The role of nanomaterial for the design of supercapacitor

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Abstract

The development of more efficient electrical storage is a pressing requirement to meet future societal and environmental needs. This demand for more sustainable, efficient energy storage has provoked a renewed scientific and commercial interest in advanced capacitor designs in which the suite of experimental techniques and ideas that comprise nanotechnology are playing a critical role. Capacitors can be charged and discharged quickly and are one of the primary building blocks of many types of electrical circuit, from microprocessors to large-sale power supplies, but usually have relatively low energy storage capability when compared with batteries. The application of nanostructured materials with bespoke morphologies and properties to electrochemical supercapacitors is being intensively studied in order to provide enhanced energy density without comprising their inherent high power density and excellent cyclability.

Keywords: Nanomaterial, supercapacitor, Redox reaction.

Resumen

El desarrollo de almacenamiento eléctrico más eficiente es un requisito ineludible para satisfacer las necesidades futuras de la sociedad y el medio ambiente. Esta demanda de más sostenible, el almacenamiento eficiente de energía ha provocado un renovado interés científico y comercial en diseños avanzados de capacitores en los cuales el conjunto de técnicas experimentales e ideas que componen la nanotecnología están jugando un papel fundamental. Los capacitores pueden ser cargados y descargados rápidamente y son uno de los principales bloques de construcción de muchos tipos de circuitos eléctricos, desde los microprocesadores hasta las fuentes de alimentación de gran-venta, pero usualmente tienen una capacidad de almacenamiento de energía relativamente baja en comparación con las baterías. La aplicación de materiales nanoestructurados con morfologías a medida y propiedades para supercapacitores electroquímicos están siendo estudiados intensamente con el fin de proporcionar una mayor densidad de energía sin que comprenda su inherente densidad de alta potencia y excelente ciclabilidad.

Palabras clave: Nanomaterial, supercapacitores, reacción Redox.

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I. INTRODUCTION

In response to the changing global landscape, energy has become a primary focus of the major world powers and scientific community. There has been great interest in developing and refining more efficient energy storage devices. One such device, the supercapacitor, has matured significantly over the last decade and emerged with the potential to facilitate major advances in energy storage. Supercapacitors, also known as ultracapacitors or electrochemical capacitors, utilize high surface area electrode materials and thin electrolytic dielectrics to achieve capacitances several orders of magnitude larger than conventional capacitors. In doing so, supercapacitors are able to attain greater energy densities while still maintaining the characteristic high power density of conventional capacitors [1, 2, 3]. The term ‘supercapacitor’ finds itself in common usage, being the trade name of the first commercial devices made by Nippon Electric Company (NEC), but ‘ultracapacitor’ is also commonly used [4, 5], originating from devices made by the Pinnacle Research Institute (PRI) for the US military.

While electrostatic capacitors have been used as energy storage elements for nearly a century, low capacitance values have traditionally limited them to low power applications as components in analogue circuits, or at most as short-term memory backup supplies. Recent developments in manufacturing techniques have changed this, however, and with the ability to construct materials of high surface-area and electrodes of low resistance has come the ability to store more energy in the form of electric charge [6, 7]. This has combined with an understanding of the charge transfer processes that occur in the electric double-layer to make high-power electrochemical capacitors possible. Supercapacitors therefore represent a new breed of technology that occupies a niche amongst other energy storage devices that was previously vacant. They have the ability to store greater amounts of energy than conventional capacitors, and are able to deliver more power than batteries. The current position of the supercapacitor is easily visualized by means of a Ragone plot, which graphically represents a device's energy and power capabilities.

The performance improvement for a supercapacitor is shown in Fig. 1; a graph termed a "Ragone plot". This type of graph presents the power densities of various energy storage devices, measured along the vertical axis, versus their energy densities, measured along the horizontal axis. In Fig. 1, it is seen that supercapacitors occupy a region between conventional capacitors and batteries. Despite greater capacitances than conventional capacitors, supercapacitors have yet to match the energy densities of mid to high-end batteries and fuel cells [8, 9]. Thus, much of the literature surveyed for this overview focuses on developing improved types or classes of supercapacitors to make their energy densities more comparable to those of batteries.

