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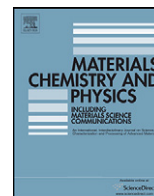
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Synthesis, characterization and electrocatalytic activity of Pt supported on poly (3,4-ethylenedioxythiophene)-V₂O₅ nanocomposites electrodes for methanol oxidation

T. Maiyalagan^{a,b,*}, B. Viswanathan^a^a National Centre for Catalysis Research, Department of Chemistry, Indian Institute of Technology Madras, Chennai 600 036, India^b Department of Chemistry, School of Science and Humanities, VIT University, Vellore 632014, Tamilnadu, India

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ABSTRACT

Platinum nanoparticles have been supported on PEDOT-V₂O₅ nanocomposite through the reduction of chloroplatinic acid with formic acid. PEDOT-V₂O₅ hybrid nanocomposites are thus found to be a good support of Pt particles as catalysts for oxidation of methanol. Surface properties and morphology of the Pt deposit on nanocomposite were characterized using XRD, SEM, EDAX and TEM analysis. EDX mapping and TEM images show the fine dispersion of Pt nanoparticle on the nanocomposite support. TEM images show 4-nm Pt nanoparticles dispersed on the nanocomposite surfaces. The electrocatalytic activity of Pt/PEDOT-V₂O₅ nanocomposite catalysts toward methanol oxidation was investigated and compared with Pt/C. Pt/PEDOT-V₂O₅ nanocomposite catalysts exhibited enhanced electrocatalytic activity when compared with commercially available Pt/C catalysts and the chronoamperometric response revealed better activity and stability of the nanocomposite electrode when compared with the Pt/C electrode.

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1. Introduction

Fuel cells are considered as one of the best options for energy conversion for the common man in the future. However, in spite of several decades of concerted attempts, this device has not yet evolved as an economically viable, socially acceptable, easily manipulative tool for energy conversion. It is known that there are a variety of barriers for the wider use of this energy conversion device [1–8]. As far as the hardware of a fuel cell is concerned; it essentially consists of three components, namely the two electrodes and the electrolyte. Pt or Pt based noble metals are employed as electrocatalysts in both the electrodes. It is therefore natural, that there are attempts to reduce the amount of noble metal loading in the electrodes. This can be achieved by suitably dispersing the noble metals on suitable electronically conducting supports keeping in view the net energy density derivable from such a device with low metal loadings. To decrease the platinum loading and to improve, the oxidation rate and electrode stability, considerable efforts have been applied to the study of electrode materials for the direct electrochemical oxidation of methanol [9–18].

Carbon is the most common catalyst support material that conducts electrons (not protons) but does not contribute to the transport of protons produced in the electro-oxidation reaction. A suitable alternative would be to develop a catalyst support that conducts both protons and electrons efficiently [19–21]. Conducting polymers possess both protonic and electronic conductivity. To overcome the lack of stability of conducting polymers, nanocomposites are being developed. The electrocatalytic activity of platinum can be improved by making nanocomposite electrodes for methanol oxidation.

There has been a great deal of interest in recent years on the preparation of conducting polymer-based nanocomposites for fuel cell applications [22–24]. Application of either conducting polymers or transition metal oxides individually, or with the nanocomposites as electrodes has been used as for methanol oxidation in direct methanol fuel cells. At this juncture, we would like to cite that recent advances have shown that electronic conducting polymers such as polypyrrole [25,26], polyaniline [27] and poly (3,4-ethylenedioxythiophene) [28] can serve as catalyst support to disperse the platinum particles and the resultant nanocomposites have excellent properties. Poly (3,4-ethylenedioxythiophene) PEDOT has a good compatibility with V₂O₅, high conductivity, good electrochemical stability as well and thus it has been studied as a Pt catalyst support for methanol oxidation and oxygen reduction [29–33].

Vanadium pentoxide (V₂O₅) has been used as an electrode material for batteries because of its intrinsic electrochemical redox

Q1 * Corresponding author at: Department of Chemistry, School of Science and Humanities, VIT University, Vellore 632014, Tamilnadu, India.
Tel.: +91 44 2257 4241; fax: +91 44 2257 4202.

E-mail addresses: maiyalagan@gmail.com (T. Maiyalagan), bvnathan@iitm.ac.in (B. Viswanathan).

activity to induceable change in the oxidation state of vanadium species [34,36,37]. Platinum and other noble metals have been found to catalyze the complete oxidation of sucrose and other sugars by vanadium (IV) in acid environments [35]. Vanadium (IV)/vanadium (III) redox couples have been used to model a redox type of fuel cell [34,35]. V_2O_5 has been used as an electrocatalyst supports for methanol oxidation [37,38].

The synthesis and electrochemical studies, of stable conducting poly (3,4-ethylenedioxythiophene) (PEDOT)- V_2O_5 nanocomposites have also been reported [39]. This nanocomposite material has been used as a catalyst support for Pt and the electrode for methanol oxidation in acid medium. The material has been characterized and studied by X-ray diffraction (XRD), elemental analysis, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and cyclic voltammetry (CV). The cyclic voltammetric technique apart from being used to characterize the composite material for accessing the electrochemical stability in acid medium has also been used to evaluate the methanol oxidation in acid medium. The chronoamperometric response was monitored to evaluate the stability of the Pt supported nanocomposite material for methanol oxidation.

