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APPLICATION OF CONJUGATED MACROMOLECULES IN RENEWABLE ENERGY STORAGE DEVICES: AN OVERVIEW.

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Abstract: The new generation of plastics or polymers called conjugated conducting polymers or macromolecules (high polymers), which could be made conductive by some structural modification called doping. Polyacetylene, Polypyrrole, polyaniline and polythiopene etc. are the examples of conjugated conducting polymers. These doped macromolecules in their modified form have wide applications in renewable energy storage devices such as electrochromic cells, batteries, charge stations etc. The potential applications of these conjugated macromolecules also includes corrosion protection, radars as well as sensors. Much research will be needed before the applications may become a reality. The research on conducting conjugated macromolecules is still rare, and the aim of this overview is to share the basic information with researchers, this article will also provide beneficial information about the application of such kind of macromolecules in renewable energy storage devices and in other important fields.

Keywords: Macromolecules, organic metals, doping, Electrochromic cells.

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INTRODUCTION

Three decades ago, the researchers discovered that, the particular class of macromolecules called conjugated polymers could become highly electrically conductive after undergoing some structural modification by doping techniques [1-6]. These conjugated macromolecules have alternating single and double bonds in the polymer chain. Due to this conjugation in their chains, it enables the electrons to de-localize throughout the whole system and hence many atoms may share them. These de-localized electrons may move around the whole system and becomes the charge carriers to make them conductive. This macromolecule can be transferred into a conducting form when electrons are removed from the backbone resulting in cations or added to the backbone resulting in anions. Cations and anions act as charge carriers and becomes mobile under the influence of an external electric field, thus increasing conductivity. Doping allows electrons to flow due to the formation of conduction bands. As doping occurs, the electrons in the conjugated macromolecules, which are loosely bound are able to jump around the polymer chain. Electric current will be produced when the electrons are moving along the polymer (macromolecule) chains. Several examples of such conjugated macromolecules are polyaniline, polythiophene, polyacetylene and polypyrrole [7-9]. These conducting polymers are also called organic metals. In future inorganic metals may replace by these conjugated polymers or macromolecules in several critical areas. The inorganic metals are not environmental friendly due to their toxicity, while organic macromolecules ie. Organic metals have potential benefit as substitute of inorganic metals. The potential applications of conjugated macromolecules (organic metals) includes corrosion protection, radars, sensors and in renewable energy storage devices such as batteries and electrochromic cells.

The Structures of Conjugated Conducting Macromolecules

Usually material can be divided into three main groups, such as conductors (metals), insulators and semiconductors. This classification of materials is on the basis of their ability to conduct or the ability to allow the flow of current. Conjugated conducting macromolecules are belongs in semiconductor category although some highly conducting macromolecules, such as polyacetylene, fall into metal range.

The structures of some conjugated conducting macromolecules are shown in figure 1. These macromolecules can be synthesized by chemical polymerization and electrochemical polymerization. In chemical polymerization, the conjugated monomers reacts with an excess amount of an oxidant in suitable solvent. The polymerization takes place spontaneously and requires constant stirring. In electrochemical polymerization technique the counter and reference electrodes are kept into the solution of diluted monomer and electrolyte in a solvent. After applying the suitable voltage, macromolecule film immediately starts to form on the working electrode.

