

# STUDY OF MORPHOLOGICAL STRUCTURE OF POLYPYRROLE

Anshika Rana

Department of Chemistry, Lovely Professional University, Punjab, India.

**Abstract:** This paper presents a comprehensive information about hydrogen fuel cells and explains their high usage round the world and elucidates the role of polypyrrole conducting polymer in successful manufacturing of hydrogen fuel cell in a compact manner. After getting thorough with this paper one can get information about certain topics such as hydrogen fuel cell's importance, the materials used in making a hydrogen fuel cells, then the paper describes polypyrrole and the morphologies that can be used in the manufacturing of hydrogen fuel cells.

**Key Words:** Energy, Fuel Cell, Hydrogen Fuel Cell, Polypyrrole (PPY), Morphology.

**Introduction:** Researchers characterize energy as the capacity to do work[1],[2],[3]. Present day development is conceivable on the grounds that individuals have figured out how to change energy starting with one structure then onto the next and afterward use it to tackle work. Individuals use energy to walk, to move vehicles along streets and boats through water, to prepare food, to light our homes and workplaces, to fabricate items, and to send space travellers into space[4]. We harness energy through different sources which have been classified broadly into two different categories i.e. Conventional and Non-conventional sources of energy[5]. Conventional sources of energy are the natural energy assets which are available in a restricted amount and are being utilized for quite a while[6]. They are called non-renewable sources as whenever they are drained, they cannot be created at the speed which can support its consumption rate. They are shaped from decaying matter more than a huge number of years[7]. These assets have been exhausted generally because of their persistent exploitation[8]. We use the conventional sources of energy at a large extent as the energy source is high, the production costs are much lower than other resources of energy and these are well known sources of energy[9] not only it has advantages but also it has more number of disadvantages like environmental pollution which is caused by fossil fuels(coal, petroleum, natural gas) combustion[10]. Due to the burning of conventional energy sources (non-renewable) particulates of anthropogenic gases[11] like carbon monoxide, carbon dioxide, hydrocarbon, nitrogen oxide, and sulphur dioxide are delivered into the air[12] which accounts for the greatest portion of the warming [13]and results in the rise of global temperature, acid rain, increase sea level, change in food supplies, changes of weather pattern, shrinking changes of water pattern and geographical changes[14]. After considering the following points there was a dire need of alternative source of energy which would overcome these challenges in order to reduce our burden on nature[15]. Hence to overcome this problem mankind came up with a different source of energy which were renewable, sustainable and dependable, they came to be known as non-conventional sources of energy

(renewable sources)[16]. These sources are an efficient measure to combat the rising demand of energy by the population of the world. Some of the non-conventional sources of energy are wind energy, solar energy, tidal energy, ocean energy and energy from waste[17],[18],[19]. One such of a kind of energy can be produce by Hydrogen fuel cells which comes under the umbrella of non-conventional[20] source of energy and is being researched on how it can be useful in different fields. These fuel cells are the best and environment friendly source of energy. Fuel cells are a drastically new and unique method of making electrical power from variety of fuels[21]. It has characteristics and components which are similar to a typical battery[22] and also work like it, however they don't run down or need re-energizing[23].They generate electricity by electrochemical reaction[24] as they converts the chemical energy from the reactant directly into electrical energy[25].Due to their prospective energy density, technological feasibility, safety, lightweight and energy storage capacity they are grabbing more and more attention to fulfil the increasing energy demands[26]. There are different kinds of fuel cells which are under evolution, each with its own benefits and likely applications[27] Some of the examples of fuel cells are Direct methanol fuel cell, Alkaline fuel cell, Phosphoric acid fuel cell, Molten carbonate fuel cell[28] and Polymer Electrolyte Membrane fuel cells whose one of the famous example is Hydrogen fuel cell[27] in which hydrogen is used as a fuel. In year 1839 William Grove was the first one who used hydrogen as a fuel in a fuel cell and demonstrated that electric current could be created from an electrochemical reaction among hydrogen and oxygen over a platinum catalyst [29],[30].Fuel cells in which hydrogen is used as a fuel are addressing the power needs from submarines to spaceships and in transportation and stationary to portable power applications [31] as it provides clean source of energy with no unfavourable ecological effect during activity as the by-products are heat and water only, it provides high-density source of energy with good efficiency, the refuelling process is very easy, it does not generate greenhouse gases and does not produce any kind of pollution[32],[33]. Hydrogen is the most prominent fuel for fuel cells. Moreover, hydrogen is referred to as one of the most plentiful substances on earth considering the different chemical species and compounds it forms with a few different elements. It is an odourless gas and involves a nontoxic nature[34] and secured up tremendous amounts in water, hydrocarbons, and other natural matter[35].It can be produced using different, domestic assets or resources—including petroleum derivatives, like flammable gas and coal (with carbon sequestration); thermal power; and other sustainable power sources, like biomass, wind, solar, geothermal, and hydro-electric power—utilizing a wide scope of cycles[36],[37].

