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Energy Storage Applications of Conducting Polymers and Its Nanocomposite : A Special Emphasis on Supercapacitor

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ABSTRACT

The implication of the conducting polymers (CPs) for various technological applications rapidly increased. Owing to the electrical conductivity approaching those of metallic conductors and other extra ordinary properties makes it distinguishable from the other synthesized materials. Herein, we discussed a broad overview of recent advances in the applications of CPs for the supercapacitor. We first focus the fundamentals of CPs, synthesis techniques and properties. We then highlight the potential supercapacitor applications of CPs, specifically polyaniline, polypyrrole and its nanocomposites with various other materials. Finally, we conclude present study by offering our perspectives on the current challenges and future opportunities for the CPs in supercapacitor applications.

Keywords: Energy Storage Devices, Supercapacitor, Polyaniline, Polypyrrole

I. INTRODUCTION

Recently, improved and advanced technologies have been changes the human life and make it lavish and comfortable. Worldwide, various scientific, academic and industrial groups are devoted their research work to develop new technologies.However, no advanced technology can work without the use of energies such as mechanical, chemical, electrical and thermal etc. As a result, more research into energy harvesting and storage is required for advancement in a variety of fields.Recently, the developed world has faced a number of serious global issues, including insufficient energy production, the availability of portable water, global warming, and so on. [1, 2]. The main cause of these serious issues is the rapidly increasing population and human standard of living. Electrical energy has become a part of everyday life. The production of electrical energy and its long-term reserves is a major and serious impediment to research. Solar energy, wind energy, tidal energy and biomass energy production are considered worrisome options. However, it has many flaws, including a large workforce, a large land business, accuracy, inefficiency, and high costs. As a result, scientists are looking for alternatives to traditional global energy sources such as super capacitors, batteries, fuel cells, and so on. [3, 4].

Recently, energy production from renewable energy sources has been increased rapidly. However, its contribution to global energy production is only low or less than 1%. The energy generated from the power plant is used for various applications such as direct lighting, cooling and communication devices [5]. Saving energy through storage devices in the absence of renewable sources requires a variety of applications. But nowadays there are insufficient efficient storage devices that can store a large number of charges and distribute them as needed. Thus, storage systems such as batteries and electrochemical capacitors (ECs) have taken more interest in saving the energy produced and have played an important role in storing maximum energy [6].

The improvement in the available storage devices with new designs and techniques are not helping to store the energy to the desired level. Therefore, utilizing new advanced technology and with new materials the properties of energy storage devices can be enhanced in desired performance. The selection of the novel materials and techniques can give us the user friendly, light weight, less hazardous, economically cheap and highly efficient energy storage devices. Concerned to the storage of energy in electrochemical form have many superior advantages such as direct energy conversion, portability, absence of moving parts and convenient for mass production. However still it has some critical issues in the developments of electrochemical energy storage devices such as environmental security, light weight, portability, efficiency and low cost etc. [7].

From the last decades the huge efforts are devoted by the many scientists and researchers to develop and enhanced the physical and chemical properties of electrochemical storage system. Electrochemical energy storage systems are broadly classified in three major types based on their properties i.e. (I) batteries, (II) fuel cells and (III) supercapacitors.

Super capacitor is an emerging and become the most promising energy storage device in recent years. Basically, the same principles are used in supercapacitors as conventional capacitors. Supercapacitors are distinguished with high surface area electrodes and thin dielectrics by conventional capacitors to obtain more capacitances. Super capacitors fall between the battery and the capacitor i.e., energy density greater than conventional capacitors and higher energy density than batteries [8].

Supercapacitors have better option for energy storage devices than batteries and fuel cells. However, it faces the challenges such as low energy density, high cost, high self-discharging rate and practical use. Thus, the researchers have scope to enhance the performance, modified electrode structure, achieved the desired thickness of the electrode layer, and porosity. Recently, carbon species (activated carbon, graphene, carbon nanotubes, etc.), metal compounds and conducting polymers are the three main types used as electrode materials for energy storage devices. As well as transition metal oxide (RuO_2, NiO, MnO_2, Co_3O_4, IrO_2 Mn_3O_4,) nanomaterials, carbon nanomaterials, binary, ternary nanocomposites, conducting polymers and conducting polymers nanocomposites and so on. Carbon species-based electrodes with high conductivity and stability usually have excellent cycling stability and high-power density as supercapacitor electrodes. However, carbon-based electrodes for supercapacitors are usually exhibits low energy density because of the limitation in energy storage mechanism. Metal compounds owing to high activity and good intrinsic electrochemical properties in supercapacitors still they have problems like low conductivity, high cost and limited natural abundance [9].

Conducting polymers (CPs), like Poly (3,4- ethylenedioxythiophene) (PEDOT), polypyrrole (Ppy) and polyaniline (PANi), have gained more attention as promising candidates for energy storage devices. CPs has the excellent and unique electronic, optoelectronic, and electrochemical features. As well as CPshave pseudocapacitive features, facile synthesis protocol, good environmental and chemical stability, tunable conductivity, low production cost, etc.Their simple components (C, H, N or S) also indicate the high affordability. CPs based devices show high specific capacitance compared with electrochemical double-layer supercapacitors, and has faster kinetics than most inorganic batteries, which can narrow the gap between inorganic batteries and carbon-based capacitors. The combination of conducting polymers and carbon materials, metal compounds is quite popular with excellent performance taking advantage of each component, shown superior performance in asymmetric supercapacitor [10, 11].

The superiority of supercapacitors decides by cyclic life which depends upon the stability of the electrode materials during charge/discharge cycles. Conducting polymers incorporated with nanomaterials attain higher stability of the electrode material in terms of cyclic life. Also, the decoration of polymer nanocomposites with nanomaterials enhances the electrochemical conductivity, thermal stability and optical and mechanical properties and large surface area to stored charges [12].

The recent development concern to the supercapacitors have been discussed in the following headings using the polyaniline and its nanocomposites as well as polypyrrole and its nanocomposites.

