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Platinum - Manganese Cobaltite- Graphene Ternary Nanocomposites as Efficient Electrocatalysts for Methanol Electrooxidation in 0.5 M H_2SO_4

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ABSTRACT: Novel ternary nanocomposites of Pt, $MnCo_2O_4$ and graphene nanosheets (GNS) with compositional formula, 20wt%Pt/xwt% $MnCo_2O_4$/GNS (where x = 0, 6, 8, 10, 15 and 20) have been prepared and investigated as electrocatalysts for methanol oxidation in 0.5 M H_2SO_4 at 25 $^{\circ}$C using cyclic voltammetry and chronoamperometry techniques. Structural characterization of electrocatalysts were carried out by X-ray diffraction (XRD) and transmission electron microscopy(TEM). In each composite, Pt followed a crystalline face-centered cubic (fcc) structure with crystallite size ranging between 6.6-8.6 nm. The Study indicates that addition of low amounts of the oxide (6-20wt%) into 20wt%Pt/GNS is greatly beneficial with regard to enhancement in accessible Pt sites, electrocatalytic activity, CO poisoning tolerance and stability of the composite. It is, further, observed that with the increase of the oxide content from 6 to 10 wt% in the composite, the rate of oxidation of methanol greatly enhances while it decreases with the higher oxide additions, 15 and 20%. At E = 0.842 V vs. RHE in 0.5 M H_2SO_4 + 1 M CH_3OH, the electrocatalytic activity of 20wt%Pt/10wt%$MnCo_2O_4$/GNS was approximately 2.6 times higher than that of the base (20wt%Pt/GNS) electrode. The CO poisoning tolerance of this electrode was also much higher than the base electrode under similar experimental conditions. Thus, ternary composite electrocatalyst with 10wt% oxide could be a potential Pt-based anode in direct methanol fuel cell.

KEYWORDS: Methanol Electrooxidation, Nanocomposites, Graphene Nanosheets, electrocatalysis, Direct Methanol Fuel Cells.

I. INTRODUCTION

Platinum-based materials are considered as potentially active anode and cathode materials in polymer electrolyte methanol fuel cells (PEMFCs). The methanol oxidation reaction (MOR: $CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$) takes place at the anode and the oxygen reduction reaction (ORR: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$), at the cathode. However, during the cell discharge process, Pt electrocatalysts undergo deactivation. In fact, the methanol oxidation intermediate, CO, gets adsorbed on the platinum surface and thereby keeps Pt active sites away from the contact of methanol molecules, as consequence of which the MOR is hindered. Also, the methanol cross-over takes place from the anode to the cathode compartment, which not only lowers the fuel utilization efficiency but also affects the cathode performance adversely. Efforts are continued to solve these two technical problems. To deal with the CO poisoning issue, the most widely accepted strategy is to use suitable Pt-based alloys such as PtRu, PtCo, PtNi, PtSn, PtPd, etc. [1-6]. However, a transition metal in the alloy may undergo dissolution during DMFCs operation. Metal ions, thus produced, can diffuse across the membrane and may undergo reduction at the cathode resulting in loss of the DMFCs performance. To overcome the problem of metal dissolution, metal oxide modified Pt particles such as Pt/RuO_2 [7-9], Pt/WO_3 [10-12], Pt/SnO_2 [13-14], Pt/MnO_2 [15, 16], Pt/CeO_2 [17,18], Pt/ZrO_2 [19], Pt/MgO [20],Pt/Co_3O_4 [21], Pt/Mn_3O_4 [22], etc. have also been investigated as active composites to improve the electrocatalytic activity of Pt for MOR. To minimize the adverse effect of methanol cross-over, researches were carried out mainly in two directions: (i) design and synthesis of Pt-based cathode materials with both higher methanol tolerance and higher ORR activity than Pt [23-26] and (ii)

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search for novel methanol tolerance and corrosion stable non Pt cathode materials with activity comparable to Pt [27-32].

