Ethanol electro-oxidation by Pt/r(GO-ZSM)/ graphite foil

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Abstract

Present study reports electro-oxidation of ethanol over platinum loaded, reduced graphene oxide – ZSM-5 composite (GO-ZSM) on graphite foil (GF). To prepare the Pt/r(GO-ZSM)/GF electrode, GO-ZSM-5 composite was prepared by simple 1:1 mechanical mixing which was coated over graphite foil and electrochemically reduced at a current density of (-)1 mA.cm^{-2}. The electro-chemical studies, such as cyclic voltammetry and chronoamperometry established that Pt/r(GO-ZSM-5)/GF electrode exhibited better tolerance towards CO-poisoning compared to Pt/rGO/GF electrode. The larger I_F:I_B value for Pt/r(GO-ZSM)/GF indicated much lesser carbonaceous accumulation on the zeolite modified electrode. The peak current density was comparable for both Pt/r(GO-ZSM-5)/GF and Pt/rGO/GF electrodes. Thus ZSM-5 was instrumental in reducing the catalyst poisoning without compromising with the current density. The findings of the investigation can prove useful in the search of solution for the problem of catalyst poisoning associated with platinum electrodes. Copyright © 2016 VBRI Press.

Keywords: ZSM-5, graphene oxide, zeolite modified electrode, CO-poisoning, cyclic voltammetry.

Introduction

Direct Alcohol Fuel cell (DAFC) is a type of fuel cell with high energy conversion efficiency and environmental affinity. It can extract the energy from alcohols by means of electro-oxidation of the alcohols **[1]**. Electro-oxidation of alcohol takes place through the formation of an adsorbed intermediate. The mechanism of ethanol is favored over that of methanol for driving a fuel cell as energy density of ethanol (316.8 kcal/mol) is almost double that of methanol (166.8 kcal/mol); ethanol can also be easily stored and handled as it is less toxic and less volatile than methanol **[2, 3]**. Besides this, ethanol production from biomass is easy and cheap; it can also be easily produced from fermentation of sugar-containing agricultural raw materials **[4]**.

The electro-oxidation of ethanol in acidic solution can produce CH_3CHO and then CH_3COOH through a weak physically adsorbed intermediate and on the other hand, CO_2 from the strongly chemisorbed intermediate by delivering 12 e- per ethanol molecule; the cell voltage being 1.145 V under standard conditions **[5,6]**. Major problems of large scale application of DAFC are high cost of platinum, slow reaction kinetics, poor selectivity and CO-poisoning associated with platinum electrodes **[7,8]**. Graphene oxide (GO) in reduced form is a good electro-catalyst for alcohol oxidation **[9]**. Electrochemical reduction of GO to reduced Graphene oxide (rGO) and electro-deposition of Pt onto rGO is a hazardless, effective and controllable method **[10]**. The oxygen content is decreased in rGO and sp^2 carbon is restored which exhibits much better electrochemical capacitance and cycling durability **[11]**. The rGO is a cheaper alternative for pure platinum by dint of high specific surface area, with unique graphitized basal plane structure having excellent electrical, mechanical and thermal properties **[12-14]**.

ZSM-5 was first synthesized by Argauer and Landolt in 1972 (U. S. Patent 3,702,886). It is an aluminosilicate zeolite of the pentasil family; it is a composite of Si, Al and O with channels of ten membered rings. It has highly ordered microporous sieve framework with pore diameters in the range of 5-10 Å and can provide a three dimensional framework for doping catalytic molecules which facilitates regular and high dispersion of metal nanoparticles **[15-17]** Because of its typical structural framework and stability, it can increase the physical and chemical stability of the electrodes even in drastic acidic and alkaline conditions and can accommodate high influx of electrogenerated species **[17]**. Presence of ZSM-5 improves the long-term cycle stability of platinum catalyst during the process of electro-oxidation of alcohol **[2]**. The present study focused on the investigation of the role of ZSM-5 in influencing the catalytic property of platinum and GO in electro-oxidation of ethanol.

Experimental

GO/GF and GO/ZSM-5/GF electrodes were prepared and their electro-catalytic behavior on oxidation of 1 M ethanol in 0.5 M H_2SO_4 was investigated by model PGSTAT128N of Autolab cylic voltammeter from Metrohm, Switzerland.