II. SUPERCAPACITOR APPLICATIONS OF CONDUCTING POLYMERS AND ITS NANOCOMPOSITE

Payami, E., et. al; developed ternary nanocomposite consisting of modified GO (GO-Fc), Mn_3O_4 nanoparticles, and polyaniline (PANI) via a simple physically mixing procedure. As synthesized ternary nanocomposite further used as a battery-type supercapacitor and obtained results reveals the promising ability via supercapacitor parameters high power density and cyclic stability [13].Röse, P. et.al; synthesized polyaniline (PANI) nanofibers via chemical oxidative synthesis route using sodium phytate as a plant derived dopant. Electrochemical properties of the synthesized PANI as electrode material for supercapacitors shows the high specific capacitance analyzed by galvanostatic charge/discharge (GCD) curves. The PANI electrode shows the capacitance retention of 67.6% of its initial value, low solution resistance (Rs) value of 281×10^{-1} Ohm and charge transfer resistance value (Rct) of 7.44 Ohm. As well as after 1000 charge discharge cycles retained 95.3% in coulombic efficiency without showing any significant degradation of the material [14].Deshmukh, P. R. et. al; prepared the polyaniline-ruthenium oxide (PANI-RuO_2) nanocomposite thin films by a chemical bath deposition (CBD) method. The PANI–RuO_2 exhibits specific capacitance of 830 Fg^{-1} with 216 $Whkg^{-1}$ and 4.16 $kWkg^{-1}$ specific energy and power respectively [15].Gui, D., et.al; synthesized three polyaniline (PANI)/grapheneoxide (GO) nanocomposite electrode materials by chemical polymerization with the mass ratio (mANI:mGO) 1000:1, 100:1, and 10:1 in ice water, respectively. The electrochemical behavior of the PANI/GO with the mass ratio (mANI:mGO)1000:1 possessed excellent capacitive behavior with a specific capacitance as high as 355.2 F g^{-1}at 0.5 A g^{-1} in 1 mol $L^{-1}H_2SO_4$electrolyte and after 1000 cycles, the specific capacitance of the composite still has 285.8 F g^{-1} [16].Mishra, A. K. et.al; synthesized graphene via hydrogen-induced exfoliation and functionalized to decorate with metal oxide (RuO_2, TiO_2, and Fe_3O_4) nanoparticles and polyaniline using the chemical route. Electrochemical performance of as-prepared nanocomposites is examined using cyclic voltammetry and galvanostatic charge discharge techniques for supercapacitor applications. A maximum specific capacitance of 80, 125, 265, 60, 180, and 375 F/g for HEG, f-HEG, RuO_2-f-HEG, TiO_2-f- HEG, Fe_3O_4-f-HEG, and PANI-f-HEG nanocomposites, respectively, is obtained with 1 M H2SO4 as the electrolyte at the voltage sweep rate of 10 mV/s. The specific capacitance for each nanocomposite sustains up to 85% even at higher voltage sweep rate of 100 mV/s [17].Khalid, M., et.al; using electrodeposition process synthesized composite thin films of polyaniline (PANI) nanofibers and graphene oxide (GO) nanoplatelets for electrochemical capacitors. An electrochemical property of thin films shows capacitance of 662 F g^{-1} at a low current density of 0.025 mA cm^2 with simultaneous high energy density (64.5 Wh kg^{-1}) and high-power density (1159 Wh kg^{-1}) [18].Viswanathan, A., et.al; synthesized reduced graphene oxide, copper oxide and polyaniline (GCP) nanocomposites by facile in-situ single step chemical method by varying the weight percentage of each of the constituent materials. The weight percentage of composites G12%: Cu_2O/CuO 40%: P48% (G12CP) exhibits the maximum specific capacitance of 684.93 Fg^{-1}, specific capacity of 821.91 Cg^{-1}, energy density of 136.98Wh kg^{-1}, and power density of 1315.76Wkg^{-1} at the current density of 0.25 Ag^{-1}. The composite shows the retention of 84% of its initial capacitance up to 5000 cycles at a scan rate of 700mVs^{-1} [19].Devadas, B., et al; Synthesized the polymer@Cdots composites by in situ chemical oxidative polymerization method and studied the specific capacitances. The specific capacitances of composites were 676 and 529 F/g for PPy@ Cdots and PANI@Cdots, respectively, at current density of 1 A/g [20].Ashokkumar, S. P., et al; reported the electrochemical performance of polyaniline (PANI)/copper oxide (CuO) nanocomposites (PCN) for energy storage device applications. The Cyclic Voltametry (CV) result shows the specific capacitance PANI is 294 F/g and 424 F/g for highest concentration PCN2 nanocomposites and GCD reveals the cyclic stability up to 4000 cycles [21].

III. CONCLUSION

In this review paper, we have discussed recent progress in the development of conducting polymers-based supercapacitor.Owing to the excellent properties of the conducting polymers it is employed for the supercapacitor applications. Worldwide various research groups devoted their research to improve the super capacitive performance of the conducting polymers. The mainly polyaniline and polypyrrole were highly studied due to some exceptional qualities compared to the other conducting polymers. We have thoroughly summaries the recent development in the fields of supercapacitor using polyaniline and polypyrrole. Finally, we conclude that the present work may be highly useful for the upcoming researcher.

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Review on Biomedicinal Applications of Ferrite Nanoparticles

Krushna J. Langade[1], Dipak A. Magar[1], Omprasad H. Sarage[2], Satish A.Dake[3], Sanjay K. Vyawahare[2]
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ABSTRACT

Ferrite Nanoparticles exhibit enormous promise in biological applications due to their capacity to accurately regulate the behaviour by an external magnetic field. Ferrite Nanoparticles are remarkable magnetic capabilities make them ideal nanoagents for a variety of applications such as targeted medication administration, MRI, biosensors, magnetic hyperthermia (MHT), magnetic separation and antibacterial agents. The issue is maintaining the high magnetism, which declines when size is reduced to the nanoscale.The manufacture of these ferrite nanoparticles is significant, with the selection of an optimum synthesis procedure playing an important role.As a result, characteristics like as shape, chemical and physical properties, and biocompatibility influence the effectiveness of ferrite nanoparticles in biomedical field. In this review article, we focuse the biological importance of Ferrite Nanoparticles.