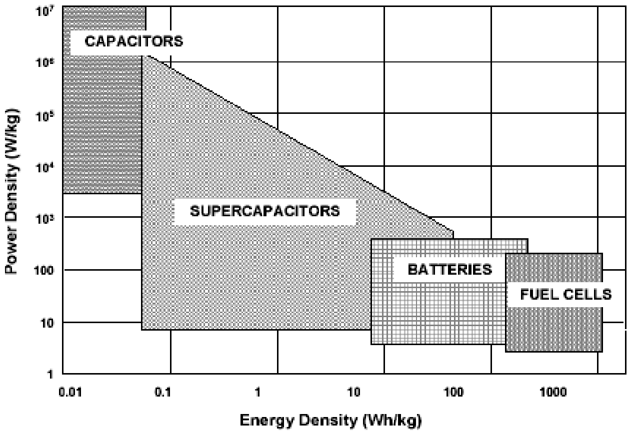

FIGURE 1. Ragone plot of energy storage devices.

Besides bridging the gap between capacitors and batteries, supercapacitors also possess a number of desirable qualities that make them an attractive energy storage option. The mechanisms by which supercapacitor store and release charge are completely reversible, so they are extremely efficient and can withstand a large number of charge/discharge cycles. They can store or release energy very quickly, and can operate over a wide range of temperatures.

Supercapacitors have only very recently begun to make themselves known as a viable energy storage alternative, and while most electrical engineers may be aware of the technology it is probable that few possess an understanding of the processes involved and the applications that are possible.

A. Background of Supercapacitor

Conventional capacitors consist of two conducting electrodes separated by an insulating dielectric material. When a voltage is applied to a capacitor, opposite charges accumulate on the surfaces of each electrode. The charges are kept separate by the dielectric, thus producing an electric field that allows the capacitor to store energy. This is illustrated in the Fig. 2 Capacitance *C* is defined as the ratio of stored (positive) charge *Q* to the applied voltage *V*.

$$C = Q/V. \tag{1}$$

For a conventional capacitor, C is directly proportional to the surface area A of each electrode and inversely proportional to the distance D between the electrodes.

$$C = \epsilon A/d. \tag{2}$$

Where is the dielectric constant.

The two primary attributes of a capacitor are its energy density and power density. For either measure, the density can be calculated as a quantity per unit mass or per unit volume. The energy E stored in a capacitor is directly proportional to its capacitance:

$$E = 1/2\, CV^2. \tag{3}$$

In general, the power *P* is the energy expended per unit time. To determine *P* for a capacitor, though, one must consider that capacitors are generally represented as a circuit in series with an external "load" resistance *R*.

The internal components of the capacitor (*e.g.*, current collectors, electrodes, and dielectric material) also contribute to the resistance, which is measured in aggregate by a quantity known as the equivalent series resistance (*ESR*). The voltage during discharge is determined by these resistances. When measured at matched impedance (R = *ESR*), the maximum power P_{max} for a capacitor is given by:

$$Pmax = v2/4 \times ESR. \tag{4}$$

This relationship shows how the *ESR* can limit the maximum power of a capacitor. Conventional capacitors have relatively high power densities, but relatively low energy densities when compared to electrochemical batteries and to fuel cells. That is, a battery can store more total energy than a capacitor, but it cannot deliver it very quickly, which means its power density is low. Capacitors, on the other hand, store relatively less energy per unit mass or volume, but what electrical energy they do store can be discharged rapidly to produce a lot of power, so their power density is usually high. Supercapacitors are governed by the same basic principles as conventional capacitors. However, they incorporate electrodes with much higher surface areas *A* and much thinner dielectrics that decrease the distance *D* between the electrodes. Thus from Eq. 2 and 3, this leads to an increase in both capacitance and energy. Furthermore, by maintaining the low *ESR* characteristic of conventional capacitors, supercapacitors also are able to achieve comparable power densities. Additionally, supercapacitors have several advantages over electrochemical batteries and fuel cells, including higher power density, shorter charging times, and longer cycle life and shelf life.

