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A Study of Supercapacitors and Gamma-Irradiation

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Abstract - A supercapacitor , sometimes known as an ultracapacitor, is a high-capacity capacitor that bridges the gap between electrolytic capacitors and rechargeable batteries. It has a capacitance value that is much larger than ordinary capacitors but with lower voltage restrictions. The gamma irradiation process uses Cobalt 60 radiation to kill microorganisms on a variety of different products in a specially designed cell. Gamma radiation is generated by the decay of the radioisotope Cobalt 60, with the resultant high energy photons being an effective sterilant. basically in study in which disused about Gamma-Irradiation, Gamma chamber, Advantages of gamma-irradiation, Supercapacitors' operational principle, Types of supercapacitors

Keyword - Gamma, supercapacitors

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INTRODUCTION

In the fields of electrical devices, transportation, and industry, this energy is critical. The energy crisis and the greenhouse effect are caused by the depletion of non-renewable energy supplies. Renewable energy resources, such as wind and solar energy, will mostly fulfill future energy requirements. Although the energy from these resources (wind and hydropower) has improved significantly in recent years, solar power remains ineffective in global energy production. However, these renewable energy sources provide a tremendous quantity of energy that cannot be stored in any way. This necessitates the development of high-capacity and decisive technologies. Electrical energy is inherently unstable and difficult to store, necessitating the use of energy storage devices to store and disperse it [1,2]. Electric energy, on the other hand, is stored in capacitors, batteries, and supercapacitors. The toxic and harmful chemical composition of the batteries endangers the surrounding environment. Battery technology is unable to penetrate crucial sectors such as lightweight gadgets, high-power electric devices, and portable electronics due to slow charge rates, limited life cycles, and poor power density [3]. Charge is stored electrostatically in capacitors, with no chemical processes taking place throughout the charging and discharging operation. Super capacitors are gaining popularity as energy storage devices that use an electrostatic mechanism and have a long charging/discharging cycle. Super capacitors, like batteries, do not need bulky electrodes, are non-toxic, and hence are environmentally benign and lightweight. Batteries and regular capacitors have lower power and energy density than super capacitors.

The notion of storing electrical energy in the double layer at the solid-electrolyte interface was first proposed by Hermann von Helmholtz in 1879. At General Electric Corporation, H. I. Becker patented the first double-layered capacitor employing carbon-based materials in the liquid electrolyte in 1957. Becker's apparatus, which needed both electrodes to be dipped in an electrolyte receptacle and was never marketed, was unfortunately ineffective. In 1969, SOHIO (Standard Oil of Ohio) produced the first electric double layer capacitor for commercial use, which used a carbon electrode in a tetra alkyl ammonium salt-based electrolyte [4]. NEC (Nippon Electric Company) [5] first introduced the new technology in 1970 as a backup power device for computer memory applications. Despite the fact that the product was on the market, it did not reach a greater specific energy density. Several attempts have been made to build supercapacitors with a better energy density while maintaining a reasonable production cost. The first pseudocapacitors were produced after the 1980s, with charges partly accumulating in a double layer and partially accumulating through faradic processes [6,7]. The first pseudocapacitive substance was ruthenium oxide (RuO2), which has a greater specific capacitance. This gave a fresh approach to the creation of large capacity supercapacitors (Cs). Due to the faradic process, pseudocapacitive materials such as metal oxide and polymers have a 10-100 times higher energy density than electric double-layer capacitors (EDLCs). Later, the whole globe got involved in the effort to replace batteries with supercapacitors. Currently, businesses such as SPEL, Maxwell, NessCap, and

SkelCap make supercapacitors for various electronic devices using carbon materials, metal oxides, polymers, and composites with a huge surface area.

Gamma-Irradiation

Irradiation of electromagnetic and elementary charge particles with high energy interacts with a substance's electronic shell, resulting in non-elastic and elastic dispersion of particles due to atom ionisation and excitation, respectively. Radiation damage is caused by these interactions, which cause nuclear processes and a change in the structure of materials. Gamma rays have the shortest wavelength, less than 10 picometers, and have energy of more than 100 keV. Gamma-rays emitted by radioactive decay typically have energies ranging from a few hundred keV to less than 10 MeV. The energy of gamma-rays from celestial sources, on the other hand, exceed 10 TeV. Because gamma-rays have the smallest wavelength, they can penetrate any gap, even subatomic ones. The potential of absorption when a gamma-ray photon interacts with matter is related to the density, absorption cross-section, and thickness of the substance. Equation 1 shows how the overall intensity of absorption drops exponentially with distance from the surface.[8]

$$I\,(x) = I_0 e^{-\mu x}$$

Where x is the distance of the incident surface from the gamma-rays in cm and μ – is the absorption coefficient.