Materials

ZSM-5 and chloroplatinic acid hexahydrate ($H_2PtCl_6.6H_2O$) used were of analytical grade. ZSM-5, with SiO_2:Al_2O_3 ratio of ~ 30, Si:Al ratio of ~ 38 and pore diameter of 5.3-5.8 Å, was procured from Greenstone, Switzerland. Chloroplatinic acid hexahydrate ($H_2PtCl_6.6H_2O$) was procured from Sigma-Aldrich. The graphite foil used as a substrate for electrode was purchased from Alfa Aesar, the purity of the foil being 98 %. The ethanol used in this investigation was procured from Changshu Yangyuan Chemical, China. Freshly triple-distilled water was used for all purposes and all experiments were carried out at the room temperature (300 K).

Preparation of graphite oxide

Graphite oxide was prepared by Hummer's Method **[18]**. 3 g of graphite flakes were mixed with 1.5 g of $NaNO_3$ and 69 mL of conc. H_2SO_4 in a beaker and stirred vigorously. The mixture was then kept at 0 °C in an ice bath for 30 s. Then, 9 g of $KMnO_4$ was added slowly in small amounts at a time, under constant stirring, keeping the bath temperature below 20 °C during the addition. The temperature of the reaction bath was raised to 30-35 °C and kept at this temperature for the next 1800 s. The mixture gradually became pasty with evolution of small amount of gas. 20 mL of distilled water was added to the resultant paste and the temperature of the solution was further increased to 98 °C and stirred constantly for another 900 s. 40 mL of distilled water and 3 mL of 30 % H_2O_2 were further added to ensure reduction of residual MnO_4^- and MnO_2 to colorless soluble $MnSO_4$. The suspension was then filtered; finally, the residue was collected and washed thoroughly with distilled water, 3 % HCl and ethanol. Graphite oxide in the form of the residue was washed and then dried in a hot air oven at 40 °C overnight.

Preparation of graphene oxide

Graphene oxide (GO) was prepared by suspending 2.5×10^{-2} g of Graphite oxide in 50 mL of distilled water and ultrasonicated for 1 h for exfoliation. The homogeneous mixture was then centrifuged at 3000 rpm for 1800 s to get a non-sediment supernatant solution [**11, 18**]. GO obtained as the residue was washed and dried.

Preparation of zeolite modified electrodes

In the beginning, graphite foil (GF) was treated in conc. HNO_3 for 1h. Then, GO was homogeneously dispersed in a solution of 5% Nafion 117 in a 20v/v dilute solution of isopropyl alcohol, under ultrasonic irradiation for 1.5 h. The catalyst ink was then painted on the pretreated graphite foil to cover an area of 1 cm^2. The other side of the foil was covered by non-conducting cello-tape; this was the GO/GF electrode.

Again, 1:1 mechanical mixture of GO and ZSM-5 was homogeneously dispersed in a 5 % solution of Nafion 117 in a 20v/v dilute solution of isopropyl alcohol, under ultrasonic irradiation for 1800 s. The catalyst ink was then painted on a pretreated graphite foil to cover an area of 1 cm^2 to get the zeolite modified electrode (ZME); the other side of the foil being covered by non-conducting cello-tape. The loading of GO was approximately 500 µg. The GO/GF and (GO-ZSM-5)/GF electrodes were dried in a desiccator overnight.

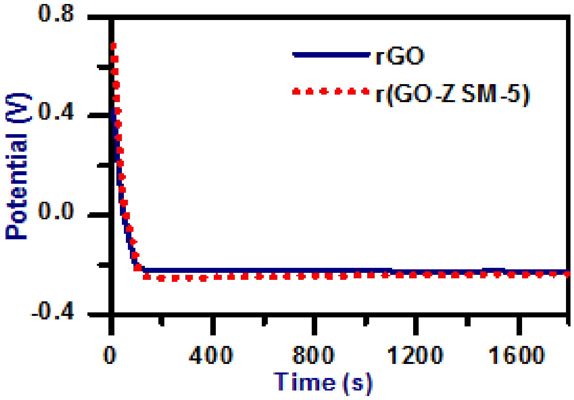

Fig. 1. Electroreduction of GO/GF & (GO-ZSM)/GF in 0.5 M H_2SO_4 at (-)1 $mA.cm^{-2}$ for 1800 s.

Electroreduction of GO to rGO

The GO deposited over the GF surface was reduced to rGO electrochemically in a bath containing 0.5 M H_2SO_4 solution by passing a current density of (-)1 $mA.cm^{-2}$ for 1800 s by means of Autolab cyclic voltammeter (**Fig. 1**). The reduced electrode was washed thoroughly by distilled water. Similarly, the (GO-ZSM-5)/GF electrode was also reduced.

