Preparation and characterization of iron-polypyrrole-carbon composite for use as methanol tolerant cathode material in direct methanol fuel cells

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Received 8 April 2013; revised and accepted 14 October 2013

Novel carbon supported iron-polypyrrole (30 wt% Fe-PPy-C) composite catalyst has been prepared by using a chemical polymerization method and investigated as electrocatalyst for the oxygen reduction reaction in 0.5 M H$_2$SO$_4$ at 25 °C. Structural and electrochemical characterizations of the catalyst have been carried out by IR, XRD, SEM, cyclic and linear sweep voltammetry, chronoamperometry and electrochemical impedance spectroscopy. Electrochemical studies have been performed in Ar- and O$_2$- saturated 0.5 M H$_2$SO$_4$ with and without 1 M CH$_3$OH at 25 °C. The study shows that the composite catalyst is oxygen reduction reaction active and stable, and does not oxidize methanol and hence can be used as an efficient methanol tolerant cathode material in direct methanol fuel cells.

Keywords: Catalysts, Composites, Iron polypyrrole carbon composite, Oxygen reduction reaction, Methanol tolerant cathode material, Fuel cells, Direct methanol fuel cells

Direct methanol fuel cells (DMFCs) have attracted considerable attention as an alternative power source to internal combustion engine for vehicles and as a replacement for batteries in portable electronic devices$^{1-10}$. Pt and Pt-based alloys are the most widely used catalysts for the oxygen reduction reaction (ORR) in DMFCs$^{5,11,12}$. These catalysts have high intrinsic activities towards both, ORR and MOR (methanol oxidation reaction)$^{13-20}$. However, there are two major problems with the use of Pt as the cathode material: firstly it is costly and less abundant on the earth, and, secondly, it suffers from activity loss due to the depolarization effect. In fact, some methanol molecules diffuse from the anode to the cathode compartment through polymer electrolyte membrane (methanol crossover) which is used to separate the two compartments of the DMFC$^{5,21}$. During the cell operation Pt cathode has sufficient potential to oxidize the methanol molecules ($E^{\circ}_{\text{CH}_3\text{OH/O}_2} = 0.016$ V vs SHE) and so, presence of any methanol in the cathode compartment would depolarize the cathode and consequently, the efficiency of the cathode and hence the cell would be diminished. Thus, the methanol crossover not only lowers the fuel utilization efficiency but also affects the cathode performance adversely$^{5,22-24}$. It is, therefore, necessary to search for novel DMFC cathode catalysts, which have good ORR performance as well as high methanol tolerance. In the last few years, several transition metal compounds such as macrocycle-based metal containing porphyrin system$^{25,28}$, chevrel phase type compounds$^{26}$ and other transition metal chalcogenides have been proposed as selective catalysts for the ORR$^{27-32}$.

Recent studies reported in literature have shown that conducting polymers, particularly polypyrrole (PPy) has great potential as support material for fuel cell catalyst due to their high ionic and electron conductivities$^{13}$. They improve dispersion of the catalyst particles and, at the same time, impart enhanced stability as well as electrocatalytic activity to the catalyst. For instance, Qu et al.$^{34}$ in electrocatalysis of methanol oxidation reaction (MOR) observed a higher catalytic stability with the Pt/PPy-MWCNTs composite electrode as compared to the Pt/MWCNTs electrode. Zhao et al.$^{35}$ demonstrated that bimetallic PtCo nanoparticles codeposited on PPy-MWCNT composite via over oxidation treatment had higher catalytic activity towards MOR, compared to that deposited on MWCNT. The application of the PPy film containing dispersed Pt and Pt/Pd nanoparticles (NPs) on ITO
glass plates has also been investigated as anode for MOR. The PPy modified electrode was found to show an enhanced electrocatalytic activity. The increase in electrocatalytic activity has been attributed to the uniform dispersion of NPs in the PPy film matrix and synergistic effect between them (i.e NPs and PPy matrix).

