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Greener method for high-quality polypyrrole

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Abstract

Conducting polypyrrole has been synthesized *via* a simple metal catalyzed process. The oxidative polymerization of pyrrole using hydrogen peroxide and a catalytic amount of iron(III) in an acidified aqueous medium afforded conducting polypyrrole in very good yield. The copper(II) or cerium(IV) catalyzed reactions under similar conditions gave poor yields. The iron(III) catalyzed reaction carried out in the absence of the acid produced low-quality polypyrrole that contain hydroxyl and carbonyl groups resulting from the nucleophilic attack of water or hydroxyl radicals.

Keywords: Polypyrrole; Catalyst; Conducting

1. Introduction

First reported in 1979 polypyrrole (PPY) stands out to be the most widely studied electronically conductive polymer [1–8]. Due to its favourable electronic properties, environmental stability and fast redox switching, polypyrrole finds applications in batteries, electronic devices, functional electrodes, electrochromic devices, optical switching devices, sensors and in many other advanced technologies [9,10]. PPY can be prepared by electrochemical as well as by wet chemical methods. Plasma polymerization [11], chemical vapour deposition (CVD) [12], and metal mediated electrochemical methods [13] are also available to obtain electronically conductive polypyrrole. Unlike these methods, wet chemical processes are in general, simpler and more amenable to bulk PPY production. Chemical synthesis of polypyrrole involves an oxidative polymerization route in which the use of oxidants such as Fe^{3+}, Ag^{+}, I_2, Br_2, AsF_5 or Cu^{2+} has been reported [14–17]. Out of all these oxidants, Fe^{3+} tends to give very good quality and highly conductive PPY powder.

The chemical synthetic routes mentioned above require more than stoichiometric amount of oxidants. For example, 1:2.5 to 1:3 molar ratio of monomer:oxidant is typically used when Fe^{3+} or Cu^{2+} is used as oxidants to polymerize pyrrole. This is an obstacle that would impede the widespread utilization of polypyrrole. To address this issue, environmentally and economically preferred catalytic polymerization pathways have been explored. One such catalytic approach is the use of enzymes to generate conducting polymers [18,19]. However, it was found that in aqueous media, enzymatic polymerization of aromatic molecules leads to the formation of low molecular weight oligomers that precipitate out easily. In order to circumvent this problem, organic solvents have been added to the aqueous medium. Furthermore, in the absence of water-soluble polyelectrolytes, branched polymeric chains of the conjugated polymers are formed which significantly lowers the conductivity. Recently, a greener route to conductive polypyrrole in an aqueous medium using the metalloenzyme Laccase was reported [20].

We have been interested in the development of environmentally benign routes to PPY and other conducting polymers. Preferred methods would use minimum amounts of the

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oxidant to yield high-quality polymer and regenerate the oxidant using harmless chemicals such as air, oxygen gas or hydrogen peroxide in an aqueous medium. The only byproduct expected in this way is water. In this respect, Toshima and Tayanagi [21] have demonstrated the use of $AlCl_3$, CuCl and molecular oxygen to catalytically polymerize pyrrole to polypyrrole. This route, however, produces a polymer that contains covalently bonded chlorine, carbonyl and C–OH groups on carbon which render a dramatic reduction of the electronic conductivity. Toshima and Ihata [22] have later shown that iron(III) catalyst together with molecular oxygen could be used to catalytically polymerize pyrrole leading to polypyrrole. The FT-IR spectrum of their product, however, contains a strong absorption at about 1700 cm^{-1} suggesting the nucleophilic attack of the water and the hydroxyl anion during polymerization. The high yield and high electrical conductivity were obtained when organic solvents with high dielectric constant were used. When water was used the conductivity of the polymer obtained was around 0.1 mS cm^{-1}. In this paper, we describe the preparation of highly conductive polypyrrole using catalytic amounts of Fe^{3+} as an oxidant and hydrogen peroxide in aqueous HBF_4 medium as the regenerator of the catalyst. The use of Cu^{2+} and Ce^{4+} catalysts was also investigated.

