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A REVIEW OF SUPERCAPACITORS AS ELECTRICAL ENERGY STORAGE DEVICES

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Abstract

The challenge of climate change on the environment leading to the massive campaign for de-carbonization has lent to global acceptance of renewable energy as a veritable alternative to the carbon-laden fossil fuels, currently in use. However, there are two major hurdles to the full implementation and adoption of renewable technologies as an alternative source of energy. The first is the low energy conversion factor of current renewable energy transducers, and the second is the spatial and temporal variability of renewable energy sources. To achieve a more sustainable society with adequate renewable energy and less environmental pollution, more versatile, robust, and efficient electric energy storage and conversion approaches are needed. Any success in the deployment of renewable energy technology, as an alternative source of energy, must rely heavily on the progress made in the development of Energy Storage Devices (ESD). This paper examines the future of supercapacitors and the development of supercapatteries as a means of mitigating the current limitations of renewable technologies. So far, batteries have been the preferred electricity storage devices, because of their portability and relatively high energy density for many applications requiring sustained power supply over a reasonable time. However, for other applications demanding large instantaneous power, like a rocket launching, current batteries become unsuitable due to their slow rate of energy release. Although new technologies such as the lithium-ion battery have been developed to improve power performance, they are still bedeviled with the same intrinsic limits. Supercapacitors on the other hand, though fundamentally, hold the promise of addressing the limitations of battery systems, fall short of high energy density considerations. Hybrid systems are, therefore, being advocated as a means of bridging the gap between the two Energy Storage Devices (ESD) technologies. The emergence of supercapatteries ESD technology which combines the positive properties of both ESDs is a step in the right direction. A lot of research effort is being made in the development of electrode materials and electrolyte characterization to improve performance and enhance affordability and commercialization.

Keywords: Supercapacitor, Supercatteries, Renewable energy, Energy storage, ESD

1. Introduction

The majority of the existing power generation technologies are based on non-renewable energy resources, such as fossil fuels, with attendant negative effects on the climate system and the environment. The duo of the decarbonization campaign and the sudden focus on intermittent renewable energy sources, like solar energy, is driving the global quest for energy storage efficiency. Experts believe that large-scale electricity storage technology can boost renewable energy applications and reduce the many intrinsic failures and weaknesses of the current grid system (Schreiber, William 2007; Hadartz and Julander, 2008; Muhammad, et al., 2022). Efficient electric energy storage will result in two major outcomes. First, it will boost the development of renewable energy technologies, and second, it will result in the de-coupling of electricity supply from the common grid and allow distributed storage opportunities for local grids or microgrids to prosper. This will greatly reduce distribution costs and enhance grid security (Javed Iqbal et al, 2021)

The demand for renewable energy resources is rising astronomically due to the rising cost and depletion of fossil fuels, and the global decarbonization campaign as a way of reducing environmental pollution. At the current level of development, renewable energy sources though abundant in supply are not readily convertible to electrical energy – the form of energy most readily available for human consumption. Hence, current renewable energy technology will not be able to satisfy the world’s energy needs. The major challenge is the low conversion factor of solar-electrical energy transducers and spatial and temporal variability of thevresources (Ewona and Obeten, 2021; Ewona, et al., 2014)).

In order to overcome these inadequacies, backup energy storage systems are needed to absorb excess energy and provide sufficient and sustained energy supply whenever required. This requires energy management strategies to guarantee that renewable energy production and supply are environmentally and economically sustainable.

To have electrical energy systems from renewable energy sources in sufficient supply and power to drive modern-day technological needs, storage facilities will be required to conserve the electrical energy in a form that can be reinvigorated to produce higher power, aside from the need to store excess energy and energy generated during hours of redundancy when such energy was not required. Because the rate of energy conversion and the power density is low, electrical energy from these sources would need to be accumulated, over time, to be enough for more demanding applications.

2. Characterisation of storage systems for renewable energy applications

Storage of electrical energy should normally be in the form that can easily be retrieved. The two main known forms that electrical energy can be stored and easily made available are electrochemical and electromagnetic forms. Each form comes with specific advantages and disadvantages as shown in section 3.

