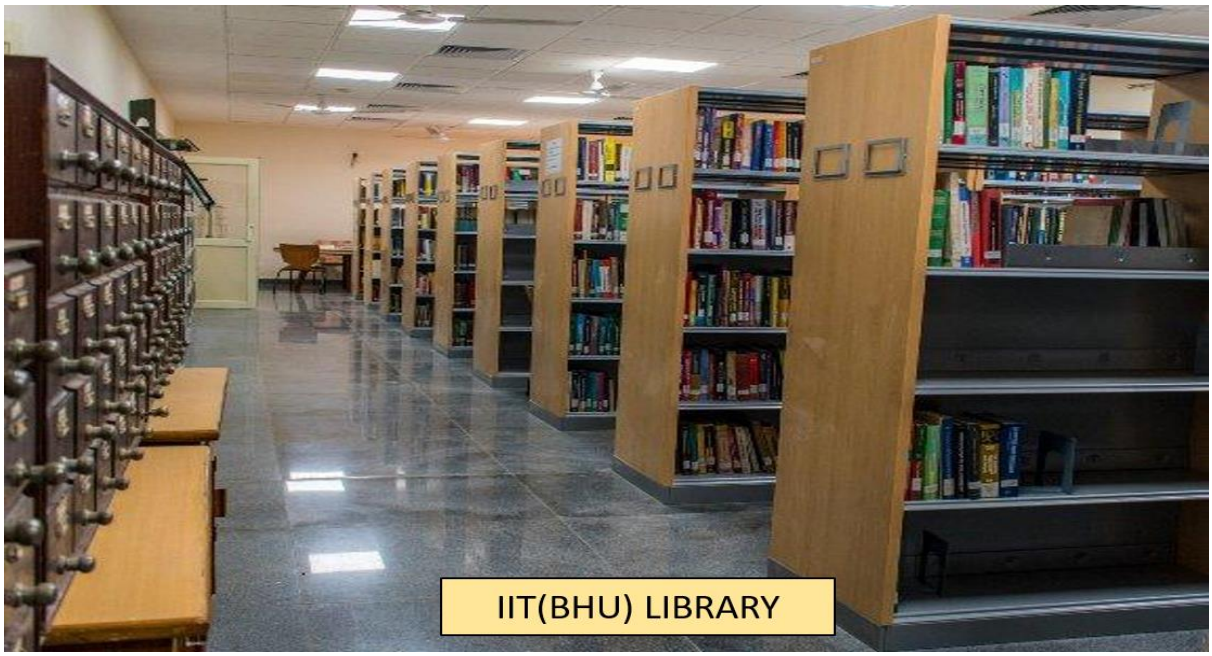
# *Chapter 1*

# *Introduction and Literature Review*



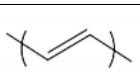
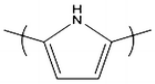
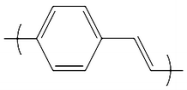
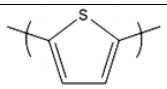
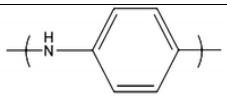
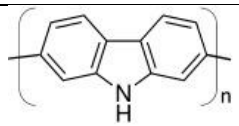

*This chapter briefly introduces the materials we chose for our research study and their related properties. It also elaborates on the general theory related to electrochemical applications. It ends with short descriptions of the available spaces and motivations for the research work.*

## 1.1 Conjugated polymer: Historical background and classification

Conjugated polymers (CPs) that conduct electricity are organic macromolecules with alternate double and single bonds along their backbone chains. Conjugated polymers are organic semiconducting materials with unique electrical and optical properties resulting from overlapping p-orbitals and delocalization of the π-electron. They are also considered 'synthetic metal,' which combines the mechanical and chemical properties of the polymer with the electronic properties of metal and semiconductor. Conjugated polymers (conducting polymer) have gained significant attention in various applications due to the vibrant superiority of compositional and morphological flexibilities, lightweight, high mechanical durability, accessible and economically favorable synthesis, easy processing, and tunable diversity [1],[2]. Research in electrically conducting conjugated polymer started in 1977 when MacDiarmid, Heeger, Shirakawa, and their co-workers investigated that the conductivity of the polyacetylene (PA), the simplest polyene, can be enhanced by several orders ( from $10^{-9}$-$10^{-2}$ to $10^{2}$-$10^{3}$ S/cm) by treating with appropriate oxidizing (iodine) and reducing agents, the so-called '**dopant**.' These scientists received the 2000 Noble Prize in Chemistry for discovering and preparing "conducting polymers."This field received the award after delivering the following noble lecture: *'Discovery of PA film: the drawing of an era of conducting polymer'* by Shirakawa; *'Synthetic metal: a novel role of the organic polymer'* by MacDiarmid; *'fourth generation of polymeric material'* by Heeger [3].

Polyaniline (PANi) was first synthesized in the mid-19$^{th}$ century by Henry Letheby in an acidic medium before the discovery of PA. PANi is highly studied and the first commercially available conducting polymer. Therefore, it is appreciable to credit all the scientists for publishing and popularizing the field of conducting polymer. Some more conducting polymers with their discovery year are given in Table 1.1.

**Table 1.1:** Various conjugated polymers and their years of discovery.

| S.N. | Polymer | Structure | Discovery year |
|---|---|---|---|
| 1 | Polyacetylene, PA |  | 1977 |
| 2 | Poly (p-phenylene), PPP |  | 1979 |
| 3 | Polypyrrole, PPy |  | 1979 |
| 4 | Poly -p-phenylenevinylene), PPV |  | 1976 |
| 5 | Polythiophene, PTh |  | 1982 |
| 6 | Polyaniline, PANi |  | 1985 |
| 7 | Polycarbazole, PCz |  | - |

Generally, the conducting polymer is categorized into four types based on their different degree of polymerization. The polymer system, which shows conductivity because of conducting filler (metal or carbon particulate), belongs to the first type. The second type belongs to that polymer system which offers conductivity due to ionic movements. The third type of conducting polymer is a redox polymer with an immobilized redox center. The polymer system having conductivity due to the conjugation of the bond falls in the fourth significant type. This type of polymer has an alternate single and double bond, creating an extended π network. The movements of electrons through π conjugation generate conductivity [1], [2]. The conducting polymers are also classified based on their chemical structure, i.e., aromatic, polyene type,

heteroatom, and mixed aromatic (heteroaromatic) system. Classifying conducting polymers based on their chemical structure is given below in table 1.2.

**Table 1.2:** Classification of conducting polymers based on their chemical structure.

| **Aromatic cycle (homo-atom)** | **Aromatic cycle with N atom** | **Aromatic cycle with S atom** | **Aliphatic** | **Aromatic cycle with the double bond** |
|---|---|---|---|---|
| Polypyrene, polynaphthalene, poly(fluorene), polyazulene. | N-atom is in the aromatic ring: **polycarbazole (PCz), polypyrrole (PPy),** polyindole (Pin), polyazepine (PAz).<br>N-atom is outside the ring: Polyanilines (PANi). | S-atom is in the aromatic ring: polythiophene (PTh).<br>S-atom is outside the aromatic ring: poly(p-phenylene sulfide) PPS | Polyacetylene (PA) | Poly(p-phenylenevinylene) (PPV) |

Polcarbazole (PCz) is an electrically conducting polymer derived from carbazole (Cz) polymerization, a tricyclic aromatic organic compound containing two fused benzene rings on either side of the nitrogen-containing five-membered ring [4]. The carbazole unit among the polymer structure is very advantageous because of the following reasons: 1) it is the entirely aromatic unit having better environmental and chemical stability; 2) carbazole containing 9H is an inexpensive raw material; 3) it contains a bridged biphenyl unit which results lower in band gap in materials; 4) easy substitution of a wide variety of a functional group on the nitrogen atom to tune the electrical, optical properties and polymer solubility. The rigidity in the PCz is imparted by the π-π electron system along its backbone, making it infusible and causing

difficulties in the process [5], [6]. Initially, it has limited application for this reason compared to the other conducting polymers. The interest in PCz has been rekindled, nevertheless, by recent developments in synthesis techniques. The substitution in PCz during the synthesis can be done in two ways having their advantage. The carbazole unit during polymerization can be substituted either at 2- and 7-positions to produce a poly(2,7-carbazole) derivative or at 3- and 6-positions to produce a poly(3,6-carbazole) derivatives with various characteristics and, consequently, various applications. The structure of the carbazole monomer and the mechanism of polymerization of carbazole are depicted in Figures 1.1 and 1.2, respectively.

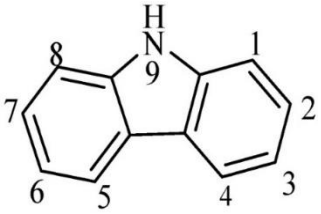



**Figure 1.1:** Structure of the Carbazole monomer.

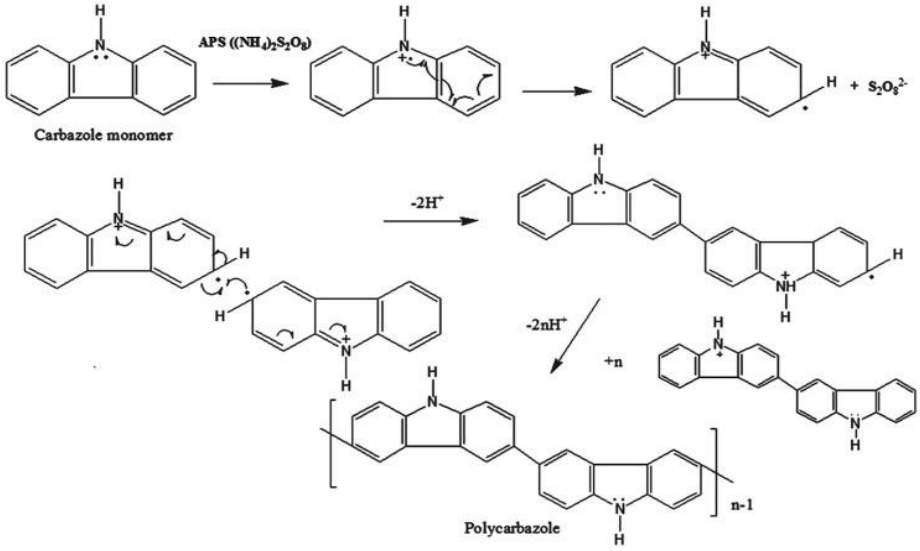



**Figure 1.2:** Mechanism of polymerization of carbazole using ammonium persulfate (APS) as an oxidizing agent [7].

Polypyrrole (PPy) is an organic conducting polymer derived from the oxidative polymerization of pyrrole monomer, a five-membered aromatic ring containing a N atom. PPy is one of the

most extensively explored π-electron conjugated polymers due to its easy synthesis, high electrical conductivity, oxidized form stability, good redox properties, excellent environmental stability and lack of toxicological issues [8]. PPy loses conductivity and charge when overoxidized since it is positively charged in its oxidized state. The exceptional inherent properties of PPy have been established to be a potential candidate for numerous applications, such as biosensors, supercapacitors, textiles, batteries, electrocatalysts, fabrics, and drug delivery applications [8], [9]. The polymerization conditions significantly influence the intrinsic characteristics of PPy. The formation of PPy-based nanocomposites using nanomaterials can enhance the processability and electrical, mechanical, and electrochemical properties of PPy. The PPy-based nanocomposites may provide improved properties similar to metals and semiconductors. The oxidative polymerization method is used to synthesize PPy, either the chemical method via solution processing or the electrochemical route through the polymer deposition at the electrode. The polymerization of pyrrole monomer takes place at the 2- and 5-position, producing poly (2,5-pyrrole), as shown in figure 1.3.