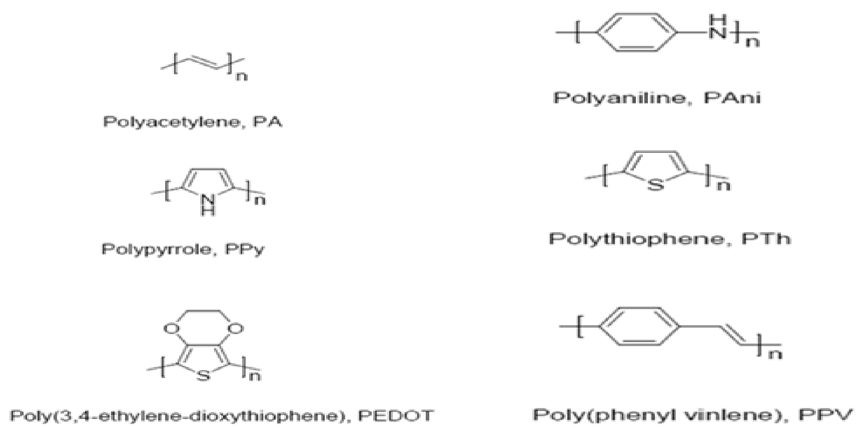

Figure: 1. Structures of some conjugated macromolecules

The figure-2 shows the comparison of conductivity of conjugated macromolecules with other materials and table-1 shows the comparison of some physical properties of these macromolecules with metals and insulators.

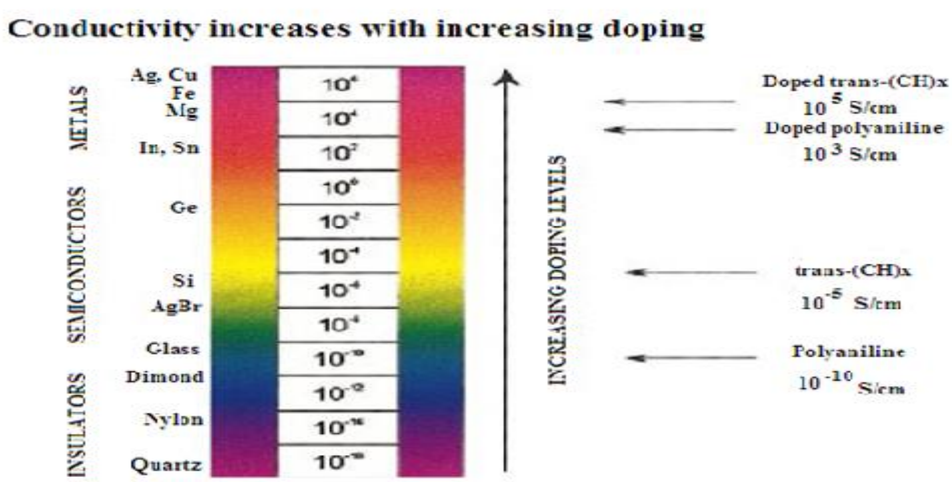

Figure2. Conductivity comparison between conjugated conducting macromolecules (Polymers) and other materials

Table 1: Comparison of physical properties of metals, insulators and conjugated conducting macromolecules.

Physical Property	Conjugated macromolecules (Polymers)	Metals	Insulators
Electrical conductivity (S/cm)	10^{-11}- 10^{3}	10^{-4} - 10^{6}	$10^{-20} – 10^{-12}$
Current carriers	Electrons of conjugated double bonds	Valance electrons of half filled orbital	Current carriers are absent
Magnetic properties	Paramagnetic	Ferro and Diamagnetic	Diamagnetic

Present and Future Potential Applications of Conjugated Macromolecules.

Potential applications for conducting polymers are numerous, since inorganic metals are toxic and can damage the environment. Following are some potential applications of conjugated conducting macromolecules.

i) Electromagnetic shielding ii) Printed circuit boards iii) Antistatic coating iv) Molecular electronics v) Electrical displays vi)Rechargeable batteries vii) Sensors viii) Electromechanical actuators, ix) 'Smart' structures

In present paper we are focusing on the potential application of conjugated conducting macromolecules in energy storage devices.

Application in batteries:

The polymer battery, such as a polypyrrole- lithium cell operates by the oxidation and reduction of the polymer backbone. During charging the polymer oxidizes anions in the electrolyte which enter the porous polymer to balance the charge created. Simultaneously, lithium ions in electrolyte are electrodeposited at the lithium surface. During discharging electrons are removed from the lithium, causing lithium ions to re enter the electrolyte and to pass through the load and into the oxidized polymer. The positive sites on the polymer are reduced, releasing the charge-balancing anions back to the electrolyte. This process can be repeated about as often as a typical secondary battery cell [10-11].

