Emergent Materials (2020) 3:347–367
https://doi.org/10.1007/s42247-020-00090-5

REVIEW

Journey from supercapacitors to supercapatteries: recent advancements in electrochemical energy storage systems

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Received: 9 June 2019 / Accepted: 20 March 2020 / Published online: 13 May 2020

Abstract

Generation, storage, and utilization of most usable form, viz., electrical energy by renewable as well as sustainable protocol are the key challenges of today's fast progressing society. This crisis has led to prompt developments in electrochemical energy storage devices embraced on batteries, supercapacitors, and fuel cells. Vast research and development are being executed worldwide on each of these systems. Although fuel cells and batteries possess higher energy density but excessive installation cost, bulkiness, low power capabilities, and short life time are major limitations till date. The performances of supercapacitors at present lie in-between these batteries and conventional capacitors, hence serve as supporting or secondary devices for uninterrupted power supply systems. Nonetheless, supercapacitors possess some indigenous qualities such as light weight, easy portability, high cycle life, and low maintenance requirement with the potentiality for high specific and energy densities. These attractive features have proposed scientific challenges that have promoted the urge for replacing conventional massive, low-lasting batteries. In recent past, nano-composite materials have been developed with improved energy density to replace the "first-generation supercaps." Moreover, hybridizing with high energy battery materials can successfully solve the existing limitation of the available supercapacitors without sacrificing their cycling performances substantially. Thus, a novel concept of "supercapatteries" (supercapacitors + batteries) has emerged combining the merits of the charge storage mechanisms of both batteries and electrochemical capacitors so as to attain improved electrochemical performances. At the same time, scientists are trying to pursue cost effective designing methods without compromising with device efficiencies. The paper outlines the progress of supercapacitor technology with special emphasis on the tuning of nature, composition, electronic, and structural designing of electrode materials and electrolytes, cell fabrication along with other related parameters that may assist in enhancing the overall electrochemical device performances.

Keywords Supercapatteries · Electrochemical energy storage · Supercapacitors · Electrode materials · Electrolytes · Nano-morphology

1 Introduction

Adverse environmental impacts of present day fossil fuels along with their restricted accessibility have stimulated serious concerns leading to extensive research to focus on discovering adequate alternatives of energy storage and conversion from various renewable as well as sustainable energy sources [1, 2]. In this circumstance, developments in electrochemical energy storage (EES) devices are enormously significant to store the electrical energy when generated in excess and to meet the ever rising demands of non-stop energy delivery [3, 4]. Till date, heavy weight and voluminous batteries are the primarily accepted and extensively employed electrochemical energy storage devices owing to their unique capability to provide high energy density (energy stored per unit volume)/specific energy (energy stored per unit mass) (30–300 Wh kg^{-1}) [4–6]. However, short life span, low specific power, pollution, and toxicity issues especially regarding their recycling and disposal after usage are the main drawbacks. But, lack of appropriate alternatives is the main cause for overlooking their

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shortcomings today. Even the high energy density offering fuel cell technology although has less environmental impacts, their bulkiness, high installation charges, and inadequate storage of fuels are major limitations for large scale applications. On the converse, conventional capacitors exhibit substandard specific energy values although they have appreciable specific power (energy delivered per unit time per unit mass)/ power density (energy delivered per unit time per unit volume) and cycle life. The performances of current supercapacitors lie in between these capacitors and batteries [6]. Thus, featherweight, flexible, portable, robust, smart supercapacitors with high specific energy and power values are in the continual search in order to substitute the conventional massive, low responsive, low-lasting rechargeable batteries soon.

Pin-point strategies for overcoming the low energy density/specific energy of supercapacitors without sacrificing their high power density/specific power and excellent cyclability have been one of the most thrusted areas of research [7, 8]. Scientists are aiming to tune the value of energy density to reach the value close to that of smart batteries [9, 10]. On the converse, extensive works are being carried out to improve the power densities of the existing batteries too [11, 12]. This has urged in delivering next generation EES with high energy density and power density for example by hybridizing the supercapacitor materials like nano-carbons with battery materials like nano-metal oxides or conducting polymers or combination of supercapacitor electrode with a battery electrode, etc. The devices of such hybrid materials or combined electrodes are now popularly called as "supercapatteries." They are expected to have the best properties of both supercapacitors and batteries.

In order to highlight the various efforts undertaken for achieving the goal, the fundamental working principles of a supercapacitor needs to be briefed initially and subsequently compared with those of batteries followed by the features/ parameters that correlate the device performance. Besides, strategies have been reviewed to emphasize on the ways by which the energy density/specific energy can be improved from the existing generation-I supercapacitors to one that they can be employed as principal EES for every days practical applications in the near future.

2 Supercapacitors: elementary facts

Improved electrochemical capacitors are also renowned "supercapacitors" or ultracapacitors have been accredited great importance due to their higher power density/ specific power compared to batteries and higher energy density/ specific energy compared to conventional capacitors along with a long cycle characteristics and improved energy-use efficacy [3, 4]. The progress of supercapacitors technology is rather interesting [13]. Around middle of 1800 AD, ideas of energy storage in the form of lead acid batteries came through the hands of French physicist Gaston Planté. Since then, many upgrading in battery sectors such as from dry cells to Ni-Cd batteries to Lead-storage batteries and so on has been carried both in theoretical sector as well as in technological aspects in that period. In 1950s, general electrical engineers started employing porous carbon electrodes for devising capacitors. H. Becker in 1957 prepared a "low-voltage electrolytic capacitor" based on porous carbon electrodes. Standard Oil of Ohio (SOHIO) Company in 1966 initially developed "electrical energy storage apparatus," followed by electrochemical capacitor with activated carbon electrodes first patented by Donald L Boosin in the year 1970. Famous Scientist, B E Conway in 1980s executed systematic research on RuO_2 based electrochemical capacitors and delineated "supercapacitor" and "battery" basic characteristics. It was in 1982 Pinnacle Research Institute (PRI) marketed the most primitive supercapacitor for military applications commercialized under the name "PRI Ultracapacitor." Ever since 1990s, Maxwell Laboratories (afterward Maxwell Technologies) introduced "Boost Caps" to address their high-power utilizations [14]. At present, supercapacitor companies from all around the globe such as Nesscap (Korea), Nippon Chemicon (Japan), ELTON (Russia) and CAP-XX (Australia), etc., are developing and marketing various models of supercapacitors for desired applications.

A typical supercapacitor (as shown in Fig. 1a) is composed of the following units: two large surface area based porous electrodes—positrode (positive electrode) and negatrode (negative electrode), ionically connected by electrolytes separated by a porous electrolyte-filled membrane. The electrodes have been named on the basis of their electrical polarities. Thus, the positive electrode carries higher or more positive potential than the negative electrode and thus current always flows from the positive to the negative electrode via the external circuit while the electrons flow in the reverse path. Since, charging and discharging are important phenomena in these charge storage devices, the above electrode terminologies helps in avoiding erroneous derivation that occur while using "anode" and "cathode" terminologies [16]. On applying voltage, the electrodes get polarized and the anions of the electrolyte form electrical double layers on the positrode while the cations form double layer on the surface of negatrode respectively at the electrode/electrolyte interface [15, 17].

In general, supercapacitors can be categorized on the basis of energy storage mechanism into two types, namely, electrical double layer capacitors (EDLCs) and pseudocapacitors respectively as depicted in Fig. 1b [15]. The EDLC-type materials store charge via ion adsorption/desorption process at the electrode/electrolyte interfaces. The electrochemically stable, high surface area-based carbon materials are commonly categorized under EDLC materials [18]. Gogotsi and co-

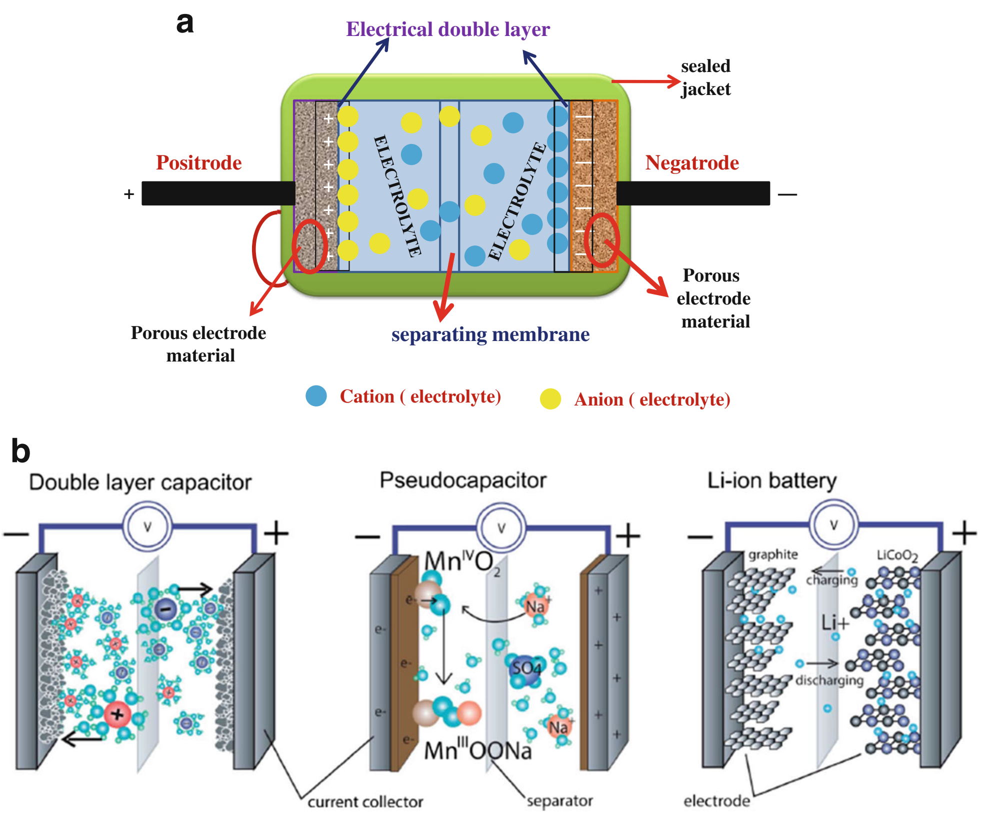

Fig. 1 **a** Schematic representation of a typical supercapacitor setup. **b** Representation of charge storage mechanism in supercapacitors (EDLC and pseudocapacitor systems) and Li-ion rechargeable battery, respectively (reprinted with permission from [15])

