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Gas Phase Electroformation of Polypyrrole

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Abstract: Gas phase electrochemical polymerization of pyrrole was investigated in which platinum electrode coated with Nafion dopant was exposed to pyrrole vapour. Homogeneous and thin conductive films were uniformly fabricated at nano level thickness. The polypyrrole obtained were characterized by cyclic voltammetry. Experimental parameters such as the Nafion concentration, polymerization time and current density were investigated. The parametric study has been investigated in order to synthesize homogeneous film in a reproductive manner.

Key words: Polypyrrole, gas phase, electrochemical deposition, cyclic voltammetry conductive polymer

INTRODUCTION

Conducting polymer such as pyrrole and aniline (Waltman *et al.*, 1984) are usually polymerised and simultaneously doped using electrochemical techniques. They can also be synthesized by chemical oxidative means, which can occur in the vapour phase. Among the conducting polymers of heterocyclic system (polypyrrole, polyaniline and polythiophene) as in Fig. 1, polypyrrole attracted most attention (Choi and Tachikawa, 1990; Christensen and Hamnett, 1990; Otero *et al.*, 1990; Novak, 1992).

The objective of this study is to make ultra thin uniform and homogeneous layers of polypyrrole film across redeposit electrodes.

Various methods of making ultra thin film across an insulating substrate have been made:

Presilanising substrate before electro deposition:

Polypyrrole (PPy) is known to be insoluble, infusible and intractable (film) after chemical or electrochemical formation. Pyrrole synthesis must be carried out directly onto a substrate material to overcome above poor mechanical properties. Electrochemically, PPy films can easily be prepared on conducting substrate (silane treated or non-silane) while chemical polymerization can be employed with insulator substrate such as glass or silica. Silane coupling agents are a broad class of surface modifying chemicals widely used as an adhesion promoter in composite materials. Organosilane treatment of the substrate promotes hydrophobic interaction, which are

important to obtain homogeneous and continuous thin PPy films. The preparation of conducting PPy-coated glass fibers in which the glass is treated with aminosilane before vapour pyrrole polymerization has been developed (Mittal, 1992; Perruchot *et al.*, 2000). The disadvantage of this technique is that organosilane is not environmental friendly.

Pulsed electrochemical deposition: Potential and galvanostatic pulse method for the deposition of conducting polymer on electrode surface is either potential or the current is change simultaneously from a value at which no monomer oxidation occurs at the electrode surface to a value above the monomer oxidation potential.

Partridge *et al.* (1996) electro deposited thin film of polypyrrole on microelectrode in which electro deposition current pulse is applied to the electrodes. The advantage of this method is that films are grown uniformly thin.

Spin coating: This is applying polymerizing solution on to the substrate and mechanically spins it around with a spin coater. This enables uniform thin coating to be formed on the substrate. A non-mechanical, electrostatic spinning (electrospinning) technique was recently developed by Huang *et al.* (1997) and Norris *et al.* (2000) when ultra fine fibers of polyaniline doped with camphorsulfonic acid and blended with polyethylene oxide were prepared. Kojima *et al.* (1997) prepared PPy/PVA/GOD composite on electrode spin-coated with PVA/GOD film by electropolymerisation of pyrrole.