2. Experimental section

2.1. Materials

3,4-Ethylenedioxythiophene (Bayer AG) was vacuum distilled before use. Vanadium pentoxide and hexachloro platinum acid was obtained from Sigma Aldrich. All other chemicals were reagent grades and were used as received. The glassy carbon (GC) disc (ϕ 3 mm dia. and ϕ 1 mm dia.) and the polishing kit were purchased from Bio Analytical System (BAS USA).

2.2. Preparation of poly (3,4-ethylenedioxythiophene)- V_2O_5 nanocomposites

Vanadium oxide (V_2O_5) powder (1 g) is mixed with 100 ml aqueous solution of hydrogen peroxide (10%). Vanadium oxide reacts with hydrogen peroxide to give $V_2O_5 \cdot nH_2O$ gels that have a layered structure [40]. These gels can intercalate organic species, such as EDOT. The monomer EDOT has been polymerised using ammonium persulphate as initiator. The intercalation of EDOT between V_2O_5 layers has been formed, while the hydrogen peroxide decomposes spontaneously in the presence of vanadium oxide.

2.3. Preparation of Pt/PEDOT- V_2O_5 nanocomposites and Pt/C catalyst

The nanocomposite powder (ca. 100 mg) was ground with a mortar and pestle and then suspended in about 20 ml H_2O . H_2PtCl_6 solution was then added in an amount slightly greater than the desired loading. The suspension was stirred at around $80^\circ C$ for 30 min to allow dispersion and aqueous formaldehyde (BDH, 37%) was added followed by heating at reflux for 1 h. The Pt supported polymer nanocomposites were collected by filtration, washed thoroughly with water, and then dried under vacuum ($25-50^\circ C$). The same procedure and conditions were used to prepare Pt/C catalyst in order to make a comparison between the Pt/C and Pt/PEDOT- V_2O_5 system.

2.4. Characterization

Powder X-ray diffraction (XRD) pattern for the catalyst was obtained on a Shimadzu XRD-6000 X-ray diffractometer using $Cu K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) source operating at 40 kV and 30 mA. Morphology and composition were characterized using a scanning electron microscope (Philips XL 30 ESEM FEG) to obtain secondary electron images as well as simultaneous electron-stimulated X-ray energy dispersive spectroscopy (EDS; PRISM IG X-ray detector, Princeton Gamma Tech, Rocky Hill, NJ) to measure the composition of the catalyst samples.

The transmission electron microscope (TEM) analyses were performed on CM12/STEM microscope operating at a 100 kV accelerating voltage. HRTEM micrographs were recorded using JEOL-3010 transmission electron microscope operating at 300 kV. To obtain TEM images, the synthesized electrocatalysts dispersed in ethanol solution were coated on a Cu-carbon grid.

2.5. Electrochemical measurements

A single glass compartment cell consisting of three electrodes was employed for the cyclic voltammetry and chronoamperometry studies. Pt wire and saturated calomel electrode (SCE) were used as counter and reference electrode respectively. A 0.076 cm^2 area glassy carbon (GC) served as the working electrode. The electrochemical studies were carried out with a potentiostat/Galvanostat Model 273 A. The

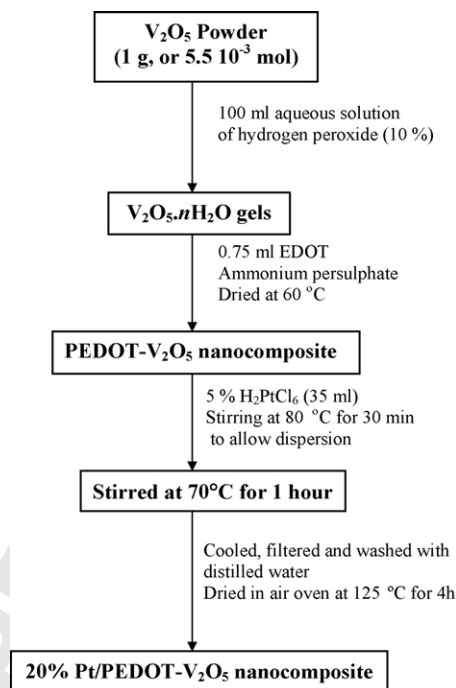


Fig. 1. Schematic representation for the preparation of 20% Pt/PEDOT- V_2O_5 nanocomposite catalyst by formaldehyde reduction method.

glassy carbon was first polished with alumina paste (procured from BAS, USA) followed by ultrasonication in water for 5 min and then polished with diamond paste ($3 \mu m$) and again ultrasonicated for 10 min in water. The composite was coated on glassy carbon electrode by taking $10 \mu l$ of Pt/PEDOT- V_2O_5 composite and dried in an oven at $80^\circ C$ for 2 min to get a thin film on glassy carbon electrode. The electrolyte was degassed with nitrogen gas before the electrochemical measurements were taken.

