO_3$ (22 m), $NaClO_4$ (17 m), $NaNO_3$ (12 m), and ammonium acetate (30 m) ^[99]. The WIS electrolyte with a mixture of two or more salts is also developed to obtain high-performance electrolytes. In particular, the ESW range of WIS electrolytes, which depends on the number of free water molecules, is increased by the mixture of salts containing common cations or anions ^[100]. The additional cations or anions coordinate with the free water molecules that constantly decompose on the electrode surface when the operating potential window crosses the water decomposition voltage (1.23 V vs. NHE), and it subsequently increases the ESW. For example, the ESW of 21 m LiTFSI electrolyte (<3 V) is increased beyond 3.1 V upon the addition of lithium triflate (7 m) ^[101]. Similarly, the mixed WIS electrolyte consisting of tetraethyl triflate (22 m) and sodium triflate (9 m) salts exhibits a wider ESW of 3.3 V that is eventually higher than that of individual salt solutions ^[102].

DES-based electrolytes are another alternative with higher ESW, low volatility, and non-flammability towards highperformance supercapacitor devices ^[103]. The DES is generally a mixture of two components with a certain mole ratio, and furthermore, it exists in a liquid phase due to a lower melting point than that of its individual components. The stronger intermolecular interactions such as hydrogen bonding, Lewis acid-Lewis base interactions, and van der Waals forces among the cation/anion and the functional groups of the organic component lead to the complex amorphous network-like structures that effectively prevent the solidification of solids [104]. In particular, the DES electrolytes achieved from the mixture of salt (metal chloride, perchlorate, sulfonamide, and ammonium/quaternary salts) and a small organic molecule with functional groups such as -OH, -C=O or -N-H are majorly stabilized with very strong hydrogen bonding interactions (~4 kJ mol⁻¹). Similarly, the mixture of electron-deficient molecules (BF₃ or AICl₃; Lewis acid) with another molecule-having electron-donating functional group (-O-, -C=O, -O-CO-O- or -N-H: Lewis base) also forms DES electrolyte, due to the Lewis acid–Lewis base interactions (~4 to >100 kJ mol⁻¹). Though the interaction energy of van der Waals forces is relatively weak (0.4 to <4 kJ mol⁻¹), they also rarely participate in the formation of DES electrolytes. The common salts employed for DES electrolytes are LiTFSI, LiClO₄, lithium difluoro(oxalato)borate, zinc perchlorate, and the functional molecules as urea, acetamide, Nsubstituted acetamide, thiourea, choline chloride, and so on. Like ionic liquids, DES electrolytes suffer lower ionic conductivity and higher viscosity. The DES electrolyte of LiTFSI: N-methyl acetamide shows an ionic conductivity of 1.35 ms cm⁻¹ and a viscosity of 78 mPa.s at 25 °C, though the ESW is high, at 4.7–5.3 V ^[105]. Furthermore, the physicochemical properties of DES electrolytes are improved by adding a fraction of water, or other organic solvents (acetonitrile or propylene carbonate) that decrease the viscosity and improve the conductivity through the ESW are slightly traded-off. The addition of 30% of water to the dual-salt DES electrolyte of urea, LiTFSI, and $Zn(TFSI)_2$ improves the conductivity to 1.85 ms cm⁻¹ from the lower value of 0.084 ms cm⁻¹, and subsequently leads to the lower viscosity of 0.139 Pa·s [106].

6. Separators

In addition to electrode and electrolyte materials, separators [107] with higher physical strength, ion permeability, and thermal and chemical stabilities are crucial for high-performance supercapacitors [108]. In the two-electrode cell and commercial supercapacitors, the separator plays a significant role in preventing any short circuit by the physical contact of positive and negative electrodes throughout the lifecycle of the device and, at the same time, it allows the free flow of ions across it [109]. Any damage to the separator component leads to the catastrophic collapse of the supercapacitor performance. A typical membrane separator should possess a low thickness, high dielectric constant, electrochemical stability, ionic mobility, macroporosity, and electrolyte wettability. Several varieties of separators are commonly used for supercapacitors that include polymer membrane-based separators, paper-based separators, and inorganic/ceramic separators. Synthetic techniques such as electro-spinning, phase inversion, and 3D printing methods are generally utilized approaches for the preparation of separators [110]. The polymer membrane-based separators are highly preferable for supercapacitors due to their low cost and higher physical and chemical stabilities. Polypropylene (commercially known as 'Celgard', a widely used separator for supercapacitors), poly(vinylidene fluoride), poly(vinyl chloride), and poly(ethylene oxide) are a few examples of polymer-based membrane separators. Based on the type of electrolyte systems (aqueous/nonaqueous), the selection of membrane separator varies; for example, the poly(vinylidene fluoride) or a copolymer of vinylidene fluoride and hexafluoropropylene is used for the organic electrolytes. However, the polymer-based separators suffer from a lower dielectric constant, which is crucial for attaining higher power and energy densities. Incorporation of ceramic materials, which inherently have a higher dielectric constant and ionic conductivity, improves the electrochemical performances of the polymer-based separators. For example, a ceramic material such as titanium dioxide is added to the poly(vinylalcohol) to improve the ionic conductivity, porosity and mechanical strength ^[111]. Similarly, the poly(vinyl butyral) with 1D aluminum oxide nanorod exhibits high porosity, high strength of >30 MPa, thermal stability up to 200 °C, electrolyte uptake of >200 wt% without swelling, and ionic conductivity of ~14 mS cm⁻¹ ^[112]. In addition to synthetic polymers, the biopolymer ^[113] (cellulose and its derivatives) and bio-membranes such as egg-shell-based materials ^[114] are also employed as separators for the supercapacitors. The paper-based separators derived from natural cellulose resources are highly preferred for large-scale fabrications, even with organic solvents, due to high porosity and mechanical stability ^{[115][116]}.

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