researchers further demonstrated that un-solvated ions are primarily responsible for charge storage in double-layer electrodes [19]. They explained the cause of large capacitance values in carbide-derived carbons (pseudocapacitors) with < 1 nm pore size owing to diffusion of de-solvated electrolyte ions through those ultra-micropores, and correlated with ion diffusion in battery electrode systems, where charge introduced through electron injection in bulk-electro-active phase gets compensated by the diffusion of de-solvated ions into its vacant lattice sites resulting in enhanced energy density [19, 20]. On the other hand, as defined by Prof. Conway group, fast, reversible surface-based faradaic reactions are responsible for charge storage in pseudocapacitor materials in comparison to batteries that engage bulk phase redox reactions and thus publish relatively slow redox kinetics [15, 20].

Extensive detailed research works consequently established that material dimensions, nature of surfaces, crystalline phases, interfaces often initiate pseudocapacitive contribution in the charge storage process in many materials that show battery type behavior (i.e., non-capacitive faradaic redox reactions) in bulk [21, 22]. As a consequence, margin between battery and pseudocapacitive materials are fast obscuring in recent days [23]. New terminologies related to pseudocapacitance classes such as “intercalation,” “redox,” and “under potential deposition” types have emerged to describe the charge storage mechanisms kinetic analysis in the emerging pseudocapacitive electrode materials, as depicted in the Fig. 2 [24]:

Intercalation pseudocapacitance is typically observed in non-aqueous electrolyte system when electrolyte ions intercalate into the channels or porous layers of the electrode material characterized by faradaic charge transfer (battery-type) with indistinct crystallographic phase modifications [21, 24]. Thus, advent of “intercalation pseudocapacitance” has significantly broadened the family of pseudocapacitive materials in last few years. Nano-systems of layered Ni $(OH)_2$ and its analogues, intercalation-type nano-TiO_2, MoO_3, Nb_2O_5, etc. are observed to belong into this category and are also often now-a-days referred to as “extrinsic pseudocapacitors” [24–27]. On the other hand, “redox pseudocapacitance,” mostly observed in aqueous electrolytes, involves faradaic charge transfer reaction with the electrochemically absorbed electrolyte ions onto near-surface of electrode materials such as MnO_2, RuO_2, majority of the metal-based chalcogenides, conducting polymers and their composites. They are often referred to as “intrinsic pseudocapacitive materials” in the literature [18, 24, 28]. Again, “under-potential deposition” pseudocapacitive mechanism is followed when one type of metal ions form an adsorbed monolayer on a different metal’s surface well above their redox potential. For example, Pb, Au, Hg layers formed on the surface of a gold electrode illustrates “pseudocapacitive under-potential deposition” process [29]. The charge storing

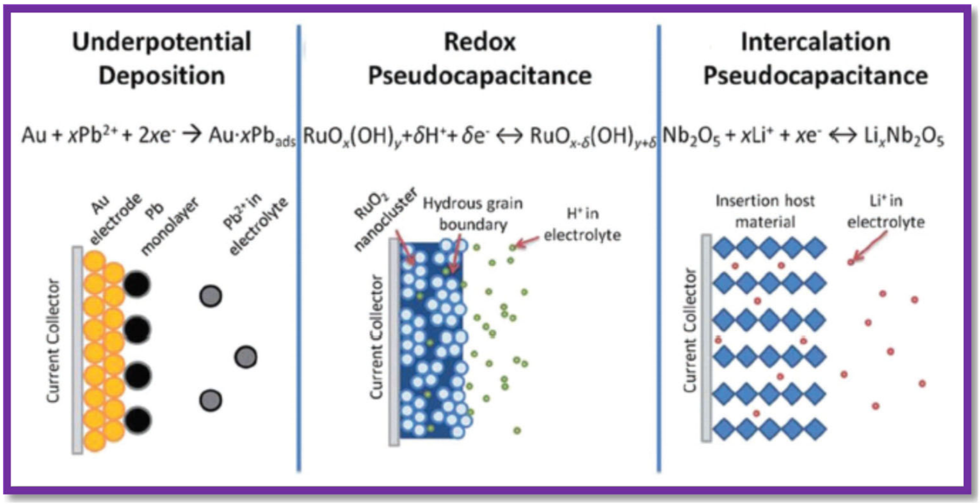

Fig. 2 Different types of reversible redox mechanisms that lead to pseudocapacitance behavior (reprinted with permission from [24])

process mainly occurs on the electrode/electrolyte interface that guarantees rapid charging and discharging kinetics and high power density in supercapacitors. The abovementioned charge storing mechanisms can operate simultaneously in many situations, depending upon the electrode–electrolyte material employed in the device [30–32].

In this regard, it is worth to delineate the mechanism of energy storage between pseudocapacitors and batteries. Pseudocapacitors involve rapid, non-diffusion controlled, surface-based electrochemical reactions with gradual and very slow as well as reversible overall phase transformation processes. The battery materials on the converse store charge within crystal lattices or porous systems via slower electrochemical reactions accompanied by rapid and distinct phase transformation, chemical modifications along with reactant-product diffusions. Thus, both of these electrochemical energy storage (EES) systems employ porous electrodes with large internal surface area for high ion-adsorption or/and surface-based Faraday reaction for faster reaction kinetics [33–35]. However, Ohmic drop in electrodes, as well as low mass transfer rate reduces the effective internal-area at high current densities [36]. The pore size distribution in a porous electrode in this regard plays a crucial role in designating the electrode characteristics [19]. It has been reported that only the micropores (of diameter less than 2 nm) can provide the largest internal specific surface area compared to mesopores (2–50 nm) and macro-pores (> 50 nm). Thus, for EDLCs, the charge storage mechanisms rely mostly on the fast adsorption/ desorption of the solvated electrolyte ions in the mesopores while pseudocapacitance and battery-type signatures arise due to slower intercalation/de-intercalation of smaller de-solvated ions or electro-active molecules in the micropores ensuing faradaic electrochemical reactions [37]. Consequently, for full utilization of the inner surface area of the micropores so as to achieve high energy density, high density of micropores are required to be designed that may lead to high energy battery-type electrodes. However, reduced pore-size slower down the kinetics of charge storage and hence lowers the device efficiency. Hence, optimization of pore-dimension distribution is essential to attain desired energy density without compromising with power density [38–40]. At this point, nano -science and nanotechnology, plays a vital role as nano-dimensions increases the surface to bulk reactivity and thus modify the existing definitions of EES materials.

Electrochemical energy storage (EES) efficiency of the above mentioned devices is guided by two important parameters, namely, specific energy or energy density and specific power or power density, respectively, denoted by the following equations [7, 15]:

$$\text{Specific energy}(E) = \frac{1}{2}C(\Delta V)^2 \tag{1}$$

$$\text{Specific power }(P) = (E/\Delta t) \tag{2}$$

where C is the specific capacitance, ΔV is the voltage window, and Δt is the discharge time respectively. Generally large values of these parameters are ideally recognized for high performance supercapacitors. Power densities and energy densities are obtained based on unit volume of the electrode material instead of its mass used in above relations [41].

In addition, a number of other essential parameters such as stable and large galvanostatic charging/discharging cycle numbers, high specific capacitance retention efficiency at varying current densities as well as at different potential scan rates and electrochemical steadiness over wide potential window and wider working temperature range are also analyzed [42, 43].

Electrochemical performances of electrodes are generally determined by cyclic voltammetry (CV), galvanostatic current charging-discharging experiments (GCD), and electrochemical impedance spectroscopy (EIS) respectively [32, 42–45]. A three-electrode cell setup is used in carrying out the above characterization experiments which comprises of working electrode, counter electrode and reference electrode respectively as shown in Fig. 3a.

Generally, CVs of EDLC-type materials display typical rectangular shape as depicted in Fig. 3b (red, dotted curve) while that for battery-type and pseudocapacitors exhibit pronounced redox peaks which remain well separated for the former (Fig. 3b, green, dashed-line curve) while in the latter, the red-ox peaks are broad and diffused (Fig. 3c, violet, bold curve) [45]. However, for the pseudocapacitors, in general, the separation of the broadened redox peaks is narrower ($< 0.059/nV$) even at a high scan rate indicating high reversibility compared to batteries where the separation of peak potential varies in a range ~ 0.1–0.2 V owing to complex factors such as diffusion-controlled processes, electrochemical irreversibility and bulk phase transition processes, etc. [46]. It can be rationalized that owing to much slower mass transport kinetics in the micropores of battery-type electrodes compared to the bulk electrolyte, the current versus voltage curves have diffusion-limiting current plateau at a steady state measurement, which are quite distinct from that of capacitor.