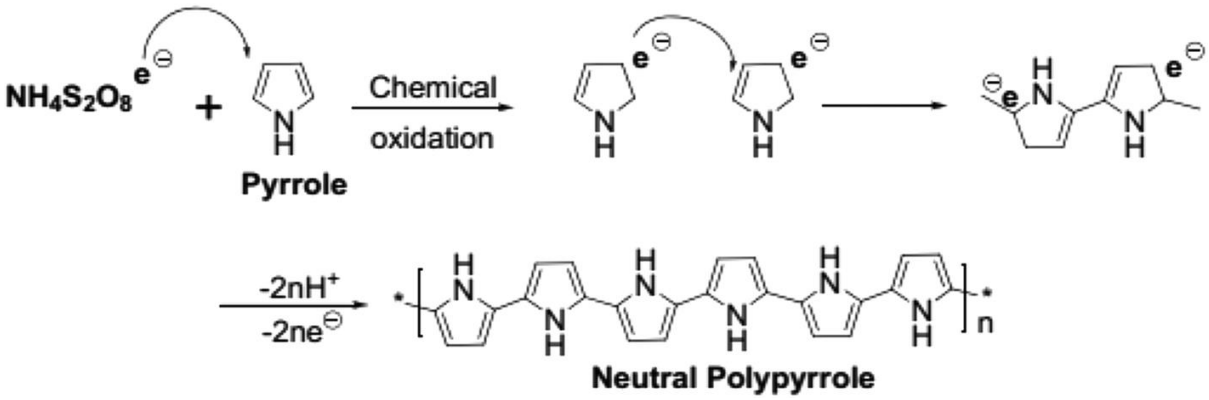



**Figure 1.3:** Synthesis mechanism of polypyrrole [10].

### 1.2 Origin and Mechanism of conductivity of conjugated polymers

Conjugated polymers (CPs) in their pure (undoped) form are the π-conjugated system known for its basic electronic structure. This structure system is formed by overlapping $p_z$ orbitals of

carbon comprising alternate single and double bonds (heteroatoms in PCz, PANI, PPy, PIN, PTh), in which the delocalization of π-electron are there along the entire polymer backbone chain. A comparison of conductivities of conducting polymer in their undoped (pure and intrinsic) and doped condition is displayed in figure 1.4. Recent research reports a significant enhancement of nearly 10 orders of magnitude in their conductivities on doping [1,11,12]. The conjugated polymer doping is a redox reaction in which the pure polymer is oxidized or reduced to its polymeric cation and anion. This results in an ionic complex having oxidized and reduced form of dopant. There is the possibility of peierls instability (coupling between elastic and electronic properties) in alternating single and double-bonded carbon atoms. Due to this, the π-band is split into two bands: the lowest unoccupied molecular orbital (LUMO) band, which is made up of the filled bonding orbital, and the highest occupied molecular orbital (HOMO), which is made up of the empty π* anti-bonding orbital giving a band gap (Eg) in electronic spectrum. (figure 1.5) [13],[14].

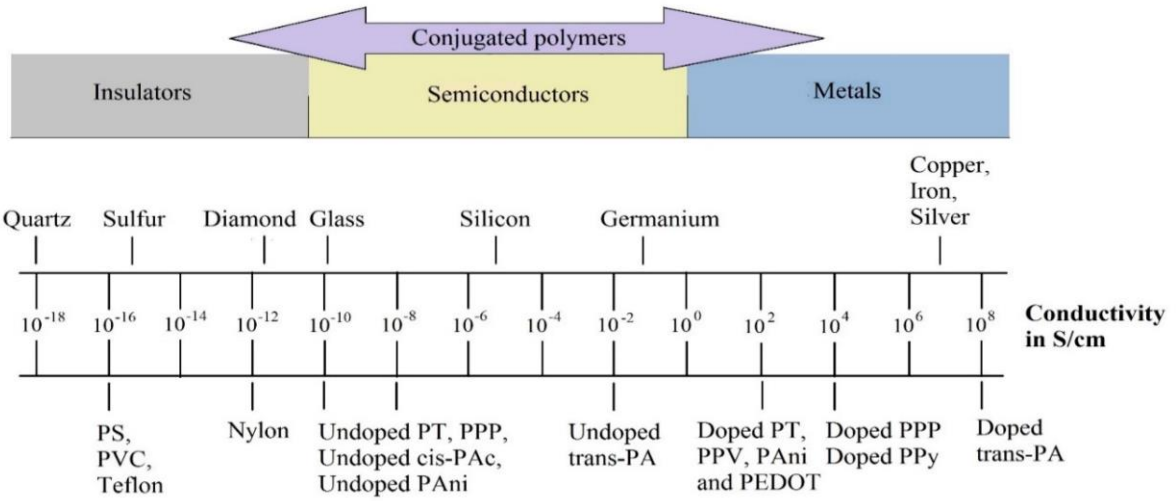



**Figure 1.4:** Range of conductivity comparison of a conjugated polymer in undoped (pure) and doped conditions [11].

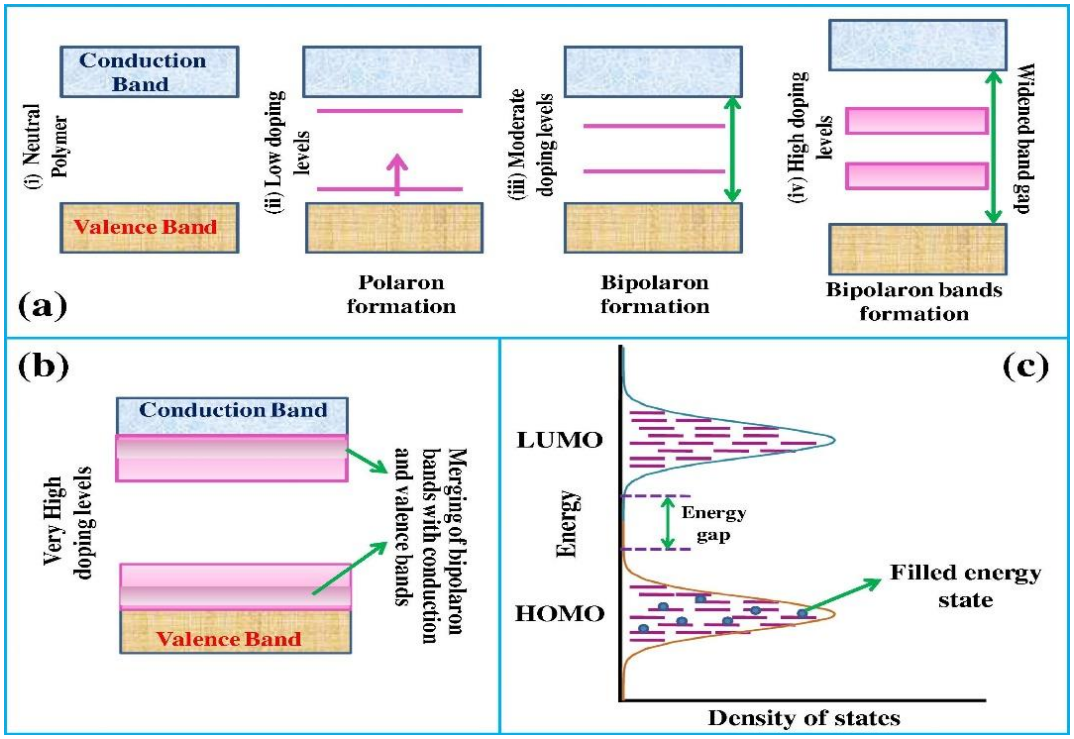



**Figure 1.5:** (a) Creation of polaron, bipolaron and bipolaron band on a different level of doping, (b) merging of the band at the high level of doping, (c) distribution of gaussian states in LUMO and HOMO of conjugated polymers [13].

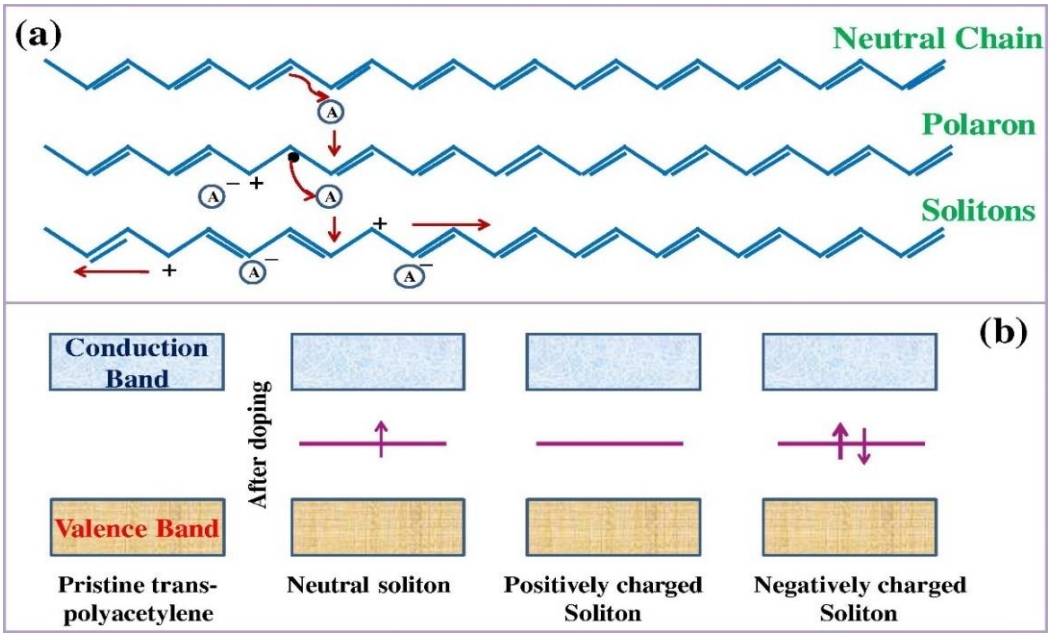



**Figure 1.6:** (a) Creation of two soliton charges on the trans-PA chain, (b) Band structure of *trans*-PA comprising of soliton with neutral, negative, and positive charge [13].

This energy distribution of LUMO and HOMO bands resembles the valence and conduction bands like traditional inorganic semiconductors. The π-electron delocalization does not affect conductivity in the pure state of polymer, so they behave as insulating materials. When these polymers are doped with electron-accepting (p-type) and electron-donating (n-type) dopants, they can be converted into conducting with increasing doping levels. The doped charges are stored in energy states such as polarons, bipolarons, and solitons due to peierls distortion in polymer chain (1D), which is attributed to their neighboring lattice distortion and charge. The generation of polaron, bipolaron, and subsequently bipolaron bands as a consequence of doping levels in several conducting polymers is shown in figure 1.5(a). On removal of an electron from the polymer backbone during doping, polaron (1/2 spin) is generated. On removing the second electron with an increasing doping level, the second polaron so formed combines with the first one to create spinless bipolarons. With increasing doping levels, the bipolaron levels finally form continuous bands as they overlap. At the very high doping level in conducting polymer, both lower and upper bipolaron bands merged with valence and conduction bands to yield metal-like partly filled bands, as shown in figure 1.5(b). A conjugated polymer cannot have a discrete energy band due to spatial disorder. Instead of serving as a charge carrier, the electron/hole will be localized within a conjugated chain with varying energy levels. Typically, a Gaussian function approximates the energy levels distribution in the HOMO and LUMO bands, as shown in figure 1.5(c).

The conjugated polymer having a degenerated ground state has a slightly different conduction mechanism as in the case of PA. In addition to polarons, the conjugated polymer contains solitary wave defects, called solitons, as charge carriers. The soliton can move freely down the chain by pairing with the nearby electron. Two charged solitons forming on the trans-PA chain are displayed in figure 1.6(a). The two charges formed in trans-PA can easily be separated due to degeneration. However, doping-induced solitons are more significant than those created by

bond alternation defects in the conduction mechanism [13]. Particularly in the case of the PA, the neutral soliton (unpaired π-electron or radical) results in the localized electron states formation in the mid of the energy band gap, which is half-filled (neutral soliton), empty in positive soliton and completely filled in case of negative solitons as shown in figure 1.6(b). The charge transport in conducting polymer occurs via the hopping mechanism [15], [16]. In an external electric field, the polaron in undoped or mildly doped polymers hops to the nearby neutral atom of the chain. In contrast, the charge carriers in doped disordered polymers (a pair of polaron and counter ion) can move between polaronic sites without altering the polymer chain.

### 1.3 Properties and limitations of conjugated polymers

Conjugated polymers have high potential and are important materials in the vast area of applications due to their following fundamental properties:

1. CPs possess long and stiff conjugated backbones (in both conducting and doped states), which can be tuned to their electronic, electrochemical, and optical property utilizing suitable modification (oxidation, dopant, and pH).

2. Unique π electron uni-dimensional conductivity and electrochemical activity enhance the electron transfer rate (ETR), lowering the potential for driving electrocatalytic reactions.

