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Electrochemical investigation of methanol electro-oxidation over GO and ZSM-5 composite in different ratios

Basu Maan Daas

Department of Chemistry,

Netaji Subhash Mahavidyalaya, Udaipur , Tripura(India)

ABSTRACT

Graphene oxide and ZSM-5 are both known to be conductive to electricity and the former is recognized to catalyze methanol electro-oxidation in acidic media and the latter is recognized to be an effective support and second catalyst. In this research work, electro-oxidation of methanol over composites of graphene oxide and ZSM-5 in different ratios is analyzed to find out the combined effect of graphene oxide and ZSM-5 in catalyzing the electro-oxidation reaction. The composites of graphene oxide and ZSM-5 analyzed are 1:0, 2:1, 1:2 and 0:1. From the cyclic voltammetric experimental data, it is found that the composite of 1:2 ratio of graphene oxide and ZSM-5 is the most effective in catalyzing methanol electro-oxidation reaction in acidic media. This information can add more to the understanding of the role of graphene oxide and ZSM-5 in methanol electro-oxidation for fuel cell applications in direct methanol fuel cells.

Keywords:Graphene oxide, ZSM-5, Electro-oxidation, Methanol, Cyclic voltammetry.

I.INTRODUCTION

The electro-oxidation of methanol (MeOH) is easier than that of ethanol and thus there has been much research about direct methanol fuel cells (DMFCs) [1,2]. DMFCs are considered a way to tackle the global energy crisis by non-conventional energy generation method for utilization in small electronic devices requiring less amount of electricity [3-12]. Graphene oxide and ZSM-5 are both known to be conductive to electricity and the former is recognized to catalyze MeOH electro-oxidation in acidic media and the latter is recognized to be an effective support and second catalyst [3,13-21]. However, the two dimensional rGO sheets have a tendency to pile together owing to π-π interaction between the individual sheets; this in turn reduces the effective surface area of rGO, consequently increasing the resistance for the influx of MeOH molecules and decreasing the catalysis [22-24]. In the preparation of GO, irreversible clustering/restacking occurs during drying due to van der Waals interactions [25,26]. The rGO sheets also possess defects which retard the overall electron transfer rate within the rGO sheets and also at the interface. The basal layers in rGO deters dispersion of electrolyte within the layers [27,28]. Thus, zeolite is used in the experimental composites to see if it can improve DMFC applications. Owing to the exceptional surface area, miniscule diffusion path lengths and readily accessible active sites ZSM-5 can promote the catalysis of MeOH electro-oxidation [29-35].

II.EXPERIMENTAL DETAILS

2.1. Instrumentation

GO was analyzed by Fourier transform infrared (FTIR) spectroscopy using Shimadzu FT-IR 8400 S. ZSM-5 was analysed by Powder X-Ray diffraction (XRD) using Rigaku Ultima IV. GO:ZSM-5/C electrodes were prepared with the ratio of GO:ZSM-5 being 1:0, 2:1, 1:2 and 0:1 and their electro-catalytic behavior on oxidation of 1 M MeOH in 0.5 M H_2SO_4 was analyzed by Autolab cylic voltammeter (CV) (model PGSTAT128N) of Metrohm, Switzerland. Electrochemical surface area (ECSA), chronoamperometric analysis (CA), and tafel plot (TP) analyses were also done by the CV.

