

## Impact of *p*-Toluenesulfonate on Polypyrrole–Cobalt Catalyst for Oxygen Reduction Reaction

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**ABSTRACT:** Polypyrrole (PPy) and polypyrrole *p*-toluenesulfonate (PPy/pTS) supported cobalt (Co) catalysts have been synthesized using *in situ* surfactant modified chemical oxidative polymerization. These catalysts have been characterized for their structure and electrocatalytic activity employing FT-IR, Raman, SEM, HRTEM, and electrochemical techniques. The influence of pTS on the morphology and oxygen reduction reaction (ORR) activity has been discussed in respect of the formation of polaronic and bipolaronic species. The impact of these species on the electrochemical performance has been studied using continuous cycling in acidic media. Overall, PPy/pTS-Co is found to be the best suitable candidate among the catalysts synthesized for this study and can become an attractive substitute as a non-noble catalyst material for cathode applications in fuel cells. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 2645–2651, 2013

**KEYWORDS:** batteries and fuel cells; catalysts; composites

Received 8 March 2013; accepted 25 April 2013; Published online 30 May 2013

DOI: 10.1002/app.39467

### INTRODUCTION

Fuel cells have been acknowledged as an environment friendly energy source and possess high power density for a wide range of technological applications. Among all the various types of fuel cells,<sup>1</sup> proton exchange membrane fuel cell (PEMFC) is believed to be the most favorable for transportation applications because of its fast startup and immediate response to changes in the demand for power and its tolerance to shock and vibration due to plastic materials and an immobilized electrolyte.<sup>2</sup> In PEMFC, platinum (Pt) is being utilized as the oxygen reduction catalyst with a much higher loading because of the very sluggish kinetics involved in oxygen reduction at cathode in comparison to the hydrogen oxidation at anode. It is well-known that Pt is not only expensive but also very scarce in resources. As a result, the so far exclusive dependence of PEMFC on Pt has been one of the major obstacles to the commercialization of this attractive new energy technique. The essential solution to this problem can be overcome by replacing the widely applied Pt with non-Pt or non-noble catalyst materials. This has attracted growing research interests during the recent years. Hence, a vital task for the commercialization of the energy conversion devices is the development of active and low-cost catalyst materials for oxygen reduction reaction (ORR).

Since Jasinski's discovery of the catalytic properties of cobalt (Co) phthalocyanines as a cathode catalyst for fuel cells,<sup>3</sup> there

has been increased research on non-precious metal catalysts such as transition metal macrocyclic compounds (e.g., Co-porphyrins<sup>4–6</sup> and iron (Fe)-porphyrins<sup>7–9</sup>) and transition metal complexes.<sup>10–13</sup> Nonetheless, transition metal whether or not is a part of the catalytic site is arguable and is of major part of discussion in the non-precious metal catalyst developing research community.<sup>14,15</sup> The ORR activity of these types of catalyst has been believed to originate from the metal–N<sub>x</sub> sites.<sup>16,17</sup> Various framework has been studied to understand the catalytic sites for ORR in presence<sup>9,14</sup> and in absence of metal centers.<sup>18,19</sup> Recently, the possible active site structure in cobalt–polypyrrole (Co–PPy) catalyst for ORR has been reported by Shi et al.<sup>15</sup> They have discussed the participation of both end-on and side-on configuration in the formation of stable oxygen adducts in Co–PPy catalyst which differ from the cobalt porphyrin and cobalt phthalocyanine systems. Morozan et al.<sup>19</sup> has reported that the control of structural morphology is critical to improve the catalytic activity of annealed polymer catalysts, which has not been of much attention in the previous works. On the other hand, Xing and Zhao<sup>20</sup> have reported that the polymerization of pyrrole in mixed-surfactant solutions is superior to the mono-surfactant systems in modulating the morphology and hence the properties of the resultant polymer. Furthermore, the doping of the ORR catalyst material having more than one heteroatom of lower electronegativity than that of carbon has shown to increase activities towards ORR than their mono

atom counterparts due to synergetic co-doping effect.<sup>21,22</sup> Yuan et al.<sup>23</sup> have reported the improvement in PEMFC performance by modifying the typical cobalt–polypyrrole–carbon (Co–PPy–C) catalyst with sulfur based organic dopant anion *p*-toluenesulfonate.

The idea of using mixed surfactant, put forward by Xing and Zhao,<sup>20</sup> has been applied in this study for synthesizing the polypyrrole (PPy) and pTS doped PPy as catalyst support for cobalt. According to Yuan et al.,<sup>23</sup> the polypyrrole chains form a twisted structure due to dopant (TsOH) induced bipolaron whereas the sulfur group doped to the polypyrrole may be helpful for entrapping Co ions in an environment rich in pyrrole-type nitrogen. However, the nature and structure of ORR active site requires further insight and discussion on how the organic dopant anion pTS affects the structure of polypyrrole and helps in improving the ORR activity.