3. Results and discussion

The synthesis of PEDOT- V_2O_5 nanocomposite is illustrated in Fig. 1. As-synthesized nanocomposite with nanometer-scale Pt particles can produce excellent fuel cell catalysts. Platinum can be dispersed in such a support that leads to a decrease in the amount of expensive noble metal used. Such composites have also improved catalytic activity for the oxidation of methanol via a better utilization of the platinum crystallites and in decreasing the poisoning effect. The typical scheme to be adopted for the preparation of Pt supported composite material is shown in Fig. 1.

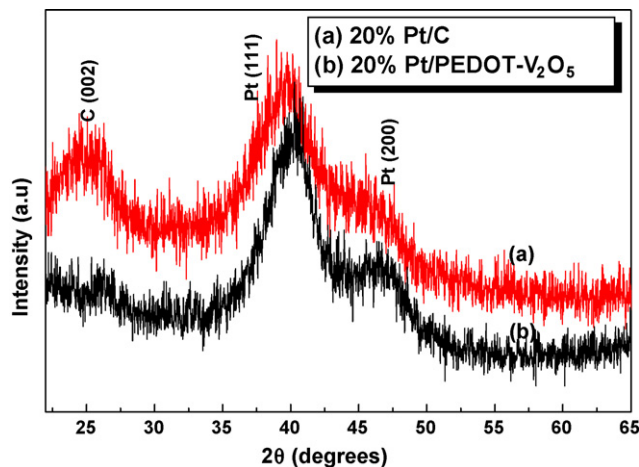


Fig. 2. X-ray diffraction powder pattern of (a) 20% Pt/C and (b) 20% Pt/PEDOT- V_2O_5 nanocomposite catalyst.

3.1. X-ray diffraction study

The powder XRD patterns for Pt/C and Pt/PEDOT-V₂O₅ nanocomposites catalysts are also shown in Fig. 2. The diffraction peak at 25° observed is attributed to the hexagonal graphite structure (002) of Vulcan carbon. Both Pt/Vulcan carbon and Pt/PEDOT-V₂O₅ electrocatalysts displayed the characteristic patterns of Pt FCC diffraction. The peaks can be indexed at 2θ = 39.8° (111), 46.6° (200) reflections of a Pt face-centered cubic (FCC) crystal structure [41].

3.2. Scanning electron microscopy (SEM)

In order to determine the morphologies and elemental distribution of the supports before and after impregnation, SEM and EDX were performed, respectively. The scanning electron microscopic (SEM) images of both V₂O₅ and PEDOT-V₂O₅ nanocomposites are illustrated in Fig. 3a-d respectively, where the latter forms a con-

tinuous and relatively homogeneous matrix with a distinct lamellar morphology. Although, the incorporation of PEDOT into the V₂O₅ leads to morphological changes in agreement with the results of XRD patterns, these can be seen only at high resolution. More significantly, the SEM images also suggest that there is no bulk deposition of polymer on the surface of the microcrystallites.

The SEM image of the nanocomposite support after impregnation with Pt is shown in Fig. 4a-b. After Pt deposition in the nanocomposite material a porous morphology has been developed which is well suited for catalyst support. The nanocomposite catalyst support not only provides ionic and electronic conductivity but also favours mass transport.

The EDX mapping image in a scanning electron microscope (SEM) of the nanocomposite support can provide information on the distribution of Pt. The typical EDX mapping image for the nanocomposite support after impregnation with Pt is shown in Fig. 4c. Fig. 4b and c shows the same area of the sample. The EDX mapping of Pt depicts the homogeneous distribution of platinum

