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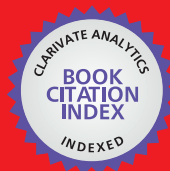
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Supercapacitors Fabrication and Performance Evaluation Techniques

Imtiaz Ahmed Khan, Litty Thekkekara, Sania Waqar, Nauman Choudhry and Sabu John

Abstract

Supercapacitors have surfaced as a promising technology to store electrical energy and bridge the gap between a conventional capacitor and a battery. This chapter reviews various fabrication practices deployed in the development of supercapacitor electrodes and devices. A broader insight is given on the numerous electrode fabrication techniques that include a detailed introduction, principles, pros and cons, and their specific applications to provide a holistic view. Key performance parameters of an energy storage device are explained in detail. A further discussion comprises several electrochemical measurement procedures that are used for the supercapacitor performance evaluation. The performance characterization section helps to determine the correct approach that should be utilized for supercapacitor device performance measurement and assessment.

Keywords: supercapacitors, electrodes, nanomaterials, fabrication methods, energy storage, performance evaluation, capacitance, and energy density

1. Introduction

The crude energy resources that power our planet are depleting and have a devastating effect on our habitat. The world has turned into an energy soaking sponge always deficient and in need of more reserves to fuel the energy shortage. Toxic fossil emissions are pounding the already battered environment resulting in global warming [1]. Planet Earth is witnessing a drastic climatic change due to this phenomenon. Abrupt weather patterns and frequent ecological calamities events are a few of the core issues arising due to these factors. Humans have realized renewable energy is the only way forward to preserve their environment for future survival. This evolution from fossil-based to renewable energy requires a long transition time and comes with its own various challenges. When renewables such as wind, sunlight, tidal, geothermal, etc., are used to generate electric energy, it requires an efficient energy storage source to ensure uninterrupted and reliable energy supply to the users. Energy storage applications have evolved to cater to various needs, from electric grid-level storage to powering small wearable on-person devices. Electric batteries, fuel cells, capacitors and supercapacitors (SCs) are vital components of energy conversion and storage systems. Electric double-layered capacitors (EDLCs), ultracapacitors, electrochemical capacitors (ECs),

pseudo-capacitors, supercapattery are other names that are used for an SC device depending upon the charge storage mechanism [2–4].

In performance metrics, a supercapacitor falls in between a conventional capacitor and a battery. The advantage that supercapacitor exhibits over other conventional batteries are mainly related to a high specific power, significantly high number of cycle life, charge–discharge efficiency, robust thermal operating window and effective handling of fluctuating input–output energy conditions [1, 5–7]. These aspects are summarized in **Table 1**.

2. Components of a supercapacitor

In fundamental form, components of a supercapacitor consist of two electrodes, an electrolyte and a separator that is identical to a conventional capacitor. Supercapacitors (SCs) are electrochemical capacitors (ECs) [9] that store charge in the electric field of electrochemical double-layer [6, 10, 11]. They are one of the favorable candidates for energy storage because of their exceptional electrochemical properties.

Depending upon the charge-storage mechanism of SCs, they can be classified into three; electric double-layer capacitors (EDLCs), redox electrochemical capacitors (RECs) and hybrid electrochemical capacitors (HECs) [10]. Electrodes of supercapacitors can be produced using various forms of carbon [12–14], metal oxides [14, 15] and conductive polymers [16, 17].

EDLCs work on the principle of energy storage by the charge separation at the electrode/electrolyte interface, and they are majorly focused on the materials based on carbon; activated carbons and graphene, carbon nanotubes [18]. While RECs are based on metal oxides, conductive polymers and doped carbon [19]. HECs combines the properties of the materials mentioned above and their working principles.

2.1 Electrode material

Electrodes are the one of the key components and the most important element in SCs. The electrochemical performance of SCs depends upon the properties of electrode materials used in their development. Plenty of researchers are working on designing low-cost, high-performance electrode materials with high stability, high specific surface area and high electronic conductivity [20]. Carbon-based materials are among the popular electrode materials for SCs, followed by conducting polymers and metal oxides, etc. [21].

