

# Polypyrrole Composites: Electrochemical Synthesis, Characterizations and Applications

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## 1. Introduction

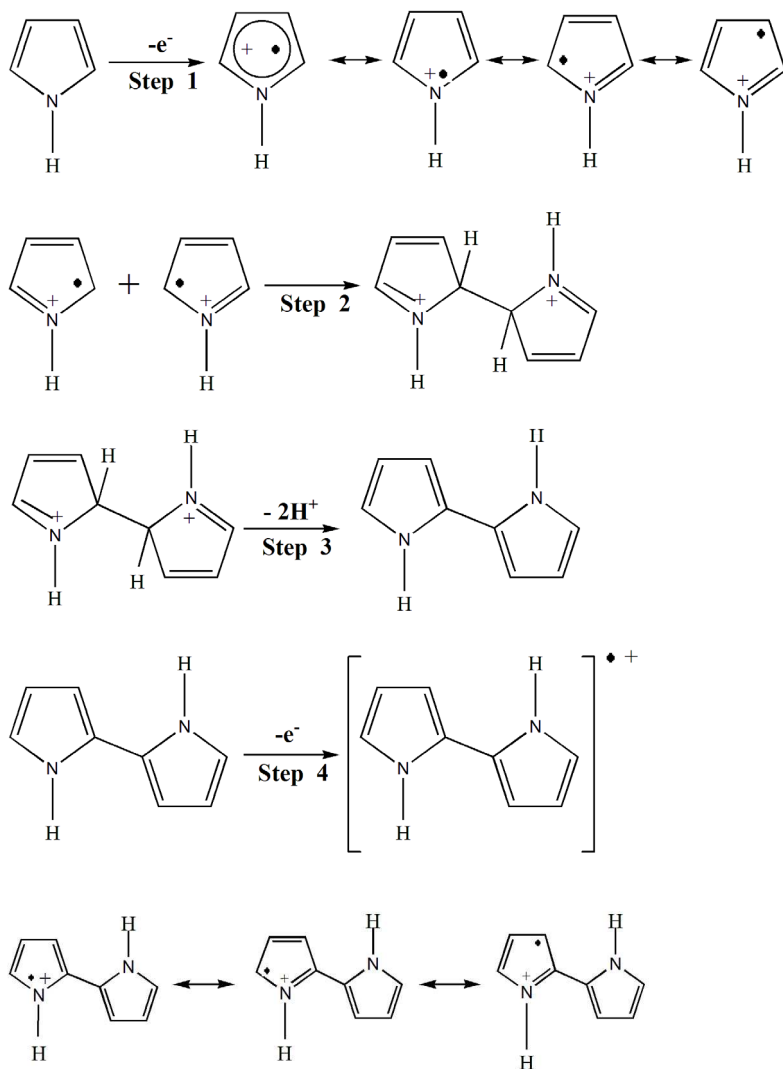
The electronically conducting polymers (ECPs), such as polypyrrole (PPy), polythiophene (PT) and polyaniline (PANI) are known to possess unusually high electrical conductivity in the doped state. Due to this, these materials have been of great interests for chemists as well as physicists since their electrical properties were reported (Diaz et al., 1979). The ECP films behave like a redox polymer and have potential applications in electrocatalysis, solar energy conversion, corrosion, electronics, etc. The redox polymer reaction is accompanied by a change in the electrical properties of the film from an insulator to an electrical conductor involving both electron and ion transport within the film (Kaplin & Qutubuddin, 1995).

Conducting polymers can be synthesized either chemically or electrochemically. Electrochemical synthesis is the most common method as it is simpler, quick and perfectly controllable. PPy is one of the most interesting conducting polymers since it is easily deposited from aqueous and non-aqueous media, very adherent to many types of substrates, and is well-conducting and stable. Electrochemical polymerization produces thin films with a thickness of few micrometers on an electrode surface (Diaz et al., 1979), while a chemical oxidation yields a fine-grained material. However, the yield and quality of the resulting polymer films are influenced by several factors, such as nature and concentration of monomer and the counter ion, solvent, cell conditions (e.g. electrode and applied potential), temperature and pH (Sadki et al. 2000; Ansari, 2006 & Pina et al. 2011).

ECPs can be modified in several ways (Juttner et al., 2004) to obtain tailored materials with special functions: (i) derivatization of the monomer by introducing aliphatic chains with functional groups; (ii) variation of the counterion, incorporated for charge compensation during the polymerization process; (iii) inclusion of neutral molecules with special chemical functions and (iv) formation of compounds with noble metal nanoparticles as catalyst for electrochemical oxidation and reduction processes.

The electropolymerization reaction is a complex process and its mechanism is still not fully understood. A number of mechanisms have been proposed (Genies et al., 1983; Kim et al., 1988; Asavapiriyant et al., 1984; Qui & Reynolds, 1992) and are comprehensively reviewed (Sadki et al. 2000; Ansari, 2006 & Pina et al. 2011). Among these, Diaz's mechanism is the most accepted one (Genies et al., 1983) and supported by Waltman and Bargon (1984 & 1985) also. In this mechanism, the pyrrole (Py) activation occurs through electron transfer

from the monomer forming a radical cation-rich solution near the electrode in several steps. Details of steps involved are given in Scheme 1.



Scheme 1.

The propagation continues via the same sequences: oxidation, coupling, deprotonation until the final polymer product is formed (Fig.1a). The electropolymerization does not give the neutral nonconducting polymer but its oxidized conducting form (doped). The final polymer chain, in fact, carries a positive charge every 3-4 Py units, which is counter balanced by an anion. The structure of the doped polymer can be given as shown in Fig.1b.

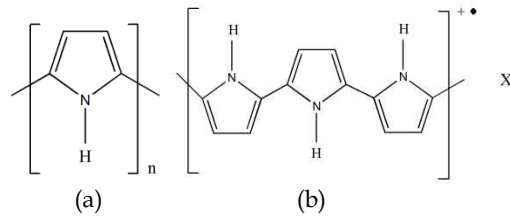


Fig. 1.

Electrochemical film formation is often followed by stoichiometric determination of the number of electrons donated by each molecule. This value is generally found to be in between 2 and 2.7, where 2 electrons serve in the film formation and the excess charge is consumed by the polymer oxidation.

The final step in the polymerization is not clear and different hypotheses have been proposed. Funt and Diaz (1991) believe that the reaction with water could be responsible for the polymerization quench. While, Street (1986) believes that the growth of the chain stops because the radical cation becomes relatively unreactive towards the chain propagation or because the reactive chain ends become sterically blocked.

This article presents an overview of electrochemical synthesis of PPy nanocomposites and their structural and electrochemical properties and applications in electrochemical devices. Applications of nanocomposites described include solar cells, fuel cells, batteries, corrosion protection coatings and super capacitors. Nanocomposites consists of PPy and one or more components, which can be carbon nanotubes, metals, oxide nanomaterials, etc.

## 2. Synthesis

### 2.1 Polypyrrole (PPy) films

PPy films are obtained through electropolymerization of Py on suitable substrates/working electrodes by using different electrochemical techniques such as cyclic voltammetry (CV), potentiodynamic, galvanostatic, potentiostatic, reversal potential pulsing technique, etc. To carry out the electropolymerization of Py, a three-electrode one-compartment cell (50 or 100 ml capacity) with provision of passing an inert gas ( $N_2/Ar$ ) into the electrolyte before the start of the oxidation and above the surface of the electrolyte during the polymerization process is employed. Saturated calomel electrode (SCE) or Ag/AgCl (saturated KCl) is used as the reference electrode. PPy composites prepared were either in the form of sandwich-type or simple films.

