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Chapter- 16

Supercapacitor: An Offer to Sustainable Green Energy

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Abstract:
With the increasing demand for sustainable green energy to minimize environmental pollution and reduce the use of fossil fuels, it is imperative to find alternative, environmentally friendly approaches to efficiently manage energy conversion and storage systems. In this context, supercapacitors or ultracapacitors have garnered significant attention, not only due to their high power density, high capacity with low internal resistance, rapid charging and discharging processes, and long life expectancy but also due to their environmentally friendly nature. The most widely used storage devices are batteries, which contain heavy metals such as zinc, lead, manganese, and mercury. These heavy metals cause long-term severe environmental pollution. In contrast, the waste management of supercapacitors is environmentally safe, as no heavy metals or harmful chemicals are used. The advent of hybrid capacitor technology and the discovery of graphene have made this technology even more attractive. This chapter briefly discusses the characteristics, basic storage principles, advantages, limitations, and scope of applications.

Introduction:

In today's world, everyone relies on energy at every second and in every aspect of life. It is impossible to imagine a day without energy. To meet our energy demands, we predominantly use fossil energy. Fossil fuels such as coal, oil, natural gas, and their derivatives like kerosene and gasoline are primarily hydrocarbons. These fuels are found in the earth's crust and formed when prehistoric plants and animals decompose due to heat and pressure. These non-renewable energy sources are used to fulfill our daily energy needs at both the industrial and domestic levels. Since the Industrial Revolution in Great Britain in the 18th century, fossil fuel consumption has increased exponentially. Today, over 80% of the world’s primary energy consumption and over 60% of its electricity come from fossil fuels.

The overuse of these hydrocarbon-rich fossil fuels has two major impacts: Firstly, the sources of these non-renewable fuels are rapidly depleting, as their formation requires a geological process that spans millions of years. Secondly, they emit greenhouse gases such as CO, CO_2, and CH_4, which cause significant environmental harm, including global warming and pollution (Wang et al., 1976; Parikh and Shukla, 1995; Gerlich and Tscheuschner, 2009). In response, scientists, engineers, and world leaders are seeking solutions to the problems posed by fossil fuels to create a healthier environment with sufficient clean energy to sustain human life and activities in the future.

This growing necessity has driven research into various types of renewable energy sources, such as solar energy, wind energy, tidal energy, hydroelectric energy, biomass energy, and nuclear energy (Rugani et al., 2011; Liu et al., 2019; Hussain et al., 2017; Demirbaş, 2006; Yüksel, 2010; Abbott,

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2012). These sources offer environmentally friendly, clean, and virtually unlimited power. However, despite the availability of these alternatives, daily energy consumption still largely depends on fossil fuels due to inherent production challenges and other issues.

In this context, energy storage devices play a crucial role. Since ancient times, various storage systems, including pumped hydro, thermal energy, compressed air, flywheels, electrochemical, chemical, and superconducting magnetic systems, have been used (Hossain et al., 2020; Sharma et al., 2009; Rehman et al., 2015; Guo et al., 2021; Olabi et al., 2021; Gür, 2018; Boom and Peterson, 1972; Mitali et al., 2022). Among them, batteries, which are electrochemical energy storage systems, are widely used in sectors ranging from industry to everyday life.

In this digital age, most energy is consumed in the form of electricity. Currently, most electric energy is generated from thermal power, which relies on fossil fuels. Since fossil fuels negatively impact the environment, scientists have developed alternative technologies to convert various non-conventional energy sources, such as hydro energy, solar energy, wind energy, and wave energy, into electricity. The advancement of electric energy storage technology is crucial to reducing the use of conventional energy and ensuring proper storage of this electrical energy.

Therefore, to address the energy crisis and its associated environmental problems, we must focus on renewable energy sources and develop low-cost, environmentally friendly energy storage systems. In this context, one critical approach is replacing batteries with capacitors, another key concept of Green Electricity.

Backgrounds:

Both batteries and capacitors can store electrical energy. Generally, a battery is a system where two electrodes, called the anode (+ve end) and cathode (-ve end), are partly immersed in a vessel filled with an electrolyte solution. Energy is stored in a battery due to a net chemical reaction between the electrode and the electrolyte, which gives it a limited life cycle. However, the main advantage of batteries is their very high energy density. Although this makes them an automatic choice and popular for energy storage, they have a very low power density.