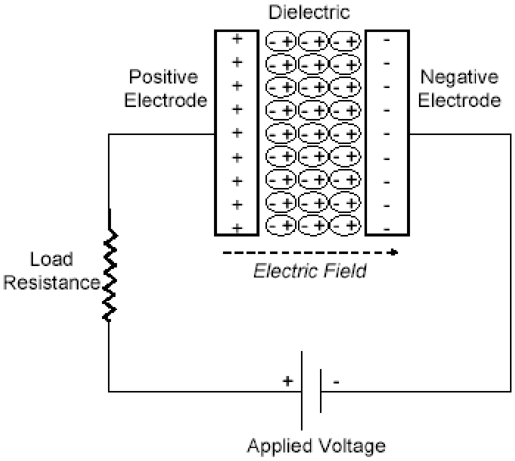

FIGURE 2. Diagram of conventional capacitor.

B. Classification of Supercapacitor

Based upon current R&D trends, supercapacitors can be divided into three general classes: electrochemical double-layer capacitors, pseudocapacitors, and hybrid capacitors. Each class is characterized by its unique mechanism for storing charge. These are, respectively, non-Faradaic, Faradaic, and a combination of the two. Faradaic processes, such as oxidation-reduction reactions, involve the transfer of charge between electrode and electrolyte. A non-Faradaic mechanism, by contrast, does not use a chemical mechanism. Rather, charges are distributed on surfaces by physical processes that do not involve the making or breaking of chemical bonds. This section will present an overview of each one of these three classes of supercapacitors and their subclasses, distinguished by electrode material. A graphical taxonomy of the different classes and subclasses of supercapacitors is presented in Fig. 3.

C. Electrochemical Double Layer Capacitor (EDLC)

Electrochemical double-layer capacitors (EDLCs) are constructed from two carbon-based electrodes, an electrolyte, and a separator. Fig. 4 provides a schematic of a typical EDLC. Like conventional capacitors, EDLCs store charge electrostatically, or non-Faradaically, and there is no transfer of charge between electrode and electrolyte. EDLCs utilize an electrochemical double-layer of charge to store energy. As voltage is applied, charge accumulates on the electrode surfaces. Following the natural attraction of unlike charges, ions in the electrolyte solution diffuse across the separator into the pores of the electrode of opposite charge. However, the electrodes are engineered to prevent the recombination of the ions. Thus, a double-layer of charge is produced at each electrode. These double-layers, coupled with an increase in surface area and a decrease in the distance between electrodes, allow EDLCs to achieve higher energy densities than conventional capacitors [10, 11]. Because there is no transfer of charge between electrolyte and electrode, there are no chemical or composition changes associated with non-Faradaic processes. For this reason, charge storage in EDLCs is highly reversible, which allows them to achieve very high cycling stabilities. EDLCs generally operate with stable performance characteristics for a great many charge-discharge cycles, sometimes as many as 10 cycles. On the other hand, electrochemical batteries are generally limited to only about 103 cycles. Because of their cycling stability, EDLCs are well suited for applications that involve non-user serviceable locations, such as deep sea or mountain environments.

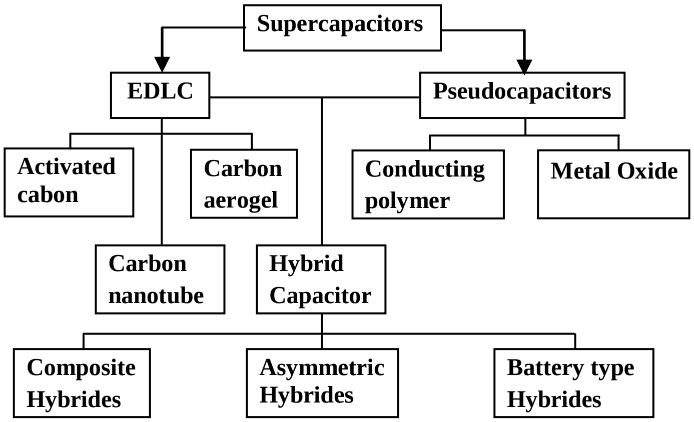

FIGURE 3. Clasification of supercapacitors.