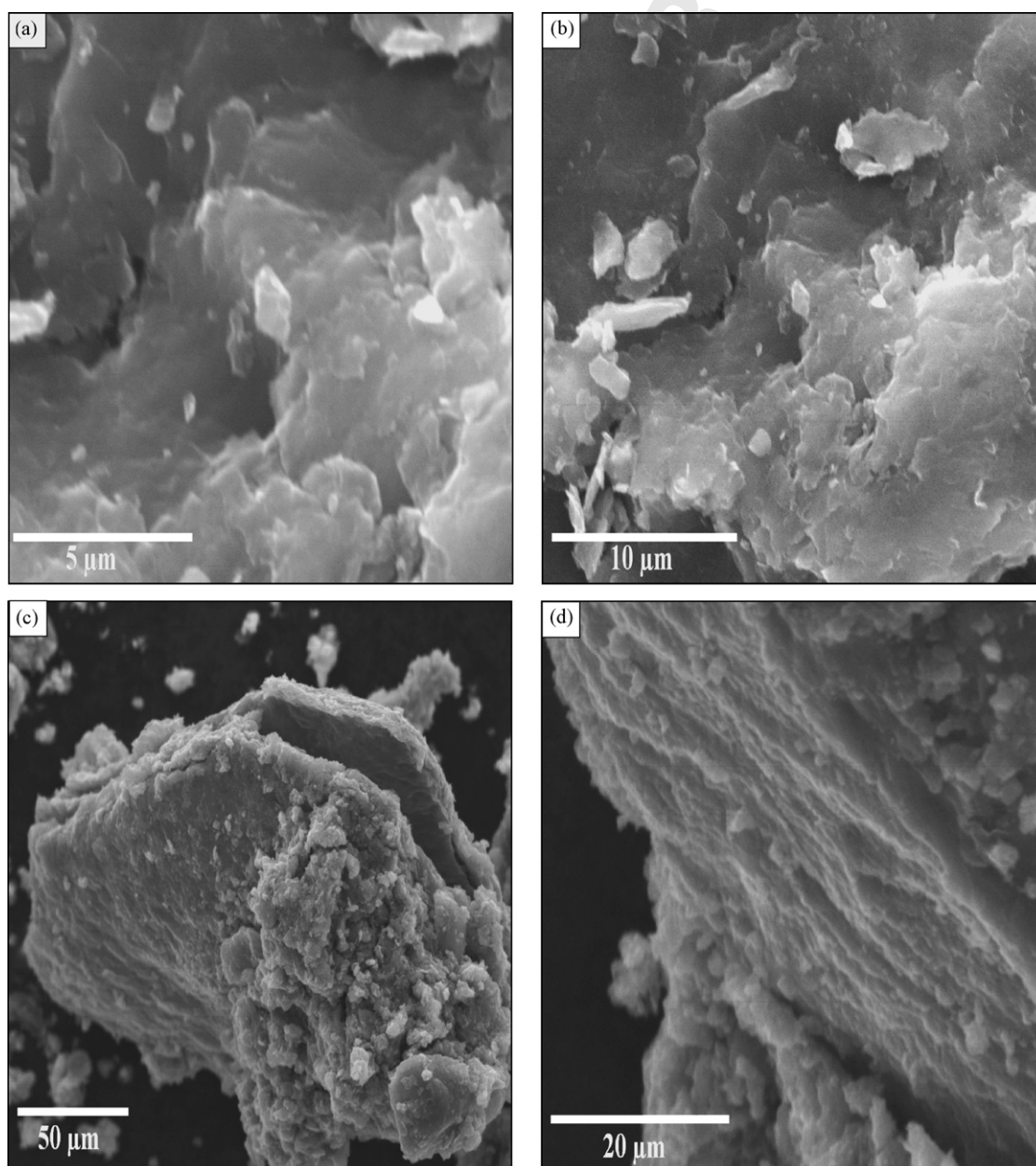


Fig. 3. SEM images of (a and b) V₂O₅ and (c and d) layered hybrid PEDOT-V₂O₅ nanocomposite support.