2. Experimental

2.1. Materials

All chemicals used were purchased from Aldrich and are of highest available purity. Pyrrole used was distilled under reduced pressure and stored at 4 °C, in a sealed-ampoule covered with an aluminum foil, under an inert atmosphere. Other chemicals used were of high purity (Aldrich Analytical Grade) and were used without further purification. Water used was distilled and deionized through Milli-Q water purification system.

2.2. Polypyrrole synthesis

A 0.671 g (1.0×10^{-2} mol) of freshly distilled pyrrole was placed in a 50-mL round-bottom flask at ~−5 °C, and stirred vigorously. An aqueous solution (20 mL) containing $FeCl_3 \cdot 6H_2O$ (0.162 g, 6.0×10^{-4} mol) and HBF_4 (2.20 g, 48 wt% in H_2O, 1.2×10^{-2} mol) was added slowly through a dropping funnel. The resulting mixture immediately turned blue with the formation of a black precipitate. A 30 mL aqueous solution of H_2O_2 (2.43 g, 35 wt% in H_2O, 2.5×10^{-2} mol) was placed in a dropping funnel and a 12 mL portion of was added drop wise to the flask; the rest of the H_2O_2 solution was added in 6 mL portions at regular intervals of 1 h each. The reaction was allowed to proceed for further 90 min (i.e., for 4 h and 30 min in total) at −5 °C. The black precipitate obtained was recovered by vacuum filtration. The precipitate was washed with a copious amount of distilled water until the effluent was colourless (~300 mL). The precipitate was dried in the oven (~70 °C) up to a constant weight. The reaction gave 0.773 g of shiny dark solid which is designated as polypyrrole A.

Other polypyrrole samples were also prepared in an identical manner but changing either the catalyst or its concentration but keeping all other parameters constant. Thus, polypyrrole samples designated as B and D were prepared by using 0.380 g of $(NH_4)_4Ce(SO_4)_4 \cdot 2H_2O$ (6.0×10^{-4} mol) and 0.102 g of $CuCl_2 \cdot 2H_2O$ (6.0×10^{-4} mol). The only difference in these three samples is the nature of the catalyst, which is $FeCl_3 \cdot 6H_2O$ for A, $(NH_4)_4Ce(SO_4)_4 \cdot 2H_2O$ for B and $CuCl_2 \cdot 2H_2O$ for C. The amounts and all other conditions have been kept constant. For the samples D, E, and F, 0.162 g of $FeCl_3 \cdot 6H_2O$ (6.0×10^{-4} mol) was used as in the procedure for the preparation of polypyrrole A. However, the amounts of acid (HBF_4, 48% in water) and/or H_2O_2 (35% in H_2O) were changed. Thus the sample D was prepared by taking 5.50 g (3.0×10^{-2} mol) of HBF_4 (48% in water) and 3.89 g (4.0×10^{-2} mol) of H_2O_2 (35% in H_2O). For the sample E the acid used was 1.2×10^{-2} mol as in A but 3.89 g (4.0×10^{-2} mol) of H_2O_2 (35% in H_2O) as in D. Sample F was prepared by taking 5.50 g (3×10^{-2} mol) of HBF_4 (48% in water) as in D but 2.43 g of H_2O_2 (35 wt% in H_2O, 2.5×10^{-2} mol) as in A.

2.3. Characterization techniques

The products obtained were characterized by FT-IR spectroscopy (JASCO FT/IR-410), Electrochemical methods (Electrochemical Impedance Spectroscopy using CH Instruments Electrochemical Analyzer), Elemental Analysis (PE-2400, Series II), and by Bulk Conductivity measurements using the standard Four-Point Probe method. The morphologies of the polymer samples were observed from scanning electron micrographs (SEM) which were recorded using a ZEISS Supra 55 VP Scanning Electron Microscope.