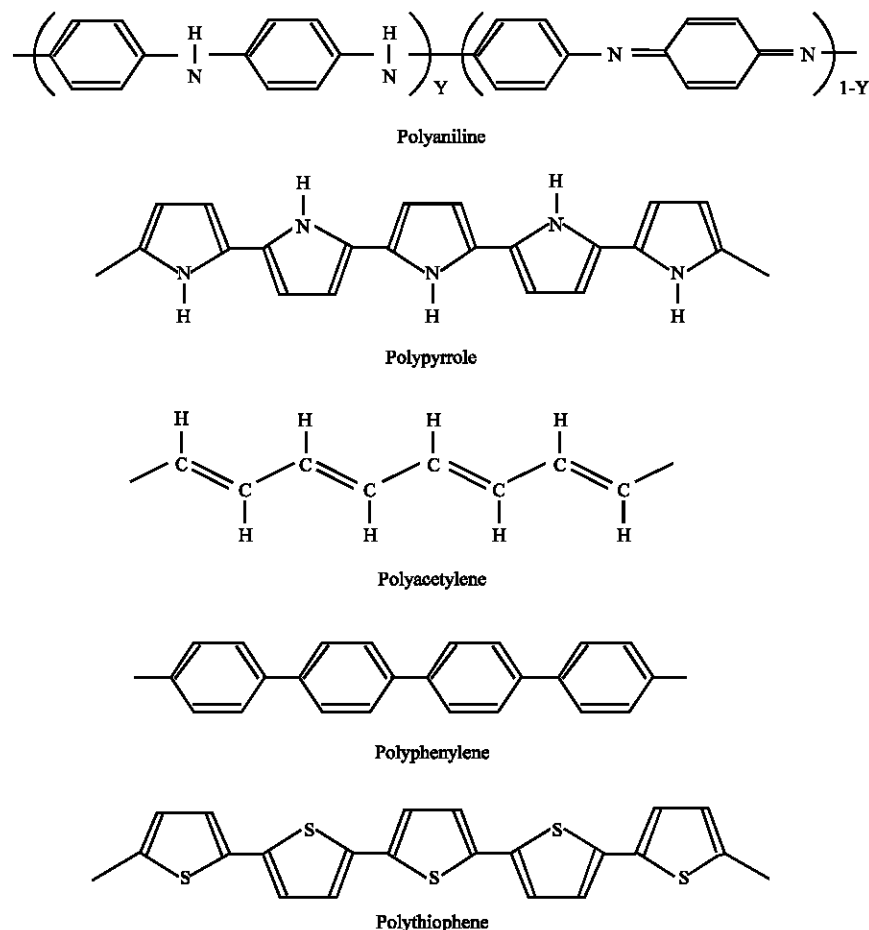


Fig. 1: Structure of some conducting polymers

Ink-jet printing: There are two main techniques of ink-jet printing: impulse and continuous. Impulse (or drop on demand) printing is used mainly in computer printers. In this method, ink droplets are squeezed when required, by application of an electrical signal, from an array of piezoelectric nozzles placed close to the substrate. In continuous technique, a continuous stream of identical ink droplets is emitted from ultrasonic nozzle operating at 64 kHz. Atkinson *et al.* (1997) used this method to print sol directly on ceramics.

In situ chemical polymerization occurs from single dips of substrate in to polymerizing aqueous solutions: Thin films of PPy were deposited *in situ* from aqueous solution of pyrrole onto the surface of various substrates. Thickness and morphology of deposited film were determined by atomic force microscopy (AFM). Avlyanov *et al.* (1997) and Wang and MacDiarmid (2001) made an *in situ* deposition of conducting polymer on

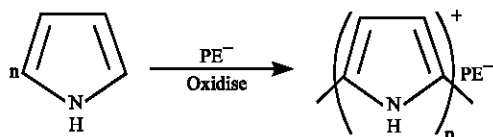
optical fiber to produce uniform thin film coatings. Poly-3, 4-ethylenedioxythiophene has been prepared on hydrophilic and hydrophobic substrate by the same group. Hohholz *et al.* (2001) and Khedkar and Radhakrishnan (1997) observed that the substrate speed during dip-coating process affects the film thickness. The limitation of this method is that only liquid solution of PPy can be deposited *in situ*.

In the study's attempts to get a better control of a thin film and uniformity of the polymer produced, a vapor phase electrochemical polymerisation of pyrrole was considered. This represented an area that has not been thoroughly investigated using electrochemical process.

In vapor phase chemical polymerisation, Khedkar and Radhakrishnan (1997) used polyethylene oxide (PE), Miyata (1986) and He *et al.* (1993) used poly (vinyl) alcohol as supporting substrate. He *et al.* (1993) also used polyurethane foam, while Najjar *et al.* (2007) and Tan and Ge (1996) used cotton thread and varied oxidants and

monomer concentration, temperature polymerisation time and solvent effects. Continuous vapour phase at a speed of 1.5 m min^{-1} was used by Xu (1995). While Najar *et al.* (2007) used 1 m min^{-1} . They all used ferric chloride as the oxidant. The disadvantage of Xu *et al.* (1995) method is that more gas are used up during electropolymerisation.