Performance indicators	Energy storage devices		
	Battery	Supercapacitor	Capacitor
Specific power (W/Kg)	<1000	500–10,000	>10 ⁴
Specific energy (Wh/Kg)	10–100	1–10	<0.1
Charge/discharge efficiency (%)	70–85	85–98	>98
Charging time	1–5 hrs	Sec–min	10 ^{–6} –10 ^{–3}
Discharging time	0.3–3 hrs	Sec–min	10 ^{–6} –10 ^{–3}
Cycle life	~1000	~500,000	>500,000

Table 1.

Performance comparison of capacitor, supercapacitor and battery. Adapted from [8].

2.1.1 Activated carbon

Carbon can be transformed in various forms with a very high specific surface area because of its highly porous structure. This is one main reason for using carbon as an electrode material. Activated carbons (ACs) have proved applications in energy storage [8]. Carbon is abundant in the environment, and its activation can be done through physical (thermal) and chemical activation. Hot gasses are used to develop the structure into ACs in physical (thermal) activation. Carbonization is usually done at very temperature ($\sim 500\text{--}1100^\circ\text{C}$). While chemical activation needs lower temperatures ($\sim 400\text{--}800^\circ\text{C}$), its pyrolysis and activation are carried out in the presence of dehydrating agents.

Depending on the hybridization, carbon has different allotropes; graphitic carbon has graphene layers, while non-graphitic carbon lacks the long-range 3-D network. The structural characters of ACs are close to the structural properties of pure graphite. ACs can be produced with different porous structures [22]; micropores (nanopores), mesopores and macropores. These pores are important in the kinetics of adsorption and do not increase the adsorption capacity. Changing the factors during carbonization and activation can lead to ACs with different porous structure areas. Conway et al. [5] reported that large pore sizes result in higher power densities while smaller pore sizes relate to higher energy densities.

2.1.2 Graphene

Graphene is a monolayer of carbon atoms packed into a honeycomb lattice and is theoretically regarded as the basis for the formation of all other sp^2 allotropes of carbon. It has excellent mechanical properties and a large surface area with great electronic transportability and thermal conductivity [23–25]. Different methods such as hummer's method [26], dispersion method [27], microwave method [28] are being used. The chemical vapor deposition (CVD) method etc., can be used for the synthesis of graphene. To enhance the capacitance performance of graphene that is synthesized by the methods mentioned above, researchers switched to doping graphene [29], conductive polymer composites [30] or oxide materials [31] to enhance the electrochemical behavior of the materials.

2.1.3 Graphite oxide and graphene oxide

Graphite oxide is a product of graphite oxidized by oxidants such as acids [32], while graphene oxide (GO) is single or few layers of graphite oxide [33]. It can be obtained when graphite oxide suspension is sonicated or stirred. Its properties can be tailored via functionalization of groups on the surface.

2.1.4 Carbon nanotubes

CNTs are another allotrope of carbon. Graphene that can be rolled at a certain axis to produce SWCNTs [34]. CNTs are chemically and thermally resilient and have the highest strength to weight ratios [35]. CNTs can be produced by various techniques, including arc discharge [36], laser ablation [37], high-pressure carbon monoxide disproportionation [38] and CVD [39]. CVD is the most common method used to synthesize CNTs. It can be produced as SWNT, DWNT and MWNT [40].

2.1.5 Metal oxides/hydroxides

Metal oxides are considered a very good material for supercapacitors because of their very high capacitance and high power, making them very attractive for

commercial applications [3]. MnO_2 [41–43], NiO [44–46], RuO_2 [47–49], $\text{Co}(\text{OH})_2$ [50] and MoC_3 [51, 52] have got interest because of their vast application for charge storage in supercapacitors. To be eligible for the use in supercapacitors, they must be conductive and can exist in oxidation states without the phase change. While, during the redox reactions, the protons should freely intercalate in and out of the material's lattice.