Recently, Bashyam and Zelenay\textsuperscript{36} demonstrated the Co-PPy composites as highly active ORR catalysts with good performance durability. It exhibited power densities of about 0.15 W cm\textsuperscript{-2} in H\textsubscript{2}-O\textsubscript{2} fuel cells without any degradation for more than 100 hours. Reddy \textit{et al.}\textsuperscript{37} examined the suitability of the cobalt-polymer-MWCNT composite electrode for the ORR in DMFCs and observed improved power density for methanol and ethanol based fuel cells as compared to previously reported non Pt based electrocatalysts. Investigations on the ORR at sandwich composite electrodes, namely PPy/PPy(Cu\textsubscript{1-x}Mn\textsubscript{x}O\textsubscript{4})/PPy\textsuperscript{38,39}, PPy/PPy(Ni\textsubscript{1-x}Co\textsubscript{x}O\textsubscript{4})/PPy\textsuperscript{40}, PPy/PPy(CoFe\textsubscript{2}O\textsubscript{4})/PPy\textsuperscript{41}, PPy/PPy(LaNiO\textsubscript{4})/PPy\textsuperscript{42}, PPy/PPy(La\textsubscript{1-x}Sr\textsubscript{x}MnO\textsubscript{3})/PPy\textsuperscript{43}, PPy/PPy(La\textsubscript{1-x}Sr\textsubscript{x}CoO\textsubscript{3})/PPy\textsuperscript{44}, and PPy/PPy(La\textsubscript{1-x}Sr\textsubscript{x}CoO\textsubscript{3})/PPy\textsuperscript{45}, were also carried out. These studies showed that the composite electrodes had excellent catalytic activities as well as remarkable stability even in acid solutions wherein mixed oxides cathodes normally undergo deactivation. All the composite electrodes studied exhibited high stability and considerably improved catalytic activities.

Metal particles supported on polymer matrix are known to have higher specific surface area and higher tolerance towards the poisoning effect of the methanol oxidation intermediate, CO\textsuperscript{35}. Considering the advantageous properties of PPy as support material and also the good ORR performance of previously used Co-PPy and Co-PPy-MWCNTs composites in fuel cells, it is desirable to carry out similar studies with other low cost non-precious metals also. In view of this, we were encouraged to synthesize the Fe-PPy/C composite by a chemical method and examine its ORR activity in 0.5 M H\textsubscript{2}SO\textsubscript{4} and 0.5 M H\textsubscript{2}O\textsubscript{2} + 1 M CH\textsubscript{3}OH solutions. Detailed results of the investigation are described herein.

Materials and Methods

Preparation and characterisation of the catalyst

The composite comprising 30wt%Fe and 70 wt% polypyrrole (PPy)/carbon nanopowder (C) was prepared following a previously reported procedure\textsuperscript{36}. The PPy/C composite was prepared by dispersing 5.0 g of C (Aldrich, 99+%, Prod. No. 633100) in glacial acetic acid (Thomas Baker, 99%) (1.25 mL) + redistilled water (40 mL) mixture. To this, 1.0 g of pyrrole (Py, Aldrich, 98%, Prod. No. 131709) was added with continuous stirring, followed by the addition of 5.0 mL of 20% H\textsubscript{2}O\textsubscript{2} (Qualigens, Prod. No. 18755) and then the mixture was stirred for 1 h. The solid residue was filtered, washed with hot distilled water and then dried in a vacuum oven at 90 °C overnight. The product (20.0 mg of PPy/C) so obtained was refluxed in water for ½ h, and then 760 µL of 0.707 M aqueous solution of hydrated iron(III) nitrate (Merck, purified) was added with stirring and heated at ~80 °C followed by addition of an alkaline sodium borohydride solution (Sigma-Aldrich, Prod. Code: 452874), dissolved in NaOH (Merck), until the pH was >10. The precipitate was filtered, washed with warm water until the pH reached 7 and finally dried in vacuum oven at ~90 °C. The 30wt%Fe/C composite was prepared similarly. The activation of carbon nanopowder was carried out by refluxing in conc. HNO\textsubscript{3} (Merck).

X-ray diffraction (XRD) patterns of the catalysts were recorded at a sweep rate of 3° min\textsuperscript{-1} on an X-ray diffractometer (Rigaku-MiniFlex-II) using Cu-K\textsubscript{a} as the radiation source (\(\lambda = 1.5418\) Å). Morphology of the compound has been studied by a scanning electron microscope (Quanta 200 FEI).