Polypyrrole (PPy) has been extensively investigated owing to its good environmental stability, high conductivity and ease of polymerisation. The properties of PPy, e.g., conductivity, strength and morphology obtained are very dependent on the dopants, conditions and mode of polymerisation employed. Various types of dopants have been incorporated into conducting polymers (CPs) during electrochemical polymerization (Adeloju and Moline, 2001; Bariscia *et al.*, 2002; Adeloju and Lawal, 2005; Ramanavièiusa *et al.*, 2005, 2006), i.e., paratoluensulfonate, tiron, polyvinylalcohol, methanesulfonate, octanesulfonate, butanesulfonate and polystyrenesulfonate (Wallace *et al.*, 2002) surfactants in solution. Sulfonated dyes have been incorporated into conducting polymers as counter ion to induce interaction with particular proteins. Complex and more delicate entities like antibodies, enzyme (Adeloju and Moline, 2001; Kueng *et al.*, 2004; Adeloju and Lawal, 2005; Chu *et al.*, 2007; Yu *et al.*, 2008) or carbon nanotubes (Wang, 2005; Rivas *et al.*, 2007) can also be directly incorporated as counter ions. Some polyelectrolytes (PE) are readily incorporated into a PPy during polymerisation according to:



Functional polyelectrolyte such as dextran sulfate chondroitin and heparin act as dopant, have been incorporated into polymer structure and they still retain their inherent bioactivity (Adeloju and Wallace, 1996).

Nafion, a polyelectrolyte also acts as dopant (counterion) in solution polymerisation. Nafion (perfluorinated sulfonate) a polymeric electrolyte has some of the following features common with other polyelectrolyte. Chemical stability, electrochemical stability, good range of conductivity, good mechanical properties and an easy method of preparation (Adeloju *et al.*, 1993).

In the course of this study we would like to report a systematic study of vapour phase electrochemical polymerisation of pyrrole using Nafion as the counterion. We investigated the effect of the following factors: Nafion

concentration, Current Density and Time. The expected benefits of this approach are that thin films are produced which will enable easy permeation during gas sensing. Thin films produced have strong adhesion to the substrate and films have high conductivity.

MATERIALS AND METHODS

Reagents and standard solutions: Pyrrole monomer (Aldrich) was redistilled and stored at -10°C Nafion (Aldrich) was used without any further purification. All other reagents were AR grade. All solutions were prepared using Milli-Q water.

Electrode preparation: The microelectrode vapour phase polymerisation set up is shown in Fig. 2. The electrode was fabricated by sealing a 50μ platinum wire in glass and sputter coating the outer glass wall with platinum to form counter electrode. The platinum disc electrodes were polished using $0.3 \mu\text{m}$ alumina (Leco) slurry on a micropolishing cloth (Buchler) and sonicated. Nafion was cast on to the working disc electrode and the ethanol evaporated at room temperature before electrochemical polymerisation in vapour phase. Electrode was placed in the cell where nitrogen was bubbled to the pyrrole monomer for vapour generation (Fig. 2) and subsequent vapour phase electrochemical polymerisation.

Instrumentation: Conducting polymer (polypyrrole) was grown on the 50μ working electrode galvanostatically using a Princeton Applied Research (PAR) Model363 Potentiostat/Galvanostat. Conducting polymer was also grown on a platinum disk electrode

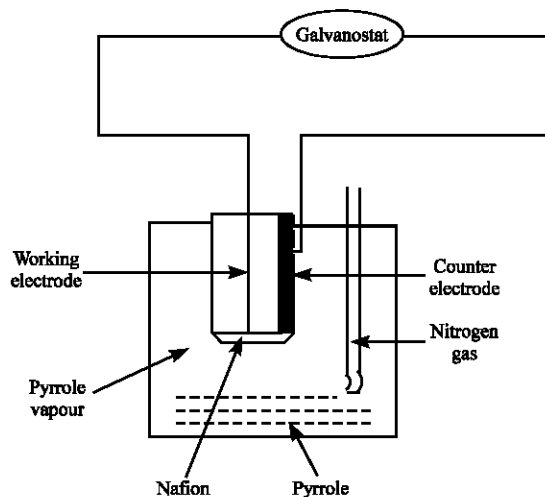


Fig. 2: Schematic diagram of vapour phase polymerization cell

(1 mm diameter) precoated with nafion and polymerization solution contains 0.5 M pyrrole and a current density of 1 mA cm^{-2} was applied for 6 min. A three-electrode system was employed for work in solution. A platinum gauss auxiliary electrode and Ag/AgCl (3 M NaCl) reference electrode were employed.