This study reports the comparative analysis of polypyrrole (PPy) and pTS anion doped PPy, synthesized using in-situ surfactant mediated chemical oxidative polymerization approach in a mixed surfactant aqueous solution for its controlled growth, and have shown that PPy/pTS–Co can be utilized as a non-precious catalyst material for ORR. The impact of addition of pTS on the structure and activity of the catalyst material has been analyzed and investigated in respect of their catalytic activity for ORR which is stable under acidic media.

## EXPERIMENTAL

### Materials

Pyrrole monomer (Fluka Chemie) was doubly distilled prior to polymerization. Ammonium persulfate (APS), sodium dodecylsulfate (SDS), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), methanol, and isopropanol (product of Merck) were of analytical grade purity and used as received. Dodecyl trimethyl ammonium bromide (DTAB) and Nafion (5 wt %) were product of Sigma-Aldrich. All solutions in the present experiment were made in de-ionized (D.I.) water (18 MΩ cm).

### Synthesis of PPy and PPy/pTS

PPy was synthesized using in-situ surfactant mediated chemical oxidative polymerization approach at room temperature (~300 K). The ratio of monomer to surfactant concentration taken for present investigation is 4 : 1. PPy was also prepared using pTS dopant in a molar ratio of 1 : 3 with respect to pyrrole monomer. In a typical procedure, 0.7915 g DTAB and 0.8651 g SDS were dissolved in a mixture containing 140 mL D.I. water and 10 mL of isopropyl alcohol (IPA). The reaction solution was stirred continuously till the solution became transparent. Then 0.83 mL of pyrrole monomer was added to the above solution and further stirred for ~30 min. For the polymerization of pyrrole, the oxidant APS (5.4768 g) was dissolved in 20 mL D.I. water and then added to the reaction mixture in small lots. The resulting precipitate was filtered and washed with copious amount of warm D.I. water and methanol repeatedly to remove the residual oxidant. PPy thus obtained was dried under vacuum at 60°C for ~24 h. PPy doped with *p*-toluenesulfonate (pTS) was synthesized using similar procedure, wherein 0.7748 g pTS was added together with pyrrole monomer to the reaction solution before the addition of oxidant (APS).

### Synthesis of PPy–Co and PPy/pTS–Co

Previously synthesized PPy was dispersed in 150 mL D.I. water using ultrasonication for ~30 min. This was followed by the addition of cobalt precursor i.e. cobalt nitrate hexahydrate (Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) in a ratio of 1 : 4 with respect to pyrrole monomer concentration taken for the synthesis of PPy. The ultrasonication was further done for 30 min and thereafter it was left for continuous stirring. For the reduction process, alkaline solution of NaBH<sub>4</sub> was added in excess to this mixture and the reaction solution was left under constant stirring for ~3 h. Then the synthesized PPy–Co catalyst was filtered and washed repeatedly with warm D.I. water and methanol until a neutral pH (~7.0) was reached. The synthesized materials were then dried overnight in vacuum at 80°C. The synthesis of PPy/pTS–Co catalyst was done using the same procedure described above for PPy–Co.

### Structural Characterizations

Fourier transform infrared (FT-IR) spectra of the powdered samples were recorded using Smart Orbit ATR Single Reflection Accessory of the Thermo Scientific Nicolet 5700 FT-IR spectrometer in the range 2000 to 650 cm<sup>-1</sup>. Raman spectra of the samples were recorded using Renishaw Raman Spectrometer, Germany with laser excitation source at 714 nm. The laser power was reduced to 2 mW to avoid destruction to the sample. All spectra were taken at a nearly identical conditions. The morphological and compositional analysis were performed using scanning electron microscopy (SEM) on a Zeiss microscope model EVO MA-10 equipped with Oxford INCA EDX microprobe. High resolution transmission electron microscopy (HRTEM) analysis of the synthesized catalysts were performed using the Tecnai G2F30 S-Twin (FEI; Super Twin lens with C s<sup>1/4</sup> 1.2 mm) instrument operating at an accelerating voltage at 300 kV, having a point resolution of 0.2 nm, and with a lattice resolution of 0.14. Image processing was performed using Digital Micrograph software (Gatan). The HRTEM samples were prepared by drying a droplet of the catalyst suspension on a carbon coated copper grid.

