

Short communication

Electronically conducting hybrid material as high performance catalyst support for electrocatalytic application

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Abstract

The electronically conducting hybrid material based on transition metal oxide and conducting polymer has been used as the catalyst support for Pt nanoparticles. The Pt nanoparticles loaded hybrid organic (polyaniline)–inorganic (vanadium pentoxide) composite has been used as the electrode material for methanol oxidation, a reaction of importance for the development of direct methanol fuel cells (DMFC). The hybrid material exhibited excellent electrochemical and thermal stability in comparison to the physical mixture of conducting polymer and transition metal oxide. The Pt nanoparticles loaded hybrid material exhibited high electrocatalytic activity and stability for methanol oxidation in comparison to the Pt supported on the Vulcan XC 72R carbon support. The higher activity and stability is attributed to the better CO tolerance of the composite material.

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1. Introduction

The attention of investigators [1–4] engaged in the development of new functional materials for current engineering applications has been attracted to hybrid 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 component is present in the form of a nanodimensional phase [5]. 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, photocatalytic and electrocatalytic systems.

Considerable interest has been devoted in recent years to develop suitable electrode materials for methanol oxidation for the possible application in fuel cells. Though, research over the past two or three decades [6–10] identified the best catalyst as Pt and Pt–Ru supported on carbon for methanol oxidation, there is lot of scope still available in developing alternate electrode materials for better activity (with lower Pt loading) and stability 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 [11–13]. The basic reason for choosing these transition metal oxides is that these oxides form respective tungsten bronzes during dehydrogenation of methanol by effectively removing the nascent hydrogen from the Pt surface. This helps to perform the dehydrogenation

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over Pt at relatively low overpotentials. Also the oxophilic nature of the oxide helps in removing the strongly adsorbed reaction intermediates from the reaction site. Though, these systems showed better activity and stability compared to Pt, the main problem is the severe leaching of the metal (W, Mo and V) under operating conditions.

The preparation of composites of the intercalation type based on polyaniline and V_2O_5 along with the establishment of their composition, structure and major physico-chemical properties have been reported [14]. Pokhodenko and Krylove reported [15] the effects of nanosize in the composites based on polyaniline and V_2O_5 . 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 oxidation [16,17] but here we report on the Pt supported on the chemically synthesised electronically conducting hybrid material based on polyaniline and V_2O_5 for electrooxidation of methanol.

2. Experimental methods

In a typical synthesis, 0.5 g of (2.38 mmol) V_2O_5 Xerogel 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 aniline monomer is oxidatively polymerised by V_2O_5 with the generation of V^{4+} . V_2O_5 not only acting as the host lattice for the intercalation of polyaniline but also act as a good oxidizing agent. The black powder was isolated by filtration, washed with acetone and dried in vacuum at room temperature overnight. By changing the aniline/ H_2O ratio and solvent amount, different stoichiometric products can be obtained [14].

To 50 mg of PANI- V_2O_5 nanocomposite, aqueous solution of hexa chloroplatinic acid (H_2PtCl_6) 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 temperature for about

1 h. The solution was filtered and the precipitate was washed well with water and it was finally dried in vacuum at room temperature overnight. The Pt loaded on Vulcan XC 72R carbon were prepared by the procedure reported in a previous report [18]. The electrochemical measurements were performed using a Potentiostan Wenking (POS 73) with Philips digital X-Y recorder (PM 8033). The Pt foil (1 cm^2) and Ag/AgCl were used as the counter and reference electrodes, respectively. The working electrode was 0.07 cm^2 glassy carbon (Bio Analytical System, USA) and Pt foil was used as the counter electrode. X-ray diffractograms were obtained for the powdered samples with a Philips PW 1130 the diffraction patterns were recorded at room temperature using a Ni filtered Cu $K\alpha$ radiation ($\lambda = 1.5418\text{ \AA}$). A scanning speed of 3° min^{-1} and a chart speed of 5 mm per degree were generally employed. The X-ray photoelectron spectroscopic studies were performed using a Perkin Elmer PHI 5500 ESCA system using Mg $K\alpha$ as the excitation source. The C,H and N analysis was done using the Heraeus CHN analyser.

3. Results and discussion

The X-ray diffraction pattern (Fig. 1a) of the PANI- V_2O_5 nanocomposite was agreeable with the one reported in [15]. Only (00*l*) reflections are observed in the X-ray diffraction pattern which is a typical pattern for quasi-crystalline layered materials. The particle size of the composite calculated using scherer equation was found to be 8 nm. In order to confirm further, the intercalation of polyaniline in V_2O_5 matrix, the XRD pattern of the physical mixture of PANI and V_2O_5 was recorded (Fig. 1b). As it is evident from the XRD pattern, there is a shift of 1° (2θ) towards the lower side of the nanocomposite in comparison to the physical mixture, which accounts for the interlayer expansion from 11.75 to 13.55 \AA .

