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SUPERCAPACITORS – BASED ON SPINEL FERRITES: A REVIEW

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ABSTRACT

With the advancement of technology and materials the requirement of the energy conversion and storage is increasing for the use in commercial as well as non-commercial sites. The inclination in the Global population and those in the Global energy crisis has led to the concerns related to the electrical energy generation and its consumption. The presented work will illustrate a recent energy storing device superconductor which has high power density and longer life than the current technologies. The supercapacitors are increasingly used for energy conversion and storage systems in sustainable nanotechnologies. The review mainly focuses on the spinel ferrites and the additional focus area includes perovskite oxide, Transition metal sulfides and other materials that have been extensively and widely employed in the fabrication of the supercapacitors. It will also lead us to the guidelines on how we can Design better energy storing devices with the higher power density and sufficient storage ability.

INTRODUCTION

With the increasing population the demand of energy is also increasing. To fulfil this requirement of energy, we need an alternative device. Nanotechnology is an advancement in the field of Technology that deals with the manipulation and regulation of substances on a nanoscale measurement (Soores et al.2018) Nanotechnology is the technology in which we deal with the contrive and arrangement of substances at nanoscale. (Soares et al.2018) Nanoparticle is an object which has dimensions in the range of nanoscale. (Anu and Saravanan Kumar 2017).

Nanomaterials are slightly different from nanoparticles; their overall dimensions including internal and external lies in the range of nanoscale. Nanomaterials have exceptional chemical and physical properties that can be considered as an asset in the field of supercapacitors.

Thus, we can say that supercapacitors are the best solution to the increasing demand. The electrochemical energy storage device supercapacitors have high energy and power density with longer life.

Supercapacitors are the devices that stores large amount of energy and have low internal resistance. It consists of an electrolyte, two electrodes and a separator. These electrodes are the most important part of supercapacitors because supercapacitors largely depend on the electrochemical properties of the electrodes, the voltage range and electrolyte; here the separator is used to electrically isolate the electrodes.

Production of supercapacitors by printing technology have utilised various Nanomaterials such as transition metal carbides, hydroxides.

Magnetic metal oxide nanoparticles represent an attractive type of materials among inorganic solids because they are cheap and easy to prepare in large amount.

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Among different magnetic materials, Spinel ferrites and inorganic perovskite oxides have superior performance as an electrode in supercapacitor applications.

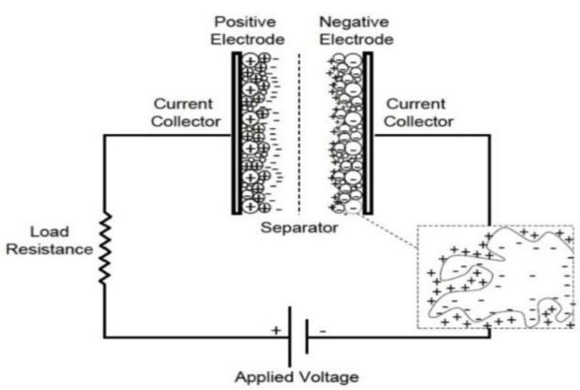
It has also been recently disclosed that spinel ferrites of different elements can be used in the formation of supercapacitors. Spinel ferrite nanomaterials have high energy density, durability, high power and long-term stability.

SUPERCAPACITOR STRUCTURE

In this cutting-edge era supercapacitor is a blessing that fulfils the demand of new technology in energy storage. Its fundamental equation is basically the same as that of the conventional capacitor that is

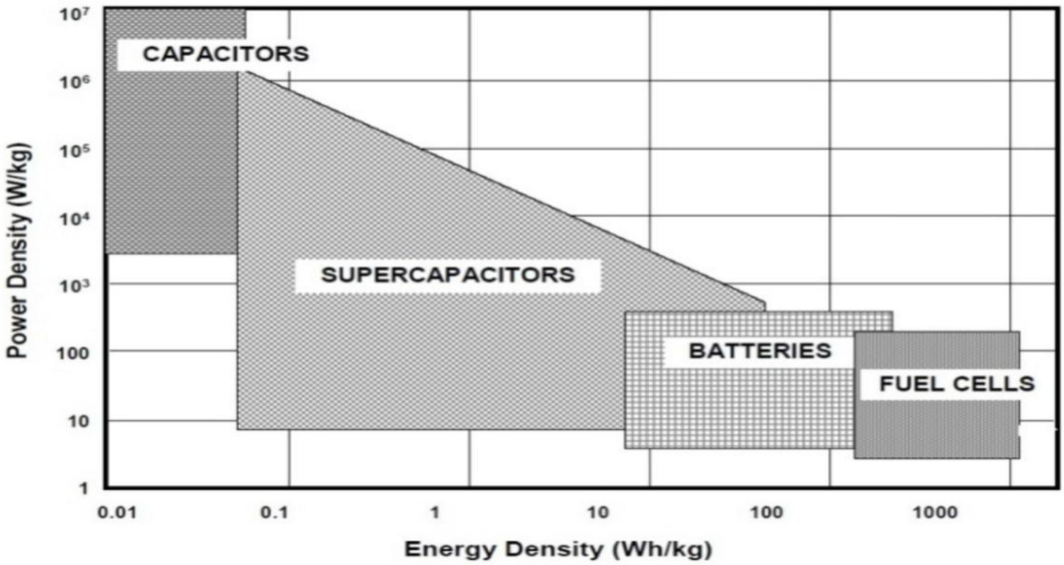
$$C = \varepsilon_r \varepsilon_o \frac{A}{D}$$