Electrodeposition of platinum

Platinum was electro-deposited on both the modified electrodes galvanostatically from a 2×10^{-3} M solution of chloroplatinic acid in 1.0 M H_2SO_4 by passing a current of (-)1 $mA.cm^{-2}$ for 100 s, by employing Autolab cyclic voltammeter to get Pt/rGO/GF and Pt/r(GO-ZSM-5)/GF electrodes (**Fig. 2**) [**11**].

Characterization techniques

GO was characterized by means of Fourier transform infrared (FTIR) spectroscopy by KBr pellet technique using Shimadzu FTIR-8400S (IR solution model) spectrophotometer (**Fig. 3**).

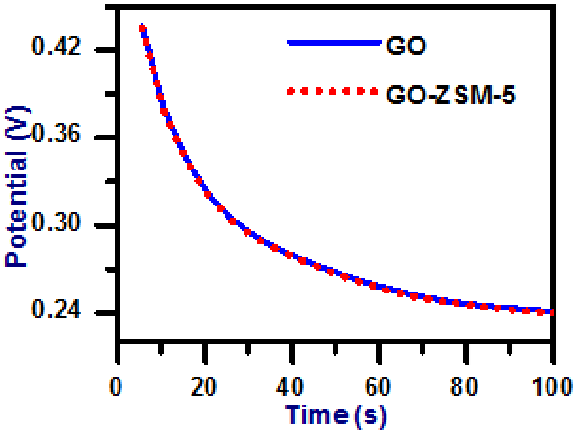

Fig. 2. Electrodeposition of Platinum on rGO/GF & Pt/r(GO-ZSM)/GF from Chloroplatinic acid hexhydrate by (-)1 mA.cm^{-2} current density for 100 s.

The powder X-Ray diffraction (XRD) of ZSM-5 was done by means of Rigaku Ultima IV employing miniflex goniometer and a Cu target with scattering slit of 4.2^0 and receiving slit of 3×10^4 m by continuous scanning with 30 kV/0.015 A of Cu Kα radiation (λ = 0.15406 nm) over a scanning range of 2θ = 5–70° with a step width of 0.05^0 (**Fig. 4(a)**).

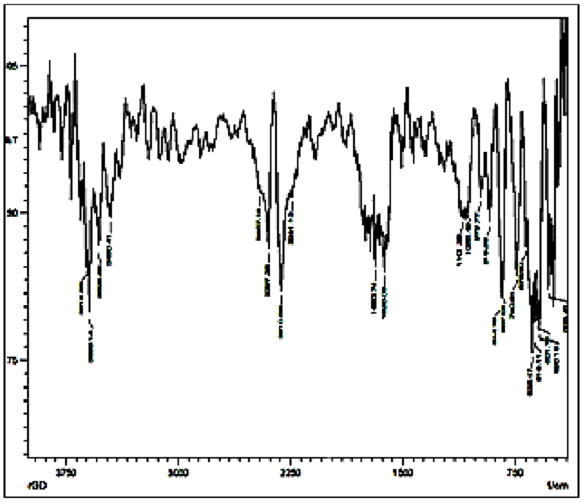

Fig. 3. FTIR spectrum of GO.

Scanning electron microscopy (SEM) (**Fig. 4(b)**) and energy dispersive spectroscopy (EDS) (**Fig. 4(c)**) analyses of the ZSM-5 procured was done by means of Jeol-JSM-6390 analyzer attached with Oxford-EDX system IE 250×Max 80.

Electrochemical studies

The electro-oxidation of 1.0 M ethanol in 0.5 M H_2SO_4 was done in presence of both Pt/rGO/GF and Pt/r(GO-ZSM-5)/GF electrodes at a scan rate of 50 mv.s^{-1} within a potential scan window of 0 to 1.2 V (**Fig. 5(a)**). The base voltammograms of blank GF in 0.5 M H_2SO_4 (**Fig. 5(b)**) and 1.0 M ethanol in 0.5 M H_2SO_4 (**Fig. 5(c)**) were also obtained to verify if any current density was generated in the absence of the catalysts under investigation. Chronoamperogram of both the catalysts at 0.4 V were done to verify their corresponding stability and turn-over number (TON) (**Fig. 6**).

Results and discussion

FTIR spectrum analysis

GO was characterized by Fourier transform infrared (FTIR) spectroscopy using Shimadzu FT-IR 8400 S (**Fig. 3**). The peaks at 360000-340000 m^{-1} for -OH stretching vibrations, at 173905 m^{-1} for C=O stretching vibration, at 158677 m^{-1} for skeletal vibration from un-oxidized graphitic domains, at 142219 m^{-1} for aromatic C=C stretching, at 122677 m^{-1} for C-OH stretching vibrations, and at 83906 m^{-1} for epoxy groups confirmed the formation of GO [**11**].