The composition of the composite evaluated from the CHN analyser (14.3% C, 1.7% H and 4.6% N) was found to be $(C_6H_4NH)_{0.41}V_2O_5 \cdot 0.5H_2O$. Fig. 2 shows the HR-TEM image of Pt loaded $(C_6H_4NH)_{0.41}V_2O_5 \cdot 0.5H_2O$ nanocom-

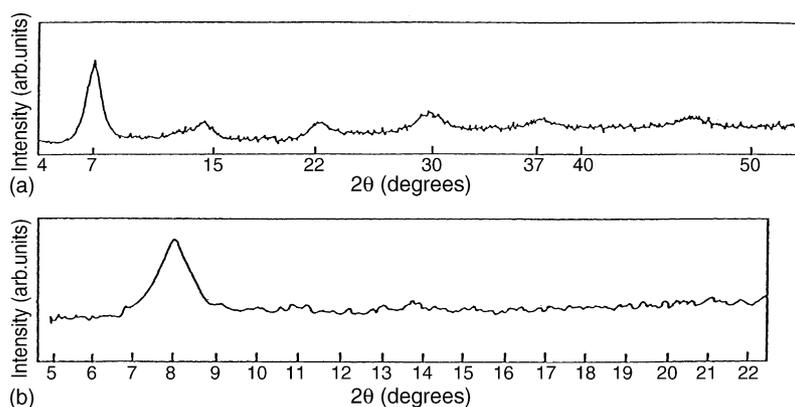


Fig. 1. X-ray diffraction pattern of (a) polyaniline- V_2O_5 ($(C_6H_4NH)_{0.41}V_2O_5 \cdot 0.5H_2O$) nanocomposite; (b) physical mixture of polyaniline and V_2O_5 .

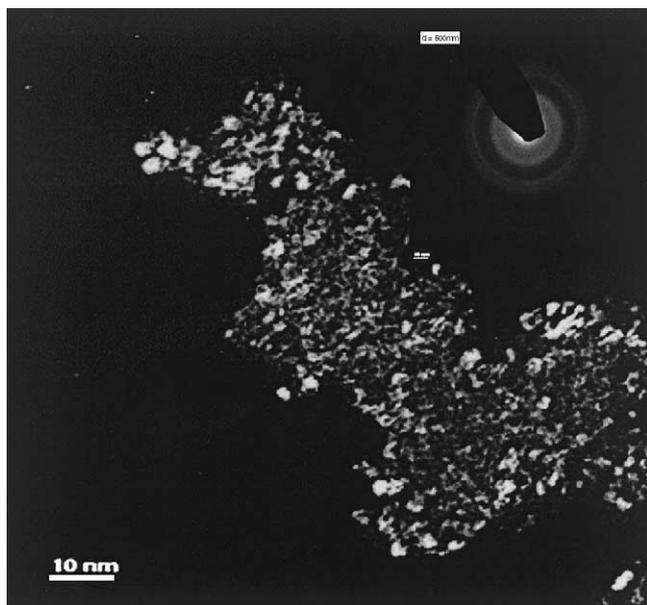


Fig. 2. HR-TEM image of Pt loaded $(C_6H_4NH)_{0.41}V_2O_5 \cdot 0.5H_2O$ nanocomposite.

posite. The dark field image clearly revealed the composite comprises of nanoparticles with an average particle size of 10 nm. The presence of Pt particles is seen as bright small spots on the nanocomposite and the *inset* shows the electron diffraction image of Pt particles. The number of concentric rings observed in the electron diffraction image suggests that the Pt particles are finely dispersed on the nanocomposite. These rings are indexed from the inside as 1 1 1, 2 0 0, 2 2 0, 3 1 1 reflectance for f.c.c. Pt.

The XPS spectra of V 2p and Pt 4f regions were recorded. The binding energy of V 2p_{1/2} at 525.3 eV, suggests that the V is present in the form of V₂O₅ in the matrix. The peak at 531.3 eV is due to the 1s O from the V₂O₅. This also revealed that the formalin that is used as the reducing agent for the Pt ions did not affect the V in the composite matrix. The binding energies of Pt 4f_{7/2} centred at 71.3 eV and Pt 4f_{5/2} centred 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 reducing agent), results in the production of fine dispersion of Pt particles on the nanocomposite. Since, the reduction was carried out at a low temperature (353 K), it did not alter the nature of the nanocomposite which is mainly reflected from the X-ray photo electron 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 was identical. But the interaction of the Pt nanoparticles with the nanocomposite needs to be investigated.

