



Pt Supported on Polyaniline-V₂O₅ Nanocomposite as the Electrode Material for Methanol Oxidation

B. Rajesh,^a K. Ravindranathan Thampi,^b J.-M. Bonard,^c N. Xanthopoulos,^d
H. J. Mathieu,^d and B. Viswanathan^{a,z}

^aDepartment of Chemistry, Indian Institute of Technology, Madras, Chennai-600 036, India

^bInstitute of Molecular and Biological Chemistry, ^cDepartment of Physics, and ^dLaboratoire de Metallurgie Chimique, Swiss Federal Institute of Technology, Lausanne CH-1015, Switzerland

The nanocomposite material prepared via the intercalation of polyaniline in V₂O₅ matrix has been used as the support for Pt in methanol oxidation reaction. The average particle size of the Pt as evaluated from the high-resolution transmission electron microscope was found to be 4 nm. The X-ray photoelectron spectroscopy analysis revealed that vanadium is present in the form of V₂O₅ and Pt in the metallic state. The activity of methanol oxidation of the Pt loaded nanocomposite electrode as evaluated from cyclic voltammetry was found to be 111 mAcm⁻² at +0.8 V vs. Ag/AgCl for a Pt loading of 50 μgcm⁻². The chronoamperometric response reveals the better activity and stability of the nanocomposite electrode compared to the bulk Pt electrode. © 2002 The Electrochemical Society. [DOI: 10.1149/1.1518610] All rights reserved.

Manuscript submitted May 28, 2002; revised manuscript received August 30, 2002. Available electronically October 16, 2002. Corrected October 18, 2002.

Considerable effort has been devoted in recent years to developing suitable electrode materials for direct electro-oxidation of methanol. Although research over the past two or three decades¹ identified the best catalyst as Pt-Ru supported on carbon for methanol oxidation, there is still much to be done in developing alternate electrode materials for methanol oxidation. Apart from Pt-Ru catalyst, materials like Pt-WO₃, Pt-MoO₃, and Pt-Ru-MO_x (M = W, Mo, and V) have been used as the electrode material for methanol oxidation.²⁻⁵ The basic reason for choosing these transition metal oxides is that these oxides can form respective tungsten bronzes by effective dehydrogenation of methanol and also the oxophilic nature of the oxide helps in removing the strongly adsorbed intermediates of methanol oxidation. Although these systems showed better activity and stability compared to the Pt, the main problem with these oxides is the severe leaching of the metal (W, Mo, and V) under operating conditions.

The attention of investigators⁶⁻⁹ engaged in the development of new functional materials for current engineering applications has been attracted to composite materials based on electrically conductive polymers and inorganic compounds. The reason for such interest is that materials of this type frequently manifest properties that cannot be achieved by the individual components, this is particularly true when one of the components is present in the form of a nanodimensional phase.¹⁰ These compounds exhibit a number of useful physicochemical properties in addition to chemical stability, opening up possibilities for their use in electrochromic devices, chemical current sources, and photocatalytic and electrocatalytic systems. The preparation of composites of the intercalation type based on polyaniline and V₂O₅ along with the establishment of their composition, structure, and major physicochemical properties have been reported.¹¹ Pokhodenko *et al.* reported¹² the effects of nanosize in the composites based on polyaniline and V₂O₅. The composite material also exhibited excellent stability under electrochemical potential conditions in acidic medium.

The Pt supported on the electrochemically synthesized polyaniline has been used as the electrode material for methanol oxidation¹³⁻¹⁵ but this is the first report on the Pt supported on the chemically synthesized nanocomposite material based on polyaniline and V₂O₅ for electro-oxidation of methanol in acid medium.

The preparation of the intercalated composite material reported, was based on two approaches, one is that the direct chemical oxidation of aniline¹⁶ (*i.e.*, *in situ* oxidative polymersiation of aniline) by xerogel of V₂O₅ and the other approach is based on the reaction of the conducting polymer independently obtained chemically with a

V₂O₅ sol. In this investigation the composite material prepared by the former method has been used as the support for Pt and used as the electrode for methanol oxidation.