2.1.6 Conductive polymers (CPs)

Conducting polymers are being explored for redox electrochemical capacitors [53–55] as they have a reversible and fast oxidation and reduction process during energy storage [3]. Due to their high capacitance and large surface area, conducting polymers are being used in supercapacitors. PANI and PEDOT are the most commonly used conducting polymers in supercapacitors.

2.1.7 Composites materials

Hybrid supercapacitors that involve a combination of carbon materials with metal oxides or conducting polymers utilize composite materials [56]. They incorporate the characteristics of both, double layer of charge and faradaic mechanisms. They display higher capacitance to other electrodes that are based on polypyrroles or CNTs [57, 58].

2.2 Electrolyte

An electrolyte is a chemical compound when dissolved in a solvent and dissociated in ions. These ions provide ionic conductivity between the positive and negative electrodes of the device, thus helps in electric charge transportation. The electrolyte plays a vital role in the supercapacitor performance, life cycle, and safety of the device. Chiefly the electrolytes used in supercapacitors are classified into three types, a) aqueous electrolytes, b) organic electrolytes, and c) ionic liquid. Each class has its distinct features related to voltage window and ionic resistance [59, 60].

2.3 Separator

A separator could be any physical barrier such as filter paper, polymeric microporous sheet or even a gel polymer electrolyte that is present between the two positive and negative electrodes to prevent electrical shorting by physical contact of electrodes. Separators should be an inert element and permeable for the electrolyte ions [61, 62].

3. Fabrication techniques

With the advancement in electrochemical supercapacitor technology, the need to design a scalable, sustainable and cost-effective electrode manufacturing method has developed too. Various techniques are being used for the fabrication of supercapacitor electrodes; every technique has merits and demerits over each other. Few commonly used ones are discussed here.

3.1 Chemical vapor deposition (CVD)

This method has gained the interest of many researchers working in this field. The main component used in this method is hydrocarbon substance, as a source of carbon. Iron, cobalt, nickel are some transition metals mainly used as catalysts. Comparatively, in the CVD method, it is easy to control the reaction process. It requires a low growth temperature and is suitable for the production of CNTs and carbon nanofibers. By optimizing the application of catalysts, this method can also align carbon nanotubes arrays [63, 64] that are used to prepare carbon nanotubes [65, 66].

3.2 Dip-coating

Dip coating is a commonly used technique to create substances. It has been reported in the most recent literature of supercapacitors [67–69]. Dip coating is a process where the substrate is dipped into a solution in the presence of a weighing roller/pressure to form a film or a coating on the surface of the substrate. The method is widely used in various industries and in the textile process [70]. It is one of the key techniques used for dyeing. The technique is highly suitable for nanomaterials for creating a thin film coating, such as bio-ceramic nanoparticles, biosensors, and nanocoated implants. The thickness of the coating material affects the adsorption and absorption of the material. The fabric structure, thickness and volume of liquid also affect its absorbance. The dip-coating process is usually followed by air-drying/curing process. The first textile-based supercapacitor was fabricated using this method [71].

The dip-coating method improves the bond between the fibers and the applied electrochemically active materials [72], thus enhance its mechanical properties. CNT/MnO₂/PVA fiber electrode was developed by forming a uniform MnO₂-PVA paste [72]. The paste was then used to dip-coat CNT fibers. The developed asymmetric supercapacitor showed a wide operating potential window of 2.0 V with the highest energy and power densities of 42.0 Wh kg⁻¹ and 19,250 W kg⁻¹, respectively. Cotton fabric was dip-coated using carbon nanofibers (CNFs) to develop flexible carbon composite electrodes in [73]. In order to enhance the electrochemical performance of the electrodes, further layers of manganese oxide (MnO₂) and activated carbon were added. Asymmetric supercapacitors (SCs) were assembled using the textile electrodes, which at low discharge rates, exhibited capacitance performance of 134 and 138 F g⁻¹ with Nafion membrane and porous paper, respectively. The stable performance of hybrid textile-based supercapacitors using a simple development approach and low-cost materials suggests the future direction for flexible energy storage applications.