Keywords: MRI; superparamagnetism; targeted drug delivery; magnetic hyperthermia; nanoferrites; toxicity.

I. INTRODUCTION

In past few years, nano-science, nanotechnology and nanostructurehave now become common words not only in science but also in daily life. Nano-materials depict, in principle, materials of which a single unit is sized (at least one dimension) between 1-100 nm (10 meter) can be accomplished by the assembly of the constituents of molecules or atoms of few angstroms or 10^{-10} m in size. Nano-materials study takes a materials science based approach to nanotechnology in materials measurement and synthesis which have been developed in support of micro-fabrication research. Materials with arrangement at the 'nanoscale' (1-100 nm) often have unique electronic, optical, mechanical properties, which are expected to be utilized in several different applications, including optical filters, sensors, low-threshold laser, biological detection and controlled drug delivery.
The research on synthesis, exploration and characterization of nanosized (1-100nm) materials were increased in the last few decades for the development of science. The term "nanoscale materials" refers to a group of substances with at least one dimension of fewer than 100 nanometers[1]. Some nanoparticles are found naturally, but artificial nanomaterials are of particular interest. Engineered nanomaterials are resources that have been developed at the molecular (nanometre) level to make use of their small size and unique features that

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aren't found in their bulk counterparts[2]. Increased relative surface area and novel quantum effects are the two main reasons why materials might have distinct properties at the nanoscale. Nanomaterials have a substantially higher surface area to volume ratio than traditional materials, which can increase chemical reactivity and weaken them[3]. Quantum effects can also play a greater role at the nanoscale in determining material properties and characteristics, resulting in unique optical, electrical, and magnetic features.

As a result, nanomaterials have important applications such as biosensors, medication delivery, energy storage, and so on. On the basis of dimensions, nanomaterials are classifieds into four different classes. The properties of nanomaterials depend on the synthesis procedure. Basically, nanomaterials are synthesized by using two different approaches, one is a top-to-down approach and the second is the bottom-up approach.

Ferrites have established their potential in several applications due to their remarkable electrical and magnetic properties and also in magnetic resonance imaging (MRI). Nanomaterials are interesting because they exhibit unique optical, magnetic, electrical, and other properties at such a small scale. These emergent features have the potential to have huge implications in sectors like electronics, medicine, and others. In comparison to bulk materials, nanoparticles exhibit significantly innovative and improved chemical, physical, magnetic, and other properties[4].

II. INTRODUCTION TO FERRITES

Ferrite exhibits ferrimagnetisms due to the super-exchange interaction between electrons of metal and oxygen ions. The opposite spins in ferrite results in the lowering of magnetization compared to ferromagnetic metals where the spins are parallel. Due to the intrinsic atomic level interaction between oxygen and metal ions, ferrite has higher resistivity compared to ferromagnetic metals. This enables the ferrite to find applications at higher frequencies and makes it technologically valuable. Ferrites are chemical compounds consisting of ceramic materials with iron oxide (Fe_2O_3) as their main component [5]. The chemical formula of ferrite is generally expressed as $MeFe_2O_4$, where 'Me' represents a divalent metal ion. (e.g. Fe^{2+}, Ni^{2+}, Mn^{2+} , Mg^{2+}, Co^{2+}, Zn^{2+}, Cu^{2+}etc). The crystal lattice of ferrite is spinel with cubic symmetry.

The crystal structure of spinel ferrite possesses two sub-lattices namely tetrahedral (A) and octahedral [B] sites. The cations can occupy either tetrahedral (A) or octahedral [B] or both sites partially. On the occupancy of cations at tetrahedral (A) and octahedral [B] sites, the spinel ferrites are known as normal, inverse and random spinel. Most important commercial spinel ferrites are cobalt ferrite and nickel ferrite have inverse spinel structureand they exhibit high electrical resistivity, high saturation magnetization, high permeability and high Curie temperature[6]. The high values of resistivity and magnetic properties are useful in making composites materials.

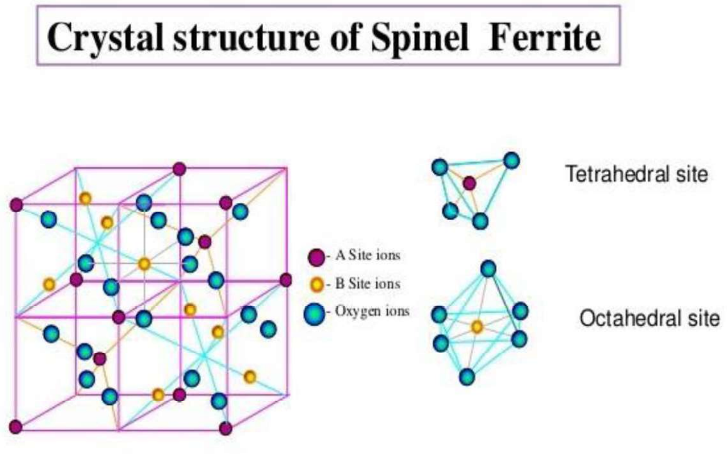

Figure 1: Crystal structure of spinal ferrite.

Among the magnetic ceramics, magnetic oxides are the most Important and rather the only relevant material from the point of view of their application .The number of mixed oxides such as ferrites, ferroelectrics, peroviskites etc, are being used in many technological applications. Ferrite are mixed metal oxide having iron oxide as their main constituent. Ferrite can be classified into three group's viz. spinal ferrite, garnet and magnetoplumbite according to their crystal structure. Spinal ferrite has the general formula MFe_2O_4, Where M is divalent metal ions like Co, Ni, Mg, Mn, Zn, Cd, Fe etc. Ferrites are the ferromagnetic oxides with combined electric and magnetic properties, which are useful in many applications such as antenna rod, transformer core, memory chips, sensors ,as catalyst, microwave devices like circulators, phase shifters, gyrator etc. Apart from their excellent elliptical and magnetic properties they have another advantage like chemical stability, easy preparation, low cost etc. They exhibit high electric resistivity, low eddy current and dielectric losses, high saturation magnetization, high curie temperature etc. These properties of ferrites are sensitive to method of preparation, cation distribution, type and nature of dopants also radiation dose, dose rate etc.