Experimental

A conventional three-electrode cell was used in all the experiments. A Pt foil (1.5 cm²) was used as the counter electrode and glassy carbon (GC, 0.07 cm²) obtained from Bioanalytical System, has been used as the working electrode. All the electrochemical measurements were performed using Wenking potentiostat (POS 73) with a Philips digital X-Y recorder (PM 8033).

Aniline (Sisco Research Laboratory, India) was used after distillation and stored dark in nitrogen atmosphere. Dowex Ion Exchange resin (H⁺ form, 50 W-X2, 50-100 mesh) was purchased from Aldrich. The hexachloroplatinic acid was purchased from M/s Hindustan Platinum Ltd., India. All other chemicals used were of analytical (AR) grade and were obtained from Sisco Research Laboratory, India or E. Merck, India.

The X-ray diffractograms (XRD) were obtained for the powdered sample with a Philips PW 1130 model. The diffraction patterns were recorded at room temperature using Ni filtered Cu K α radiation. The particle size was calculated using Scherrer equation ($\tau = 0.897/\beta \cos\theta$). The X-ray photoelectron spectroscopic (XPS) studies were performed using a Perkin elmer PHI 5500 ESCA system using Mg K α as the excitation source. The microscopic features of the sample were observed with Philips EM430 ST operated at 300 kV. The bulk Pt on the electrode was analyzed by inductively coupled plasma atomic emission spectrometer (ICPAES) model 3410 ARL after calibration with standard solution containing known Pt content. The Pt was extracted from the electrode by boiling in aqua regia. The composition of the nanocomposite was evaluated using a Hereaus CHN analyzer.

Preparation of PANI-V₂O₅ nanocomposite.—A known weight, 0.5 g of (2.38 mmol) V₂O₅ xerogel¹⁶ in the form of fine powder was added to 85 mL of 3.5 wt % of distilled aniline aqueous solution. The mixture was stirred at room temperature for 16 h in air. The black powder was isolated by filtration, washed with acetone, and dried in a vacuum at room temperature overnight. By changing the aniline/H₂O ratio and solvent amount, different stoichiometric products can be obtained.

Loading of Pt on Pani-V₂O_{5N} nanocomposite.—To 50 mg of Pani-V₂O₅ nanocomposite, aqueous solution of hexachloroplatinic acid (H₂PtCl₆) was added and it was refluxed at 353 K for about 30 min and then excess of 30% formalin was added as the reducing agent. The resulting solution was again refluxed at the same tem-

^z E-mail: bviswanathan@hotmail.com

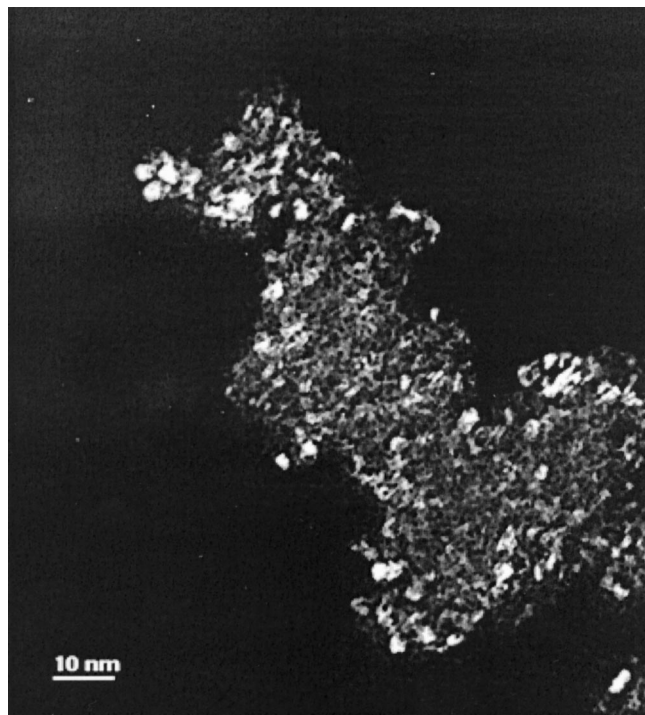


Figure 1. HR-TEM image of Pt loaded on $(C_6H_4NH)_{0.41} V_2O_5 \cdot 0.5H_2O$ nanocomposite.

perature for about 1 h. The solution was filtered and the precipitate was washed well with water and dried in a vacuum at room temperature overnight.