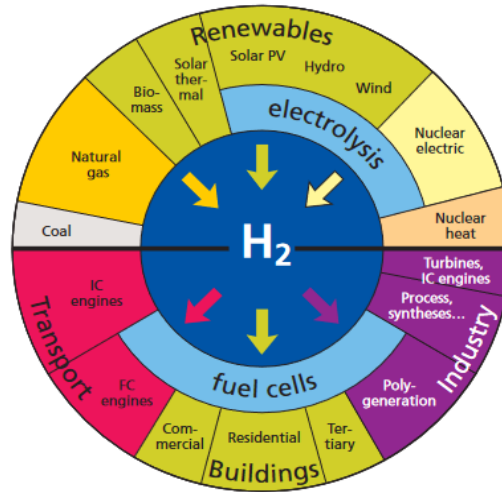


Figure 1: The above pictorial representation, represents the use of Hydrogen (H<sub>2</sub>) as a primary source of energy in different sectors[38].

### STRUCTURE AND WORKING OF FUEL CELL

The structure of any kind of fuel cell consists of three columns: anode, cathode, and an electrolyte layer which is in contact with an anode and a cathode on one or the other side[39]. Electrolyte plays a role of principle section for any fuel cell because it tells about the nature, attributes and its activity[40]. A fuel enters the anode, and an oxidant enters the cathode. These are isolated by a specifically conductive electrolyte. Conduction through the electrolyte can happen one or the other way: anode to cathode or cathode to anode depending upon the fuel cell[41].

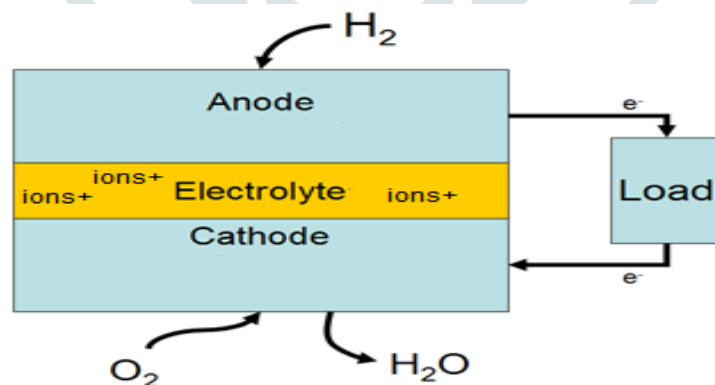


Figure 2: The figure represents the basic structure of the Hydrogen Fuel Cell having three pillars anode, cathode and electrolyte and how electrolyte is connected to anode and cathode[42].

All the fuel cell work on the same concept, just the fact that the fuel and electrolytes vary from fuel cell to fuel cell. One such type of fuel cell is Hydrogen Fuel Cell. In Hydrogen Fuel Cell technology, a process known as reverse electrolysis takes places which is responsible for reaction between oxygen and hydrogen[43].

Hydrogen gas is supplied to the electrode which is covered with a metal, like platinum or platinum alloy [44] which plays a role of catalyst and increases the rate of separation of hydrogen particles into atoms and the ionization (stripped of electrons) of these molecules into hydrogen particles (H+, or protons)[45].

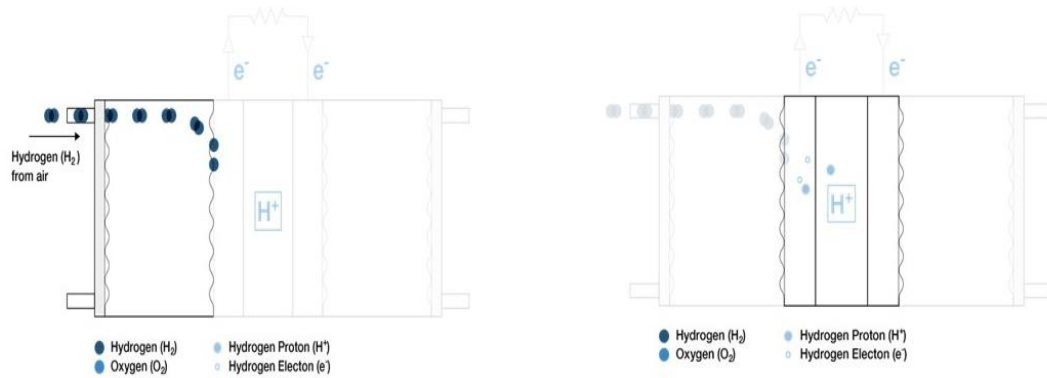


Figure 3: Schematic representation of (a) Hydrogen gas is entering into the fuel cell through the anode side (b) Hydrogen molecules gets separated into ions [46].

Assuming, a circuit is associated between anode and cathode, the electrons can go through the circuit and give power to any load that is associated as a feature of the circuit[47].



The hydrogen particles (protons) that are created from the hydrogen at anode travel through the electrolyte in the fuel cell to the cathode. On the other hand, oxygen gas is being forced through the catalyst, where it forms two oxygen atoms. These particles have a strong negative charge, which gets two hydrogen protons through exchange membrane[47],[25],[50].