Cyclic voltammetry was recorded in 0.1 M NaNO_3 of the modified electrode. This was run on BAS 100 to monitor the polymer grown, its anodic current and the anodic potential recorded. The CV of bear electrode in 0.1 M NaNO_3 was ran before casting of Nafion and after the polymerisation to ensure there was no polymer on the electrode before subsequent gas phase polymerisation.

RESULTS AND DISCUSSION

The steps involved in electrochemical polymerisation of simple polypyrrole have been elucidated (Adeloluju *et al.*, 1993) and are shown in Fig. 3. In solution polymerisation the CV shows that it is electro active and the oxidation and reduction peaks is shifted when compared with the CV obtained in vapour phase

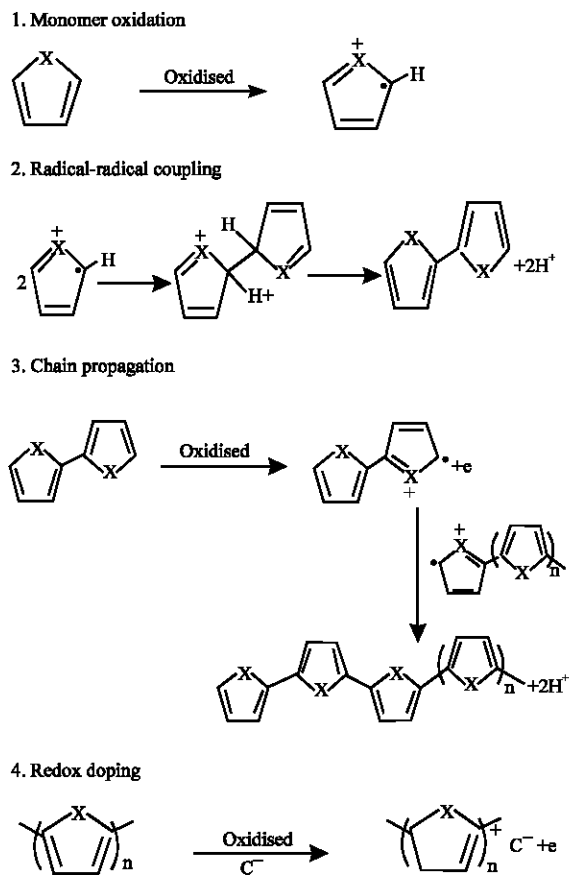


Fig. 3: Nucleation/growth mechanism for heterocyclic conducting polymers

(Fig. 4). In electrochemical oxidation of pyrrole, the oxidation potential, the concentration of monomer and counterions, polymerisation time and temperature play a role in determining the physical and chemical properties of the PPy. The reactants are transported to the electrode surface and the product (dimer, oligomers, polymer) are either deposited (film) or transported away from the surface. The presence of polyelectrolyte may affect one or both of these processes. The reproducibility of the PPy film is limited by the thickness and the porosity of Nafion film.

Nafion is adsorbed on the microelectrode before polymerisation is initiated. Sulfonate group within the Nafion complex act as counterions, facilitating the deposition of the conducting polymer (PPy/Nafion) (Fig. 5). A consistent procedure (of polymerisation) was adopted to ensure that the working electrode was placed at the same position in the cell (Fig. 2). We investigated the effect of Nafion concentration; polymerisation time, temperature and current density by running CV of Nafion/conducting polymer produced in 0.1 M NaNO_3 solutions.

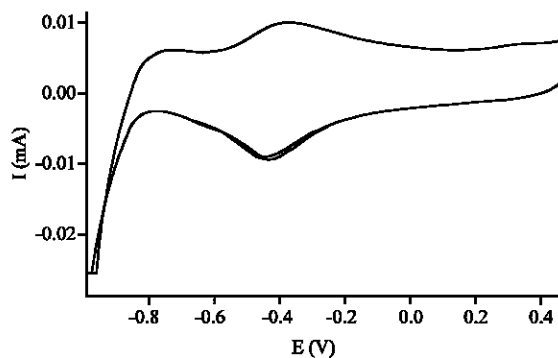


Fig. 4: Cyclic voltammogram of PPy/Nafion coated 1 mm Pt disc electrode in 0.1 M NaNO_3 solution