From CV, one can calculate specific capacitance (C_s) of EDLC and pseudocapacitor materials using the following equations:

$$\mathrm{Cs} = \left(\frac{1}{ms}\right)(\Delta \mathrm{V})\int_{V1}^{Vn} idV \qquad (3)$$

where $\int (idV)$ is the integrated area of the CV curve, s is the potential scan rate ($\mathrm{V\ s^{-1}}$), ΔV is the voltage window, V_n and V_1 are the extreme limiting values of voltage scans, and "m" is the active electrode materials mass on both electrodes (g). The common unit of gravimetric capacitance is "$\mathrm{F\ g^{-1}}$." Similarly, areal and volumetric capacitances also can be determined in terms of "$\mathrm{F\ cm^{-2}}$" and "$\mathrm{F\ cm^{-3}}$,"respectively [47]. The capacitance thus obtained from the above equations is associated with potential scan rate, discharge rate, and operating frequency [48]. The value of capacitance obtained for a 3-electrode cell is actually the value of the working electrode only while that for a 2-electrode cell is contributed by two electrodes connected in series and hence the corresponding masses and volumes should be accordingly considered so as to obtain the consequent performances accurately [45].

Galvanostatic charging-discharging (GCD) experiments measured also accomplish values of specific capacitance (C_s) of the electrode material in a similar cell setup following the Eq. (4), considering the same notations of the terms used above [32, 42–45]:

$$\mathrm{Cs\ (wt)} = \frac{\boldsymbol{I}}{\boldsymbol{m}\ (\Delta \boldsymbol{V}/\Delta \boldsymbol{t}))} \qquad (4)$$

where I is the constant current applied for the measurement of the GCD. The experiment also helps in illustrating the stability of the electrode for large cycle numbers in particular working potential windows under fixed current densities. The typical

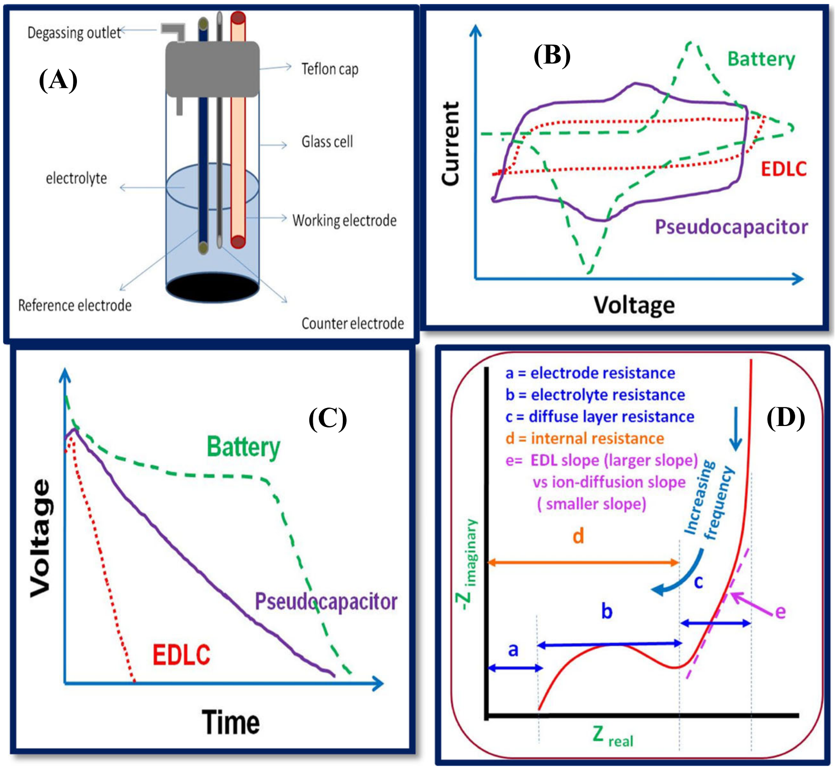

Fig. 3 **a** A typical 3-electrode cell set-up for carrying out electrochemical characterization experiment. **b** Typical cyclic voltammograms of EDLC (red curve), pseudocapacitor (violet), and battery (green). **c** Typical galvanostatic discharge plots of EDLC (red, curve 1), pseudocapacitor (black, curve 2), and battery (blue, curve 3). **d** Nyquist plot for a typical supercapacitor electrode material

characteristics of GCD curves are highlighted in Fig. 3b. Both EDLC (red, dotted curve) and pseudocapacitors (violet, bold curve) exhibit linear voltage versus discharge time relationship at a constant discharge current although the former has a sharper slope than the latter due to its smaller capacitance and shorter discharge time. Batteries (green, dashed-line curve) on the other hand normally exhibit constant voltage for an appreciable period of time during charging or discharging process and then drop suddenly owing to phase transformation phenomena [4, 49].

Supercapacitors are differentiated from batteries based on their operational characteristics: (a) charge–discharge response times that may be as fast as in the order of few seconds compared to long hours for batteries; (b) sloping and symmetric nature of GCD profiles; (c) generally high cycle life (> 10,000 or more, which of course depends on the purpose of application) compared to conventional batteries (500–1000 cycles) [50–52].

EIS is another technique to characterize batteries and supercapacitors using frequency as probe [53]. The measured impedance is represented as a Nyquist plot that contains three distinct segments—the intercept at the real axis (abscissa), semicircle in the high frequency area, and the linear part in the low frequencies region. Nyquist plots (in Fig. 3d) can also be employed to understand the charge transfer kinetics in EDLC, pseudocapacitors, and battery materials successfully adjoined with the above electrochemical studies [54]. Corresponding fitting Nyquist curves based on the circuit model with constant phase elements (Z_{CPE}) and series of resistors provide information about charge transfer resistance, double-layer capacitance connected in parallel configuration and diffusion process at low frequency application (CPE_w). The Z_{CPE} follows the equation: $Z_{CPE} = [T_{CPE}\ (i\omega)^n]^{-1}$,where n and T_{CPE} are the CPE exponents and coefficients, respectively. The ω refers to the angular frequency and $i = (-1)^{1/2}$. CPE exponential value of ~ 1 represents an ideal capacitive behavior.

Most of the typical EDLCs are expected to display vertical (~ 90°) straight line (in the low frequency) region that starts from the real part (*Z*') axis without any semicircle (high-frequency region) as they are devoid of faradic and ion-diffusion processes. Since charging process occurs via electrical double-layer formation which has a fast kinetics, larger slope of the line in the low-frequency region is indicated while sluggish ion-diffusion limited process as typically shown by common battery materials display small slopes. However, many reported conventional EDLC materials such as various carbonaceous materials show small-semicircles owing to their surface-functional groups or/and doped redox-active heteroatoms that participate in faradic charge transfer processes [55, 56]. Pseudocapacitors, ideally, due to very fast surface-controlled Faradic reactions, should display very small semicircle, followed by a vertical line with phase angle of or less than ~90° due to capacitive behavior [57]. Again, a typical battery owing to phase transformation coupled with faradaic charge transfer process undergoes sluggish ion diffusion kinetics, and thus displays a much larger semicircle than a pseudocapacitor, followed by almost 45° aligned straight line [58, 59]. However, the actual results often vary and deviate depending upon the charge transfer kinetics of electrode/electrolyte interfaces [60].

One often uses a Ragone plot (Fig. 4) to evaluate the relative device performance of various electrochemical energy-storage systems by plotting the specific energy (in Wh kg^{-1}) values at different specific power (W kg^{-1}), both calculated in logarithmic forms of the fabricated device and then compare it with the performances available in the literature [61]. The currently existing EES systems exhibit much inferior performances compared to that hydrogen or gasoline combustion engine positioned in the upper right–hand side having very high energy density and power density[62–64]. However, only because of the non-renewable nature of the employed fossil fuels in these combustion engines and their adverse effects on the environment are triggering the urge for upgrading the qualities of the EES devices. The plot represents that the EDLCS and other symmetric supercapacitors bridge the gaps of power density and energy density between batteries, and conventional (solid-state and electrolytic) capacitors. Advent of nanomaterials and use of asymmetric electrode configurations in different electrolytes, especially in organic ionic electrolytes has considerably improved the performances. Hybrid materials composed of different nature but with complementary properties often offer synergic performances and improved activities than their individual components. In this connection, these modified systems bestowed with combined merits of supercapacitors and rechargeable batteries that are to be categorized under "supercapatteries" will surely open up better prospects in the near future [61].

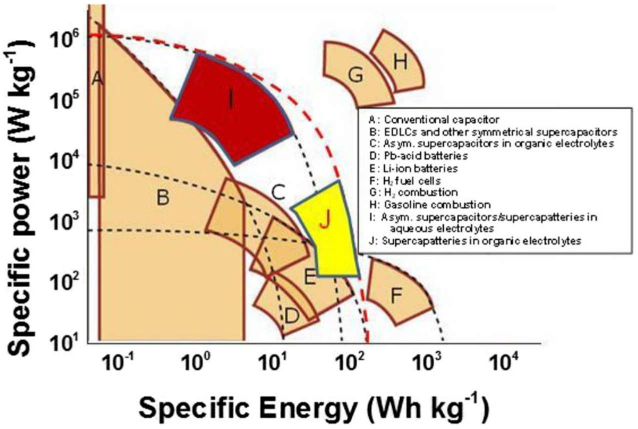

Fig. 4 A typical Ragone plot (reprinted with permission from [61])

3 Parameters controlling the performances of supercapacitors

A number of factors influence the efficiencies of supercapacitors that have been summarized in Fig. 5 and briefly outlined in the following paragraphs.