Generally, the electropolymerization is carried out on noble metals or inert materials such as Pt, Au, glassy carbon (GC), or indium tin oxide (ITO). It is because of the fact that the standard oxidation potential of pyrrole is fairly high ( $E_{ox} = 0.70$  V vs. SCE) and so, when scanning the potential the dissolution of most of metal supports takes place prior to the oxidation of monomer is reached and, thus, the electropolymerization reaction is inhibited. However, when we are using supports which are oxidizable, for example, Fe, Zn, Al, etc, as the working electrode, it is necessary to find new electrochemical conditions for slowing the dissolution of the working electrode without preventing electropolymerization. Recently, a new electrosynthesis process of PPy films on oxidizable metals Al and Fe has been reported (Bazzaoui et al. 2005). In this process, the formation of homogeneous and strongly adherent

PPy films is achieved in only one step using an aqueous medium containing saccharin and Py. Similarly, Bazzaoui et al. (2006b) obtained PPy coating on Fe by the use of an aqueous solution of 0.1M sodium saccharinate and 0.5M Py.

Various techniques have been employed to prepare composite films of PPy with pure metals, oxides (pure as well as mixed valence ones), anions (simple as well as complex ones), etc. It is difficult to describe all of them here. However, efforts would be made to include as much as possible those techniques which have repeatedly been used in preparation of different composites.

## 2.2 Functionalized PPy film

The functionalized PPy films can be obtained in mainly two ways. The first involves the polymerization of a functionalized monomeric molecule. The second technique makes use of the anion exchange properties of the oxidized form of the polymer.

The functionalization of a monomer Py molecule can be carried out by introducing a substituent on the nitrogen atom or on its 3, 4 positions. N-substituted pyrroles are excellent electropolymerizable monomers for the preparation of polymer films containing active centres. A series of Py-substituted pyridine, 2,2'-bipyridine, 1,10-phenanthroline and 2,2':6-2''-terpyridine ligands and their corresponding Ru(II), Fe(II), Re(I), Cu(I), Cu(II), Co(II), Ni(II), Rh(III), Mn(III), Pd(II), Zn(II), Ag(I) and Ir(III) complexes have been synthesized. In most cases, films of PPy bearing these complexes can be obtained by anodic electropolymerization of the monomer. There are also two types of Py-substituted metallic tetraphenylporphyrins ( $M=Ni^+$ ,  $Zn^+$ ,  $Co^+$ ,  $Cu^{2+}$ ,  $Mn^{2+}$ ); one involving the connection of the Py group directly on the phenyl group, the other through a flexible chain. The efficiency of electropolymerization seems to be lower for complexes in which the Py is connected directly to the macrocycle. With this configuration, steric hindrance and mesomeric effects limit the efficiency of the electrochemical polymerization process (Deronzier & Moutet, 1996). Recently, Diab and Schuhmann (2001) synthesized  $Mn^{2+}$ -meso-tetracarboxyphenylporphyrin linked via a spacer chain to a Py unit using electropolymerization method. Abrantes et al. (2000) prepared substituted Mn and Fe metalloporphyrins with two Py groups bonded in lateral chains through the electropolymerization under potentiodynamic condition.

The literature suggests that 3-substituted Py molecules would require a less anodic potential for their oxidation and would be more conductive than the N-substituted PPy. However, Py monomers substituted at the 3-position with metallic complexes are limited in literature; only two examples are cited here, the first one involves ferrocene derivatives, and the second one an entwining phenanthroline Cu(I) complex (Deronzier & Moutet, 1996).

The functionalized PPy films can also be obtained by carrying out electropolymerization of Py in a medium containing an anionic species as the supporting electrolyte. Following this procedure PPy has been doped by several metallic tetraphenylporphyrin, tetrasulphonates or carboxylates ( $Co^{II}$ ,  $Fe^{II}$ ,  $Mn^{II}$ ) and metallic phthalocyanine, mono and tetrasulphonates ( $Co^{II}$ ,  $Fe^{II}$ ,  $Cu^{II}$ ). Some other complexes have also been incorporated by this technique. For instance, PPy films containing cobalt salts, thiomolybdate anions, nickel and palladium complexes of maleonitriledithiol, heteropolyanions, a chromium oxalate complex, an iron trisphenanthroline sulphonic acid complex or ferri/ferrocyanide and Prussian blue have been prepared by electropolymerization in a medium containing these anions as supporting electrolyte. All these works has been cited in (Deronzier & Moutet, 1996). It is expected that the polymer frame would be formed around the trapped anion and retains it strongly.

However, such electrode materials are less stable than those in which the substituents are covalently attached to the polymeric skeleton, owing to some exchange of dopant anions with counter-anions of the electrolyte.

### 2.3 PPy-metal composite films

Several methods have been reported on modification of conducting PPy by metal catalysts (Juttner et al., 2004). They can be put into the following four main categories:

1. Composite layers of metal particles embedded in PPy are formed in a two-step process: electropolymerization of Py followed by an electrochemical deposition of the metal from a solution containing its own ions. Electrodeposition of the metal by this method leads to the formation of metal crystallites on the surface of PPy film, while the amount of the metal tends to zero inside the film. Using this technique PPy/metal composites prepared are: PPy/Pd (Mangold et al., 2004; Chen et al., 2006) PPy/Pt (Vork & Barenrecht, 1989; Bouzek et al., 2000; 2001), PPy/Pt or PPy/Pt+Pb (Del Valle et al., 1998), Pt-based alloy/PPy (Becerik & Kadirgan, 2001).
2. Insertion of colloidal metal particles in the course of electropolymerization of the PPy film. For the purpose, a solution of nanodispersed metal particles is separately prepared by suitable chemical reduction method. To this solution, the polymer monomer is added for the electropolymerization. Both PPy and metal particles are deposited simultaneously. Using this technique PPy/Pt electrocatalysts were obtained by Bose & Rajeshwar (1992) and Del Valle et al. (1998).
3. Insertion of a suitable metal complex anion as a counterion in the PPy film during the electropolymerization process and subsequent electrochemical reduction of the complex metal anion into the metal. Using this technique PPy/metal composites prepared are: PPy/Pt (Vork & Barenrecht, 1989; Bouzek et al., 2000; 2001) Cu/functionalized PPy (Pournaghi-Azar et al., 1999), PPy/PtClO<sub>4</sub><sup>-2</sup> (Zhang et al., 2005a), PPy/[Fe(CN)<sub>6</sub>]<sup>3-</sup> (Pournaghi-Azar et al., 2000), PPy/[Fe(CN)<sub>6</sub>]<sup>4-</sup> (Raouf et al., 2004). Methods, 2 and 3, results a homogeneous distribution of the metal within the whole PPy film.
4. PPy-metal nanoparticle composites were electro-co-deposited from a solution containing Py, metal salt as source of metal ions, a suitable neutral salt as supporting electrolyte and small amount of a suitable additive to achieve stability of the metal complex salt. For examples, PPy-Au (Rapecki et al., 2010), PPy/Ni (Haseko et al., 2006), PPy/Fe (Chipara et al., 2007), PPy/Co (Ikeda et al., 1983) and Pd/PPy/foam-Ni (Sun et al., 2010) are some examples of nano composites obtained by this technique.

### 2.4 PPy-Oxide composite films

Sandwich-type composite films of PPy and an oxide (Ox) having composition, PPy/PPy(Ox)/PPy, onto a GC electrode were obtained by a sequential electrodeposition method. For the purpose, two electrolyte solutions (A and B) were used. Solution A contained 0.10M Py and 0.05M K<sub>2</sub>SO<sub>4</sub> and that solution B contained 0.10M Py, 0.05M K<sub>2</sub>SO<sub>4</sub> and 8.33 g L<sup>-1</sup> oxide powders. The first layer of PPy (~2.1 μm thick) was obtained onto graphite (G)/GC electrode in solution A by carrying out electrolysis at *j* (current density) = 5.0 mA cm<sup>-2</sup> for 100 s under unstirred condition. After electrolysis, G/PPy electrode was removed from the cell, washed with distilled water, dried in air and then introduced into the cell containing solution B and electrolysis was again carried out at *j* = 20 mA cm<sup>-2</sup> for 200

s under stirred condition so as to obtain a second layer of PPy(Ox) (~16  $\mu\text{m}$  thick). The polymer coated G electrode [G/PPy/PPy(Ox)], so obtained, was washed with distilled water, dried and reintroduced in the former cell containing solution A to electrodeposit the third and final layer of PPy (~4.2  $\mu\text{m}$  thick); electrolysis condition being  $j = 5.0 \text{ mA cm}^{-2}$ ,  $t=200 \text{ s}$ , unstirred. Prior to electrodeposition of PPy, the electrolytes (solution A & B) were degassed for 45 min by bubbling Ar and maintained under Ar atmosphere during the electrodeposition process also.