Electrode fabrication.—The electrodes for the electrochemical measurements were fabricated by dispersing the unloaded or Pt loaded nanocomposite in 200 μ L of deionized water and 25 μ L of 5 wt % Nafion solution was then added and ultrasonicated for 20 min. A known amount of suspension was added onto the glassy carbon (GC) electrode and solvent was slowly evaporated which results in unloaded or loaded GC/PANI- V_2O_5 -Nafion nanocomposite electrode. The electrochemical characteristics of the unloaded nanocomposite has been evaluated by cyclic voltammetry (CV) by running the voltammogram in 1 M H_2SO_4 between -0.2 and $+0.8$ V at 50 mV/s. The methanol oxidation has been carried out using the Pt loaded nanocomposite material as the electrode in 1 M H_2SO_4 /1 M CH_3OH under the same experimental conditions adopted for the unloaded nanocomposite. The chronoamperometric experiments were also performed by polarizing the electrode at $+0.4$ V and $+0.6$ V vs. Ag/AgCl electrode.

Results and Discussion

The XRD pattern (not shown) of the PANI- V_2O_5 nanocomposite was agreeable with the one reported in the literature.¹⁶ The particle size of the composite calculated using Scherer equation was found to be 8 nm. The interaction of the polyaniline in the V_2O_5 layers has been confirmed from the interlayer expansion from 11.75 to 13.55 Å.

The composition of the composite evaluated from the CHN analyzer (14.3% C, 1.7% H, and 4.6% N) was $(C_6H_4NH)_{0.41} V_2O_5 \cdot 0.5 H_2O$.

Pt loaded on Pani- V_2O_5 nanocomposite.—Figure 1 shows the high resolution transmission electron microscopy (HR-TEM) image of the Pt loaded $(C_6H_4NH)_{0.41} V_2O_5 \cdot 0.5 H_2O$ nanocomposite. The