Super capacitors are also known as ultracapacitors and can also be called an electrochemical dual layer capacitor. It is clear from the fundamental equation that the capacitance is directly proportional to the area of electrodes and is inversely proportional to the distance between the electrodes.



Supercapacitors stores electrostatic energy. These devices have a very high power density if we compare them with the batteries however they have low energy density. So, these devices can be used in the places where there is a high and unforeseen power demand.

Unlike charges attract each other when the voltage is applied to the system. The separator is vital as the ions in the electrolyte diffuse across it into the pores of the electrodes. However, the recombination of the iron is prevented by these electrodes because of their specific design. The increase in the area is due to the double layer coupled with them and also the decrease in the distance between the electrodes, resulting in the high energy density as compared to the conventional capacitors. Here the process is non-faradic process So these supercapacitors possess a large number of charging and discharging cycles as well as have high reversible stored charge. The aqueous electrolytes that are used in supercapacitors include Sulfuric acid and Potassium hydroxide. In the supercapacitors charge is stored at the interface of liquid electrolyte and high surface electrode. Every solid liquid interface has this charge separation. The conventional capacitors as Compare to these supercapacitors have low energy and power density, Whereas the latter has high power density and low energy density than battery. Thus, we can say that a supercapacitor is a combination of properties of the conventional capacitor as well as the battery. The power density of various devices are shown as under: -



LITERATURE REVIEW

Spine ferrites are metal oxide compounds which can only be obtained from magnetite i.e. Iron Oxide (III)(Fe_3O_4). They have good magnetic and electrical properties, due to which it has broad application in high density data storage, Drug delivery, sensors, hyperthermia of cancer, Magnetic resonance imaging.

Besides these applications, rise in the demand of an energy storage device which must smaller, lighter and cheaper is accomplished by the supercapacitors made of spinel ferrites. The crystal structure of ionic oxides, mainly iron oxides, allow visibility of complex composition of magnetic ordering. This kind of magnetic ordering is known as ferrimagnetism. These materials (ferrimagnetic) have two spins i.e. up spin and downspin as well as their net magnetic moment of all directions is not zero. For the various neighbouring sub-lattices, the atoms magnetic moment are opposed to each other, nevertheless the opposing moment are unbalanced (O'handley 2000; Cullity and Graham 2011).

Spinel ferrites are distinguished via the nominal composition MFe_2O_4 , Where M denotes divalent cations such as copper, nickel, manganese, zinc etc ; also M can be substituted by different metal ions. The ferric ions can be substituted by x-ray divalent cations such as aluminium, chromium etc.

The spinal structure of it originates from $MgAl_2O_4$ which owns a cubic structure. This crystal was first discovered by Bragg and Nishikawa (Ashour et al.2014).

In the spinal letters Every cell has a cubic structure and consists of eight MeFe2O4 molecules. the large O2- ions a face centred cubic lattice which has two kinds of interstitial sites: -

a) Tetrahedral sites enclosed via 4 oxygen anions (A-site)

b) Octahedral sites enclosed via 6 oxygen anions (B-site)

(Shah et al. 2018; Yadav et al. 2018; Kefeni et al.2018).

Ferrite can be classified into three categories on the basis of cation distribution. The general formula for the possible distribution of metals is (Cullity and Graham 2011):-

$$\left(M_{\delta}^{+2}Fe_{1-\delta}^{+3}\right)\left[M_{1-\delta}^{+2}Fe_{1+\delta}^{+3}\right]O_4$$

Where δ is degree of inversion. Bracket () Is used to represent a positive ion that occupy the tetrahedral sites, while those inside the brackets [ ] occupy the octahedral sites.
The three different categories of spinel ferrites are:

1.Normal spinel (δ = 1) : -
The formula becomes
$(M^{2+})\ [Fe_2]O_4$
and the divalent metal ions are in tetrahedral sites.
Example: $ZnFe_2O_4$ and $CdFe_2O_4$

2. Inverse spinel ferrite (δ = 0)
the formula becomes
$(Fe^{3+})[M^{2+}\ Fe3^{+}]\ O_4$
In this case the iron is equally divided between the tetrahedral and octahedral sites and divalent metal ion occupy octahedral sites.
Examples: - $NiFe_2O_4$
and $CoFe_2O_4$

3. Intermediate ferrite (0 < < 1)
In intermediate ferrites the M and Fe^{3+} the ions are distributed uniformly over the tetrahedral and octahedral sites.
Example: - . $MnFe_2O_4$ (Cullity and Graham 2011)

Spinel MFe_2O_3 where M is Co, Zn and Mn

In the last few years researchers studying the application of spinel ferrite and derivatives. Spinel ferrites has Nominal composition MFe_2O_3, Where M can be zinc, copper, manganese, nickel and Cobalt.