3.3 Electrochemical deposition

This is a technique where the electrons are transferred through anions and cations under the external electric field. To form a plating layer, a redox reaction takes place on an electrode [74]. Electrochemical deposition is extensively used to improve the capacitive properties of fiber electrodes by forming nanostructure crystals or conductive polymers. With highly capacitive active materials, this method simplifies the composition between carbon nanotube-based fiber.

3.4 Inkjet printing

Inkjet printing is considered an important breakthrough in manufacturing energy storage devices, particularly in supercapacitors. Over the other fabrication

techniques, inkjet printing technology has various advantages such as controlled material deposition, low cost, and compatibility with a variety of substrates [75]. Le et al. [76] fabricated graphene electrodes with inkjet printing of graphene oxide, followed by thermal reduction and found that the electrochemical performance of inkjet printing is favorably comparable to other methods. Graphene oxide dispersed in water was used as an ink to develop a graphene-based inkjet printed supercapacitor [77]. The specific capacitance of up to 192 F/g and the loss of capacitance less than 5% was observed after the repeated bending cycles of the device. SWNT inks were used through an inkjet printer on a cloth fabric to produce thin-film electrodes. These films were then sandwiched between polymer electrolytes to develop supercapacitors. The performance of the printed SWNT supercapacitor was remarkably improved in terms of its specific capacitance of 138 F/g, power density and energy density, with the addition of RuO₂ nanowires [78].

3.5 3D printing

The 3D printing technology could produce low-cost 3D printed platforms for various applications. As electrochemical 3D systems have recently been explored, there has been a particular focus on the development of supercapacitors [79, 80]. The 3D technique is one effective way to improve the overall energy performance of stretchable supercapacitors without compromising their mechanical properties [81], and is also famous to improve the energetic areal performance of micro-supercapacitors [82]. Zhu et al. [83] reported the fabrication of 3D printed aerogel for supercapacitor applications using the 3D printing fabrication method. The developed supercapacitor exhibited exceptional capacitive retention and power densities. A highly flexible electrochemical double-layer capacitor was developed in a single continuous manufacturing process using the 3D printing method [84]. All the components of the supercapacitor were fabricated in a grid pattern. Electrochemical performance and flexibility of the 3D printed supercapacitors were investigated using the mechanical bending tests, which were found excellent with the retention of 54-58% of its initial capacitance at 50 mV s⁻¹ scan rate. Moreover, they proved that the 3D printing technique has good reproducibility and can develop various electronic devices.

3.6 Spray coating

The spray coating technique is generally preferred for large scale production because there is no restraint in the size of the substrate and polymer utilization. This technique is a substitute for the conventional spin coating method [85]. An aerosol is formed, as the printing ink comes out through a nozzle [86]. However, spray coating application for active materials is faced with issues like high film thickness and roughness [87]. Thus, researchers are concerned about improving the morphology of an active layer by means of solvents with high boiling points [88].

Li et al. [89] used the spray coating technique to deposit the silver electrode. They altered the morphology of spray-coated silver electrodes by hydrochloric acid Solvent Vapor Annealing (SVA). They provided a promising technique to prepare large-scale PSC for the fabrication of printed electronics. In another study, Sprayable ink based on activated carbon and single-layer graphene flakes was reported in [90]. Ink deposition through spray coating enhanced the electrolyte accessibility to the electrode surface area. The superior rate capability with the specific energies of 31.5 Wh/kg and 12.5 Wh/kg was displayed at specific powers of 150 W/kg and 30 kW/kg, respectively.

There are many other techniques deployed by scholars to fabricate supercapacitor electrodes that include screen printing [91, 92], vacuum filtration [93, 94], electroless deposition [95], electrospinning [96], blade coating [97], carbonization [98], sol-gel [99, 100] etc.