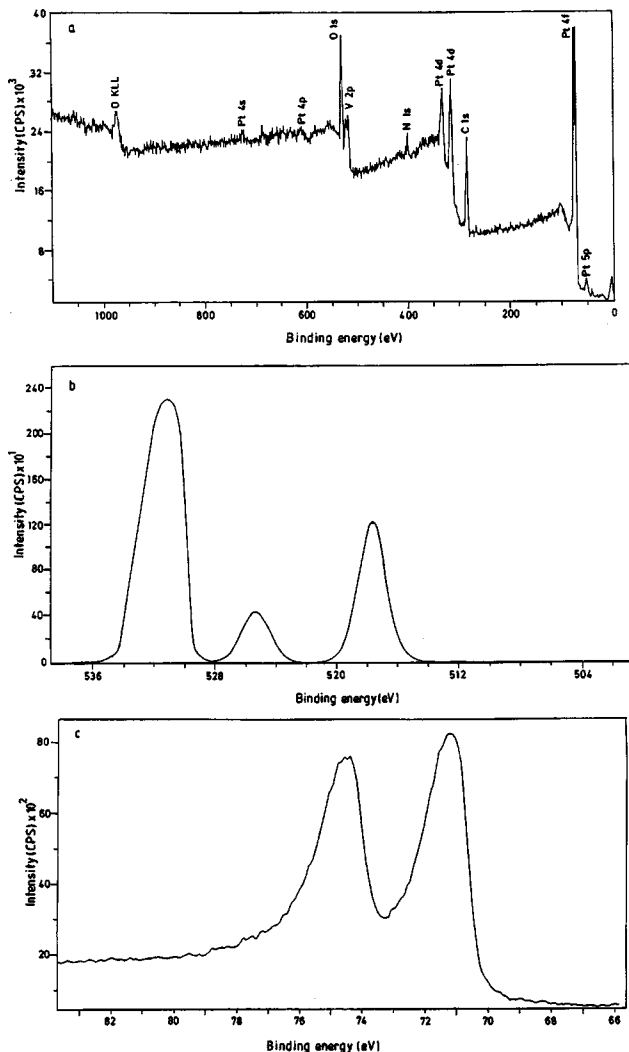


Figure 2. (a) The survey scan XPS spectra of Pt loaded on $(C_6H_4NH)_{0.41} V_2O_5 \cdot 0.5H_2O$ nanocomposite. XPS spectra of (b) V 2p and O 1s and (c) Pt 4f in Pt loaded $(C_6H_4NH)_{0.41} V_2O_5 \cdot 0.5H_2O$ nanocomposite.

dark field and the bright field images clearly reveal the composite comprises of nanoparticles. The presence of Pt nanoparticles is seen as bright small spots on the nanocomposite.

XPS study on Pt loaded $(C_6H_4NH)_{0.41} V_2O_5 \cdot 0.5H_2O$ nanocomposite.—Figure 2a shows the survey scan of the Pt loaded nanocomposite material. It is evident from the spectra that the survey scan is similar to that of the spectra obtained for the PANI- V_2O_5 nanocomposite. But apart from the strong signals due to V 2p, O 1s, N 1s, and C 1s, a very strong signal due to Pt 4f and 4d is also seen. To see in detail the nature of the V and Pt, the V 2p and the Pt 4f regions were recorded (Fig. 2b and c). Figure 2b shows that though the binding energy of V 2p_{3/2} centered at 517.6 eV, the peak due to V 2p_{1/2} is not clearly seen. However, the deconvoluted spectra clearly revealed the peak due to V 2p_{1/2} at 525.3 eV, which once again suggests that the V is present in the form of V_2O_5 in the matrix. The peak at 531.3 eV is due to the O 1s from the V_2O_5 . This also revealed that the formalin used as the reducing agent for the Pt ions did not affect the V in the composite matrix. Figure 2c shows the Pt 4f expanded region. The binding energies of Pt 4f_{7/2} centered at 71.3 eV and Pt 4f_{5/2} centered at 74.5 eV suggest that Pt ions are reduced to the metallic state. The XPS results revealed that the present method of deposition of Pt (using formalin as a reducing

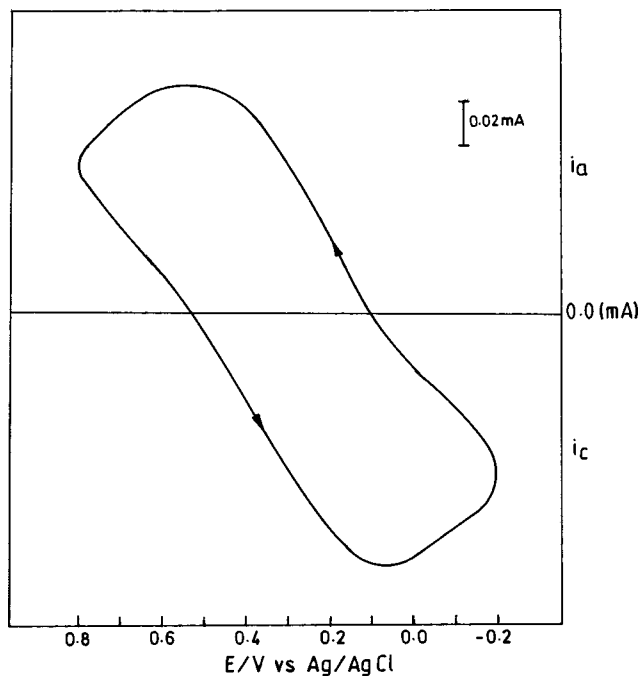


Figure 3. CV of $(C_6H_4NH)_{0.41} V_2O_5 \cdot 0.5H_2O$ nanocomposite electrode in 1 M H_2SO_4 at 50 mV/s.

agent), results in the production of fine dispersion of Pt particles on the nanocomposite. Because the reduction was carried out at a low temperature (353 K), it did not alter the nature of the nanocomposite which is mainly reflected in the X-ray photoelectron spectra of V 2p in Pt supported composite. The X-ray photoelectron spectra of V 2p in the Pt loaded nanocomposite and the composite without platinum (not shown) was identical. But the interaction of the Pt nanoparticles with the nanocomposite needs to be investigated.

