Advancing Energy Storage Technology through Hybridization of Supercapacitors and Batteries: A Review on the Contribution of Carbon-Based Nanomaterials

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Abstract. Fast depletion of fossil fuel and other non-renewable energy resources with their negative environmental impact have raised the quest for eco-friendly and sustainable energy resources. Sustainable energy resources such as solar and wind energy are periodical. Therefore, such energy resources can only be effectively utilized with advanced energy storage technology. Currently, various energy storage technologies such as batteries and supercapacitors are available with various energy storage properties. For instance, batteries are characterized with high energy and low power density. On the other hand, supercapacitors are low energy and high power density devices. The high power density of supercapacitors results to their faster charging and discharging capability compared to batteries. While batteries can accommodate higher energy compared to supercapacitors. Therefore, to obtain single energy storage material/device with both high energy and power density is a challenge in the energy storage sector. However, various efforts have been made to address this challenge through combinations of various materials or devices. For instance, carbon-based nanomaterials such as graphene and carbon nanotubes have been extensively studied in design of supercapacitors for high energy storage density. While supercapacitors and batteries have been hybridized on the effort to obtain energy storage device with both high energy and power density for advanced energy storage technology. Therefore, this review looks into the contribution of carbon-based nanomaterials in improving energy storage density of supercapacitors and their hybridization with batteries as the way forward to obtain energy storage materials/devices with both high energy and power density for advanced energy storage technology.

Keywords: Battery, Supercapacitor, Carbon and Nanomaterials
1. Introduction

Energy is eventually used in all humans’ day to day activities. The significant increase in the world population has resulted in high demand for energy resources. Although fossil fuel is the major source of energy, it is fast depleting due to high consumption and fast increasing population [1, 2]. Due to the production of greenhouse effects by fossil fuel, it places danger on global warming [3, 4]. This has led to the innovation of clean and sustainable energy such as renewable energy resources [5, 6]. The renewable energy resources such as wind and sunlight energy are periodical – for instance, sunlight might be at the peak in the day and lowest in the night [7]. It is worth noting that as energy generation is important, appropriate energy distribution and storage have great roles to play in the energy sector, which can be achieved with advanced materials as shown in Fig. 1. Therefore, for constant availability of renewable energy, high electrical energy storage devices such as batteries are required [8]. However, the high cost of batteries used in renewable energy storage systems makes such energy cost ineffective [9].

![Figure 1. (a) The Applications of Advanced Materials in Energy System (Hudaya, [10])](image)

In addition, despite the higher energy density of batteries compared to other energy storage technologies, their long charging and discharging duration are still challenges facing the effective utilization of batteries in energy storage applications. These limitations of batteries placed capacitor energy storage technology as better candidate for energy storage as a result of their large power density, quick charging and discharging cycle [11, 12]. Capacitors have the capability to store and release large amount of energy in a simple device that can last over millions of cycles [13] due to their high power density. Therefore, to designing a single energy storage device that simultaneously characterized by high power and high energy density has been a challenge facing energy storage technology. Since various energy storage technology have different power and energy storage capacity, hybridized energy storage system can lead to high energy storage device. For instance, a hybrid circuit of an electrical energy storage system consisting of electrostatic capacitors (ESCs) and electrochemical capacitors (ECCs) is merging technology for storing energy from renewable resources [14]. Hybridization of battery, hybrid capacitor and supercapacitor for electric vehicles has been investigated with improved performance [15]. It is believed that such hybrid energy storage systems are compromised. At high power delivery frequency from the generating source such as sunlight (during the day), high power density capacitor can absorb the energy and transfer to battery at a rate compatible to the battery. While at low power delivery frequency (during the night), capacitor can be by-pasted to store directly to the battery [14]. Such energy storage system is an advanced energy storage technology for effective utilization of renewable energy and other applications such as electric vehicles, boost inverter, DC converter, motor inverter etc.
From the ongoing discussion, appreciable energy storage density and high temperature resistance is required to obtain compatible hybridization of capacitors and batteries. Carbon-based materials such as graphene and carbon nanotubes have revealed promising properties in boosting energy storage density of capacitors. According to Uyor et al. [16], such materials have been extensively used in studying various energy storage related technologies such as lithium ion batteries [17,18] and supercapacitors [19-21]. The extensive use of these materials is due to their excellent thermal, mechanical, electrical properties etc. Therefore, this review considered the role of such carbon-based materials in enhancing the energy storage density of supercapacitors. The review went further to look at advancement in energy storage technology through hybridization of capacitor and battery electrodes as a way forward to bridge the gaps of low energy density of capacitors and low power density of batteries. Therefore, this review is aimed at creating a platform for future advancement in the study of energy storage techniques.

