

V₂O₅-MWNT NANOCOMPOSITE AS A PROMISING SUPPORT FOR PLATINIUM IN METHANOL ELECTRO - OXIDATION

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Introduction

Direct methanol fuel cells are very important as a clean, low cost and portable power source because of several environmental problems in traditional energy producing systems. Compared to the hydrogen fueled PEMFCs, direct methanol PEMFCs are more compact and can be used in power portable electric devices. Platinum is the most active electro-catalyst for the electro-oxidation of methanol. However, pure platinum is a poor anode catalyst for methanol electro-oxidation at lower temperatures. This is because CO and various other carbonaceous intermediates are generated and block the active sites of the platinum catalyst during methanol electro-oxidation [1,2]. Making alloys with a second or a third metal is a convenient way to modify the electro-catalytic properties of platinum. Pt-Ru alloy is considered to be the best available anodic material for DMFCs [3]. 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 [4-8]. One of the reasons for choosing these transition metal oxides is that these oxides form tungsten bronzes during dehydrogenation of methanol by effectively removing the hydrogen from the Pt surface. This helps to perform the dehydrogenation over Pt at lower over potentials. Also the oxophilic nature of the oxide helps in removing the strongly adsorbed reaction intermediates from the reaction site.

In this study we proposed vanadium oxide / multi-wall carbon nanotube nanocomposite as a promising material for using as the support for Pt nanoparticles in methanol electro-oxidation.

experimental

Materials

All the chemical were of analytical grade. V₂O₅ and H₂PtCl₆.6H₂O were purchased from Aldrich. Also home made carbon nanotubes were used. Methanol, ethylene glycol and sulphuric acid were obtained from merck and the 5%wt solution of nafion was bought from alfa aesar.

Preparation of electro- catalysts

Firstly, the MWNT's were functionalized with a mixture of sulphuric acid and nitric acid with a ratio of 3:1. Secondly, the functionalized MWNT's were dispersed well in 2-propanol in an ultrasonic bath. Next, a solution of vanadium oxide in 2-propanol was mixed well with the above suspension at 80°C

and dried in an oven over night. The resulted nanocomposite of vanadium oxide and MWNT's were introduced into a microwave oven and heated several times.

The Pt/V₂O₅-CNT catalyst was synthesized by polyol process. Briefly, the carbon nanotubes were dispersed in ethylene glycol and mixed well with aqueous solution of hexachloroplatinic acid. Next, the reaction was conducted at 130°C under reflux for 3h. Then the resulted catalyst was washed with ample amount of water and dried in a vacuum oven at 100°C for 6h.

Also, the same procedure as the above was repeated for the preparation of Pt/CNT catalyst.

Electrochemical measurement

A conventional three electrode cell was used with a glassy carbon electrode (0.0314cm²) as working electrode, a Pt plate (5.2 cm²) as counter electrode and a saturated calomel electrode as the reference electrode. The CV experiments were carried out using 0.5 M H₂SO₄ solution in the absence and presence of 1M CH₃OH at a scan rate of 50 mV/s.

Results and Discussion

The electro-catalytic activities for methanol oxidation on the Pt/CNT and Pt/CNT-V₂O₅ catalysts were analyzed by cyclic voltammetry, CO-stripping and chronoamperometry experiments. The voltammograms of Pt/CNT and Pt Pt/MWNT-vanadium oxide electrodes are shown in Fig. 1. It is appear in fig.1 that the onset potential of methanol electro-oxidation for the catalyst are almost the same but the peak current densited in forward scan improves from 88 mA/cm² for Pt/CNT to 164 mA/Cm² in Pt/CNT-V₂O₅. This confirms that the vanadium oxide nanoparticles increase the platinum catalytic activity in methanol electro-oxidation.