The most important considerations and operational characteristics of Energy Storage Devices (ESD) are based on two properties: their energy density and power density. The energy density is quantified based on its wattage hour (Wh). Hence, the gravimetric energy density of an ESD system is defined as the amount of energy that can be stored in the system per unit mass(kg). In the same way, the gravimetric power density of a system is defined as the amount of power(W) that the system can supply per unit mass(kg) (Herzog et.al. 2010).

Practical energy storage and supply systems require that the ESD possesses the following characteristics.

1. Quick charge/ discharge rates
2. High energy density
3. High power density

However, where there is a stable and constant power supply, the most important property of the system would be its energy density. This means that the system can supply the load’s requirements for a relatively long period of time. but, when the load profile is characterized by some transient behavior, instantaneous power requirements become more important, and the most important property of the system will be its power density.

3. Types of Energy Storage Devices (ESD)

Effective Energy Storage Devices (ESD) are designed with materials such that electrodes demonstrate efficient electrochemical performance supported by efficient electrolyte architecture for facile transport of ions and electrons.

There are two basic forms of storing electrical energy for easy conversion to electrical power. Electrical energy can either be stored as chemical potential energy or as electromagnetic potential energy.

A. Electrochemical Systems

Electrochemical systems employ the use of electrolytes as storage media for electrical energy. The common forms are batteries and electrochemical condensers. The basic advantage of electrochemical energy storage is that it ensures high energy density (Suresh et al 2021). A common example is a battery. Battery systems are characterized by high energy storage density, stable charge and discharge features but low power density. The greatest concern in the application of battery systems is related to ionic and electronic transport, kinetic barriers, phase mobility, reactivity, degradation, and stability issues – and all these are related to materials and interface properties. One of these challenges is a chemical reaction that leads to battery degradation and aging. Degradation or aging is due to gassing and normally comes with overcharging, though, this can be mitigated using appropriate battery management systems with overvoltage protection. (Schiffer et.al., 2007 Glavin et. al., 2007).

B. Electromagnetic Systems

Electromagnetic energy can also be stored in the form of an electric field or a magnetic field, the latter is typically generated by a current-carrying coil. Practical electrical energy storage technologies include Electrical Double-Layer Capacitors (EDLCs or ultracapacitors) and superconducting magnetic energy storage (SMES).

Among electromagnetic storage systems which store electrical energy in an electric field sustained by a dielectric material are capacitors, EDLCs, or supercapatteries. Supercapatteries are actually hybrid systems that combine the features of both batteries and supercapacitors to improve performance. Supercapacitors possess unique properties that can complement other energy storage technologies in hybrid electric energy systems. They are characterized by their fast charge and discharge capability, highly reversible process functionality, high recyclability, and high power density but relatively low energy density compared to batteries. Hence, integrating a supercapacitor into the energy system can positively affect the system's operation stability (Altiparmakis & Däumling 2013).

4. The capacitor

A capacitor is an electrical device that stores charge when an electrical field develops between two electrically charged electrode plates. It is therefore characterized by its ability to store energy in an electric field developed through the accumulation of electric charge. The capacitor's ability to accumulate electric charge and store electric energy is defined by its capacitance. There are generally three categories of capacitors namely: electrostatic, electrolytic, and electrochemical. The electrostatic capacitor is the conventional capacitor. It is made up of two conducting plates with an isolator between the plates. The insulator serves as the dielectric where electrical energy is stored as charges. In an electrolytic capacitor, a conductive electrolytic salt replaces the dielectric and makes direct contact with the electrodes. In this way, the effective plate distance is reduced hence, increasing the capacitance of the capacitor. On the other hand, an electrochemical capacitor has porous electrodes where an electrolyte replaces the dielectric. This helps to increase the capacitance even more. They are known by different names such as supercapacitor, ultracapacitor, pseudocapacitors, or double-layer capacitors (Atcitty, 2006)

The basic configuration of a capacitor provides that one plate is held at a positive potential, while the other is negative. The potential difference, V between the two plates is directly proportional to the distance between the plates, d, and to the strength of the electric field, E through the relationship:

$$V = E \cdot d. \text{ ------------------------------------ } (1)$$

The capacitance of the capacitor, C is the ratio of charge, Q to the potential difference, V (Tipler, 2007).