Types of ferrites

Types	Structure	General formula	Example
Spinal	Cubic	$M^{II}Fe_2O_4$	M^{II}=Cd,Co,Mg,Ni,Zn etc.
Garnet	Cubic	$Re^{II}Fe_2O_{12}$	Re^{II}=Y,Sm,Eu,Cd,Tb,Dy,etc.
Magnetoplumbite	Hexagonal	$Me^{II}Fe_2O_{19}$	(Er,Tm and Lu)

Ferrites are ferromagnetic in structure as originally proposed by Neel.It play an important part in the field of telecommunication, electronic, entertainment digital computer industries. Since the appearance of the first commercial ferrite product was in about 1945. The unique property of these ferrites is high magnetic permeability and high electrical resistivity. The required properties of ferrite may be classified as intrinsic and extrinsic. Number of applications depends on the extrinsic properties.

Nickel ferrite

Nickel Ferrite is a significant magnetic material with a wide range of applications, including ferrofluid fabrication, catalysis, and magnetic refrigeration. It is one of the most important soft ferrites, with low conductivity, low eddy current losses, and excellent chemical stability, mechanical hardness and electrochemical consistency[7]. Additionally, nickel ferrite's bulk phase is entirely made up of inverse spinel structures. The structure and morphology (form, size, and surface topology) of ferrite nanostructures may be precisely controlled by modifying the composition as well as the techniques of synthesis, according to the researchers. Various procedures for creating ferrite nanostructures have been developed over the years, including solid state, sol-gel, thermal decomposition, co-precipitation, hydrothermal, and mechanical milling. Despite several concerted attempts, a highly efficient and precise process for synthesis of ferrite nanostructures is still a long way off. Furthermore, no association has been discovered between the compositions, cationic distributions in the structure, electric and magnetic characteristics of ferrite nanostructures. This ferrite is an inverted spinel ferrite, with eight units of $NiFe_2O_4$ incorporated within the spinel structure's cell. Half of the ferric ions preferentially occupy tetrahedral sites, whereas the other half preferentially occupy octahedral sites. As a result, the compound is represented by the formula $(Fe^{3+})_A\ [Ni^{2+}Fe^{3+}]_BO_4^{2-}$.

The magnetic characteristics of nickel ferrite are comparable to those of magnetite and maghemite. Composition and microstructure, which are susceptible to the synthesis preparation technique, have an impact on the characteristics of synthesised materials. Furthermore, the magnetic properties of $NiFe_2O_4$ nanoparticles are very size-dependent. The creation of $NiFe_2O_4$ nanoparticles with the best magnetic characteristics is already generating a lot of attention. Numerous techniques have been devised to create nanocrystalline nickel ferrite, including sol-gel, organic gel-thermal decomposition, hydrothermal, co-precipitation, gel assisted hydrothermal routes, thermolysis, wet chemical co precipitation approach, microemulsion, and microwave synthesis [8]. Nickel ferrite nanoparticles are suitable for photocatalytic and waste water applications due to their large band gap and modern saturation magnetization. The performance of devices utilised in sensing and biological applications, such as contrast agents for magnetic resonance imaging and heat mediators for magnetic fluid hyperthermia, may be implemented due to the large tuning ability of nickel ferrite[9].

The following are the main applications of nickel iron oxide nanoparticles:

- Resistant suspension for levitated railway systems
- In the process of preparing nickel cermet for the anode layer of solid oxide fuel cells
- Magnetic recording medium with a high density
- Magnetic refrigeration
- As a catalyst, magnetic liquid, and microwave absorbers
- In lithium nickel iron oxide cathodes for lithium micro batteries
- In electrochromic coating, polymers, and fabrics.

III. LITERATURE REVIEW

The co-precipitation process was used to make nickel ferrite nanoparticles. To identify the structure of $NiFe_2O_4$ nanoparticles, an X-ray diffraction pattern was employed. FT-IR analysis revealed the existence of $NiFe_2O_4$ nanoparticles. Scanning Electron Microscopy was used to examine the surface morphology of $NiFe_2O_4$ nanoparticles. Transmission Electron Microscopy might be used to measure the particle size of nickel ferrites nanoparticles. The research sought to investigate the dielectric characteristics of nickel ferrite nanoparticles at various frequencies and temperatures, such as dielectric loss and dielectric constant. The magnetic characteristics of nickel ferrites were also investigated. XRD confirmed that $NiFe_2O_4$ nanoparticles corresponded to the cubic spinel structure. $NiFe_2O_4$ nanoparticles have an average particle size of 28nm. The dielectric investigations revealed that frequency had a detrimental influence on both the dielectric constant and the dielectric loss[10].

The $NiFe_2O_4$ nanoparticles were manufactured by the hydrothermal technique and the inhibition of surfactant on the particle growth is explored. It demonstrated that the products were pure $NiFe_2O_4$ and also nanoparticles develop with increasing the temperature, whereas surfactant hinders the particle growth under the same circumstances. The average particle size was evaluated by the TEM micrographs and found to be in the range of 50-60 nm that reduced up to 10-15 nm in the presence surfactant. Nano sized nickel ferrite particles were produced with or without surfactant aided hydrothermal techniques. The findings revealed that with rising in the temperature, the crystallinity of nanoparticles is enhanced. In the presence of surfactants, the crystallinity of $NiFe_2O_4$ nanoparticles reduced in comparison with surfactant - free produced samples. All of the nickel ferrite nanoparticles were superparamagnetic at normal temperature[11].