### Electrode Preparation and Electrochemical Studies

Catalyst slurry was prepared for fabricating the electrode catalyst layer. This slurry was a well-mixed suspension of 10 mg of the active material (catalyst) with 100 μL of diluted Nafion solution (5 wt %) and 400 μL of isopropanol : D.I. water (50 : 50) mixture. To coat the glassy carbon disk electrode with catalyst slurry, a drop of the material was carefully dropped on the disk electrode so that it covers only the top surface of the electrode and subsequently the electrode was left to dry in air.

Electrochemical measurements such as cyclic voltammetry (CV) and linear sweep voltammetry were carried out using AUTO-LAB PGSTAT 302N controlled with NOVA 1.7 computer interface. A three electrode one compartment cell was used for electrochemical measurements. The working electrode was catalyst coated glassy carbon disk electrode (0.07 cm<sup>2</sup>). A silver/silver chloride (Ag/AgCl) electrode and Pt sheet were used as the reference and auxiliary electrode, respectively. Electrolyte solution consists of aqueous solution of 0.5M H<sub>2</sub>SO<sub>4</sub>. The electrochemical tests were performed in both under ultrapure (99.999%) nitrogen (N<sub>2</sub>) and (O<sub>2</sub>) saturated solution. The electrolyte solution was purged with either N<sub>2</sub> or O<sub>2</sub> for ~30 min prior to any

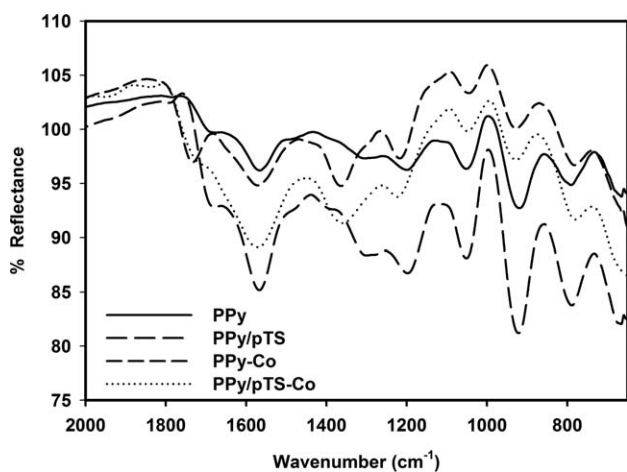


Figure 1. FT-IR spectra for PPy, PPy/pTS, PPy-Co, and PPy/pTS-Co.

electrochemical measurements. The cyclic voltammetry was carried out in the range of  $-0.2$  to  $1.0$  V versus Ag/AgCl electrode at various scan rates viz. 10, 20, 50, 100, and 200,  $\text{mV s}^{-1}$ . A linear sweep voltammetry at a slow scan rate ( $\sim 5$   $\text{mV s}^{-1}$ ) was also performed. These cyclic and linear sweep voltammetry were used to measure ORR activity of materials of this study in  $\text{O}_2$  saturated aqueous solutions. All measurements were carried out at room temperature.

## RESULTS AND DISCUSSION

### FT-IR and Raman Spectroscopic Investigations

Figure 1 shows the FT-IR spectra of PPy, PPy/pTS, PPy-Co, and PPy/pTS-Co. The representative peaks of polypyrrole, i.e., the pyrrole ring vibration, C-N stretching and breathing vibrations of pyrrole ring have been observed at 1550, 1300, and  $1200$   $\text{cm}^{-1}$ , respectively. The =C-H in plane and out of plane vibrations have been observed at 1050 and  $790$   $\text{cm}^{-1}$ ,

respectively, whereas the C-C out of phase deformation vibration is seen at  $920$   $\text{cm}^{-1}$ . The peak arising at  $1361$   $\text{cm}^{-1}$  in PPy-pTS and PPy/pTS-Co sample is due to sulfonic acid group of the pTS anion. Apart from these characteristic peaks, a shift is observed in some of the peak positions. In particular, the breathing vibration of pyrrole ring and C-N stretching vibrations were shifted to higher wavenumber for PPy-Co and PPy/pTS-Co. Since cobalt is likely to be placed in proximity of the nitrogen atoms in either  $\text{M-N}_4$  or  $\text{M-N}_2$  type conformation, it affects largely the C-N and pyrrole ring vibrations.