3.1 Electrode material

It is undoubtedly a serious mission to explore smart electrode materials for supercapacitors with outstanding electrochemical signatures. The elementary operational principle urges the electrode materials and electrolyte to have well-organized, smooth contacts, so that faster transport of ions/charges occurs in the bulk of electrode as well as at electrode-electrolyte interfaces in order to realize outstanding capacitances [16, 65, 66]. Both energy and power densities can be modified largely through judicious choice and designing of electrodes and electrolytic medium employed [67]. Thus, it is obvious that characteristics of the supercapacitors are essentially dictated by the electrode material and the electrolyte employed. Depending on the purpose of usage, the devising and designing of supercapacitors are done accordingly with suitable electrode materials [68]. For example, carbon-based nanomaterials including activated carbons, various 3D carbon nano-forms, meso-porous carbons, carbon nanofibers and nanotubes, functionalized graphenes, etc. store charge via EDLC-type mechanism that though exhibit low capacitance but can efficiently withstand large number of fast and stable charging/discharging cycles. [69]. On the other hand, pseudocapacitors display superior specific capacitance values compared to EDLCs although with lower charging/discharging efficiency [24, 70, 71]. Generally, transition metal based compounds and conducting polymers along with their derivatives exhibit characteristic pseudo-capacitance behavior because of tunable semi-conductor electronic structure, easily accessibility and varying multiple oxidation states [72–75]. Nevertheless, metal oxides and analogues are susceptible to environmental contaminations, undergoes huge volume fluctuations and irreversible phase transitions during GCD cycles The conducting polymer on the other hand are easily decomposed, and their solubility as well as processability have contributed to huge issue for commercialization. The fabrication design, crystalline/ amorphous phases, water content, morphology in various nano-dimensions plays important roles in determining the charge storing capabilities [76]. They are ideally planned so as to undergo minimal structural deformations during execution of large GCD cycles to signify good electrochemical reversibility. Sluggish ion transport kinetics and undesired volume/ phase changes in pseudocapacitive materials are considerably overcome using superior nanocomposite structural transformations and use of hybrid materials in many cases [77–80].

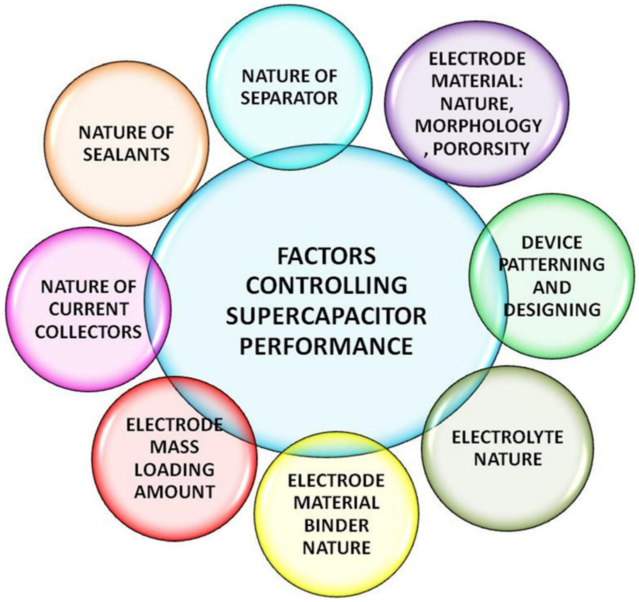

Fig. 5 Schematic representation of some of the important factors controlling the performance of supercapacitors

In the recent past, fundamental differences between pseudocapacitive and battery-type/non-capacitive electron transfer processes have been re-defined by the band model as illustrated in Fig. 6. Non-capacitive (battery-like) electron transfer process arise due to occurrence of significantly close energy states between localized redox active sites, as a result of which the electrons move among these different sites within a very small potential range leading to sharp and narrow peak-shaped cyclic voltammograms as shown in Fig. 6a [16, 65]. Such systems work well with Nernst Equation, provided surface concentration of reactants and products are considered at any instant of time during the reaction. Conversely, capacitive faradaic process involves continuous electron transfer over relatively wide voltage in semiconductor systems with delocalized electrons actively connected over a range of active redox sites forming a band of energy states [71]. Thus, a nearly invariant current over a wide potential window results in quasi-rectangular CV signature, characteristic for pseudocapacitors as represented in Fig. 6b [66].

Pseudocapacitive and battery materials can often be distinguished, from their quantitative kinetics analysis using Power law by considering the total CV current (**i**) as the combination of both adsorption/desorption (diffusion controlled and capacitive currents [5, 79].

$$\mathrm{i(V)} = \mathrm{k}_1\nu + \mathrm{k}_2\nu^{1/2} \tag{5}$$

where $k_1(\nu)$ and $k_2(\nu^{1/2})$ denote the capacitive current and adsorption/desorption current, respectively. The above equation is represented in a simplified form as follows:

$$\mathrm{i} = \mathrm{a}\nu^{\mathrm{m}} \tag{6}$$

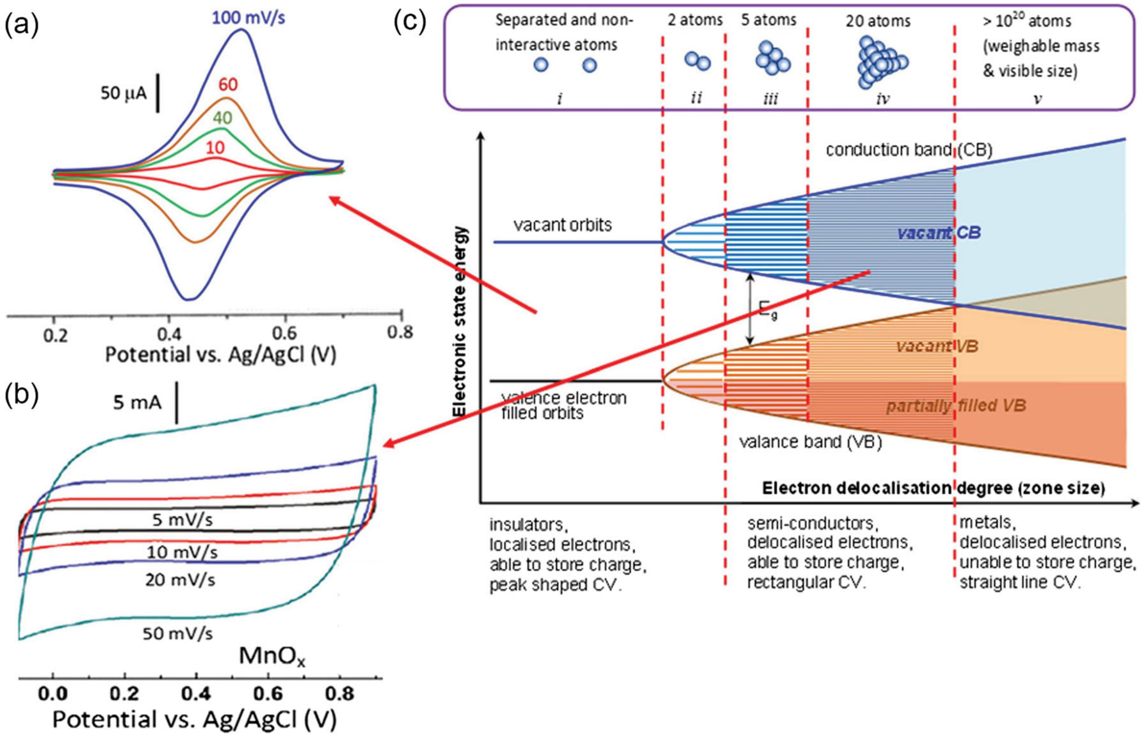

Fig. 6 Schematic representation of correlation of cyclic voltammograms based on relative nature of energy states for **a** non-capacitive and **b** capacitive electron transfer processes (reprinted with permission from [66] (open access))

where "a" and "m" are adjustable parameters and ν is potential scan rate (mV s^{-1}). The "m" value can be obtained from the slope of log(i) versus log(ν) plot at a fixed potential (V). Here, value of the "m" (0.5 or 1) explains two discrete behavior of the electrode material. For $m = 0.5$, the charge storage mechanism is dominated by faradic adsorption/desorption of ions from electrolyte to electrode, i.e., diffusion controlled process typical for battery type electrode materials while for $m = 1$ charge storage mechanism is mainly non-faradic capacitive or non-diffusive controlled process as commonly observed for EDLC electrode systems [79].

However, many nano-dimensional battery-type electrodes designed with specific electrode engineering and structural pattern, exhibit m value > 0.5 designating the fact that the therein occurring redox process is not purely ion-diffusion-controlled. Thus to get proper distinction between battery and pseudocapacitive materials, all the electrochemical signatures should be explored over a wide ranges of potential sweep rate and current densities. An ideal pseudocapacitive material should show invariant electrochemical signatures with material size or film thickness [24]. Correct interpretation of the meaning of "$m \sim 1$" highlight either a capacitive process (i.e., EDLC) or a process not limited by ion diffusion that may well possibly be because of small electrode dimension/ thickness with dominating surface process with very fast redox kinetics [24, 81]. In such cases, other electrochemical techniques such as EIS may side-by-side assist in determining the plausible mechanism of charge storage in these electrode materials. Thus, the concept of "pseudocapacitance" which was initially mentioned as "fast surface based faradaic reactions" have been re-defined as the phenomenon that originates from the transfer of partially delocalized valence electrons present in all semiconducting materials [66].

