JETIR.ORG ISSN: 2349-5162 | ESTD Year : 2014 | Monthly Issue
JOURNAL OF EMERGING TECHNOLOGIES AND INNOVATIVE RESEARCH (JETIR)
An International Scholarly Open Access, Peer-reviewed, Refereed Journal

A review on patent analysis of polyaniline (PANI) nano composites for potential applications

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Abstract:

Polyaniline (PANI) a well-known conducting polymer finds many potential applications in various fields such as energy storage, anticorrosion paints, supercapacitors and electrical devices. Nano composite metal oxides, organic-inorganic added to PANI matrix enhances structural modifications which in turn helps to enhance the electrical properties. Proper weight percentage with suitable nano fillers into PANI matrix tune the material properties for efficient technological applications. A detailed patent review analysis on PANI composites presented in this paper which helps to understand the importance of the material.

Keywords: Polyaniline, Nanocomposites, conductivity.

I. INTRODUCTION

Conducting polymers have been accruing immense attention for the recent decades in both academic and research fields for their extraordinary unique electrical and electronic properties.[1] Conducting polymers, also known as intrinsically conducting polymers (ICPs), are a class of organic polymers that can conduct electricity. Unlike traditional insulators like plastics, ICPs possess unique properties that allow them to behave like metals or semiconductors. This fascinating ability opens a vast range of potential applications in various fields. The conductivity of conducting polymers can range from that of semiconductors to that of metals, depending on the specific polymer and its doping level. The electrical, optical, and mechanical properties of conducting polymers can be easily tuned by doping, which involves introducing electron donors or acceptors into the polymer chain. Conducting polymers can be processed into various forms, such as films, fibres, and tubes, using a variety of techniques, including chemical synthesis, electrochemical polymerization, and spin coating. Compared to traditional conductors like metals, conducting polymers are lightweight and flexible, making them attractive for applications in flexible electronics. Some of the most common ICPs are Polyacetylene (PA), Polypyrrole (PPy), Polythiophene (PTh) and Polyaniline (PANI). These CPs are the class of organic materials with a prospective application such as energy storage [1], solar cell [2], microelectronic devices, piezoelectric actuators [3], sensors [4] and optoelectronic gadgets [5]. Numerous papers [7-17] recently reported on the preparation of conducting polymer nanocomposite contains metal oxide nanostructures, including ferrates, Zno, MnO_2, SnO_2 , TiO_2 and others. CPs might function as conductive supports among polymer chains, increasing the conductivity of the nanocomposites.

Polyaniline (PANI) is a conducting polymer and organic semiconductor of the semi-flexible rod polymer family. The compound has been of interest since the 1980s because of its electrical conductivity and mechanical properties. Polyaniline is one of the most studied conducting polymers. When doped with acids or other dopants, PANI's conductivity can rival that of metals, making it suitable for electronic applications. Depending on the dopant and oxidation state, PANI's conductivity and color can be adjusted, offering versatility for diverse applications. Compared to other conducting polymers, PANI exhibits good resistance to environmental factors like temperature and light, enhancing its practical use. PANI can be synthesized through various chemical and electrochemical methods, making it readily available and scalable for production. This has piqued the interest of numerous investigators owing to their extremely high conductivity, distinctive conduction mechanism, ease of synthesis, simple polymerisation, and excellent thermal stability [4,5,7]. PANI tops the list of conductive polymers because of the following reasons, easy synthesis, low cost, good conductivity, excellent wave absorption, special doping mechanism and electrochemical performance. [18].

II. Materials, Methods and Analysis:

A. Anticorrosive paint:

i. The preparation method of graphene oxide/polyaniline/titanium dioxide nanocomposite and polyaniline nano anticorrosive paint

Nano anti corrosive paint prepared Using sodium hydroxide solution or ammonia sprit as dispersing agent and titanium dioxide is excellent and environmentally friendly. The invention belongs to the technical field of metal anti-corrosion such as aluminium alloy, and in particular to a kind of graphene oxide/polyaniline/dioxy Change the preparation method of titanium nanometre composite material and polyaniline nano anticorrosive paint. To reach first purpose, the preparation of graphene oxide of the invention/polyaniline/titanium dioxide nanocomposite Method, comprising steps of