The intercalated nanocomposite $(C_6H_4NH)_{0.41}V_2O_5 \cdot 0.5H_2O$ (without Pt) has been examined for electrochemical stability by cycling the electrode between -0.2 and $+0.8$ V in 1 M H₂SO₄ for 3 h, with a scan rate of 50 mV s^{-1} . In the first cycle, the composite exhibited an anodic peak at $+0.5$ V

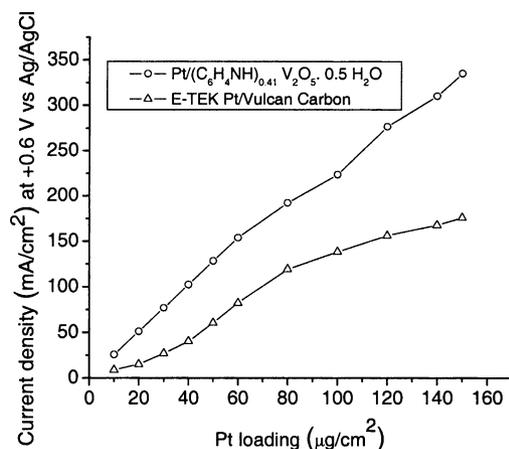


Fig. 3. Variation of current density (current densities were measured at $+0.6$ V for CVs run in 1 M H₂SO₄/1 M CH₃OH between -0.2 and $+0.8$ V) with Pt loading.

in the forward scan (with a peak current of $65 \mu\text{A}$) and a cathodic peak at $+0.1$ V in the reverse scan (with a peak current of $67 \mu\text{A}$). The final cycle at the end of 2 h exhibited peaks at the same potentials in the forward and the reverse scan with a peak current of 62 and $63 \mu\text{A}$. This revealed that the intercalated nanocomposite exhibited excellent electrochemical stability under the present experimental conditions.

Fig. 3 shows the variation in performance of methanol oxidation current densities with Pt loading on Pt loaded $(C_6H_4NH)_{0.41}V_2O_5 \cdot 0.5H_2O$ nanocomposite and Pt/Vulcan carbon based electrodes. It is evident that for the nanocomposite based electrode, as the Pt loading increases there is a continuous increase in activity from 26 mA cm^{-2} (Pt = $10 \mu\text{g cm}^{-2}$) to 335 mA cm^{-2} (Pt = $150 \mu\text{g cm}^{-2}$). But in the case of Pt/Vulcan XC 72R carbon electrode the activity increase was from 12 mA cm^{-2} (Pt = $10 \mu\text{g cm}^{-2}$) to 176 mA cm^{-2} (Pt = $150 \mu\text{g cm}^{-2}$). This revealed that the nanocomposite electrode exhibited nearly two times higher activity compared to the Pt/Vulcan XC 72R carbon electrodes.

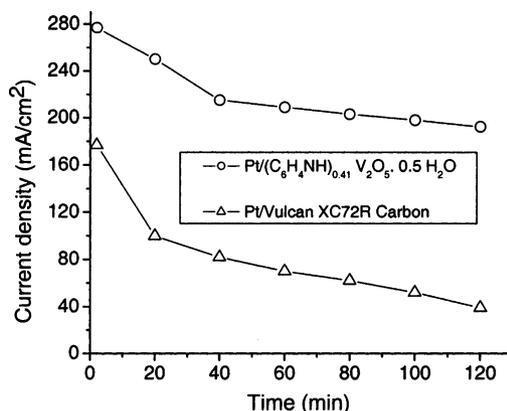


Fig. 4. Variation of current density with time in 1 M H₂SO₄/1 M CH₃OH at $+0.6$ V vs. Ag/AgCl (Pt = $120 \mu\text{g cm}^{-2}$).