Electrochemical characteristics of the $(C_6H_4NH)_{0.41} V_2O_5 \cdot 0.5 H_2O$ nanocomposite.—Figure 3 shows the CV of the unloaded nanocomposite ($(C_6H_4NH)_{0.41} V_2O_5 \cdot 0.5H_2O$) run in 1 M H_2SO_4 after 2 h of continuous cycling at 50 mV/s. The composite exhibited a broad peak at +0.5 V in the forward scan and a slightly narrow peak at +0.1 V in the reverse scan. There is a peak potential difference of 400 mV between the forward and the reverse scan, but there is no observable decrease in the current response between the first scan and the scan at the end of 2 h. The nature of the voltammogram also remained constant. These clearly suggest that the vanadium oxide in the nanocomposite did not undergo any appreciable leaching in the acid medium under the present operating conditions. Another interesting feature is that the voltammogram did not resemble either PANI or V_2O_5 present in the composite. Polyaniline normally¹³ displays two pairs of peaks under similar conditions. The enhanced stability of the composite is due to the interaction between the organic component¹⁶ and the inorganic oxide. The interlayer expansion of the V_2O_5 layers (from XRD results) confirms the compound is an intercalated compound; the enhanced stability and the alteration in the redox potential of the composite demonstrate that the nanodimension of the composite plays an important role for the alteration in the electrochemical property of the composite compared to the individual components. The broad peak also possibly suggests that the particles present in the composite are fine in nature.¹⁴ We did not observe any appreciable difference in the CV of the nanocomposite in the presence of methanol.

Evaluation of methanol oxidation on Pt loaded $(C_6H_4NH)_{0.41} V_2O_5 \cdot 0.5H_2O$ nanocomposite.—Figure 4a shows the CV of Pt loaded $(C_6H_4NH)_{0.41} V_2O_5 \cdot 0.5H_2O$ nanocomposite (GC/PANI-

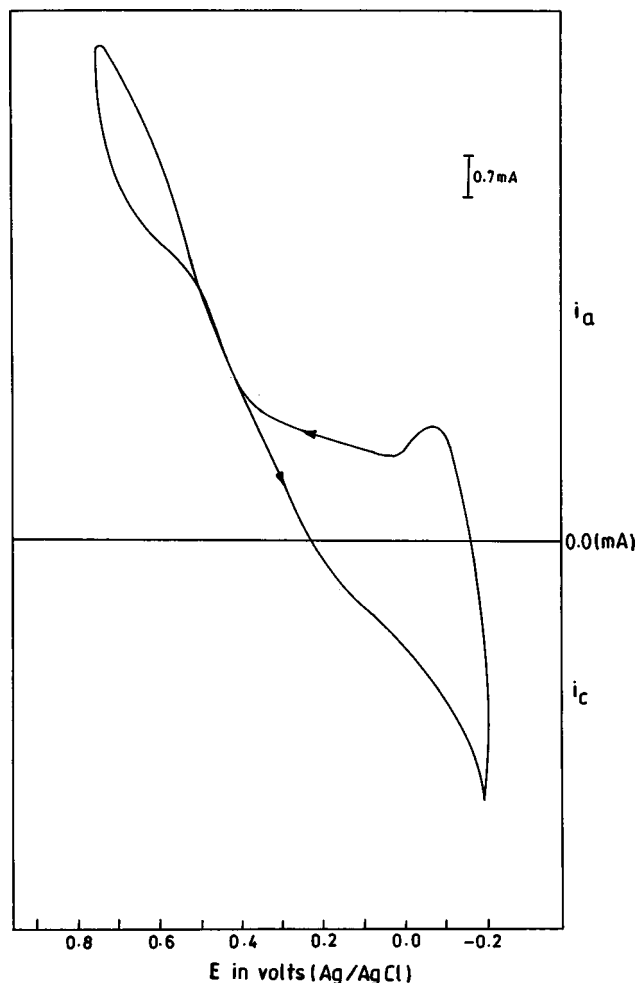


Figure 4. CV of Pt loaded $(C_6H_4NH)_{0.41} V_2O_5 \cdot 0.5H_2O$ nanocomposite electrode in 1 M $H_2SO_4/1$ M CH_3OH at 50 mV/s.