4. Performance evaluation

4.1 Governing equations

Chen & Dai [101] explained the electrochemical supercapacitors governing equations for performance evaluation when charge cumulates at electrode and electrolyte interface. The capacitance (C) being represented by Eq. (1):

$$C = \epsilon_r \epsilon_0 \left(\frac{A}{D} \right) \quad (1)$$

Where ϵ_r is the electrolyte dielectric constant, ϵ_0 is the dielectric constant of the vacuum, d is the effective thickness of the double layer (charge separation distance), and A is the electrode surface area. The overall capacitance (C_c) of the entire device or cell and the normalized capacitance (C_{NOR}) of an electrode or electrode materials can be expressed via Eqs. (2) and (3):

$$\frac{1}{C_c} = \frac{1}{C_{(p+)}} + \frac{1}{C_{(n-)}} \quad (2)$$

$$C_{\text{NOR}} = \frac{C_i}{P_i} \quad (3)$$

where $C_{(p+)}$ and $C_{(n-)}$ represent the capacitance of the positive electrode and negative electrodes' capacitance, respectively. C_i is the capacitance of the device or electrode materials (individual electrode). P_i could be the parameter either related with the weight (resulting in gravimetric capacitance, F/g), the area (resulting in aerial capacitance, F/cm²) or the volume (resulting in volumetric capacitance, F/cm³) of the electrode or electrode materials to achieve the normalized capacitance values. In the case of a symmetric device, the capacitance of the positive electrode $C_{(p+)}$ must equal that of the negative one $C_{(n-)}$. Thus, the capacitance of the complete cell or device is half of the capacitance of each individual electrode (C_i), that is, $C_i = C_{(p+)} = C_{(n-)}$

$$C_c = \frac{C_i}{2} \quad (4)$$

The energy density (E) and power density (P) can be calculated using Eqs. (5) and (6):

$$E = 0.5 CV^2 \quad (5)$$

$$P = \frac{V^2}{4R_{\text{ESR}}} = \frac{E}{t_{\text{discharge}}} \quad (6)$$

Where V is the operating voltage, R_{ESR} is the equivalent series resistance of the device, and $t_{\text{discharge}}$ is the discharge time.

4.2 Cell setup for supercapacitor testing

The supercapacitor testing is carried out through an electrochemical workstation (EW), which contains electronic hardware units of potentiostat and galvanostat. It also contains a frequency response analyzing unit as an option to characterize electrochemical impedance spectroscopy. The user-specified counter electrode (C_E) potential is precisely controlled against the working electrode (W_E) potential, and the current response being observed in potentiostatic mode. In contrast, the flow of current is accurately maintained between working and counter electrodes in galvanostatic mode.

The cell setup for supercapacitor performance output characterization consists of three and two-electrode configurations. Two electrode test cell design gives the real output performance of the supercapacitor device, i.e. the obtained results include both electrode contributions towards the capacitance value. On the other hand, the latter is used to derive effective electrode material performance results. This means the results that are acquired through a three-electrode setup are exclusively due to the working electrode (the electrode understudy) and do not include any invasion from another electrode.

It is easy to extract output information for individual electrodes while using two-electrode cell assembly for symmetrical devices, but difficult to obtain such information accurately for the asymmetric device since using two-electrode methods is not feasible. The main reason for not recommending a two-electrode configuration for asymmetric devices is that accurate contribution to overall capacitance values arising from two different electrodes cannot be distinguished. A three-electrode cell should be used in such scenarios if individual electrode performance is studied in an asymmetric supercapacitor [102]. The three-cell setup consists of a working electrode, a counter electrode, and a reference electrode, while in the two-electrode setup, there are two electrodes; one is positive, and the other is negative, separated by electrolyte-soaked porous membrane.

4.3 Electrochemical techniques employed for supercapacitor characterization

The critical performance parameters of a supercapacitor are measured using three main electrochemical techniques, which include cyclic voltammetry (CV), Galvanostatic Charge/Discharge (GCD, also known as constant current charge/discharge) and Electrochemical Impedance Spectroscopy (EIS). Electrochemical workstation is used for all these techniques to quantify key factors such as voltage, current, time, equivalent series resistance and capacitance in three or two-electrode configurations. From the measurement results, the power and energy values of the tested device can be calculated through mathematical Equations [103].