(1) using sodium hydroxide solution or ammonia spirit as dispersing agent, graphite oxide ultrasound is removed into obtain graphene oxide.
(2) graphene oxide is added to the organic sulfonic acid solution of aniline, stirring 10h ~ 16h obtains graphene oxide/polyphenyl Amine nanocomposite.
(3) nano-titanium dioxide is added to having for step (2) resulting graphene oxide/polyaniline nano-composite material in machine sulfonic acid solutions, stir 10h ~ 16h, successively through centrifugation, washing, dry to obtain graphene oxide/polyaniline/titanium dioxide nanometre Composite material. [Patent refrence-19].
Compared to the prior art, the invention has the advantages that and the utility model has the advantages that;

1. Raw material is cheap and easy to get, and graphene
2. oxide/polyaniline/titanium dioxide nanocomposite and polyaniline nano are anti- The preparation process of rotten coating is simple and easy to control.

(2) present invention gained anticorrosive paint is water paint, environmental-friendly, can be used for the anti-corrosion of the metal materials such as aluminium alloy Coating；

(3) graphene oxide can improve film forming, shielding and the dispersibility of polyaniline paint, poly- to give full play of The excellent antiseptic property of aniline；

(4) nano-titanium dioxide can improve film forming, shielding and the adhesion of polyaniline paint, may additionally facilitate coating pair The light degradation of water environment microorganism, to improve the antiseptic property of polyaniline paint and environment resistant.

ii. A kind of polyaniline graphene nano composite anticorrosion coating and preparation method

This patent describes a new type of anti-corrosion coating made with a polyaniline graphene nanocomposite material. The coating offers several advantages over existing solutions. The combination of graphene and polyaniline provides both physical and chemical barriers against corrosion. Graphene's strength and insulating properties block corrosive agents, while polyaniline's passivation and conductive blocking capabilities hinder electrochemical corrosion. Graphene strengthens the coating, making it more resistant to scratches and other damage. The coating contains no heavy metals and uses less solvent, making it more environmentally friendly. The coating can be produced using readily available equipment and requires minimal steps.Overall, this patent presents a promising new solution for anti-corrosion coatings with advantages in performance, environmental impact, and production simplicity.

The preparation method of the polyaniline graphene nano composite anticorrosion coating, is carried out as follows

1) component A preparation: Under the protection of nitrogen, epoxy resin and first are sequentially added by formula rate to reactor In solvent, high-speed stirred Levelling agent, defoamer, filler, wetting dispersing agent are sequentially added after dispersed by formula rate to continue High-speed stirred 0.5-2 hours, dispersed and finely ground rear discharging, sealing is kept in dark place in the cool.

2) component B preparation: Under the protection of nitrogen, curing agent and eigenstate are sequentially added by formula rate to reactor Polyaniline graphene composite material, stirring at low speed; It is molten by formula rate addition second in the state of being kept stirring for after dispersed Agent, is uniformly dispersed and is discharged after finely ground, sealing is kept in dark place in the cool

3) it is 1 to weigh mass ratio:0.25-1:0.5 component A and component B, after being uniformly mixed, stands 30 minutes, obtains To polyaniline graphene nano composite anticorrosion coating. .[20 -patent reference]

Compared with prior art, the present invention has following prominent effect.

1) in polyaniline graphene nano composite anticorrosion coating of the present invention, doped polyaniline graphene nano is answered Condensation material is made in the way of in-situ polymerization, using alkalization dedoping technique, i.e., dedoping reaction system is carried out in alkaline environment Obtain insulating properties polyaniline in eigenstate graphene nanocomposite material. The polyaniline-coated graphene-structured of gained, from molecular level On ensure that the individual layer or few number of plies of graphene disperse, polyaniline graphene nanocomposite material can be improved in dicyandiamide solution The compatibility of solubility, raising and coating system, is conducive to graphene to be uniformly dispersed in paint-based bottom to play its mechanical property Can, metal-graphite alkene-graphene conductive network

is effectively blocked, further suppresses the generation of electrochemical corrosion. This is nano combined Material can in coating stable dispersion, neither influence coating, paint film appearance, be also conducive to the performance of composite property.

2) in nano-composite corrosion proof paint of the present invention, on the one hand graphene improves the mechanical property of resin, separately On the one hand form isolation layer and physical shielding effect is provided, the cavity that can fill up paint film prevents corrosive medium from entering Metal Substrate BodyA; And polyaniline can prevent the electric charge transfer in corrosion process and ion diffusion, and its amido knot with metal formation passivating film Structure will participate in the cross-linking reaction of Curing Process of Epoxy, further increase the compactness of paint film. The two synergy causes The Corrosion Protection of the coating is lifted well.