3. The solubility, conductivity, electrochemical, and other properties of CPs can be easily altered by synthesizing desired substituted polymer or incorporating suitable components like fillers and dopants.

4. Conjugated polymers have the vibrant superiority of compositional and morphological, structural flexibilities, and tuneable diversity.

5. CPs have the merits of cost-effectiveness, processibility, and non-toxic and environmentally friendly nature.

6. High surface area and probable porosity of the conjugated polymer film are required for effective ionic transport, easy electrolyte diffusion, and more readily available redox active sites for reactions.

7. The homogeneity of the conducting property throughout the polymer thickness controls the concentration profile of the catalyst's active site.

Apart from these properties, the real-world application of conjugated polymer is limited because of some undesired but significant properties like aerial oxidation, poor processability, poor conductivity and poor stability. The stiffness of the conjugated polymer backbone resists dissolving and melting, resulting in poor processability. First, linear, planner and strong packing of conducting polymers lead to maximizing the interaction forces to offer significant crystallinity. Therefore, a very strong interaction between CP and solvent is required to overcome interchain forces for dissolution. Secondly, due to doping, the electrostatic forces between chains in the case of charged conducting polymer are much stronger than van der Waals interactions between the chains. Third, there is minimal entropic gain ($\Delta S$) during the dissolution of conjugated polymer since these processes do not significantly increase conformational freedom. Therefore, several methods are used to improve properties and modify the conjugated polymer to overcome these limitations by forming their nanocomposites, as discussed in the next section.

### 1.4 Conjugated polymer nanocomposites: Improved properties

Conjugated polymers are the subject of intensive research due to their exceptional qualities, such as high tuning capabilities of electrical, mechanical, and optical properties, easy synthesis and fabrication, and superior environmental stability to traditional inorganic materials.

However, CPs have several limitations in their pure state, but they can be conquered through the composite formation with other suitable materials to improve their properties. Composites of CPs with transition metals, carbon-based materials, metal oxides, TMDs, and other materials are investigated for deep and thorough analysis. The structural characteristics significantly influence the performance of the composites [17]. The design of CP-based nanocomposites, from laboratory to industrial scale, depends on the variety of their incredibly wide-ranging applications. Moreover, the preparation process and conditions significantly impact the CP characteristics. New CP composite materials can be synthesized using various methods, including chemical functionalization, vapor polymerization, and template-oriented synthesis, *in-situ* CP composite formation. Figure 1.7 shows the structure of the CPs and the synthesis of polymer nanocomposites via different methods using various fillers (metal nanoparticles, metal oxides ($WO_3$, NASICON-structured oxides), carbon nanomaterials, MOF, 2D materials). NASICON stands for sodium superionic conductors with the generic formula $A_nB_2(PO_4)_3$, where A is sodium and B is typically a transition metal ion or element. Also, CP composites are synthesized using other methods, including electrochemistry, photo-chemistry, radiolysis, chemical, radical, plasma polymerization, emulsion and radial polymerization, etc. The two most common methods among them are chemical and electrochemical techniques [18]. The conjugated polymer composites are formed by mixing or incorporating filler into the poly matrix. The incorporation can be done at the monomeric or polymeric level, depending on the applications. Monomers and CPs can be functionalized with various substances to modify their characteristics. The main polymer chain's chemical and physical properties, particularly its electrical and mechanical capabilities, are improved by incorporating the substituents in addition to its functionality. CPs serve as the principal component of composites that contain a minimum of one secondary part, which could be an inorganic, organic, or biological species [19]. These substances include nanoparticles (NPs), metal ions, **metal and metal oxide**

**nanostructures, NASICON-structured materials**, carbon materials, metallophthalocyanine-containing molecular species, and biologically active substances like enzymes, proteins, antibodies, and antigens. A new composite material is synthesized with the intention of observing unique, distinctive features that are not present in the individual components. Consequently, it is crucial to synthesize composite materials utilizing a synergetic approach. The properties of the nanocomposites will depend on the composition ratio, as CP nanocomposites show interfacial adhesion between CPs and the secondary component.

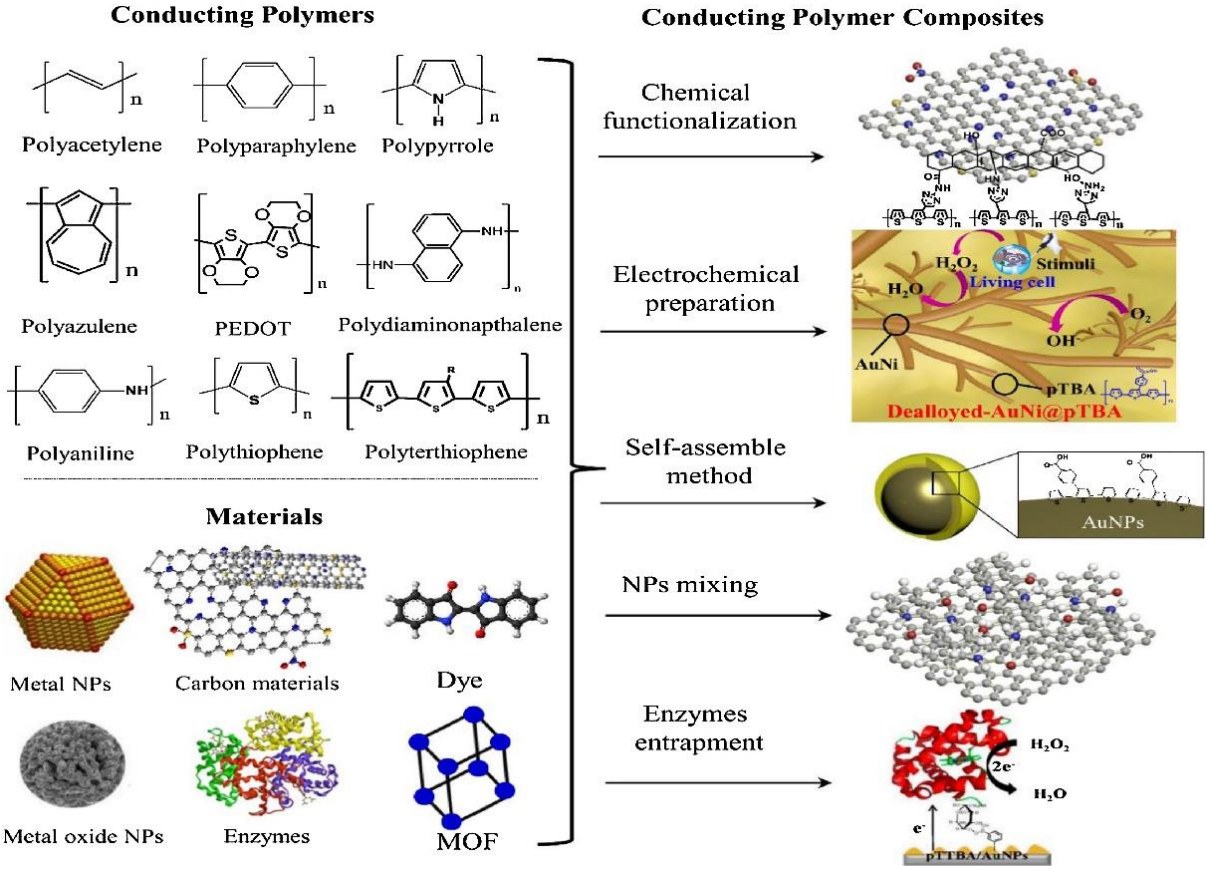



**Figure 1.7:** Various techniques to synthesize the conjugated polymer nanocomposites using CPs and nanomaterials [19].

Due to their synergistic effects, conjugated polymer composites have numerous applications, such as energy storage, fuel cells, biomedical, electrical, catalysis, electronics, optoelectronics, and electrochemical areas [19],[20], [21], [22]. Figure 1.8 shows applications of conjugated polymer nanocomposites in various areas.

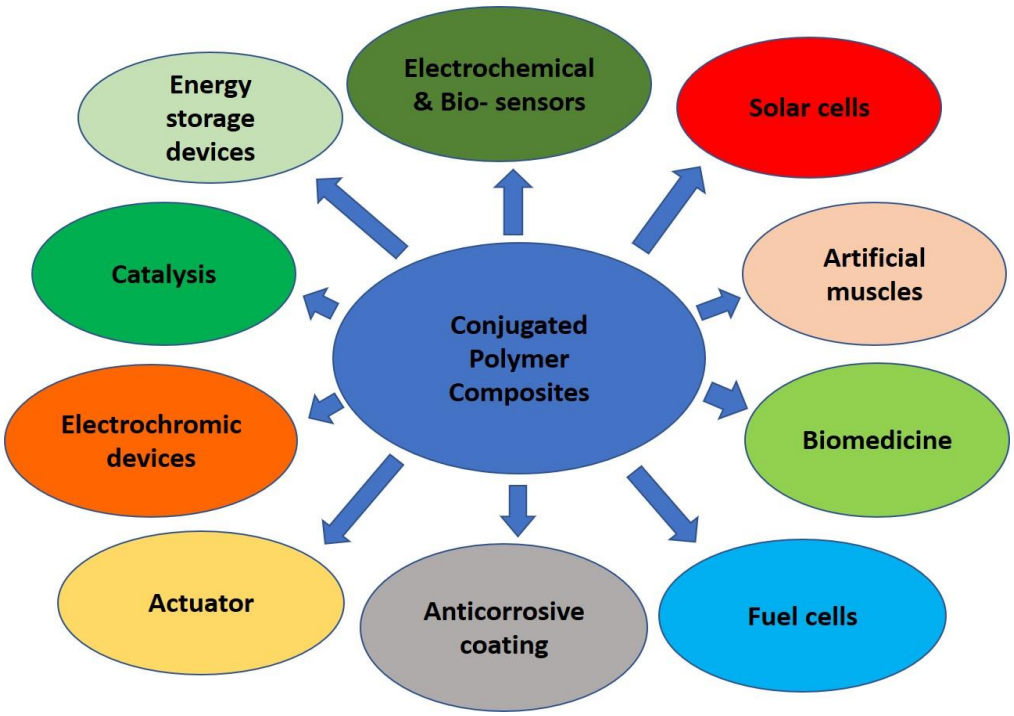



**Figure 1.8:** Different areas of applications of conjugated polymer nanocomposites.

## 1.5 Electrochemical applications of conjugated polymer nanocomposites

CPs possess a higher redox activity and electron affinity than ordinary organic polymers. The length and size of CPs affect their general physical properties, which are also defined in terms of molecular weight [23]. The CP chains, which are insoluble in an aqueous solution, are primarily responsible for the chemical properties of polymers. Most commonly, CPs are synthesized by monomer oxidation using oxidizing agents or electrochemical polymerization methods. Initially proposed by Diaz et al. in 1981, the original PPy synthesis mechanism promoted polymerization by continuously expanding chains by side-to-side coupling of

cationic radicals of monomeric to form oligomer radicals [24]. Electrochemical doping of CPs can result in the oxidation of CPs, producing a p-doped state and the reduction of CPs, generating an n-doped form. They are particularly fascinating candidates for electrochemical devices because of the exceptional properties created in CP-carbon composites. CP-based nanocomposites have been used for various electrochemical applications such as electrocatalysis, electrochemical sensing, fuel cell, supercapacitor and batteries because of their cost-effectiveness, light weight, mechanical flexibility, conductivity and electroactive properties. The high conductivity of conducting polymers boosts the catalytic activity by improving the charge transfer efficiency at the interface of electrolyte and electrode.