4.3.1 Cyclic voltammetry (CV)

Cyclic voltammetry is a versatile, dynamic electrochemical method for evaluating the electrochemical capabilities of a device or material through electrode kinetics and charge storage mechanism happening at the electrode/electrolyte interface. Both three and two electrode configurations can be used in a CV experiment to measure various parameters. Working electrode potential is measured against a reference electrode which maintains a constant potential. Distinct shape CV graphs are generated (rectangular/quasi-rectangular) as shown in **Figure 1a**, with time-dependent current on the vertical axis and predetermined voltage window on the horizontal axis, when a fixed rate linear varying voltage is swept between two predetermined upper and lower electric potential values. The scan is forwarded and reversed

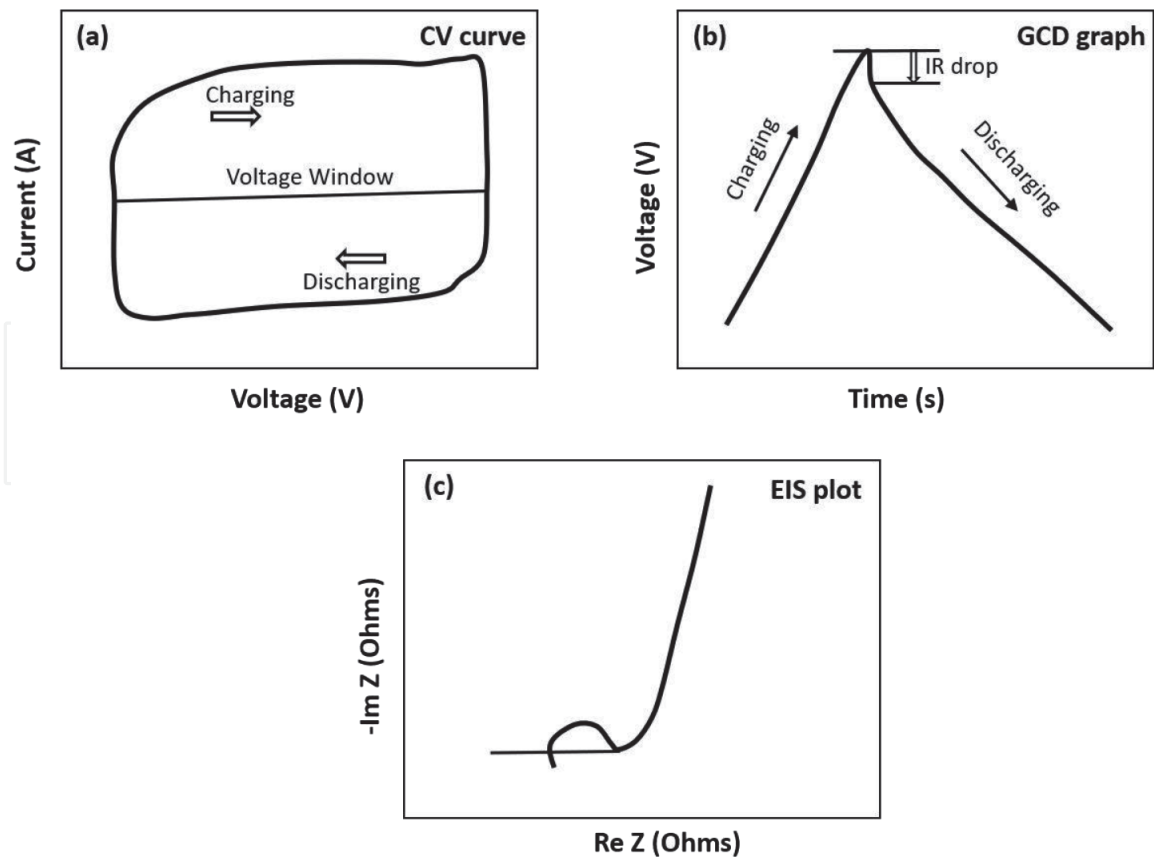


Figure 1.
 Typical profiles of a) CV, b) GCD, and c) EIS of a supercapacitor.

between this voltage bracket, also known as operating potential or voltage window. This voltage window value depends upon the type of electrolyte used, as the voltage range should not surpass the stable voltage operating window of the electrolyte.