In this area conjugated conducting polymers promises to have a great commercial impact. The design of commercial rechargeable battery is shown in figure 3. General batteries have several components, the electrodes in batteries allow for collection of current and transmission of power and the electrolyte provides a physical separation between the cathode and anode, and also provides a source of cations and anions to balance the redox reactions. There are many issues, not related to conjugate conducting macromolecules that affect battery performance, such as electrolyte stability and stability of counter half- cell reaction, and compatibility between the electrolyte and the materials. In case of lead –acid battery, in its discharge state both the positive and negative electrodes become lead sulfate and the electrolyte such as sulfuric acid becomes primarily water. The discharge process was driven by the conduction of electrons from the negative electrode back into the cell at the positive electrode in external circuit. In the fully charged state, the negative electrode consists of lead and positive electrode lead oxide, with the electrolyte of concentrated sulfuric acid. During discharge, H^+ produced at negative electrode moves to the electrolyte solution (H_2SO_4) and then is consumed into the positive electrode, while HSO_4^- consumed at both electrodes. The reverse occurs during charging. Those motion can be electrically driven proton flow or by diffusion through the electrolyte. Since the density is greater when the sulfuric acid concentration is higher, the liquid will tends to circulate by convection. Therefore a liquid medium cell tends to rapidly discharge. In such batteries repeated cycles of partial charging and discharging will increase startification of electrolyte, reducing capacity and performance of the battery because of the lack of acid on top limit electrode activation. Again excessive charging of such batteries cause explosion.

The conjugated conducting polymers can be used as active materials in batteries. Owing to their low density, it was thought that batteries with power densities much higher than those of ordinary lead-acid battery could be readily obtained. Since the charge on macromolecule backbone is distributed over three or four repeat units, the charge capacity per unit mass of conducting polymers is marginally better than that of metals. Conducting polymer batteries were investigated by BASF/VARTA and Allied Signal. Bridgestone has marketed a button-sized battery using conjugated polymer polyaniline and lithium. Polyaniline and lithium-based high-power density batteries use the high potential difference between lithium and the polyaniline to achieve high power densities, although stability and self life. Such batteries can be use as energy storage devices at solar energy, tidal energy and wind energy generation stations. Conducting polymer based batteries show promise, but much work needed to be done.

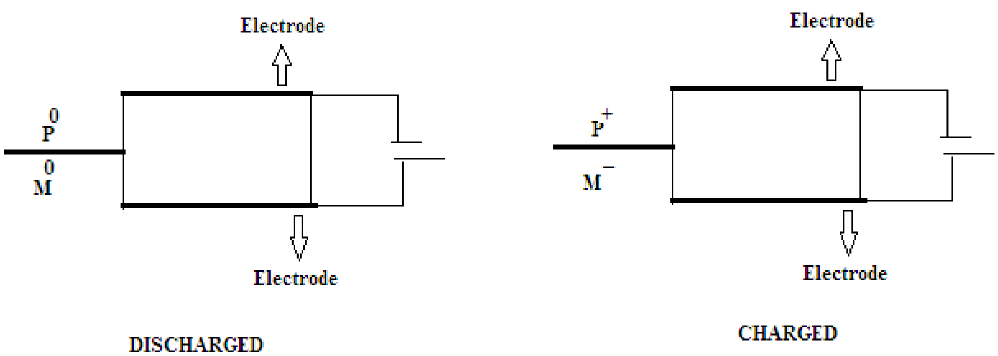

Figure 3 : General Battery Design

Electrochromic cells:

Electrochemical cells are used to go from opaque to transmissive at selected region of the electromagnetic spectrum. The electro- magnetic spectrum covers an immense range of wave length. Some major spectral regions are γ-ray region, X-ray region, visible and ultraviolet region, infrared region, microwave region and radiofrequency region. The operation of an electrochromic cell is shown in figure 4. The electrochromic window is similar to a battery with some additional requirements. This electrochemical window contain at least one electrode which must be transparent to the incident electromagnetic spectrum, the cathode material must be electrochemically reversible, the ion-conducting electrolyte must not provide only physical separation between cathode and anode, a source of both cations and anions to balance redox reactions but must also be transparent to the given region of the spectrum; and the anode material must also be electrochemically reversible. The ion-conducting electrolyte in electrochromic cell is generally inorganic salts dissolved in solvents. The ion-conducting electrolyte acts as a source and sink for the ions as the various redox processes take place and maintains ionic contact between the materials. Conjugated conducting polymers also have an application in electrochromic cells, attenuating various regions of the electromagnetic spectrum. There is a great deal of data indicates that conducting polymers are good materials can be used in electrochromic cells. In particular, polyaniline, polypyrrole and polythiphene have been cycled more than 1000 times. This data although good for evaluating differences between polymers, may not accurately reflect the performance of conducting polymers in a sealed, self contained device. This is because the counter half-cell reaction and those devices often require complete oxidation/reduction . this device usually starts to degrade at 10 to 100 times fewer cycles than conducting macromolecules studied by cyclic voltammetry.

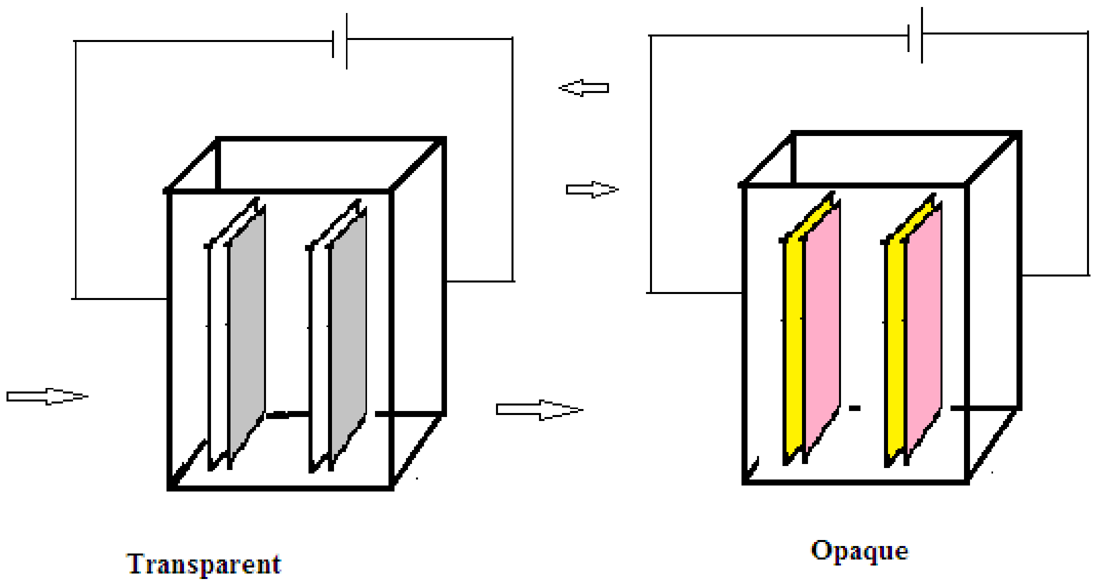

Figure 4: Electrochromic window operation

This does not necessarily mean that polymer is degrading as, either the counter half cell reaction or limited amount of electrolyte may control the lifetime of the devices. However, whereas a 20% drop in charge capacity might be acceptable in a battery, a 20% decrease in a contrast ratio for electrochromic cells may be unacceptable. The evaluation of conducting conjugated macromolecules for battery and electrochromic application should be similar to the actual condition.

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