$NiFe_2O_4$ was synthesized by two methods – chemical sol gel method and the high frequency plasma chemical synthesis and magnetic properties, crystalline size, specific surface area of synthesized products was characterized. The average particle size of nano powders obtained by the sol-gel method self-combustion method is in the range of (25-40) nm and ferrites synthesized in plasma have wider particle size distribution range (10-100) nm with some particles of 200 nm. The magnetic properties of sample obtained by the sol gel self-combustion method differ from those of the plasma products. Dense material from the plasma nano powders forms at 1000 degree Celsius but from the sol gel self-combustion nano powders at 1200degree Celsius[12].

The citrate precursor technique was used to create $Ni_{0.5}M_{0.5}Fe_2O_4$ nanoparticles. At 400 degrees Celsius, the citrate precursor was annealed. An X-ray diffractometer was used to characterise the annealed powders. The observed XRD data was further investigated, revealing that particles annealed at temperatures up to 450 degrees Celsius had a cubic spinel structure, but particles produced at temperatures above 450 degrees Celsius have a tetragonal spinel structure. Sharp variations in particle size, lattice constant, magnetism, and retentivity were detected in the temperature range 450-500 degrees Celsius, indicating that growth differs at temperatures above and below a critical temperature in this range. The characteristics of nano size ferrite samples are highly dependent on the temperature of production[13].

$NiFe_2O_4$ nanoparticles were synthesized using co-precipitation method. The X-Ray diffraction was used to determine the structure of nickel ferrite nanoparticles. The fact that $NiFe_2O_4$ nanoparticles belonged to cubic spinal structure was established by XRD. The presence of nickel ferrite nanoparticles was confirmed by FT-IR spectrum. The details of surface morphology of $NiFe_2O_4$ nanoparticles were obtained by scanning electron microscopic analysis. SEM analysis showed that nanoparticles agglomerated to form spherical-shaped particles. The particle size was determined by Transmission electron microscopy. The average particle size of $NiFe_2O_4$ nanoparticles was found to be 28 nm. The work aimed at investigation of the dielectric properties such as dielectric loss and dielectric constant of $NiFe_2O_4$ nanoparticles at varied frequencies and temperature. From the dielectric studies it became evident that the frequency negatively impacted both the dielectric constant and the dielectric loss as decreased with increase in the frequency[14].

IV. SYNTHESIS METHODS

SOL-GEL TECHNIQUE

The sol-gel method of synthesizing nanomaterials is very popular and is widely employed to prepare ferrite materials[15-16]. The interest in this synthesis technique arises due to the possibility of synthesizing nano ferrite materials at very low temperatures; precursors are very simple chemical reagents, good stoichiometric control, special instruments are not needed, dopant ions can be quickly introduced into the resultant material and less agglomeration of grains in the product. The main advantage is one can get uniform nanoparticles with good quality by the sol-gel approach. The chemical reaction is carried out by dissolving the citric acid and metal nitrates in a minimum quantity of distilled water at room temperature. The citrate precursors are usually preferred due to their low solubility and low decomposition temperature. Generally, in order to achieve a complete reaction within the shortest time period and at the lowest possible temperatures, mixing of the component cations on an atomic scale is necessary. The mixture is heated in order to evaporate excess amount of water. Then the gel was dried at 150^0Cand as a result of which, the dry gel self-ignited to form intended ferrite powder. Throughout the auto-combustion process, exothermic redox chemical reaction along with fuel oxidation and decomposition of nitrates take place. The gasses like N_2 and CO_2 emerge, supporting the formation of nano ferrite powder.

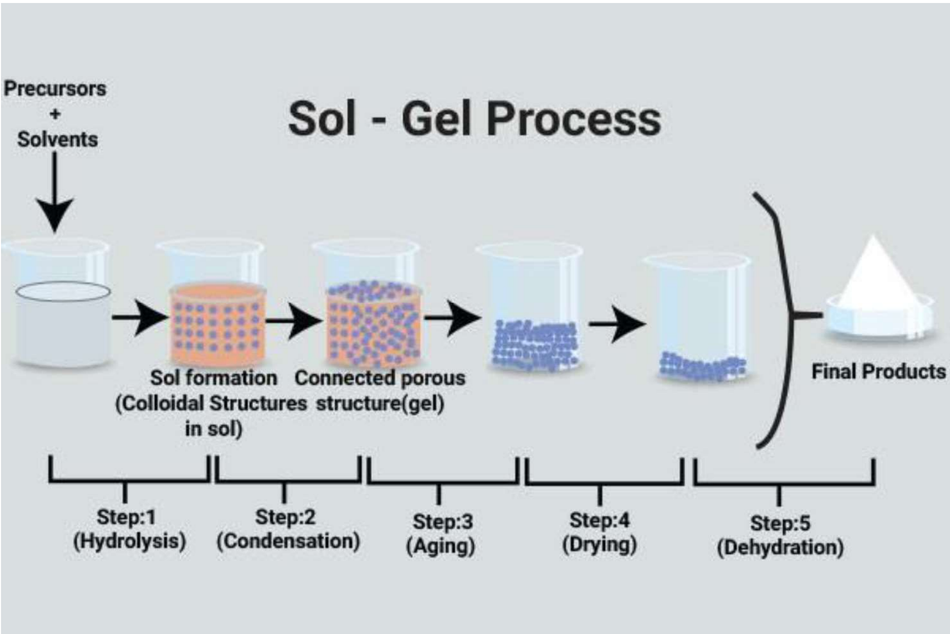

Figure 2. Sol-gel technique

The advantages of this technique are as elucidated below[17-18].

- The intimate mixing of the elements in gel form results in reaching the ingredients in a short period of time.
- Grinding procedure is not required to achieve homogeneous single phase ferrites, which avoids contamination (high product purity).
- The precise size control of the particles is also strength of a sol-gel processing.
- The possibility of controlling the porosity of the product material is highly attractive. (High crystalline ferrite nanoparticles)
- It is attributed to more uniform phase distribution in multicomponent systems like ferrites.