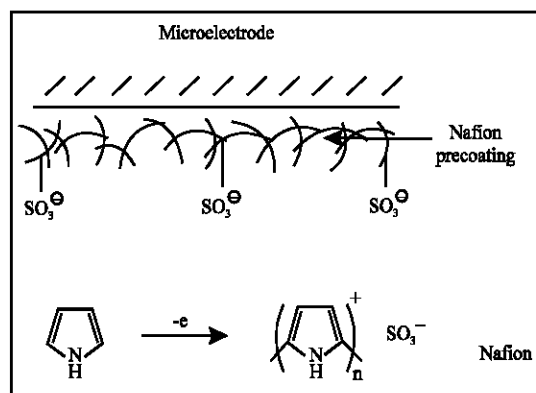


Fig. 5: Polymer-Nafion growth mechanism for heterocyclic conducting polymers

Table 1A: Effect of nafion concentration 50%nafion constant time (5 min)

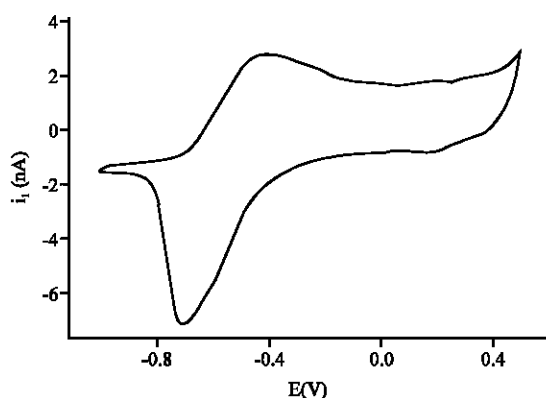
Current density (mA cm ⁻²)	Anodic current ip(a) (μA)	Anodic potential Ep(a) (V)	Cathodic current ip(c) (μA)	Cathodic potential Ep(c) (V)	ip(a)/ip(c)	Ep(a)-Ep(c) ΔEp
5	0.02	0.15	0.03	-0.49	0.80	0.64
10	0.958	-0.20	0.45	-0.43	2.09	0.23
20	1.37	0.20	0.50	-0.38	2.74	0.58
30	2.16	0.10	0.83	-0.70	2.60	0.80

Table 1B: Effect of nafion concentration 100%nafion constant time (5 min)

Current density (mA cm ⁻²)	Anodic current ip(a) (μA)	Anodic potential Ep(a) (V)	Cathodic current ip(c) (μA)	Cathodic potential Ep(c) (V)	ip(a)/ip(c)	Ep(a)-Ep(c) ΔEp
5	0.610	0.13	0.20	-0.01	3.05	0.14
10	0.78	0.15	0.50	-0.25	1.56	0.40
15	0.958	-0.16	0.70	-0.28	1.19	0.12
20	1.04	0.00	0.75	-0.32	1.38	0.32

Table 2: Effect of polymerisation time 75%nafion at 10 mA cm⁻²

Time (min)	ip(a) (μA)	Ep(a) (V)	ip(c) (μA)	Ep(c) (V)	ip(a)/ip(c)	ΔEp = Ep(a)-Ep(c)
5	1.20	-0.07	0.50	-0.38	2.4	0.31
10	1.25	0.09	0.66	-0.25	1.8	0.34
15	2.50	0.38	0.708	-0.40	2.8	0.78



Mode: Cyclic, Start Pot'l: 500 mV, End Pot'l: 500 mV, Rate: 100 mV sec⁻¹, Step W: 20 ms, Upper L: 500 mV, Lower L: 1000 mV, Cycles: 4

Fig. 6: Cyclic voltammogram of PPy/Nafion coated Pt disc microelectrode in 0.1 M NaNO₃ solution

The electrochemical properties of CP-PE display the expected oxidation-reduction response (Fig. 6). The anodic and cathodic peak current is measured as we varied the Nafion concentration, time of polymerisation, current density and temperature.