Following similar method several sandwich-type binary composite electrodes of PPy and a mixed oxide belonging to both spinel and perovskite families, namely  $\text{CoFe}_2\text{O}_4$  (Singh et al., 2004; Malviya et al., 2005a & b),  $\text{Cu}_x\text{Mn}_{3-x}\text{O}_4$  ( $x = 1.0 - 1.4$ ) (Nguyen Cong et al., 2005; 2002a; 2000),  $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$  ( $x = 0.3 \& 1.0$ ) (Nguyen Cong et al., 2002b; 2003, Gautier et al., 2002),  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$  ( $0 \leq x \leq 0.4$ ) (Singh et al., 2007a),  $\text{LaNiO}_3$  (Singh et al., 2007b) and  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  ( $0 \leq x \leq 0.4$ ) (Singh et al., 2007c) were prepared.

## 2.5 Other composites

**Preparation of PPy/Chitosan:** PPy/Chitosan composite films have been electrochemically synthesized on the Pt electrode from an aqueous solution containing 4.0  $\text{mg ml}^{-1}$  chitosan, 0.3M oxalic acid and 5 mmol Py (as monomer) by using cyclic voltammetry method (Yalcinkaya, 2010). A standard 3-electrode cell containing two platinum sheets for use as the counter and working electrodes and an Ag/AgCl (saturated with KCl) electrode as the reference electrode was employed to carry out the electrolysis. The potential was scanned from - 0.60 to + 0.90 V at scan rate of 50  $\text{mV s}^{-1}$ . Chitosan is a natural polymer and exhibits characteristic properties, such as chemical inertness, high mechanical strength, biodegradability, biocompatibility, high quality film forming properties and low cost (Yalcinkaya et al., 2010). The proposed structure of the composite is shown in Fig.2.

**Preparation of PPy/PANI:** 0.02M Py was polymerized in 0.25M  $\text{H}_2\text{SO}_4$  solution at 1.0 V under inert atmosphere for 30 min. The electrode was washed with distilled water and dried at 60°C. 0.1M pure ANI (aniline) was then electrochemically polymerized in 0.25M  $\text{H}_2\text{SO}_4$  solution at 0.8 V using PPy coated electrode as working electrode under inert atmosphere for 30 min (Hacaloglu et al., 2009). Similarly, the PANI/PPy composite was prepared. In this case first of all, 0.1M pure ANI solution was polymerized. The polymer films obtained were washed with distilled water several times to remove unreacted monomer as well as the electrolyte and subsequently dried in vacuum.

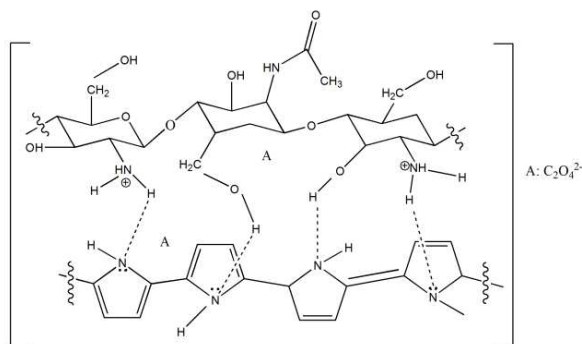


Fig. 2. Structural representation of the PPy/Chitosan composite

### 3. Characterization

#### 3.1 Thermal Gravimetric Analysis (TGA)

TGA is frequently used to quantify the amount and thermal stability of PPy in the composite and also to know whether there occurs some interaction between PPy and the other constituent of the composite. The TGA curve of the electrochemically synthesized PPy/chitosan composite on Pt electrode in air showed two stages of the weight loss (Yalcinkaya et al., 2010). The first stage of the thermal degradation was observed at 150-200°C and was attributed to removal of the dopant molecule (oxalate ion) from the polymer structure. The decomposition of chitosan chain was indicated by minimum weight loss in temperature range 300-370°C. On the other hand, the maximum weight loss observed at 380-400°C was attributed to the degradation and interchain crosslink of the composite. The comparison of results of the PPy/chitosan composite with those obtained from chitosan suggests that an interaction occurs between chitosan and PPy.

Similarly, The TGA analysis of SnO<sub>2</sub>-PPy nanocomposite from 25 to 700°C exhibited two weight losses (Cui et al., 2011). The first weight loss, in the temperature range of 25-250°C, attributed to desorption of physisorbed water, while the second in the range of 250-700°C, attributed to the oxidation of PPy. Bare SnO<sub>2</sub> does not show any weight change in the whole temperature range of the investigation, while the pure PPy is burnt off. So, on the basis of weight change before and after the oxidation of PPy, the SnO<sub>2</sub> content in the composite was estimated. TGA analyses of the S/PPy composite, bare S and PPy powder indicated (Wang et al, 2006) that S is burnt completely on temperature up to 340°C, followed by the oxidation of PPy in the second stage on temperature above 340°C. The weight loss in the second stage was about 40wt% which represents the amount of PPy in the S-PPy composite. TGA measurements were performed in air. The nanocomposites, SnO<sub>2</sub>-PPy and S/PPy were prepared by chemical polymerization.

#### 3.2 Scanning Electron Microscopy (SEM)

The morphology of the composite strongly depends upon the nature as well as the method of preparation. From the SEM analyses of pure PPy and its composites it was observed that morphology of the PPy changed significantly when the composite was formed. As, in the case of the PPy/chitosan composite, the SEM image of composite was significantly different compared to that of PPy (cauliflower-like spherical shape) or chitosan (smooth surface) (Yalcinkaya et al, 2010). On the other hand, HRTEM (High Resolution Transmission Electron Microscope) images of pure PPy and graphene nano sheet (GNS)/PPy composite obtained by chemical method (Zhang et.al., 2011) showed that pure PPy has the amorphous structure, while the PPy is homogeneously surrounded by GNS in the composite. The particle size of PPy/GNS was found to be smaller than pure PPy.

#### 3.3 X-Ray Diffraction (XRD)

The XRD pattern of GNS/PPy exhibited diffraction peaks at  $2\theta \approx 24.5^\circ$ ,  $26^\circ$  and  $42.8^\circ$ . The diffraction peaks at  $2\theta \approx 24.5^\circ$  and  $42.8^\circ$  correspond to (002) and (100) planes of graphite like structure while that the peak at  $2\theta \approx 26^\circ$  corresponds to amorphous PPy (Zhang et al., 2011). In the GNS/PPy composite, as GNS percentage increased, the broad peak shifted from  $2\theta \approx 26^\circ$  to  $24.8^\circ$ , implying that interaction occurs between GNS and PPy. The Au/PPy core-shell nanocomposites (Liu and Chuang, 2003) displayed a broad maximum at  $2\theta \approx 25.1^\circ$  ( $d = 3.5 \text{ \AA}$ ) which was ascribed to the closest distance of approach of the planar aromatic rings of PPy

like face to face Py rings. However, the XRD of pure PPy film electrodeposited on Au substrate showed the broad maximum at the lower angle, i.e. at  $2\theta \approx 19.0^\circ$  ( $d = 4.7\text{\AA}$ ). This may be caused due to scattering from side-by-side Py rings. The estimated values of the coherence length from the Scherrer equation were 11.03 and  $9.73\text{\AA}$  for Au/PPy nanocomposite and electrodeposited PPy on Au, respectively. The higher coherence value obtained for Au/PPy nanocomposite clearly indicates increased crystallinity and crystalline coherence, which would contribute to the higher conductivity of PPy.

The pure PPy exhibited a broad diffraction peak at  $2\theta \approx 24.6^\circ$ , which is characteristic peak of amorphous like PPy, while the diffraction pattern of PPy/ $\text{Y}_2\text{O}_3$  (30wt% oxide) composite was the same as  $\text{Y}_2\text{O}_3$  and PPy. It indicated that PPy deposited on the surface of  $\text{Y}_2\text{O}_3$  particles has a little effect on crystallization performance of  $\text{Y}_2\text{O}_3$  (Vishnuvardhan et al., 2006).