When gamma-rays contact with matter, they leave their energy behind in three ways:

1. Photoelectric effect
2. Compton scattering
3. Pair production

The sum of the σ cross-sectional of these three processes is known as the atomic absorption coefficient (μa).

$$\mu_a = \sigma_{photo} + \sigma_{comp} + \sigma_{pair}$$

Gamma matter interaction also includes photo fission, Rayleigh, and Thomson scattering processes, to a lesser degree.

Gamma chamber:

Defects such as cluster, point, Frenkel, and columnar are well-known to be created by gamma-irradiation. K.E. is transferred to one of the atoms, and the excess energy is sent to the system of free and bound electrons at the same time. Frenkel pair defects are formed when an atom with a high K.E. is formed.[9]

It became common for medical and industrial use to use gamma emitters such as cobalt-60 (Co-60). Natural cobalt is the first step in the production of radioactive cobalt. Only 0.001% of the earth's crust contains cobalt-rich ore, making it an extremely scarce commodity. The great energy of the gamma rays and the extended half-life of 5.27 years make it the best source of gamma radiation. Commercially, Co-60 is utilized in industrial radiation processing units, and its isotopes are employed as a radiation source in non-contact industrial applications, such as in refining and food and soaps and mining. Gamma sources are widely utilized in the paper industry for a variety of thickness measurement applications.

Flat surfaces and homogeneous dimensions are required for use in ion beam treatment or implantation. Any sort of material may be used, as long as it is uniform. The first step in ion irradiation is to generate an ion beam with a keV energy and then to accelerate it to a MeV or GeV energy range. As a result, a high-vacuum accelerator is needed, as well as a beam transport optics system. Materials of any sort may be used in gamma-irradiation, since homogeneity is not required. Compared to ion beam irradiation, gamma irradiation is a lot less expensive.

Gamma-irradiation was performed at the InterUniversity Accelerator Centre (IUAC) in New Delhi, India, for this study. Gamma rays are produced by using the Co-60 source. There is a calibration certificate from Mumbai, India's Board of Radiation and Isotope Technology (BRIT). This is the gamma chamber at IUAC. Gray is the gamma dosage unit used in this investigation (Gy). One joule of energy is absorbed by one kilograms of matter for every one joule of energy.

Advantages of gamma-irradiation:

1. The gamma technique is capable of sterilizing a broad range of items.
2. Products that have been bombarded with gamma radiation may be utilized right away.
3. Control is simple and accurate in the Gamma-irradiation process.
4. Finally, a record of the faults is kept for future reference.
5. Five. Gamma-ray radiation is inexpensive to begin with.

Supercapacitors' operational principle

Capacitors are categorized into three types- electrostatic, electrolytic, and electrochemical capacitors depending upon their fabrication and charge accumulation mechanism. Two metallic plates detached in electrostatic capacitors by an insulating medium. When the potential is applied, the opposite nature of charges move towards one another and gather on the electrodes whose polarity is deliberated by the applied field polarity. The electrostatic capacitors give very low capacitance in order of pico or nanofarads. The Electrolytic capacitors contain supplementary electrolytic content besides dielectric medium, where it has two electrodes, the metal foil has a thin layer of oxide taken as the anode which serves as a dielectric layer and conducting electrolyte serve as the cathode itself. During the charging process it is used to polarize the charges. The electrolytic capacitors give more capacitance than electrostatic capacitors up to millifarads. The electrochemical capacitors represent the ceramic type capacitors. To achieve craved capacitance, the electrochemical capacitors are made of ferroelectric materials blended with ceramic material. The ceramic type capacitors are devoted, rugged, and have excessive capacitance as compared to electrostatic and electrolytic capacitors. For these reasons, electrochemical capacitors are used in electronic circuits also in the military for different purposes.[10-11]