Cobalt ferrite $CoFe_2O_3$, nanoparticles: -

The most common ferromagnetic nanoparticles of Cobalt ferrite $CoFe_2O_3$ Has an inverse spinel structure where Co^{2+} Ion is situated at B-site and Fe^{3+} positive Ion located at both A and B sites. These ferrite materials have an interlacing structure of metal ions with positive charge and divalent oxygen ions with negative charge. Cobalt ferrite is suitable for sensing devices as well as active and passive microwave devices due to its versatility and high resistance. It is Cubic in structure which belongs to Fd^3m space group. Cobalt ferrite is an insulator with resistivity rho(ρ) $=10^5$ ohm metre And magnetic moment μ =3.7 μ_B also it has some disadvantages also like high volume change and high resistivity.

$CoFe_2O_4$ nanoparticles enhance positive capacitance of composite electrode and have an innumerable electrochemical activity, due to which energy and power densities of a supercapacitor increased. Reddy et al. (2018 a) used ZnO to increase the electrochemical properties of Co Fe_2O_4 i.e. ZnO@ Co Fe_2O_4 nanocomposite electrode in a 3M KOH aqueous solution. This experiment results in in enhanced capacitance of electrode with magnificent energy density. this electrode showed excellent cycling stability and if it ain't about 91% of its specific capacitance after 1000 cycles.

Zinc Ferrite $ZnFe_2O4$:

Due to eco-friendly nature of zinc ferrite, it's cost-effectiveness and strong redox process, it is the most common material for electrochemical applications. However, due to its lower conductivity, volume fluctuations during charge and low cycling stability make it inappropriate for efficient supercapacitors.

To overcome all these disadvantages the conducting material added to zinc ferrite to increase its conductivity and to enhance cycling stability. It is important to mention that conducting network of graphene with the formation of nanocomposite is the main reason for its highest specific capacity and good rate ability.

The high conductance of nanoplatelets of graphene with the nanocomposite structures made it efficient transport of charge as well as develops the electrodes capability rate. It can be used as an electrochemical capacitor with an excellent capacitance and high-performance rate.

Israr et al.(2018) Synthesized or nanocomposite material of zinc ferrite by adding platelets of graphene.

Manganese Ferrite $MnFe_2O_3$

Spinel $MnFe_2O_3$ have high electrochemical activity, fast valence state response ability. It is cheap, easily available an eco-friendly material. so, so spinel MN ferrite NPs has been lately examined as proper electrodes for batteries based on Lithium and sodium ions and SCs (Xiao et al.2013; Sankar and Selvan 2014,2015; Lin and Wu 2011) but it has some disadvantages also like it has low rate capability and cycling stability due to the small electrical conductivity and the continuous effect of iron insertion/ de insertion during charging/ discharging process. (Cheng et al.2011; Guan et al. 2015; Wang et al. 2014 a).

Because of the integrated advantages of quantum dot, it can be assumed that if we decrease the size of spinal MN ferrite into quantum scale, the surface area and the electrochemical active sites will be e highly developed in addition to rapid surface controlled pseudo-capacitance behaviour with reduction in the Ion carrying route (Su etal. 2018). Apart from this, the electrode has a super performance rate owing to the integration Between the great capacitance and extraordinary cycling stability.

Su et al.(2018) have Show the successful preparation of Mn ferrite@ Nitrogen- Doped graphene by solvothermal method, which results in enhanced capacitance as well as excellent life cycle prepared electrodes. these prepared electrodes are well suitable for energy storage applications.

CONCLUSION

Supercapacitors provide an excellent power performance. Research is going on continuously to increase energy density and voltage of these supercapacitors. Supercapacitors have an exceptional power performance and also has large number of charging and discharging cycles which makes it suitable to be used in the vehicle applications. Supercapacitors have widened electrode material spinel ferrites and evaluated their performance and outlined their advantages as well as disadvantages in the application of these supercapacitors significantly. In these recent years it has spread its roots towards latest technologies Smartphones and energy collection. In this particular review we have evaluated their performance and also have mentioned the advantages in the application of supercapacitors. However, there are other materials such as mixed magnetic oxides and transition metal sulfides also their composites that can be widely used for the upcoming energy storage applications.

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