### 3.4 Infra Red (IR)/Raman/UV-visible absorption spectroscopy

Zhang et al., (2011) recorded the FTIR of pure PPy and PPy/GNS composite and observed that most of peaks, which correspond to PPy, get shifted towards the left when GNS was introduced. This was considered to an association of graphene to the nitrogenous functional group of PPy backbone. The FTIR spectra of PPy-Ag composite showed (Ayad et al., 2009) peaks at  $1560$  and  $1475\text{ cm}^{-1}$ , which correspond to the C-C and C-N stretching vibrations of PPy ring, respectively. The peak position of the composite showed a little shift towards the higher wave number compared to pure PPy. It was probably due to interaction between PPy and Ag particle and improvement of doping level of the polymer.

Raman spectra of PPy/GNS composite exhibited two prominent peaks, at  $\sim 1590$  (G band) and  $1350$  (D band)  $\text{cm}^{-1}$  which get broadened with increasing amount of GNS in the composite suggesting that the nanocrystalite size decreases due to the phonon confinement (Zhang et al., 2011). A broad peak at  $1051\text{ cm}^{-1}$  and two small peaks at  $933$  and  $981\text{ cm}^{-1}$  observed for pure PPy and PPy/GNS composite are the characteristic peaks of PPy. In the case of S-PPy composite, peak at  $\sim 500\text{ cm}^{-1}$  corresponds to the S particle and the peak between  $800$  and  $1700\text{ cm}^{-1}$  corresponds to the PPy nanoparticle suggesting that S-PPy contain both the sulphur (S) and conductive PPy elements (Wang et al., 2006). The Raman spectra of MWCNT exhibited the bands at  $\sim 1350\text{ cm}^{-1}$  (D band) and  $\sim 1580\text{ cm}^{-1}$  (G band), (Fang et al., 2010). The ratio of D to G band is associated with extent of defect present in the MWCNT and is sensitive to molecular interaction. After PPy deposition D/G ratio decreased which was prominent in short-pulse deposition than that of continuous deposition method. This decrease in D/G ratio is associated with reduction of disorder at the MWCNT surface. Further, Raman spectra of PPy/CNT composite did not produce any additional peaks except the characteristic peaks of CNT and PPy (Kim et al., 2008a). This suggests that no new chemical bond is formed between CNT and PPy in composite and no chemical change in PPy composite occurs.

UV-visible absorption spectra of the composite PPy-CdS with different CdS contents clearly indicated two absorption bands at  $300\text{-}400\text{ nm}$  and  $700\text{-}1000\text{ nm}$ . The former absorption band was assigned to the  $\pi\text{-}\pi^*$  transition and the latter, to the oxidation state of the film. There occurs an increase in absorption of the composite material with CdS concentration, which implies that electronic structure of PPy is affected by CdS (Madani et al., 2011). Sharifirad et al. (2010) prepared PPy on Cu in three aqueous media (citric acid: CA, sodium acetate: SA and sodium benzoate: SB) and recorded their UV-visible spectra. The UV spectra of PPy/Cu in CA showed two absorption peaks at  $295$  and  $460\text{ nm}$ , assigned to the  $\pi\text{-}\pi^*$



transition and to the formation of perninfreaniline form (PB) and the spectra of PPy/Cu synthesized in SA and SB indicated a shoulder respectively at 360 and 350 nm, which was assigned to the formation of polybenzoic salt.  $AuCl_4^-$  nano complex showed a band at ~308 nm which disappeared after addition of Py monomer and a new band of  $\pi-\pi^*$  transition of PPy appeared in the region 400-500 nm with absorption maximum at 463 nm, showing the formation of Au/PPy nanocomposite with core-shell structure (Liu & Chuang, 2003). The UV-visible absorption spectrum of pure PPy indicated (Konwer et al, 2011) a weaker absorption at 330 nm ( $\pi-\pi^*$  transition) and stronger absorption at 570 nm (bipolar state of PPy). The PPy/EG (expanded graphite) composite showed a red shift in UV visible spectrum suggesting that EG assists the polymerization in such a way that it maintains a higher conjugation length in the chain of the PPy and there may be possible some coupling between conjugation length of PPy and EG. Estimate of the optical band gap of PPy found by using equation,  $E_g^{opt} (eV) = 1240/\lambda_{edge}(nm)$ , was 2.17 eV, while it decreased to 1.85-1.93 eV in PPy/EG with addition of EG.

**3.5 Electrochemical impedance spectroscopy (EIS)**

A conductive polymer electrode is a porous material. Various equivalent circuits have been applied to present impedance behavior of the conducting polymer electrodes (Passiniemi & Vakiparta, 1995). But till now, no general equivalent circuit that can satisfy all electrolyte-conducting polymer configurations has been reported. In literature, (Levi & Aurabch, 1997, 2004; Lang & Intzelt, 1999; Mohamedi et al., 2001) different equivalent circuit models have been used to treat the experimental data and some of them are given in Fig.3; wherein subscripts 'sl' and 'ct' represent the surface layer and the charge transfer and symbols:  $Z_w$ ,  $C_{int}$  and  $Z_{FLW}$  and  $Z_{FSW}$  represent Warburg impedance, capacitor due to intercalation and finite length and finite space Warburg type elements, respectively; other symbols have their usual meaning.

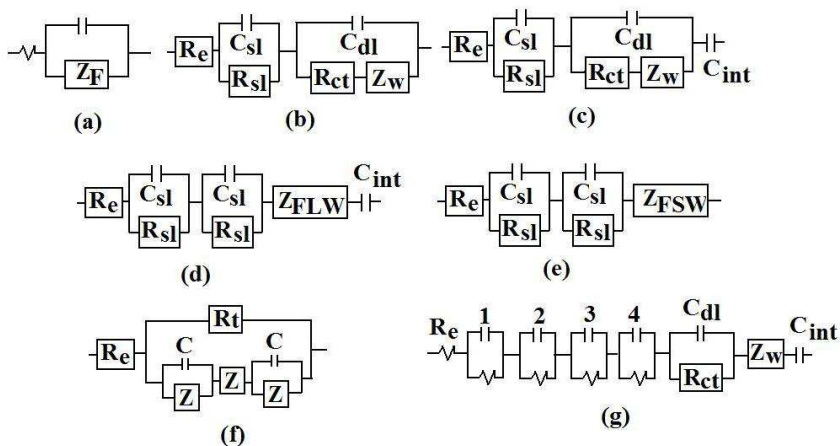


Fig. 3. Equivalent circuit (EC) models: (a)Randle's EC model; (b-d) Modified Randle's EC (analogs for ion-intercalated electrodes); (e) Meyers EC Model (analog for mixed particle porous electrode); (f) EC model of polymer film electrodes; (g) Voigt and Frumkin and Melik-Gaykazyan (FMG) model (for interfacial boundaries of lithiated graphite electrode).

The EIS spectra (i.e. Nyquist plots) of several composites such as S/T-PPy (Tubular PPy) and S/G-PPy (Granular PPy) (Liang et al., 2010), PEDOT/h-PPy (Poly 3,4-ethylenedioxythiophene/horn like-PPy) (5:1) (Wang et al., 2007), PPy films on DuPont 7012 carbon composite (Li et al., 2005), S-PPy (Wang et al., 2006) and Si/PPy (9:1) (Guo et al. 2005) reported in literature displayed a small semi-circle at high frequencies and a straight line at lower frequencies. The observed linearity at low frequencies has been ascribed to the anion diffusion in the composite matrix and the semicircle in the high frequency region, to the contact resistance and charge transfer resistance. Only in the case of PEDOT/h-PPy, a line indicating a capacitive behavior related to the film charging mechanism at low frequencies was observed.