2.2. Chemicals, reagents & working electrodes

Graphite powder, carbon felt (C-felt) and H_2PtCl_6 were purchased from Alfa-Aeser (India); ZSM-5 from Greenstone, Switzerland; $KMnO_4$, $NaNO_3$, H_2SO_4, HCl, and 30% H_2O_2 from Merck (India). Freshly triple-distilled water was used for the whole experiment. Graphene oxide was prepared as done in my previous works [36,37]. GO/C, [GO:ZSM-5]/C (2:1), [GO:ZSM-5]/C (1:2), and ZSM-5/C electrodes were prepared as done in my previous work [38]. The ratio of GO and ZSM-5 in the electrodes were maintained by taking mechanical 1:0, 2:1, 1:2 and 0:1 mixtures by weight. These electrodes were electrochemically reduced to rGO/C, r[GO:ZSM-5]/C (2:1), r[GO:ZSM-5]/C (1:2), and rZSM-5/C electrodes on a bath containing 0.5 M H_2SO_4 solution, by passing a current of (-)0.001 mA/cm^{-2} for 30 min and washing thoroughly by deionized water. Then, platinum (Pt) was galvanostatically electrodeposited on all the rGO/C, r[GO:ZSM-5]/C (2:1), r[GO:ZSM-5]/C (1:2), and rZSM-5/C electrodes to obtain the working electrodes, Pt/rGO/C, Pt/r[GO:ZSM-5]/C (2:1), Pt/r[GO:ZSM-5]/C (1:2), and Pt/rZSM-5/C, by passing (-)0.001 A/cm^2 for 100 s through a 2×10^{-3} M solution of chloroplatinic acid ($H_2PtCl_6.6H_2O$) in 1.0 M H_2SO_4 with each of the electrodes dipped separately.

III. EXPERIMENTAL RESULTS

In the FTIR spectrum of GO (Fig.1) peaks at 3600 - 3400 cm^{-1}, 1740 cm^{-1}, 1590 cm^{-1}, 1420 cm^{-1}, 1230 cm^{-1} and 840 cm^{-1} can be attributed to -OH stretching vibrations, C = O stretching vibration, skeletal vibration from un-oxidized graphitic domains, aromatic C = C stretching, C-OH stretching vibrations, and epoxy group respectively confirming the formation of GO [38,39].

In the X-ray diffractogram of ZSM-5 (Fig. 2) the pattern matched with the characteristic diffraction pattern with hkl peaks of (011), (020), (051), (101), (301), (501) and (503) at $2\theta = 22.99^0$ to 25^0 [40-42]. This confirmed the purity and authenticity of the purchased ZSM-5.

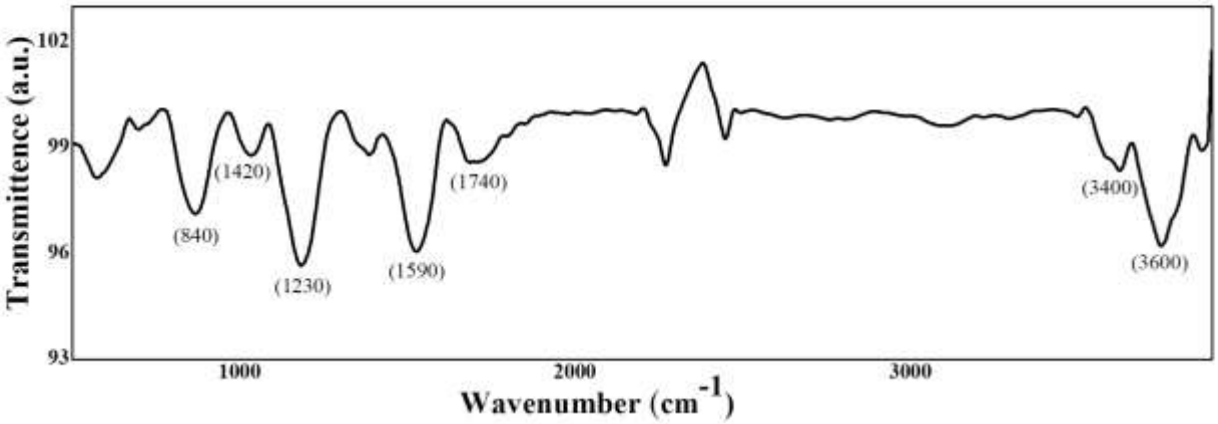

Fig. 1: FTIR spectrum of GO.