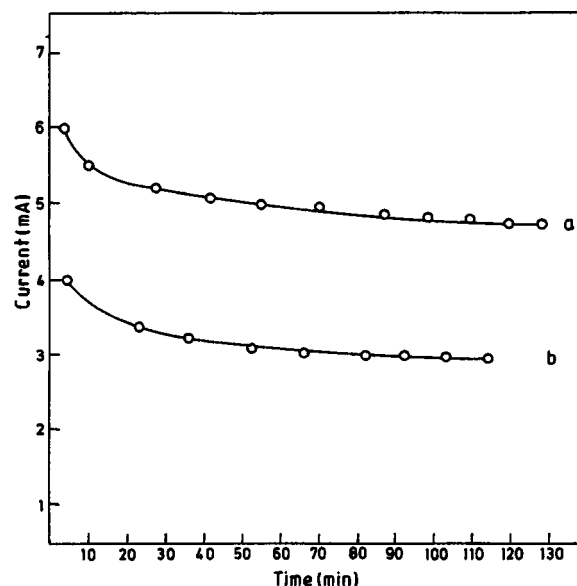


Figure 5. Chronoamperometric response of Pt loaded $(C_6H_4NH)_{0.41} V_2O_5 \cdot 0.5H_2O$ nanocomposite electrodes polarized at (a) +0.6 V and (b) +0.4 V in 1 M $H_2SO_4/1$ M CH_3OH .

V₂O₅-Naf/Pt) in 1 M H₂SO₄ scanned between -0.2 and +0.8 V and run at 50 mV/s. The presence of Pt is evident from the broad peak at -0.2 V vs. Ag/AgCl, which is due to the hydrogen adsorption on Pt. The broad peak suggests that the Pt particles are finely dispersed¹³ on the nanocomposite. Figure 4b shows the CV of Pt loaded (C₆H₄NH)_{0.41} V₂O₅·0.5H₂O nanocomposite (GC/PANI-V₂O₅-Naf/Pt) in the presence of 1 M H₂SO₄/1 M CH₃OH run at 50 mV/s. It is evident from the voltammogram that the onset of methanol oxidation starts at 50 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 111 mA/cm² at +0.8 V for a Pt loading of 50 μg/cm². In the reverse scan there is a slight decrease in the current between +0.8 and +0.6 V, the superposition of the voltammogram between +0.5 and +0.4 V probably suggests the tolerance of nanocomposite electrode toward the strongly adsorbed intermediates. Normally the onset of methanol oxidation will be around +0.2 V vs. Ag/AgCl for the Pt deposited on polyaniline¹³ electrode. In the present investigation, the shift of the onset potential for methanol oxidation toward the less positive side probably suggests that the vanadium pentoxide present in the matrix might have helped in the bifunctional mechanism. Although the activity observed in the present investigation is fairly high for the present 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 V₂O₅, but the present method of the intercalation of the polymer reduces the polymer conductivity, which might effect the charge transfer at the electrode/electrolyte interface. However, supporting the currently synthesized material on the high surface area carbon material may improve the dispersion further and the catalytic activity.

Chronoamperometric response of the Pt loaded (C₆H₄NH)_{0.41} V₂O₅·0.5 H₂O nanocomposite.—Figure 5a and b show the chronoamperometric response of the Pt loaded (C₆H₄NH)_{0.41} V₂O₅·0.5H₂O nanocomposite (GC/PANI-V₂O₅-Naf/Pt) in 1 M H₂SO₄/1 M CH₃OH. It is evident from Fig. 5a that the decrease in the percentage activity at the end of 2 h when the electrode was polarized at +0.6 V was 23% and the decrease in the activity of the loaded composite electrode when the electrode was polarized at +0.4 V (Fig. 5b) was 20%. These results reveal that the difference in the decrease in activity was slight, which suggests the better stability of the V₂O₅ even at +0.6 V. In bulk Pt electrode the initial activity of 10 mA/cm², decreased to 0.7 mA/cm² in less than 10 min. The rapid decay of the activity of the bulk Pt electrode for methanol oxidation suggests the severe poisoning of the electrode surface (not shown).