The EIS study of sandwich-type composite film electrodes of PPy and a mixed valence oxide have generally produced more or less similar Nyquist plots. Each Nyquist curve indicated a capacitive behavior at low frequencies, a small semicircle (or an arc) at high frequencies and more or less a linear curve at intermediate frequencies. The observed semicircle at high frequencies is considered to be produced due to contribution of the charge transfer reaction (Singh et al., 2004). In some cases, no semicircle corresponding to the charge transfer reaction is observed (Malviya et al., 2005; Singh et al., 2007a); in these cases the charge transfer resistance is thought to be much smaller than the sum of the film and solution resistances. In fact, at higher frequencies, the diffusion of anions ( $\text{ClO}_4^-$ ,  $\text{Cl}^-$  or  $\text{SO}_4^{2-}$ ) into the polymer matrix dominates the impedance results and that a conventional semi-infinite Warburg response is observed. At relatively lower frequencies, the  $\Delta Z_{\text{im}}/\Delta Z_{\text{real}}$  value increases with decreasing frequency and that the impedance response results a capacitive-type behavior. Thus, a change over seems to take place from the semi-infinite Warburg regime to the finite Warburg regime with the variation of frequency from high (100 KHz) to a low value (20 mHz).

The spectra obtained were analyzed by fitting the equivalent circuits,  $R_s(\text{RQ})Q'$ ,  $R_s(\text{R}_1\text{Q}_1)(\text{R}_2\text{C}_2)(\text{R}_3\text{C}_3)\text{C}_4\text{W}_4$ ,  $R_s\text{QWC}$ ,  $\text{LR}(\text{RQ})(\text{RQ})\text{Q}$  and  $\text{LR}(\text{RQ})(\text{RQ})$ , where  $R_s$  is solution resistance,  $Q$  is constant phase element,  $W$  is Warburg resistance and  $C$  is capacitance. The apparent diffusion coefficient ( $D_a$ ) for transport of anions particularly  $\text{SO}_4^{2-}$  in the polymer matrix were also estimated at varying potentials. Estimates of  $D_a$  values for  $\text{SO}_4^{2-}$  anions at a constant potential,  $E = -0.1$  V vs SCE in deoxygenated 0.5M  $\text{K}_2\text{SO}_4 + 5\text{mM}$  KOH at 25°C were 1.1, 12.1, 2.5, 0.7,  $0.60 \times 10^{-7}$   $\text{cm}^2 \text{ s}^{-1}$  in binary composites of PPy and  $\text{LaNiO}_3$ ,  $\text{LaMnO}_3$ ,  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ ,  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  and  $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ , respectively.

### 3.6 Cyclic Voltammetry (CV)

During the CV, the PPy film electrode-electrolyte system involves the redox couple,  $\text{PPy}^+/\text{PPy}$  (Kaplin & Qutubuddin, 1995), where PPy is the neutral species (associated with three to four monomer units) and  $\text{PPy}^+$  is the radical cationic species or polaron (one positive charge localized over three to four monomer units). In the oxidized state, the PPy is positively charged and so, some anions get migrated from solution into the polymer matrix so as to maintain electroneutrality. Similarly, on reduction, as electrons are injected and the positive charge on the polymer chain disappears, some anions leave the PPy matrix and enter into the solution. The formation of a second redox couple,  $\text{PPy}^{++}/\text{PPy}^+$ , has also been proposed (Genies and Pernaut, 1985) to explain two reduction peaks observed in some CVs.  $\text{PPy}^{++}$  is the dicationic species or bipolaron. The counterion concentration will be greater for a PPy film containing both polaron and bipolaron species than for a film containing only polaron species (Kaplin and Qutubuddin, 1995).

The preparation method strongly influences the electrochemical reaction activity of PPy. CVs of PPy films deposited on GC by using three different methods, constant current, constant potential electrolysis and CV, at the scan rate of 100 mV/s in the potential region from -0.20 to 1.02 V vs. Ag/AgCl in 0.1M PBS (Phosphate buffer saline) have shown that the galvanostatically deposited polymer film had the greatest electrochemical activity than that of potentiostatically deposited film. A triple layer of PPy films on the GC electrode, obtained by sequential electrodeposition method, has the worst redox capacity (Lee et al., 2005).

The charge transport properties in the PPy matrix depends upon the nature and concentration of the doping anions. The charge transport properties of a triple layer of PPy films on the GC electrode, obtained by sequential electrodeposition method, were examined by CV under Ar atmosphere in Py-free 0.15M KA (A = Cl<sup>-</sup>, PF<sub>6</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>) solution at a scan rate of 10 mVs<sup>-1</sup> from -0.8 to +0.8 V/SCE (Nguyen Cong et al., 2005). The changes in shape and characteristics of CVs were observed with doping anions. For instance, the increase of the anodic peak potential (E<sub>pa</sub>) in sequence Cl<sup>-</sup> (150 mV/SCE) < ClO<sub>4</sub><sup>-</sup> (380 mV/SCE) < PF<sub>6</sub><sup>-</sup> (440 mV/SCE < NO<sub>3</sub><sup>-</sup> (490 mV/SCE) < SO<sub>4</sub><sup>2-</sup> (520 mV/SCE) is accompanied by a drop in the peak current intensities. In fact, in its oxidized state the PPy incorporates the doping anions in order to neutralize the positive charges (dications, i.e. bipolaron) created on its backbone by the electropolymerization process. The switching between the oxidized and reduced states implies the deintercalation/intercalation of these anions, whose ability to move depends on their nature. This explains the changes in shape of the CVs.

Recently, CVs of sandwich-type electrodeposited composite films of PPy and CoFe<sub>2</sub>O<sub>4</sub> on graphite (G) having structure G/PPy/(PPy(CoFe<sub>2</sub>O<sub>4</sub>)/PPy in Ar-deoxygenated 0.5 M KOH containing K<sub>2</sub>SO<sub>4</sub> as a dopant anion indicated a broad anodic and a broad cathodic maxima corresponding to establishment of the redox couple, [PPy<sup>+</sup>. SO<sub>4</sub><sup>2-</sup>]/[PPy + SO<sub>4</sub><sup>2-</sup>] (Singh et al., 2004), transport of doping anion being a diffusion controlled one. Features of CVs of pure PPy and composite electrodes were similar. Similar results were also found from the study of CVs of similar sandwich type composites of PPy with LaNiO<sub>3</sub> (Singh et al., 2007b), La<sub>1-x</sub>Sr<sub>x</sub>MnO<sub>3</sub> (0 ≤ x ≤ 0.4) (Singh et al., 2007a), Cu<sub>1.4</sub>Mn<sub>1.6</sub>O<sub>4</sub> (Nguyen Cong et al., 2002a), Ni<sub>x</sub>Co<sub>3-x</sub>O<sub>4</sub> (x = 0.3 and 1.0) (Nguyen Cong et al., 2002b).

Very recently, CVs of nanocomposite systems, MnO<sub>2</sub>/PPy, SO<sub>4</sub><sup>2-</sup> (Sharma et al, 2008), PPy<sub>Cl</sub> (PPy films doped with Cl<sup>-</sup>), Cl<sup>-</sup> and PPy<sub>ClO<sub>4</sub></sub> (PPy films doped with ClO<sub>4</sub><sup>-</sup>), ClO<sub>4</sub><sup>-</sup> (Sun et al., 2009) and PEDOT/c-PPy, ClO<sub>4</sub><sup>-</sup> and PEDOT/h-PPy, ClO<sub>4</sub><sup>-</sup> (Wang et al., 2007) have shown that the specific capacitance of composites are greatly enhanced in comparison with those obtained for their respective constituents elements/materials. Further, the CV curves of PEDOT/h-PPy and PPy doped with ClO<sub>4</sub><sup>-</sup> have rectangle like (i.e. ideal) shapes while CV curves for MnO<sub>2</sub>/PPy, PPy doped with Cl<sup>-</sup> and PEDOT/c-PPy are non ideal.

## 4. Applications

### 4.1 Corrosion protection coatings

Conductive polymers are presently being considered as potential materials for corrosion protection of metals. They can substitute conventional protection materials such as chromates and phosphates used in the electroplating and paint industries with stronger more resistant and environmentally friendly coatings. The traditional anticorrosion materials provide excellent corrosion protection coatings but their toxicity has been severely questioned.