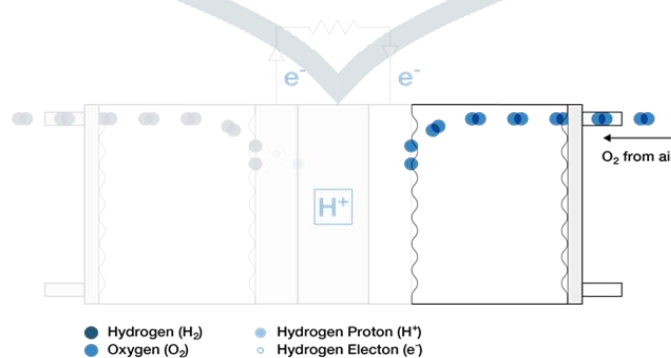


Figure 4: Oxygen gas entering into the fuel cell from the cathode side[46].

At last, the electrons at the same time travel through the anode and clear their path through an outside circuit generating power(electricity), eventually getting back to the cathode side of the fuel cell.

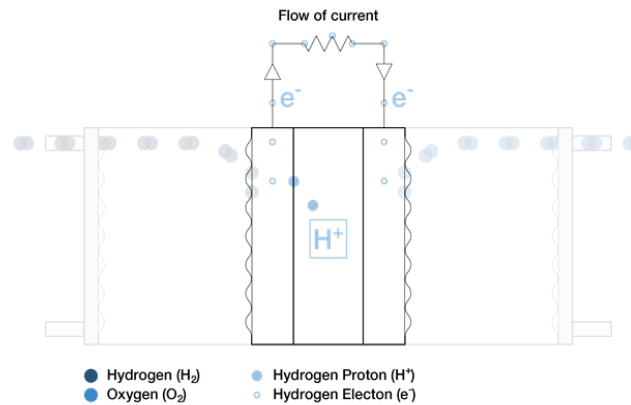


Figure 5: Flow of current due to the travelling of electrode within the cell[46].

## COMPONENTS OF HYDROGEN FUEL CELL

### 1. Proton Exchange Membrane

In Hydrogen fuel cell, Proton Exchange Membrane is required that will convey the hydrogen ions, proton, from the anode to the cathode without passing the electrons that were eliminated from the hydrogen molecules[51]. This membrane should be made up of that material which is able to conduct protons as ionic conductivity is very important. In addition to high conductivity membrane material should be resistive to chemical attacks, robust and durable. Sulfonated polymers such as Nafion are the most suited material for the membranes and there is per fluorinated as back-bone and sulfonated side chains. This polymer material combines the proton conductivity and the high mechanical strength represents by represented by hydrophilic micro-phase of the sulfonic acid and hydrophobic polymeric phase of the per fluorinated back-bones respectively[52].

### 2. Gas diffusion layer

Gas diffusion layer (GDL) is used for multi-tasking like used to supply hydrogen and air (fuel) to the anode, gather electrons obtained by the chemical reaction with the cathode, and drained moisture over electrolytic membrane and water created by the cycle. Carbon paper and carbon fabric is for the most part utilized because of different prerequisites including gas permeability, conductivity, corrosive obstruction, and mechanical strength[53].

### 3. Catalyst layer

The catalytic layer is an important material that enhance the reaction of oxygen and hydrogen[54]. It is generally made up of platinum nano particles because it is superb for fuel cell with comparatively clean reactants[55]. A layer is added on both the sides of the membrane the anode layer on one side and the cathode layer on the other. Customary catalyst layers incorporate nano-sized particles so that most extreme surface space of the platinum can be presented to the hydrogen or oxygen[54],[56]. The platinum catalyst is blended

with ion conducting polymer (ionomer) and sandwiched between the film and the GDLs. On the anode side, the platinum catalyst empowers hydrogen particles to spilt into protons and electrons and on the cathode side, it empowers reduction of oxygen by responding with the protons created by the anode, delivering water. The ionomer blended into the catalyst layers permits the protons to go through these layers[56],[57].

#### 4. Bipolar plates

Every segment of the fuel cell should be planned appropriately – else, you risk diminishing energy unit execution. The bipolar plates are named "bipolar" on the grounds that they have stream(flow) fields on the two sides. This plan is advantageous when you have membrane electrode assemblies' gatherings (MEAs) on both sides[58]. Bipolar plates have reactant stream channels on the two sides, shaping the anode and cathode compartments of the fuel cell on the opposite sides of the bipolar plate. They work as fuel and oxidant distributor inside the cell, and separate the individual cells in the stack, gather the current, divert water from every cell, humidify gases, and keep the cells cool. To all the while play out these capacities - explicit plate materials and plans are needed. Many sorts of metallic plates, including aluminium, steel, titanium, and nickel. Metallic plates[56] are appropriate for large scale manufacturing and can be made into thin layers, which brings about lightweight. Graphite-carbon composite plates have been made utilizing thermoplastics or thermosets with conductive fillers. These materials are chemically stable and are reasonable for large scale manufacturing procedures, for example, pressure forming, transfer moulding, or shaping.