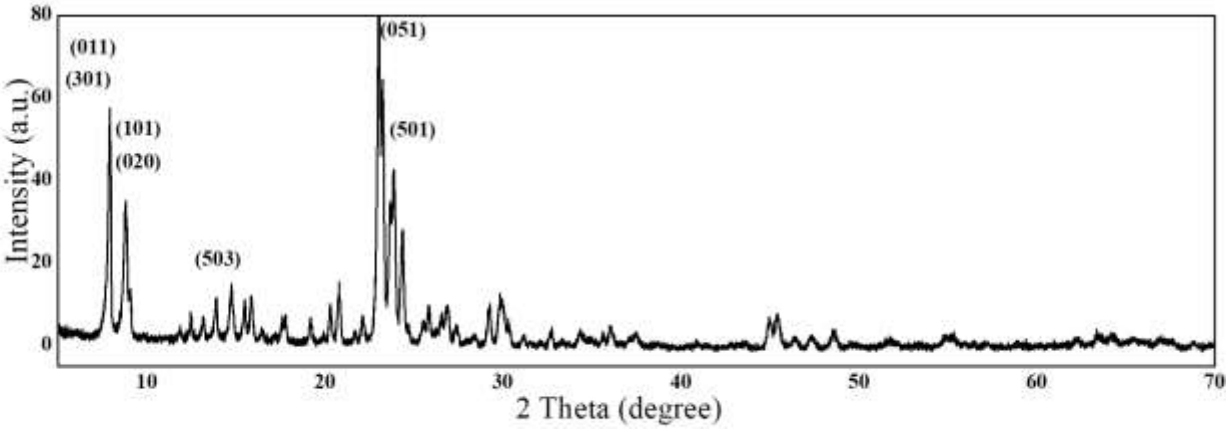

Fig. 2: X-ray diffractogram of ZSM-5.

The ECSA (Fig. 3) of Pt/rGO/C, Pt/r[GO:ZSM-5]/C (2:1), Pt/r[GO:ZSM-5]/C (1:2), and Pt/rZSM-5/C electrodes are reported in Fig. 1. The calculated ECSA of Pt/rGO/C, Pt/r[GO:ZSM-5]/C (2:1), Pt/r[GO:ZSM-5]/C (1:2), and Pt/rZSM-5/C electrodes were found to be 89.6, 96, 103.6 and 81.9 cm^2/mg respectively.

The CV (Fig. 4) of 1 M MeOH oxidation in 0.5 M H_2SO_4 catalyzed by Pt/rGO/C, Pt/r[GO:ZSM-5]/C (2:1), Pt/r[GO:ZSM-5]/C (1:2), and Pt/rZSM-5/C. The forward peak current density (I_f) of Pt/rGO/C, Pt/r[GO:ZSM-5]/C (2:1), Pt/r[GO:ZSM-5]/C (1:2), and Pt/rZSM-5/C electrodes were found to be 0.018, 0.024, 0.038 and 0.016 A/cm^2 while backward peak current density (I_b) are 0.005, 0.008, 0.015 and 0.005 A/cm^2 respectively; the I_f / I_b ratio for Pt/rGO/C, Pt/r[GO:ZSM-5]/C (2:1), Pt/r[GO:ZSM-5]/C (1:2), and Pt/rZSM-5/C electrodes being 3.6, 3.0, 2.5 and 3.2 respectively.

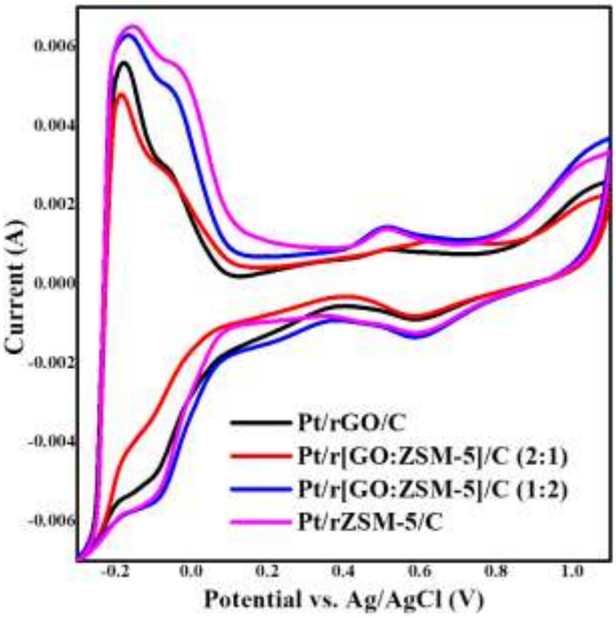

Fig. 3: ECSA of Pt/rGO/C, Pt/r[GO:ZSM-5]/C (2:1), Pt/r[GO:ZSM-5]/C (1:2), and Pt/rZSM-5/C electrodes in 0.5 M H_2SO_4.

