Properties of Polyaniline/Activated Carbon Composite for High-Performance Applications in Batteries

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Abstract-The **Properties** study, of polyaniline/activated carbon composite for high applications *batteries* performance in was successfully investigated. Results/findings, showed that sample I (700°C and ratio of 25g: 1g) had the highest conductivity. This suggested that Polyaniline is one of the conductive materials that can increase the electrical conductivity in batteries and also activated carbon could be produced from coconut shells and it had electrical conductivity value of $2.36 \times 10^{-8} \pm 5.39 \times 10^{-10}$ ms/cm. Also, the value of the electrical conductivity of Polyaniline/activated carbon from this study lies in the area of the electrical conductivity value of the semiconductor material, which is at a value of 10-8 ms/cm to 103 ms/cm. Hence, Polyaniline/activated carbon has the potential to be used as conductive material in batteries. The researchers suggested the following recommendations: Use of Polyaniline/ carbon might increase electrical activated conductivity of cell batteries through proper carbonization, activation and synthesis, the use of potassium carbonate KHCO₃ as activation reagent is more environmentally friendly instead of the common KOH which is very corrosive and poses some environmental concerns, Polyaniline should be used for high performance batteries that demands environmental safety and reliability, etc.

Indexed Terms- Activated carbon, Polyaniline, Batteries, Electrical conductivity, Reagent

I. INTRODUCTION

Polyaniline (PANI) is a conducting polymer of the semi-flexible rod polymer family which was discovered in the early 1860s by light foot through oxidation of aniline. It behaves like an organic semiconductor that has good electrical conductivity measured in the units. According to Winter et al., (2018) Polyaniline (PANI) is a famous conductive polymer, and it has received tremendous consideration from researchers in the field of nanotechnology for the improvement of sensors, optoelectronic devices, and photonic devices.

Liang et al.,(2018) claimed that PANI can be doped easily by different acids and dopants because of its easy synthesis and remarkable environmental stability. This review focuses on different preparation processes of PANI thin film by chemical and physical methods. Several features of PANI thin films, such as their magnetic, redox, and antioxidant, anti-corrosion, and electrical and sensing properties, are discussed in this review. PANI is a highly conductive polymer. Given its unique properties, easy synthesis, low cost, and high environmental stability in various applications such as electronics, drugs, and anti-corrosion materials, it has attracted extensive attention. The most important PANI applications are briefly reviewed at the end of this review in previous work, researchers focused on producing conductive polymers, which are achieved in the fields of optics, electronics, energy, and so on. Basic types of conductive polymers are obtained through high-precision molecular design and a suitable preparation process. Polyaniline (PANI) was first known as black aniline and came in different forms depending on its oxidation level. Furthermore, PANI is known for its simplicity, environmental stability, and ability to be doped by protonic acids.

Tamez, Modesto and Julie (2002) stated that a *battery* is a device that contains active cells, stores energy and then discharges it by converting chemical energy into electricity. Batteries also can be electronic component of a system that converts chemical energy into electrical energy to provide a static electrical charge for power. *It is* also collection of one or more cells whose chemical reactions encourage a flow of electrons in different directions in a circuit. Batteries nowadays are one of the most important components of electronic appliances and are used in almost every portable electronic gadget. From Drones to phones, and tablets to automobile EVs, one common electronic component you find is the battery.

A polymer-based battery uses organic materials

instead of bulk metals to form a battery. Currently accepted metal-based batteries pose many challenges due to limited resources, negative environmental impact, approaching and the limit of progress. Redox active polymers are attractive options for electrodes in batteries due to their synthetic availability, high-capacity, flexibility, light weight, low cost, and low toxicity. Recent studies have explored how to increase efficiency and reduce challenges to push polymeric active materials further towards practicality in batteries.

II. STATEMENT OF THE PROBLEM

From finding it is being discovered that; during the production of lithium-ion batteries, hydrofluoric acid is used. This acid is very corrosive and can cause severe burns and lung damage if inhaled. Lithium-ion batteries contain as significant amount of heavy metals such as lead, mercury and cadmium which are toxic to humans and wildlife's. Lithium-ion batteries are said to have low energy density. lithium-sulfur batteries contain polysulfide's which after a while dissolves into the electrolyte causing its corrosion.