Raman spectroscopy is very important tool to investigate the molecular structure of the prepared catalyst. Figure 2 shows the Raman spectra of PPy, PPy/pTS, PPy-Co, and PPy/pTS-Co samples. The peaks arising at 934 and  $1045$   $\text{cm}^{-1}$  have been ascribed to bipolaron (dication) and polaron (radical cation) structure, respectively. The broad peak near  $1317$   $\text{cm}^{-1}$  is considered to be an overlap of antisymmetric C-H in plane bending and antisymmetrical C-N stretching. The peak at  $1585$   $\text{cm}^{-1}$  is attributed to C=C stretching. One important observation comes out from the present investigation is that the PPy/pTS shows significant polaronic and bipolaronic peaks as compared to PPy. This enhancement in peaks has been related to the increase in number of bipolarons due to the addition of pTS anion into the PPy matrix. In a recent report,<sup>24</sup> we have observed the higher doping level for pTS anion doped PPy. This shows that there are more number of polarons and bipolarons taking part into the conduction thus increasing the overall conductivity of pTS anion doped PPy. Yuan et al.<sup>23</sup> have also reported that the addition of pTS in PPy/C shows increase in the number of bipolarons which causes maximum conformational defects such as twists and links in the polymer structure. The transition metal is considered to occupy a position inside the PPy matrix in either  $\text{M-N}_4$  or  $\text{M-N}_2$  configuration. The intensity of C=C stretching vibration decreases when addition of cobalt takes place in the PPy or PPy/pTS structure, however, the

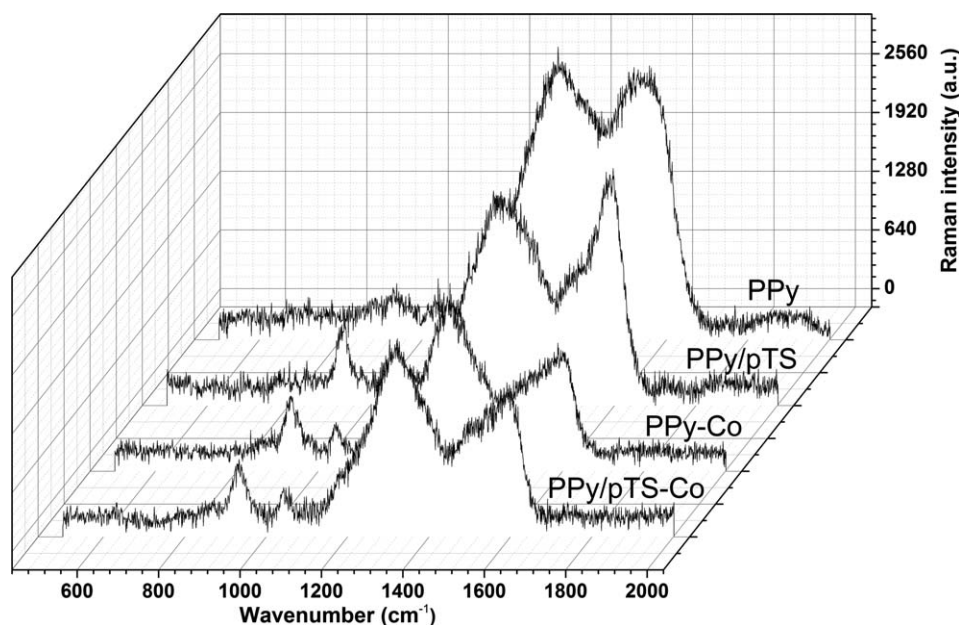
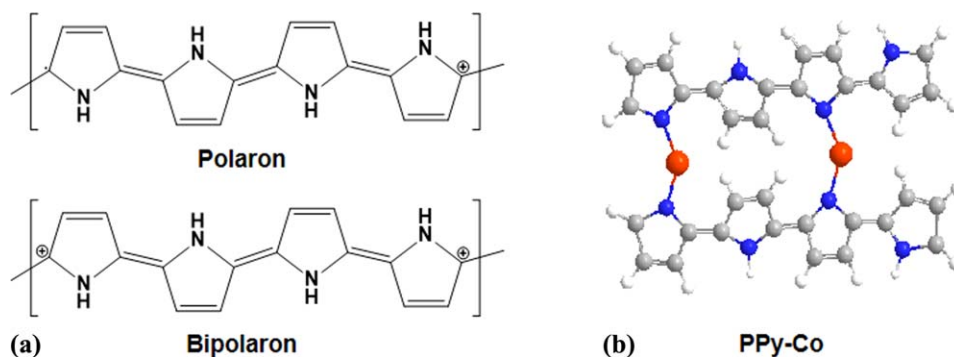


Figure 2. Raman spectra of PPy, PPy/pTS, PPy-Co, and PPy/pTS-Co.