To achieve better utilization of Pt, the latter is generally obtained in highly dispersed form on different high surface area carbon supports, such as activated carbon, Vulcan XC-72 carbon black, mesoporous carbon, carbon nanofibers, carbon nanotubes, graphitized materials as well as graphene [13, 17,33-41]. It is found that Pt-based catalysts loaded on graphene support exhibit superior catalytic activity and CO poisoning tolerance for methanol electrooxidation [35, 40]. Very recently, Singh and coworkers introduced (2-10wt%) a complex transition metal oxide (Co_3O_4, $NiCo_2O_4$, $FeCo_2O_4$, $MnCo_2O_4$ Or $MnMoO_4$) into the 40wt%Pd/GNS nano-composite and observed greatly enhanced catalytic activity as well as CO poisoning tolerance of the catalyst toward MOR in alkaline solutions; the effect, however, being the greatest with 8-10wt% oxide [42, 43]. This result encouraged us to prepare nanocomposites of Pt, GNS and $MnCo_2O_4$ and investigate their electrocatalytic properties toward MOR in 0.5 M H_2SO_4 with aimed to produce an efficient and CO poisoning tolerance Pt-based electrocatalyst for MOR. Detailed results of the investigation are described in the present report.

II. EXPERIMENTAL

A. *Preparation and characterization of electrocatalysts:*

First of all, the required amount of graphene (18-24 mg) was dispersed into 35 ml of redistilled water by sonication of the suspension for 1 h. To this added calculated amount of $MnCo_2O_4$ (1.8-6.0 mg), sonicated for 1.5 h, added 796 µL of 0.0386 M of $H_2PtCl_6.6H_2O$, again sonicated for 0.30 h and then added sodium borohydride with continued sonication. Left the whole content for over-night, centrifuged and then dried overnight at 100°C. Transition metal complex oxide was prepared by a previously reported hydroxide preparation method using metals sulphate as the precursors [44]. Graphene was freshly prepared from the sodium borohydride reduction of graphite oxide (GO) [35], which was prepared following the modified Hummers and Offenmans method [45]. Nanocatalysts, thus prepared, were 20wt%Pt/ x wt%$MnCo_2O_4$/GNS (x = 0, 6, 8, 10, 15 and 20). To simplify, the nanocomposites, 20wt%Pt/ x wt%$MnCo_2O_4$/GNS, are represented as Pt/ x MC/GNS in the text.

The catalyst electrodes were obtained by dropping the catalyst suspension in ethanol-water (2:1) mixture on pretreated glassy carbon (geometrical area = 1.0 cm^2) as previously described [42]. When the catalyst suspension on GC was dried, 10 µL of 1 % Nafion solution (Alfa Aesar) was dropped over it so as to enhance the adherence of the catalyst film with the support. The catalyst loading on GC was maintained 0.3 mg cm^{-2} (≡ 0.06 mg cm^{-2} of Pt). The structural characterization of hybrid materials was carried out using an X-ray diffractometer (XRD) (Model: Thermoelectron) and a transmission electron spectrometer (TEM) (Model: TECNAI G^2 FEI). The CuK_α (λ = 1.54184 Å) was used as the radiation source.

B. *Electrochemical measurements:*

A conventional three-electrode-single-compartment Pyrex glass cell having pure Pt-foil and saturated calomel (SCE) as auxiliary and reference electrodes, respectively, were employed in the study as described previously [42]. A potentiostat/galvanostat (Model 273A, PARC, USA) was used to study the cyclic (CV) and chronoamperometry (CA) of the electrocatalyst in 0.5 M H_2SO_4 at 25 °C. Potentials mentioned in the text are referred against the reversible hydrogen electrode.

CV of each hybrid electrocatalyst has been recorded at a scan rate of 50 mVs^{-1} between -0.058 and 1.542 V vs. RHE in 0.5 M H_2SO_4 and -0.058 and 1.342 V vs. RHE in 0.5 M H_2SO_4 + 1 M CH_3OH at 25°C. Prior to recording the voltammogram, each electrode was cycled for five runs in the electrolyte. CA experiments were performed at a constant potential (E = 0.742 V vs. RHE) in M H_2SO_4+ 1 M CH_3OH. All experiments related to methanol oxidation were performed in Ar-saturated 0.5 M H_2SO_4 + 1 M CH_3OH.