In energy storage systems, two terms are essential—energy density (or specific energy) and power density (or specific power). The first term refers to the amount of energy stored per unit mass or volume, while the second refers to the power per unit mass. Simply put, energy density indicates how much energy a system contains, and power density indicates how quickly it can discharge its energy. A system with a large energy density but low power density can deliver energy over a more extended period.

A conventional capacitor stores energy by charging and discharging, and since no chemical reaction is involved, it can be used millions of times, theoretically, even infinitely. It is a two-terminal electrical component. In general, when a dielectric (insulating) medium is placed between two parallel conducting plates, a capacitor is formed. Suppose the surface area of the parallel plates is A, the distance between the two plates is d, and the permittivity of the dielectric medium is ε_0. In that case, the capacitance (C) of this parallel plate capacitor will be:

$$C = \varepsilon_0 A/d \quad (1)$$

Now, if the capacitor is connected to a voltage difference V, it will become charged. The amount of electrical energy (E) stored in the capacitor can be expressed as:

$$E = \frac{1}{2}CV^{2}. \quad (2)$$

Thus, more capacitance means more energy stored in the capacitor. Generally, the capacitance of a conventional capacitor is very small (~µF), and as a result, the energy stored in it is also small. We would require huge dimensions to achieve a large capacitance (~F), which is practically impossible. Unlike a battery, a capacitor has low energy density but high power density, meaning it can deliver or absorb energy very quickly once it begins to discharge or charge. Therefore, both batteries and conventional capacitors have their respective advantages and disadvantages.

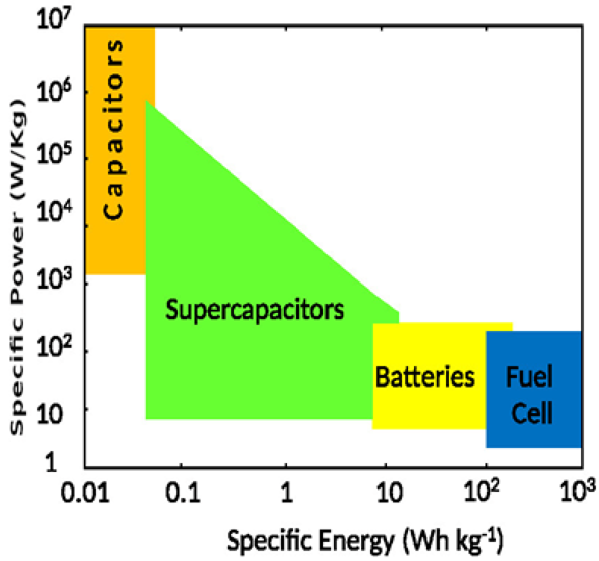

Figure 1. Ragone plot of energy storage device (Kotz and Carlen, 2000).

The technology of supercapacitors, or ultracapacitors, helps to bridge the gap between batteries and dielectric capacitors in terms of energy density and power density, as indicated in Figure 1 (Kotz and Carlen, 2000). Advances in supercapacitor technology have made it possible to achieve large capacitance (~F) in very small dimensions by utilizing electrode materials with high surface area and thin electrolytic dielectrics (Conway, 1999; Kotz and Carlen, 2000; Burke, 2000; Chu and Braatz, 2002; Aricò et al., 2005). The characteristics of high power density, moderately high energy density, exceptionally long life cycles, a wide thermal range (-40°C to 70°C), low weight, and low maintenance costs, compared to secondary batteries or conventional dielectric capacitors, make supercapacitors an attractive energy storage device (Wang et al., 2009). Compared to electrolytic capacitors, supercapacitors can store 10 to 100 times more energy per unit volume or mass. Since no chemical reaction occurs during charging and discharging, they can endure significantly more charge cycles compared to rechargeable batteries and accept and deliver charge much faster.

Classification of Supercapacitors and Energy Storage Mechanism:

Supercapacitors can be divided into three categories based on their charge storage mechanism: (1) Electrochemical Double Layer Capacitor (EDLC), (2) Pseudo-capacitor, and (3) Hybrid Capacitor. Figure 2 illustrates the taxonomy of supercapacitors based on storage mechanisms and electrode materials (Hadjipaschalis et al., 2009).

Electrochemical Double Layer Capacitor (EDLC):

The charge storage mechanism of an EDLC is a non-Faradaic process, similar to that of a conventional capacitor, where charges are accumulated electrostatically, and no charge transfer occurs between the electrode and the electrolyte. Consequently, the capacitance originates at the electrode-electrolyte interfaces. In electrochemical double-layer capacitors, an electrolyte (a mixture of positive and negative ions dissolved in a solvent, such as water) is used between two carbon-based electrodes instead of the dielectric medium used in conventional capacitors. For example, aqueous solutions of KOH, H_2SO_4, or Na_2CO_3 are common electrolytes. A separator allows ions in the electrolyte solution to diffuse into the electrode's pores with the opposite charge. A schematic diagram of an EDLC is shown in Figure 3.