#### 5. Gaskets

The gaskets which are the sealing part fundamentally affects wellbeing and safety, reliability, durability, practical execution, and cost of a fuel cell. Using hydrogen gas as a fuel can cause two unique sorts of security worries in fuel cells: getting away (leakage) of hydrogen from the fuel cell because of insufficient sealing and blending of hydrogen with oxygen (air) inside the cell because of a deformity (rupture) in the membrane[59] and this can results in reduction in the performance of the fuel cell and damage of fuel cell stack which can cause safety issues[60] so to prevent such kind of internal fuel leakage problems gaskets are used. These gaskets are insert between of pipes or equipment devices or by bolting or tightening it by other methods[61]. The polymers discovered to be reasonable for gasket applications because of their thermal stability and strong chemical resistance incorporate fluorocarbon polymer, polyacrylate rubber, nitrile elastic and its mixes, ethylene propylene rubber, neoprene rubber, butyl rubber, fluoro silicone rubber, urethane rubber and, silicone rubber[62]. In every part of hydrogen fuel cell, different materials are used for example carbon-graphite composite and platinum like metals in catalytic layer, different polymers like fluorocarbon polymer, polyacrylate rubber, nitrile elastic and its mixes, ethylene propylene rubber, neoprene rubber etc in gaskets and conducting polymers example polypyrrole in bi-polar plates and proton exchange membrane.



## POLYPYRROLE AND ITS USES IN HYDROGEN FUEL CELL

After the year 2000, when MacDiarmid, Heeger, and Shirakawa got Nobel prize for their contribution in creating polyacetylene as a conducting polymer[63], there was a boost in the research of conducting polymers and one of those extensively researched polymer is conducting polypyrrole. Polypyrrole (PPy) is an electroconductive polymer from the class of the remarkable materials which join metallic and semiconductor properties with such polymeric qualities as adaptability, strength, and versatility[64],[65]. It is an intrinsically conducting polymer which is synthesized by the oxidation of pyrrole[66] (heterocyclic aromatic organic compound) monomer by different methods. It is having each central carbon atom is  $Sp^2$  hybridized attached to unhybridized p-orbitals with  $\pi$ -electrons or pair of unpaired electrons due to which it shows unique electrical properties. The aromatic ring lies at the right angle to the unhybridized p-orbital and overlap to form electronic cloud below and above where the electrons are delocalized along the backbone of polymer chain which acts as smooth passage for the movement of electrons with greater mobility which results in the conduction process with greater ease[67].

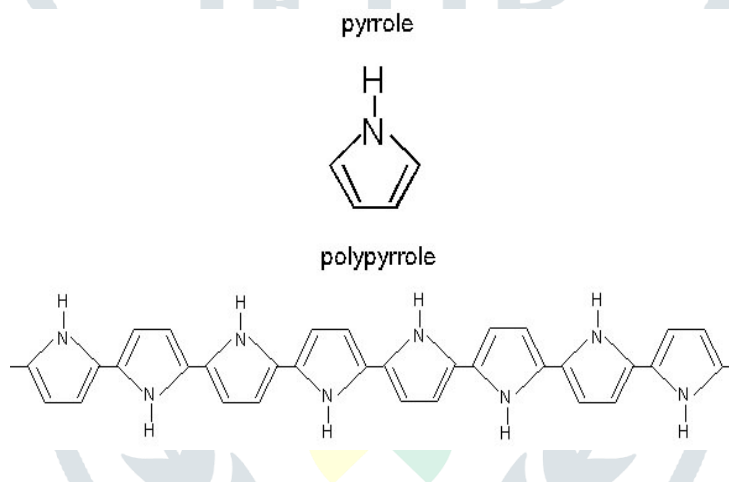


Figure 6: Polypyrrole synthesised from polymerization of pyrrole monomer[68].

Due to its ease of synthesis, compatibility, surface modification and electrically conductivity it can be used in hydrogen fuel cell[69] bipolar plates and electron exchange membrane of hydrogen fuel cell which are described in the following headings:

### 1. Bi-Polar Plates

In a Hydrogen fuel cell, bipolar plates contribute 80% of the size and weight roughly 45% of the framework cost[70]. The fundamental prerequisites for bipolar plates are gas impermeability, low volume, less cost, corrosion resistive, light weight, easy synthesis and most important good electrical conduction [71]. For this requirement metals are the perfect match and can provides good thermal conductivity, electrical conductivity, mechanical stability and can be recycle but are not resistive to corrosion [72],[73] which can be defined as deterioration of the material on reaction with the oxygen present in the environment[74]. So, Polypyrrole layer is used over metals because of its high adherence, high conductivity, high stability, simple electrosynthesis process, and environmental friendly and anti-corrosive property [75],[76],[77]. There are many reasons behind the anti-corrosive property of Polypyrrole. The very first reason is when there is a contact between metal and