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III. RESULTS AND DISCUSSION

A. *X-Ray diffraction:*

XRD patterns of Pt/GNS, Pt-10MC/GNS, and Pt-20MC/GNS shown in Fig. 1 show that all the three composite catalysts exhibit the three characteristic diffraction peaks at $2\theta \approx 40^{\circ}$, 46.5° and 68.2° which can be indexed respectively to the (111), (200) and (220) planes of the face-centered- cubic (fcc) phase of pure Pt [40, JCPDS 04-0802]. This is a typical characteristic of Pt/MC/GNS containing up to 20wt% of MC. The broad peak between $2\theta = 24^{\circ}$ and $2\theta = 26^{\circ}$ is the characteristic (002) diffraction peak of GNS [35]. It is further observed that the diffraction peaks are slightly displaced toward the higher angle with the oxide addition, the magnitude of shift being $\approx 0.3^{0}$. This suggests that the oxide somehow influences the crystalline lattice of Pt. It is noteworthy that no characteristic diffraction peaks of the spinel oxide were indicated in Fig.1. It is worth-mentioning that XRD's of Pd/MCo_2O_4-GNS (where M = Mn, Fe, Co, or Ni) also indicated diffraction peaks for Pd only; they did not indicate any diffraction peaks for spinel oxides or their constituent metals/ oxides, however, the XPS study of these hybrid materials clearly demonstrated the presence of respective spinel oxide in the surface layer of the catalysts [42]. The crystallite size of Pt, as estimated using Scherrer equation and the most intense diffraction peak, (111), were 8.5, 7.2 and 6.6 nm in case of Pt/GNS, Pt/10MC/GNS and Pt/20MC/GNS, respectively.

B. *TEM:*

TEM photographs of MC/GNS and three representative electrocatalysts, namely Pt/GNS, Pt/ 10MC/GNS and Pt/ 20MC/GNS are taken and reproduced in Fig. 2 (A, B, C, & D). The oxide molecules on the GNS support are well dispersed in the form of nano-granules with sizes ranging between ~20 and ~50 nm (Fig. 2A). On the other hand, Pt deposit on GNS follows cluster morphology (Fig.2B). Moreover, the cluster morphology changes to a granular morphology with 10wt% oxide addition (Fig. 2C) and that the GNS surface looks to be uniformly covered by well dispersed nanoparticles (NPs). Thus, the oxide decreases agglomeration of Pt NPs. However, the higher addition of the oxide (20wt%) reverts back grannular morphology into cluster morphology(Fig. 2D).

The high-resolution TEM (HRTEM) photographs of Pt/GNS and Pt/10MC/GNS shown in Fig. 2(a & b) exhibit clear lattice fringes with the interplanar spacings of 0.211 and 0.215 nm corresponding to the (111) plane of the fcc Pt, which clearly substantiates the highly crystalline character of metallic Pt NPs. Average particle sizes of Pt NPs, as estimated from TEM photographs, are found to be 6.2-8.7, 4.9-5.0, and 4.3-5.0 nm for Pt/GNS, Pt/10MC/GNS and Pt/20MC/GNS, respectively. The XRD also showed similar values of the average Pt particle sizes in hybrid materials.

C. *Cyclic Voltammetry:*

Surface redox behavior of the electrocatalysts: CVs of hybrid electrodes in Ar-saturated 0.5 M H_2SO_4 (without methanol) were recorded under identical experimental conditions. Voltammograms, so obtained, show similar features, which are characteristic of polycrystalline Pt [21,22, 33, 37]. Each curve has the hydrogen adsorption- desorption region in the potential region from ~0.33 to -0.058 V (vs RHE), two anodic peaks respectively at 0.649-0.598V and 0.971-0.982 V (vs RHE), and a cathodic peak at 0.650-0.625 V (vs RHE). A typical voltammogram for Pt/10MC/GNS is shown in Fig. 3.

Anodic Peaks, I ($E_p \sim 0.64$ V vs. RHE) and II ($E \geq 0.85$ V vs RHE), can be attributed to the electrochemical adsorption of OH^- (i.e., $OH^- \rightarrow OH_{ads} + e^-$) [21, 33,] and the formation of Pt oxide ($Pt\text{-}OH_{ads} + OH^- \rightarrow Pt\text{-}O + H_2O + e^-$) [21,33, 46], respectively. Whereas the cathodic Peak, III (E_p = 0.650-0.625 V vs. RHE) is produced due to the electrochemical reduction of Pt-O, formed under anodic conditions, into elemental Pt (i.e., $Pt\text{-}O + H_2O + 2e^- \rightarrow Pt + 2OH^-$) [21,33, 46].