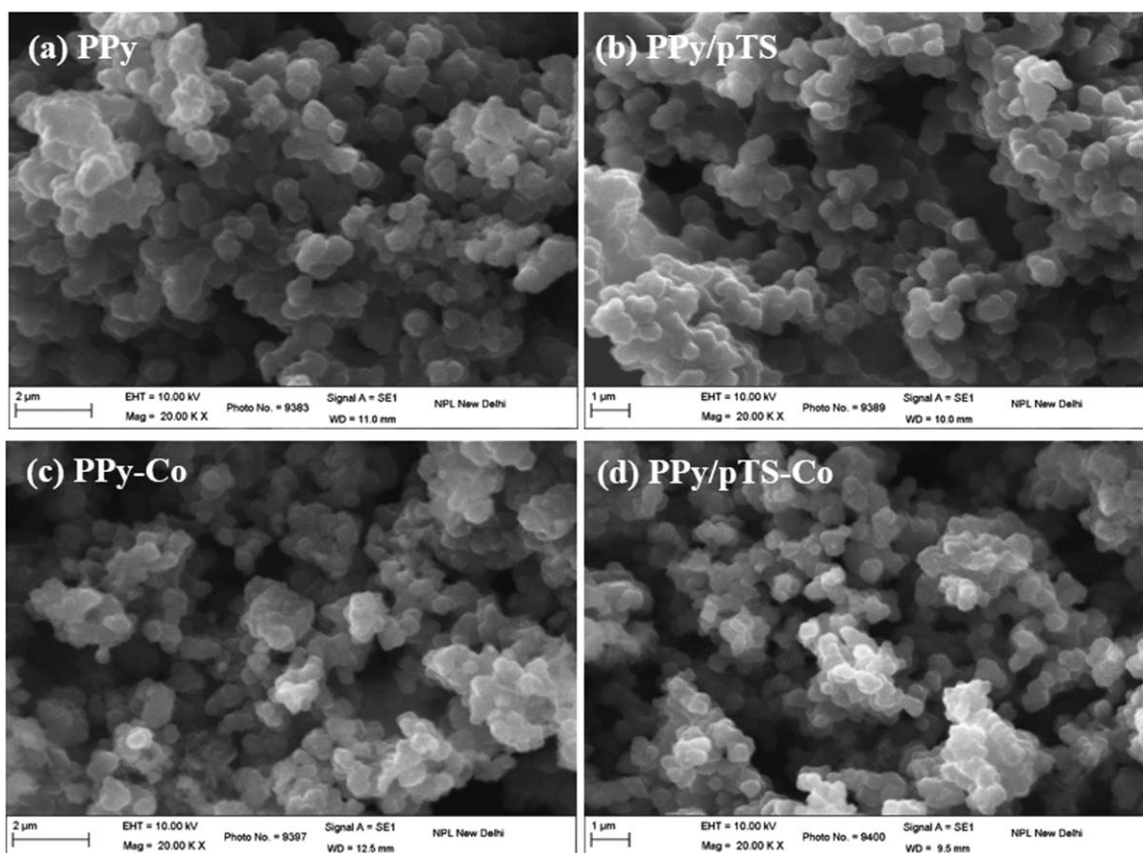
**Scheme 1.** (a) Polaronic and bipolaronic forms of polypyrrole; (b) the structure of PPy-Co in a periodic M-N<sub>2</sub> type configuration. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

bipolaronic and polaronic peaks remain as is. Scheme 1(a,b) represents the structure of polaronic and bipolaronic forms of PPy and PPy-Co, wherein Co is surrounded by polymer in an M-N<sub>2</sub> fashion. Scheme 1(b) depicts that the bipolaronic form is more favored in forming catalytic center owing to increase in net positive charge generated on carbon atoms adjacent to the nitrogen.

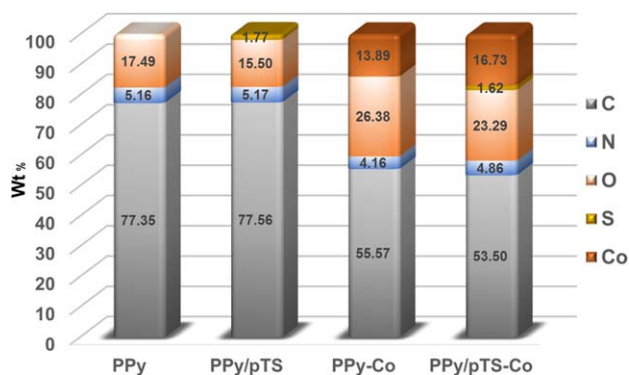
#### Morphological and Elemental Analysis

Figure 3(a–d) shows SEM micrographs of the samples; PPy, PPy/pTS, PPy-Co, and PPy/pTS-Co, respectively. Small spherical/globular particles have been seen in the micrographs of all the samples, without any substantial change in the morphology. However, there is a small difference in particle size of PPy and PPy/pTS sample. The size of the particle is in the range of  $\sim 0.5$  to  $0.7$