A conductive organic coating forms a physical barrier against corrosive agents and a passive layer on the metal surface. The corrosion protection efficiency of this organic coating can be

greatly improved by introducing organic or inorganic materials embedded within the polymer structure by electropolymerization. It is reported that the composites with micron- and submicron ceramic particles such as  $\text{TiO}_2$  (Ferreira et al., 2001),  $\text{WO}_3$  (Yoneyama et al., 1990),  $\text{Fe}_3\text{O}_4$  (Garcia et al., 2002),  $\text{MnO}_2$  (Yoneyama et al., 1991) and  $\text{Zn}_3(\text{PO}_4)_2$  (Lenz et al., 2007) with PPy improved the mechanical and corrosion resistance of the coatings.

Electrochemically polymer (PANI+PPy) coated stainless steel plates showed improved corrosion resistance with acceptable contact resistance under proton-exchange membrane fuel cell (PEMFC) condition (Joseph et al., 2005). Recently, it has been demonstrated (Ren & Zeng, 2008) that a bilayer conducting polymer coating, composed of an inner layer of PPy with large dodecylsulfate ionic groups and an external PANI layer with small  $\text{SO}_4^{2-}$  groups, reduced the corrosion of the type 304 stainless steel, used for bipolar plates of a PEMFC, much more effectively than the single PPy coatings in 0.3M HCl. Besides these, some PPy-based composites such as PPy-CMC (carboxymethylcellulose), PPy-SDS (sodium dodecylsulfate), PPy-TiNT (Titanate nanotube) and PPy-zinc phosphate were observed to protect steel (Herrasti & Ocoan, 2001), 1Cr18Ni9Ti stainless steel (Zhang & Zeng, 2005), stainless steel type 904L (Herrasti et al., 2011), and AISI 1010 steel (Lenz et al., 2007) surfaces effectively from corrosion, respectively. Electrochemically prepared PPy- $\text{WO}_4^{2-}$  (Sabouri et al., 2009), PPy/PANI (Panah & Danaee, 2010) and Pt/PPy (Rahman, 2011) composite films provided noticeable corrosion inhibition for carbon steel, whereas PPy- $\text{TiO}_2$  (Lenz et al., 2003), PPhe (polyphenol)/PPy (Tuken et al., 2004), PPy-P (Hosseini et al., 2007), PPy-DGEBA (Riaz et al., 2007), PPy- $\text{PMo}_{12}\text{O}_4^{3-}$  (Kowalski et al., 2008), and PPy-PANAP (poly(5-amino-1-naphthol)) (Bereket & Hur, 2009) provided better protection for corrosion of mild steel.

PPy-based coatings were also found to reduce the corrosion of oxidizable metals such as Fe (Bazzaoui et al., 2006; Bazzaoui et al., 2005; Lee et al., 2005), Al (Bazzaoui et al., 2005; Lehr & Saidman, 2006a; 2006b) and Al alloys (Lehr & Saidman, 2006a; 2006b). The efficiency of corrosion protection of PPy depends on the nature of the doping agents (Balaskas et al., 2011).

Electrochemically deposited PPy films on Cu displayed good protection against Cu corrosion in a 3.5% NaCl solution (Herrasti et al., 2007). The effectiveness of the protection is enhanced when the PPy film is electrosynthesized from a solution of dihydrogen phosphate (Redondo & Breslin, 2007) or sodium saccharinate (Bazzaoui et al., 2007).

PPy films electrodeposited onto Ni-Ti alloy employing sodium bis(2-ethylhexyl) sulfosuccinate (Aerosol OT or AOT) solutions improved the corrosion performance of the alloy at the open circuit potential and at potentials where the bare substrate suffers pitting attack (Flamini & Saidman 2010). PPy coatings on Mg alloy AZ91D, obtained respectively from aqueous solutions of a dicarboxylic organic acid salt (Turhan et al., 2011a) and sodiumsalicylate (Turhan et al., 2011b) by cyclic voltammetry (CV) method, demonstrated good corrosion protections of the alloy.

## 4.2 Fuel cell

In a fuel cell, the fuel (hydrogen, natural gas, methanol, ethanol, etc.) is electrochemically oxidized at the anode, whereas the oxidant (oxygen from the air) is reduced at the cathode. Because of difficulties involved in the production, storage, and distribution of hydrogen, the use of alcohols (methanol, ethanol, etc.) as hydrogen carrier is preferred and the resulting cell is called as the direct alcohol fuel cell (DAFC). Thus, the overall efficiency of a DAFC depends upon the efficiencies of both the electrode reactions (e.g. alcohol oxidation and

oxygen reduction). The mechanism of oxygen reduction reaction (ORR) is very complex. The most accepted mechanisms in acid media are, the direct four electron pathway ( $O_2 + 4H^+ + 4e^- \leftrightarrow 2H_2O$ ,  $E^\circ = 1.229 V_{SHE}$ ) and a series two-electron pathway ( $O_2 + 2H^+ + 2e^- \leftrightarrow H_2O_2 + 2H^+ + 2e^- \leftrightarrow 2H_2O$ ). The ORR and Methanol/Ethanol oxidation reaction (MOR/EOR) are traditionally catalyzed by Pt or Pt-based alloys dispersed on high surface area carbon support materials.

PPy has been investigated as carbon-substitute supports for fuel cell catalysts. Polymer-supported metal particles present the higher specific surface area and the higher tolerance to poisoning due to the adsorption of CO species, in comparison to the serious problem of poisoning of bulk and carbon supported metals. Moreover conducting polymers are not only electron conducting, but also proton conducting materials, so they can replace Nafion in the catalyst layer of the fuel cell electrode and provide enhanced performance also.

#### 4.2.1 PPy-based anodes

Several PPy-based anodes for fuel cells have recently been prepared and investigated for their applications in DAFCs. Most of them are described briefly in following lines.

In the MOR, Pt nano-particles decorated PPy-MWCNTs composite electrodes showed higher catalytic stability than Pt/MWCNTs binary catalyst, due to the synergic interaction between PPy and the carrier (Qu et al, 2010). Zhao et al. (2008a) demonstrated that the Pt nano-particles deposited on PPy-C with naphthalene sulfonic acid as dopant exhibit better catalytic activity than those on plane carbon in fuel cells. They also reported (Zhao et al., 2009) that bimetallic Pt-Co nano-particles co-deposited on PPy-MWCNT composite via over-oxidation treatment had higher catalytic activity towards methanol oxidation. Further, the MOR was observed to improve on the Pt-Fe/PPy-C catalyst compared to commercial Pt/C catalyst (Zhao et al., 2008b).

Mohana Reddy et al. (2008) examined the suitability of the cobalt-polymer-MWCNT composite electrode for the ORR in DMFCs and DEFCs by using Pt-Ru/MWCNT and Pt-Sn/MWCNT, respectively, as anode electrocatalysts. The study indicated an improved power densities for hydrogen, methanol and ethanol based fuel cells compared to the previously non Pt based electro-catalysts. Hammache et al. (2001) observed a higher catalytic activity for MOR on the dispersed gold micro particle on PPy coatings on Fe than a bare gold electrode in acidic media.

The application of PPy film containing nanometer-sized Pt and Pt/Pd bimetallic particles on ITO glass plates has also been investigated as anode for MOR. The modified electrode was found to exhibit significant electrocatalytic activity. The enhanced electrocatalytic activities may be due to the uniform dispersion of nanoparticles in the PPy film and a synergistic effect of the highly dispersed metal particles so that the PPy film reduces electrode poisoning by adsorbed CO species (Selvaraj et al. 2006). A Pd/PPy/Pd/G generated by sequential electrodeposition method (Ding et al., 2011) showed a satisfactory electrocatalysis toward the formic acid oxidation.