Electrocatalysis is a process in which an electrochemical reaction occurs at the electrolyte-electrode interface by enhancing electron transfer rates. Additionally, because the entire reaction consumes less energy, it is possible to develop new technological applications. The electrode surface can also be utilized to regenerate an electrocatalyst for homogenous electron transfer. These species are also recognized as redox mediators and are very useful, for example, in sensor design, **electro-oxidation, HER**, $CO_2$ reduction, oxygen evolution reaction (OER), and electrosynthesis [21]. Using an electrocatalyst during the organic synthesis process can decrease energy costs, stoichiometric amounts of redox reagents can be avoided, and safety is improved. Both ideas fit in well with the present synthetic organic electrochemistry's emphasis on green chemistry. Most materials for electrocatalytic applications are composed of noble or precious metals or transition metal elements, either in the form of alloys or pure electron-conducting metals and electronic semiconductors. Because of this, there has been a lot of investigation into the possibility of substituting pricey precious metals with less expensive organic conjugated polymers. Since they both involve π-conjugated CP layers comprising aromatic moieties and heterocycles with precise molecular structures and empty spaces, well-defined 2D covalent organic polymers and organic carbon frameworks, for instance, behave

like CPs. CPs can have inherent properties of electrocatalysis for some redox reactions. Incorporating metals, metal oxides, and other nanomaterials into these CPs interchain cavities will allow for the generation of electrocatalysts with improved activity. Redox mediators can also be immobilized using CPs, enhancing the homogenous electron transport in the catalytic cycle. A CP matrix can be combined with heterogeneous catalysts, such as catalytic metal nanoparticles and metal oxides, to generate a catalytic electrode [25]. It is an efficient method for reducing the size of the particle and increasing the surface area (and consequently, the reduction of noble metal loading), improving electrocatalytic activity. CPs also have potential utility in electrocatalytic reactions such as HER [26], [27], $O_2$ reduction [25], oxygen evolution reaction (OER) [26], chemosensors [28], and biosensors [29]. The utilization of CPs may lead to future commercial applications because precious metals generally catalyze these reactions. As a result, they are excellent candidates as catalysts for various redox reactions due to their high conductivity and other previously discussed properties. Modern methods like density functional theory are used to understand the deep insight into the electrocatalytic reactions.

Conjugated polymers are also used in energy storage applications like batteries and supercapacitors, along with energy conversions, as discussed above. Various polymer composites, including polypyrrole, polyaniline, and polyacetylene with fillers (nanomaterials), are used as electrodes in batteries. $MnCo_2O_4$-doped PPy composites are used as anode in lithium-ion batteries [30] due to their lightweight, high-performance rate and exhibit reasonable stability. These batteries are used in mobile phones, electric vehicles, and tablets. The conjugated polymer-based supercapacitors have high charge storage efficiency; hence they can store large amounts of electrical energy (up to ~1000 F/g). Supercapacitors have active electrodes based on conducting polymer composites because of their high conductivity, flexibility, stability, and low cost. Various electrochemical applications of conjugated polymer nanocomposites are displayed in figure 1.9.

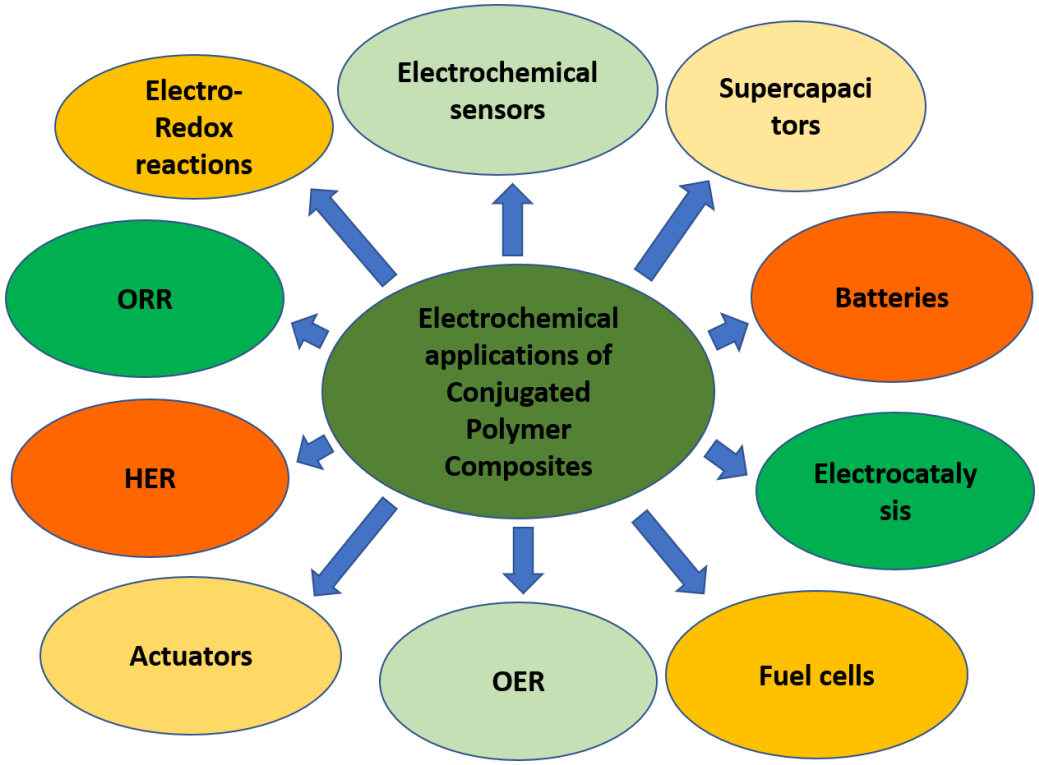



**Figure 1.9:** Different areas of electrochemical applications of conjugated polymer nanocomposites.

### 1.6 Renewable energy and hydrogen ($H_2$) production

Energy is one of the most critical concerns for developing a sustainable society in the 21$^{st}$ century. Developing clean and sustainable energy systems is extremely urgent due to the global energy demand and associated environmental issues [31], [32]. The usage of fossil fuels will continue to rise as the world's energy demand increases from 17 TW in 2010 to 27 TW by 2040, further accelerating the $CO_2$ accumulation in the environment. Although petroleum and fossil fuels can still meet the world's energy needs in the future decades, their finite supplies and unfavorable climate effects make it impossible to achieve long-term development objectives [33]. As a result, we must look for a renewable and clean energy system to solve both the energy crisis and the current severe environmental pollution issue. As sustainable alternatives to traditional fossil fuels, renewable energy sources (such as wind, solar, and hydraulic power) have been studied during the past few decades; however, their use is typically constrained by

spatial and temporal intermittencies and low efficiency of energy delivery [34]. Therefore, further feasible options for energy conversion and storage are required.

Hydrogen ($H_2$) is thought to be the promising next-generation energy carrier and source to alter the current energy structure of the world in the future because it has carbon-free emissions and the highest volumetric energy density. $H_2$ has a much higher energy density of 120-142 MJ $kg^{-1}$. Instead of fossil fuels, hydrogen can be used directly without further treatment as fuel gas. It can also store extra energy by incorporating fluctuating renewable electricity into the modified energy system. Therefore, developing a technology for hydrogen production is vital for the future of the hydrogen economy and clean energy. Generally, $H_2$ can be produced from natural gas, biomass, (gasified) coal, or water. Steam methane reforming and coal gasification, which often require fossil fuels and high temperatures and result in heavy energy consumption, low-purity hydrogen products, high costs, and undesired $CO_2$ emissions, have historically dominated industrial hydrogen production [35]. The large-scale hydrogen demand cannot be fully fulfilled by biomass, although it is renewable and can be transformed into various fuels, including ethanol, biodiesel, and methanol. As a result, environmentally friendly and efficient hydrogen production techniques should be developed, such as photoelectrochemical [36] and electrochemical [37] methods of $H_2$ production, which have the advantages of an unlimited source, highly pure hydrogen production, and the capacity for large-scale production. However, the electrochemical pathway of $H_2$ production is more tempting because of the increased flexibility, application, and hydrogen generation efficiency compared to those achieved from a photoelectrochemical system.

There are two main electrochemical techniques used for $H_2$ production. First, **electrocatalytic oxidation** of organic molecules (**formic acid (FA)**, methanol, ethanol), and second electrocatalytic **hydrogen evolution reaction (HER),** which are used in fuel cells. However, FA electro-oxidation is more feasible and attractive because of better proton transport on the

catalyst with thermodynamic voltage, less hazardous, recyclable, and non-inflammable than methanol or ethanol [38]. Since Troostwijk and Diemann initially discovered water electrolysis in 1789, it has received much attention from researchers worldwide. However, the amount of hydrogen produced electrochemically through HER only accounts for <5% of the total supply. Therefore, promoting electrochemical $H_2$ production toward widespread commercialization is a severe challenge. When combined with renewable energy sources, water electrolysis (or water splitting electrochemically) is a practical method of producing hydrogen. [39]. It has numerous benefits, including abundant water supplies, steady yield, high $H_2$ purity (>99%), and the viability of large-scale implementation.

### 1.7 Conjugated polymer nanocomposites: An effective electrocatalyst

CPs were discovered more than 40 years ago. Since then, they have been used increasingly in various technological fields, including the metallization of dielectrics, electromagnetic shielding, primary and secondary batteries, electrochromic systems, antistatic coatings, etc. One of their most noticeable features is the ability of CPs to catalyze various electrode processes. An ideal electrocatalyst possesses high electrical conductivities, electroactive properties, and large specific surface areas. CPs fulfill these criteria along with the merits of being environmentally friendly and their processability. CPs have been extensively researched as intrinsic electrocatalysts because of their exceptional delocalized conjugated architectures throughout the chain and their excellent electrical and electrochemical properties [40]. To be more precise, the high electroactive properties and conductivity of CPs enable them to use as the catalyst for the redox reactions needed for electro-oxidation of FA, HER, OER, dye-sensitized solar cells (DSSCs), biosensors, and fuel cells, among other devices [41], [42]. CPs often have tunable, narrow bandgaps. Additionally, many CP catalysts are easily fabricated into flexible films and have strong biocompatibility, making them easier to use in flexible devices and electrode systems. CPs are conductive supports that can immobilize other catalysts to

enhance or extend their functionality. CP catalysts, both intrinsic and composite, can be synthesized electrochemically or chemically in the form of powders and films. For electrocatalysis, CP-based films can be employed directly as electrodes, but their powders need to be loaded with sticky binders onto the surfaces of current collectors. CP-based catalysts must be nanostructured or combined with cocatalysts and/or other highly conductive materials to increase their activity and/or stability [43]. CP-based catalysts are inexpensive and efficient and can be synthesized easily on a large scale. Due to these facts, CPs have been the subject of in-depth research in recent years and have significant applications in catalysis. The investigations on CP-based catalysts have not yet been thoroughly analyzed and published in a journal. Most commonly used CPs for electrocatalysis include PANI, PCz, PPy, PTh, and their derivatives.

A thin coating of a CP can be applied to the surface of the substrate electrode of particular solution species to enhance the electrode kinetics. These electrocatalytic reactions, which occur at conducting polymer electrodes, are a rapidly expanding area of study and could have a wide variety of unanticipated applications in several fields of applied electrochemistry. At least three processes during the electrocatalytic conversion of solution species should be considered when using CP-modified electrodes. First, an electron transfer that occurs heterogeneously inside the polymer film and between the CP layer and electrode. As is usual, charge-compensating anions and solvent molecules move throughout the CP film during this process, and there may also be conformational changes to the polymer's structure. Numerous factors influence the rate of this process. Among them, the electrical conductivity of a CP layer, the rate of electron self-exchange inside polymer chains and/or clusters, and the movement of anions within polymer films appear significant. The second phase, which leads to the electrocatalytic conversion, is the diffusion of species present in the solution into the area where the reaction occurs. This procedure can be more complicated than simple electrode reactions when the electrocatalytic conversion occurs inside the CP layer. Then, it is essential to consider species diffusion within

the film and any possible electrostatic interactions between these species and the polymer film. Last, solution species and CP participate in a chemical (heterogeneous) reaction [44].

The site of the electrocatalytic reaction appears to be the central area of interest, both theoretically and practically. The electrocatalytic process should occur at the outer side of the CP/electrolyte interface if the charge transfer within the conducting polymer layer moves considerably quicker than the mass transfer and electrochemical conversion of reactive species. When the mass transfer and electrochemical reaction occur more quickly than the electron transfer in the CP, an electrocatalytic process occurs at the inner substrate electrode/CP interface, provided that the permeability of a porous CP layer is high enough to permit the reacting species and solution ions to pass through. Lastly, if the rates of the two processes mentioned above are equivalent, the electrocatalytic process will occur within the CP layer. In this case, the depth of the reaction zone within the CP layer will depend on the equilibrium between charge and mass transfer and the rate of electrocatalytic conversion. The issue of the site of an electrocatalytic process is often seen as a matter of metal-like (at the CP/electrolyte interface) or semiconductor-like (either within the polymer layer or at the inner substrate electrode/CP interface) behavior or, in another way, chemical vs. redox catalysis, respectively [44].