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 [9-10]. A higher ratio indicates more effective removal of the poisoning species on the catalyst surface. In fig. 1, the ratio of forward scan peak current density to the current peak of backward scan improves from 0.67 to 0.87 be cause of using nanocomposite of vanadium oxide nanoparticles and multiwall carbon nanotubes as the catalyst support. This shows that vanadium nanoparticles improve oxidation and removal of intermediate chemical species from methanol electro-oxidation reaction on platinum active sites. This is also confirmed from CO-stripping results in fig. 2. The results showed that the onset potential of CO electro-oxidation on the Pt/CNT-V₂O₅ is 25 mV less than Pt/MWNT which means that the former shows higher CO tolerance. This is another evidence for improvement in Bi-functional mechanism as a result of V₂O₅ addition on the carbon nanotubes. The cyclic voltammetry results in a 0.5M H₂SO₄ aqueous solution in absence of CO are compared in fig. 3. Two peaks in the potential range from -0.2 to .1 V are related to hydrogen desorption from the electrode active sites. By comparing the corresponding hydrogen desorption peak areas, it will be appeared that the

electrochemical active surface area (EAS) is varied from 125 in case of Pt/CNT to 186 for Pt/CNT-V₂O₅. This can be explained by formation some new active sites for methanol electro-oxidation as a result of vanadium oxide nanoparticles existence. Chronoamperometry curves for two mentioned catalysts are presented in fig.4. It can be clearly seen that after 5600 s, Pt/CNT shows more decreases in current density compare to Pt/MWNT-V₂O₅. This gives one an idea about easier removal of methanol oxidation reaction intermediates from the active sites, which causes the second catalyst to be more stable than first one. The results are also confirmed by the cyclic voltammetry diagrams in fig.1 and CO-stripping curves from fig. 2.

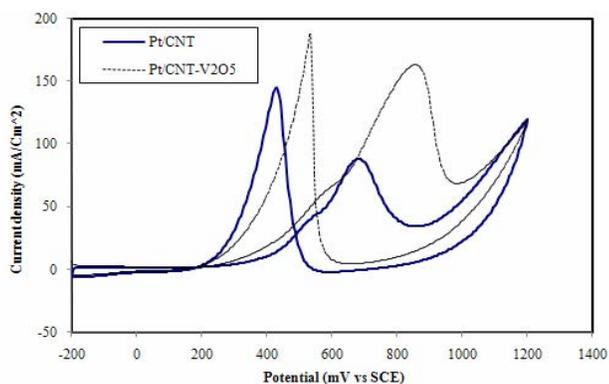


Fig.1 Cyclic voltammograms for Pt/CNT and Pt/CNT-V₂O₅ at scan rate of 50mV/s in 0.5M H₂SO₄ and 1M Methanol

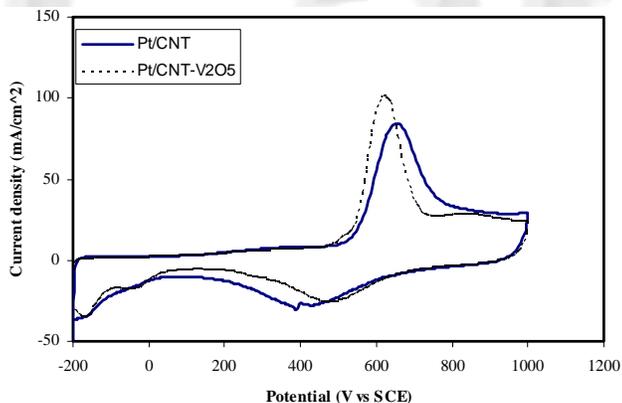


Fig. 2 CO-stripping curves for Pt/CNT and Pt/CNT-V₂O₅ at scan rate of 50mV/s. in 0.5M H₂SO₄

Conclusion

In this paper we proposed V₂O₅-MWNT nanocomposite as a promising support for platinum based catalyst in methanol electro-oxidation in acidic media as the anodic reaction in direct methanol fuel cells (DMFCs). The V₂O₅ nanoparticles were composite with MWNT by a solid state reaction with the aid of microwave radiation. The Pt/MWNT-V₂O₅ was synthesized by polyol process. The results show that methanol is oxidized on the Pt/V₂O₅-MWNT properly with an onset potential of 0.35 V vs. SCE and peak current density of 164

mA/cm². These are significantly better than the results of Pt/CNT catalysts. On the other hand, the presence of V₂O₅ causes to increase of catalyst stability against adsorbed carbonaceous intermediates. These are because of synergetic effect of V₂O₅ in Bi-functional mechanism and formation of new of active sites at interfaces between platinum and vanadium oxide nanoparticles.