- Exothermic decomposition of precursor provides heat to the solid-state reaction, thus reducing the external temperature required for the ferrite formation in shorter time.
- Fine particle size and uniform particle size distribution
- Simple equipment and simple synthesis process
- It is a cost effective method.

Among the available chemical methods, sol-gel is a simple technique without much- complicated procedure and produce ferrite nanoparticles of high purity at minimum cost.

Solid-State Technique

The solid-state approach is extensively utilised for the production of single crystal and polycrystalline powders of transition metal phosphates and arsenates and monovalent cations[19]. This is a typical method for producing polycrystalline material from solid reagents. This approach use a chemical reaction to generate a new solid with a well-defined structure from solid starting ingredients. Fine grain metal compounds are mixed, pelletized, and heated at a given temperature for a certain amount of time. Extreme circumstances, such as high temperature and pressure, are required for some metal compounds, such as metal oxides or salts, to begin reactions in a molten flux or a rapidly condensing vapour phase. This method is also known as "shake and bake" or "heat and beat" chemistry. Characterizing the reaction rate in solid state synthesis is especially critical. Because approaches for purifying produced solids are extremely constrained, solid-state processes must be completed. The rate of the solid-state reaction is determined by the reaction circumstances, which include the structural qualities, shape, and surface areas of the reactants, the rate of diffusion, and the thermodynamic parameters of the process. The chemical precursors and preparation procedures determine the chemical and physical characteristics of the final products. Metal compound reactions are initiated by an energy source and propagated by the heat emitted during the synthesis of products and byproducts in this approach. The downsides of this approach are its slowness and high energy requirements. In reality, the reaction takes place at high temperatures (500-2000 degrees Celsius) for several hours and continues for several days. Heating at these temperatures may cause the target chemical to breakdown[19].

Hydrothermal technique

The hydrothermal technique is a novel approach for producing nanocrystalline inorganic materials. It is characterised as a homogeneous or heterogeneous reaction that occurs under high temperature and pressure in the presence of aqueous solvents, resulting in the development of solid compounds that are generally insoluble under normal circumstances. It is a low-cost and environmentally friendly approach. Temperature, water, pressure, and reaction time are therefore the three required physical parameters in hydrothermal processing. This synthesis method is also known as a solvothermal procedure, which indicates that additional solvents are employed in addition to water. In a typical experiment, the precursor material is dissolved in a suitable solvent and transported to an autoclave, which is a stainless-steel tank. In such experiments, water is frequently selected as the solvent. After the transfer is complete, the vessel is firmly sealed and exposed to heat treatments. For the synthesis of simple nanostructures, the temperature is set between 80 and 250 degrees Celsius. The supercritical solvent interacts with the precursor material at these extreme temperatures, resulting in the creation of products. Surfactants, in addition to precursor materials, are used in such reactions to create a nanostructure with the appropriate shape. Furthermore, the technique of simplicity and beauty is being forgotten[20]. The hydrothermal approach was used to create aluminium phosphate nanosheets[21].

Application of nanoferrites in biomedical sciences

Ferrite nanoparticles notably ferrites have attracted a lot of interest in recent years due to their uses in various sector and particularly in biomedical field where there improved magnetic characteristics enable diversity in imaging diagnosis and therapy. There are several varieties of ferrites that have been synthesized and presented for diverse uses but ferrite based on cobalt, nickel, and zinc has shown potential for biomedical applications due to strong magnetic biocompatibility and anisotropy[22]. With the objective of increasing the response in magnetic hyperthermia therapies and other biomedical applications, a nanoparticle system based on nickel ferrites has been studied.Monodispersed ferrites nanoparticles with varied proportions of Ni^{2+} ions and sizes have been created using an improved synthesis based on the thermal decomposition method and the seed-growth methodology. It has been demonstrated that structures with low Ni^{2+}cation percentages promote saturation magnetization levels and a decrease in the magnetic anisotropy constant[23]. Recently, magnetic nanoparticles (MNPs) have demonstrated significant promise in biological applications.

Among other uses, MNPs can be utilised as protein separators, contrast agents for magnetic resonance imaging (MRI), medication delivery systems, and heat generators. MNPs have a wide variety of uses and may be utilised for both treatment and diagnostic at the same time. To have a satisfactory performance for both purposes, the qualities and characteristics of the magnetic material should be adjusted (diagnosis and treatment). In the scientific literature, there are several publications on the use of MNPs as heat producers in magnetic fluid hyperthermia or contrast agents for MRI diagnosis or cancer therapy. Despite the fact that both uses are the consequence of magnetic fields interacting with one another[24].

Targeted drug delivery

The low toxicity and good biocompatibility of magnetic nanomaterials form them suitable materials for targeted drug delivery. Magnetic nanoparticles are widely used in targeted drug delivery applications. The direct intake of medicine affects non-targeted healthy organs to overcome these problems targeted drug delivery becomes a standard and promising technique nowadays. The other healthy tissues are not affected by any medicine in the case of targeted drug delivery application[25-26]. Magnetic nanoparticles have excellent magnetic properties which reveal the reduction of nanomagnets concentration in blood. The coating and doping of suitable components increase the effectiveness of magnetic nanoparticles in drug delivery applications.Spinel ferrites nanoparticles have received a lot of interest for their use as a drug delivery agent under the control of an external magnetic field because of their simplicity, effectiveness, ease of manufacture, and capacity to adjust their characteristics for specific biological applications[27–28]. German scientist Paul Ehrlich (1854–1915) introduced the idea of a "magic bullet" that would only kill sick tissue around a century ago[29]. The current history of drug delivery began to use microencapsulated drug particles in the 1950s[30]. The volume of papers in this biological field has significantly expanded since that time.