2. Brief Overview of the Carbon-Based Nanomaterials

Graphene nanosheets (GNs) and carbon nanotubes (CNTs) are typical examples of carbon-based nanomaterials. These materials have excellent properties which make them desired materials for energy storage application. Their small size, high aspect ratio and surface area [12], good mechanical, electrical and thermal properties [22,23] have given these carbon-based materials edge over other conventional materials. GNs is a 2D carbon based nanomaterial with carbon atoms bonded in sp² structure [24,25]. GNs is characterized with high electrical conductivity, Young Modulus and strength. While CNTs is a 1D carbon-based material with high conductivity, strength and thermal stability [26]. These carbon-based nanomaterials easily change the structure and properties of materials in which they are incorporated [27,28]. Therefore, the nanomaterials have been greatly used to improve the thermal stability and conductivity [29], mechanical and electrical properties [30,22] of polymeric materials. However, one of the challenges facing such materials are incompatibility and agglomeration in most matrices. This is due to strong cohesive interaction, Van der Waals force of attraction and π-bond between individual particles of such nanomaterials [31,32]. These often negatively influence the properties of the resultant materials in which they are incorporated since their excellent properties strongly depend on the state of dispersion in the matrix [33,34]. Notwithstanding, it has been shown that surface modification of such nanomaterials enhances the behavior of the materials in which they are incorporated [35,36].

3. Effect of Carbon-Based Nanomaterials on High Energy Storage Density of Supercapacitor

Supercapacitor closed the disparity between conventional capacitor (low energy density) and battery (low power density). It lay midway between this two energy storage technologies. Supercapacitors are mainly classified into three; that is electric double layer capacitors (store charges electrostatically), pseudo capacitors (store charges electrochemically – redox or faradaic reaction) and hybrid capacitor (store charges both electrostatically and electrochemically). Supercapacitors store higher amount of energy compared to conventional capacitors and higher power density compared to batteries. This has raised their demand in energy storage application. A single cell supercapacitor is made up of two electrodes and electrolyte. The electrolyte is made up of positive and negative charges which accumulate at the surfaces of the electrodes (in case of electrostatic mechanism) or by charge transfer between electrodes and electrolyte (in the case of electrochemical mechanism). On the other hand, electrodes used for supercapacitors are made with various forms of materials. For instance, carbon-based materials (such as activated carbon, aerogel carbon etc), metal oxides (such as MnO₂, LiFePO₄ etc) and conducting polymers (such as polyaniline, polypyrrole etc) are all used for supercapacitors’ electrodes [37]. Carbon-based electrodes for supercapacitor application have been widely studied due to their wonderful electrical conductivity, low cost and availability. Carbon-based electrodes which often have capacitance in the range of 100 F g⁻¹ to 200 F g⁻¹ has been advanced to 300 F g⁻¹ with the recent used of hierarchical porous carbon having various range of pores interconnected and arrange in a hierarchical order [38]. Although appropriate interconnected pores is essential for high capacitance, appropriate balance between the porosity and electrical conductivity is an important factor for simultaneous high capacitance and good rate performance [39]. Capacitance and electrical conductivity/resistivity have direct and inverse relationship with the energy store (E) and power deliver (P)
of a single cell supercapacitor as shown in equation 1 and 2 respectively, which are very important parameters to evaluate a supercapacitor [39].

\[ E = 0.5CV^2 \]

\[ P = \frac{V^2}{4R} \]

Where C (farads) is the total capacitance, V (volts) is the voltage of the cell and R (ohms) is equivalent series resistance.

The excellent properties of carbon-based nanomaterials such as graphene nanosheets (GNS) and carbon nanotubes (CNTs) have raised the study of electrodes made with such nanomaterials in respect to the capacitance and energy storage of supercapacitors. For instance, Zhang et al. [40] separately modified reduced graphene oxide with ruthenium oxide and polyaniline for anode and cathode respectively in fabrication of asymmetric supercapacitor. The authors obtained higher energy density of about 26.3 W h kg\(^{-1}\) compared to commercially available supercapacitors, which often have energy density less than 10 W h kg\(^{-1}\). This shows significant improvement in energy storage density of a supercapacitor using graphene-based electrodes. A very high energy storage density of a supercapacitor which increase from about 85.6 W h kg\(^{-1}\) to 136 W h kg\(^{-1}\) at room temperature and 80°C respectively have also been reported by Liu et al. [41] using graphene-based electrodes. They authors achieved the high supercapacitor performance using curved graphene sheets, which promoted un-restacking face to face graphene sheets with high surface capacitance and surface area. The results obtained by various research show significant contribution of graphene-based electrodes on energy storage density of supercapacitors. In a study carried out by Kim et al. [42], activated graphene-based carbon was used as electrodes for supercapacitor. High specific capacitance of about 174 F g\(^{-1}\) was achieved in an ionic liquid electrolyte and energy density of about 74 W h kg\(^{-1}\) using the graphene derived carbon electrode with hierarchical pore structures. According to the authors, the results was credited to especial pores structures, which was achieved through structural modification and the high surface area of the carbon-based materials.