Above mentioned capacitors, however, are not made for the industrial level use for energy storage purpose but they are found in the electronic system for coupling and filtering AC signals. EDLCs are next-generation capacitors that contain carbon materials that serve as cathode and anode detached by an aqueous and non-aqueous electrolyte. In EDLCs, the charge accumulation mechanism relies on the collection of the charges or ions on the surface of the electrode materials and electrolyte solution followed by the applied potential difference. The collected charges create an electric double layer separated by a distance of a few Angstrom. The schematic of the energy storage mechanism of a conventional electrochemical capacitor is illustrated. The charge accumulation mechanism of carbon-based electrodes determined by the generation of two different layers of charge or ions represent the Helmholtz double layer at the ,electrode/electrolyte interface. When a potential difference is given, the ions in the electrolyte with the opposite polarity are adsorbed on the electrode, which forms the double layer. The charge accumulation at the electrode/electrolyte interface is on account of the integrated consequence of electrochemical adsorption and coulombic interaction. The amount of charge stored corresponding to the applied potential is called capacitance. The capacitance is calculated by the ratio of the charges stored to the applied voltage as given in equation 1.1;

$$C = \frac{Q}{V} \quad \text{..............................(1.1)}$$

Where, Q – the amount of charge stored per unit mass on the electrode and V – operating potential window. In conventional capacitors, capacitance (C) is directly and inversely proportional to the surface area of each electrode and distance between the two electrodes, respectively;[12]

$$C = \frac{\varepsilon_r \varepsilon_0 A}{d} \quad \text{.........................(1.2)}$$

Where, εr – relative permittivity of the medium in the EDL, εr – permittivity of vacuum, A – specific surface area of the electrode, and d– thickness of the EDL, The capacitance is higher when the area is larger to store charges and the distance between separated charges is small. The energy storage capability of the capacitor is deliberated by the following equation 1.3;

$$E = \frac{CV^2}{2} \quad \text{.........................(1.3)}$$

Where, E – energy density and V – the potential window of electrochemical capacitors, The power density is nothing but the energy released per unit time. To calculate the power density internal resistance across the internal component of supercapacitors such as active electrode material, electrolyte and separator are need to be considered. This resistance is called equivalent series resistance (ESR), determined from the potential drop (IR drop) during the discharge process and therefore limits the maximum energy and power of supercapacitors. The power density is calculated by the equation 1.4;

$$P = \frac{V^2}{ESR} \quad \text{.....................................(1.4)}$$

Where, P – power density and V – maximum cell voltage.

Conventional capacitors have low E and high P as compared to batteries, which means the battery can reserve extra energy than capacitors but fail to release power quickly whereas a capacitor stores less energy very rapidly and it can deliver power quickly and generally have high P. From equation 1.2 and 1.3, C and E of supercapacitors can be enhanced with the high surface area and high applied potential. The capacitance obtained from the supercapacitors in the order of Farads which is greater than the above-mentioned capacitors.

Types of supercapacitors:

Supercapacitors are classified into three types, namely EDLCs, pseudocapacitors, and hybrid capacitors based on their charge storage system that involve non-faradic, faradic, and mixture of these two processes, respectively. In the non-faradic process, charges are collected on the surface of the active electrode by a physical process that does not involve any breaking or making chemical bonding. However, in the faradic process, redox reactions occur with the movement of charges between electrode and electrolyte. The EDLCs and pseudocapacitors store charges by using carbon and transition metal oxide or conducting polymers based materials respectively. However, the hybrid capacitors store charges with both mechanisms i.e. faradic and non-faradic processes. [13]

- **EDLCs(electric double layer capacitors):**

The EDLCs are electrochemical capacitors that reserve energy owing to the accumulation of charges at the electrode/electrolyte interface. The EDLCs are constructed by two carbon-based electrodes, electrolytes, and separators that obstruct the straight connection between the electrodes. The energy accumulation process in EDLCs is non-faradic, there is no charges are transferred through electrode and electrolyte. At the time of charging, electrons transport from the negative to the positive electrode via the external loop. In the electrolyte, captions proceed towards the negative electrode whereas anions move to the positive electrode. During the discharging business, electrons and ions migrate in the reverse direction. The schematic of the energy storage mechanism in EDLCs. The oppositely charged ions form a double-layer of charges separated by atomic-scale distance. This process is highly reversible. The capacitance is achieved in EDLCs owing to the high surface area of carbon-based electrodes. The EDLCs give high P and magnificent cyclic stability due to the absence of charge transfer chemical reactions. Von Helmholtz first proposed the concept of a double-layer model in the 19^{th} century, which stated that oppositely charged ions are formed on two layers at the electrode/electrolyte interface disengage by an atomic scale distance. Helmholtz's mock-up failed to show the relation between capacitance and voltage because he did not consider the different distribution of charges due to the resistance of the electrolyte. Later on, Gouy and Chapman remodelled the Helmholtz mock-up, which states that ions are movable in the electrolyte solution. The ions with the opposite charge to that of the electrode are dispersed in a region called diffuse layer having a thickness greater than that of atomic-scale distance. Further, Stern proposed the new model by incorporating the Helmholtz mock-up with Gouy and Chapman mock-up. He stated that the layers are formed by the compact layer owing to the adsorption of ions near the surface of electrodes and diffuse layer into the bulk of active material .Thus, total capacitance (C) can be calculated by equation 1.5