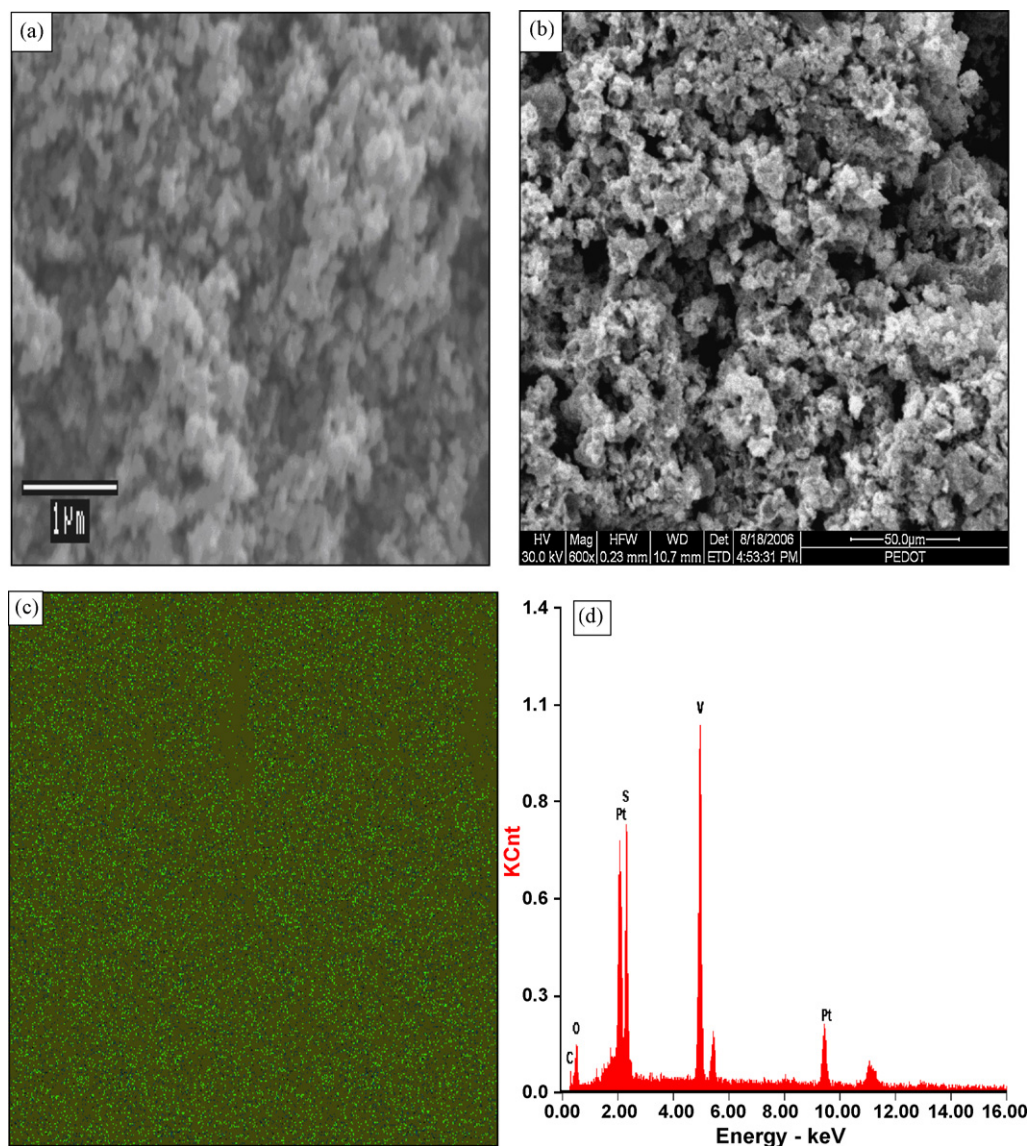


Fig. 4. SEM images of (a and b) 20% Pt/PEDOT-V₂O₅, (c) the corresponding EDX mapping of Pt on PEDOT-V₂O₅ nanocomposite support and (d) EDX-element distribution.

in the nanocomposite, which indicates better catalyst dispersion. The EDX spectrum shown in Fig. 4d substantiated that the catalyst support consisted of Pt and V.

3.3. Transmission electron microscopy (TEM)

A more accurate observation of particle morphology and structure can be realized using transmission electron microscopy (TEM) as illustrated in Fig. 5. The TEM image of Pt/C catalyst was shown in Fig. 5a and the average Pt particle size was 3.1 nm. The TEM image of PEDOT-V₂O₅ nanocomposite support was shown in Fig. 5b. The Pt particles are well dispersed on the nanocomposite support was shown in Fig. 5c and d. The average Pt particle size was found to be around 2.3 nm. TEM image of Pt/PEDOT-V₂O₅ nanocomposite catalyst reveals Pt nanoparticles dispersed throughout the nanocomposite support.

3.4. Electrochemical characteristics of the Pt/PEDOT-V₂O₅ nanocomposite catalysts

The electrochemical behavior of Pt/PEDOT-V₂O₅ nanocomposites and Pt/C catalysts was studied in 1 M H₂SO₄ as shown in

Fig. 6. The potential window was extended to the onset potential for oxygen evolution to enable a better comparison to be made. The hydrogen adsorption rate is more pronounced on the Pt nanoparticles; possibly because of the presence of highly reactive Pt (111) facets, which is evident from the observation of broad hydrogen adsorption-desorption features in the nanocomposite catalyst. Table 1 lists the electrochemical surface areas (ESA) of Pt/PEDOT-V₂O₅ and Pt/C catalyst. Comparing the electrochemically active surface area of the nanocomposite catalyst to the Pt/C showed a promising result. It is found that the Pt/PEDOT-V₂O₅ nanocomposites electrode has a higher ESA (94.6 m² g⁻¹ Pt) than does the Pt/C electrode (70.2 m² g⁻¹ Pt). Its active surface area was found to be higher than that of the commercial JM Pt/C catalyst.

3.5. Evaluation of methanol oxidation on Pt/PEDOT-V₂O₅ nanocomposite catalysts

Fig. 7a shows the cyclic voltammogram of Pt supported PEDOT-V₂O₅ nanocomposite (GC/PEDOT-V₂O₅/Pt) in 1 M H₂SO₄; 1 M methanol scanned between -0.2 and +1.2 V and run at 50 mV s⁻¹. It is evident from the voltammogram that the onset