The FT-IR spectra were recorded by preparing polypyrrole–KBr pellets using 1:20 mass ratio of polypyrrole:KBr. Electrochemical impedance spectroscopic (EIS) studies of polypyrrole samples were performed as follows. Freshly synthesized samples were allowed to dry under laboratory environment. Then a liquid-like paste was prepared using PPY and concentrated H_2SO_4 solution and a drop of this solution was placed carefully on the Pt tip of the Pt disc electrode (CH Instruments, $r = 1$ mm) or a few drops were allowed to spread on a pre-cleaned ITO (Indium doped tin oxide, resistivity 10 Ω cm^{-1}) to obtain a thin film of ~0.1 mm thickness. EIS studies were performed using three-electrode configuration in one-compartment cell. The background electrolyte used was a dry nitrogen purged 0.1 mol dm^{-3} H_2SO_4(aq) solution and the reference electrode used is Ag(s)/AgCl(s)/KCl(aq, saturated) ($E° = +0.222$ V at 298 K with respect to SHE) and the counter electrode is a Pt wire sealed in kel-F (CH Instruments). The EIS spectra were recorded at selected DC potentials with a constant 10 mV AC perturbation in the frequency domain 0.1 mHz to 10 MHz. The Nyquist plots obtained were analyzed using the dual-rail transmission line model proposed by Albery et al. [23–27] and further perfected by Ren et al. [28–31].

3. Results and discussion

3.1. *Effect of oxidant in the catalytic polymerization of pyrrole*

The polymerization of pyrrole using hydrogen peroxide can be accomplished using all three catalysts, *viz*., Fe^{3+}, Ce^{4+} and Cu^{2+}, though the yields obtained during 4 and 1/2 h of reaction time under the conditions stated in Section 2 are not the same for the three catalysts. The preparative conditions of these samples A−F together with polypyrrole yields obtained are summarized in Table 1.

The yield obtained (based on the amount of monomer used) with Fe^{3+} as the catalyst is the highest (80%−90%; see PPY A, D, E, and F), and that with Ce^{4+} is low (<18%), but with Cu^{2+} it is very poor (∼4%). The yields for polymers B (from Ce^{4+} catalyzed process) and C (from Cu^{2+} catalyzed process) were calculated assuming that their chemical structures were similar to those of polymer A. However, for polymer B, the elemental analysis suggested the presence of ceric residues, as already pointed out in the syntheses of related polymers (i.e., polythiophenes) when strong ceric oxidants have been used [32]. The reaction carried out under identical conditions as those for polymer A, but in the absence of any catalyst (i.e., pyrrole, HBF_4 acid and H_2O_2 in water) did not give any precipitate, but only a dark solution. The darkening of the solution indicates a slow polymerization process possibly initiated by acid as reported by Salmon et al. [33]. The standard electrode potentials of Pt/Fe^{3+}(aq), Fe^{2+}(aq), H^+(aq); Pt/Ce^{4+}(aq), Ce^{3+}(aq); Pt/Cu^{2+}(aq)/Cu(s) and Pt/H_2O_2(aq), H_2O(l), H^+(aq) at 298 K are +0.77 V, +1.61 V, +0.34 V and +1.78 V, respectively [34]. The polymerization of pyrrole follows oxidative initiation step and the standard electrode potential for Pt/pyrrole, pyrrole radical cation is around +0.70 V [35]. Since the concentrations of the acid and the oxidized form of the redox couple are the same in all three cases, it can be assumed that the standard electrode potentials reflect the thermodynamic tendency of H_2O_2 to regenerate the oxidized form of the catalyst in each case. In pure thermodynamic perspective hydrogen peroxide is also capable of polymerizing pyrrole but the kinetic limitations disfavor the reaction. Both Fe^{3+}(aq) and Ce^{4+}(aq) are indeed capable of polymerizing pyrrole and the minute amount of these oxidants used does the reaction. The hydrogen peroxide present in the medium regenerates the oxidized form of the metal ion, and the polymerization cycle continues. The relative yields of the polymer obtained in these two cases show the tendency of hydrogen peroxide to regenerate the oxidized form: it is much easier to regenerate Fe^{3+} from Fe^{2+} than to regenerate Ce^{4+} from Ce^{3+}. In the case of Cu^{2+} as the oxidant, there are three possible redox couples, Cu^{2+}(aq)/Cu(0); Cu^{2+}(aq), Cu^+(aq) and Cu^+(aq)/Cu(0) though Cu^+ is highly unstable in the aqueous medium. Their standard electrode potentials at 298 K are +0.34 V, +0.16 V and +0.54 V, respectively [34]. It is, therefore, obvious that Cu^{2+} on its own is incapable of producing polypyrrole from pyrrole. However, Cu^{2+} can act as a homogeneous catalyst to facilitate the decomposition of hydrogen peroxide by decreasing the activation energy for the oxidative