$\mu\text{m}$  in PPy and it is  $\sim 0.3$  to  $0.5 \mu\text{m}$  for PPy/pTS. The introduction of pTS is found to affect the particle size restricting it to  $<0.5 \mu\text{m}$ . Since the addition of pTS increases the formation of bipolarons, more charges get accumulated on a smaller size particle of the polymer. The elemental composition of all the samples is shown in Figure 4. Cobalt is present in the sample PPy-Co and PPy/pTS-Co apart from carbon, oxygen, and nitrogen which are present in all the prepared catalyst samples. The decrease in carbon and nitrogen content after reduction of cobalt in the matrix can be associated with the rupture of larger polymer chains into smaller ones in a reducing medium. Cobalt content in PPy/pTS-Co sample is found to be more in amount than in PPy-Co sample. This can be due to the addition of sulfur containing dopant in PPy which helps in making associations with cobalt ions



**Figure 3.** SEM images of (a) PPy, (b) PPy/pTS, (c) PPy-Co, and (d) PPy/pTS-Co.

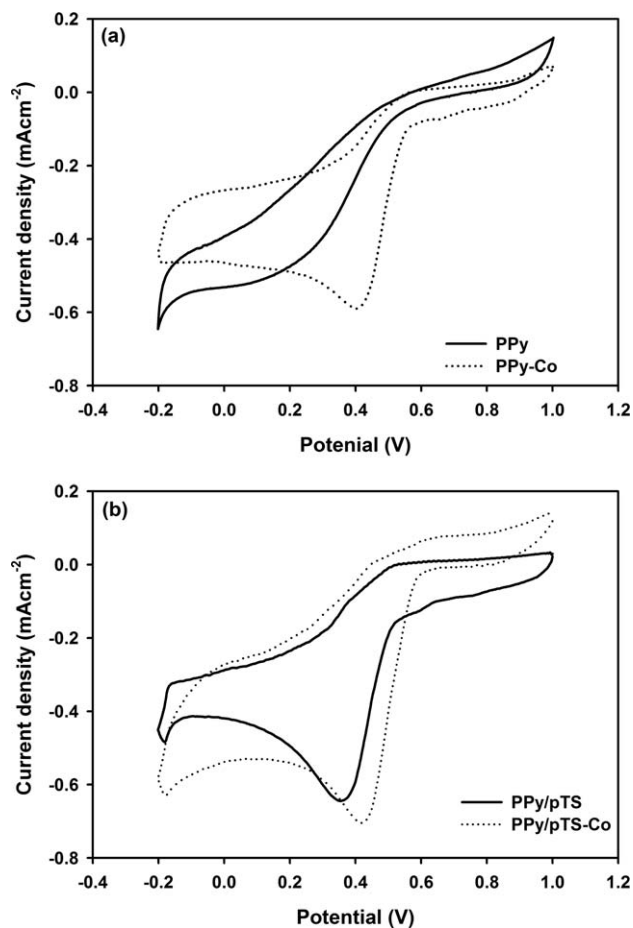


**Figure 4.** A schematic representation of the composition of elements present in PPy; PPy-pTS; PPy-Co; and PPy/pTS-Co using EDAX. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

together with nitrogen containing polymer PPy. Figure 5(a,b) shows HRTEM images of PPy-Co sample as a representative result. The occurrence of interplanar lattice spacing of 0.22 and 0.28 nm [marked by parallel lines in Figure 5(a,b)] correspond to (0 0 4) and (1 1 0) planes, respectively, reconfirms the presence of cobalt in the amorphous polymer matrix.