The literature now accessible contains several studies and research papers employing nanoparticles made of silica[31-32], gold, polymers, and other materials. It follows that since a variety of nanoparticles can be employed, magnetism isn't a need when building a drug delivery nano system. However, the application of magnetic nanoparticles in medication delivery has received significant interest recently[33]. The typical drug delivery approach from non-specific cell and tissue distributions with metabolic instability results in total body toxicity and decreased therapeutic effectiveness[34]. Spinel ferrite nanoparticles' capacity to enclose cytotoxic medicines within the polymer matrix and distribute them to cells is another noteworthy characteristic[35–36]. Spinel ferrite nanoparticles may transport medications without spilling and can quickly reach the target tumour location with the aid of an external magnetic field, helping to successfully treat cancer cells while avoiding normal cells[37]. Up till it reaches the sites of action, the medicine will be released and have therapeutic effects. Multifunctional nanoparticles, which contain semiconductors (for cell imaging), anticancer medicines, spinel ferrite nanoparticles, and biocompatible coating agents, are very useful for cancer therapy. It has been established that $CoFe_2O_4$ nanoparticles with lauric acid caps might be exploited as a potential drug delivery agent with pH-sensitive release[38]. Spinel ferrite nanoparticles may also be made more stable and have less hazardous effects on cells by being coated or capped with biocompatible materials. Spinel ferrite nanoparticles need to be completely demagnetized after being exposed to an external magnetic field in order to be employed for magnetically driven medication delivery.They can also maintain colloidal stability and avoid aggregation as a result, which enables them to be employed in biological applications[39]. One of the hypothesised causes of spinel ferrite nanoparticle aggregation is magnetic attraction between the particles[40].

Magnetic hyperthermia

Magnetic hyperthermia is one of the promising cancer treatments based on the heating ability of nanoparticles. Chemotherapy, radiotherapy, etc are some cancer treatments but these treatments have some drawbacks like these treatments affect normal tissues[41]. To overcome this problem, the use of magnetic hyperthermia is widely increased in the biomedical field. In this treatment, only cancer tissues of cells are killed with the help of an applied magnetic field and do not affect normal tissues or cells. The specific absorbance rate (*i.e.*SAR) value reveals the heating rate of nanoparticles[42]. Hyperthermia, a mild increase in temperature to 40-43 degree Celsius, can trigger the death of cancer cells and boost the effects of radiation and chemotherapy. However, the fulfilment of its full potential as a therapeutically relevant therapy approach was limited due to its inability to heat malignant cells efficiently and locally. This obstacle can be avoided by the intravenous introduction of magnetic nanoparticles focused at cancer cells that aggregate in the tumour, followed by the use of an alternating magnetic field to increase the temperature of nanoparticles situated in the tumour tissue. This tailored approach allows locally heating cancer cells, at the same time, without injuring surrounding normal tissue, which potentially boosts the effectiveness and safety of hyperthermia. The most common materials for magnetic hyperthermia are magnetite or maghemite nanoparticles.

Magnetic nanoparticles can be administered to the tumour by intra-tumoral, intra-arterial, intra-cavitary, intravenous injection. There oral delivery is not possible since most of the nanoparticles will be excreted from the body. Intra-tumoral and intra-cavitary injection localises magnetic particles in the tumour and can lead to efficient heating of primary tumours. Although the following routes of administration are well suited for certain circumstances, intravenous injection is the most adaptable delivery strategy for a wide spectrum of oncological disorders. When magnetic particles of iron oxide are given in this way, the accumulation of nanoparticles of tumour partially depends on the impact of increase permeability and retention[43]. This phenomenon refers to the tendency of nanoparticles to mainly collect in tumours due to the permeability of their vasculature and inadequate lymphatic drainage. Target ligands (antibodies and their fragments, ligands of particular receptors located on the surface of tumour cells, peptides, and aptamers) linked with the magnetic particles might improve the absorption of nanoparticles by malignant cells[44].

Their predominant concentration in malignantneoplasms leads to targeted local heating of tumours and the preservation of adjacent normal tissues under the influence of an alternating magnetic field. Despite the encouraging findings of preclinical trials of magnetic hyperthermia, there are several unanswered challenges in this area. This includes the establishment of optimal limits of magnetic field strength and frequency, their correlation with the duration of treatment, the toxicity of, magnetic nanoparticles (including the dependence of toxicity on the presence of specific ligands that improve the accumulation of magnetic particles in tumour cells), and determining their optimal concentration in the affected organ.

MRI and cancer diagnosis

There are several motivations for creating technology that can detect cancer in its earliest stages because early detection is linked to a favourable result with any sort of therapy[45]. Due to the availability of curative therapy, stage 1 cancer discovery is often linked with a 5-year survival rate higher than 90%[46,47]. Cancer may currently be found using a number of medical tests, including blood, urine, or imaging methods. When cancer is just a few millimetres (e.g., MRI) or centimetres (e.g., PET) in diameter, when it already contains more than a million cells, conventional imaging techniques often identify it. To address this drawback, molecular imaging has recently been proposed. Recent advancements in nanotechnology, molecular cell biology, and imaging technologies made it feasible to create this novel imaging modality. While magnetic resonance imaging (MRI), which offers the best spatial resolution when compared to other techniques and is noninvasive or at the very least minimally invasive, is of particular interest, molecular imaging imaging applies to a variety of imaging techniques such as Positron Emission Tomography (PET), computed tomography, or ultrasound.

Implementation of iron-based nanoparticles increased MRI sensitivity due to buildup of iron in the liver produced by selective action of the hepatobiliary system. Nanoparticles have been lately exploited by biologists, pharmacologists, physicists, doctors as well as pharmaceutical business. There are roughly 20 clinically approved nanomedicines utilized for the therapy. Some examples are Abraxane, an albumin-bound form of paclitaxel with cobalt of mean particle size of approximately 130nm that is used to treat breast cancer and Doxia, also based on Cobalt, is used for the treatment of refractory ovarian cancer and AIDS-related Kaposi's sarcoma and it consist of nanoparticles with a polyethylene glycol coating. A fundamental aspect of nanoparticles delivery systems is their potential to boost transport systems is their ability to enhance the concentration of anticancer medicines in tumor cellssince certain nanoparticles passively accumulate in tumor's after their intravenous injection. Nanoparticles may pass via microscopic capillaries and are taken up by cells, which allow efficient drug accumulation at target locations and also sustained and regulated release of medications at target areas over a period of days and weak[45].