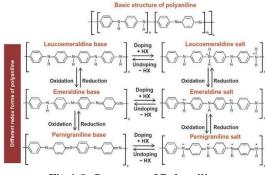


Fig.1.0: Structure of Polyaniline

III. MOLECULAR FORMS OF PANI

Polyaniline exists in three fundamental forms differing in the degree of oxidation. The intermediate form, emeraldine salt, is produced directly by the oxidative polymerization. One half of nitrogen atoms in the polymer chain are present as secondary amines, the other as protonated imines. The completely oxidized form, blue pernigraniline salt, is observed as an intermediate during the oxidation, which takes place in the presence of excess oxidant and converts to the emeraldine form after the oxidant has been consumed and the reaction completed. The oxidation of aniline, for example, with ammonium peroxydisulfate, under acidic conditions yields the polyaniline salt (emeraldine hydrogen sulfate). Sulfuric acid and its ammonium salt are by-products. When transferred to alkaline media, emeraldine salt transforms to a corresponding blue emeraldine base. This important transition, when a conducting form converts to a nonconducting one, is discussed in detail below. The pernigraniline salt yields similarly a violet pernigraniline base. The reduction of emeraldine produces a yellowish leucoemeraldine base. Some studies indicate that leucoemeraldine may also exist in salt and base forms. The salt would be produced, however, only under strongly acidic conditions . Polyaniline is a true polymer. Weight-average molecular weights determined by gel-permeation chromatography in N-methylpyrrolidone are of the order of tens thousands and exceptionally even higher. The lower is the polymerization temperature, the higher is the molecular weight. The polymer fraction is often accompanied by oligomers that are produced at the beginning of aniline oxidation. One has also to realize that the chromatography refers only to the soluble part of the oxidation product, which typically amounts to 40-50 wt% (35). Any product of aniline oxidation is thus composed of aniline oligomers, soluble polyaniline fraction, and insoluble component, and only their mutual proportions differ depending on reaction conditions.

IV. DISCUSSIONS

Valuable Properties of Polyaniline

 Physical Properties: PANI has various physical properties, depending on its three forms, where these forms show different colors according to their chemical nature. PANI appears white/clear or colorless if the polymer form is leucoemeraldine, and if the polymer type is pernigraniline, it gives blue to violet color, and if the polymer form is emeraldine, it gives blue color if it is basic and gives green color if it is salt form. PANI also has good electrical conductivity only in the emeraldine form, and the other types do not show significant conductivity. As for solubility, all forms of PANI are insoluble in water, acetone, ethanol, and other solvents, but are soluble in dimethylformamide, dimethyl sulfoxide, and N-methyl-2-pyrrolidone.

- Optical Properties: The optical properties of PANI are used to study the
- oxidation level and protonation process of the polymer. Huang and MacDiarmid observed that when leucoemeraldine was converted from its base form to its salt form, a blue shift occurred from 3.94 to 4.17 eV. This shift occurred due to the excitation of electrons between the locally occupied upper molecular orbital (HOMO) to the lower unoccupied molecular orbital (LOMO), where the absorption peak was observed at 2.1 eV . Barbero and Kötz studied the optical properties of PANI films deposited on gold, and two absorption states appeared in the UV-visible region of the oxidized state of the polymer, the first at 3.8 eV (which is due to the π - π * transition*) and the second at 2.75 eV (which is related to the n-to- π^* transition), as it has one absorption band at 1.5 eV near infrared and is due to the transition entering the band . For emeraldine conductive PANI in its salt form, there are predictions of molecular orbital calculations, where these studies show the presence of a single broad polaron band within the band gap. This band is half full, resulting in a signal in the ESR scan. Calculations of this band structure are consistent with the observed UVvisible and infrared spectra. The emeraldine salt in their compact coil structure shows three bands: the first band at 330 nm, which is assigned to $(\pi - \pi^*)$ band transitions), and two visible-region bands at 430 nm, which is attributed to ($\pi \rightarrow$ polaron band), and 800 nm, which related to (polaron $\rightarrow \pi^*$).
- Mechanical Properties: PANI shows a noticeable difference in mechanical properties according to the polymerization method from which it was