Electrochemically active surface area (ECSA): The ECSA of an electrocatalyst not only provides important information regarding the number of electrochemically active sites per gram of the catalyst, but also is crucial parameter to compare different electrocatalytic supports. In the case of Pt and Pt-based alloys/composites, the hydrogen adsorption/desorption peaks observed in the voltammogram are usually employed to estimate ECSA of the catalyst. For the purpose, the hydrogen adsorption peaks of each voltammogram are taken for ECSA determination in the present study. The integrated area under the adsorption peaks in the voltammogram (as shown in Fig. 3 by dashed line) has

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been considered as the total charge (Q_H) concerning H^+ adsorption, and used to determine ECSA by employing the relation [23, 33],

$$ECSA\ (cm^2\ mg^{-1}of\ Pt) = Q_H\ (\mu\ C)/\ 210\ (\mu\ C\ cm^{-2})\ .\ Pt\ loading\ (mg.\ cm^{-2})$$

Estimates of the ECSA were ~ 937, ~ 2842, ~ 2990, ~ 3,791, ~ 3,320 and ~ 2876 $cm^2\ mg^{-1}$of Pt respectively for Pt/GNS, Pt/6MC/GNS, Pt/8MC/GNS, Pt-10MC/GNS, Pt/15MC/GNS and Pt/20 MC/GNS. The result shows that the EASA of Pt/GNS significantly increases with introduction of the oxide, the magnitude of increase, however, being the greatest with 10MC. Thus ,it could be concluded that addition of a controlled amount of the oxide improves the percent utilization of Pt, showing beneficial effect from electrocatalysis standpoint. Estimates of particles size are very close for all the samples, particularly oxide containing ones and so, a larger EASA could be attributed to an enhanced dispersion of Pt. Thus, the addition of oxide produces much more accessible Pt sites for efficient catalytic activity in comparison with GNS used as alone as the catalyst support.

Methanol electrooxidation Fig. 4 gathers CV curves of Pt/GNS and Pt/xMC/GNS recorded at the scan rate of 50 mV s^{-1} in the potential region from -0.058 to 1.342 V vs. RHE in Ar-saturated 0.5M H_2SO_4 + 1M methanol at 25˚C. Each CV curve indicates the two characteristic methanol oxidation current peaks: one observed in the positive (i.e. forward) ($I_{p,f}$) and the other one in negative (i.e., reverse) ($I_{p,r}$) going scan [34, 37, 47,48]. It is mentioned that there appears no controversy regarding the origin of the forward oxidation peak, while diverse opinions are available in literature for the origin of the oxidation peak observed in negative going scan. It is considered that the freshly chemisorbed species coming from methanol adsorption is oxidized in the forward scan whereas in the reverse scan, the oxidation peak is primarily associated with the removal of the residual carbon species formed in the forward scan [34, 48-51]. The residual carbon species are oxidized according to the following reaction:

$$Pt.OH_{ads} + Pt{=}C{=}O \rightarrow CO_2 + Pt + H^+ + e^-$$

However, some researchers believe that both the oxidation peaks, observed on the forward and reverse scans have been originated from the oxidation of the same chemical species, i.e., freshly adsorbed methanol species [52-55].

CV curves were analyzed and estimates of the onset potential (E_{OP}), the peak current density (j_p) and the peak potential (E_P) for each curve are given in Table 1.

Table1: Results of the cyclic voltammetry study of methanol electroxidation on Pt-based ternary nanocomposites in Ar-saturated 0.5M H_2SO_4 + 1M methanol at 25˚C. Scan rate = 50 mV s^{-1}; Geometrical area of each electrode = 0.5 cm^2; Catalyst loading = 0.30 (≡ 0.06 mg cm^{-2} of Pt) mg cm^{-2}.

