



Graphene-Manganite-Pd Hybrids as Highly Active and Stable Electrocatalysts for Methanol Oxidation and Oxygen Reduction



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ABSTRACT

Hybrids of graphene nanosheets (GNSs) with Pd and MMn_2O_4 ($M = Mn \text{ \& } Co$) have been prepared and investigated as electrocatalysts for the methanol oxidation (MOR) and oxygen reduction (ORR) reactions in 1 M KOH at 25 °C. Results show that incorporation of Mn_3O_4 (or $CoMn_2O_4$) into 40wt%Pd/GNS increases the electrocatalytic activity toward both the reactions (MOR and ORR) greatly; the observed enhancement in the activity being much higher with $CoMn_2O_4$ addition. It is observed that at an anodic potential, $E = 0.610 \text{ V vs RHE}$, 8wt% $CoMn_2O_4$ addition improves the methanol oxidation current density of 40wt%Pd/GNS by more than 3 times. Similarly, at $E = 0.90 \text{ V vs RHE}$, 5wt% $CoMn_2O_4$ addition improves the ORR activity of 40wt%Pd/GNS nearly two times. The stability of the active hybrid electrode is also found to be outstanding under both MOR and ORR conditions. Similar stabilities have not been found with other fuel cell catalysts. In a chronoamperometry experiment at $E = 0.626 \text{ V vs RHE}$, the methanol oxidation current observed on Pd-8% $CoMn_2O_4$ /GNS at 2 min decreased by only ~5% at 120 min.

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1. Introduction

Increased interests towards improvement in the efficiency of direct methanol fuel cells (DMFCs) for use in very small to mid-sized applications have been shown during recent years [1,2]. One major problem in DMFCs is the sluggish kinetics of methanol oxidation (MOR) [3–5]. Pt and its alloys are considered as the most active electrocatalysts for the MOR [2,4] as well as the oxygen reduction reaction (ORR) [6,7]. However, the cost and scarcity of platinum are not suitable for commercial applications [2,3]. Also, Pt undergoes deactivation under anodic condition due to blockage of its active sites by the adsorbed methanol oxidation intermediate, CO [2,3,8]. It is, therefore, desired to search for efficient and robust catalysts based on abundant non-precious metals, catalytic activities of which toward the MOR/ORR are comparable to or greater than platinum.

To improve the kinetics of MOR and increase the range of metals other than Pt as catalysts, the study of electrocatalysis of the MOR has resorted to in alkaline solutions [3,8,9]. Among the non-Pt metal catalysts investigated, Pd is considered as an efficient and a potential substitute for Pt [8,10]. The research work has been carried

out to improve the catalytic efficiency of Pd through alloying with metals, such as Pt [11], Ni [8,12], Ag [1,8], Au [8,13], Sn [8,14], Ru [8,15], Ru-Sn [8,16], Fe [17], Co [8,18], etc. and produce in the form of highly dispersed nanoparticles (NPs) on high surface area carbon supports, such as Vulcan XC-72R carbon black [8,12], carbon nanotubes (CNTs) [8,19,20], carbon microspheres (CMSs) [8,21], hollow carbon spheres (HCSs) [22], nanowire arrays (NWAs) [8,23], tungsten carbide (WC) adsorbed on XC-72R carbon [17] and graphene nanosheets (GNSs) [11,12,14–16,24]. Compared to other fuel catalyst supports, the GNS is low cost and has high surface area (ca. 2630 $\text{m}^2 \text{ g}^{-1}$). Also, its application as support material is superior to other carbon supports for fuel cell metal catalysts [24,25].

Efforts are also continued to develop new low cost active and stable electrocatalysts for the ORR and several new cathode materials such as nitrogen-doped graphene [26,27] transition metal mixed oxide-graphene [27,28], Pd- MCo_2O_4 /graphene [29] and MnO_2 -based nanostructures [30] have recently been discovered as active ORR catalysts.