prepared. Emeraldine salts prepared by electropolymerization method are highly porous and have poor mechanical properties. In addition, PANI films prepared by electropolymerization method have poor mechanical properties, so they are not used frequently. As for PANI prepared from solutions, it is more rigid and is widely used as films and fibers, because it has less porosity and better mechanical properties. The first to study the mechanical properties of PANI are Wei et al., where they noticed that a layer of PANI with a thickness of 0:07 + 0:03 mm at a temperature of 25° C and under nitrogen atmosphere showed a storage modulus of ~200 MPa.

- Electrical Properties: PANI is an attractive conductive polymer that is widely used in the electrical field, because it has good electrical conductivity in its emeraldine salt form. When the acid is added with the basic emeraldine of PANI, it works on protonating the imine group's nitrogen, thus converting it into a salt, thus turning from the non-conductive form to the electrically conductive polymer [37]. Generally, the range of PANI conductivity is from $\sigma \leq 10-10$ S/cm (undoped base emeraldine) to $\sigma \ge 10$ S/cm (doped salt emeraldine) [76, 77]. The process of improving the electrical conductivity or increasing the number of different properties of PANI simultaneously is coupled with the doping process of the polymer. In recent decades, many researchers in the world have tended to dope PANI with various classes of chemical compounds for use in different applications. The purpose of this is to improve the electrical conductivity of the new compounds prepared (polymer compounds) to be used in that application.
- Anti-Corrosion Properties: Corrosion is a chemical change to the metal due to the environmental influences surrounding it, and it is one of the major problems facing the various processes that use the metal as a base element in their applications. Many materials have been used to end or reduce the corrosion process, and one of these materials is PANI, which was first reported in the 1980s . PANI was used to effectively protect steel from oxidation (corrosion) when it was used with fuel cells at the same time. Research and studies have

proven that preparing layers of sulfate with PANI is much better and more suitable for reducing the corrosion of steel than layers of PANI with phosphate. The materials prepared from PANI molybdate and PANI tungstate as coating materials to reduce steel corrosion were studied by Kamaraj et al. Likewise, with nickel-plated steel, the PANI coating showed great protection for this steel from corrosion. In addition, Mirmohseni and Oladegaragoze used PANI-coated iron in different corrosive environments to study the corrosion potential and corrosion current.

- Semiconducting Properties: PANI is considered one of the most promising materials in the field of electronics due to its good conductivity of electrons. The results of electrical and thermal conductivity of the ionic liquid of PANI showed that this polymer is a p-type semiconductor, and the diode of PANI was prepared by Yakuphanoglu and Şenkal. On the other hand, PANI films doped with boric acid were prepared, then the electrical properties of these films were examined. It was found that PANI films doped with boric acid show semi-conductive properties, and its electrical conductivity was found $1:02 \times 10-4$ S/cm at room temperature. The optical band gap of the PANI films doped with boric acid was 3.71 eV. Because of these semiconducting properties, PANI is widely used in organic field transistors and in solar batteries.
- Capacitive Properties: PANI has been widely used in recent years in various electrical and electronic devices, especially electrical storage devices, such as the super capacitor. PANI has contributed to improving the properties of these energy-saving devices due to the rapid oxidation and reduction reactions that occur in a large part of the polymer material. PANI gives a good capacitive response and produces superior specific energies compared to double-layer capacitors. Moreover, PANI has a stronger effect than inorganic batteries and also has remarkable electrical conductivity.

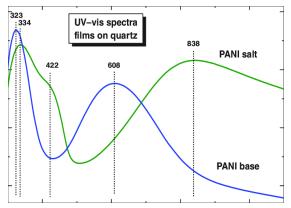


Fig.1.1. UV-vis spectra of original polyaniline salt film obtained after polymerization, and spectrum of corresponding polyaniline base



Fig.1.2. Application Area of polyaniline



Fig.1.3. Application Area of polyaniline in Alkaline Batteries



Fig.1.3. Application Area of polyaniline in Dry Cell Batteries

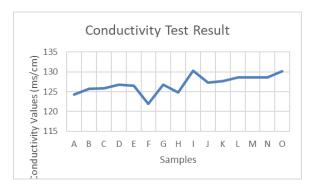
V. CONDUCTIVITY TEST

The polyaniline (emeraldine) sample was passed through a conductivity test to check the degree of conductivity using a Techmel dds-11a conductivity meter. Sample was in liquid form.