electronically conducting polymer (PPY) there is a generation of an electric field which restricts the movement of electrons from metal to an oxidizing which results in the prevention of corrosion[78]. There is another mechanism known as controlled inhibitor release mechanism which also tells why polypyrrole act as protecting agents against corrosion. According to this mechanism doping of Conducting Polymer (PPY) can be done in various ways to control the electrolytic environment adjacent to the metal surface. When PPY layer is coated on metal there is galvanic coupling between the PPY and metal. At cathode reduction of PPY takes place followed by the release of the doping anions whereas at anode oxidation of metal takes place. With the reduction of  $O_2$  takes place simultaneously on the PPY coating leading to the reoxidation of PPY and the production  $OH^-$ . Here the process of self-healing takes place which depends on the nature of metal and the anions of dopant. In metals like steel ,platinum, copper, aluminium formation of oxide is initiated or the doping anions act as inhibitors[79] hence, PPY layer act as anti-corrosive agent.

## 2. Membrane

A significant advancement happened in 1959 when Perfluorosulfonic acid (PFSA) was found as a strong and an effective polymer layer material with huge proton conduction. This is a mixture of hydrophobic Teflon acid as a principal chain and hydrophilic sulfonic acid as a side chain[80]. In disdain of various advantages like amazing proton conductivity even at high working temperatures up to 463.15 K, the perfluorosulfonic acid-based layers face a few challenges like expensive materials, change in shape during water uptake and mechanical and chemical degradation on long thermal exposure[81],[82]. These difficulties have become a main thrust for the improvement and considerable interest in developing alternative [80]. Therefore class of material, conducting polymers, can be utilized to create a permeable electrolyte membrane because of their high strength, high chemical and corrosive resistivity, simplicity of manufacture, light weight, and design flexibility in correlation with semiconductor and metallic materials[83].Hence, Polypyrrole can be used to modify these membrane as polypyrrole is having high catalytic, possess good environmental stability ,chemically extremely resistant, high surface and good electro-conductive properties[84].After coating the bipolar plates and the electrolytic membranes, the polypyrrole which was observed in the end are described in the following paragraphs.

### MORPHOLOGY OF POLYPYRROLE USED IN HYDROGEN FUEL CELL

The below mentioned morphologies are those which were observed under the Scanning Electron Microscope after finding the morphology of the polypyrrole which was used in bi-polar plates, electrodes, membrane, and catalyst of the fuel cell. Morphology is a structural study which is emphasized on the structure of the polymer i.e., how the monomeric units are arranged in a polymeric chain and relationship between polymers. This physical study determines the chemical composition, configuration, and molecular arrangement from nano-level to macro-level[85],[86].Sombatmankhong.et.al developed a porous structured polypyrrole for the



application of electrode in fuel cell using electropolymerisation of pyrrole monomer which results in PPY films consists of irregular and compact deposition of porous PPY of pore diameter 18-65  $\mu\text{m}$  [87].

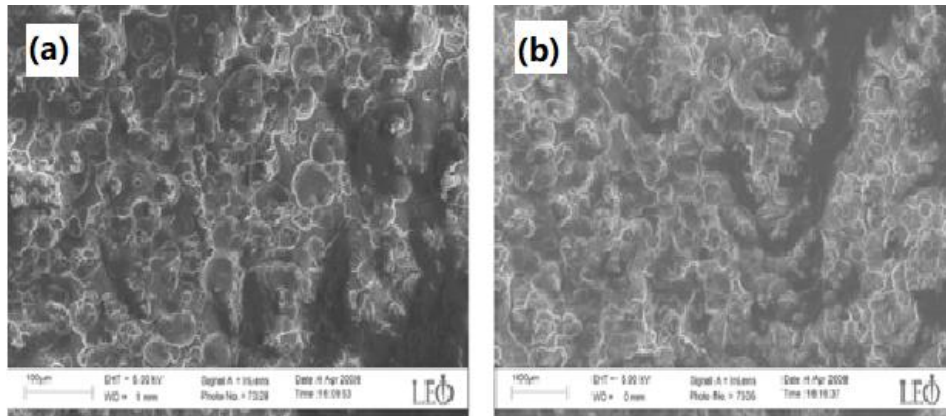


Figure 7: Structure of PPY films consist compact and irregular deposition of PPY[87].

The porous structured PPY films as electrode improved power density which also improves the cell performance[87]. Similarly, In the instance of bi-polar plates Ren et.al reported the electrodeposition of polypyrrole coating on stainless steel for bipolar plates from a alkaline solution of pyrrole monomer (0.2M) and sodium dodecylsulfate as a supporting electrolyte using constant current and cyclic voltammetry technique .It is observed that PPY coating done by constant current results in the formation of compact structure of uniform growth and on the other hand deposition done through voltammetry technique results in the formation of non-uniform deposition because the polymerization is somehow disturbed and intermediates like short chains and oligomers were developed for reduction process[88].