Powder XRD analysis

The powder X-Ray diffraction (XRD) of ZSM-5 was done using Rigaku Ultima IV (**Fig. 4a**). The pattern obtained matched with the standard diffraction pattern; the peaks d011, d020, d051, d101, d301, d501 and d503 within 2θ = 22.99^0 to 25^0 corresponded to the characteristic peaks of ZSM-5 and possessed comparable values of relative intensities as reported in the literature **[19-21]**.

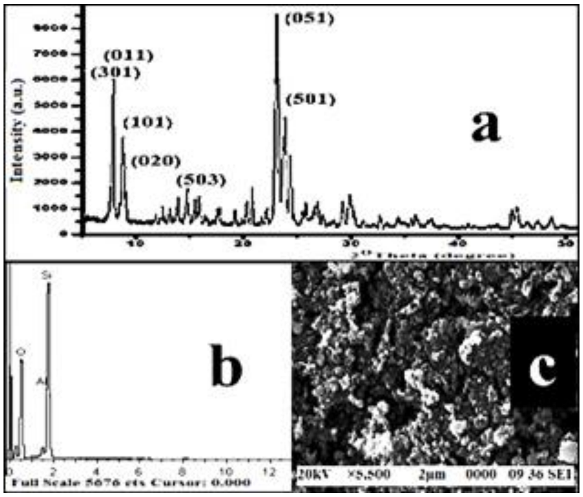

Fig. 4 XRD pattern (a), EDS pattern (b**)** and SEM image (c) of ZSM-5.

EDS and SEM analyses

EDS analysis of ZSM-5 proved the presence of all the elements of ZSM-5 and revealed that the weight percentage (wt%) of Si, Al and O in ZSM-5 were approximately 58, 20 and 22 % respectively; which established the purity of the zeolite used in the investigation (**Fig. 4b**). SEM of ZSM-5 showed the particle size of the zeolite in the order of 20 nm which was calculated by scaling the size of the smaller particles under magnifying glass and diving by 5500 as the reported snap was magnified 5500 times (**Fig. 4(c)**).

Cyclic voltammogram analysis

The mass activity (MA) of platinum in electro-oxidation of 1.0 M ethanol in 0.5 M H_2SO_4 catalyzed by Pt/rGO/GF and Pt/r(GO-ZSM)/GF were found to be about 147 mA.mg^{-1} and 144 mA.mg^{-1} respectively which were comparable (**Fig. 5(a)**).