Catalyst	EASA (cm^2/mg Pt)	Pt utilization / %	E_{op} /V	E_p / V	J (mA/ cm^2)	At E=0.842 vs RHE		
						j (mA $cm^{-2)}$	MA (mA mg^{-1})	SA (mA cm^{-2})
Pt/GNS	~ 937	~ 20	0.675	0.953	21.44	15.40	256.7	0.27
Pt/6MC/GNS	~ 2,842	~ 60	0.335	0.946	45.47	30.74	512.3	0.18
Pt/8 MC/GNS	~ 2,990	~ 63	0.346	0.956	58.38	39.64	660.7	0.22
Pt/10MC/GNS	~ 3,791	~ 80	0.330	1.020	73.31	40.51	675.2	0.18
Pt/15 MC/GNS	~ 3,320	~ 70	0.391	0.962	57.47	36.57	609.5	0.18
Pt/20 MC/GNS	~ 2876	~ 61	0.357	0.942	31.11	20.66	344.3	0.12

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Table 1 shows that addition of the oxide from 6 to 20wt% decreases the E_{op} on the base electrode (Pt/GNS) by 284-345 mV. Further, with the exception of the electrocatalysts, Pt/10MC/GNS, the anodic peak potential (Ep) for MOR on Pt/xMC/GNS marginally shifts (3-67 mV) towards the positive potential in comparison with the base electrocatalysts but, the oxidation peak current values increases markedly, the increase being the greatest with 10wt% of the oxide. Thus, results show that introduction of the oxide into the Pt/GNS matrix improves the MOR greatly. The I_p observed on Pt/10MC /GNS was more than 3.4 times higher than that on Pt/GNS. For better comparison, the MOR current density produced at a constant anodic potential, E = 0.842 V vs. RHE and the scan rate of 50 mV s^{-1} in Ar-saturated 0.5 M H_2SO_4 + 1 M methanol and at 25˚C on different electrocatalysts investigated in the study are listed in Table 1. Results shown in this table demonstrate that the Pt/10MC/GNS electrocatalyst (j = 40.51 mAcm^{-2} or 675.2 mA mg^{-1}of Pt) is approximately 2.6 times greater than the base, Pt/GNS electrocatalyst (j = 15.40 mAcm^{-2} or 256.7 mA mg^{-1} of Pt). Therefore, the performance of Pt/10MC/GNS on the electrochemical oxidation of methanol can be considered superior to that of Pt/GNS catalysts. Estimates of the Pt mass activity (MA = observed current (mA)/Pt mass (mg)) and specific activity (SA = MA/EASA (cm^2.mg^{-1})) of electrocatalysts given in Table 1 show that the Pt mass utilization efficiency of the catalyst is greatly improved (40-60%) with introduction of the oxide into the Pt/GNS matrix, which is mainly due to improvement in Pt NPs dispersion on the oxide/GNS support. The percent Pt-utilization (= 100 x observed EASA, m^2 g^{-1}/ 471 m^2 g^{-1}) was estimated by considering the surface area for 100% utilization of 1 g Pt as ~ 471 m^2 g^{-1}.

Chronoamperometry: To evaluate the electrocatalytic activity and stability of electrocatalysts, namely Pt/GNS, Pt/8MC/GNS, Pt/10MC/GNS, and Pt/15MC/GNS, the chronoamperometry tests were carried out in an Ar-saturated 0.5M H_2SO_4 + 1M methanol at 25˚C under a constant potential of 0.724 V vs. RHE (Fig.5). As displayed in Fig.5, the polarization currents for catalysts rapidly decreased at the beginning, possibly due to the formation of poisonous species, such as CO_{ads} during the methanol oxidation reaction. Nevertheless, the current decay for the reaction on Pt/xMC/GNS composite electrodes was significantly slower than that on the Pt/GNS electrode. The observed current on Pt/10MC/GNS was higher than that on Pt/8MC/GNS, Pt/15MC/GNS or Pt/GNS during the whole chronoamperometry experiment. At the end of the experiment, the quasi-steady current (I_s) value displayed on Pt/10MC/GNS was 26.98 mA mg^{-1}, which is ~ 1.5, ~ 3.9 and ~ 5.4 times of the value found on Pt/8MC/GNS (I_s= 18 mA mg^{-1}), Pt/15MC/GNS (I_s= 6.9 mA mg^{-1}) and Pt/GNS (I_s= 4.89 mA mg^{-1}), respectively. The results from current decay and I_s demonstrated that the composite electrodes with 8-15% oxide had better activities and stabilities than the base electrode under the same conditions. The improved long-term durability of the composite electrodes may be ascribed to the role of oxide molecules. This study also shows that the catalytic performance of the Pt/10MC/GNS electrode is the best one among the present series of electrocatalysts investigated.