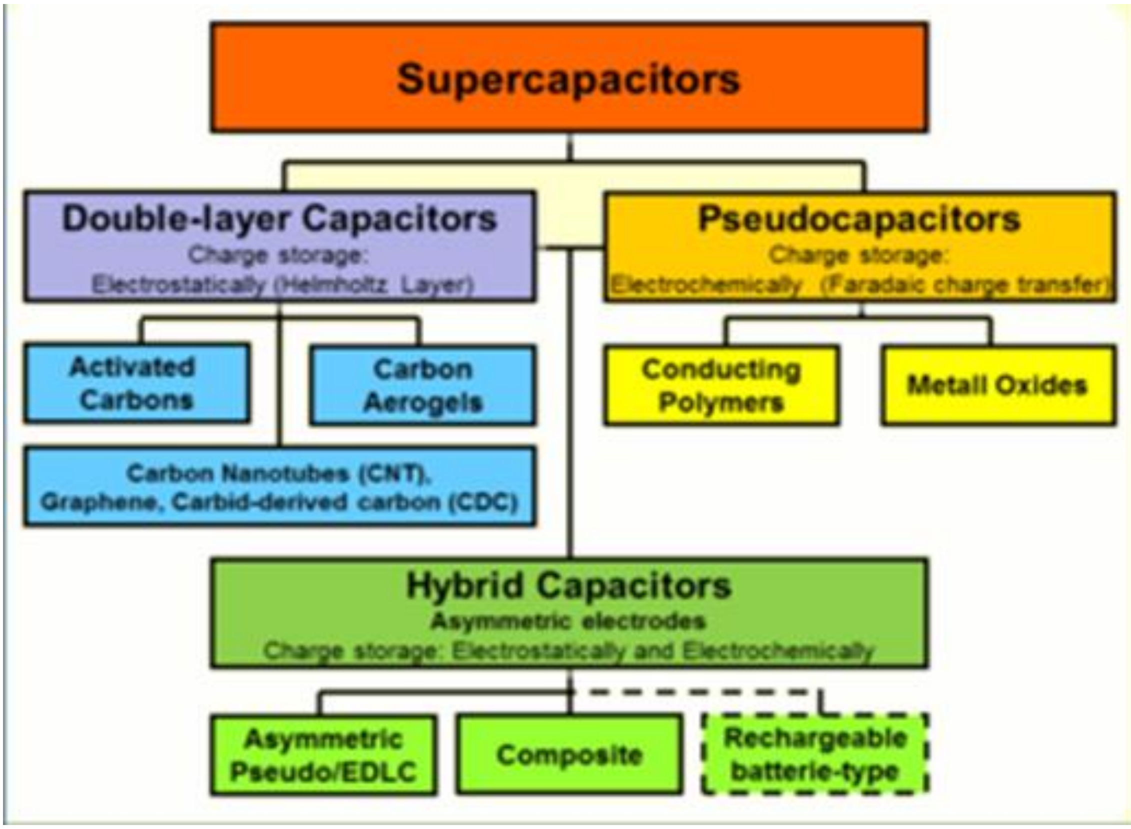

Figure 2. Classification of supercapacitors based on storage mechanism and electrode materials (Hadjipaschalis et al., 2009).