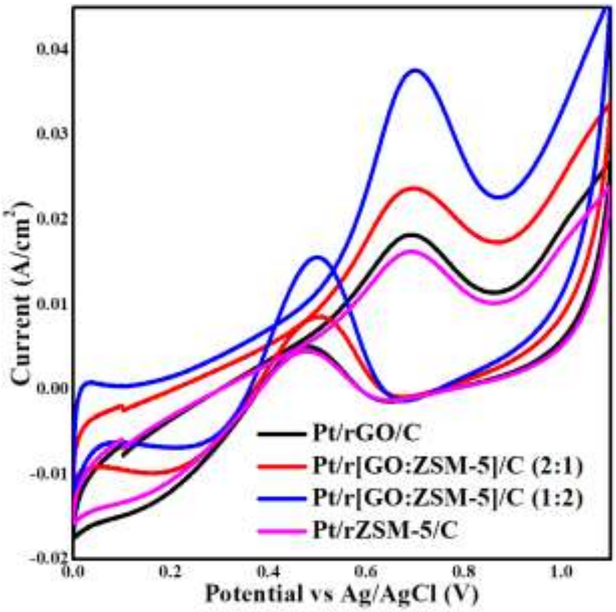

Fig. 4: CV of 1 M MeOH oxidation in 0.5 M H_2SO_4 catalyzed Pt/rGO/C, Pt/r[GO:ZSM-5]/C (2:1), Pt/r[GO:ZSM-5]/C (1:2), and Pt/rZSM-5/C electrodes.

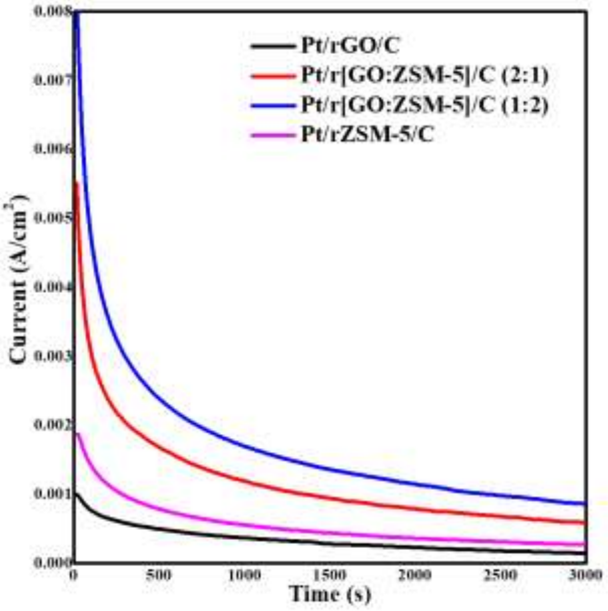

Fig. 5: CA of Pt/rGO/C, Pt/r[GO:ZSM-5]/C (2:1), Pt/r[GO:ZSM-5]/C (1:2), and Pt/rZSM-5/C electrodes in 1 M MeOH and 0.5 M H_2SO_4 at 0.4 V for 3000s.