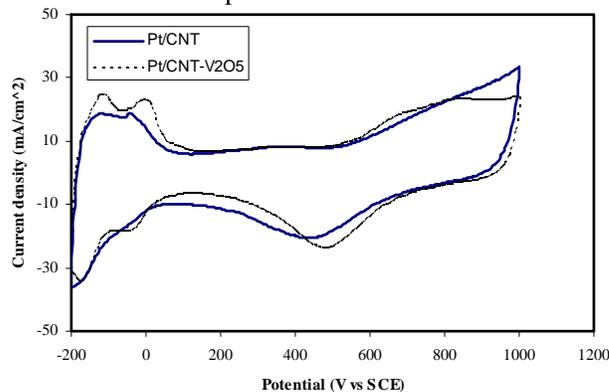


Fig. 3 Cyclic voltammograms for Pt/CNT and Pt/CNT-V₂O₅ at scan rate of 50mV/s in 0.5M H₂SO₄

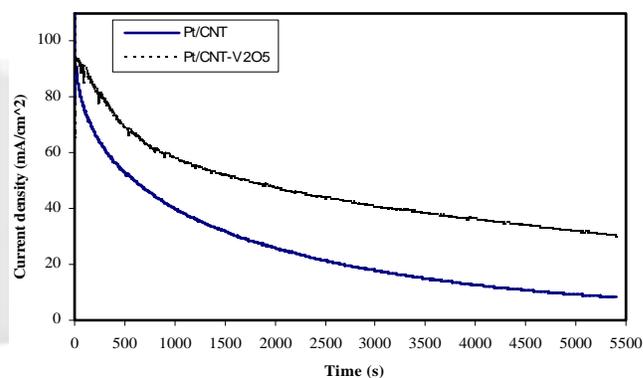


Fig.4 Chronoamperometry diagrams for Pt/CNT and Pt/CNT-V₂O₅ in 0.5M H₂SO₄ and 1M Methanol

References

- [1] W. Zhou, Z. Zhou, S. Song, W. Li, G. Sun, P. Tsiakaras, Q. Xin, *Appl.Catal. B: Environ.*, (2003), 125, 273.
- [2] Y.X. Chen, A. Miki, S. Ye, H. Sakai, M. Osawa, *J. Am. Chem. Soc.*, (2003), 125, 3680.
- [3] S. Wasmus, A. Kuver, *J. Electroanal. Chem.* 461 (1999) 14.
- [4] K.W. Park, K.S. Ahn, Y.C. Nah, J.H. Choi, Y.E. Sung, *J. Phys.Chem. B*, (2003), 107, 4352.
- [5] H. Zhang, Y. Wang, E.R. Fuchini, C.R. Cabrera, *Electrochem. Solid-State Lett.*, (1999), 2, 437.
- [6] P.K. Shen, A.C.C. Tseung, *J. Electrochem. Soc.* (1994), 141, 3083.
- [7] T. Maiyalagan, F. Nawaz Khan, *Catalysis Communications*, (2009), 10 433
- [8] P. Justin, G. Ranga Rao, *Catalysis Today*, (2009), 141, 138.
- [9] Z. Liu, J.Y. Lee, W. Chen, M. Han, L.M. Gan, *Langmuir* (2004) ,20, 181.
- [10] Y. Mu, H. Liang, J. Hu, L. Jiang, L. Wan, *J. Phys. Chem. B*, (2005) 109, 22212.