$C = Q/V$ (Farads) ----------------------------(2)

Or

$V = Q/C$ (Volts--------------------------------(3)

Differentiating Equation (3) we get

$dV(t)\,dt = 1/C \cdot dQ/dt = 1/C \cdot I$ ----------(4)

Notice that, at constant current, the voltage is proportional to the inverse of capacitance. However, there is a limit to the voltage increase, for a particular capacitor. The maximum voltage at which a portion of the insulating material between the two conductor plates becomes electrically conductive and a short circuit channel develops is known as its breakdown voltage (Product guide, 2009).

In actual terms, capacitance is defined by

$C = \varepsilon A/d$ ----------------------------------- (5)

Where,
C = Capacitance
ε = permittivity of the dielectric
A = Cross-sectional area
d = separation between the two plates

It can be seen from Equation (5) that the capacitance of the capacitor can be increased by maximizing the effective cross-sectional area and reducing the effective electrode separation.

Figure 1. shows the frequency-dependent profile of a typical supercapacitor. It can be observed that as the frequency increases, the capacitance rises rapidly. The reason is that as the applied electric field changes the ions are not able to speed up to reach the depth of the electrode pores as quickly as the change occurs (Rafik et.al, 2007). This is why the variation in current does not follow frequency fluctuations.

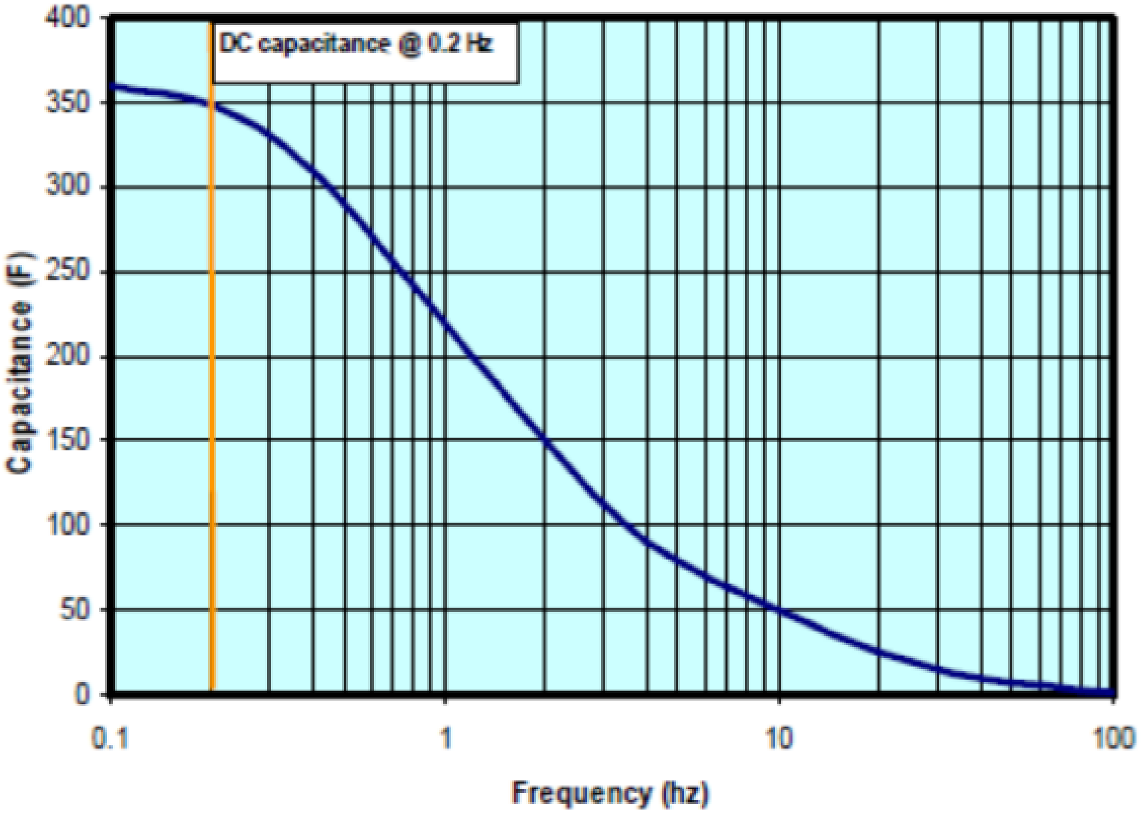


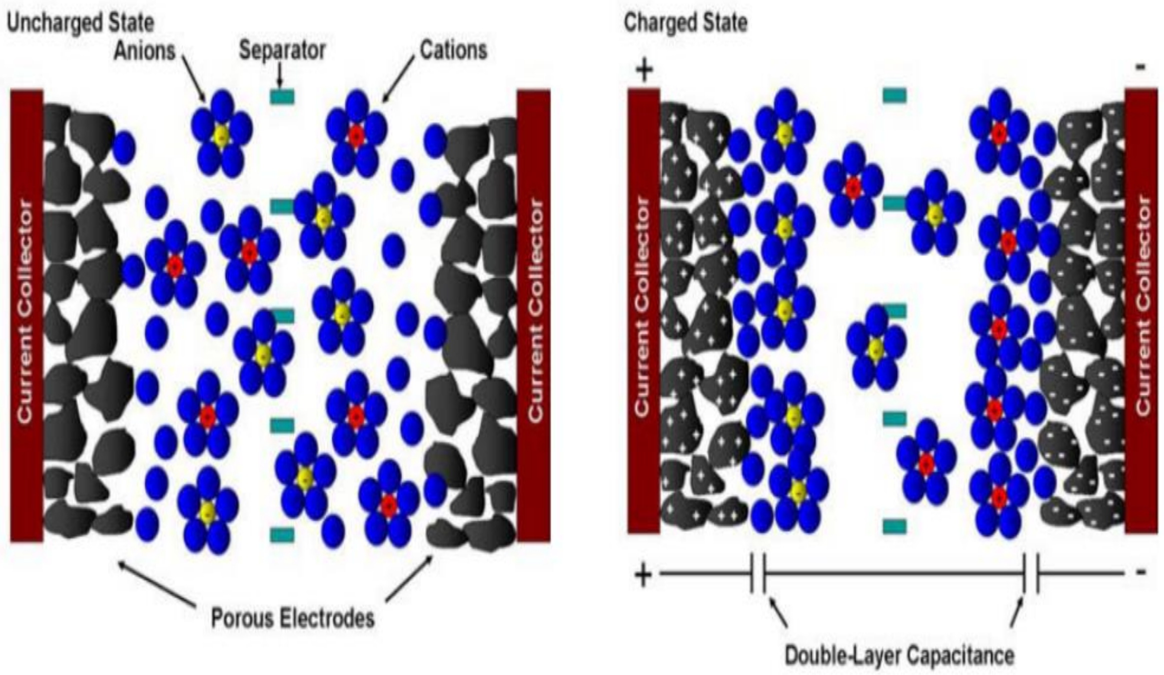
Figure 1: Capacitance as a function of applied frequency (Product guide, 2009).