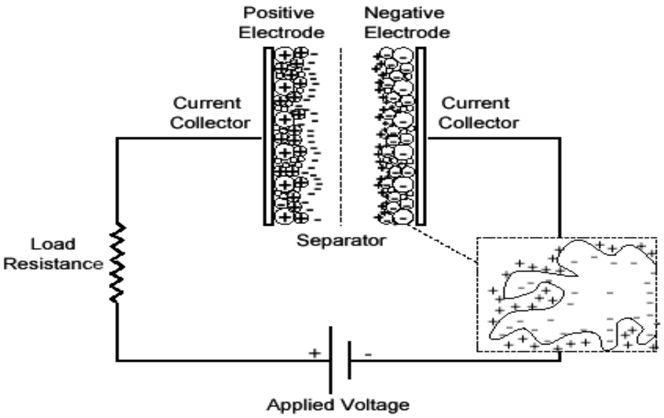

FIGURE 4. Schematic of EDLC.

The performance characteristics of an EDLC can be adjusted by changing the nature of its electrolyte. An EDLC can utilize either an aqueous or organic electrolyte. Aqueous electrolytes, such as H_2SO_4 and KOH, generally have lower ESR and lower minimum pore size requirements compared to organic electrolytes, such as acetonitrile [12, 13]. However, aqueous electrolytes also have lower breakdown voltages. Therefore, in choosing between an aqueous or organic electrolyte, one must consider the tradeoffs between capacitance, ESR, and voltage. Because of these tradeoffs, the choice of electrolyte often depends on the intended application of the supercapacitor. While the nature of the electrolyte is of great importance in supercapacitor design, the subclasses of EDLCs are distinguished primarily by the form of carbon they use as an electrode material. Carbon electrode materials generally have higher surface area, lower cost, and more established fabrication techniques than other materials, such as conducting polymers and metal oxides. Different forms of carbon materials that can be used to store charge in EDLC electrodes are activated carbons, carbon aerogels, and carbon nanotubes.

D. Pseudocapacitor

In contrast to EDLCs, which store charge electrostatically, pseudocapacitors store charge Faradaically through the transfer of charge between electrode and electrolyte. This is accomplished through electrosorption, reduction-oxidation reactions, and intercalation processes. These Faradaic processes may allow pseudocapacitors to achieve greater capacitances and energy densities than EDLCs.

There are two electrode materials that are used to store charge in pseudocapacitors, conducting polymers and metal oxides. The charge transfer that takes places in these reactions is voltage dependent, so a capacitive phenomenon occurs. There are two types of reactions that can involve a charge transfer that is voltage dependent. One is redox reaction and another is adsorption of ions. In a redox reaction involving an oxidant, *ox*, and reductant, *red*, of the form,
$\boldsymbol{ox + ze^{-}=red}$, the potential, E, is given by the Nernst equation as

$$E = E0 + RT/ZF \ \ln \ [\check{R}/1 - \check{R}] \ . \tag{5}$$

E0 is the standard potential, *R* is the gas constant, *T* is the absolute temperature, *F* is the Faraday constant, and $\check{R}$ is defined as *[ox] / ([ox]+[red])*,(where square brackets denote species concentrations). The amount of charge *q* (given by the product *zF*), is therefore a function of the potential *E*. Differentiation of Eq. 5 thus produces a pseudocapacitive relation.