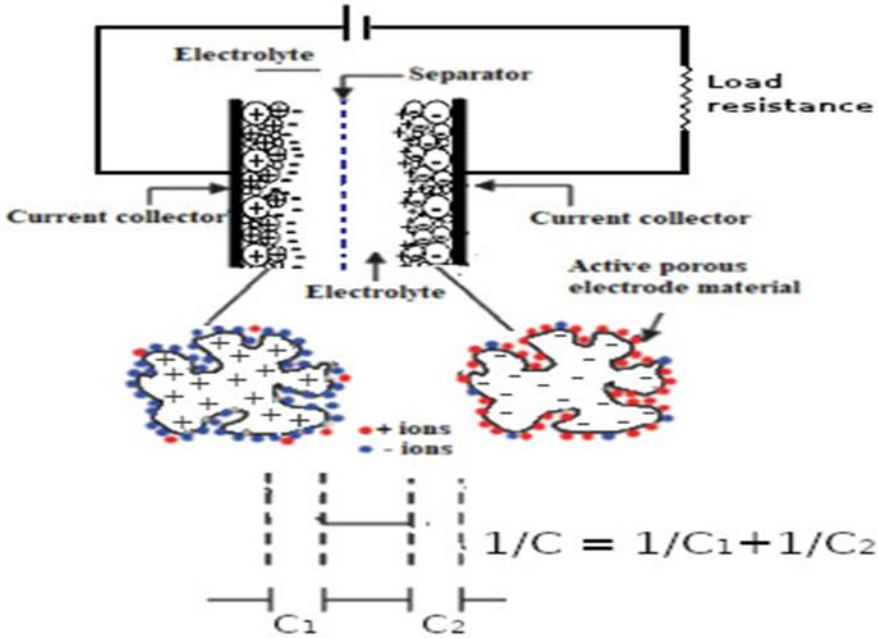

Figure 3. Schematic diagram of an EDLC with porous electrode materials (Zhang and Zhao, 2009).

In EDLCs, electrodes are engineered so that the recombination of ions or charges at the electrode-electrolyte interface is prevented (Shi et al., 2011). When voltage is applied, a double-layer of charge is formed due to the accumulation of ions in the electrode (e.g., negative ions) and solvated ions (e.g., positive ions) in the liquid electrolyte, which diffuses through a separator. A monolayer of polarized solvent molecules separates these. This double-layer acts approximately as the dielectric layer in a conventional capacitor, with a thickness of a single molecule. Therefore, the capacitance can be calculated using equation (1), which yields a very large value due to the minimal thickness (d) and large surface area (A). To achieve high storage capacity, it is essential to control the specific surface area, pore size, and enhance electrical conductivity (Wang et al., 2012).

Due to this charge storage mechanism, EDLCs achieve higher energy densities than conventional capacitors (Conway, 1999; Kotz and Carlen, 2000; Burke, 2000). Since, in EDLCs, each electrode-electrolyte interface acts like a capacitor, as shown in Figure 3, the system can be considered as two capacitors in series. This results in the cell capacitance (C), given by equation (3), where C_1 and C_2 represent the capacitances of the first and second electrodes:

$$C = C_1\, C_2/(C_1 + C_2) \qquad (3)$$

Here, C_1 and C_2 are the capacitances of the capacitors formed at the electrode-electrolyte interface, which depend on the nature of the electrode and electrolyte. The characteristics of EDLCs largely depend on surface area, pore size distribution, shape, structure, and conductivity. Electrodes with a porous structure exhibit a high specific area. Due to their higher surface area, lower cost, stability under high current loads, low internal resistance, and fabrication flexibility, carbon materials in different forms—such as activated carbons, carbon aerogels, carbon nanotubes, and graphene—are generally used as electrodes (Frackowiak and Beguin, 2001; Shi, 1996; Wang et al., 2001; Frackowiak and Beguin, 2002; Du et al., 2005; Gao, 2017; Zhang et al., 2014).

The electrolyte may be either aqueous or organic, depending on the intended application of the supercapacitor. No chemical changes occur since there is no charge transfer between the electrolyte and the electrode. Due to this, EDLCs are highly reversible and can operate for many charge-discharge cycles (as many as 10^6 times) with stable performance. Because of their cycling stability, EDLCs are well-suited for applications in non-user-serviceable locations, such as deep-sea or mountain environments (Conway, 1999; Kotz and Carlen, 2000; Burke, 2000).

Pseudo-capacitor (PC):

The energy storage mechanism of pseudocapacitors (PC) is based on a Faradaic charge process, which involves the transfer of charge between the electrode and electrolyte due to the oxidation or reduction of a chemical species. These Faradaic processes can be either reversible or irreversible. In reversible processes, no new chemical species are produced during redox Faradaic reactions, while in irreversible Faradaic processes, new species are generated. Generally, compared to electric double-layer capacitors (EDLCs), pseudocapacitors exhibit higher specific capacitance and energy density. However, pseudocapacitive electrodes commonly show poor electrical conductivity, restricting and slowing Faradaic reactions. This leads to lower power performance, reduced cycle life, and poorer mechanical stability than EDLCs (Hu et al., 2006; Ke et al., 2005). Notably, the response of pseudocapacitive materials is similar to that of double-layer capacitors. Conducting polymers and metal oxides are typically used for configuring pseudocapacitors.