### 1.7.1 Principles and figures of merit of electrocatalyst

An electrocatalyst is a catalyst that modifies the activation energy of an electrochemical process. The potential at which a reaction occurs is related to the activation energy in electrochemical reactions in a similar way as the activation energy of a chemical reaction associated with the energies of reactants and products (figure 1.10). An electrocatalyst reduces the activation energy of an electrochemical reaction, frequently decreasing the electric potential at which the reaction usually occurs. As a result, electrocatalysts commonly alter the potential

at which redox reactions occur [45]. Alternatively, an electrocatalyst is a facilitator of a particular chemical reaction at the surface of an electrode. Transferring electrons from one chemical species to another causes electrochemical processes. Electrochemical transformations are more likely to occur when favorable interactions at the electrode surface reduce the voltage needed to effect these changes. [46]. The Sabatier principle states that the bonding energy between the catalyst and the reactant should be optimum, the primary criterion in developing and selecting electrocatalytic materials. Activity, stability, and selectivity are the three prominent figures of merit that can be used to evaluate electrocatalysts.

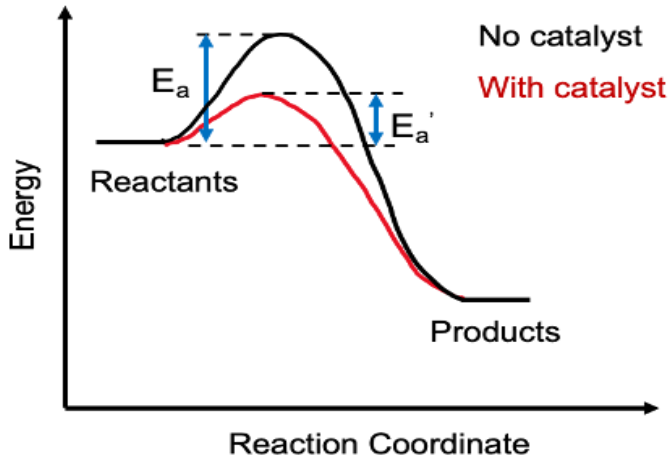



**Figure 1.10:** Potential energy diagram for a reaction. An electrocatalyst reduces the activation energy of an electrochemical reaction, frequently lowering the electric Potential at which the reaction occurs (Courtesy: Wikipedia).

### 1.7.2 Polymer nanocomposites as an electrocatalyst for electro-oxidation of formic acid

Fuel cells (the galvanic device that transforms chemical energy into electrical energy) are emerging as viable energy conversion technologies that operate in hydrogen or hydrogen-rich fuels with low $CO_2$ emissions [47]. Proton exchange membrane fuel cells (PEMFC) have drawn the most attention among them as a result of their superior qualities, including high open-circuit potential (OCP), least fuel crossover effects, high efficiency of energy conversion, and effective electro-oxidation of small organic molecules like formic acid (direct formic acid fuel cell-

DFAFC), ethanol (direct ethanol fuel cell - DEFC), methanol (direct methanol fuel cell - DMFC), etc. at low temperatures [48]. Direct formic acid fuel cells (DFAFC) with polymer electrolyte membranes have been studied for more than ten years and are currently a significant field of research for portable power systems. The DFAFCs have shown an advantage over the direct methanol FCs (DMFCs) and the long-investigated $H_2$–FCs (HFCs). Since the DFAFCs have a more significant theoretical OCP (1.48 V) than DMFC (1.21 V), the voltage gain is likely to be more pronounced. Also, FA (as a fuel) has lower toxicity, a faster oxidation rate, and a smaller crossover across the membrane, allowing for thinner membranes and a greater fuel concentration.

The following criteria must be satisfied by the electrocatalysts used in the oxidation of formic acid: high electrocatalytic activity, safety, affordability, high electrical conductivity, high tolerance to poisonous species, increased physical and electrochemical stability without particle agglomeration, component migration and loss, surface oxidation state change, carrier corrosion, etc. CP-based nanocomposites are a specific kind of hybrid electrocatalysts for fuel cell applications that combine the advantageous features of CPs and nanomaterials. The better electronic conductivity of CPs supports this increased emphasis over the past two decades compared to the traditional carbon-based catalyst. Additionally, the catalysts' improved electrocatalytic activity and stabilization of fuel cell performance are significantly influenced by their large surface area and characteristic synergistic effects with the metal NPs/metal oxide [49]. Although the high catalytic activity of low-Pt nanoparticles on polymers makes them valuable, much effort has been spent on fabricating Pt-free catalysts on CPs. For CP-supported hybrid catalysts, numerous research groups have successfully developed various synthetic techniques, including metal NPs, metal oxides, and multimetallic NPs, that can be employed as anodes, cathodes, and electrolyte membranes [50]. CPs, including PANi, PPy, PIn, and PCz, have recently shown promise for use in the electrocatalysis of FAO, and numerous Pt/CPs

composites have been developed for FA oxidation [51]. An exceptional improvement in the Pt catalyst's particle distribution and surface area was linked to the electro-oxidation of formic acid, which showed a remarkably improved activity at Pt/CPs composites [52]. PANi, PPy, and PTh for electro-oxidation of FA are the main focus of the investigations of CPs as a host material of Pt nanoparticles. It has been revealed that PIn and its derivatives make excellent supports for Pt and noble-metal free (nanomaterials based on metal oxides) catalysts in the electro-oxidation of FA, where the synergistic interaction between nanomaterials and PIn can increase the reaction's selectivity via dehydrogenation pathway [53]. However, among PPy, PIn, PTh, and PCz, PCz has drawn attention because of its potential industrial uses in electroluminescent applications, light-emitting diodes, electrocatalysis and rechargeable batteries. PCz also has merits of good conductivity, environmental stability, photoconductivity, and electrochromic properties [54]. The fact that carbazole might be considered a pyrrole or indole derivative is another area of interest for PCz. The PCz has a specific conductivity ($7.5x10^{-3}$ S $cm^{-1}$), excellent electrochemical activity, environmental resilience and robust adherence to the electrode substrate. Pt/PCz/GC and Pt-Ru/PCz/GC, display higher catalytic activity toward FA electro-oxidation than their counterparts.[54] The onset oxidation potential of FA is dramatically reduced, while the oxidation current density at a low potential is significantly increased. The synergistic effect between PCz and metal nanoparticles (Pt, Pt-Ru) is primarily responsible for the improved electrocatalytic activity. Further evidence that PCz can act as an effective promoter for the electro-oxidation of FA on Pt/PCz and Pt-Ru/PCz catalysts as it significantly weakens the CO adsorption strength over catalysts and the adsorbed CO on the PCz modified catalysts can be more easily electro-oxidized.[54]

#### 1.7.2.1 Mechanism of electro-oxidation of formic acid

Most of the recent studies state that Pt-based materials predominated in the FAO, the primary oxidation reaction in DFAFCs. This may have been initiated from the assessable attraction of

Pt surfaces for the deprotonation of FA to formate, which, according to basic Brnsted-Lowry acid-base principles, is FA's conjugate base. According to reports, the electro-oxidation of FA follows a triple pathway mechanism (direct pathways, indirect pathways and formate pathways) that begins with the adsorption of formic acid [51], [53]. Dehydrogenation (direct path), which involves the direct oxidation to $CO_2$, is preferred because it uses less energy and doesn't produce any toxic intermediates. The indirect (undesired) path involves the "non-faradaic" dissociation (dehydration) to produce CO, which is poisonous for catalytic surfaces. A considerable percentage of active catalytic sites are consumed by CO emission, potentially deactivating FAO. Third, the adsorbent may undergo dehydrogenation to bridge-adsorbed as formate (formate pathways). The chemical equation below shows the different paths of electro-oxidation of FA [53].

(1) Direct pathways

$$HCOOH + S \rightarrow 2H^+ + CO_2 + 2e^- \qquad \text{(eq. 1.1)}$$

(2) Indirect pathways

$$HCOOH + S \rightarrow S\text{-}CO + H_2O \qquad \text{(eq. 1.2)}$$

$$S + H_2O \rightarrow S\text{-}OH + H^+ + e^- \qquad \text{(eq. 1.3)}$$

$$S\text{-}OH + S\text{-}CO \rightarrow CO_2 + S + H^+ + e^- \qquad \text{(eq. 1.4)}$$

(3) Formate pathways

$$HCOOH + S \rightarrow HCOO\text{-}S + H^+ + e^- \qquad \text{(eq. 1.5)}$$

$$HCOO\text{-}S \rightarrow CO_2 + S + H^+ + e^- \qquad \text{(eq. 1.6)}$$

where S is the catalytic substrate that includes Pt, Pd, PIn-$SnO_2$, $TiO_2$, CPs nanocomposites, and other catalysts.

By biassing the potential significantly to the positive side (high energy) until the catalyst surface gets hydroxylated, the oxidative desorption of CO enables the catalytic surface to be recovered as active for FAO. The simple explanation of both approaches explains why the alterations intended to stimulate consuming the FAO entirely in a direct pathway are becoming increasingly popular. When it comes to Pt-based catalysts, boosting the basicity of the Pt surface with a chemisorbed oxygen layer can gradually impart an increase in recognized activity (6-7 fold increase) for the Pt surface toward the FAO dehydrogenation pathway [55]. The oxygen needed for increased oxidation of CO at a substantially lower voltage might be provided by combining the Pt surface with various nanostructures of transition metal oxide [56].

During electrocatalytic FA oxidation, Pt and other metal-based catalysts are well known to be very susceptible to adsorbed CO poisoning. Strongly adsorbed CO on the Pt and other metal-based catalyst surfaces can prevent the active sites from catalyzing, drastically reducing efficiency. Many efforts have been made worldwide to incorporate cocatalysts to promote adsorbed CO oxidation. Conjugated polymer nanocomposites are the potential candidates which facilitate the oxidation of adsorbed CO species on the catalyst surface. Therefore, for electro-oxidation at a lower potential, CPs nanocomposites are employed to increase the catalytic activity and stability during FA oxidation. [51], [52], [53], [56]. Figure 1.11 displays the mechanism of FA electro-oxidation on conjugated polymer nanocomposite-based Pt/PANi/GC electrodes.

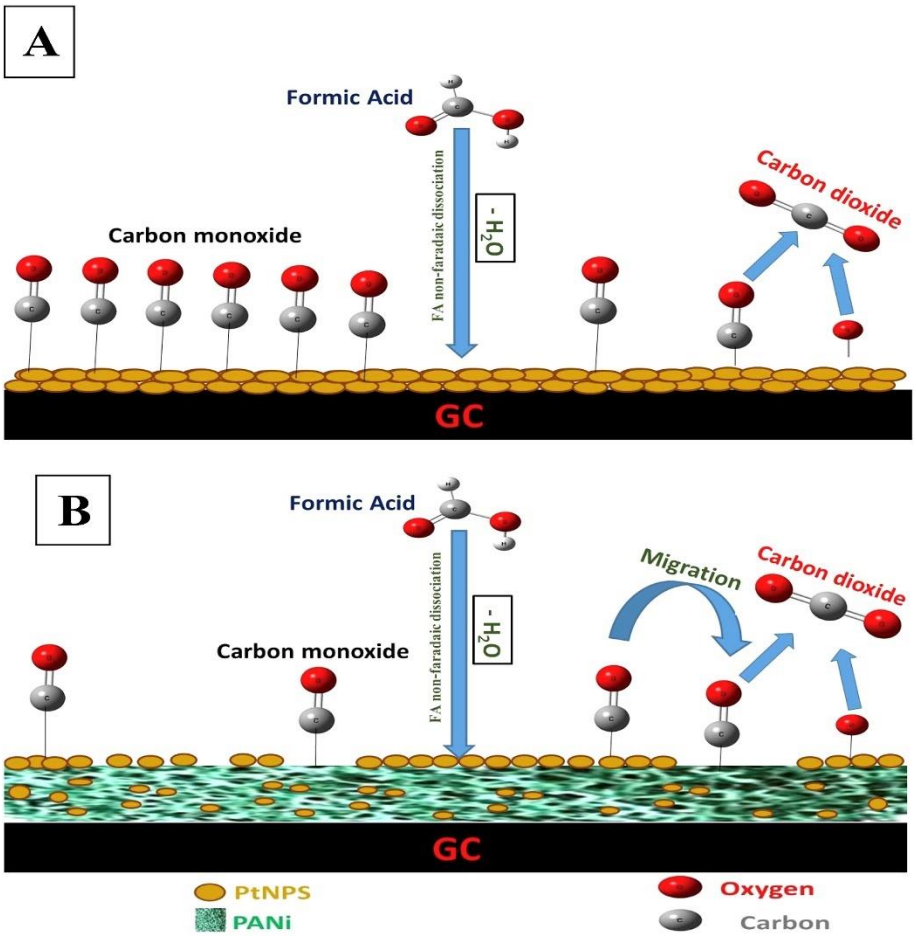



**Figure 1.11:** A schematic for the electrode poisoning during indirect pathways of FAO at (a) Pt/GC and (b) Pt/PANi/GC electrodes where the amount of adsorbed CO is reduced, and PANi may even trap CO more effectively [51].