On the other hand, CNTs has also been extensively studied for application as supercapacitor electrodes. In a study carried out by Guo et al. [43], supercapacitor electrode containing CNTs embedded carbon nanofiber was developed. The supercapacitor gave specific capacitance of about 310 F g\(^{-1}\). The capacitance was twice that of pure carbon nanofiber electrode due to the presence of CNTs. The presence of CNTs increased the conductive networks of the electrode for charge transfer with improved supercapacitor performance. Polyaniline/CNTs composites have also been developed by Gupta, Miura [44] with significant enhanced capacitance for supercapacitor application. The authors recorded specific capacitance and energy storage density of about 485 F g\(^{-1}\) and 2250 W kg\(^{-1}\) respectively. The developed materials also showed cyclic stability over tested duration. High specific capacitance of about 328 F g\(^{-1}\) has also been recorded using polyaniline/CNTs composites as electrodes [45]. Various high capacitance and energy storage density of supercapacitors have been reported using GNs or CNTs based electrodes such as 480 F g\(^{-1}\) [46], 130–165 F g\(^{-1}\) [47], 1126 F g\(^{-1}\) [48] etc. The achieved results were due to the effective properties such as high surface area, large aspect ratio, high electrical and thermal conductivity of the carbon-based nanomaterials. The hybrid materials discussed in this section have always shown better performance compared to their respective individual materials. However, studies still need to be conducted to obtain optimal supercapacitor electrodes’ performance using these carbon-based nanomaterials for further improvement of energy storage technology.

4. Hybridization of Energy Storage Devices

As various materials are being hybridized to improve energy storage performance of the resultant materials as discussed in the previous section, various energy storage techniques are also being hybridized to improve energy storage performance. Studies have been conducted on the hybridization of different energy storage technology such as supercapacitors and batteries for various applications [49,50]. According to Dubal et al. [37], combination of different energy storage mechanism such as capacitor and battery in a single device can enhance energy storage performance of such device compared to their individual
component as shown in Fig. 2. The figure is a case study as adopted from Dubal et al. [37], where energy storage equations and charge-potential profile of a single electrode; capacitor, battery and hybridized system are depicted. Battery which have a high energy density can store energy twice that of capacitor which have high power density as shown in Fig. 2. When these two energy storage technologies with different energy storage mechanism are merge together in a single device, high energy storage density and high-power density can be simultaneously achieved in one device as shown in Fig. 2c. Hence, the total stored energy in such device will be the energy stored in a capacitor system plus the energy stored in the battery system. This gives rise to high energy storage capability of such hybrid device. In addition, such hybrid energy storage system requires high applied voltage, which will directly enhance the energy stored in such device since the voltage is directly proportional to the energy stored in a device. However, to achieve this, energy storage density of capacitors must be appreciably raised, which has been demonstrated using GNs and CNTs based electrodes. In addition, interfacial and kinetic challenges must be addressed to fully utilized the benefit of such hybrid energy storage system for advanced energy storage technology.

![Figure 2](image-url)

**Figure 2.** (a) Schematic illustration of single (a) capacitor electrode (b) battery electrode and (c) hybridized capacitor and battery system with their charge-potential profile and the resultant equations for energy storage (Dubal et al. [37]).

5. **Conclusion and Recommendations**

This brief review has been able to look at the contribution of carbon-based nanomaterials such as graphene nanosheets (GNs) and carbon nanotubes (CNTs) on the capacitance and energy storage density of supercapacitors. It was noted that such nanomaterials have significant influence on the improvement of supercapacitors’ performance following the reports on the published literature. The paper went further to look at hybridization of capacitors and batteries as the way forward in achieving high energy and high-power density simultaneously in a single device for advancement of energy storage technology. It is recommended that further studies should be conducted to optimized supercapacitor electrodes’ performance, synergetic effect of the hybrid materials/devices, cyclic stability of the supercapacitor, proper balance of electrical conductivity and porosity of electrodes made with GNs and CNTs for optimal performance and applications.

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