In the urge to enhance the specific capacitance and energy density of the devices, various pseudocapacitive materials including nano-structured transition metal oxides/chalcogenides/pnictogenides and analogous compounds, conducting polymers like polyaniline, polypyrrole, polythiophene and their derivatives, have been blended with carbon based EDLC materials to form their nano-composites and aimed to satisfy the criteria of achieving better device performances compared to pristine components through enhanced surface area, faster charge transport features, suitable pore size distribution characteristics, etc. [82]. It is amazing to find that among various metal oxides, RuO_2 shows the best result and accordingly various nano-composites of it have been designed to obtain superior product [42, 77]. However, this metal oxide is highly expensive and so mainly engaged in designing of micro-supercapacitors with high energy storage efficiencies that require low amount of electrode material [83–86]. Taking these facts into consideration, abundant, cost effective nano-composite materials with large surface area, ion-adsorption capacity, porosity, reversible multi-electron transfer properties, are ideal claimant for supercapacitor applications [84–87].

While designing electrode materials for high energy density factors, it is equally important to tune its characteristics that would promote smooth interfaces for restoring high power densities. The intrinsic conductivity and charge transport characteristics should be accordingly controlled through appropriate choice of blenders, binders, current collectors, additives, and electrolytes for supplying energy at high rates [88, 89].

It is worth to mention that for effective storage of massive amount of charge in short charging time, maximum utilization of electrode materials is very essential. Fast ionic as well as electronic transports are also extremely important in this regard. Nowadays, colloidal clusters systems are being employed that have effectively exhibited very high specific capacitances (~ 5000–10,000 F g^{-1}) [90]. Such colloidal materials are prepared using in situ electrochemical activation of transition metal salts and available rare earth metal salts in alkaline electrolyte using electrical bias [91, 92]. These systems employ multiple-electron faradaic redox reactions that result in ultrahigh specific capacitance much larger than one-electron capacitances as available in the literature. The authors emphasized on the fact that existence of multiple forms such as ion-clusters, colloidal ions, nano-sized matter principally influenced multi-electron transfer owing to presence of larger number of redox active sites that led to such high energy storing capacity. Therefore, these classes of electrode materials are expected to yield devices with high power as well as energy densities [90].

Nonetheless, the existing methods of electrode fabrication limit their electrochemical stabilities especially for large cycle numbers and therefore restrict their usage only to those set-ups that require momentary high energy and power density applications. Figure 7 depicts innovative designing strategies such as morphology modification, dimension control of electrode materials, composite formation approach, doping and functionalization, coating, and encapsulation procedures as well as electrolyte adaption to enhance the performance of upcoming next generation EES systems [93, 94].

3.2 Binder-free electrode designing

In the recent past, binder-free “super-cap” electrode morphologies are being designed to compete with the difficulties confronted with added binders such as Nafion, etc. traditionally employed today to hold these electrode materials tightly to current collector. Thus, rational designing of self-supported electrodes is a big challenge today [95, 96].

3.3 Mass loading of electrode materials and electrode thickness

Electro-active materials loading on the electrode (generally ~ 10 mg cm^{-2}) on the current collector is important for obtaining optimal specific capacitance [97, 98]. Higher loading may reduce the ion diffusion, charge transport and hence specific capacitance. Likewise, too small amount of the electrode material may also mislead electrode characteristics [99]. The thickness of an electrode also plays a vital role in the performance of a supercapacitor [100]. For a particular application like hybrid vehicles, the electrodes thickness should be of the order of less than 150 μm and the large fraction of micropores should be of diameter 10–20 A° [15]. Therefore, it is essential to consider the thickness of the electrode in relevance to its applicability. [101, 102]

3.4 Role of electrolytes

Proper choices of electrolytes are equally vital in order to widen the operating voltage window, lower equivalent series resistance, and increase charge transport of the system [103]. Aqueous electrolytes are advantageous owing to high-ionic conductivity, low cost, non-flammability, and for convenient assembly in air, in comparison to organic electrolytes, which are observed to be poor conductive, expensive, highly flammable and more eco-toxic. Neutral aqueous electrolytes however, hold lower production-cost, high ionic conductivity, and non-flammability along with eco-friendly properties are being promoted lately, but show narrow potential window, maximum of ~ 1.6 V. Several attempts have been tried to address the above limitation, by replacing aqueous electrolyte with organic or quasi-solid-state electrolyte to relieve their dissolution. Lately, gel polymer electrolyte with less water content based on polyvinyl alcohol (PVA) and LiCl have yielded appreciable results [104]. In the recent past, ionic liquids are being employed with appreciable wide voltage range as high as ~ 4 V (Table 1). The problems of self-discharge have been recently studied can be eliminated with proper choice of electrolytes [101]. Such problems can easily be overcome employing organic electrolytes and assembling device under moisture-free environment [116, 117].

3.5 Separators

Choice of suitable separators is based on its facilitation of easy permeability of ions and should on the other hand be insulating in nature. The separator materials must be inexpensive, chemically inert to maintain electrolyte’s stability and conductivity; more permeable to

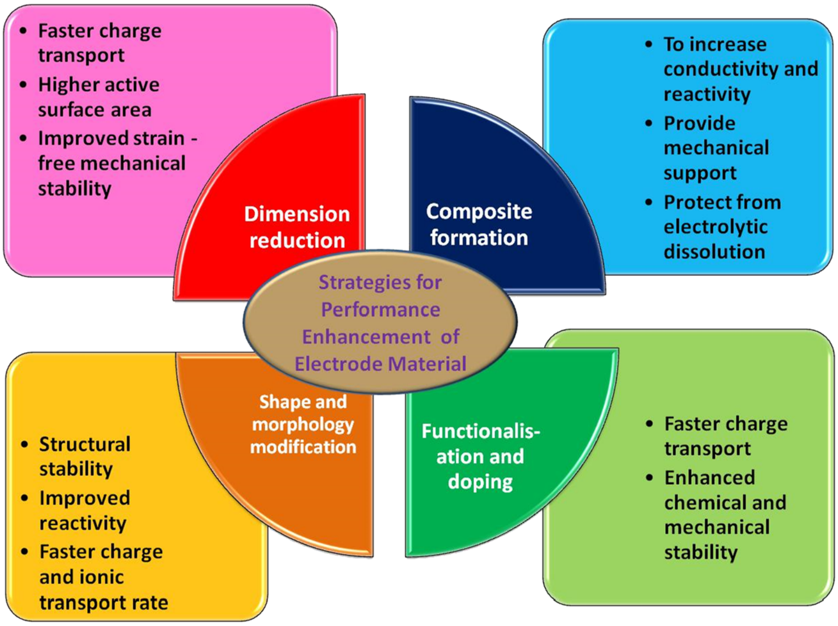

Fig. 7 Generalized strategies for performance enhancement of electrode materials for EES systems

electrolyte ion with least ionic resistance; minimum swelling, appreciably mechanical resistant to pressure or volume fluctuations; easily wetted by electrolytes. Moreover, it should not introduce any undesirable interference to the work environment, such as humidity, gases, and especially air that are often susceptible towards getting trapped into the pores. Filtration papers to polymer membranes are employed for the purpose. Ideally, separators are saturated with electrolyte before assembling of cells. For efficient contact, polymer separators often are sandwiched in-between the electrodes and then soaked with electrolytes [118]. Several factors such as porosity, membrane thickness, electrical and mechanical characteristics of the separators play decisive role in the device efficiency. In recent past, high performance supercapacitor setups especially where polymeric electroactive electrolytes such as sulfonated polyaniline (S-PANI), a water-soluble conducting polymer, is employed, the separator is a semi-permeable membrane that preferentially blocks the migration of electrolyte ions between the two electrodes and thus prevents self discharging of the devices. This is because in absence of semi-permeable membrane as a separator, a charged device can readily face self discharging process as the oxidized S-PANI (electrolyte ions) get reduced by the cathode [119]. Several other instances are also available

Table 1 Examples of symmetric and asymmetric supercapacitors

Two electrode configuration	Negatrode	Positrode	Electrolyte used	Voltage window (V)	Ref
Symmetric	MnO_2	MnO_2	Polyvinyl pyrrolidone-$LiClO_4$ gel electrolyte	1.6	[105]
	ZnO/carbon	ZnO/carbon	6 M KOH	1	[106]
	Phosphorus-doped carbon/CNT composites	Phosphorus-doped carbon/CNTcomposites	2 M H_2SO_4	1.5	[107]
	Sulfurized graphene	Sulfurized graphene	Ionic liquid	3.2	[108]
	Polyaniline	Polyaniline	1 M H_2SO_4	0.5	[109]
Asymmetric	Activated carbon	MnO_2	0.1 M K_2SO_4	1.2	[110]
	Activated carbon	MnO_2/CNT	0.5 M Na_2SO_4	2	[111]
	Graphene hydrogel	Vertically aligned MnO_2 nanoplates on Ni foam	0.5 M Na_2SO_4	2	[112]
	Activated carbon	MnO_2–Pd–CNTs–NF	BMIM-PF_6/DMF	3	[113]
	Activated nano-carbons	CNTs	Ionic liquid	3.5	[114]
	Graphite	Activated carbon (AC)	$LiPF_6$/organic carbonate	4.0	[115]

in the literature—such as flexible ionic electrolyte-based graphene-supercapacitors [120].