Table 1
Preparative conditions for polypyrrole samples A−F together with percentage yields obtained

PPY	A	B	C	D	E	F
Amount of pyrrole used	0.671 g (1.0×10^{-2} mol)	0.671 g (1.0×10^{-2} mol)	0.671 g (1.0×10^{-2} mol)	0.671 g (1.0×10^{-2} mol)	0.671 g (1.0×10^{-2} mol)	0.671 g (1.0×10^{-2} mol)
Amount and nature of catalyst used	0.162 g of $FeCl_3 \cdot 6H_2O$ (6.0×10^{-4} mol)	0.380 g of $(NH_4)_4Ce(SO_4)_4 \cdot 2H_2O$ (6.0×10^{-4} mol)	0.102 g of $CuCl_2 \cdot 2H_2O$ (6.0×10^{-4} mol)	0.162 g of $FeCl_3 \cdot 6H_2O$ (6.0×10^{-4} mol)	0.162 g of $FeCl_3 \cdot 6H_2O$ (6.0×10^{-4} mol)	0.162 g of $FeCl_3 \cdot 6H_2O$ (6.0×10^{-4} mol)
Amount of acid HBF_4 (48 wt% in water) used	2.20 g (1.2×10^{-2} mol)	2.20 g (1.2×10^{-2} mol)	2.20 g (1.2×10^{-2} mol)	5.50 g (3.0×10^{-2} mol)	2.20 g (1.2×10^{-2} mol)	5.50 g (3.0×10^{-2} mol)
Amount of H_2O_2 (35 wt% in water) used	2.43 g (2.5×10^{-2} mol)	2.43 g (2.5×10^{-2} mol)	2.43 g (2.5×10^{-2} mol)	3.89 g (4.0×10^{-2} mol)	3.89 g (4.0×10^{-2} mol)	2.43 g (2.5×10^{-2} mol)
% Yield based on monomer	86%	<18%	∼04%	87%	85%	82%
% Yield based on catalyst	1433%	<300%	∼67%	1450%	1417%	1367%

The total volume of the reaction mixture, temperature, and reaction time are 50 mL, −5 °C, and 4.5 h, respectively.

polymerization of pyrrole by hydrogen peroxide. This could explain the reason as to why Cu^{2+}/H_2O_2 system gave some polymer though the yield was very poor. The poor yield obtained in 4 and 1/2 h is probably due to kinetic limitations.

It is interesting to compare the percentage yields of Fe^{3+} catalyzed process under different conditions (see PPY A, D, E and F). The increase of acid concentration or hydrogen peroxide concentration or both hardly shows any effect on the percentage yields obtained when the monomer and the catalyst concentrations were held constant. This is because the amount of hydrogen peroxide used in case A is sufficient to regenerate required amount of Fe^{3+}(aq) to polymerize almost all monomer present. The amount of acid used in this case is sufficient to keep the medium acidic enough to accelerate the polymerization reaction by activating the α-C in the pyrrole moiety. The absence of carbonyl or hydroxyl bands in the FT-IR spectra (*vide infra*) confirms the role of acid in preventing the nucleophilic attack of pyrrolium radical cations produced by water molecules. The nucleophilic attack of water on the polymer during its polymerization is a serious problem in the preparation of conducting polymers (particularly polypyrrole) from the aqueous medium [36]. The procedure developed in this work successfully solves this problem as well.