3) In nano-composite corrosion proof paint of the present invention, resin solid content height, the viscosity for inventing described polyaniline graphene nano composite anticorrosion coating are low, prepare and apply the use of curing agent and solvent can be reduced during material,

4) polyaniline graphene nano composite anticorrosion coating of the present invention is free of heavy metal component, and application is more Extensively, practicality is stronger.

5) the preparation process step of polyaniline graphene composite material and nano-composite corrosion proof paint of the present invention is few, Operation is mainly temperature control and liquid agitation, and technological process is simple , To pressure and no requirement (NR), therefore to instrument and equipment requirement Low, generally conventional container and paint production plant can reach the requirement, be adapted to large-scale production.

B. BATTERIES:

i. Graphene/Polyaniline/Sulfur composite cathod material and preparation method therof lithium sulfur battery.

In lithium sulfur battery cathode and a lithium sulphur battery graphene/ polyaniline/sulfur nano-particles are used as base body and packages. The graphene/polyaniline/sulfur composite cathode material preparation method comprises preparing polyaniline/sulfur nano-particles, carrying out oxidation grapheme package to the polyaniline/sulfur nano-particles, carrying out water heat treatment to the packaged material. These materials endow good cycle performance and rate capability to the lithium sulfur battery. The graphene/polyaniline/sulfur composite cathode material has excellent conductivity and structure stability, is simple in preparation method and is suitable for industrial production.[21]

ii. Polymer Electrolyte Composition for Lithium Battery Comprising Electrospun poly (vinylidene Fluoride)- Conducting polymer Derivatives Composite nano fibrous Membranes and Lithium Battery Employing the same

This lithium-ion battery consists of vinyldenefloride (poly electrospun), to get the improved ion migration and conductivity conducting polyaniline derivatives composite nano fibrous membranes are provided. This provides electrochemically stable window and improves the performance of the battery. This battery conists of electrospun poly(vinylidene floride), poly (o-phenylenediamine),poly(n-methylaniline)and polyaniline. These are in included in the amount of 0.1 – 10.0wt %. Based on tatal weight of a mixture of poly(vinylidene fluoride) and conducting polyaniline derivative. [22].

C. SUPER CAPACITORS:

i. Supercapacitor electrodes with highly oriented and close-packed graphene sheets and methods of production

This patent describes a novel method for producing supercapacitor electrodes using highly oriented and close-packed graphene sheets. These electrodes offer several advantages over conventional graphene-based electrodes. The electrodes can be made with a thick layer of graphene, leading to increased energy density. The graphene sheets are tightly packed, resulting in a higher volumetric capacitance. The method prevents individual graphene sheets from re-stacking, maximizing their surface area available for electrolyte contact. The method allows for control over the porosity and pore size of the electrodes. The invention also describes a supercapacitor incorporating the newly developed electrodes. These supercapacitors are expected to exhibit:

- High specific capacitance: Due to the increased surface area and efficient electrolyte access, the electrodes can store more energy per unit weight.
- High energy density: The thick electrodes and dense packing of graphene sheets contribute to a higher energy storage capacity per unit volume.
- Improved power density: The well-aligned graphene sheets facilitate fast charge and discharge cycles.

Overall, this invention presents a promising approach for developing high-performance supercapacitors with enhanced energy and power densities.

This patent discloses a method for producing an electrolyte-impregnated layered graphene structure for use as a supercapacitor electrode. The method involves preparing a polyaniline (PANi) dispersion, then mixing it with a graphene oxide (GO) dispersion to form a composite material. This composite is then spread onto a current collector and dried, followed by a thermal reduction step to convert GO to reduced graphene oxide (rGO) and partially reduce PANi. The resulting structure exhibits highly oriented layered graphene with embedded PANi nanofibers, leading to improved electrochemical performance.

The first step is to mix particles of an anode active material (e.g., activated carbon), a conductive filler (e.g., graphite flake), and a resin binder (e.g., PVDF) in a solvent (e.g., NMP) to form an anode slurry. On a separate basis, particles of a cathode active material (e.g., activated carbon), a conductive filler (e.g., acetylene black), and a resin binder (e.g., PVDF) are mixed and dispersed in a solvent (e.g., NMP) to form a cathode slurry.