3.6 Current collectors

Generally, chemically resistant and mechanically durable low costing metals (e.g., aluminum and stainless steel, Tantalum, etc., are used as current collectors on which the electrode materials are adhered using suitable binder [5]. It is important that the adherence of active materials on current collectors is good otherwise; high resistances and easy detachment of the electrode material would result in poor electrochemical performances [118]. Thus, to increase conductivity, porosity as well as surface area, nanoporus separators have also been fabricated in the recent past [121].

3.7 Sealants

Sealants play supplementary role in hybrid supercapacitors to restrict performance loss [122]. Sealant functions as a blockage to the outside contaminants like air, water, chemicals which can cause electrolyte degradation and unwanted surface oxidation of electrodes. Moreover, it can increase the shunt resistance between cells linked in assembly and therefore, detoriated the overall effectiveness of the system. Thus, proper sealing of supercapacitors is an essential [123]. Polymeric materials are mostly employed as sealants owing to their excellent covering features moisture resistant-ability, flexibility, etc. [124].

3.8 Device patterning

Energy storage systems with patterning-assembly technology are developing rapidly in recent years for designing compact and flexible electronics [125–127]. In order to fabricate 2D or film-type supercapacitors, the patterning approach facilitates improvement in device performance by utilizing high surface-to-volume ratio and also avoiding the need for binders or separators. Furthermore, the assembly also endorses high extent of materials bending and stretching. These characteristic features are crucial for fabricating multifunctional flexible gadgets such as wearable computers, electronic books and cell phones with high electrical performance [128]. In addition, 3D structured hierarchical morphologies with optimal porosity with optimal ratios of micro- to meso- and macro-pores from 1D or 2D highly conductive materials are being achieved using innovative fabrication techniques exhibiting improved device efficiencies aimed for purpose-specific applications [129]. Multiple supercapacitors cells stacking open up possibilities for wider voltage operation and thus avoid the limits of a single device, although complications such as heating effects, poor cycle durability arise. However, cells charging in parallel configuration and then discharging in series configuration can be effective as potential solution of the above problem; although, tailoring of such configuration in practical sense would be a challenge! Another recent engineering approach involves application of bipolar electrodes in assembly of two individual EES cells where multiple cells are internally stacked in series via bipolar electrodes that has been found to be a very cost-effective way of increasing energy density of devices [16].

4 Development of next-generation supercapacitors

Symmetrical supercapacitors typically consist of two identical electrodes separated by an electrolyte. Some of examples for symmetric electrochemical capacitors are provided in Table 1 [105–109]. These devices uses identical electro-active materials as electrodes that results in lowering manufacturing price and also simplifies fabrication procedure besides providing the charging ability in both directions. As only one type of electrode fabrication is required, the economic benefit encourages scalable production for next-generation EES. In addition, employing symmetrical electrodes often reduce the chance of unwanted side reactions between the electrolyte or electrolyte additives or the electrodes, that also improves safety as well as cyclic stability [130]. However, there are some limitations of symmetric cell configuration. For example, further understanding of charge-storage mechanism in symmetrical electrodes is highly desirable, as certain amount of reversible activity during the charge/discharge reactions fails, blocks active sites and thus reduces efficiency. Still the cost effective as well as easily available high energy electrode materials of mass production are waiting for commercialization. Several symmetric electrodes require complex pre-treatments before cell fabrication for better working voltage range. Even, the theoretical specific energy densities of symmetric cells are generally low in contrast to asymmetric ones owing to narrow working potentials, thus restraining their practical applications [130].

Thus, the desire for higher energy density, wider working potential window and improved electrochemical stability has resulted in designing “asymmetric supercapacitors” (ASCs) [128]. Typical ASCs consist of two different types of electrodes; often a porous EDLC-type carbon electrode and a pseudocapacitive electrode to result higher energy and power density due to the non-identical potential changes in the two electrodes (Table 1) [110–114]. The use of faradaic electrodes significantly contributes to the pseudocapacitance, besides widening the potential window while the EDLC electrode provides high energy delivering efficiency. Moreover, the longer discharge period and dissimilar discharge profiles provide higher specific power/ power density and specific energy/energy density to the ASCs [110–115, 128, 129].

In case of asymmetric supercapacitors, although one electrode performs more as a faradaic electrode with obvious anodic and cathodic peaks, the CV and GCD curves of the full cell generally exhibit more capacitive-like behavior although with some obvious deviations from ideal capacitive characteristics. This can be achieved by careful control of mass loading of the electrode materials. If C_p and C_n stand for the capacitances of the positive and negative electrodes respectively, then the total capacitance (C_t) for an asymmetric supercapacitor is calculated as follows [131]:

$$\frac{1}{C_t} = \frac{1}{C_p} + \frac{1}{C_n}$$

Therefore, the total capacitance of ASC is mainly limited by the electrode with the lower value of the specific capacitance. As described for aqueous electrolyte hybrid capacitors, the negative electrodes used are mainly carbon-based EDLC electrodes, whose specific capacitance is generally much lower than that of the positive electrode. Thus, if one can replace the carbon-based EDLC negative electrode of low specific capacitance with a faradaic system of higher specific capacitance, this represents a promising approach to increase the total energy density of a capacitive asymmetric supercapacitor [131, 132].

Here, we present an illustration to discuss the way of fabrication and performance testing of an asymmetric supercapacitor composed of MnO_2 nanowire/graphene composite (MGC) and graphene electrodes. At first, three-electrode-based CV characterization is employed to assign the stable potential ranges of both the electrode materials as shown in Fig. 8a, and their specific capacitances are determined [133]. Here, a platinum foil and a saturated calomel electrode have been used as counter and reference electrodes respectively in neutral aqueous Na_2SO_4 electrolyte. CV signatures of both the MnO_2 nanowire/graphene and the pristine graphene electrodes exhibited nearly rectangular and almost mirror-image current responses over operating potential in between 0.0 to 1.0 V and − 1.0 to 0.4 V, respectively, demonstrating ideal capacitive activities and electrochemical stability. The stable working voltage range for the MGC//graphene asymmetric supercapacitor as shown in Fig. 8b stands to 2.0 V considering the higher and lower potential limits of the MnO_2 nanowire/graphene electrode (+ 1.0 V) and the graphene electrode (− 1.0 V) respectively. The asymmetric cell arrangement for the above system has been represented in Fig.8c [133]. The cell reported enhanced energy density of 30.4 Wh kg^{-1} compared to those of symmetric supercapacitors based on graphene//graphene (2.8 Wh kg^{-1}) and MGC//MGC (5.2 Wh kg^{-1}), respectively. In addition, high power density (5000 W kg^{-1} at 7.0 Wh kg^{-1}) and appreciable GCD cyclic stability were achieved.

Moreover, to achieve optimum performance, charge balance estimation between the positive and the negative electrodes can be considered. Total charge stored in each electrode (Q_{el}) is obtained by the product of the specific capacitance (C_{el}), the active mass (m), and the potential window (ΔE_{el}) of each electrode as follows:

$$Q_{el} = C_{el} \times m \times \Delta E \tag{7}$$

To achieve the charge balance condition $Q^+ = Q^-$, a mass balance as per following is required:

$$\frac{m_{(+)}}{m_{(-)}} = \frac{C_{el(-)} \times \Delta E_{el(-)}}{C_{el(+)} \times \Delta E_{el(+)}} \tag{8}$$

Hence, the optimal mass ratio between the two electrodes $m_{(+)}/m_{(-)}$ can be attuned for attaining best performance of an asymmetric supercapacitor.

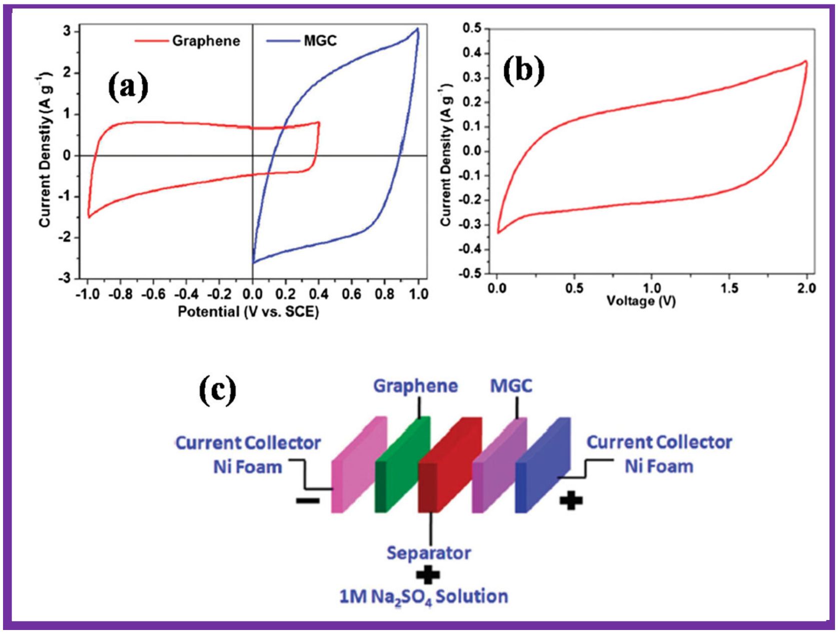

Fig. 8 **a** CV curves of graphene and MnO_2 nanowire/graphene electrodes and **b** CV curve for MnO_2 nanowire/graphene(MGC)//graphene asymmetric supercapacitor recorded at a potential scan rate of 10 mV s^{-1} in three-electrode cell set-up using 1 M Na_2SO_4 aqueous electrolyte solution. **c** Schematic representation of asymmetric cell assembly with as MnO_2 nanowire/graphene as positive electrode and graphene as negative electrode, respectively (reprinted with permission from [133])