By using sophisticated porous electrode materials with large effective surface areas instead of the usual homogeneous conductor plates, far higher capacitance values can be achieved. When conventional dielectrics are replaced with electrolytes that have mobile ions, charge separation is reduced to molecular dimensions making them more compact.

5. Supercapacitor fundamentals

Supercapacitors are excellent energy buffers that are very necessary for applications that function with large electrical power and high pulse current due to their high capacitance and low impedance characteristics. The large storage capacitance provides enough power required during start-up and a steady supply during transient operation. When connected in parallel, a supercapacitor can smoothen the transient characteristics and thus improve the efficiency of an ordinary battery supply. The supercapacitor either supplies large current pulses that occur during engine start-up or absorbs excess current during regenerative braking. The capacitor also has low internal impedance, which is useful in pulsed power applications (Schönberger, 2022; Harper and Ellenbogen, 2006; Datasheet, Bootscap Ultracapacitors, 2009).

The basic features of a supercapacitor are similar to those of conventional capacitors as shown in section 4. A typical example of a double-layer supercapacitor is shown in figures 2 A and B below.



A B

Figure 2: Principal sketch of a double layer supercapacitor, uncharged state at the left, 2A charged state to the right 2B (Atcitty, 2006).

When a voltage is applied to the electrodes, the corresponding electric field will cause ions in the electrolyte to move toward the electrode surfaces as shown in figure 2B. The electrode surfaces are made from materials that do not react with the ions. This ensures that both the electrolyte and the electrode do not degenerate with time.