E. Hybrid Capacitor

Hybrid capacitors attempt to exploit the relative advantages and mitigate the relative disadvantages of EDLCs and pseudocapacitors to realize better performance characteristics. Utilizing both Faradaic and non-Faradaic processes to store charge, hybrid capacitors have achieved energy and power densities greater than EDLCs without the sacrifices in cycling stability and affordability that have limited the success of pseudocapacitors. Research has focused on three different types of hybrid capacitors, distinguished by their electrode configuration: composite, asymmetric, and battery-type respectively.

F. Materials for Supercapacitor

The critical components of supercapacitors include the electrodes, electrolyte and the separator. The characteristics of electrode materials for supercapacitors include high cyclability, long-term stability, high surface areas, and resistance to electrochemical oxidation/reduction. The focus seems to be, however, on achieving high surface areas with low 'matrix' resistivity. Carbonaceous materials have been particularly popular owing to their large surface areas. High temperature heat-treatment of active carbon precursors such as coconut shells, wood powders, coal tar, resins and resorcinol-formaldehyde and related polymers yield active electrode materials with surfaces ranging between 1000 and $1500m^2/g$, that result in capacities as high as 500F/g in alkaline electrolytes. Another class of materials includes modified carbon and carbon-composites such as activated carbonpolyacene, platinized activated carbon, polyoxometallate modified carbon and carbon-inert particulate material which have led to capacitance values between 150 and $200F/cm^2$. Besides, conducting metal oxides such as RuO_2 and IrO_2 yield capacities of the order of $150–250\mu F/cm^2$, which happen to be several times larger than the carbon-based capacitors. These values arise from pseudocapacitance believed to occur between the surface ruthenium ions and protons. Indeed, substantially high specific capacitance values near 768F/g have been achieved when amorphous $RuO_2.xH_2O$ is used as the electrode material [14, 15, 16]. Activated glassy carbon and high surface area gold are planar or extended area electrode materials that provide both high and short pulse charges. The absence of porous character associated with the electrode structure and/or the absence of any faradaic process is required for short pulse capacitors with their overall capacitance arising from electrical double-layer. Conducting polymers are complementary materials to carbon and metal oxides. A wider voltage window is achieved with derivatized polythiophenes in non-aqueous solutions. However, long-term stability is still a problem. Recently, nitrides of molybdenum, titanium and iron, carbon nanotubes and glutarsonitrile have been reported to yield energy densities of the order of 10Wh/kg when used with carbon electrodes. The electrolytes used are $LiClO_4$, $NaClO_4$, $LiAsF_6$, and quarternary phosphonium salts. The choice of electrolytes demands the requirement for hermetic seals. This has led to the use of solid polymer electrolytes which are usually ionomers. Donor polyether solvents such as polyethylene oxide (PEO), where anions are usually not coordinated to the solvent molecules unless through hydrogen bonding to hydroxyl end groups are quite frequently used along with a plasticizer.

G. Why Nanomaterial?

The size quantization effect in semiconductor nanoparticles (also called nanoclusters, nanocrystals and quantum dots); the research of nanostructure has become a flourishing field in material science. One can obtain smaller, lighter, cheaper and faster devices with greater functionality while using less row materials and consuming less energy by using nanotechnology. Nanotechnology is the almost invisible science of construction on scales of a billionth of a meter. The optical properties of nanocrystals are defined by their size and surface chemistry and they differ drastically from those of the bulk solids. Nanomaterials exhibit highly exotic properties and their industrial demand is steadily increasing. The properties of nanomaterials are:

- High surface to volume ratio and surface energy
- High mechanical strength and microhardness
- Large specific heat
- Large thermal expansion
- High catalytic activity
- Enhanced self diffusion
- High magnetic susceptibility and
- High sintering rate etc.

As the Surface to volume ratio is high hence the surface area will be increased by incorporating the nanomaterials and the capacitance will be increased.

II. CONCLUSIONS

In conclusion it is summarized that by incorporating nanomaterials the capacitance will be increased due to it's high surface to volume ratio and low matrix resistivity. We are doing some synthesis of nanomaterial like $SrRuO_3$ and $CaRuO_3$ for the application in the supercapacitor.

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