Exceeding the voltage limit will start the electrolysis process of an electrolyte, and this reaction will govern the cell chemistry, thus resulting in deteriorated cell performance [104]. Different scan rates (mV/s) are also employed during CV analysis; this voltage/potential change speeds during the experimental setup. The scan rate has a considerable impact on capacitance values and graphs obtained. It is mainly related to electrode kinetics, as the decrease in specific capacitance is associated with limited ion transfer due to increased scan rate [102]. At slower scan rates, the CV graphs also show better rectangular charts. Eq. (7) can be used to calculate the capacitance values of a super cache capacitor when the CV technique is used in two-electrode assemblies [105].

$$C_{wt} = \frac{4 \int_{V_1}^{V_2} i dV}{ms\Delta V} \quad (7)$$

where is the integrated area of the CV curve, V is ($2 \times$ the voltage window, from E1 to E2 = $(|E2 - E1|)$ in volts (V), s is the scan rate (V/s), m represents the mass (g) of active materials on both electrodes [105].

The multiplication factor of 4 should be replaced by 2 in the three-cell setup to calculate the gravimetric capacitance.

4.3.2 Galvanostatic charge–discharge (GCD)

GCD is another heavily deployed technique to calculate capacitance, power, energy densities, the equivalent series resistance of the supercapacitor device or

material. It also helps in identifying parameters such as the life cycle and the stability of the device during that period [103]. In this method, a constant positive current is applied to the working electrode at the start, so it is charged to its peak voltage value that is specified in the voltage window, and voltage response is recorded against charging time. Once fully charged, a constant negative current is applied to the device, so it is discharged to its lower voltage value, and voltage response against discharge time are noted [105]. The GCD profile formed for a supercapacitor is triangular, as shown in **Figure 1b**. Eq. (8) can be used to calculate areal capacitance (F/cm^2) in a two-electrode assembly [105];

$$C_A = \frac{4I}{A \left(\frac{\Delta E}{\Delta t} \right)} \quad (8)$$

where I is the current in amperes (A), $\left(\frac{\Delta E}{\Delta t} \right)$ represents the slope of the discharge curve from IR drop, and A is the area in cm^2 of the two electrodes.

4.3.3 Electrochemical impedance spectroscopy (EIS)

This technique provides beneficial information such as impedance, frequency response on capacitance, electrode/electrolyte interface related phenomena such as charge transfer, and mass transport. EIS is also known as AC impedance spectroscopy and dielectric spectroscopy. In this method, a low amplitude ACs, signal (voltage-potentiostatic or current control-galvanostatic) is superimposed on a steady-state signal over a variable frequency range, and its effect is studied on the impedance of the device [102]. The data is usually presented on a Nyquist plot (**Figure 1c**) where the real and imaginary impedance of the device is shown. Calculating capacitance via EIS test using traditional method basically relies on imaginary complex impedance part $\text{Im}(Z)$ and is shown in Eq. (9) [103].

$$C_{\text{Tf}} = -\frac{1}{2\pi f \text{Im}(Z)} \quad (9)$$

Where f is usually the lowest applied frequency value.

5. Conclusion

Supercapacitors provide promising solution to the future energy storage devices. Various materials and fabrication options are available for the development of supercapacitors. Key performance parameters and their assessment criteria have been reviewed in this chapter.

Extensive research has been conducted in the past decade on supercapacitors with quite significant progress. Although inspiring results have been achieved in this field; yet the energy storage devices still require further enhancement in device fabrication techniques to achieve uniformity, scalability, and consistency in performance evaluation to satisfy commercial demands. It is expected that future research and developments will address these challenges.

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Conflict of interest

The authors declare no conflict of interest.

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