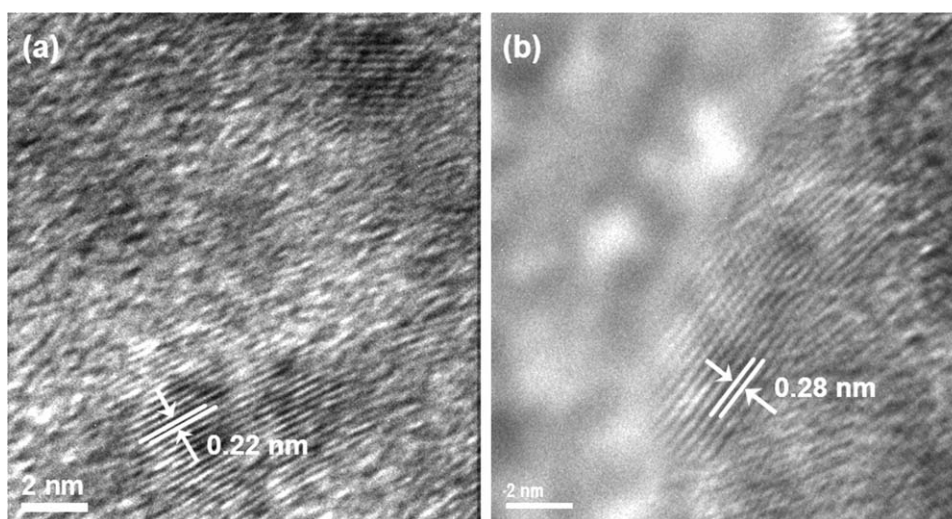
### Cyclic Voltammetry

The catalytic activity of all the samples towards ORR has been analyzed using cyclic voltammetry (CV) in nitrogen and oxygen saturated aqueous solution of 0.5M H<sub>2</sub>SO<sub>4</sub> in a three-electrode cell configuration. The criterion for ORR activity can be related to the negative cathodic peak,  $E_{p,c}$  or  $E_{ORR}$  corresponding to the oxygen reduction reaction. The higher the ORR activity, the closer the  $E_{p,c}$  to the thermodynamic potential of 1.2 V.<sup>25</sup> It is evident from Figure 6(a), that the PPy and PPy-Co samples show a reduction current in the presence of oxygen, however, no noticeable response is observed under N<sub>2</sub> saturated solution (data not shown). In the cathodic scan, PPy shows reduction current but no ORR peak is observed, however, PPy-Co shows an ORR peak at ~0.4 V. Moreover, the onset potential for PPy-



**Figure 6.** Typical cyclic voltammograms for the ORR at the (a) PPy and PPy-Co, and (b) PPy/pTS and PPy/pTS-Co modified electrodes in an oxygen-saturated aqueous solution of 0.5M H<sub>2</sub>SO<sub>4</sub>. Scan rate: 20 mV s<sup>-1</sup>.

Co is higher than that of PPy which is due to the effect of introduction of cobalt in the PPy matrix. The appearance of ORR peak ( $E_{ORR}$  ~0.4 V) in the cathodic region towards the thermodynamic potential of ORR (~1.2 V) is due to the

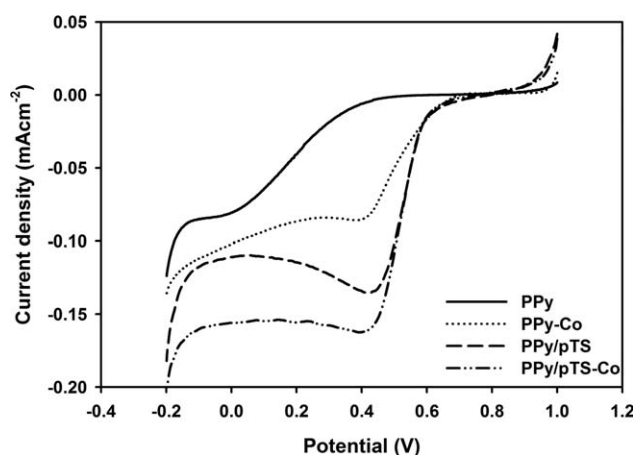


**Figure 5.** HRTEM images of PPy-Co sample showing interplanar lattice spacing (marked by parallel lines) of (a) ~0.22 nm and (b) ~0.28 nm of cobalt in the amorphous polymer matrix.