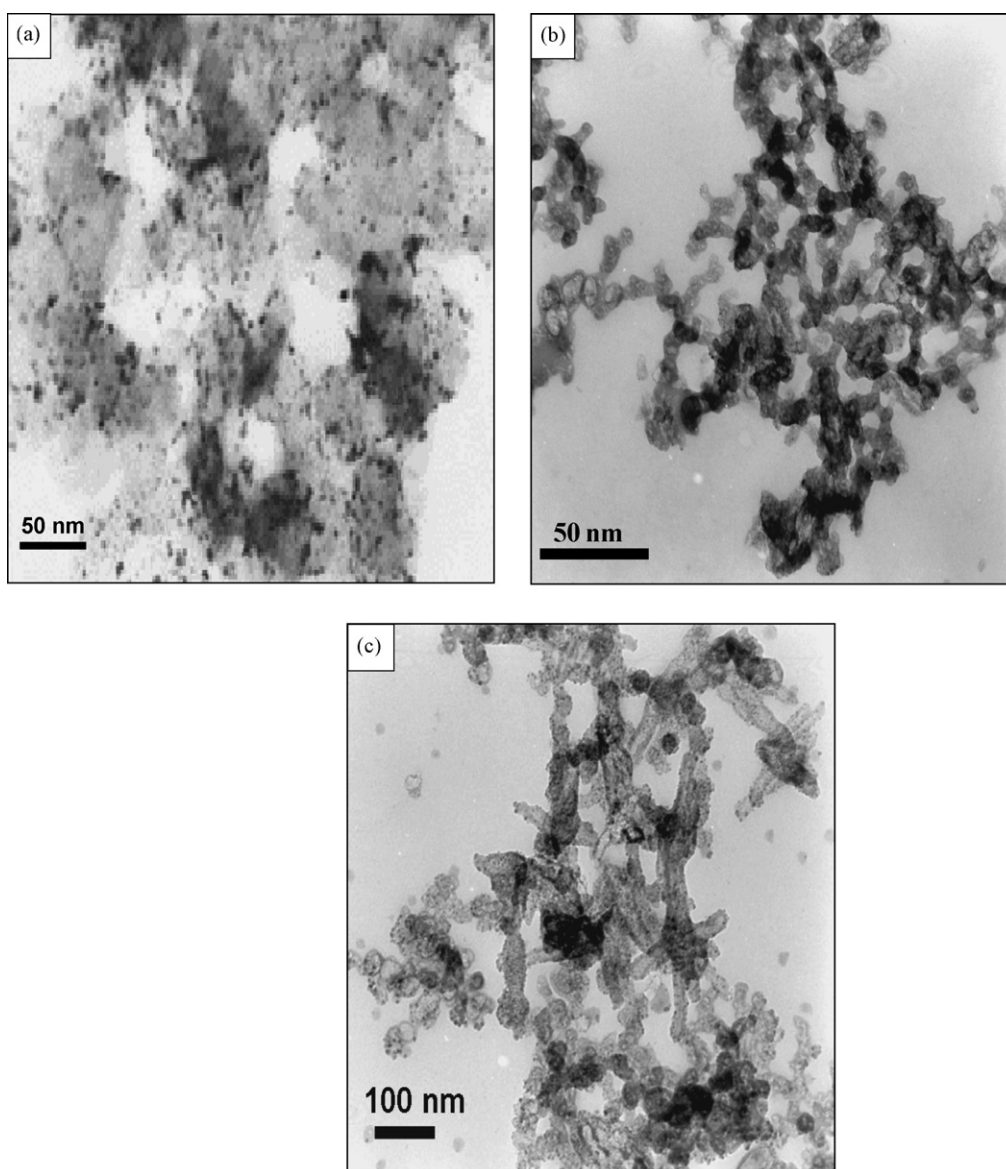


Fig. 5. TEM images of (a) 20% Pt/C (b) PEDOT-V₂O₅ nanocomposite and (c and d) Pt/PEDOT-V₂O₅ catalyst.

of methanol oxidation starts at 300 mV and the current increases linearly with the applied potential and does not exhibit any peak in the forward scan and reaches a maximum current density of 56.4 mA cm⁻² for a Pt loading of 10 μg cm⁻². In the reverse scan, it has found that there is a great decrease in the current and there is a superposition of the voltammogram between +0.8 and +1.0 V which probably suggests the tolerance of nanocomposite electrode toward the strongly adsorbed intermediates. The ratio of the forward anodic peak current (*I_f*) to the reverse anodic peak current (*I_b*) can be used to describe the catalyst tolerance to accumulation of carbonaceous species [42–46]. A higher ratio indicates a more effective removal of the poisoning species on the catalyst surface. The *I_f*/*I_b* ratio of Pt/PEDOT-V₂O₅ is 1.14, which is higher than that of Pt/C (0.80), thus showing a better catalyst tolerance of PEDOT-V₂O₅

nanocomposite. Also the activity of the Pt/PEDOT-V₂O₅ and Pt/C catalysts was presented quantitatively in Table 1.

The potentials of methanol oxidation and vanadium redox couples are shown in Fig. 8. The normal potentials of the probable intermediates in the methanol oxidation are also included. The redox potential of vanadium (VO²⁺/V³⁺) is +337 mV (versus SHE) which lies above the electrode potential of methanol oxidation favours oxidation of methanol. Also vanadium redox couple has also been extensively used in batteries [47,48].

In the present investigation, the increased methanol oxidation activity probably suggests that the vanadium pentoxide present in the matrix might have helped in the bifunctional mechanism. This is due to V₂O₅ functioning as Ru does in Pt-Ru/C catalysts because oxygen-containing species could easily form on the sur-

Table 1
Electrocatalytic activity of Pt/PEDOT-V₂O₅ and Pt/C catalysts for methanol oxidation.