Very recently [29], we have synthesized new 40wt%Pd- MCo_2O_4 /GNS ($M = Mn, Co, Ni$) hybrid materials and investigated them as electrocatalysts for both MOR as well as ORR in 1 M KOH. These hybrids exhibited superior ORR activities with 5 wt % and superior MOR activities with 10 wt % oxide content. Among the hybrid catalysts investigated, the Pd- $xMnCo_2O_4$ /GNS exhibited the best performance for both ORR and MOR reactions. The catalytic

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activity and stability of the catalysts containing MnCo_2O_4 were superior to Pt in 1 M KOH. These results encouraged us to prepare hybrids of GNS and Pd with Mn-based spinel-type oxide (e.g. Mn_3O_4 , FeMn_2O_4 , CoMn_2O_4 or CuMn_2O_4) and characterize them for use as electrocatalysts for MOR and ORR in 1 M KOH. The oxides were prepared by three methods, co-precipitation [31] precipitation [32] and sol-gel [33]. Preliminary investigations showed that the hybrids prepared with oxides, obtained by the precipitation method, were superior to ones obtained by other methods. The optimized oxide compositions in the hybrid catalyst for exhibiting the superior ORR and MOR activities were 5 and 8 wt%, respectively. This is due to fact that the oxide interacts with Pd nanoparticles strongly. So, the higher oxide additions can enhance agglomeration of Pd nanoparticles, resulting in an adverse effect on the catalytic activity. This is also apparent from the electrochemical active area (EASA) of the hybrid materials which decreases at higher amount (i.e., 10wt%) of the oxide addition; values of the EASA being ~ 233 , ~ 369 and $\sim 283 \text{ cm}^2$ per mg of Pd for Pd-5wt% CoMn_2O_4 /GNS, Pd-8wt% CoMn_2O_4 and Pd-10wt% CoMn_2O_4 , respectively.

Herein, we present details of results of the investigation on hybrids of GNS and Pd with the base oxide (Mn_3O_4) and with active CoMn_2O_4 .

2. Experimental

2.1. Preparation and Characterization of Electrocatalysts

40wt%Pd- x wt% MMn_2O_4 /GNS (where M = Mn & Co and x = 5 & 8) catalysts were synthesized by dispersing required amounts of graphene and a mixed oxide, as per formula of a particular hybrid, into 40 mL ethylene glycol and adding 6.6 mL of 0.01 M PdCl_2 , details of which are described elsewhere [29]. Transition metal complex oxides were prepared by a previously reported hydroxide precipitation method [32]. Metal sulphates were used as precursors. Graphene was freshly prepared from the sodium borohydride reduction of graphite oxide (GO) [25]. The latter was also prepared by us using the modified Hummers and Offenmans method [34]. For simplicity, hybrid materials, 40wt%Pd- x wt% MnMn_2O_4 /GNS, 40wt%Pd- x wt% CoMn_2O_4 /GNS and 40wt%Pd/GNS are hereafter written as Pd- x MnM/GNS, Pd- x CoM/GNS, and Pd/GNS, respectively.

The hybrid electrodes were prepared by dropping the catalyst suspension in ethanol-water (2:1) mixture on pretreated glassy carbon disk (dia = 0.3 cm, area = 0.07 cm^2) as previously described [29]. When the catalyst suspension on GC was dried, $1.4 \mu\text{L}$ of 1% Nafion solution (Alfa Aesar) was dropped over it so as to enhance the adherence of the catalyst film. In the case of the ORR study, the loading of each catalyst on GC was maintained 0.6 mg cm^{-2} ($\equiv 0.24 \text{ mg cm}^{-2}$ of Pd), while it was 0.3 mg cm^{-2} ($\equiv 0.12 \text{ mg cm}^{-2}$ of Pd) for the MOR study. The structural characterization of hybrid materials was carried out using an X-ray diffractometer (XRD: Thermoelectron, $\text{CuK}\alpha$ radiation, $\lambda = 1.54184 \text{ \AA}$), X-ray photoelectron (XPS: AMICUS) and transmission electron (TEM: TECNAI G^2 FEI) spectrometer. All XPS spectra recorded were referenced to C 1s (234.6 eV). For the TEM study, hybrid catalysts were dispersed in methanol and then placed on 'holey' carbon film- supported on copper grid (Icon Analytical Equipment PVT. LTD., Prod. Code 01810).