The second step includes coating the anode slurry onto one or both major surfaces of an anode current collector (e.g., Cu or Al foil), drying the coated layer by evaporating a solvent (e.g., NMP) to form a dried anode electrode coated on the Cu or Al foil. Similarly, the cathode slurry was coated and dried to form a dried cathode electrode coated on Al foil.

The third step involves laminating the anode/Al foil, porous separator layer and cathode/Al foil together to form a 3-or 5-layer assembly, which is cut and divided into the desired dimensions and stacked to form a rectangular structure (as an example of a shape) or rolled into a cylindrical cell structure.

The rectangular or cylindrical laminate structure is then enclosed in a laminated aluminum plastic envelope or steel housing.

A liquid electrolyte is then injected into the laminated housing structure to produce a supercapacitor cell[23].

The above discussion clearly shows that each of the prior art methods or processes for produces graphene electrodes with high specific surface areas.

ii. Continuous process for producing electrodes for supercapacitors having high energy densities

This patent describes a novel method for manufacturing supercapacitor electrodes with highly oriented and close-packed graphene sheets. The resulting electrodes offer significant improvements over conventional graphene. Thick graphene layers lead to increased energy density.Densely packed graphene sheets result in higher volumetric capacitance. The method prevents sheet re-stacking, maximizing surface area for electrolyte contact. The method allows for control over electrode porosity and pore size. This invention presents a promising approach for developing high-performance supercapacitors with significantly enhanced energy and power densities. The method's flexibility and control over electrode properties offer potential for further optimization and advancements in energy storage technology.

supercapacitor cell is typically made by a process that includes the following steps

a) The first step is mixing particles of the anode active material (e.g. activated carbon), a conductive filler (e.g. graphite flakes), a resin binder (e.g. PVDF) in a solvent (e.g. NMP) to form an anode slurry. On a separate basis, particles of the cathode active material (e.g. activated carbon), a conductive filler (e.g. acetylene black), a resin binder (e.g. PVDF) are mixed and dispersed in a solvent (e.g. NMP) to form a cathode slurry.

b) The second step includes coating the anode slurry onto one or both primary surfaces of an anode current collector (e.g. Cu or Al foil), drying the coated layer by vaporizing the solvent (e.g. NMP) to form a dried anode electrode coated on Cu or Al foil. Similarly, the cathode slurry is coated and dried to form a dried cathode electrode coated on Al foil.

c) The third step includes laminating an anode/Al foil sheet, a porous separator layer, and a cathode/Al foil sheet together to form a 3-layer or 5-layer assembly, which is cut and slit into desired sizes and stacked to form a rectangular structure (as an example of shape) or rolled into a cylindrical cell structure.

d) The rectangular or cylindrical laminated structure is then encased in an aluminum-plastic laminated envelope or steel casing.

e) A liquid electrolyte is then injected into the laminated structure to make a supercapacitor cell.[24]

The present invention provides a highly innovative and elegant process to overcome this graphene sheet re-stacking issue. This invented process completely eliminates the need to go through slurry coating, drying, and compressing procedures. Instead of forming a slurry containing an environmentally undesirable solvent (i.e. NMP), the process entails dispersing graphene sheets in a liquid electrolyte to form a slurry of electrode active material-liquid electrolyte mixture. This mixture slurry is then injected into pores of a conductive foam-based current collector; no subsequent drying and compressing are required and no or little possibility of graphene sheets re-stacking together. Furthermore, graphene sheets are already pre-dispersed in a liquid electrolyte, implying that essentially all graphene surfaces are naturally accessible to the electrolyte, leaving behind no “dry pockets”. This process also enables us to pack graphene sheets (with electrolyte in between) in a highly compact manner, giving rise to an unexpectedly high electrode active material tap density.