Catalyst	Pt loading (μg cm ⁻²)	Q _H (mC)	Electrochemical surface area (ESA) (m ² g ⁻¹ of Pt)	<i>I_f</i> / <i>I_b</i>	Methanol oxidation activity (mA cm ⁻²)
Pt/PEDOT-V ₂ O ₅	10	99.53	94.62	1.14	57
Pt/C	10	73.77	70.2	0.90	14

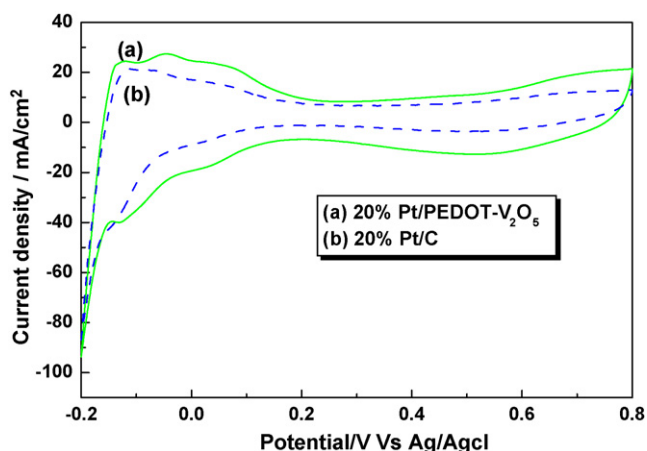


Fig. 6. Cyclic voltammograms of (a) Pt/C and (b) Pt/PEDOT- V_2O_5 nanocomposite catalysts in 1 M H_2SO_4 at a scan rate of 50 mV s^{-1} .

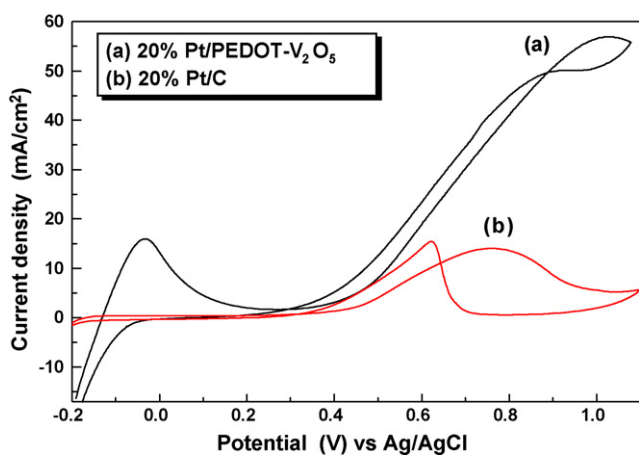


Fig. 7. Cyclic voltammograms of (a) Pt/PEDOT- V_2O_5 nanocomposite and (b) Pt/C electrode in 1 M $H_2SO_4/1 \text{ M } CH_3OH$ at 50 mV s^{-1} .

face of V_2O_5 . Due to the higher affinity of vanadium oxides toward oxygen-containing species, sufficient amounts of OH_{ad} to support reasonable CO oxidation rates are formed at lower potential on V_2O_5 nanocomposite sites than on Pt sites. The OH_{ad} species are necessary for the oxidative removal of CO_{ad} intermediates. This effect leads to a higher activity and longer lifetime for the overall methanol oxidation process on Pt/PEDOT- V_2O_5 nanocomposite. Based on the experimental results, to illustrate the enhanced activity of methanol electro-oxidation a tentative reaction mechanism

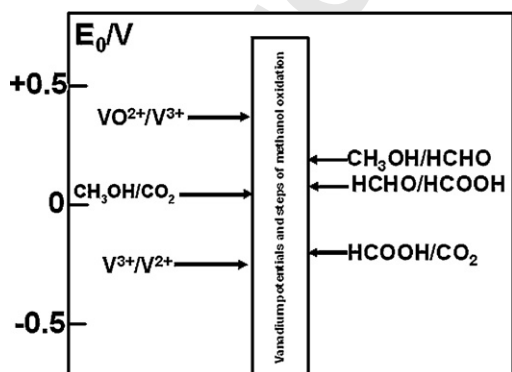
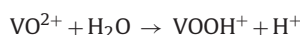
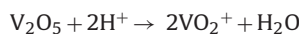


Fig. 8. Electrode potentials of methanol oxidation intermediates and vanadium redox couples [37].

is proposed as follows, $CH_3OH_{ad} \rightarrow CO_{ad} + 4H^+ + 4e^-$



3.6. Chronoamperometric response of the Pt/PEDOT- V_2O_5 nanocomposite catalysts

Fig. 9 shows the chronoamperometric response of Pt/PEDOT- V_2O_5 and Pt/C electrodes at a constant potential of +0.6 V versus Ag/AgCl in 1 M H_2SO_4 and 1 M CH_3OH . The methanol oxidation activity and the stability for Pt/PEDOT- V_2O_5 nanocomposite based electrode were found to be higher than that of Pt/C electrode. The porous PEDOT- V_2O_5 nanocomposite leads to the high dispersion of Pt particles on its surface and also the porous morphology of the nanocomposite is favourable for the transport of methanol in the catalyst layer. The conducting poly (3,4-ethylenedioxythiophene) not only acted as an excellent electronic support for Pt particles but also aided an increased stability of the layered transition metal oxide, under the electrochemical operating conditions.