Electrode preparation

The catalyst was transformed into the film form on a glassy carbon (GC) support by the ink painting method. Prior to use, the GC support was polished with alumina powder and then pre-treated in phosphoric acid. The ink was prepared by sonicating 8 mg of the catalyst with a 1600 µL mixture of Nafion solution (1%, Alfa Aesar) and redistilled water (1:1) for 15 min. The ink, thus prepared, was dropped at the pre-treated GC surface (1 cm x 1 cm) to cover the entire plate uniformly and dried in air. The mass of catalytic film was 0.3 mg cm\textsuperscript{-2}. Electrical contact with the catalytic film on GC electrode was made with the help of a conductive silver paste (Eltecks, Code No: 18755), a thin copper wire and Araldite epoxy (Petro Araldite Pvt. Ltd.) as previously described\textsuperscript{46,47}. Only 0.5 cm\textsuperscript{2} surface of the catalytic film was used for the study and the rest was isolated with Araldite.

Electrochemical studies

A three-electrode single compartment Pyrex glass cell was used to carry out electrochemical
investigations. The reference and auxiliary electrodes were SCE (0.242 V vs. SHE) and pure Pt-foil (~8 cm²), respectively. Values of the potential mentioned herein are against the SCE electrode only. Electrochemical studies, namely cyclic (CV) and linear sweep (LSV) voltammetries, were carried out on a computer controlled (EG&G PAR, model: 273 A) potentiogalvanostat. CV and LSV of the electrocatalyst were recorded in Ar and O₂ saturated 0.5 M H₂SO₄ with and without 1 M CH₃OH. The electrochemical impedance spectroscopy (EIS) study of the catalyst film electrode in Ar and O₂ saturated 0.5 M H₂SO₄ with and without 1 M CH₃OH was carried out with an ac voltage amplitude of 10 mV using an electrochemical impedance system (EG&G, PAR) provided with a lock-in-amplifier (model 273A) and P-4HP computer. The frequency range used in the study was from 0.005 to 20 × 10³ Hz and softwares employed were ‘Power Sine’ and ‘ZsimpWin version’ 3.00.

Results and Discussion

Characterisation of the catalyst

IR spectra of the PPy, PPy-C and Fe-PPy-C composite were recorded in the region 4000-400 cm⁻¹ and are shown in the Fig. 1. The broad and strong band at ~3425 cm⁻¹ corresponds to N-H stretching vibration of polypyrrole. The bands at ~2926, ~1622 cm⁻¹ are due to C-H and C=C stretching vibration, respectively and those at ~1555 and ~1460 cm⁻¹ can be assigned respectively to C-H stretching and C-N stretching vibrations of PPy. The bands at ~1380 and ~920 cm⁻¹ refer to respectively, C-C vibration and C-H out-of-plane vibration. Further, IR spectra of PPy, PPy-C and Fe-PPy-C appear to be similar but most of the stretching IR bands observed in the case of Fe-PPy-C are found to shift to the higher wave number, which indicates that there is shifting of electron density from the pyrrole ring to the iron.

Figure 2 depicts the XRD patterns for PPy-C and Fe-PPy-C recorded between 20 = 30° and 80°. The XRD pattern of PPy-C does not indicate the presence of any diffraction peak, while that of the composite Fe-PPy-C containing one prominent peak at 2θ = 51° (d = 1.789) indicates the presence of Fe in the ternary composite (JCPDS file: 23-0298). The absence of any prominent peak in the XRD of the binary composite (PPy-C), shows that PPy-C is present in amorphous phase.

SEM images of the catalyst, Fe-PPy-C, were taken at different magnifications and are reproduced in the Fig. 3. The amorphous nature of the composite is also clearly visible from the scanning electron micrographs.

Cyclic voltammetry

Cyclic voltammetry (CV) of the Fe-PPy-C/GC electrode was recorded at the scan rate of 50 mV s⁻¹ in Ar-saturated 0.5 M H₂SO₄ with and without 1 M CH₃OH at 25 °C (Fig. 4). For comparison, the cyclic voltammogram of Fe-C/GC at 50 mV s⁻¹ in Ar-saturated 0.5 M H₂SO₄ is also given in the inset of Fig. 4. The potential range used for the CV study was
from -0.2 to +1.3 V (vs. SCE). Similar features of CV curves in the absence and presence of 1 M CH₃OH in the electrolyte, indicate that the methanol electrooxidation reaction does not take place at the catalyst electrode during potential cycling condition. Thus, the electrode, Fe-PPy-C/GC, is quite resistant to methanol oxidation and hence can be used as a methanol tolerant electrode. Based on the Pourbaix diagram of Fe, a pair of broad anodic and cathodic peaks observed respectively at ~0.55 V and ~0.36 V vs SCE (Fig. 4) is due to the formation of Fe(II)/Fe(III) redox couple.