Further to note that beside proper choice of electrode materials for ACS, the role of electrolyte employed is very crucial as that could assist in optimizing the power as well as energy densities of the devices to large extent [134, 135]. Although aqueous electrolytes are cheaper, more accessible and conducting than organic counterparts, these non-aqueous electrolytes can function reversibly over wider as well as stable electrochemical operating voltage windows and over wide temperature ranges (e.g., from − 30 to 70 °C) than those of aqueous systems [136]. However, the potential windows of organic electrolytes as well as ionic liquids are essentially controlled by several key factors, such as nature of solvents, conducting salts (i.e., cation and anion), trace amounts of water and contaminants, etc. [137, 138]. Nonetheless, widening of voltage window not only improves energy density but also enhances the output voltage which is indispensible for smart energy storage systems as it minimizes the required number of devices for series combination to provide high output voltage. In addition to the above measures, further steps to improve the energy density and power density of next-generation supercapacitors, requires minimization of self-discharge phenomenon [139]. Self-discharging in supercapacitors leads to fast loss-rate of charge, creating concerns for durable charge storage behavior. In the recent years in-depth studies revealed that self-discharge of EDLCs due to the capacitive carbon electrodes can be lowered by fabricating the asymmetric types. [140].

As studies progressed, additional strategies have come up with innovative ideas that resulted in systems termed as “hybrid supercapacitors” as primarily proposed by Cericola and Kötz that paved the way of development of subsequent generations of supercapacitors [141]. Hybrid supercapacitors are the combinations of EDLC-type or pseudocapacitor electrode with a battery-type electrode, so as to display more enhanced characteristics than the corresponding combining components and get enhanced capacitances [142, 143]. The combination of these two charge storage processes together constitutes the mechanism of energy storage in hybrid supercapacitors. The hybrid capacitors generally resemble the signatures of capacitors. Hybrid supercapacitors can be constituted with same material but with different morphology with varying mass ratios, electrode thickness, thus displaying different charge storing behavior as well. On contrary to symmetrical EDLCs, the hybrid type display superior specific capacitance with elevated rated voltage and higher specific energy. [144]. The hybrid supercapacitors exhibit the ability to store a large amount of charge furnished at high power rates compared to rechargeable batteries [145]. Hence, hybrid supercapacitors promise to be an alternative option to rechargeable batteries for high power density [146]. Figure 9 represents the reported remarkable specific energy values achieved by various hybrid electrode materials that have been studied in the recent years [146, 147].

Amatucci group first proposed $Li_4Ti_5O_{12}$/acetonitrile/AC system to achieve more than 10 Wh kg^{-1} working at potential window of 3.2 V with good power capability [147]. In the recent past, hybrid devices have been developed with pre-lithiated activated carbons or polyacene as negative electrode while employing AC as the positive electrode respectively that achieved cell voltages as high as 4 V with energy density greater than 30 Wh kg^{-1} [115, 148]. Thus, such large volumetric energy density is responsible for the driving force for commercialization irrespective of higher cost of fabrication than existing EDLCs [149, 150]. The mode of fabrication of two typical supercapacitor devices—asymmetric supercapacitor and hybrid supercapacitor can be easily clarified schematically in Fig. 10. Asymmetric supercapacitor devices can have four probable configurations such as (i) EDLC positive electrode and pseudocapacitive negative electrode, (ii) pseudocapacitive positive electrode and EDLC negative electrode, (iii) both positive and negative electrodes made of EDLC electrodes (A and B) but of different EDLC electrode materials ($A \neq B$), (iv) both pseudocapacitive positive electrodes (A and B) but of different pseudocapacitive electrode materials ($A \neq B$). On the other hand, “hybrid supercapacitors” generally have one battery electrode and one capacitive electrode (EDLC or pseudocapacitive), respectively [23].

Recent explorations resulted in hybrid supercapacitors comprising of one battery-type electrode with Li-intercalating phase and the other capacitor electrode are considered as “lithium-ion capacitors” [151, 152]. Here, the battery-type electrode generates high energy density while the capacitor electrode enhances the power capability of the device. Besides $LiCoO_2$ or $LiMn_2O_4$ are also reported as alternate positive electrodes employed in similar hybrid devices that resulted in high power hybrid-Li-ion battery (supercapattery) [152]. The reported energy density of a Lithium ion capacitor in commercialized form is approximately 20 Wh.kg^{-1}, roughly four times higher than an EDLC and five times lower than a lithium-ion battery [153]. Nonetheless, here also such cell-designing did not meet the full utilization of specific energy density of the battery-type electrodes owing to sluggish redox kinetics and therefore needs advanced theoretical and technological re-evaluation. However, there is still plenty of room for substantial improvement. For instance, use of high conducting composite materials minimizes the kinetic mismatch problem of the electrodes in these hybrid devices. In addition, annealing the carbon electrode at 700 °C considerably enhanced the durability of the Li-ion capacitors [154]. Even, pre-doping of Li into nano-carbon electrode has been rigorously explored to undertake the production expenditure and safety issues [155]. It revealed that (i) wide voltage window up to ~ 4 V avoiding excess charging, (ii) irreversible capacity of negative electrode can well be controlled, (iii) electrode resistance gets minimized [5]. Several experimentations have been aimed to optimize the combinations of the negative and positive electrode materials that may synergistically enhance the cell activity [156–159].

To overcome the problems with Li-ion capacitors, nano-hybrid capacitors have come up in last few years. These “nano-hybrid capacitors” provide superior energy density compared to Li-ion capacitors along with increased stability

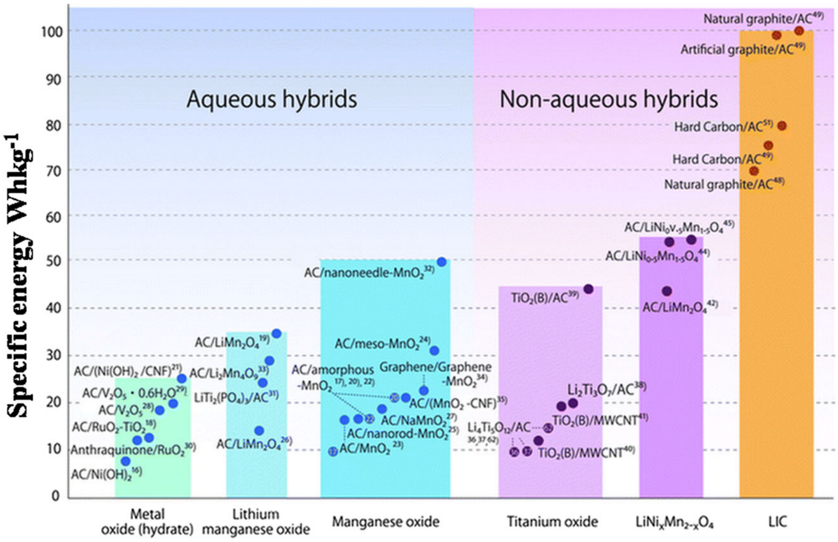

Fig. 9 Plot displaying comparative variation of specific energy for various types of hybrid composite systems (reprinted with permission from [146])

and safety especially while working at very high current densities [160]. Figure 11 represents strategies of designing hybrid devices through proper choice of capacitor and battery-type electrodes so as to obtain supercapacitor-battery-type hybrid devices [161]. For illustration, high energy and high power hybrid devices have been reported by combining a nitroxide-polymer redox supercapacitor (PTMA) with a Li-ion battery material ($LiFePO_4$), where the polymer component controls the device's charge process and makes $LiFePO_4$ voltage more negative by virtue of its ultra-fast electrochemical response leading to higher working potential window [162].