$$\frac{1}{C} = \frac{1}{C_c} + \frac{1}{C_d} \quad \text{.................................} (1.5)$$

Where, Cc – capacitance of compact layer and Cd – capacitance of diffuse layer.The carbon-based electrodes are electrochemically inert at all operating potential. The decomposition potential of electrolytes is very important in determining the operating voltage range of EDLCs.

- **Pseudocapacitors:**

Pseudocapacitors are the second kind of supercapacitors. The storage mechanism of pseudocapacitors is situated on the movement of charges within the electrode and the electrolyte by rapid and reversible surface redox reactions. When a potential is given to the electrodes, faradic reactions occur on the surface of electrodes which transfer charges between the electrode and the electrolyte. The transition metal oxides/hydroxides like CuO, MnO_2, Co_3O_4, and conducting polymers like polyaniline and polypyrrole are widely used as pseudocapacitor electrode materials. The pseudocapacitors store energy on the surface of the electrode as well as in the bulk of electrode hence produces more capacitance as compared to EDLCs. Also, the charge storage capacity of pseudocapacitors is more than EDLCs, which means they provide higher energy density than the EDLCs. However, pseudocapacitors suffer from low cycle life than EDLCs because of the depletion of active electrode material throughout in electrochemical redox reactions.

- **Hybrid capacitors:**

Although the carbon and carbon derivative used in EDLCs give a very better surface area as compared to pseudocapacitive materials, but EDLCs exhibit relatively low Cs which impedes further application in supercapacitors with low E. The E of pseudocapacitors is more than that of EDLCs, but the pseudocapacitors have limitations such as short lifetime, low electrical conductivity, and P because of their faradic reactions. To overcome the limitations of EDLCs and pseudocapacitors, the third type of supercapacitors developed are known as hybrid capacitors. They are formed through the incorporation of EDLC and pseudocapacitive materials exploiting both non-faradic and faradic mechanisms to reserve charges. The hybrid capacitor electrodes can achieve higher Cs, E, P, and capacity retention than EDLCs or pseudocapacitor electrodes. Incorporating the benefits of various materials approach by optimizing each component to form composite, should be an advantageous approach to raise the supercapacitive performance.[14-15]

The composite electrode consists of the combination of two carbon-based materials or a composition of two conducting polymers or a combination of two metal oxides (mixed metal oxides). The carbon and carbon derivatives have a high surface area which increases the contact between pseudocapacitive materials and electrolyte, whereas Faradic reactions increase the charge storing capability of composite electrodes. Asymmetric hybrid capacitors consist of one EDLCs and another pseudocapacitors electrode in the same cell. The hybrid capacitor possesses high capacitance with improved E than EDLCs and good capacity retention than pseudocapacitors.

CONCLUSION

The use of gamma-irradiation is expected to be an effective technique for improving the supercapacitor performance of CuO thin films prepared by the CBD method, "with great potential for using gamma-irradiated CuO devices in space applications in small spacecrafts, in delivery of high pulse for ignition systems, in high power communication throughout interplanetary missions, and in conventional electronics".

Prepared CuO thin films were exposed to gamma radiation at different doses successfully. gamma-irradiation, the CuO thin films retained its monoclinic structure. However, a decrease in crystallite size is observed at 100 kGy doses because of crystallite fragmentation, perversion of the lattice from their initial states, and diminished interfacial energy between the CuO crystallites. Gamma-irradiation increased the specific capacitance of CuO thin films due to the irregular swelling of woollen-like morphology as irregular swelling helps improving the ions transport rate by filling the cracks observed in the pristine sample.

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