**Electrocatalytic activity**

The electrocatalytic activity of the Fe-PPy-C/GC electrode towards ORR in Ar and O₂-saturated 0.5 M H₂SO₄ has been determined by recording the linear sweep voltammetry (LSV) curves at the scan rate of 5 mV s⁻¹ in the potential range, 0.60 to -0.50 V at 25°C (Fig. 5). The apparent ORR current density
values (observed current, mA/geometrical surface area, cm$^2$) obtained at $E = -0.2$ and $-0.3$ V were 0.36 and 0.56 mA cm$^2$, respectively. These current values have been obtained by subtracting the current densities observed at the electrocatalyst in Ar-saturated 0.5 $M$ $H_2SO_4$ from those observed at the same electrocatalyst in $O_2$-saturated 0.5 $M$ $H_2SO_4$ under similar polarization conditions.

To verify the diffusion controlled nature of the ORR, linear sweep voltammetry (LSV) experiments have been performed with the rotating disk electrode (RDE) in $O_2$-saturated 0.5 $M$ $H_2SO_4$ at 25 °C. Results shown in Fig. 5 (inset) demonstrate that as the electrode rotation is increased from 250 to 1600 rpm, the LSV curve shifts considerably towards the higher ORR region, indicating thereby that the ORR is the diffusion controlled.

### Electrochemical impedance spectroscopy

The EIS study of the catalyst electrode was carried out at varying potentials chosen in the potential range, 0.10 to $-0.20$ V, in Ar- and $O_2$-saturated 0.5 $M$ $H_2SO_4$, and $O_2$-saturated, 0.5 $M$ $H_2SO_4 + 1 M$ $CH_3OH$. The potentials chosen for the present study fall in the ORR region. The frequency range used was from 100 kHz to 5 MHz. Before recording each spectrum, the electrode was first kept at the applied potential for 300 s. The obtained EIS spectra are shown in Fig. 6. Each EIS spectrum appears to be an arc of semicircle. However, a careful perusal of these figures indicates that each EIS spectrum, in fact, consists of two semicircles, one at the higher frequency region (Inset of Fig. 6 (a)) and the other one at the intermediate and low frequency region, which overlap each other. The arc, produced at high frequencies is found to be independent of the applied potential, while the arc produced at intermediate and low frequencies depends upon the applied potential.

Features of EIS spectra of the electrode, recorded in Ar and $O_2$ saturated 0.5 $M$ $H_2SO_4$, appear to be similar as is evident from Fig. 7 (a). However, at a particular potential, the diameter of the semicircle observed in the Ar-saturated 0.5 $M$ $H_2SO_4$ seems to be much larger than that observed in $O_2$-saturated 0.5 $M$ $H_2SO_4$. A considerable decrease in the diameter in presence of $O_2$ can be ascribed to the occurrence of ORR. The diameter is a measure of the charge transfer reaction ($R_{ct}$), which is inversely proportional to the rate of the reaction. Further, the diameter of the semicircle does not change significantly (Fig. 7 (b)) in the presence of 1 $M$ $CH_3OH$ in 0.5 $M$ $H_2SO_4$, which indicates that the MOR on this electrode is almost nil. These results corroborate the findings of the CV study.

The obtained EIS spectra, were simulated using a common and best-fit electrical equivalent circuit, $R_a(R_1Q_1)(R_2Q_2)$. The parallel ($R_1Q_1$) combination describes the properties of the composite in the bulk, while the parallel ($R_2Q_2$) combination is associated with the ORR. The symbols $R_a$, $R_1$ and $R_2$ represent the solution resistance ($\Omega$ cm$^2$), film resistance ($\Omega$ cm$^2$) and charge transfer resistance ($\Omega$ cm$^2$) and $Q_1$ and $Q_2$ represent constant phase elements (CPE) ($F$ s$^{-n}$ cm$^{-2}$) for the composite (bulk) and the composite/solution interface, respectively. Based on the proposed circuit model, the EIS spectrum obtained agree reasonably well with the experimental curve. Simulated and experimental curves in “Nyquist mode” and “Bode mode” are given in Fig. 8. Estimates of the circuit parameters and values of the double layer capacitance ($C_{dl}$), estimated using the relationship, $Q_2 = (C_{dl})^n [(R_1)^{-1} + (R_{ct})^{-1}]^{1-n}$, are given in Tables S1 and S2 (Supplementary Data).