V. CONCLUSION

In this reviews article, the use of magnetic hyperthermia, targeted medication delivery, and nanoferrite in MRI was briefly discussed. Nanoferrites are a great choice for all of these biological applications due to their superb characteristics and adjustable magnetic behaviour. The main issues that need to be addressed when employing different nanoferrites for biomedical applications to increase effectiveness are stability and biocompatibility. Although there have been many in vitro research on nanoferrites, there haven't been many clinical trials on the substance.

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Methods of Preparation of Nanoparticles : A Review

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ABSTRACT

Nanotechnology attracts huge attention in recent research field. The development in technology in the preparation of nanomaterials gives extra interest in this research field. Many fields of research such as Physics, chemistry, material science, medical sector, pharma sector and many more carry out research in this field. Many scientists and researchers made significant development in the preparation of nanomaterials. The properties of materials in its bulk form are totally different than the properties in nano size. These nanoparticles show interesting properties. Due to quantization of electronic states the properties which depends upon size of the materials such as magnetic, optical shows apparent changes. Other properties such as thermal, electrical and mechanical properties change due to high surface to volume ratio of these nano sized materials.in this review different methods of preparation of nanomaterials are discussed.

KEWORDS: Nanoparticles, Electrolyte, Suspension, electro deposition.

I. INTRODUCTION

Nanoscience or nanotechnology is the science of very very small particles which are less than 100 nanometer size. Hence the nanomaterials are also very small in size. There are various techniques for the synthesis of nanomaterials. These methods are broadly synthesized into two types. Top-down approach and bottom-up approach. These methods are further divided into Physical methods, chemical method and biological methods. Synthesis of nanomaterials depends upon various factors such as Temperature, Pressure, Time, material size and shape, pH Value and environment. We will discuss some of the methods for the preparation of nanomaterials.

II. CHEMICAL VAPOR DEPOSITION

In this method of preparation, a solid material is deposited from a vapor by some chemical reaction occurs on the heated substrate material. This method nis primarily used in semiconductor industry in the preparation of thin films.in this method the chemical reaction taking place between some organometallic compound to be deposited on the substrate material.

By products are removed by carrier gas flow through the reaction chamber.to avoid desired chemical reaction the substrate surface temperature, pressure deposition time are carefully selected. The material obtained is high purity in nature. The decomposition can enhance with the plasma.[12]

III. ELECTRON BEAM LITHOGRAPHY

It is very expensive method. The rate of this reaction is very slow.as the material is subjected in a great stress in this method there occurs some surface defects.

IV. BALL MILLING

This is the physical method of synthesis of nanomaterial. The simple mechanism in this method is to grind and blend materials to form the desired nanomaterials. The hollow cylindrical shell which rotates about its own axis of rotation. This axis may be inclined or horizontal.it is partially filled with the ball which is made up of ceramics, stainless steel or rubber. These balls form the grinding media. The inner surface of the shell is coated with an abrasion resistant material. Generally, rubber is used as it causes less wear in mills. The key properties of grinding medial which are taken into consideration are size, density, Hardness and composition. There are mainly two types i.e., grate type and overall type. There are many advantages of this method. Some of them are lost cost, this is suitable for both batch and continuousoperation, material of any hardness can be grounded. This method is used in synthesis of metal oxide nanomaterials in the gas detection. Some chemicals, ceramics, raw materials can also be grinded by using this method.

V. SOL GEL PROCESS

It is a bottom-up approach of synthesis. A sol is a colloidal suspension in which solid particles are suspended in liquid solvent. A gel is a semi rigid mass that forms when the solvent form the sol begins to evaporates.it is a multi-stepped chemical reaction which is used in recently used in the field of material science and technology.[14]

The process generally starts with mixing of metal alkoxides in a suitable solvent at a high temperature. The metal oxide or metal chlorides are the precursors in this method. The hydrolysis reaction takes place in this method. Hence in this method metal oxo or metal hydroxy polymers are formed. A base is added in the reaction because it is very important to control the PH of the solution to avoid the co precipitation catalyst is used to start the reaction. Hydrolysis, condensation, growth of particles and collection of the particles are the steps in this method of preparation. The rate of the reaction depends on the temperature.it is a one of the cheap methods. High purity products are formed in this reaction.in powder synthesis smaller particle size and morphological control takes place. The cost of the raw materials i.e., chemicals may be high in this method. A very close monitoring is required in this method as this is a multi-step reaction.

This method has a wide applications.it can be used to produce powders and fibers.by using this method we can deposit thin films on different surfaces.it is used in drug delivery systems. we can make UV protection gels by using this method.it is suitable for producing lubricants and scratch free materials.

VI. ELECTRODEPOSITION

It is a liquid phase chemical method of synthesis of nanomaterials.it is a bottom-up approach.it is a most suitable method for depositing thin film from aqueous solution. The reaction is based on the discharge of metal ions which are present in the electrolyte ate cathode surface. The metal ions accept the electron from the electrically conducting material and there is a deposition of metal atoms. The thin films are formed by this method are strong and uniform. certain properties such as electrical resistivity, Hardness are strongly affected by the size of grains.

This method has a high utilization rate of the raw materials.it is a low energy consumption process.in this method we can precise the film thickness, morphology and doping. This method is used in the deposition of few atoms or up to large dimensions.

VII.LASER VAPORIZATION

In this method a pulse of high-power LASER beam is used to vaporize the given material. Thesetup assembly consist of anultra-highvacuum chamber with inert or reactive gas, laserbeam, atarget and a substrayte.by using this method the cluster of any material can be made. A powerful LASER beam evaporates the solid surface and the formation of cluster of atoms takes place. They condense on called substrate. This method is also known as LASER Ablation. The particle size depends upon the gas pressure.

VIII. SUMMARY

Nanomaterials are used in variety of applications in recent decades. This field of Nanotechnology is very dynamic in nature. There are various methods to preparation of particles. scientists and researchers find many methods to prepare nanoparticles and research is still going on.

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