The electrons are seen accumulating on the negative electrode while leaving behind a vacancy of electrons on the positive electrode. The opposite ions in the electrolyte are thereby separated into electrodes with opposite polarities and accumulated there. These form a second conducting layer between the electrolyte and the electrodes, but with a very small gap – normally of a few nanometers. The Ionic layers formed at the electrode surfaces give rise to the effective double layer of charges which gives the double-layer capacitor its name. By comparison, the gap or phase boundary between the ionic layer and the electrode is the analog of the dielectric layer of a conventional capacitor (Prophet, 2003). Consequently, a capacitance is established within this layer, and energy is stored in the electric field.

A thin isolation membrane is used to separate between the electrodes of the supercapacitor where the mobile ions are made to fuse into. The porous electrodes are then bonded to current collectors, which are further connected to the external metal leads from the positive and negative terminals of the device. Because there is no chemical reaction taking place in the electrolyte, degradation due to charging/discharging cycles does not occur. This raises the lifetime of the device to more than 1 million cycles. The large surface area has the advantage of offering low internal resistance to current, resulting in low losses. And because the cycle efficiency is high, internal heating is low.

Figure 3 shows that the capacitance of the supercapacitor varies with the terminal voltage, contrary to a conventional capacitor. The physical understanding of this phenomenon is not well understood, but many researchers believe that it could be due to a reduction in the distance separating the charges at the phase boundary occurring between the electrode and the electrolyte as the voltage increases (Rafik et.al, 2007).

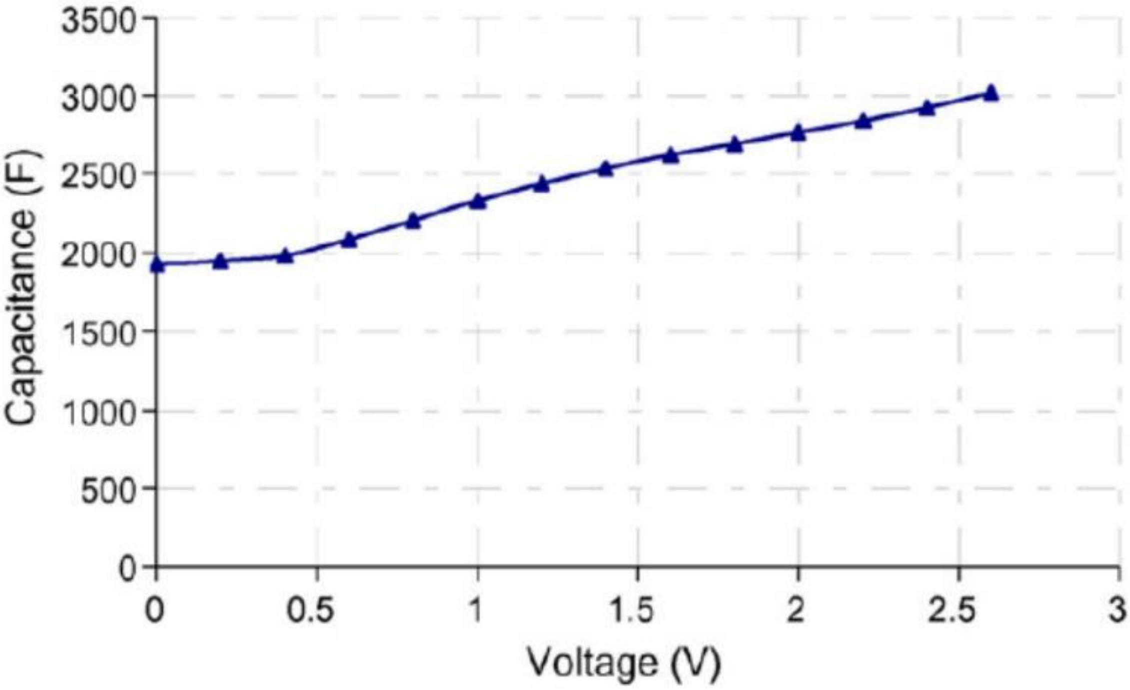


Figure 3: Capacitance as a function of voltage for a typical supercapacitor (Rafik et.al, 2007).