Conclusions

The Pt loaded on PANI-V₂O₅ nanocomposite has been evaluated as the electrode for methanol oxidation in acid medium. The electrode exhibited a fairly high catalytic activity of 111 mA/cm² at +0.8 V vs. Ag/AgCl with a Pt loading of 50 μg/cm². The particle size of the Pt loaded composites was found to be 8-10 nm as evaluated from the HR-TEM. The XPS results on the Pt loaded nanocomposite revealed that the vanadium oxidation state was not affected during the reduction of Pt ions and the Pt was found to be in the metallic state. The chronoamperometric response revealed that the stability of the Pt loaded composite electrode for methanol oxidation did not vary much, when the electrode was polarized at +0.6 and +0.4 V, which suggests that V was stable even at +0.6 V. Though, the observed activity is fairly high for the extent of loading of Pt, the activity can further be increased. The probable reason for this is the conductivity of the composite system. Though the conductivity of the composite system is higher than that of the crystalline V₂O₅, the intercalation of the polymer reduces the conductivity of the polyaniline. This might effect the charge transfer at the electrode/electrolyte interface. But, supporting the synthesized material on the carbon can improve the catalytic activity.

The Indian Institute of Technology assisted in meeting the publication costs of this article.

References

1. A. B. Anderson and E. Grantscharava, *J. Phys. Chem.*, **99**, 9143 (1995).
2. S. Wasmus and A. Kuver, *J. Electroanal. Chem.*, **461**, 14 (1999).
3. H. Zhang, Y. Wang, E. R. Fuchini, and C. R. Cabrera, *Electrochem. Solid-State Lett.*, **2**, 437 (1999).
4. P. K. Shen and A. C. C. Tseung, *J. Chem. Soc. Faraday Trans.*, **90**, 3089 (1994).
5. P. K. Shen and A. C. C. Tseung, *J. Electrochem. Soc.*, **141**, 3083 (1994).
6. A. K. Shukla, M. K. Ravikumar, A. S. Arico, G. Candiano, V. Antonucci, N. Giordano, and A. Hamnett, *J. Appl. Electrochem.*, **25**, 528 (1995).
7. C.-G. Wu, D. C. DeGroot, H. O. Marcy, J. L. Schindler, C. K. Kannewarf, Y. J. Liu, W. Hirpo, and M. J. Kanatzidis, *Chem. Mater.*, **8**, 1992 (1996).
8. M. G. Kanatzidis, L. M. Tonge, and T. J. Marks, *J. Am. Chem. Soc.*, **109**, 3797 (1987).
9. H. Masbah, D. Timet, M. Craspin, R. Erre, R. Satton, and H. Van Damme, *J. Chem. Soc. Chem. Commun.*, **1985**, 935.
10. R. Bissenensar, D. C. DeGroot, J. L. Schindler, C. P. Kannewarf, and G. Kanatzidis, *J. Chem. Soc. Chem. Commun.*, **1991**, 205.
11. M. G. Kanatzidis and C. G. Wu, *J. Am. Chem. Soc.*, **111**, 4139 (1989).
12. V. D. Pokhodenko, V. A. Krylov, Y. I. Kurys, and O. L. Posudievsky, *Phys. Chem. Chem. Phys.*, **1**, 905 (1999).
13. H. Laborde, J. M. Leger, and C. Lamy, *J. Appl. Electrochem.*, **24**, 219 (1994).
14. H. Laborde, J. M. Leger, and C. Lamy, *J. Appl. Electrochem.*, **24**, 1019 (1994).
15. A. Malinauskas, *Synth. Met.*, **107**, 75 (1999).
16. V. D. Pokhodenko and V. A. Krylove, *Synth. Met.*, **41-43**, 533 (1991).