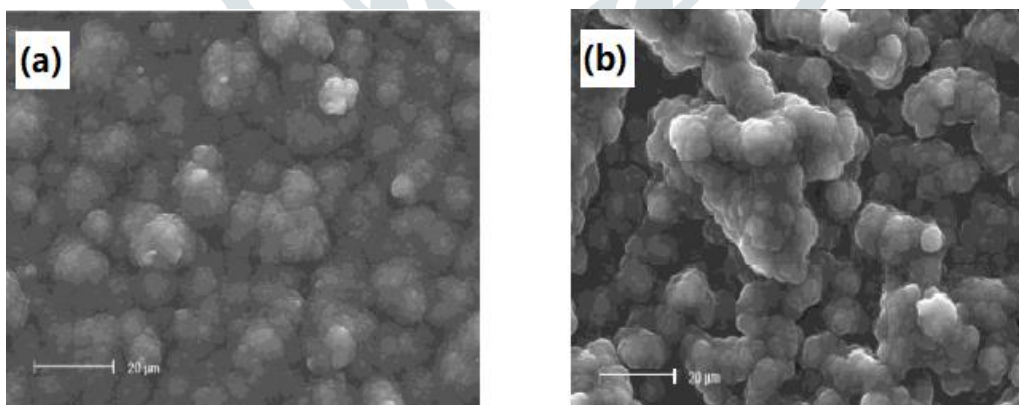


Figure 8: Surface morphology of polypyrrole due to (a) constant current supply (b) cyclic voltammetry[88].

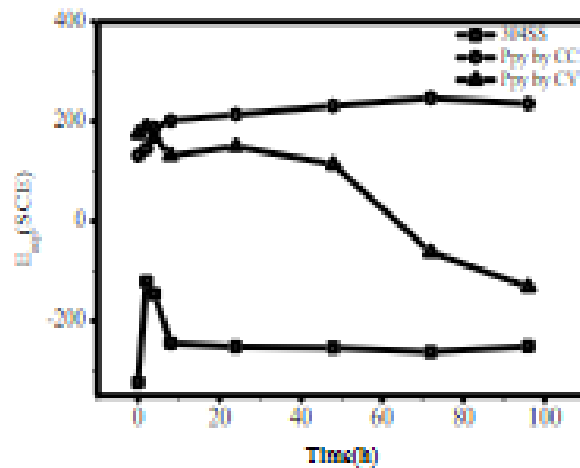


Figure 9: Representation of time vs open circuit potential for PPY coating done on bare steel by cyclic voltammetry method [88].

From the potential ( $E_{ocp}$ ) versus time cure for PPY coated steel and bare steel it is seen that for the steel there is an increase at initial stage of  $E_{ocp}$  and then decreased up to  $-230\text{mV}$  (SCE) and on the other the  $E_{ocp}$  value for PPY coated steel increases during initial 4h of immersion and then decrease rapidly up to  $-97\text{mV}$  (SCE). These above results clearly indicates that steel coated with PPY with the help constant current technique,  $E_{corr}$  value stayed around  $220\text{mV}$ (SCE) for the immersion in corrosive solution hence coating of PPY over steel for bi-polar plates could furnish with good anodic protection and physical barrier[88]. Pan.et.al reported that single PPY coating was done on copper through cyclic voltametric. The polymer coatings expanded the corrosion capability of copper by more than  $250\text{ mV}$  (SCE). Comparing, the  $R_p$  of the copper with PPY covering was almost two significant degrees better than that of the single copper. The potential static estimations at the cathode activity capability of PEMFC demonstrated that no debasement was distinguished in the single PPY coatings. In addition, the impedance of the covering was higher than that of exposed copper[89].

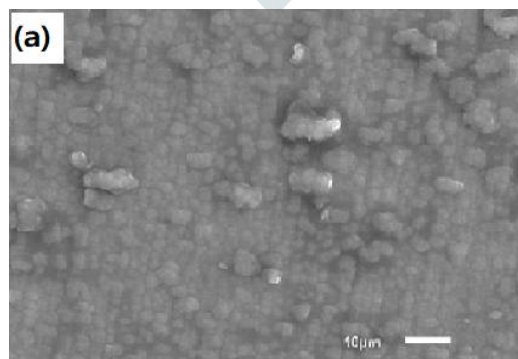


Figure 10: Surface morphology of single layer of PPY[89].

The PPy film over copper was dense which consist of ball shaped(grains) particles with the uniform morphology. The shape and size of the particles is related to the synthesis method. All in all, the development of PPY movies might be related with reaction of oxygen evolution. It is seen that the oxidation of pyrrole monomer began at 1.3 V of potential on copper electrode and overlapped the reaction of oxygen evolution which started around at the capability of 1.5 V. The development of PPY was related with continuously increment of current from the second to fifth cycles. This wonder is credited to the way that the oxygen evolution reaction ought to likewise share a part of total current, since the PPY films is viewed as a perfect catalyst for the O<sub>2</sub> evolution reaction[89],[90]. Stainless steel fulfils large numbers of the prerequisites for fuel cell bipolar plates. Metal oxide development prompts contact resistance, and metal disintegration can cause pollution of the membrane electrode assembly (MEA). These issues can be settled by covering steel plates with corrosion resistive and conductive layers. In this examination, 304 stainless steel was covered electrochemically with the conducting polymers polypyrrole (PPY). Cyclic voltammetry was utilized for the polymerization and deposition of this polymers. The polymer-covered steel plates were tested for corrosion which showed improved corrosion resistance with satisfactory contact resistance[91].