In another approach, the simultaneous as well as homogeneous combination of faradaic (battery-type) and capacitive materials (as depicted in Fig. 11, bottom-most figure) in the form of a single electrode, commonly termed as "BatCap electrode," and finally combined it with the capacitive one

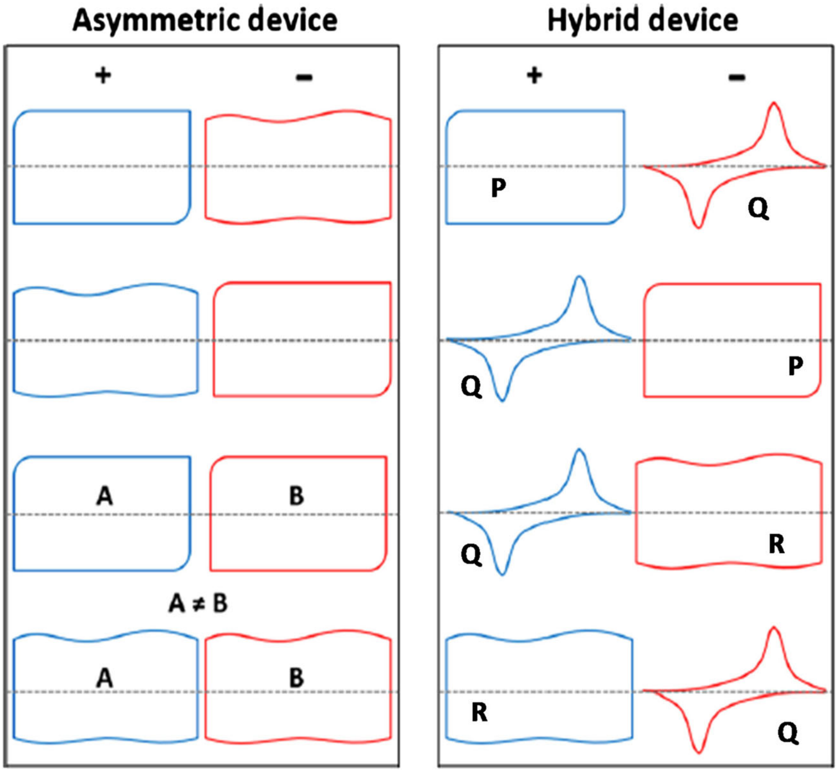

Fig. 10 Generalized cyclic voltammograms for different device configurations of asymmetric supercapacitors and hybrid supercapacitors with A and B are representing different electrode materials. For hybrid devices, P, Q, and R represent EDLC, battery and pseudocapacitive-type electrodes, respectively (reprinted with permission from [23])

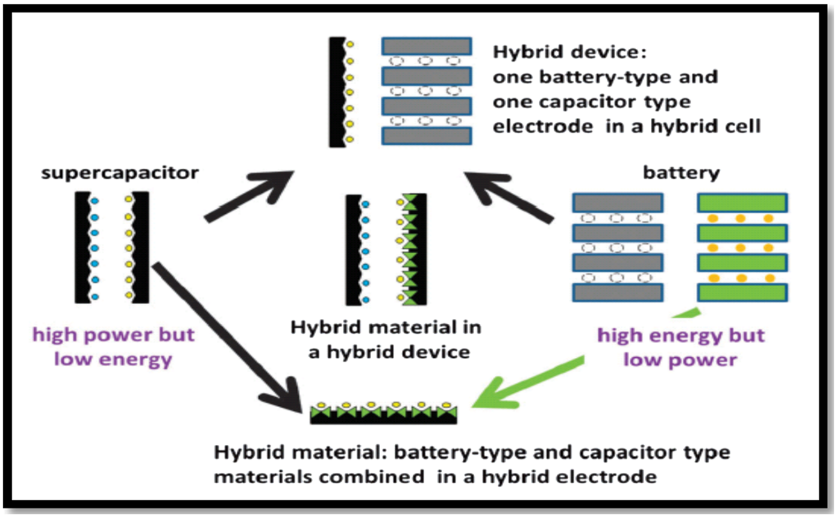

Fig. 11 Schematic representations of different possible hybridization approaches between supercapacitor and battery electrode materials to achieve hybrid electrodes and devices (reprinted with permission from [160])

have been adopted to improve the overall electrochemical kinetics of this class of EES systems [162].

Detailed studies have revealed that total energy stored in hybrid devices is the total contribution of energy storage by both the electrodes. These systems exhibit much improved power density values in comparison to typical pseudocapacitors or battery-type electrodes due to enhanced electron transfer rate by the "capacitor component" triggers a better and high rated charge transfer reaction in the "battery component." Thus, integrating electrode materials having EDLC type (supercapacitor-type) characteristics with electroactive (redox) materials of battery-type features results in hybrid materials, electrodes and devices with improved energy as well as power performances have been generically termed as "supercapbatteries" or "supercapatteries" [16, 161]. Thus, the present scenario of EES research stands that meticulous designing of the electrodes and electrolytes have considerably improved the device performances [163]. These supercapatteries category as depicted in the Fig. 12 are showing the light of hope of improving the thermodynamics and kinetics of conventional supercapacitors so as to achieve the state of their commercialization in the near future.

5 Fabrication of advanced multifunctional next-generation supercapatteries

Along with improving electrochemical performance of supercapacitors, research have been focused on the integration of improved generations of supercapacitors, i.e., supercapatteries/supercabatteries with versatility such as flexibility, wearability for their usage in portable devices and adding smart functionalities such as self-charging and self-healing for robust-field applications of defense, aeronautics, and aerospace engineering. Zhu and co-workers reported electro-deposited WO_3 as a smart electrode material with correlated optical properties that can be effective for devising electrochromic supercapacitors for buildings, vehicles and satellites [164]. Microsupercapacitors with fractal-planar architecture have been fabricated for miniaturized electronics [165, 166]. Liu and co-researchers have reported a photo-switchable microsupercapacitors based on the diarylethene-graphene film in the recent past [167]. Besides, "Electrochemical flow capacitor" with the provision of two external reservoirs with blend of electrolyte and carbon material have also been devised that can sustain a large number (hundreds of thousands) of charge-discharge cycles [168]. Even supercapacitors with photoactive layer incorporated into a single device that has offered capabilities of self-charging upon illumination with self-storage of charge [169, 170]. Similarly, using the concepts of Seebeck effect, thermally activated ion diffusion and temperature dependent electrochemical redox potential, thermal-self-charging supercapacitors have come up. The

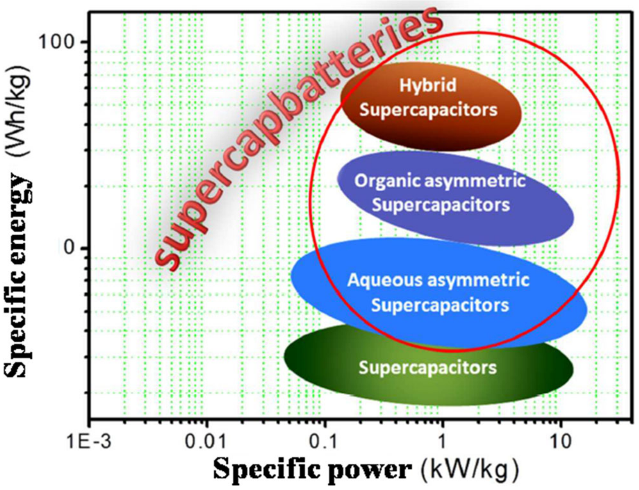

Fig. 12 Ragone plot comparing the recent status of supercapacitors with supercapatteries that comprises of aqueous electrolyte-based organic-electrolytes based asymmetric supercapacitors and hybrid supercapacitors (reprinted with permission from [160])

two electrodes are maintained at dissimilar temperatures to produce large voltage from thermo-electric conversion. This technique can be effective in utilizing the wasted heat loss in electronic devices [171, 172]. Lately, pseudocapacitor and piezoelectric material integrated-supercapacitors have been designed for self-charging energy storage devices as well [173]. For withstanding high stress and regain flexibility, robustness in wearable supercapacitors, shape-memory supercapacitors have been designed which on heating above a critical temperature can help in regaining the original shape of the supercapacitor, is mainly handful for military and space applications. [174–176].

6 Conclusions

Thus, the above overview narrates that considerable developments based on supercapacitor technology have come up in the recent years but still there are considerable challenges for upgrading the efficiency and utilization of next generation supercapatteries. Lately, better understanding of the challenges and the technological progress has brought revolution in these electrochemical energy storage devices. Recent advancements based on motivating works on in situ developing novel electrode materials are making better technological impression that redefines the limit of supercapacitors efficiency. Furthermore, use of suitable electrolytes and redox additives; electrode binders, sealants, current collectors, etc. have become enormously important for obtaining proficient supercapacitors. In addition, device-patterning for effective usage of electro-active material, smooth ion-adsorption/desorption process, and high conductivity are crucial parameters to generate high value of real capacitance for portable, miniature and targeted supercapacitors. Lately realized asymmetric and hybrid supercapacitor concepts have considerably assisted in widening the device operating voltage window with judicious choice of electrolytes. The supercapattery-type electrode materials with ultrafast electron/ion transfer in presence of appropriate electrolytes as well as smart cell architecture have also paved the way for advanced electrochemical performances. These systems have offered superior charge transport kinetics along with high GCD cycling durability and electrochemical stability. This approach has widened the domain for choices of designing of electrodes for desired EES applications. Device innovation and integration with multifunctional activities including piezo-electric, self-healing, thermally/photo-self-charging, electrochromic-supercapatteries are attracting great attention for future durable, maintenance-free EES designs for the near future.

However, there are still a number of technical challenges that are yet to be addressed for commercializing high performance supercapacitors at scalable level. Issues related to complicated charge-storage mechanisms in composites, physicochemical processes existing at the electrolyte/electrode interfaces along with controlling high self-discharge rates especially during device-static condition are yet to be addressed. Concerns related with enhancing mechanical flexibility and stability, durability, production and installation costs, susceptibility to extreme-weather conditions, etc. are the present barriers to large scale commercialization of the EES devices and have yet been seriously attended.

Nonetheless, recent statistics announces that the rate of enthusiasm at which scientists and technologists have put their hands together to overcome the existing challenges to achieve high energy and power density, it is not too far that next-generation supercapacitors in the form of supercapatteries will reach the height of achievement that would be well beyond what rechargeable batteries and EDLCs can individually attain.

Acknowledgments DM acknowledges Chandernagore College, Chandannagar, Hooghly, West Bengal, Pin-712136, India, for providing permission to do honorary research and Jadavpur University for infrastructural facilities.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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