Hybrid Capacitor:

Both Faradaic and non-Faradaic processes are used in hybrid capacitors to capitalize on the relative advantages and mitigate the drawbacks of EDLCs and pseudocapacitors. This concept achieves higher energy and power densities compared to EDLCs and higher cycle stability compared to pseudocapacitors. Depending on electrode configurations, there are three types of hybrid SCs: Composite, Asymmetric, and Battery-type. In battery-type hybrid capacitors, a battery electrode is used along with a supercapacitor electrode to achieve higher energy density, similar to batteries, while maintaining higher specific power, faster charging-recharging processes, and longer cycle life, like supercapacitors (Li et al., 2005).

Advantages and challenges of supercapacitors:

Advantages: Supercapacitors have several advantages over batteries:

- **High power density:** Compared to lithium-ion batteries (150 W kg^{-1}), supercapacitors display a much higher power delivery (1–10 kW kg^{-1}) as charging and discharging rates are much faster (~0.1–1 sec) than those of batteries (~hours) (Kusko and Dedad, 2007; Uzunoglu and Alam, 2006).

- **Long life expectancy:** No or negligibly minor chemical charge transfer reactions occur during charging and discharging. The life cycle of a supercapacitor is almost infinite (500,000–1,000,000 cycles) with no maintenance and a life expectancy of up to 30 years, whereas lithium-ion batteries have 1,000–10,000 cycles with a life expectancy of only 5–10 years (Conway, 1999; Burke, 2000; Zhang et al., 2009).
- **Long life:** Unlike rechargeable batteries, which experience self-discharge and corrosion, supercapacitors maintain their capacitance and recharging capabilities for several years (Burke, 2000).
- **Wide thermal range:** Supercapacitors can function effectively at a typical operating temperature of -40°C to 70°C. This is advantageous for military applications, where reliable energy storage is required to run proprietary electronic devices under all temperature conditions during warfare.
- **Environmental friendliness:** Supercapacitors are environmentally friendly as no hazardous or toxic materials are used, making the disposal of waste materials safe and easy.

Challenges:

Despite having many advantages over batteries, this technology has some limitations and faces several challenges:

- **Low energy density:** When compared with batteries (> 50 Wh kg^{-1}), supercapacitors have a low energy density (about 5 Wh kg^{-1}). This characteristic limits their use where a large energy capacity is required.
- **High cost:** One of the significant challenges for energy storage commercialization is the high costs of raw materials used as electrodes, electrolytes, and separators. Two common electrode materials used for commercial purposes, carbon materials with a high surface area and RuO_2, are costly, which makes supercapacitors costly (Burke, 2000).
- **High self-discharging rate:** The high self-discharging rate (about 10–40% per day) also hinders their practical uses.

Applications and scope:

With the advantages of high power density and an extensive lifecycle, supercapacitors are suitable for applications where high-power pulses for a short duration and many rapid charge/discharge cycles are required. Applications such as electric vehicles, digital cameras, mobile phones, GPS tracking systems, Bluetooth communication devices, digital communication devices, memory backup, medical equipment, forklifts, cranes, elevators, electrical tools, pulsed laser techniques, regenerative braking or burst-mode power delivery systems, uninterruptible power supplies, alarm and security systems, and storage of solar energy (Ming et al., 2010; Miller, 2006; Reddy and Reddy, 2003; Tehrani et al., 2017; Miller and Simon, 2008; Hu and Wang, 2003; Kim et al., 2015) are a few areas where supercapacitors are highly competitive choices. Under pulsed load conditions, supercapacitors act as filters that relieve peak stresses on the battery by supplying power to the system in short energy bursts. After delivering the pulse current, the battery quickly recharges the supercapacitor between pulse cycles. A parallel battery-supercapacitor connection greatly enhances peak power, considerably reduces internal losses, and extends the discharge life of the battery. With several advantages, supercapacitors have the potential to be a solution in the fields of energy conversion and storage systems by either replacing or complementing batteries.

Summary and Conclusion:

High power densities, quick charging and discharging processes, and exceptional cycle stability make supercapacitors a promising candidate in green energy solutions. This chapter briefly overviews supercapacitors and illustrates how they bridge the gap between capacitors and batteries. The basic charge storage mechanisms for different types of supercapacitors are discussed briefly. Although supercapacitors have many advantages, they face numerous challenges in practical applications. The discovery of graphene and carbon nanotubes has accelerated the development of this technology. With the constant advancement of new technologies and ongoing research into new materials for electrodes and electrolytes, supercapacitors are becoming a viable solution to the ever-increasing demand for clean, sustainable energy.

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