Effect of nafion concentration: Polypyrrole formation increases with increase in Nafion concentration 50% Nafion could not affect vapour polymerisation for more than 10 min but the anodic current increased as we increased the time. This could be due to the very thin Nafion film (Adeloju and Wallace, 1996). The 75% Nafion has better reproducibility than those of 100 and 50% in 5 min of polymerisation as seen in their change in ip (a) in Table 1A, 1B and 3B. This might be due to moderately thick nafion film produced by this concentration. This is in agreement with the trend of oxidant concentration used

by Tan and Ge (1996), He *et al.* (1993), Khedkar and Radhakrishnan (1997), Dall'Acqua *et al.* (2006) and Kaynak *et al.* (2008) in vapour-phase formation of polypyrrole, where the thickness of PPy formed increased with increasing concentration of Ferric chloride (Tan and Ge, 1996; Khedkar and Radhakrishnan, 1997; Dall'Acqua *et al.*, 2006; Kaynak *et al.*, 2008). Microelectrodes render voltammetry possible in moderately thick polyelectrolyte Nafion. There is higher anodic current in 75% Nafion compare to those of 100% and 50%. The anodic current increases in all the Nafion concentration as we increased the time and the current density.

Effect of polymerisation time: The thickness of pyrrole film formation increases with time as seen in the value of ip (a) in Table 2, the ip (a) increased as we increased the polymerization time. This shows that polypyrrole formation in vapour phase is fast and falls in the same trend obtained by Tan and Ge (1996), Khedkar and Radhakrishnan (1997) and Kaynak *et al.* (2008) in their vapour phase polymerization of polypyrrole.

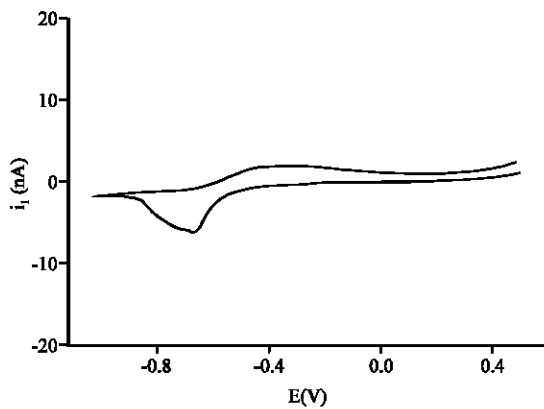
Effect of current density: As we increased the constant time, in Table 3A and B ip (a) and Fig. 7A, B, C the ip (a) increased with the increase in current density. At 10 min constant time, ip (a) increases from 1 to 2.7 μA and while in 5 min constant time ip (a) increases from 0.416 to 1.45 μA. This shows an increase in polypyrrole formation as we increased the current density. The formation of PPy is slower in vapour phase when compared to solution phase. Adeloju and Wallace (1996) deposited PPy film on electrode array using anodic current density of 0.05 mA cm⁻² for 1.5 min.

Table 3A: Effect of current density 75% nafion constant time (10 min)

Current density (mA cm ⁻²)	ip(a) (μA)	Ep(a) (V)	ip(c) (μA)	Ep(c) (V)	ip(a)/ip(c)	ΔEp = Ep(a)-Ep(c)
5	1.00	-0.08	0.60	-0.23	1.60	0.15
10	1.25	0.09	0.66	-0.25	1.80	0.34
15	2.50	-0.08	1.25	-0.50	2.00	0.42
20	2.70	0.18	1.45	-0.50	1.86	0.68

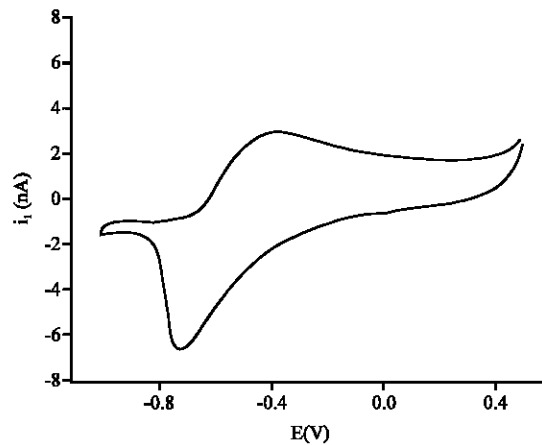
Table 3B: Effect of current density 75% nafion constant time (5 min)

Current density (mA cm ⁻²)	ip(a) (μA)	Ep(a) (V)	ip(c) (μA)	Ep(c) (V)	ip(a)/ip(c)	ΔEp = Ep(a)-Ep(c)
5	0.416	-0.33	0.625	-0.60	0.66	0.27
10	0.833	-0.33	1.60	-0.57	0.718	0.24
15	0.96	-0.30	1.25	-0.57	0.76	0.27
20	1.45	-0.02	1.33	-0.20	1.09	0.18