#### 4.2.2 Oxygen Reduction Reaction (ORR)

As early as in 1983, Bull et al. observed that Fe tetrasulfonated phthalocyanines-doped PPy film on GC electrode catalyzes the reduction of  $O_2$  at potentials 250-800 mV less negative than at bare GC or at PPy-coated GC electrode. Co-doped PPy films on metal electrodes also showed the electrocatalytic activity for  $O_2$  reduction (Ikeda et al., 1983). Osaka et al. (1984)

studied the ORR at the PPy film electrode containing Co(III) tetrakis(sulfophenyl)porphine and observed a 4 electron reduction of  $O_2$  to  $H_2O$  in  $H_2SO_4$ , contrary to the 2 electron reduction which usually occurs in this system in homogeneous state. The ORR at the GC/PPy/CoTSP ((tetrasulfonatophthalocyaninato)cobalt) electrode in 0.05 M  $H_2SO_4$  showed approx. 0.5 V more anodic onset potential than the value obtained with a GC electrode in 0.05 M  $H_2SO_4$  containing  $10^{-3}$  M CoTSP (Osaka et al., 1986). The electrodeposited Pt particles on PPy films were also active for the ORR (Vork and Barendrecht, 1989). PPy films containing nanometer-sized Pt particles (PPy/Pt), electrosynthesized from a solution containing Py and colloidal Pt particles, exhibited high catalytic activity towards the ORR (Bose & Rajeshwar, 1992). The ORR study has also been carried out on PPy films doped with anionic Co-species (Seeliger & Hamnett, 1992), tungstophosphate anions (Dong & Liu, 1994), Fe/Co phthalocyanines (Coutanceau et al., 1995), ferriporphyrin (FeTPPS) (Wu et al., 1999), meso-tetra(4-sulfonatophenyl)porphine (TPPS4) (Johanson et al., 2005), and anthraquinone-2,7-disulfonate (AQDS) (Zhang et al., 2007). These modified electrodes exhibited good activity towards the ORR. The PPy-cobalt complex-modified C particles displayed electrocatalytic activity for four-electron reduction of  $O_2$  and the catalyst showed high stability against degradation after use for several hours (Yuasa et al., 2005). The catalytic reduction of molecular oxygen on the PPy-Mn phthalocyanine film (GC/ITO-coated glass support) indicated the participation of the Mn center of the PPy in the reduction of molecular oxygen (Rodrigues et al., 2005). The ORR displayed a pathway of irreversible 2-electron reduction to form  $H_2O_2$  on the PPy/AQDS (anthraquinonedisulfonate) composite film on GC at all electrolyte pH employed, the pH 6.0 buffer solution being a more suitable medium for the reduction of dioxygen (Zhang & Yang, 2007).

Recently, it has shown (Ding & Cheng, 2009) that electrochemically produced  $MnO_2$ -PPy composite material is ORR active in 0.5M  $H_2SO_4$  when compared to the pure PPy. Template-synthesized Co porphyrin/PPy nanocomposite in a neutral medium catalyzes the ORR mainly through a 4-electron pathway, exhibiting excellent electrocatalytic activity (Zhou et al., 2007). Also, Pd-PPy/C nanocomposite efficiently catalyzes reduction of oxygen, with resistance to methanol oxidation, directly to water through a four-electron pathway (Jeyabharathi et al., 2010). C-supported CoPPy composite material exhibits the Tafel slopes, -110 -120 mV (Millan et al., 2009). Very recently, Zhao et al. (2011) observed an enhanced electrocatalytic performance for the ORR on the AQS (anthraquinone-2-sulfonate)/PPy composite modified graphite electrode.

Investigations on the ORR at sandwich composite electrodes of PPy and  $Cu_{1.4}Mn_{1.6}O_4$  (Nguyen Cong et al., 2000; 2002a), PPy and  $Ni_xCo_{3-x}O_4$  (Gautier et al., 2002; Nguyen Cong et al. 2002b), PPy and  $CoFe_2O_4$  (Singh et al., 2004), PPy and  $LaNiO_3$  (Singh et al., 2007a), PPy and  $La_{1-x}Sr_xMnO_3$  ( $0 \leq x \leq 0.4$ ) (Singh et al., 2007b) and  $La_{1-x}Sr_xCoO_3$  (Singh et al., 2007c) were also carried out. The results have shown that the composite electrode had excellent catalytic activities as well as remarkable stability even in acid solutions wherein mixed oxide cathodes normally undergo deactivation.

### 4.3 Rechargeable batteries

Among the various types of rechargeable batteries, the Li/S battery system is a very attractive candidate for rechargeable Li-batteries due to its high theoretical specific capacity of  $1672 \text{ mAhg}^{-1}$  and theoretical power density of  $2600 \text{ Wh kg}^{-1}$  based on S active materials. The use of S as a cathode material is advantageous because of its abundance, low cost, and

environmental friendliness. As S is an insulating material, the cathode material is combined with 30-55% carbon black (Jin et al., 2003; Song et al., 2004) of the total weight of the electrode materials. Recently, PPy has been used as an additive to improve the performance of anode and cathode materials in Li-ion batteries (Guo et al., 2005; Pasquier et al., 1999; Veeraraghavan et al., 2002; Wang et al., 2006).

Very recently, Liang et al., (2010) observed that the morphology of the PPy combined with S shows a significant effect on the dispersion status and electrochemical behaviour of S. When S was highly combined with two types of PPy, G-PPy and T-PPy, by in-situ oxidation and co-heating methods, the cycle durability of the composite was more favourable with the T-PPy matrix in comparison with G-PPy matrix. Guo et al. (2005), for the first time, prepared a series of novel Si/PPy composites by high-energy mechanical milling techniques. These anode materials had high capacities characteristic of the Li-Si alloy system but substantially improved cyclability compared to bare Si anodes.

Metal oxide powders such as  $\text{LiCoO}_2$  (Ohzuku & Ueda, 1994),  $\text{LiMn}_2\text{O}_4$  (Tarascon et al., 1994),  $\text{LiNiO}_2$  (Kanno et al., 1994), and  $\text{V}_2\text{O}_5$  (Leroux et al., 1996) have been considered as promising candidates for positive electrode materials in rechargeable Li batteries having high energy densities. In order to prepare these oxide electrodes, a conducting matrix and a binder are usually mixed with the oxide powder. PPy can serve as both as the conductor and binder. In view of this, composite electrodes of  $\text{LiMn}_2\text{O}_4$  and PPy were prepared and studied for the charge-discharge properties of electrodes for 3V class (Gemeay et al., 1995) and also 4V class (Kuwabata et al., 1999) of Li-batteries. Results show that the PPy works well as a conducting matrix for the redox reaction of  $\text{LiMn}_2\text{O}_4 \leftrightarrow \text{Li}_{1-x}\text{Mn}_2\text{O}_4 + x \text{Li}^+ + x \text{e}^-$  as well as like a capacitor and contributed to the capacity of the  $\text{LiMn}_2\text{O}_4/\text{PPy}$  composite.

Recently,  $\text{LiFePO}_4$  has emerged as an important cathode material for lithium-ion batteries due to its high theoretical capacity (170 mAh/g), high potential (3.4 V versus Li/Li+), low cost, natural abundance and environmental friendliness of Fe. Bare  $\text{LiFePO}_4$  is an insulator with an electrical conductivity of about  $\sim 10^{-11}$  S/cm. To improve the electrical conductivity efforts have been made. Since PPy is a conductive polymer and also has lithium storage capacity in lithium-ion cells, a coating of PPy on the  $\text{LiFePO}_4$  particles would increase the electrical conductivity of the  $\text{LiFePO}_4$ . With this idea, Wang et al (2005) prepared a series of PPy- $\text{LiFePO}_4$  composite materials. The PPy- $\text{LiFePO}_4$  composite electrodes demonstrated an increased reversible capacity and better cyclability, compared to the bare  $\text{LiFePO}_4$  electrode. The thin PPy film has also been used to make Li-batteries lighter and more flexible than the existing ones for portable electronic equipments. Wang et al. (2008) prepared highly flexible, paper-like, free-standing PPy and PPy- $\text{LiFePO}_4$  composite film electrodes and observed that the cell with PPy- $\text{LiFePO}_4$  composite film had a higher discharge capacity beyond 50 cycles (80 mAh/g) than that of the cell with pure PPy (60 mAh/g).