3.2. Characterization of the polymers obtained

Since the best yield is obtained when a catalytic amount of Fe^{3+}(aq) and H_2O_2 is used in the polymerization of pyrrole the further characterizations have been done with polymers obtained by this method, i.e., polypyrrole samples A, D, E and F. Table 2 shows the most probable molecular formulae calculated through elemental analysis data together with bulk conductivity values of the samples.

The molecular formulae closely resemble the partially oxidized conducting form of polypyrrole carrying one polaron per four monomer units in the polymer. It is interesting to note that despite the repeated excessive washings of the products obtained the polymer samples seem to contain some trapped acid in its conducting form. The FT-IR spectra of these samples also have the "tail of the electronic absorption band" (see below).

Table 2
The most probable molecular formulae calculated through elemental analysis data together with bulk conductivity values of polypyrrole samples prepared using pyrrole, HBF_4 and Fe(III)/H_2O_2 with different molar ratios

PPY	Most probable molecular formulae	Conductivity/S cm^{-1}
A	$[C_4N_1H_{3.294}(BF_4)_{0.265}Cl_{0.040}]_n$	0.99
D	$[C_4N_1H_{3.474}(BF_4)_{0.300}Cl_{0.018}]_n$	0.08
E	$[C_4N_1H_{3.369}(BF_4)_{0.260}Cl_{0.040}]_n$	0.20
F	$[C_4N_1H_{3.519}(BF_4)_{0.310}Cl_{0.019}]_n$	0.11

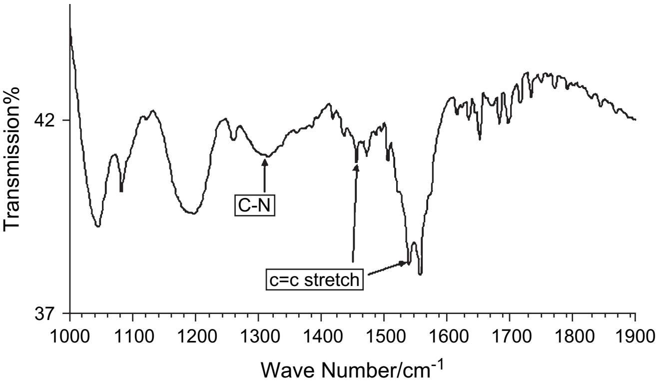

Fig. 1. Typical FT-IR spectrum of polypyrrole samples in 1000–2000 cm^{-1} region.

Fig. 1 shows the characteristic FT-IR spectrum of polypyrrole samples obtained. The presence of conjugated π-electron system gives broad bands in the FT-IR spectrum of electronically conductive polymers. The broad band in the range 4000–2000 cm^{-1} which is known as "tail of the electronic absorption band" is characteristic of the conducting form of polypyrrole is clearly visible in our polymer samples [37]. The bands centered at 1550 cm^{-1} and 1480 cm^{-1} can be assigned to be due to C═C (str.) vibrations [37]. The shoulder at 1385 cm^{-1} is due to N–C (str.) vibration and that at 1300 cm^{-1} is due to deformation vibration [37]. The absence of strong absorption around 1700 cm^{-1} and at 1600 cm^{-1} indicates the absence of carbonyl groups whether isolated or conjugated [37]. The strongly acidic medium prevents the nucleophilic attack of water molecules or hydroxyl radicals with the polymer backbone thus enabling the formation of extendedly conjugated polymer. The acidic medium also stabilizes Fe(III) in the aqueous medium or otherwise Fe(III) tends to precipitate as $Fe(OH)_3$(s) due to its hydrolysis. The control experiment involving the identical PPY A synthesis conditions but *without* the HBF_4 gave 0.238 g of black precipitate containing polypyrrole and $Fe(OH)_3$. The IR spectrum of this PPY gave a strong and large band at 1685 cm^{-1} indicating the presence of carbonyl groups. Thus good quality polypyrrole can only be produced from aqueous medium if the medium is sufficiently acidic.

