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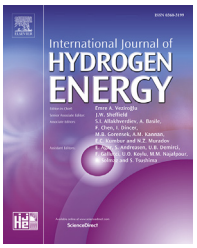

Palladium-ruthenium alloy nanoparticles dispersed on $CoWO_4$-doped graphene for enhanced methanol electro-oxidation

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ABSTRACT

Highly dispersed nanoparticles (NPs) of Pd and Pd-Ru alloys on the 10 wt% $CoWO_4$-doped GNS (graphene nano sheets) support have been obtained by a microwave-assisted polyol reduction and investigated for their application as efficient electrode materials for methanol oxidation reaction (MOR). Structural and electrocatalytic surface characterization of hybrid materials were carried out by XRD, TEM, XPS, cyclic voltammetry and chronoamperometry. Pure $CoWO_4$ and $CoWO_4$-doped GNS follow the monoclinic crystal structure and the Pd NPs (6–7 nm) dispersed on $CoWO_4$-doped GNS follow the face-centered cubic crystal structure. It is observed that with the increase of Pd loading from 5 to 20 mg on the support, the onset potential (E_{op}) for MOR shifts negatively and the MOR current density increases, the magnitude of shift in E_{op} and increase in the MOR peak current density being the greatest in the case of 15 mg Pd loading. Introduction of Ru from 0.6 to 2.0 mg into 15 mg Pd on the catalyst support, the apparent activity of the active catalyst, 15Pd/10 wt% $CoWO_4$-GNS improved further, the magnitude of improvement, however, being the greatest (≈50%) with 1.0 mg Ru. Thus, novel 15Pd-1.0Ru/10 wt%$CoWO_4$-doped GNS can be a promising electrode material for MOR in alkaline solutions.

Introduction

In recent years, an increased interest has been shown towards the improvement of the efficiency of direct methanol fuel cell due to its advantage of low operating temperature (<100 °C), easy transportation and storage, high energy efficiency and fast start-up of fuel [1–6]. Pt and Pt alloys are the best catalysts for the methanol oxidation [7–17] but, they are costly and have limited abundance in nature. Besides, the Pt anode gets poisoned during the MOR due to blockage of the active centers by the CO molecule formed as the oxidation intermediate [18,19]. Efforts are continued to solve this CO poisoning issue. The most widely accepted strategy has been to use a suitable non-platinum metal, such as Pd with suitable amounts of transition metals and deposit the same on high surface area carbon supports, such as carbon microspheres [19,20], nanowires [19,21], multiwalled carbon nanotubes [19,22–26], GNS (graphene-nano-sheets) [27–37], Nitrogen-doped graphene [25,38,39] etc. A number of bimetallic alloys, namely, Pd-Co [40,41], Pd-Ni [24,42,43], Pd-Cu [44–47], Pd-Au [48], Pd-Ag [49], Pd-Pt [2,10,11], Pd-Ru [50–53] and ternary composites [53,54] have recently been reported as active electrocatalysts for MOR.

Among fuel cell catalyst supports used, the GNS is low cost and considered superior to other carbon supports [28,30]. The presence of a controlled amount of oxide in the GNS support is

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known [31,35,55] to improve the electrocatalytic properties of Pd towards the methanol oxidation reaction in alkaline solutions.

Complex oxides [56,57] belonging to the wolframite family, mainly $CoWO_4$ is an important class of material which has recently been found to display bifunctional activity towards the evolution [58] and reduction of oxygen [59] in alkaline solutions. To enhance the electrocatalytic activity vis-à-vis CO poisoning tolerance, Pd was deposited on the GNS support doped by $CoWO_4$. Preliminary investigations have shown that the oxide doped GNS support is superior to that without doped one and that the 10 wt% $CoWO_4$-doped GNS support produced the greatest electrocatalytic effect compared to other $CoWO_4$-doped GNS. Further, the presence of alloying metal, Ru, is well known [52,60,61] to improve the catalytic efficiency of Pd towards the oxidation of alcohols. Therefore, a systematic investigation was undertaken to optimize, first the palladium mass and then mass ratio of palladium and ruthenium on the 10 wt% $CoWO_4$-doped GNS support so as to obtain a promising electrode material for MOR. Detailed results of the investigation are reported in this paper.