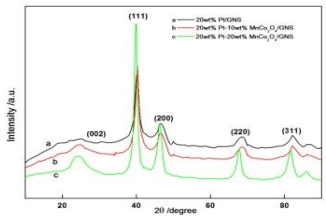
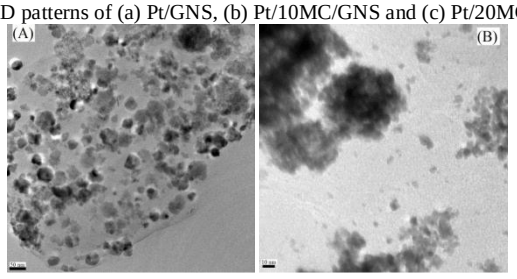


Fig.1. XRD patterns of (a) Pt/GNS, (b) Pt/10MC/GNS and (c) Pt/20MC/GNS.



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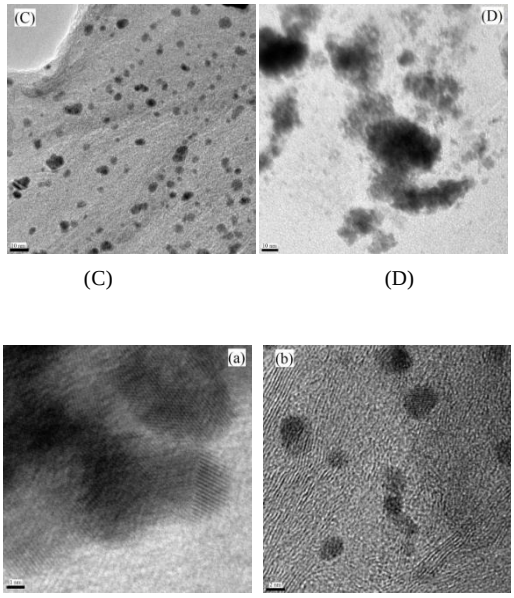

(C) (D)

(a) (b)

Fig.2. TEM images of (A) MC/GNS, (B) Pt/GNS, (C) Pt/10MC/GNS & (D) Pt/20MC/GNS and HRTEM images of (a) Pt/GNS and (b) Pt/10MC/GNS.

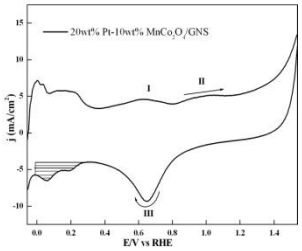

Fig.3. Typical cyclic voltammogram of Pt/10MC/GNS in Ar-saturated 0.5M H_2SO_4 at 50 mVs^{-1}.

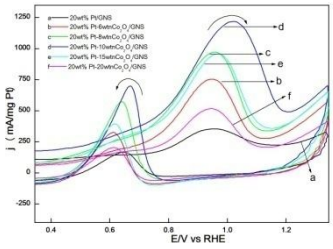

Fig.4. Cyclic voltammograms of Pt/xMC/GNS (x = 0, 6, 8, 10, 15 & 20 wt%) at 50 mVs^{-1} in Ar-saturated 0.5M H_2SO_4 + 1M CH_3OH (25°C).

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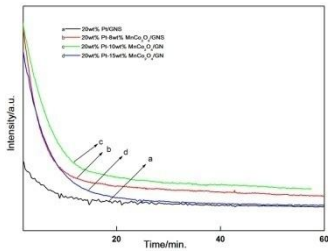

Fig.5. Chronoamperograms of Pt/xMC/GNS (x = 0, 8, 10 & 15 wt %) at 0.842V vs. RHE in Ar-saturated 0.5 M H_2SO_4 + 1M CH_3OH (25°C).

IV. CONCLUSION

The study demonstrates that low additions of the oxide (6-10wt%) greatly improve not only the electrocatalytic activity but CO poisoning tolerance of the composite too. The composite electrode containing 10wt% of the oxide exhibited the greatest MOR activity and excellent CO poisoning tolerance vis-à-vis stability in 0.5 M H_2SO_4 + 1 M CH_3OH. The electrocatalytic activity, CO poisoning tolerance and stability performances of Pt/10MC/GNS were much superior to Pt/GNS. Our study demonstrates that the support, $MnCo_2O_4$/GNS is much superior to GNS alone for obtaining better dispersion and hence enhanced MOR activity of Pt. Thus, $MnCo_2O_4$/GNS could be used as a novel potential support for Pt in direct methanol fuel cells.

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