6. Limitations of the supercapacitor

Though supercapacitors are heralded for their high-power densities, the following weaknesses limit their wide applications:

i. Low energy density, due essentially to size limitations which makes the device bulky (Jimena, **2020**).
ii. High self-discharge rate due to large surface area reduces useful storage time (Diab, et. al., 2009; Yang and Zhang, 2011).
iii. Very low internal resistance can result in very high current discharge which if short-circuited can damage the device or be harmful.
iv. Uneven charging due to connecting many supercapacitors in series when higher voltage is desired; leading to a reduction of the effective capacity.

v. The voltage across a capacitor varies a lot with the charge level. This means that a dc converter is needed to maintain a constant output voltage from a supercapacitor storage system.
vi. It is impossible to extract the entire energy content from the capacitor while keeping the output voltage within practical limits. This further reduces the effective energy density of a supercapacitor.

7. Hybridization considerations

The apparent limitations of various standalone Energy Storage Devices, ESDs such as supercapacitors and battery systems, in meeting contemporary energy needs, especially about their strengths at differing extremes of the energy requirements, have encouraged the development of hybrid ESDs. The desired hybrid system is expected to meet the following basic operational requirements:

1. The system should be able to supply a nearly constant mean current.
2. Internal ohmic losses should be kept to the minimum
3. Terminal voltage dips should be avoided
4. In the case of supercapacitor-battery pair, both should be matched and ensure the supply of steady dynamic current to the load with zero average.

During high load demand, for instance, both the battery and the supercapacitor supply charge to the load, while during low load demand, the battery supplies both the load and recharges the supercapacitor. This reduces the voltage and current ripple of the ESD.

7.1. Hybrid storage systems

Although supercapacitors and batteries are being extensively used in ESDs, their stand-alone efficiencies are still not enough to meet the increasing quest for more energy supply. Hybrid ESDs therefore, employ a combination of both battery and supercapacitors storage methods to enhance performance and overcome their inherent limitations. Hybrid energy storage systems that combine the features of both are advocated to bridge the performance gap between the two technologies. In this way, surplus energy is stored when the demand is low, and more energy is released when instantaneous energy demand is high. The search for more efficient and advanced materials to further improve the energy storage capabilities of the supercapacitor-battery pair hybrid systems has also received tremendous attention.

The hybrid systems, which incorporate the characteristics of both supercapacitor and battery technologies are now popularly called Supercapatteries. Supercapatteries combine both capacitive and battery-like behavior, thereby deriving the benefits of both storage mechanisms. These ESD materials possess intermediate ion intercalation between pseudocapacitive and battery materials. It poses a nonideal polarization like that of a battery while it can be discharged completely. The nematodes in supercapattery are usually made of carbonaceous materials and their composites due to their high surface area, electrochemical stability, electrical conductivity, and high porosity. This combination provides an outstanding energy storage performance. (Arshid, et al, 2021).

7.2. Specialised materials for supercapattery (scap) development

Supercapattery deals with the electrochemical characterization of battery-type charge storage materials. Current efforts are being made to develop materials to enhance the energy density and efficacy of existing supercapacitors. The common areas of interest in achieving this goal are more towards improving the electrode material characteristics in order to improve ionic mobilities in electrolyte insulators than in the need to improve the dielectric characteristics of existing supercapacitors. The following research approaches are aimed at achieving the aforementioned objectives.

A. Electrodes

i. Layered double hydroxide as electrode material for high-performance supercapattery

Efficient electrodes are an important consideration in designing efficient storage systems in supercapattery. Layered double hydroxides (LDH) are a class of synthetic clay with cationic layers comprising anions in the hydrated interlayer. LDH are great materials for making efficient electrodes for supercapatteries, due to their tunable composition, structure, and morphology. Transition metal oxides/hydroxides are excellent in building LDH materials because they provide better capacity and enhanced stability, due to their faradic mechanism (Aruni et al., 2021).

ii. Metal-based ternary nanocomposites

The design of new electrode materials from Metal-based ternary nanocomposites, which help to improve the energy density requirement in supercapacitors has been successful. Metal-based ternary nanocomposites are active materials that can enhance the specific capacitance and electrochemical conductivity, and also improve the thermal and chemical strengths of electrode materials. The advances of ternary electrode materials based on noble metals with transition metals and conducting platforms such as carbonaceous materials and conducting polymers are still being explored.

iii. MXene

The materials for the design of electrodes that demonstrate efficient electrochemical performance supported by efficient architecture for facile transport of ions and electrons are becoming topical in the design of high-performing Energy Storage Devices, ESDs. 2D MXenes have shown promise as an efficient electrode material due to their high surface area, extra active sites, and interlayer spacing. Hence, the future of nanomaterials based on MXene are promising (Ghulam et al., 2021).

iv. Metal/metal oxide thin film electrodes for supercapatteries:

The practical constraints on performance enhancement and long-term stability of supercapacitors, as ESDs, have triggered vigorous research efforts in the direction of metal oxides-based nanostructures with different morphologies, new materials composites through doping, mixing or chemical processing, hybridization with other composites for enhanced surface area and more efficient surface redox reactions, and nanocomposites fabrication.