Experimental

Hybrid catalyst preparation

Graphite in powder form was used as precursor for GNS preparation. First of all, graphite is converted to graphite oxide (GO) using the modified Hummers and Offenmans method [28,62], details of which are given elsewhere [28]. GO is then reduced by the $NaBH_4$ (Sigma Aldrich CAS 16940-66-2) chemical reduction method. Cobalt tungstate has been prepared by a co-precipitation method using precursors, cobalt acetate (Extra pure, Merck, India) and sodium tungstate (AR BDH) [58]. The support material, 10 wt% $CoWO_4$-GNS was prepared by adding 90 mg of GNS and 10 mg of $CoWO_4$ powder into 40 mL double distilled water, ultrasonically mixing and then drying. xPd/10 wt% $CoWO_4$-GNS hybrids (where x = 5, 10, 15 and 20 mg) were prepared by a microwave assisted polyol reduction [31]. In a typical procedure, 20 mg of the support material was taken in 40 mL ethylene glycol (EG, Merck), ultrasonicated for 1 h and then, to this 5–20 mg of Pd (0.01 M $PdCl_2$, Merck) was added with ultrasonication. The $PdCl_2$ solution was prepared with 0.05 M HCl. The pH of this mixture was adjusted ~10 by using 0.8 M KOH (Merck) solution. The resulting mixture was exposed with microwave radiation for 5 min at 800 W power with a break of 15 s after every 30 s, left overnight, centrifuged, washed with acetone and then dried in vacuum oven at 100 °C over night. Similarly, 15Pd-yRu/10 wt% $CoWO_4$-GNS (where y = 0.6, 0.8, 1.0, 1.4 and 2.0 mg) hybrid materials were prepared by the same method using 15 mg Pd, y mg Ru and 20 mg of the support material. For simplicity, 10 wt% $CoWO_4$ doped-GNS has been represented as $CoWO_4$-GNS in the text.

Electrode preparation

The catalyst ink was prepared by dispersing 3 mg of the catalyst powders in 600 μL of ethanol-water (2:1) mixture through ultrasonication for 30 min. 30 μL of the suspension was placed on a pre-treated glassy carbon plate (GC ≈ 0.5 cm^2) and dried in air. 10 μL of 1% Nafion solution (Alfa Aesar) was then dropped over the catalyst film on GC. The catalyst loading on GC was kept 0.3 mg cm^{-2}. The electrical contact of the catalyst/GC electrode was made as described previously [31].

Material characterization

Structural characterization of the catalysts has been performed using X-ray diffractometer (Thermo Electron: Radiation Source, CuK_α with $\lambda = 1.541841$ Å), transmission electron microscope (TEM: TECNAI G^2 FEI) and AMICUS-X-ray photoelectron spectrometer (XPS). For TEM pictures, the catalyst was dispersed in ethanol and a drop of this suspension was placed onto a carbon coated copper grid (Icon Analytical Equipment PVT. LTD., Prod. Code 01810) and dried.

Electrochemical characterization

As described previously [31], a conventional three electrode single-compartment Pyrex glass cell having pure Pt-foil and saturated calomel electrode (SCE) respectively as auxiliary and reference electrode were employed in the study. The electrolyte and instrument used in the study were 1 M KOH and Biologic potentiostat/galvanostat (SP-150), respectively. Cyclic voltammetry (CV) and chronoamperometry (CA) experiments on the hybrid electrodes have been performed in the potential region, 0.17–1.27 V vs. RHE at 50 mV s^{-1} in 1 M KOH with and without containing methanol (25 °C). Prior to recording the voltammogram, each electrode was cycled for five runs in the electrolyte. CA experiments were performed in the electrolyte, 1 M KOH + 1 M CH_3OH at a constant anodic potential. All CV and CA experiments were performed in an Ar-deoxygenated solution. The potential values mentioned in the text are given against RHE only.

Results and discussion

XRD

XRD powder patterns of GNS, $CoWO_4$, $CoWO_4$-GNS, 15Pd/$CoWO_4$-GNS and 15Pd-1.0Ru/$CoWO_4$-GNS recorded between $2\theta = 20°$ and 80° are shown in Fig. 1. The broad peak between $2\theta = 24°$ and $2\theta = 26°$ is the characteristic diffraction peak (002) of GNS [41]. It is noteworthy that XRD of samples, $CoWO_4$ and $CoWO_4$-GNS seem to be similar and that 2θ and corresponding d values of all the diffraction lines of both the samples excellently match with those reported for pure $CoWO_4$ possessing the monoclinic crystal structure with space group, 'P2/a (13)' [JCPDS files 15-0867] [58]. Fig. 1 further shows that both the hybrids, 15Pd/$CoWO_4$-GNS and 15Pd-1.0Ru/$CoWO_4$-GNS exhibit the three characteristic prominent diffraction peaks at $2\theta \approx 40°$, 46.5° and 68.2° which correspond to the (111), (200) and (220) planes of pure Pd phase with the face-centered-cubic (fcc) structure [19,32]. The observation of Fig. 1 shows further that characteristic diffraction peaks for the pure oxide have been suppressed in presence of Pd on the oxide doped

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