The Scanning Electron Micrograph (SEM) of the PPY samples F is depicted in Fig. 2. It is characterized by uniform

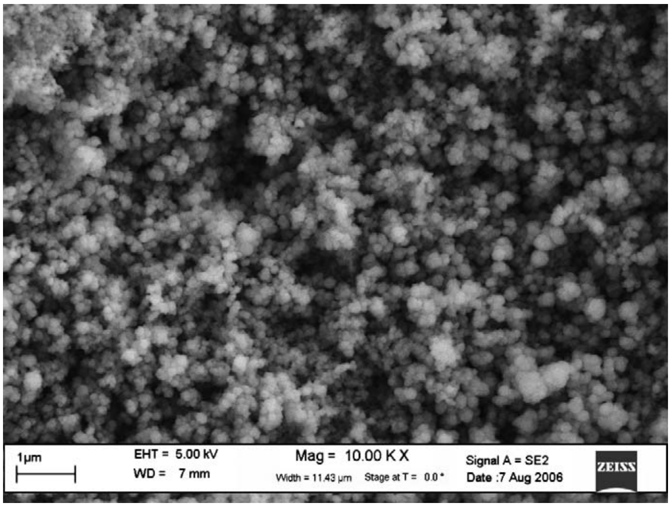

Fig. 2. SEM image of polypyrrole sample F.

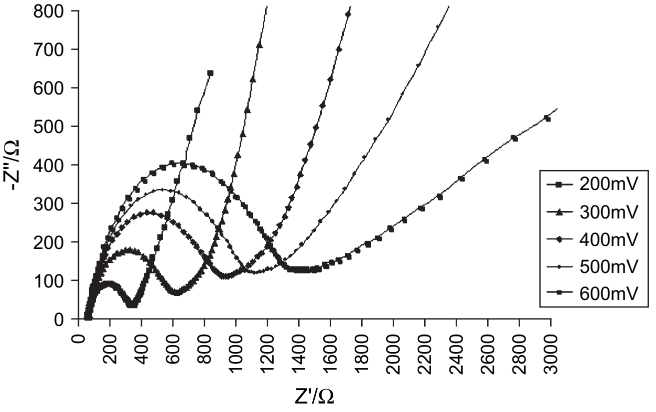

Fig. 3. The Nyquist plots for PPY F electrode in 0.1 M H_2SO_4 at specified DC potentials. The reference and counter electrodes are Ag(s)/AgCl(s)/KCl(aq, 3 M) [$E = 0.222$ V at 298 K] and Pt wire, respectively.

texture of surface morphology where dark spots represent porous areas while the white spots indicate material surface. As is clearly visible in Fig. 2 the pores are distributed homogeneously in this sample allowing ready access to solution species in all directions. This may enable a faster mobility for ions within the polymer. Indeed, the electron transport kinetics of the sample is fast as confirmed by electrochemical impedance spectroscopy (see Fig. 3). The surface morphology seen from SEM pictures of samples A, D, and E is not very different from that observed for sample F. They all show mushroom type structure with some variations in sizes and shapes of black and white areas.

3.3. Electrochemical Impedance Spectroscopic studies of polypyrrole samples

The Electrochemical Impedance Spectroscopic (EIS) studies provide further useful information on the nature of electronic and ionic conductivities of the polypyrrole samples. Fig. 3 depicts the Nyquist plots for PPY F (prepared using Fe(III)/H_2O_2) in 0.1 M H_2SO_4 in the frequency range 1 mHz to 10^5 Hz at specified constant DC potentials superimposed with 5 mV AC potential amplitude. The trends look the same for samples A, D, and E. The experiments were performed in three-electrode configuration where the Ag(s)/AgCl(s)/KCl(aq, 3 M) [$E = 0.222$ V at 298 K] and Pt wire served as the reference and counter electrodes, respectively.