To ensure long cycle life and safety, the use of graphite, among carbon materials, as anode for the Li-ion battery is favoured, however carbonaceous anodes exhibit capacity loss during the first intercalation step. To minimize the capacity loss the graphite electrode was coated by a thin PPy film, the later is found to decrease the initial  $E_{\text{rev}}$  capacity loss of the graphite anode (Veeraraghavan et al., 2002). The decrease in the  $E_{\text{rev}}$  capacity loss has been ascribed to the reduction in the thickness of the solid electrolyte interface (SEI) layer. PPy/C (7.8%) gives the optimum performance based on the  $E_{\text{rev}}$  capacity loss and the discharge capacity of the composite.

The research work on the use of PPy as electrode material of the aqueous based power sources has recently been also commenced. Grgur et al. (2008) obtained PPy thin film on

graphite electrode in 0.1M HCl galvanostatically and characterized as cathode material for the aqueous based rechargeable zinc batteries. Results have shown that Zn/PPy cell have potentially promising characteristic.

#### 4.4 Supercapacitor

PPy offers a greater degree of flexibility in electrochemical processing than most conducting polymers, and consequently the material has been the subject of much research as a super capacitor or battery electrode (Snook et al., 2011). Due to greater density, polymer had a high capacitance per unit volume (400-500 Fcm<sup>-3</sup>). Combining PPy with polyimide (a dopant of high molecular weight) is claimed to improve the charge storage property (Iroh & Levine, 2003), due to the polyimide matrix protecting the PPy from oxidative degradation. Polyimide is cathodically electroactive, whereas PPy is anodically electroactive.

MWCNT coated with PPy has also been used in supercapacitor. The maximum value of 163 F g<sup>-1</sup> has been obtained for MWCNTs prepared at 600°C and modified by a PPy layer of 5 nm, whereas it is only 50 F g<sup>-1</sup> for the pristine nanotube (Jurewicz et al., 2001). PPy/GNS composite is a promising candidate for supercapacitor to have higher specific capacitance, better rate capability and cycling stability than those of pure PPy. The specific capacitance of PPy/GNS composite based on the three electrode cell configuration is as high as 482 F g<sup>-1</sup> at a current density of 0.5 A g<sup>-1</sup> (Zhang et al., 2011).

PPy doped with nafion ions or ClO<sub>4</sub><sup>-</sup> exhibits a specific capacitance of 344 or 355 F g<sup>-1</sup>. Cycle life experiments revealed that the nafion material retains 98% of the original capacitance after 3000 cycles whereas that doped with ClO<sub>4</sub><sup>-</sup> retains only 70% over this period (Kim et al., 2008b). The PPy active films doped with ClO<sub>4</sub><sup>-</sup> ion in NaCl solution demonstrates an ideal supercapacitor behavior, i.e. rectangle-like CV shape at scan rates from 5-200 mV s<sup>-1</sup>, linear galvanosttic charge/discharge curves at currents loads from 0.5 to 2 mA and stable cyclic property. However, dopings with Cl<sup>-</sup> ions give rise to nonideal property of supercapacitor (Sun et al., 2009).

PEDOT/PPy composite can be used as an electrochemical supercapacitor electrode material. This composite electrode produced the specific capacitance as 230 Fg<sup>-1</sup> in 1M lithium perchlorate aqueous solution and 290 F g<sup>-1</sup> in 1M KCl aq solution (Wang et al., 2007). A pulsed polymerized Py film obtained on the polished graphite plate has been reported to exhibit very high capacitance (400 Fg<sup>-1</sup>) and high energy density (250 Wh h kg<sup>-1</sup>) and can be used as supercapacitor. Stability tests performed on this pulse polymerized PPy electrode yield long cycle life upto 10,000 cycles, the charge/discharge current density being 5mA cm<sup>-2</sup> (Sharma et al., 2008).

#### 4.5 Solar cells

Literature reveals that the increased application of the PPy material has been made, during recent years, in solar cells, particularly in dye-sensitized solar cells (DSSCs) to improve the overall energy conversion efficiency and also to reduce the cost of the cell. Recently, PPy was synthesized by vapour phase polymerization and traditional electrochemical polymerization and employed as counter electrode in a DSSC. Both PPy and Pt electrodes showed good catalytic behaviour in DSSCs (Xia et al., 2011). The composite, PPy/graphite on ITO glass also showed favourable catalytic activity for I<sub>2</sub>/I<sup>-</sup> redox reaction (Xiaoming et al., 2011). The overall energy conversion efficiency of the DSSCs based on the ruthenium dye (N719) with PPy/graphite composite counter electrode reached 6.01% under simulated AM



1.5 irradiation (100 mW/cm<sup>2</sup>), which was 92% of the energy conversion efficiency of the DSSCs with Pt electrode.

Photoelectrochemical and electrochemical behavior of gold electrode modified with bilayers of PPy and PANI have been investigated in acid solutions (Upadhyay et al., 1995). Both PPy and PANI films on gold exhibit photo electrochemical activity, with the former showing a considerably high activity than the latter. PEC solar cells based on nanostructured ZnO/dye/PPy/ film electrode display excellent properties as anode in the conversion process of light to electricity (Hao et al., 2000). PPy was prepared on Ru-dye sensitized TiO<sub>2</sub> nanoporous film and solar cell was constructed using gold as the counter electrode with PPy acting as the hole conductor (Cervini et al., 2004). Photodevices comprising covalently grafted PPy films on surface modified mesoporous TiO<sub>2</sub> substrates via 3-(trimethoxysilyl) propyl methacrylate were fabricated and tested their performances with a counter electrode having a thin layer of gold (Senadeera et al., 2006). Significant enhancements in photoresponses were observed with the above additives in PPy than the reported devices comprising TiO<sub>2</sub>/PPy. Hybrid Cu-In disulphide/PPy photovoltaic structures prepared by electrodeposition exhibited (Bereznev et al., 2005) significant photovoltage and photocurrent under standard white light illumination. Electrodeposited Cu-In-Se/PPy PV structures exhibited the formation of a n-p barrier between the n-CuInSe and p-PPy layers (Bereznev et al., 2006). The PPy encapsulated TiO<sub>2</sub> nanotube array (PPy/TiO<sub>2</sub> NTs) electrode was also synthesized (Zhang et al., 2008) by electropolymerization to encapsulate PPy inside the TiO<sub>2</sub> nanotube channels and walls in order to enhance the photocurrent density.

## 5. Conclusion

Different electrochemical methods for obtaining pure PPy, functionalized PPy and PPy composites are briefly described. Structural and electrochemical characterizations of new conductive materials and their application in solar cells, fuel cells, batteries, super capacitors and in corrosion protection have been highlighted. Studies available in literature have shown that the PPy has been used as carbon-substitute, particularly in fuel cells and batteries and found to greatly improve their performances. The use of active films or composites of PPy is very effective in enhancement of the capacitance of the supercapacitors. The PPy and its composites such as PPy/graphite have also shown favourable catalytic activity for I<sub>2</sub>/I<sup>-</sup> redox reaction. The PPy film has also improved the efficiency of the photo anodes in dye-sensitized solar cells significantly. PPy and PPy-based coatings are proved to be very effective inhibitors in the corrosion of oxidizable metals and alloys, stainless steels, mild steel, etc. Besides these, PPy films are being used in other areas such as sensors, bio-fuel cells, etc.

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## 7. References

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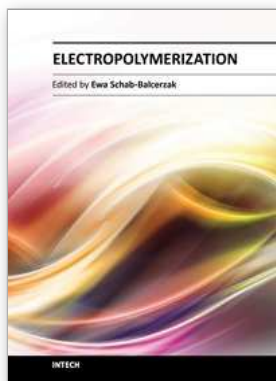


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## **Electropolymerization**

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In recent years, great focus has been placed upon polymer thin films. These polymer thin films are important in many technological applications, ranging from coatings and adhesives to organic electronic devices, including sensors and detectors. Electrochemical polymerization is preferable, especially if the polymeric product is intended for use as polymer thin films, because electrogeneration allows fine control over the film thickness, an important parameter for fabrication of devices. Moreover, it was demonstrated that it is possible to modify the material properties by parameter control of the electrodeposition process. Electrochemistry is an excellent tool, not only for synthesis, but also for characterization and application of various types of materials. This book provides a timely overview of a current state of knowledge regarding the use of electropolymerization for new materials preparation, including conducting polymers and various possibilities of applications.

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