### 1.7.3 Polymer nanocomposites as an HER electrocatalyst

Hydrogen ($H_2$) is regarded as a renewable, clean energy source and environmentally safe fuel due to its high volumetric energy density and environmentally friendly combustion by-product water. A simple and efficient approach for producing $H_2$ is water electrolysis. The HER and OER can be seen as components of the water electrolysis reaction. Electrocatalysts are essential to reduce both HER and OER overpotentials and make water-splitting less energy-intensive. Pt noble metals group is considered the best catalysts for HER, but their high cost and labor-intensive manufacturing processes have inhibited their use. HER catalysts must be affordable

and effective to meet various $H_2$ requirements. Catalysts based on conjugated polymer nanocomposites can be considered appropriate alternatives to noble-metal catalysts. CPs, including PANI, PPy, PEDOT, and PTh, have good electrical conductivity, low cost, high stability, and high charge storage capacity, and might be anticipated to behave as HER electrocatalysts [57]. Although efficient electrocatalysts for the HER, such as CPs, have weak conductivity, the catalyst's conductivity is critical in catalytic reactions to ensure electron transport. As a result, conducting polymers are regarded as an appropriate matrix that can improve conductivity while stabilizing the catalysts. Additionally, conducting polymers may exhibit catalytic activity on their own. CPs can act as high-surface-area substrates to hold nanomaterials with additional active-site, hence boosting HER activity. However, research on conjugated polymers as electrocatalysts is not investigated much. The conjugated polymer with a heteroatom, such as N, may have a very high potential for HER electrocatalysts due to its highly efficient electron-transfer ability and superior electrical conductivity [26]. Due to its high conductivity, significantly high electrochemical surface area, and outstanding stability, PPy is frequently used to modify catalysts. Uniquely, the C-N bonds in the PPy-based electrocatalysts can act as the active centers for HER. The transition metal (TM)-N coordinate bonds can easily be formed for CPs like PPy and PANi because the lone pairs of electrons of N atoms can provide effective sites to coordinate with 3d transition metal ions (TMIs). It is strategic to fabricate high-performance CP-based electrocatalysts by doping TMIs because of the strong driving ability of electron transfer of the TM-N coordinate bonds, which offers an abundance of active centers for electrocatalytic HER [26]. An excellent electrocatalytic activity of CPs-based composites was obtained by incorporating and hybridizing with metal-based precursors like metals, metal alloys, and their oxides, sulfides, phosphides, carbides, and nitrides into the conjugated polymer [58].

### 1.7.3.1 Mechanism of electrocatalytic HER

The HER, one of the electrochemical reactions that have received the most significant attention, is the half-reaction at the cathode for water electrolysis. Three possible main steps can be taken in the electrochemical HER process to convert protons in acidic media or water molecules in an alkaline medium to $H_2$ on the surface of an electrode with a minimum external voltage applied. (figure 1.12). Since the HER is a two-electron transfer process, the energy barriers of each step must be lowered by using active catalysts. The Volmer-Tafel or the Volmer-Heyrovsky mechanism is involved in the adsorption/desorption of a hydrogen intermediate (H*), which is one of the well-recognized mechanisms for the HER in acidic solution [59], [60], [61]. The Volmer reaction is the first step, where an electron and a proton combine to form an adsorbed hydrogen atom (H*) on the surface of the electrode. The proton sources are the hydronium cation (H3O+) in the acidic medium and the water molecule in the alkaline medium. After that, either the Tafel reaction, the Heyrovsky reaction, or both may result in the formation of $H_2$. Another proton combines with the H* during the Heyrovsky step, subsequently interacting with a second $e^-$ to form $H_2$. In the Tafel step, two nearby adsorbed H* atoms combine on the surface of the electrode to release $H_2$. The overall HER can be written in the following steps:

1. Volmer step (hydrogen adsorption)

$$H^+ + e^- \rightarrow H^* \quad (\text{acidic condition}) \qquad \text{(eq. 1.7)}$$

$$H_2O + e^- \rightarrow H^* + OH^- \quad (\text{alkaline condition}) \qquad \text{(eq. 1.8)}$$

2. Heyrovsky step (desorption)

$$H^* + H^+ + e^- \rightarrow H_2 \quad (\text{acidic condition}) \qquad \text{(eq. 1.9)}$$

$$H_2O + e^- + H^* \rightarrow H_2 + OH^- \quad (\text{alkaline condition}) \qquad \text{(eq. 1.10)}$$

3. Tafel step (chemical desorption)

$$H^* + H^* \rightarrow H_2 \quad \text{( both acidic and alkaline condition)} \qquad \text{(eq. 1.11)}$$

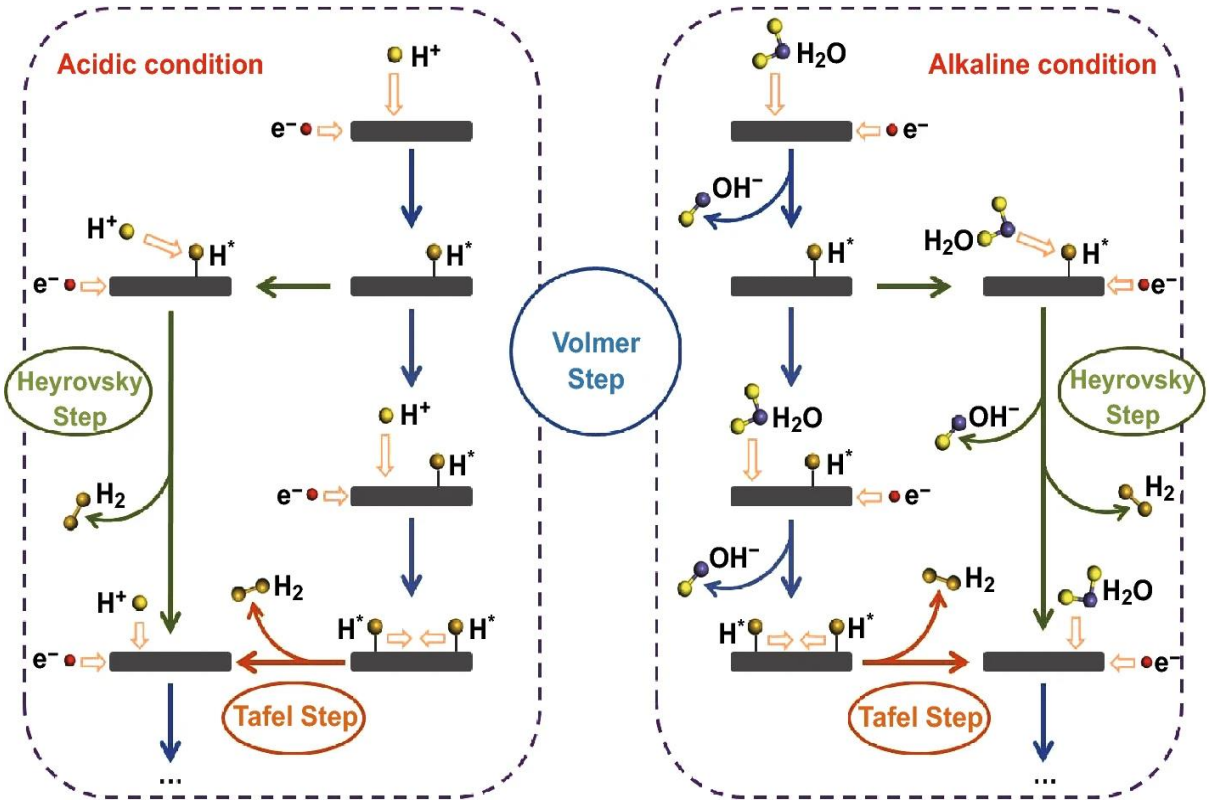



**Figure 1.12:** HER mechanism on the electrode's surface in acidic and alkaline conditions (Data extracted from Ref. [61]).

The Tafel slope (*b*) represents the potential necessary to change the current density by a factor of 10, revealing the HER mechanism. When the chemical desorption (combination) reaction is the slowest step and the Volmer or discharge reaction is fast, the b of 29 mV $dec^{-1}$ would be obtained and provided by $b = 2.3RT/2F = 0.029$ V $dec^{-1}$ at room temperature. The *b* would be 39 mV $dec^{-1}$ and provided by $b = 4.6RT/3F = 0.039$ V $dec^{-1}$ at room temperature if the discharge reaction is fast and electrochemical desorption (Heyrovsky step) is the slowest step. In the case of a slow discharge reaction, then *b* would be 116 mV $dec^{-1}$ and calculated as follows: $b = 4.6RT/F = 0.116$ V $dec^{-1}$ at room temperature.

### 1.7.3.2 Evaluating parameter for the electrochemical performance of electrocatalyst

The electrochemical water splitting is seen as the combination of two half-cell reactions: HER and OER. The overall reaction is given below

$$H2O \rightarrow H_2 + {}^1/_2\, O_2 \qquad \text{(eq. 1.12)}$$

The free energy change ($\Delta G^o$) for converting one $H_2O$ molecule into $H_2$ and $O_2$ is +237.2 kJ/mol of $H_2$ at STP. The expansion of gas also requires some extra work ($T\Delta S^o$); therefore, the enthalpy change ( $\Delta H^o = \Delta G^o + \Delta TS^o$) in the process is +286 kJ/mol of $H_2$. Splitting water requires converting this thermodynamic value into a reversible electrochemical cell voltage, $\Delta E^o_{rev}$ = 1.23 V at 1 atm.

In order to drive the electrochemical water splitting, the applied potential should be higher in practicality than this theoretical reversible thermodynamic value of 1.23 V. The overpotential ($\eta$) of the electrocatalyst is the additional excess potential required to over this 1.23 V. When reaction intermediates are formed at the surfaces of both electrodes ($\eta_a$ and $\eta_c$), it is employed to overcome the kinetic barrier imposed by the high activation energy and overcome specific solution resistance and other barriers ($\eta_{other}$). Therefore, the operating voltage ($E_{op}$) supplied for water splitting is as follows

$$E_{op} = 1.23\ V + \eta_a + \eta_c + \eta_{other} \qquad \text{(eq. 1.13)}$$

Of course, '$E_{op}$' can be reduced by designing a promising electrocatalyst and improving the electrochemical cell. An excellent electrocatalyst possesses a lower overpotential. The applied potential is given by the Nernst equation in an electrochemical reaction as follows

$$E = E^0 + \frac{RT}{nF}\ln\frac{[\mathrm{Ox}]}{[\mathrm{Red}]} \qquad \text{(eq. 1.14)}$$

where numerous parameters have usual meanings, [O] and [R] are the concentration of oxidizing and reducing agents, respectively. It means that the $\eta$ is the difference between the applied (actual) potential and the potential in equilibrium ($E_{eq}$), i.e., $\eta = E - E_{eq}$.

Some important kinetic parameters are essential to evaluate the catalytic activity of an HER electrocatalyst which are defined below:

**1.7.3.2 (a) Onset potential and overpotential**

As previously indicated, the applied potential necessary for HER will be much higher than theoretical values; the voltage difference between the applied and theoretical values is known as the overpotential. Higher electrode activity is associated with an electrocatalyst having a lower overpotential. The three primary components of overpotential are resistance overpotential, concentration overpotential, and activation overpotential. The HER catalyst has an intrinsic property called activation overpotential, which can be significantly reduced by selecting the appropriate electrocatalysts. The differential in ion concentration between the electrode surface and bulk solution leads to the concentration overpotential. Therefore, it only reduces partially by agitating the electrolyte to promote ion diffusion. Resistance overpotential (junction overpotential) is the potential difference between the reference and working electrodes. It causes a further drop of voltage, which can be eliminated by IR compensation (also known as an Ohmic drop compensation), resulting in an accurate overpotential.

$$E_{corrected} = E_{uncorrected} - IRs \qquad \text{(eq. 1.15)}$$

Using LSV measurements, the polarisation curves can be determined by plotting the applied potential vs. the current density. Two significant metrics can be found by evaluating the polarisation curve: the onset potential at which the reaction begins and the $\eta$ at which the current density (*j)* equals to 10 mA $cm^{-2}$.