D. APLLICATIONS AND REAL-LIFE EXAMPLES:

From the study of the above-mentioned patents following progressive applications of conducting polymer nano composite material with reference to poly aniline are gathered (collected) and are discussed.

i. BATTERIES

One of the important major applications of this material is batteries. Polyaniline (PANI) is a promising material for battery electrodes due to its unique properties:

- High conductivity: These are readily conducting electricity, crucial for efficient charge transport in batteries.
- Redox activity: This can switch between different oxidation states, allowing it to store and release energy through reversible chemical reactions.
- Low cost and environmental friendliness: This is relatively inexpensive and can be synthesized from readily available chemicals.
- Flexibility and adaptability: This can be easily processed into various forms like films, fibers, and composites, adapting to different battery designs.
- While PANI alone doesn't meet the high energy density needs of **Li-ion batteries**, but the combination with other materials like metal oxides or carbon will improve conductivity and cyclability.[21][22]

ii. SUPERCAPACITORS:

PANI shines in supercapacitors, devices that store energy through rapid surface-based charge accumulation. Its high capacitance and fast charge/discharge cycles make it suitable for applications like short-term energy buffering and electric vehicle power delivery. some specific applications of polyaniline-based supercapacitors are; 1. Portable electronics: Due to their high-power density and fast charging/discharging capabilities, PANI supercapacitors can be ideal for power sources in devices like smartphones, wearable electronics, and medical implants. 2. Electric vehicles: Supercapacitors can complement batteries in electric vehicles by providing rapid bursts of power for acceleration and regenerative braking, extending battery life and improving overall efficiency. 3. Grid energy storage: Supercapacitors can store energy from renewable sources like solar and wind during peak generation times and release it back to the grid when needed, stabilizing the power supply, and reducing reliance on fossil fuels. 4. Memory backup systems: Supercapacitors offer reliable and long-lasting backup power for critical systems like data centres and emergency equipment, ensuring uninterrupted operation during power outages. 5. Flexible and wearable electronics: The inherent flexibility of PANI makes it suitable for developing bendable and conformable supercapacitors for integration into smart textiles, healthcare devices, and other emerging applications.[23][24]

iii. POLYANILINE-BASED ANTICORROSIVE PAINT

Polyaniline-based anticorrosive paint is a type of paint that uses polyaniline, a conductive polymer, to protect metal surfaces from corrosion. It has several advantages over traditional paints, including:

- Superior corrosion protection: Polyaniline can form a passive film on the metal surface that prevents corrosion-causing agents from reaching the metal. This film can also self-heal, repairing minor scratches and damage.
- Electrical conductivity: Polyaniline can conduct electricity, which can be used to provide cathodic protection to the metal surface. This means that an electrical current is applied to the metal to prevent it from corroding.
- Environmental friendliness: Polyaniline is a relatively environmentally friendly material compared to some traditional corrosion inhibitors, such as chromates.

Here are some of the applications of polyaniline-based anticorrosive paint:

- Marine and offshore structures: Polyaniline-based paint is often used to protect ships, oil rigs, and other structures that are exposed to saltwater.
- Pipelines and tanks: Polyaniline-based paint can be used to protect pipelines and tanks that transport or store corrosive materials, such as oil and gas.
- Bridges and buildings: Polyaniline-based paint can be used to protect bridges, buildings, and other structures that are exposed to the elements.
- Aircraft: Polyaniline-based paint can be used to protect aircraft from corrosion, especially in areas such as the landing gear and wing flaps.

Polyaniline-based anticorrosive paint is a relatively new technology, but it has the potential to revolutionize the way we protect metal surfaces from corrosion. It is a more effective and environmentally friendly alternative to traditional paints, and it can be used in a wide variety of applications.[19][20]

III. SCOPE FOR FUTURE STUDY

Extensive research has been done in past four decades on PANI along with different composites like metal oxides, organics dopants and other materials as filler to tune its electrical properties. From the previous work, PANI remains good material to explore for device applications. There is a plenty of scope to explore PANI at nano scale filler with different composite material weight percentage using transition metal oxides, doping of rare earth elements and lanthanide oxides which alter materials properties for new potential applications. Gamma and Electron irradiation on PANI nano composites provides an insight into space applications and its shielding properties for various technological uses. With all this literature work. Still PANI nano composites is better materials to explore for future efficient device applications.

IV. CONCLUSION

Patents granted in recent years on polyaniline nano composites are studied and reported the recent developments. These nanocomposites find excellent applications as supercapacitors, anticorrosion paints and energy storage devices. From previous studies, electrical properties of polyaniline composites can be tunned accordingly with proper choice of dopant and controlling of parameters during synthesis. PANI exhibits good resistance towards atmospheric effects helps for practical applications. Previous work on PANI showed that a promising material for researches to explore more on future potential technological applications**.**

unique properties and adaptability make it an asset for scientists and engineers to explore and unlock its full potential in shaping the future of technology.

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