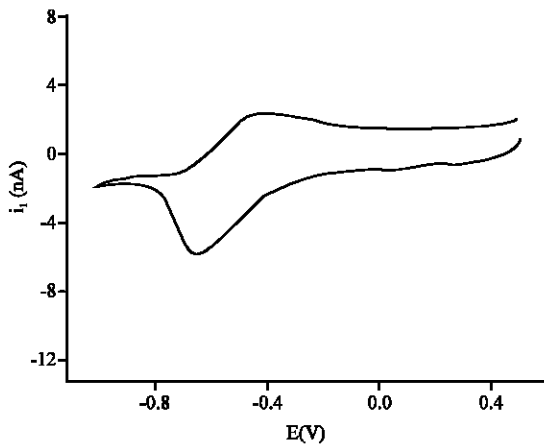
Mode: Cyclic, Start Pot'l: 500 mV, End Pot'l: 500 mV, Rate: 100 mV sec⁻¹, Step W: 20 ms, Upper L: 500 mV, Lower L: -1000 mV, Cycles: 4 (4:13 PM, Mon, Aug 19, 1996)

Fig. 7A: Cyclic voltammogram of PPy/Nafion coated Pt disc electrode made at 5 mA cm⁻² 15 min in 0.1 M NaNO₃ solution



Mode: Cyclic, Start Pot'l: 500 mV, End Pot'l: 500 mV, Rate: 100 mV sec⁻¹, Step W: 20 ms, Upper L: 500 mV, Lower L: -1000 mV, Cycles: 4 (7:18 PM, Fri, Aug 16, 1996)

Fig. 7C: Cyclic voltammogram of PPy/Nafion coated Pt disc electrode made at 8 mA cm⁻² 20 min in 0.1 M NaNO₃ solution



Mode: Cyclic, Start Pot'l: 500 mV, End Pot'l: 500 mV, Rate: 100 mV sec⁻¹, Step W: 20 ms, Upper L: 500 mV, Lower L: -1000 mV, Cycles: 2 (2:18 PM, Mon, Aug 19, 1996)

Fig. 7B: Cyclic voltammogram of PPy/Nafion coated Pt disc electrode made at 5 mA cm⁻² 20 min in 0.1 M NaNO₃ solution

Effect of temperature: The effect of temperature on polymerisation of pyrrole was greater when the temperature was above 60°C (Table 4). When the temperature was lower than 60°C there could be two possible causes for the low anodic and cathodic current of the PPy/Nafion in NaNO₃, first the vapour pressure of pyrrole was low at low temperature, which reduced the pyrrole concentration in the vapour phase, so that less PPy was produced. Secondly the diffusion of pyrrole vapour in Nafion was slow at low temperature so that less PPy was produced. The low diffusion rate could lead to formation of PPy with a structure in favour of low anodic and cathodic current. While when the temperature was high, the vapour pressure of pyrrole was high and the rate of diffusion was high so that there was increase in PPy formation. This is contrary to general trend of chemical polymerization occurring in solution in which the conductivity of PPy is enhanced at lower temperature (Adelolu *et al.*, 1993). This is also in contrast with

Table 4: Effect of polymerisation temperature

Temp. (°C)	ip(a) (µA)	Ep(a) (V)	ip(c) (µA)	Ep(c) (V)	ip(a)/ip(c)	ΔEp = Ep(a)-Ep(c)
25	0.437	0.05	0.34	-0.62	1.280	0.67
40	0.479	-0.37	0.83	-0.56	0.577	0.20
60	0.489	-0.29	0.84	-0.62	0.582	0.23
80	0.560	-0.30	1.21	-0.56	0.462	0.28

electrochemical polymerisation of polypyrrole dodecylsulfate, which was prepared at 5 and 10°C. This shows better electroactivity, a homogenous surface and globular surface morphology (Bocchi *et al.*, 1987).

CONCLUSIONS

A high uniform PPy coating was formed via vapor phase electrochemical polymerisation on the substrate electrode through porous Nafion (polyelectrolyte) Nafion has been used as dopant and optimum concentration with better reproducibility was 75%. The formation of polypyrrole increased as we increased polymerizing time and current density. High temperature above 60°C also supported increase in electroformation of polypyrrole.

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