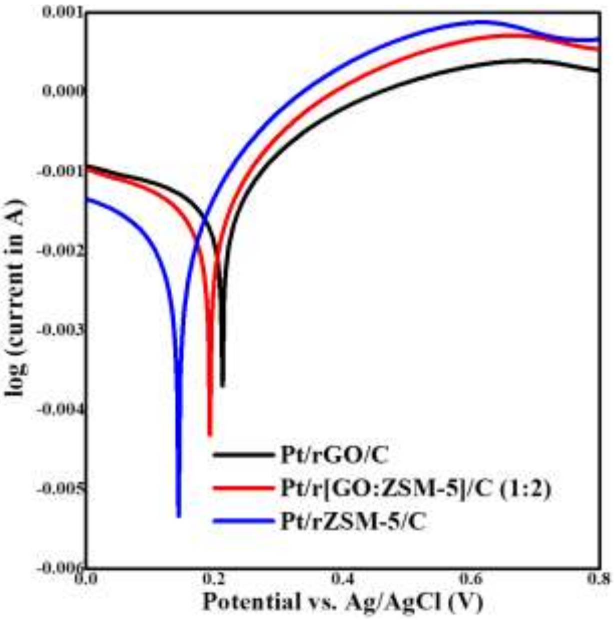

Fig. 6: TP of Pt/rGO/C, Pt/r[GO:ZSM-5]/C (1:2) and Pt/rZSM-5/C in 1 M MeOH and 0.5 M H_2SO_4.

The CA (Fig. 5) of Pt/rGO/C, Pt/r[GO:ZSM-5]/C (2:1), Pt/r[GO:ZSM-5]/C (1:2), and Pt/rZSM-5/C electrodes in 1 M MeOH and 0.5 M H_2SO_4 at 0.4 V for 3000s were done. The current density decreased for all the electrodes but after 3000s the current density was found to be maximum for Pt/r[GO:ZSM-5]/C (1:2) electrode. The turn over number (TON) calculated from the electro chemical data with the current density at 3000 s; TON was found to be maximum for Pt/r[GO:ZSM-5]/C (1:2) electrode [43,44].

The TP (Fig. 6) of Pt/rGO/C, Pt/r[GO:ZSM-5]/C (1:2) and Pt/rZSM-5/C electrodes in 1 M MeOH and 0.5 M H_2SO_4 gave the corrosion potential (E_{corr}) and the corrosion current density (i_{corr}) at the point of intersection of extrapolated cathodic and anodic tafel slopes. The Pt/r[GO:ZSM-5]/C (1:2) electrode was not considered here as the CV and CA experimental data showed that Pt/r[GO:ZSM-5]/C (1:2) electrode was the one with highest catalytic possibility. The Pt/r[GO:ZSM-5]/C (1:2) electrode was found to possess highest i_{corr} and lowest E_{corr} in the TP.

IV.DISCUSSION

It is seen that ECSA and I_f increases in the ascending order of Pt/rGO/C < Pt/rZSM-5/C < Pt/r[GO:ZSM-5]/C (2:1) < Pt/r[GO:ZSM-5]/C (1:2) electrodes. This shows that the electrodeposited Pt nanoparticles (PNPs) were of smallest size in case of the Pt/r[GO:ZSM-5]/C (1:2) electrode resulting maximum active surface area which in turn resulted in maximum cyclic voltammetric current density for the said electrode. From the CA experimental data, it is seen that the residual current after a time period of 3000 s was maximum for Pt/r[GO:ZSM-5]/C (1:2) electrode as well as the TON calculated is seen to be maximum. From the TP experimental data, it is seen that in case of Pt/r[GO:ZSM-5]/C (1:2) electrode maximum current was generated at minimum potential which strengthens the statement that Pt/r[GO:ZSM-5]/C (1:2) electrode is the most capable electrode of all the working electrodes [3,43].

V. CONCLUSION

From the electrochemical investigation of methanol electro-oxidation over Pt/rGO/C, Pt/r[GO:ZSM-5]/C (2:1), Pt/r[GO:ZSM-5]/C (1:2), and Pt/rZSM-5/C electrodes in acidic medium proves that the composite of GO and ZSM-5 in the ratio of 1:2 is the most potent catalyst for methanol electro-oxidation. As a further scope of work it may be concluded that there is enough scope of investigation more ratios of GO:ZSM-5 to identify the optimum ratio for catalyzing methanol electro-oxidation in acidic media.

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