### 1.7.3.2 (b) Tafel slope

The Tafel slope is the slope of the linear region in the Tafel plot (log |current density| vs. overpotential), which can be created by replotting the matching LSV curve.

$$\eta = a + b \log(j_0) \qquad \text{(eq. 1.16)}$$

The Tafel equation, where $\eta$ is overpotential, $a$ is the Tafel constant, $b$ is the Tafel slope, and $j_0$ is current density, gives the linear relationship between overpotential and log| $j_0$|. Notably, the HER reaction process can be understood on the catalyst surface by observing the Tafel slope. Theoretically, the Volmer, Tafel steps, and Heyrovsky in HER have Tafel slopes of 120, 30, and 40 mV dec-1, respectively. Catalytic efficiency and possible HER reaction pathways are frequently described using the Tafel slope. The smaller overpotential essential to increase the same current density with a lower Tafel slope value suggests a faster charge-transfer kinetics.

### 1.7.3.2 (c) Exchange current density ($j_0$)

The exchange current density of a reaction is the current density at the equilibrium potential, where the anodic current and the cathodic current are equal. The exchange current density ($j_0$), which depends on the characteristic catalytic activity of the electrode material, is obtained under equilibrium conditions when it is anticipated to be zero. It can be determined from the deduced linear portion of Tafel plots with the X-axis connection. Basically, $j_0$ represents the inherent activity of transferring charge between electrolyte and electrode, and catalyzing a reaction enhances the $j_0$. Higher electron transfer rates and exceptional kinetic performance correlate with larger exchange current density values. In 0.5 M $H_2SO_4$, for example, the current densities of HER on Hg, Ti, and Pt surfaces are around $10^{-9}$, $10^{-5}$, and 1 mA $cm^{-2}$, respectively, illustrating the variations in their characteristic activity [59], [61].

### 1.7.3.2 (d) Gibbs free energy of adsorption and volcano plot

Since the catalysis process occurs via the adsorption of reacting species ($H_2O$) on the catalyst electrode surface, the examination of Gibbs free energy of adsorption ($\Delta G_{ads}$) is an important parameter to compare the catalytic performance of various electrocatalysts. A plot of $j_0$ as a function of DFT-calculated Gibbs free energy for hydrogen adsorption ($\Delta G_{adsH^*}$) is shown in figure 1.13. This plot acquires a volcano shape with Pt at the top of the plot, having the highest current density and $\Delta G_{adsH^*}$ close to zero.

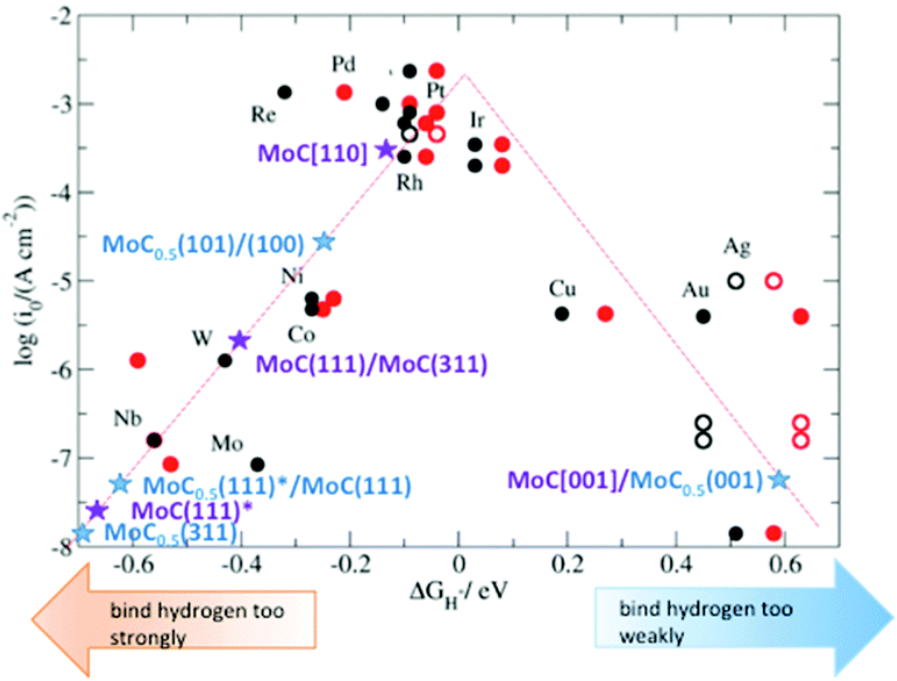



**Figure 1.13:** A volcano plot for an experimentally determined $j_0$ for hydrogen adsorption on the surface of a catalyst as a function of DFT-calculated Gibbs free energy for hydrogen adsorption ($\Delta G_{adsH^*}$) (Data extracted from Ref. [62])

### 1.7.3.2 (e) Faradic efficiency

Faradic efficiency is the efficiency of an electron taking part in a redox reaction in the electrochemical system. It is calculated as the ratio of experimentally produced $H_2$ and theoretical $H_2$ amount in the case of the HER process.

### 1.7.3.2 (f) Stability

In terms of practical application, stability, or durability, is a crucial characteristic of a catalyst since it shows its capacity to retain its original activity after a long period. The stability may be investigated by monitoring the variation in current density at an applied overpotential or the change in overpotential at a constant current density over time. Galvanostatic or potentiostatic electrolysis and repeating cyclic voltammetry (CV) or linear sweep voltammetry (LSV) are two electrocatalytic techniques for measuring stability. Since LSV curves are typically recorded before and after the investigation of the stability test, if the catalyst drops its activity rapidly, the overpotential will be increased. The galvanostatic (or potentiostatic) method involves keeping track of how the electrocatalyst's potential (or current density) changes over time while maintaining a constant current density (or overpotential). Longer periods with no potential (or current) change imply excellent stability.

### 1.7.3.2 (g) Turnover frequency (ToF)

ToF is the ability of the catalyst to convert reactant into the product per active catalytic sites per unit area. Since the calculation of the number of accessible active sites is quite complex, it is not always correct.

### 1.7.3.2 (h) Electrochemical active surface area (ECSA)

ECSA is required to compare the electrochemical performance of various nanostructured materials. An electrode with a nanostructure typically has a greater ECSA than the geometrical area of an equivalent flat electrode. Two alternative methods can often be used to measure the ECSA of HER electrocatalysts: the electric double layer capacitance ($C_{dl}$) and coulombic charge of a specified surface faradic reaction.

### 1.8 Conjugated polymer nanocomposites: Next-generation supercapacitor

The demand for energy storage technologies (such as supercapacitors and batteries) having high power and energy densities is rising as the portable electronics market grows rapidly. Although batteries can produce large energy density, they have a small power delivery or absorption rate, which limits their use in applications requiring rapid power. Traditional capacitors have a very high power density but a much inferior energy density than batteries. Electrochemical capacitors, also called supercapacitors, can fill the gap between conventional capacitors and batteries (figure 1.14). While offering more power than batteries, a typical supercapacitor has a much higher energy density than traditional capacitors. Recent significant efforts have been made to increase the energy density to a level comparable to or higher than that of batteries without losing the power density. [63].

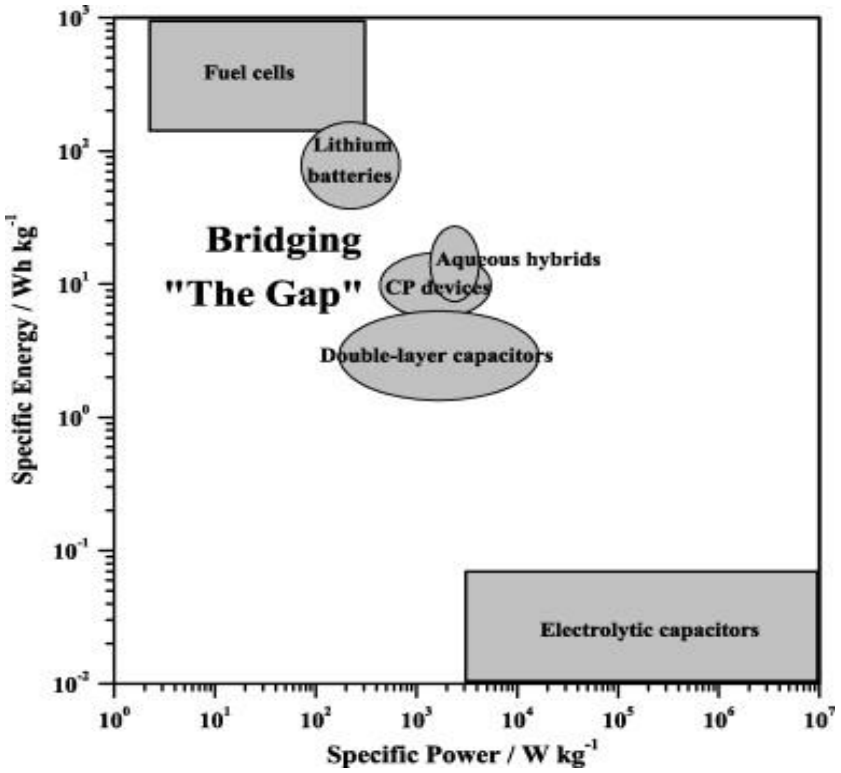



**Figure 1.14:** Ragone plot for various energy storage devices; CP stands for conjugated polymers. [65]

Exploiting innovative materials and techniques to tune materials' structural and electrochemical properties is of great importance to increasing supercapacitors' performance significantly and fulfilling the constantly rising energy demand in diverse technologies. CPs are a novel category of promising materials essential for the next-generation supercapacitor. CPs are regarded as the most potential materials compared to transition metal oxide/hydroxides due to their high conductivity, easy synthesis, high specific capacitance, structural diversity, environmentally friendly nature, and high flexibility. Highly π-conjugated polymeric chains are seen in CPs. PPy, PANI, PTh, and their derivatives are some of the most intriguing CPs for supercapacitors. Neutral conjugated polymers typically have conductivities between $10^{-10}$ and $10^{-5}$ S $cm^{-1}$. However, using electrochemical or chemical redox reactions, so-called "doping," they could be modified in a broad range of up to $10^{4}$ S $cm^{-1}$. The dopants and doping level applied significantly impact the resulting conductivity. Doping is reversible in CP, which converts its backbone into negative(n-doping) or positive (p-doping) charge carriers. To maintain the charge neutrality of the CPs, counter ions with opposing charges would be trapped or released from them [64]. High specific capacitances ($C_{sp}$), such as PPy, offers upto 620 F $g^{-1}$, 750 F $g^{-1}$ in the case of PANI, are provided by CPs, which store energy via the process of doping-de-doping related to reversible redox reactions [65]. CP-based electrodes, however, typically have poor cycle stability because of the volume fluctuations brought on by the doping-dedoping processes. Improvement in cycling stability and energy storage capacity can be added to CPs by forming composites with various materials such as metal oxides/hydroxides, carbon, and innovative 2D materials [66].

The ongoing development of CP-based nanocomposites in various arrangements (powders, films, fibers, hydrogels and foams) offers significant opportunities to achieve different types of novel architectured advanced supercapacitors with high functions, has so far aided progress

toward advanced supercapacitors [63]. Three configurations are possible for supercapacitor devices manufactured from conjugated polymers.[65]

Type I (symmetric), where both electrodes are made of the same polymer.

Type II (asymmetric), utilizing two polymers with different levels of doping and electroactivity.

Type III (symmetric) in which both electrodes have the same polymer, with the positive electrode in p-doped form and the negative electrode in n-doped form.