2.2. Electrochemical Measurements

As mentioned earlier [29], a conventional three-electrode single-compartment Pyrex glass cell and pure Pt-foil as auxiliary and saturated calomel electrode (SCE) as reference electrode were employed in the study. A potentiostat/galvanostat (Model 273A,

PARC, USA) was used to study the cyclic (CV) and linear sweep (LSV) voltammeteries and chronoamperometry (CA) of the catalyst. Potentials mentioned in the text are referred against the reversible hydrogen electrode ($E^\circ = -0.828 \text{ V vs. SHE}$).

CV of each hybrid catalyst has been recorded at a scan rate of 50 mVs^{-1} between 0.37 and 1.17 V vs. RHE in 1 M KOH with and without containing methanol at 25°C . The upper limit of the scan range was kept to only 1.17 V to avoid any oxidation of carbon. Prior to recording the voltammogram, each electrode was cycled for five runs at the potential scan rate of 50 mV s^{-1} in 1 M KOH. All experiments related to methanol oxidation were carried out in Ar-saturated 1 M KOH + 1 M CH_3OH .

To investigate the ORR, the LSV study on hybrid catalysts has been carried out in O_2 -saturated and deaerated 1 M KOH at 25°C . The potential range and scan rate employed were 0.37 – 1.17 V vs. RHE and 2 mV s^{-1} , respectively. To obtain O_2 -saturated and deoxygenated solutions, pure O_2 and Ar gas were bubbled for 45 min, respectively. A slow flow of O_2 was maintained over the electrolyte (O_2 -saturated 1 M KOH) surface during the recording of LSV so as to ensure its continued O_2 saturation. Prior to investigation of the ORR activities, the loading of hybrid materials on the GC disk electrode (3 mm) was optimized for producing the highest and reproducible diffusion limited current density. The catalyst loadings between 0.6 and 0.9 mg cm^{-2} produced reproducible LSV curves with a diffusion limited current density close to 5 mA cm^{-2} (rotation = 1600 rpm). Finally, the catalyst loading on the GC disk was kept at 0.6 mg cm^{-2} for the ORR study. All LSV curves of the present investigation have been corrected for the background current (i.e., the current produced under identical conditions in Ar-saturated 1 M KOH). The ORR current densities given in the text and figures are normalized with respect to the geometrical area (A) of the catalyst.

In the case of methanol oxidation, the CA experiment was performed at a constant anodic potential in Ar-saturated 1 M KOH + 1 M CH_3OH solution, while in the case of oxygen reduction, it was performed at a constant cathodic potential in O_2 -saturated 1 M KOH.

3. Results and Discussion

3.1. XRD

Fig. 1 gathers XRD patterns of Pd/GNS, Pd-5MnM/GNS, and Pd-5CoM/GNS. This figure shows that all the three hybrids exhibit the

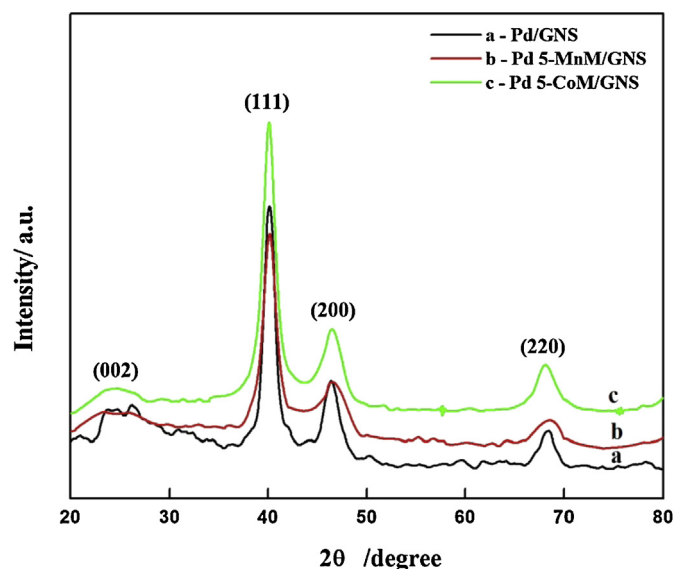


Fig. 1. XRD patterns of (a) Pd/GNS, (b) Pd-5MnM/GNS and (c) Pd-5CoM/GNS.

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