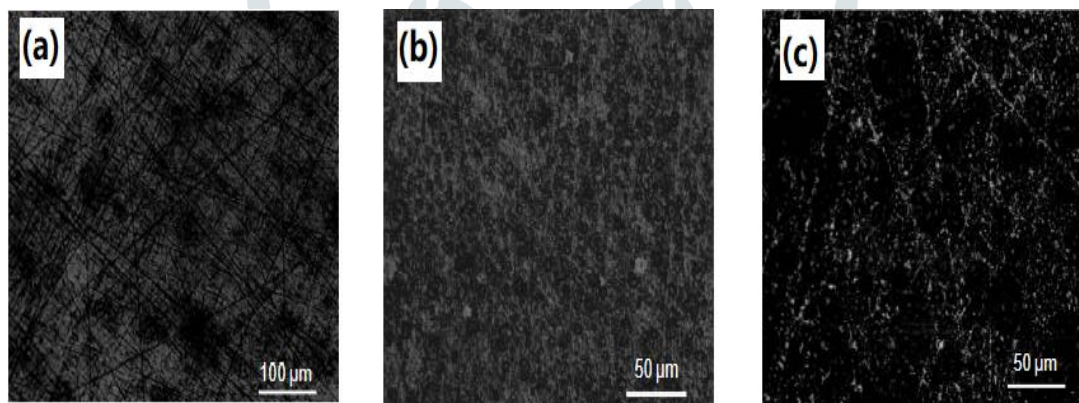


Figure 11: At 20 mV/s PPY developed on 304 stainless steel at different cycles(a) 3<sup>rd</sup> cycle (b) 8<sup>th</sup> cycle and (c) 15<sup>th</sup> cycle [91].

The comparison of corrosion and current densities between bare steel and polymer coated steel is done and the graph is below in fig 12 which depicts that corrosion current density of PPY coated steel is  $10^{-6}$  A/cm<sup>2</sup> and for bare steel is  $10^{-7}$  A/cm<sup>2</sup>. The potential of coated steel shifts towards the more positive value relatively to uncoated steel the formation of oxide is under the film which retards the further corrosion of the material [91],[92].

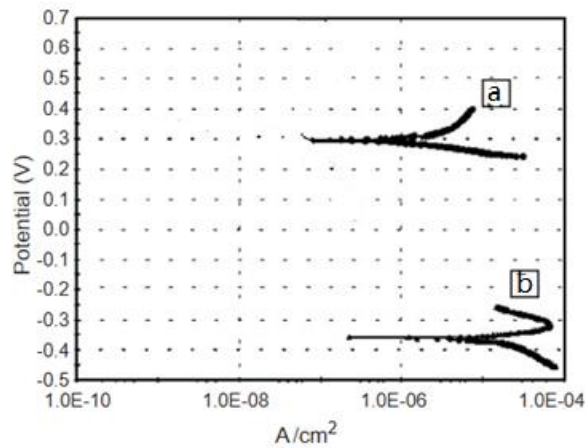


Figure 12: comparison of corrosion current densities between coated steel with PPY(a) and uncoated steel(b) [91].

As PPY used for the coating of materials for bi-polar plates it can be used in the field of catalyst and reported by many researchers like Xia et.al reported an easy electrochemical polymerization technique for the preparation of polypyrrole (PPy) nanowires on Pd altered Nafion layers. Curiously, with modifying the deposition potential and temperature, we can undoubtedly tune the PPy nano wires from confused nano designs to all around requested vertically adjusted nano wires. The different PPy nanowires show comparable electronic conductivity however assorted hydrophobicity/hydrophilicity [93].

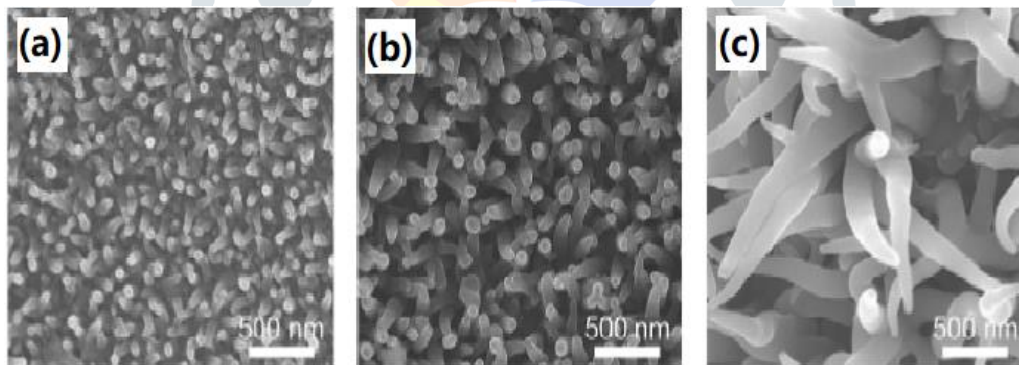


Figure 13: Morphological structure of polypyrrole at various polymerization temperature [93].