Due to good electrical conductivity, low cost, and abundance, metal oxides are aggressively being explored as positive electrodes for supercapatteries. Among them, ruthenium oxide (RuO2), manganese oxide (MnO2), and cobalt oxide (Co3O4) are more prominent due to their high energy and power densities, and cyclic stability (Mohammad et al., 2021).

v. Binary metal oxides for supercapattery devices

A family of Binary Metal Oxides (BMOs) generally represented by ABxOy (where A and B represent metallic elements such as Ni, Co, Zn, Mn or Fe, etc.) are efficient electrode materials for supercapattery devices. Low cost, easy synthesis, less toxicity, multiple oxidation states, better electronic conductivities, and higher theoretical capacities are the attractive features of BMOs (Iqbal, et al., 2021).

vi. Carbonaceous nanocomposites for supercapattery

Supercapattery poses a nonideal polarization like that of a battery while it can be discharged completely. The negative electrodes in supercapattery are usually made of carbonaceous materials and their composites due to their high surface area, electrochemical stability, electrical conductivity, and high porosity. Various carbonaceous materials such as reduced graphene oxide, carbon nanotube, and activated carbon are being used as electrodes in supercapattery (2021, Ewona and Obeten (2021).

vii. Conducting polymeric nanocomposite for supercapattery

Owing to the facile synthesis routes, cost-effective processes, and high specific capacitance with enhanced mechanical stability, the nanocomposites of conductive polymers have gained considerable research attention in developing efficient supercapatteries. Various nanostructured materials such as carbon with its derivatives, metal oxide, transition metal oxide, chalcogenide, and MXene, when incorporated into conducting polymers show superior electrochemical performance due to their synergistic properties (Meenakshi et al., 2021, Ewona and Obeten, 2021).

B. Electrolytes

Aqueous solid and gel electrolytes for supercapattery

Research for electrolytes for enhanced ESDs is not as aggressive as the search for electrode materials. However, the quest for developing environment-friendly materials for Supercapacitors ESDs for enhanced energy density and efficacy of existing supercapacitors is in the works, currently. The polymer electrolytes have significant potential advantages, such as a three-dimensional network, microstructure, porous morphology, controlled pore structure, self-healability, environment-friendly, and nontoxic nature. Aqueous solid and gel electrolytes are a unique combination of conventional polymers and organic conductors. Furthermore, polymer electrolytes improved the rate capability, cycle life, specific capacitance, energy density, and power density of supercapacitors and supercapattery. Recent studies on flexible polymer hydrogel electrolytes as functional materials have provided new hope for the development of environment-friendly supercapacitors and supercapatteries (Shahid et al., 2021; Seim, 2011).

8. Future possibilities

It has been observed that supercapacitors have excellent electrical power densities as shown in figure 4, but, at present, their energy densities are very low. In fact, it is about 1% of a typical Li-ion battery.