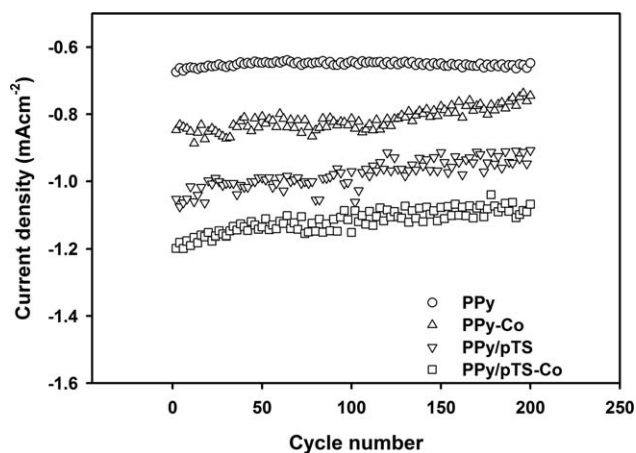
insertion of Co in the PPy matrix which serves as a good catalytic material than PPy. Figure 6(b) shows the catalytic activity of PPy/pTS and PPy/pTS-Co sample in oxygen saturated acidic environment. It was noticed that the PPy/pTS shows oxygen reduction tendency giving an ORR peak at  $\sim 0.35$  V without the support of cobalt. However, the addition of cobalt to the PPy/pTS follows the same effect in shifting the cathodic peak potential ( $\sim 0.42$  V) towards 1.2 V as seen in PPy-Co. Nevertheless, PPy/pTS itself shows good ORR activity but the  $E_{\text{ORR}}$  is lower ( $\sim 0.35$  V) than that for PPy/pTS-Co ( $\sim 0.42$  V). Overall, PPy/pTS-Co catalyst is superior in terms of higher current density and high peak potential relative to other synthesized samples and hence can be validated as a catalyst for ORR. Similar improvement in the activity towards ORR has been found by researchers when polymer samples have been synthesized altogether with pTS anion.<sup>23</sup> However, the cause of this improvement is related to the increase in N content, but the correlation between S content and catalytic activity is still unclear.<sup>23</sup> In a recent study, the addition of organic dopant anion (pTS) to the PPy makes the latter a better ordered matrix having higher doping level.<sup>24</sup> This increase in the doping level is related to the increase in polarons and bipolarons taking part in the conduction process which makes the PPy a planar quinoid chain.<sup>26</sup> Further, in a DFT study made by Xi et al.<sup>27</sup> on PPy-Co catalyst, it has been suggested that the PPy-Co having a periodic structure would have a good ORR catalytic ability. It has been discussed earlier that the pTS influences the PPy structure and makes the polymer chain a planar rigid framework, which increases the periodicity in the PPy-Co catalyst and helps in improving the catalytic activity of the same. Further, PPy/pTS also shows ORR activity which can be due to the addition of sulfur containing group in the PPy chain, increasing the oxygen adsorption tendency and hence catalyzing the reaction in a synergetic way as reported by researchers in other co-doped materials.<sup>22</sup>

### Linear Sweep Voltammetry

To gain further insight into the catalytic activity of the samples of the present investigation, linear sweep voltammetry has been performed at a scan rate of  $5 \text{ mV s}^{-1}$  (Figure 7). A substantial reduction current is observed for all the samples in the cathodic



**Figure 7.** Linear sweep voltammograms for the ORR at the PPy, PPy-Co, PPy/pTS and PPy/pTS-Co modified electrodes in an oxygen-saturated aqueous solution of  $0.5 \text{ M H}_2\text{SO}_4$ . Scan rate:  $5 \text{ mV s}^{-1}$ .



**Figure 8.** Stability measurement of the PPy, PPy-Co, PPy/pTS, and PPy/pTS-Co samples.

scan. Addition of cobalt to the PPy matrix shows increase in current density towards lower potential range. The maximum current density is observed for PPy/pTS-Co sample. PPy sample synthesized without pTS dopant anion has an onset potential of ORR at  $\sim 0.38$  V which is much lower than the onset potential of ORR for other three samples ( $\sim 0.62$  V). However, PPy/pTS has reduction current almost equal to or more than the reduction current as observed for PPy-Co.

The stability of the samples have been tested under  $\text{O}_2$  saturated  $0.5 \text{ M H}_2\text{SO}_4$  solution for 200 cycles at a scan rate of  $50 \text{ mV s}^{-1}$ . The peak current density at the cathodic scan related to ORR is plotted as a function of number of cycles in Figure 8. It is evident from this figure that all the samples show a stable reduction current up to 200 cycles but the peak current density is maximum for sample PPy/pTS-Co.

### CONCLUSIONS

Influence of aromatic sulfur based dopant (pTS) on the ORR activity of PPy and PPy-Co based catalyst samples has been investigated in acidic media. The structural modification in PPy chain due to the addition of pTS as well as its effect on the ORR activity has been discussed with reference to the previous studies. The formation of bipolarons in polymer matrix has increased the tendency of PPy chain to become planar thereby increasing the net positive charge on the adjacent carbon atoms favoring the adsorption of oxygen resulting into more ORR activity. The entrapment of Co in PPy and PPy/pTS matrix possess Co- $\text{N}_x$  type structure. The presence of sulfur in PPy/pTS matrix helps in stabilizing the cobalt in the polymer chain. It can be concluded that PPy/pTS-Co is the better ORR catalyst for cathode application in fuel cells.

### ACKNOWLEDGMENTS

The authors are thankful to Director, National Physical Laboratory, New Delhi for his kind permission to publish this study and to Drs. R. B. Mathur, S. K. Dhawan, A. K. Srivastava, and Sukhbir Singh for providing their experimental facilities. A Kumar and R. Singh are thankful to Council of Scientific and Industrial Research (CSIR), Government of India, New Delhi for the award of Junior



Research Fellowship and Emeritus Scientist Fellowship, respectively. Financial assistance from CSIR, New Delhi under grant No. 21(0756)/09/EMR-II is gratefully acknowledged.

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