The plots have a common shape of a high-frequency semicircle, intermediate frequency 45° line representing the "classical" finite-length Warberg diffusion element Z_D, and a low-frequency almost vertical capacitive line. The last two features are the typical impedance behaviour of an ideal dual-rail transmission line model proposed to account for the impedance behaviour of electronically conducting polymers. The first intercept on the x-axis is, typically, due to the solution resistance R_s. It is independent from the applied potential for a given cell configuration and is typically 50 Ω for our system. The Z_D is characterized by the diffusional time constant (τ_D), the diffusional pseudo capacitance (C_D) and the diffusion resistance R_D, where $R_D = \tau_D/C_D$ and the quantitative relationship between Z_D and the its characteristic circuit elements is given by:

$$Z_D = \frac{\tau_D}{C_D}\frac{\coth(j\omega\tau_D)^{1/2}}{(j\omega\tau_D)^{1/2}}, \quad \text{where } j = \sqrt{-1},$$

the angular frequency $\omega = 2\pi f$ where f is the linear frequency in Hz.

The intermediate frequency linear relation with 45° inclination is due to the ion diffusion control and the vertical pure capacitive region at $\omega \to 0$, is due to the limitations of ion diffusion in the film. The difference between the intermediate and low-frequency limiting real impedance values ($R_{\text{high}} - R_{\text{low}}$) is one-third of the polymer film's ionic resistance R_I. The factor of one-third comes from the approximation for the $\coth(j\omega\tau_D)^{1/2}$ at small values of $(j\omega\tau_D)^{1/2}$ (note that $\coth x = 1/x + x/3$ for small x). As $\omega \to \infty$, the semicircle observed in the Nyquist plot has been assigned due to the kinetic control corresponding to the rate-determining region of charge transfer. The diameter of the semicircle thus gives the resistance for interfacial electron transfer, R_ρ. The R_ρ and R_I calculated at various DC potentials are shown in Table 3.

The data reveal that the polymer is in its highly conductive partially oxidized form at DC potentials in the range of +300 to +600 mV (with respect to SHE). Increasing the potential overoxidizes the polymer decreasing its electronic conductivity. The ionic conductivity also follows the same trend. Similar trend is observed in the negative DC potentials (not shown in the figure). At sufficiently positive potentials polypyrrole is in its conducting state but lowering the potential injects electrons to the polymer, resulting in the formation of the neutral non-conducting form of polypyrrole. At sufficiently negative potentials (below −700 mV) the EIS spectra do not follow the usual trend shown above. The polymer is too resistive to conduct electrons and hence current sampling is not possible. The results are in very good agreement with the potential dependent electrical conductivity reported for electrochemically prepared polypyrrole.

Table 3
The solution resistance R_s, electron transfer resistance R_ρ and ionic resistance R_I calculated at various applied DC potentials for PPY F [prepared using Fe(III)/H_2O_2] electrode

DC potential/mV [with respect to Ag(s)/AgCl(s)/KCl (3 M, aq)]	DC potential/mV [with respect to SHE]	R_s/Ω	R_ρ/Ω	R_I/Ω
+200	+422	54	280	138
+300	+522	54	648	750
+400	+622	54	946	1989
+500	+722	52	1180	2721
+600	+822	51	1539	5271
+700	+922	54	2509	14,550

4. Concluding remarks

A catalytic method is presented for the large scale synthesis of polypyrrole from the aqueous medium. The best catalyst is found to be Fe(III) and 1:0.06 molar ratio of monomer to catalyst is sufficient to effect the reaction. The catalyst can be regenerated in acidic medium using H_2O_2. The regenerator alone is thermodynamically capable of polymerizing pyrrole, but kinetic limitations hinder the reaction. The polymer formed is free from nucleophilic attack of water or hydroxyl radicals due to the acidity of the medium. The reaction carried out in the absence of acid generates iron(III) hydroxide and low-quality polymer containing hydroxyl and carbonyl groups. FT-IR, bulk conductivity measurements using the Four-Probe Technique and the Electrochemical Impedance Spectroscopy are in good agreement providing evidence for the formation of good quality of polypyrrole. Some polymer samples show electronic conductivities around $1\ \mathrm{S\,cm^{-1}}$ (Table 2). We are presently developing environmentally benign routes to other types of conducting polymers.

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