Although the activity observed in the present investigation is fairly high for the same loading of Pt, the activity can be further increased. The probable reason for this is the conductivity of the nanocomposite system. The conductivity of the nanocomposite system might be higher than the crystalline V_2O_5 and the conductivity of polymer nanocomposite is less than pure conducting polymer. This is due to the conducting polymer intercalation of the layered V_2O_5 which reduces the polymer conductivity, which might affect the charge transfer at the electrode/electrolyte interface. However, the synthesized material incorporated on the high surface area carbon material may improve the dispersion further and enhance the catalytic activity.

During fuel cell operation, electrons and protons generated are found to migrate through the electrode layer. The electrode layer must exhibit good electronic and protonic conductivities to minimize resistive losses in the cell. Commonly used carbon supports (Conductex 975 and Vulcan XC-72) are good conductors of electrons. Carbon based catalyst by itself, however, cannot conduct

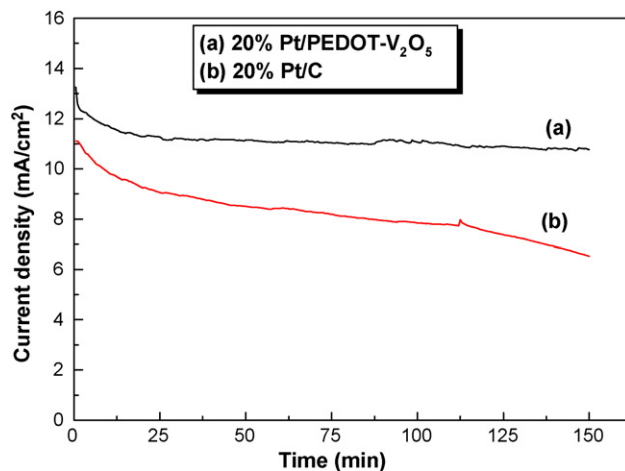


Fig. 9. Chronoamperometric response of (a) Pt/PEDOT- V_2O_5 nanocomposite electrodes and (b) Pt/C polarized at +0.6 V in 1 M $H_2SO_4/1 \text{ M } CH_3OH$.

protons. Introduction of ionomer such as Nafion has been used in the electrodes to improve the protonic conductivity. Nafion solution is used to enhance the three-phase boundary; the electrodes are adhered to the polymer membrane by hot pressing, not in a fused state, but in a simple physically close contact state. Thus, the polymer membrane is simply brought into simple contact with the electrodes in a plane, which has a limit in improving the utilization of the platinum catalyst. Further, Nafion solution itself is expensive and thus increases the cost of the electrodes.

The present conducting polymer nanocomposite provides both protonic conductivity and ionic conductivity and it removes the barrier of a three-phase boundary. The high porosity of nanocomposites is desirable and favourable in fuel cell electrodes because they allow for dispersion of a maximum amount of catalyst particles. They also provide sufficient porosity in the support to enable access of electrolyte to catalyst particles without blocking transport of fuel. Electrode materials designed with these considerations in mind are expected to exhibit maximum activity for fuel cell reactions and could form the basis of a new generation of power sources with a much higher performance than existing devices.

4. Conclusion

The Pt supported PEDOT-V₂O₅ nanocomposite has been evaluated as the electrode for methanol oxidation in an acid medium. The nanocomposite electrode exhibited a fairly high catalytic activity of 28 mA cm⁻² at a Pt loading of 10 μg cm⁻². Electron microscopic studies show the Pt supported PEDOT-V₂O₅ nanocomposite shows a porous morphology, which favours methanol diffusion. TEM investigations showed good dispersion of Pt nanoparticles on PEDOT-V₂O₅ nanocomposite with an average particle size of 2.3 nm. The results also suggest that polymer nanocomposite acts as a better catalyst support than the carbon support material by enhancing methanol oxidation. The Pt/PEDOT-V₂O₅ catalyst synthesized and studied in this work display a series of interesting properties like (a) the presence of vanadium atom(s) is beneficial in several catalytic and electrocatalytic processes (b) vanadium oxide (VO²⁺/V³⁺) redox couple which favours oxidation of methanol. Further, the high electrocatalytic activity of the Pt/PEDOT-V₂O₅ catalyst can be attributed to the high dispersion of the Pt nanoparticles and the porosity of the catalyst improved the capability of mass transport of methanol in the electrode. The results also suggest that, the polymer nanocomposite acts as a better catalyst support than the carbon support material by enhancing methanol oxidation. Future studies will focus on the development of carbon with PEDOT-V₂O₅ nanocomposite supported Pt catalyst and the testing of the composite anode in DMFC.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.matchemphys.2010.01.003.

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