	Result	
	Value(ms/cm)	
Runs		
	13.09	
1		
	13.03	
2		
	13.07	
3		
	13.06	
Mean		

The conductivity result of the activated carbon and the synthesized polyaniline. Result

Sample Value(ms/cm) А 124.3 В 125.7 С 125.8 D 126.7 Е 126.5 F 122.0 G 126.8 Η 124.8 Ι 130.3 J 127.3 Κ 127.7 L 128.6 М 128.6 Ν 128.6 0 130.1



CONCLUSION

The study, Properties of polyaniline/activated carbon composite for high performance applications in batteries was effectively carried out. Results/findings, showed that sample I (700°C and ratio of 25g: 1g) had the highest conductivity. This suggested that Polyaniline is one of the conductive materials that can increase the electrical conductivity in batteries and also activated carbon could be produced from coconut shells with electrical conductivity value of $2.36 \times$ $10^{-8} \pm 5.39 \times 10^{-10}$ ms/cm. Also, the value of the electrical conductivity of activated carbon from this study lies in the area of the electrical conductivity value of the semiconductor material, which is at a value of 10-8 ms/cm to 103 ms/cm. hence, Polyaniline/activated carbon has the potential to be used as conductive material.

RECOMMENDATIONS

The following recommendations are suggested based on the study:

- 1) Use of Polyaniline/ activated carbon might increase electrical conductivity of cell batteries through proper carbonization, activation and synthesis.
- The use of potassium carbonate KHCO₃ as activation reagent is more environmentally friendly instead of the common KOH which is very corrosive and poses some environmental concerns.
- Polyaniline should be used for high performance batteries that demands environmental safety and reliability.
- This research could also be done in future using different conducting polymers such as polyacetylene, polypyrole, polyindole, and other advanced software for generalization.

REFERENCES

- Liang, G., Qin, X.& Zou, J., (2018). Electrosprayed Silicon-Embedded Porous Carbon Microspheres as Lithium-Ion Battery Anodes with Exceptional Rate Capacities, (12)7: 424-431.
- [2] Lai. J., YiY., &Zhu, P. (2016). Polyaniline-based glucose biosensor: A review Journal of Electroanalytical Chemistry, (78)2: 138-153.
- [3] Hu, J., Jia, F., &Song, Y.F. (2017). Engineering high performance polyoxometalate/PANI/MWNTs nanocomposite anode materials for lithium-ion batteries. Chemical Engineering Journal, (32)6: 273-280.
- [4] Ge, D., Yang, L., & Honglawan, A. (2014). In situ synthesis of hybrid aerogels from singlewalled carbon nanotubes and polyaniline nanoribbons as free-standing, flexible energy storage electrodes. Journal of Chemistry of Materials, 26(4): 1678-1685.
- [5] Wu, H., Yu, G., & Pan, L. (2013). Stable Li-ion battery anodes by in-situ polymerization of conducting hydrogel to conformally coat silicon nanoparticles. Journal of Nature Communications, (4): 1943
- [6] Xia, X., Chao, D., & Qi, X, (2013). Controllable growth of conducting polymers shell for constructing high-quality organic/inorganic core/shell nanostructures and their opticalelectrochemical properties. Journal of Nanotechnology letters, (13).
- [7] Aluminum Air Battery, Foiled Again. Web. 17 July 2002. Tamez, Modesto & Julie H. Yu. "Aluminum-Air Battery."
- [8] Nishide, Hiroyuki, Takeo & Suga (2005). "Organic Radical Battery". The Electrochemical Society Interface. Retrieved 3 November 2011.
- [9] Winter M, Barnett B, Xu K. (2018). Before Li ion batteries. Journal of Chemical Reviews, 118(23): pp. 11433-11456.