Fig. 4 shows the chronoamperometric response of Pt/(C₆H₄NH)_{0.41}V₂O₅·0.5H₂O and Pt/Vulcan XC 72R carbon electrodes at a constant potential of +0.6 V versus Ag/AgCl in 1 M H₂SO₄ and 1 M CH₃OH. The decrease in methanol oxidation activity was found to be 29% for Pt/(C₆H₄NH)_{0.41}V₂O₅·0.5H₂O nanocomposite based electrode at the end of 2 h, whereas the decrease in activity at the end of 2 h for the Pt/Vulcan XC 72R carbon was found to be 78%. And more interestingly, though the initial activity of Pt/(C₆H₄NH)_{0.41}V₂O₅·0.5H₂O was only 1.5 times higher than the Pt/Vulcan XC 72R carbon electrode, the methanol oxidation activity at the end of 2 h was found to be nearly five times than the Pt/Vulcan XC 72R carbon electrode. This clearly demonstrated that the activity and the stability for methanol oxidation were found to be higher than the Pt/Vulcan XC 72R carbon electrode.

4. Conclusions

The Pt loaded conducting polyaniline intercalated vanadium pentoxide nanocomposite exhibited excellent activity and stability for methanol oxidation compared to the Pt loaded on the commercial Vulcan XC 72R carbon support. The conducting polyaniline not only acted as an excellent electronic support for Pt particles but also aided for an increased stability of the layered transition metal oxide, under present electrochemical operating condition. A more detailed investigation on the role of V₂O₅ as a co-catalyst for methanol oxidation is currently under progress. The present preliminary investigation encourage to employ this material as electrocatalyst not only in direct methanol fuel cells (DMFC) but also for hydrogen oxidation in proton exchange membrane fuel cells (PEMFC), when the hydrogen gas is contaminated with CO. Currently we are investigating on the effect of electronic conductivity of the nanocomposite and Pt–Ru deposited intercalated nanocomposite for evaluating the electrocatalytic activity of methanol oxidation.

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References

- [1] C.-G. Wu, D.C. DeGroot, H.O. Marcy, J.L. Schindler, C.K. Kannewarf, Y.J. Liu, W. Hirpo, M.J. Kanatzidis, *Chem. Mater.* 8 (1996) 1992.
- [2] H. Masbah, D. Timet, M. Craspin, R. Erre, R. Satton, H. Van Damme, *J. Chem. Soc. Chem. Commun.* (1985) 935.
- [3] R. Bissensar, D.C. DeGroot, J.L. Schindler, C.P. Kannewarf, G. Kanatzidis, *J. Chem. Soc. Chem. Commun.* (1991) 205.
- [4] M.G. Kanatzidis, C.G. Wu, *J. Am. Chem. Soc.* 111 (1989) 4139.
- [5] M.G. Kanatzidis, L.M. Tonge, T.J. Marks, *J. Am. Chem. Soc.* 109 (1987) 3797.
- [6] K.Y. Chan, J. Ding, S. Cheng, K.Y. Tsang, *J. Mater. Chem.* 14 (2003) 505.
- [7] B. Rajesh, K. Ravindranathan Thampi, J.M. Bonard, N. Xanthopoulos, H.J. Mathieu, B. Viswanathan, *Fuel* 81 (2002) 2177.
- [8] S. Wasmus, A. Kuver, *J. Electroanal. Chem.* 60 (1999) 14.
- [9] B. Rajesh, K. Ravindranathan Thampi, J.M. Bonard, A.J. McEvoy, N. Xanthopoulos, H.H. Mathieu, B. Viswanathan, *J. Power Sources* 133 (2004) 155.
- [10] B. Rajesh, K. Ravindranathan Thampi, J.M. Bonard, N. Xanthopoulos, H.J. Mathieu, B. Viswanathan, *J. Phys. Chem. B.* 107 (2003) 2701.
- [11] K.W. Park, K.S. Ahn, Y.C. Nah, J.H. Choi, Y.E. Sung, *J. Phys. Chem. B* 107 (2003) 4352.
- [12] H. Zhang, Y. Wang, E.R. Fuchini, C.R. Cabrera, *Electrochem. Solid-State Lett.* 2 (1999) 437.
- [13] P.K. Shen, A.C.C. Tseung, *J. Electrochem. Soc.* 141 (1994) 3083.
- [14] V.D. Pokhodenko, V.A. Krylov, Y.I. Kurys, O.L. Posudievsky, *Phys. Chem. Chem. Phys.* 1 (1999) 905.
- [15] V.D. Pokhodenko, V.A. Krylove, *Synth. Met.* 41–43 (1991) 533.
- [16] H. Laborde, J.M. Leger, C. Lamy, *J. Appl. Electrochem.* 24 (1994) 219.
- [17] A. Malinauskas, *Synth. Met.* 107 (1999) 75.
- [18] T. Ioroi, N. Fujiwara, Z. Siroma, K. Yasuda, Y. Miyazuki, *Electrochem. Commun.* 4 (2002) 442.