The magnitude of $R_2 (= R_{ct})$ decreases and hence the rate for the ORR increases with the increase in potential in the cathodic direction (Supplementary Data Tables S1 and S2). The conductivity (bulk) of the composite film (= 1/$R_1$) increases with an increase in the cathodic potential. The increase in bulk conductivity of the film may be ascribed to the migration of $SO_4^{2-}$ from the polymer matrix to the
Fig. 6 – (a) Complex impedance diagram of Fe-PPy-C at varying potentials in Ar-saturated 0.5 \( M \) \( \text{H}_2\text{SO}_4 \). [Temp. = 25 °C]. (b) Complex impedance diagram of Fe-PPy-C composite at varying potentials. \([E = 0.10, 0.05, 0.0, -0.05 \text{ and } -0.10 \text{ V vs SCE})\) in \( \text{O}_2 \)-saturated 0.5 \( M \) \( \text{H}_2\text{SO}_4 \); Temp. = 25 °C. (c) Complex impedance diagram of Fe-PPy-C composite at varying potentials. \([E = -0.10, -0.15 \text{ and } -0.20 \text{ V vs SCE})\) in \( \text{O}_2 \)-saturated 0.5 \( M \) \( \text{H}_2\text{SO}_4 \); Temp. = 25 °C.

Fig. 7 – (a) Complex impedance diagram of Fe-PPy-C composite in Ar and \( \text{O}_2 \)-saturated 0.5 \( M \) \( \text{H}_2\text{SO}_4 \) at \( E = -0.1 \text{ V vs SCE} \). [Temp. = 25 °C] (b) Complex impedance diagram of Fe-PPy-C composite in \( \text{O}_2 \)-saturated 0.5 \( M \) \( \text{H}_2\text{SO}_4 \) with and without containing 1 \( M \) \( \text{CH}_3\text{OH} \) at \( E = 0.0 \text{ V vs SCE} \). [Temp. = 25 °C].
solution. It is known that when a positive potential is applied to the PPy/\text{SO}_4^{2-}\) (solution) system, \text{SO}_4^{2-}\) ions diffuse from solution into the PPy matrix and the reverse occurs when a negative (i.e. cathodic) potential is applied\(^{37}\). In fact, the migration of \text{SO}_4^{2-}\) takes place so as to make the PPy matrix electrically neutral. Further, the \(C_{\text{dl}}\) of the composite/solution interface seems to be independent of the applied potential in the ORR. This shows that the nature of the catalyst surface does not change practically with the applied potential in the ORR region. Also, the presence of methanol in the electrolyte does not seem to influence the \(C_{\text{dl}}\) of the catalyst/electrolyte interface significantly. Further, the plot \(E\) vs log \((1/R_{\text{ct}})\) shows a linear relation with slope ~173 mV in 0.5 \(M\) \(\text{H}_2\text{SO}_4\) and ~170 mV in 0.5 \(M\) \(\text{H}_2\text{SO}_4 + 1 M\) \(\text{CH}_3\text{OH}\), which are close to the slope (~175 mV) obtained from the Tafel polarization study.

**Chronoamperometry**

Chronoamperogram of the Fe-PPy-C electrode recorded at \(E = -0.3\) V in \(\text{O}_2\)-saturated 0.5 \(M\) \(\text{H}_2\text{SO}_4\) for five hours indicated that the oxygen reduction current density increases with polarization time showing a constancy in about 2 hours. This result clearly demonstrates that the electrode is quite stable under the employed experimental conditions.

**Conclusions**

The study has shown that the Fe-PPy/C hybrid material prepared by chemical polymerization method is ORR active and quite stable. Also, it does not practically oxidise methanol in 0.5 \(M\) \(\text{H}_2\text{SO}_4\). So, it can be used as an active methanol tolerant cathode material in direct methanol fuel cells.

**Supplementary Data**

Supplementary data associated with this article i.e., Tables S1 and S2, are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_52A(11)1383-1390_SupplData.pdf.

**Acknowledgement**

One of authors (Madhu) thanks the University Grants Commission (UGC), New Delhi; India, for the award of Rajiv Gandhi National Fellowship to carry out the investigation. The authors also thank the Council of Scientific and Industrial Research (CSIR), New Delhi; India, for financial support through research grant (No. 01(2320)/09-EMR-II).
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