

Electronically Conducting Hybrid Nanomaterial as High Performance Catalyst Support for Methanol Oxidation

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Introduction

Considerable interest has been devoted in recent years to develop suitable electrode materials for methanol oxidation in fuel cells. Though, research over the past three decades identified¹ the best catalyst for methanol oxidation as Pt and Pt-Ru supported on carbon, there is still a lot of scope for developing alternate fuel cell electrode materials to achieve better activity, lower Pt loading and higher stability²⁻⁵. 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 electrode materials for methanol oxidation⁶. 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 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. On the other hand, intercalated composites of polyaniline (PANI) and V₂O₅ are known⁷. Here we report the Pt supported electronically conducting hybrid polyaniline and V₂O₅ composite for the electrooxidation of methanol.

Experimental Section

In a typical synthesis, a known amount of V₂O₅ xerogel in the form of fine powder was added to a known amount of distilled aniline dissolved in water. 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 vacuum at room temperature overnight. By changing the aniline/H₂O ratio, different stoichiometric products have been obtained.

To 50 mg of PANI-V₂O₅ nanocomposite, an aqueous solution of hexa H₂PtCl₆ was added and it was refluxed at 353 K for about 30 min. before adding an excess of 30% formalin as a reducing agent. The resulting solution was again refluxed at the same temperature for about 1h. The solution was filtered and the precipitate was washed thoroughly in water and it was finally dried in vacuum at room temperature overnight.

Results and Discussion

The physical properties of the synthesized material were characterized using XPS, XRD, HR-TEM, EPR and by Thermo Gravimetric Analysis (TGA).

Figure 1 shows the variation in performance of methanol oxidation current densities as a function of Pt loading on Pt loaded (C₆H₄NH)_{0.41} V₂O₅ · 0.5 H₂O nanocomposite and Pt/Vulcan carbon electrodes. It is evident that for the nanocomposite electrode, as the Pt loading increases there is a regular increase in activity from 26 mA/cm² (Pt=10 μg/cm²) to 335 mA/cm² (Pt=150 μg/cm²). But in the case of Pt/ Vulcan XC 72R carbon electrode, the activity increased from 12 mA/cm² (Pt=10 μg/cm²) to 176 mA/cm² (Pt=150 μg/cm²) only. This revealed that the nanocomposite electrode exhibited nearly two times higher activity compared to the Pt/Vulcan XC 72 R carbon electrodes.

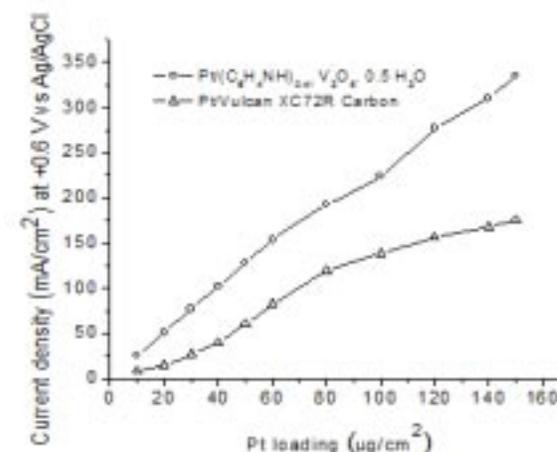


Figure 1. Variation of current density* with Pt loading.

*Current densities were measured at +0.6 V for CV's run in 1M H₂SO₄/1 M CH₃OH between -0.2 V and +0.8 V vs Ag/AgCl. Scan rate: 50 mV/s.

The chronoamperometric response of Pt/(C₆H₄NH)_{0.41} V₂O₅ · 0.5 H₂O and Pt/Vulcan XC 72 R carbon electrodes at a constant potential of + 0.6 V vs Ag/AgCl in 1 M H₂SO₄ and 1 M CH₃OH was also evaluated. The stability of the nanocomposite electrode (in terms of current density) was found to be nearly 5 times better than the electrodes based on the commercial catalyst.

References

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