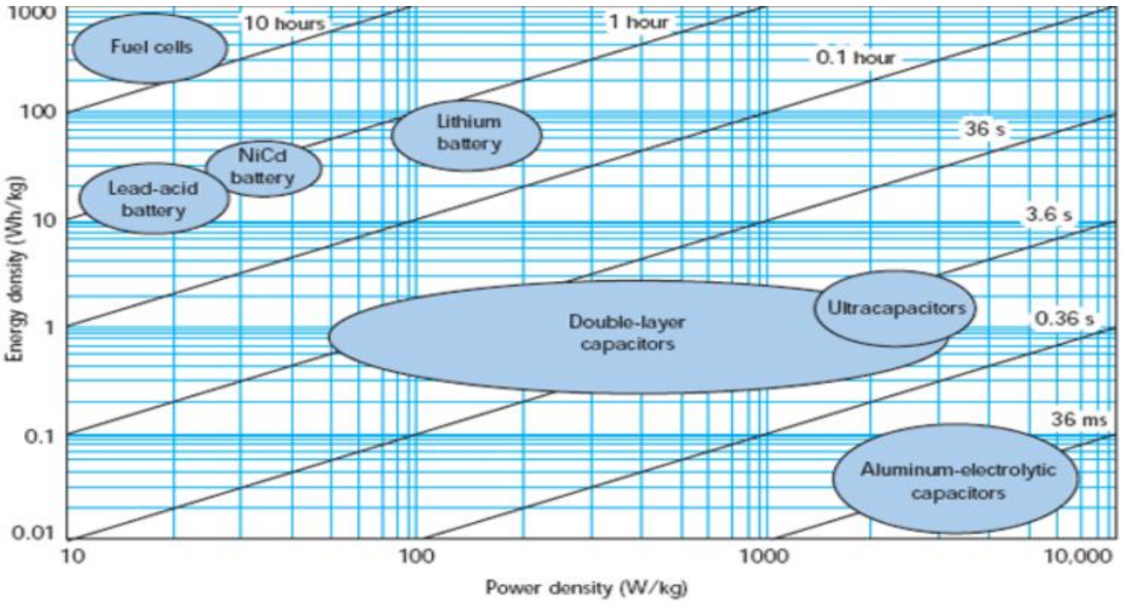


Fig. 4: Ragone plot of specific gravimetric energy densities against specific gravimetric power densities for different energy storage technologies (Rafik et.al, 2007). The incline lines show the discharge times into a specific load.

Low energy density is therefore a major factor inhibiting the growth of supercapacitors for mass energy storage. Ongoing research is, therefore, aimed at an efficient way of combining the best properties of both supercapacitors and battery. A lot of progress is being made already. This seems to be the best way to go at the moment – the way leading to high-power and large energy densities, little cycling degradation, and a wide range of operating temperatures. Supercapatteries using various forms of nanostructured carbon-based electrodes, such as carbon nanotubes and graphene, have also shown very promising results. Graphene is often used as the negative electrode to improve ion transfer efficiency. (Product guide, 2009; Lee, et al., 2011; Kuperman, et. al., 2011; Sikha, et. al., 2005; Sikha, et. al., 2004).

The introduction of a graphene-based lithium capacitor which combines the properties of a supercapacitor and a Li-ion battery is producing fantastic results (Gebre, 2009). Such devices have shown energy densities close to those of Li-ion batteries. There are great prospects for obtaining high power and energy densities, and a long operating lifespan at affordable prices.

In some applications, it is observed that a battery and a supercapacitor can be used be used effectively in one storage systems, if connected in parallel. This will produce a smaller, cheaper, and longer-lasting ESD than using a battery alone. There are applications where a smaller current is required during the running cycle but a supercapacitor may be needed to deliver short bursts of high power, such as when starting a machine or accelerating a moving device. In this case, a supercapacitor in parallel with a small battery will be sufficient for the load requirements. When charging, the supercapacitor helps to smoothen out unwanted current pulses that could have damaging effects on the battery, thus prolonging the battery shelve life (Dougal et.al., 2002).

9. Conclusions

The major challenges in the renewable energy sector are in the areas of effective conversion of energy from other forms to electrical energy. At present, the preoccupation for most researchers is the role of batteries in energy storage and reuse. This is considered against the backdrop of immediate challenges such as inadequacy of both energy and power densities, charge and discharge rates, conversion efficiency, shelve life, etc. To bridge this gap, greater effort is devoted to the development of electrode materials and electrolyte characterization. Herzog et.al., 2010 argue that the success of the deployment of renewable energy technology, as an alternative source of energy, relies heavily on the progress made in the development of Energy Storage Devices (ESD).

The electrochemical and electromagnetic methods of electrical energy storage have been identified as potential methods for the development of excellent ESDs though each is characterized by opposite limitations. The supercapacitor which stores energy in an electromagnetic field has excellent power density but low energy density. On the other hand, the battery system which stores electrical energy as charges in an electrolyte has a high energy density, as against low power density. Hybrid storage systems, which combine the positive properties of both technologies, are being explored. To achieve this, emphasis is being laid, more on the electrode material development with appropriate electrolytes to replace the conventional dielectrics in capacitors and create what is now called supercapatteries.

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