In addition, CP-based anodic electrodes and carbon- and lithium-based cathodic electrodes can also be used to form asymmetric (or hybrid) devices.[65]

### 1.8.1 Principles, classification and mechanisms of supercapacitors

The electrochemical capacitor, which has a higher $C_{sp}$ value than ordinary capacitors, is an energy storage device that stores and releases energy by transferring electron charges at the electrode and electrolyte interface. Essentially, an electrochemical cell or supercapacitor consists of two positive and negative electrodes, an aqueous electrolyte, and a separator that facilitates the flow of ions between them. Electrochemical supercapacitors are categorized into three types based on their charge storage mechanisms: Electric Double Layer Capacitors (EDLC), Pseudocapacitors, and Hybrid capacitors.

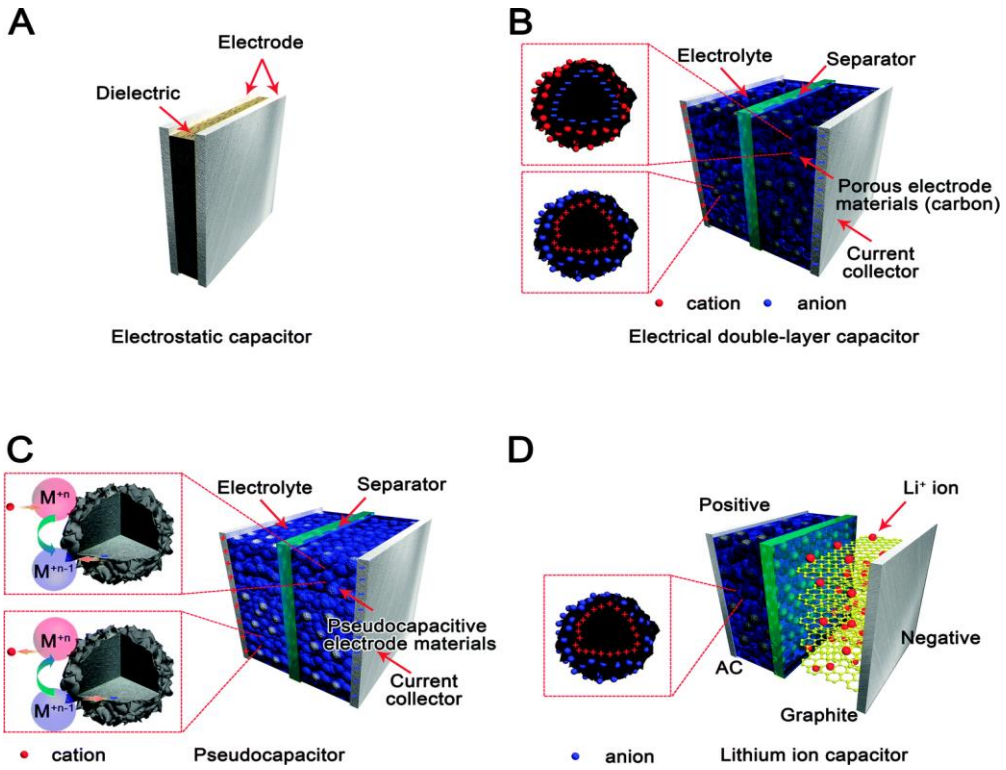



**Figure 1.15:** (a) A conventional capacitor, (b) an EDLC, (c) a pseudocapacitor, and (d) a hybrid capacitor. (data extracted from [67])

(1) EDLCs, in which the capacitance is produced at the electrode/electrolyte interface due to electrostatic charge separation (figure 1.15(b)). The electrode materials are frequently manufactured from highly porous carbon-based materials to improve charge storage capacity.

(2) Pseudocapacitors store the charges through rapid and reversible faradaic redox reactions (figure 1.15(c)).

(3) Hybrid ESs are those that store charges via both faradaic and EDL processes (figure 1.15(d)). Due to the combination of one capacitive electrode and the other rechargeable battery-based electrode, these devices are called hybrid ESs.

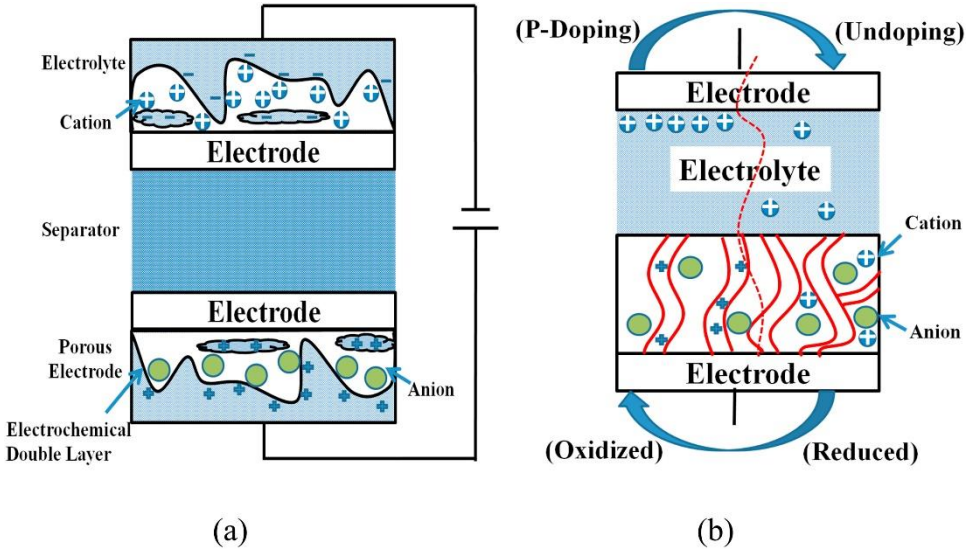



**Figure 1.16:** Schematic illustration of a mechanism for (a) an EDLC and (b) a pseudocapacitor (Extracted from Ref. [68]).

The mechanism of charge storage is different for an EDLC and a pseudocapacitor. The electrostatic interaction between ions on the surface area of active electrodes and electrolytes is the basis for energy storage in EDLCs (Figure 1.16(a). In EDLC systems, a significantly faster charge-discharge process can occur in just a few seconds. An EDLC having a thickness of around 1 nm consists of a compact Helmholtz layer, a electrolytes diffusive layer (thin electrolyte regions (diffusion layers) adjacent to the electrodes where there are gradients of the ion concentration), and a space charge layer corresponding to the electrode. Since the electrochemical activity and kinetics of the electrode dictate the effectiveness of the EDLC, electrode materials with a high specific surface area, substantial porosity, and appropriate pore dispersion are necessary [68]. In pseudocapacitors, the electrolyte ions and electrode materials experience a rapid and reversible Faradaic redox process on the surface and in bulk close to the surface (Figure 1.16(b)). Pseudocapacitors typically have higher capacitance values than EDLCs. Still, their kinetics are slower because the energy storage phenomena occur both at the surface and in bulk. While the charge/discharge process in an EDLC only appears on the

electrode surface. Materials used frequently in pseudocapacitors include CPs, metal oxides, and mainly transition metal oxides [68].

### 1.8.2 Evaluating parameter for the performance of supercapacitor

#### 1.8.2(a) Specific capacitance ($C_{sp}$)

A good supercapacitor should have a high value of $C_{sp.}$ It can be calculated using the formula $C_{sp} = C_T/m$. where $C_T$ is the total capacitance and m is the mass of materials loaded electrode. The $C_{sp}$ can be determined by both the CV and GCD curve as per the following equation

$$C_{sp} = 1/(m\upsilon\Delta V)*\int i.dV \qquad \text{(from CV method)} \qquad \text{(eq. 1.17)}$$

$$C_{sp} = idt/m\Delta V \qquad \text{(from GCD method)} \qquad \text{(eq. 1.18)}$$

where $i$ represents the current, $\Delta V$ stands for the potential window, and $\upsilon$ represents the scan rate.

#### 1.8.2(b) Energy density and power density

The theoretical energy density ($E$) and theoretical power density (P) of a supercapacitor are expressed, respectively

$$E = \tfrac{1}{2}C_{sp}V^2 \qquad \text{(eq. 1.19)}$$

$$P = {}^1/4mR_{cell}*V^2 \quad \text{or} \quad P = E/dt \qquad \text{(eq. 1.20)}$$

Where $R_{cell}$ is the equivalent series resistance and dt is discharge time.

These two equations suggest that these four quantities, V, $C_{sp}$, m, and $R_{cell}$ are the critical parameter determining the supercapacitor's performance. The energy and power densities of the supercapacitor must be enhanced by raising V and $C_{sp}$ values while lowering m and $R_{cell}$ values. An increase in cell voltage would have a higher impact on improving the energy and power

densities than raising capacitance or lowering resistance because both are related to the square of the operational voltage.

### 1.8.2(c) Cycle life

Cycle life is a critical parameter used to measure stability, determining how well the supercapacitor performs. The electrode is subjected to charge/discharge cycling in a specific electrolyte as part of standard test procedures for stability analysis. Higher cycle life is associated with the excellent performance of supercapacitors.

### 1.8.2(d) Self discharge rate

Self-discharge rates, associated with charged electrodes' potential losses during a storage period, are an issue concerning the performance of supercapacitors. Current leakage during the self-discharge process causes a voltage drop in the cell, which could limit the usage of supercapacitors for some particular applications that need steady energy retention over a long time.

## 1.9 Scope of the work and objectives of the thesis

The hunt for renewable energy-based catalytic and storage materials with care for the environment has emphasized the development of such catalytic and storage materials with noble metal-free compositions. This thesis briefly reviews the use of CPs, such as PCz and PPy, and their composites for energy conversion and storage electrochemically. The exceptionally uncommon combination of properties like organic-based composition, metal-like electrical properties, vibrant superiority of structural compositional and morphological flexibility, tunable diversity, each synthesis, and low cost has inspired researchers worldwide to propose its various applications in almost all directions of Science and Technology. The CPs-based composites formed by the hybridization with various nanomaterials have improved properties and are used in various electrochemical applications like electrocatalytic and charge storage. Nevertheless,

there is still much more research yet to be explored. For instance, most electrocatalytic materials for electro-oxidation and HER are based on precious noble metals: their high cost, limited reserve and metallic corrosion in harsh conditions (acidic and basic) limit their uses. Conjugated polymer-based composite materials (noble metal-free) for electrochemical application (energy conversion and storage) using polymer (PCz and PPy) as primary components with high performance and efficiency are less reported to date. This is because of the poor conductivity and processability of the pristine conjugated polymer. Also, the electrochemical catalytic conversion and energy storage based on pure CPs have low performance compared with precious and other metal-based materials. Therefore, we integrated our research objective based on the idea of hybrid/composite materials formation to address these issues. The nanocomposite of CPs (PCz and PPy) with earth-abundant noble metal-free materials viz WO3, NASICON-structured (NFS and Ni-doped NFS) are investigated for electrochemical applications (catalytic conversion and energy storage) to achieve the benchmark performance of the noble metal and other precious materials. Similarly, the availability of metal-based semiconductors, which are environmentally harmful, gives a chance to choose CPs as an alternative due to their comparable band alignment and environmentally friendly nature. Optimizing and tuning the properties of CPs nanocomposites can enhance their performance many folds having practical use and similar to noble metals. Therefore, another scope of CPs nanocomposites is to find alternatives to costly electrochemical materials (noble metals based) with similar performance. Apart from these, another objective is to select and optimize a simple and easy synthesis route for practical and efficient application.

In view of the above discussion of the scopes, the objectives of this thesis are

1. To synthesize the low-cost and environmentally friendly conjugated polymer for the electrochemical catalytic conversion and charge storage application.

2. Prepare and optimize the CPs nanocomposites by incorporating a varying amount of earth-abundant metal oxides for enhanced formic acid electro-oxidation.
3. To prepare the NASICON-structured nanomaterials as filler by choosing earth-abundant low-cost precursors to enhance the number of active sites for electrochemical application.
4. To Synthesize and optimize nanocomposites of CPs with NASICON-structured nanomaterials for enhanced electrocatalytic and charge storage performance.
5. Doping of Ni into the NASICON-structured nanomaterials to further enhance the electrocatalytic and charge storage performance.

This thesis mainly focuses on the preparation and electrochemical application of conjugated polymer-based nanocomposites. The choice of CPs and fillers materials is based on their potential in electrochemical application with the merits of being noble metal-free, low-cost, earth-abundant, environmentally friendly, and easy to synthesize. The outcomes are exciting and encouraging.