It is observed that the arranged PPy nanowires can fundamentally work with the mass transport and improve the catalyst usage by enhancing the transport of oxygen and water. These factor together make a conspicuous exhibition improvement of hydrogen fuel cell[93]. Similarly, Carbon materials, particularly Vulcan XC-72 carbon dark, are the most generally utilized catalyst support in fuel cells. A few inconveniences of these type of catalyst, be that as it may, limit the catalytic performance, prompting decreased cell performance and durability: low protection from corrosion at high potential, micropores prompting restricted to surface accessibility, impermeability to gases and fluids, and no proton conductivity. In this way, improvement of carbon materials is vital for commercialization of fuel cells. Because of remarkable metallic/semiconductor characteristics alongside superb ecological stability, easy combination, and high conductivity, polypyrrole



(PPy), an individual leading polymer, has been viewed as the most encouraging option in contrast to carbon catalyst in fuel cells. PPy used in both anode and cathode catalyst in fuel cells[94].

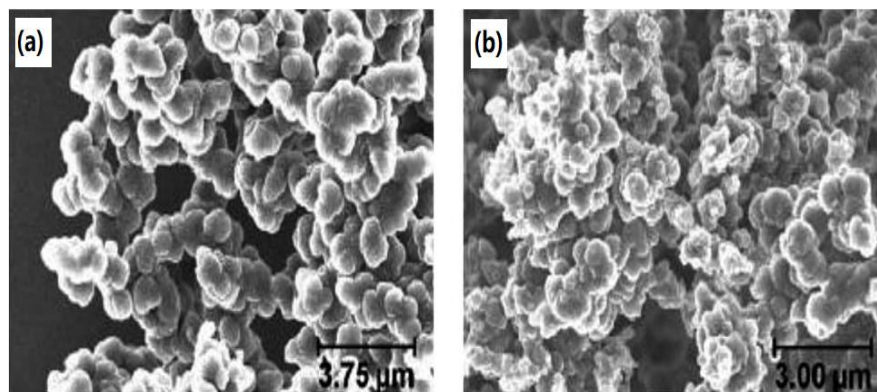


Figure 14: SEM images of morphology of PPy coating [94].

Huang.et.al reported that three polypyrrole (PPy) tests were combined by means of insitu chemical oxidative polymerization to observe their applications as another cathode catalyst support material for fuel cells. The electrochemical stability of the PPy analyte and carbon supports (Vulcan XC-72) were inspected by cyclic voltammetry (CV). Small anodic current i.e., 1.8 V was observed in case of PPy samples as compared to carbon material, demonstrating their resistance towards oxidation under high potential. Among the PPy samples blended in this examination, PPy-3 showed the most elevated electrical conductivity ( $1.67 \text{ S cm}^{-1}$ ) and BET surface space of  $69.6 \text{ m}^2 \text{ g}^{-1}$ . The PPy support is exceptionally resistive towards oxidation at potential as high as 1.8 V[95].

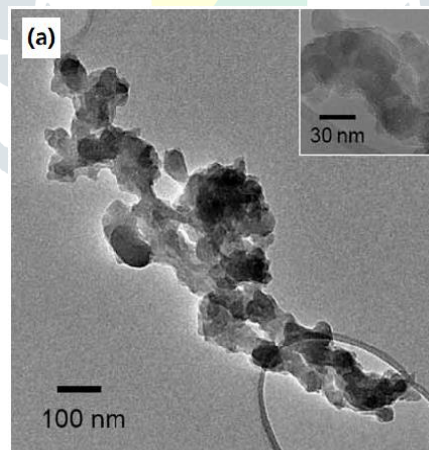


Figure 15: Transmission electron micrographs of PPy-3 support [95]

## CONCLUSION

Hydrogen Fuel Cells are considered one of the most competent alternatives to the conventional fuel sources due to their eco-friendly nature as they emit only oxygen and water as a biproduct, we do not have to recharge the hydrogen fuel cell the way we recharge conventional batteries, they meet the ends of requirement of energy



from as small as a laptop to the rocket due to their scalable property in size and versatility. For the versatility of the hydrogen fuel cell, one class of material plays a major role which are conducting polymers such as Polypyrrole. Conducting polymers which are known for their versatility and cost efficiency are replacing metals and hence are being replaced in different field. Due to Conducting polymers' characteristics they are useful in different field and are hence applied in multifarious fields. Hydrogen fuel cell is also one of the areas in which Polypyrrole (conducting polymer) shows its important presence. Polypyrrole can be used to coat the parts of fuel cell like bi-polar plates, membrane, catalyst, and electrode because of its non-corrosive property and highly proton conduction like properties. Polypyrrole is seen to be present in different morphologies like granular, thin sheets and tubular. Polypyrrole provide good conduction, durability and protection from corrosion which improves the life of the fuel cell and make it more efficient.

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