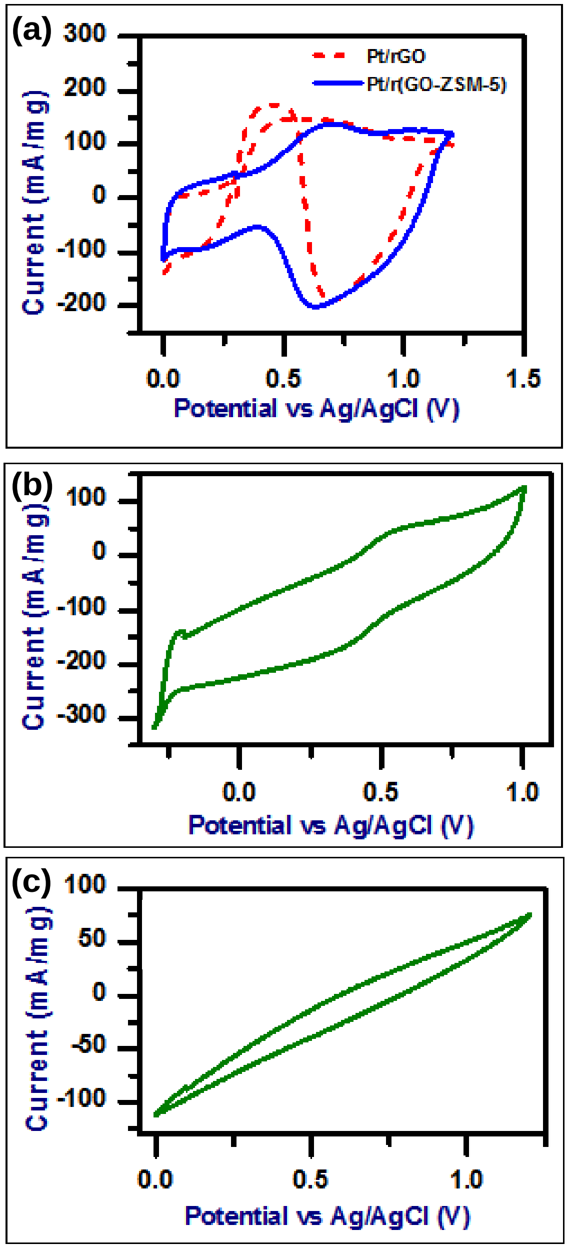

Fig. 5. Cyclic voltammogram of electro-oxidation of EtOH at 50 mv.s^{-1} scan rate (a); base voltammograms of blank GF in 0.5 M H_2SO_4 (b); and in 1.0 M EtOH and 0.5 M H_2SO_4 (c).

Mass activity (MA) is the current (in mA) recorded per unit mass of the loaded catalyst (in mg); the catalyst being platinum. The ratio of the forward and backward peak currents (I_F:I_B) for the Pt/rGO/GF catalyst was found to be 0.9. But I_F:I_B for Pt/(rGO:rZSM-5)/GF catalyst was found to be remarkably high (5.3) which showed that resistance to carbonaceous poisoning in case of the zeolite modified electrode (ZME) was more than five times higher compared to that of Pt/rGO/GF. This could be due to the higher separation and exposure of GO and platinum in the zeolite matrix due to the inherent microporous sieve structure of ZSM-5.

It has been reported by many electrochemists that presence of Ru-OH can facilitate release of CO_2 from adsorbed CO (CO_{abs}) by releasing proton and electron thereby reactivating the catalyst surface for further reaction **[22-30]**. So, the higher resistance to CO poisoning by ZME can be explained in the similar line as ZSM-5 also has hydroxyl (–OH) groups in its framework that can facilitate release of CO_{ads} from active sites as CO_2 which clears the electrode surface for next cycle of electro-oxidation reaction mechanism. The introduction of ZSM-5 was found to significantly accelerate the process of ethanol electro-oxidation by clearing the active sites quickly.

The base voltammograms of blank GF in 0.5 M H_2SO_4 (**Fig. 5(b)**) and 1.0 M ethanol in 0.5 M H_2SO_4 (**Fig. 5(c)**) gave the pattern of hysteresis that showed no peak in current density. In the former voltammogram, no recognizable peak in current density was observed and in the latter, it was confirmed that without the presence of the acid electrolyte electro-oxidation reaction of ethanol didn't occur. This established that the forward and backward current density peaks were produced by the electro-oxidation reaction of ethanol on the electrode surface, only in the acidic medium. Another observation from the latter voltammogram was that the hysteresis pattern was broad which also dictated the shape of cyclic voltammogram for ethanol electro-oxidation (**Fig. 5(a)**).

Chronoamperogram analysis

Chronoamperograms of GO/GF & (GO-ZSM)/GF, in 1.0 M ethanol in 0.5 M H_2SO_4 at 0.4 V, were comparable.

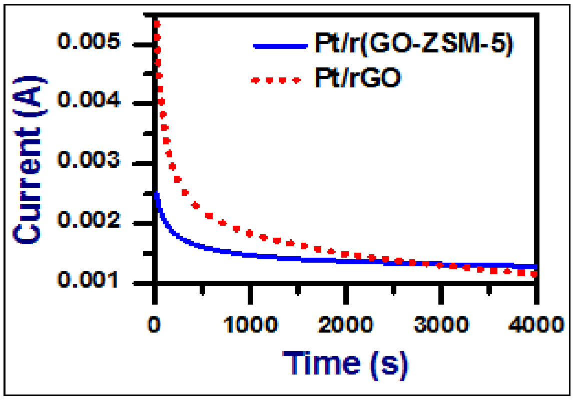

Fig. 6. Chronoamperagrams of GO/GF & (GO-ZSM)/GF in 1.0 M EtOH and 0.5 M H_2SO_4 at 0.4 V.

It was found that the stability of Pt/r(GO-ZSM)/GF electrode increased than that of Pt/rGO/GF electrode after 3000 s which established the fact that the composite catalyst got better than the catalyst without ZSM-5 in catalyzing ethanol electro-oxidation after a particular time period. After 3000 s of electrocatalysis, the current density is considered to be in a steady-state. Turn-over number (TON) was calculated from the current density at 3500 s by using the following equation,

$$\text{TON} = \text{Molecules/Sites} = \frac{\mathrm{i} \times 6.023 \times 10^{23}}{\mathrm{nF} \times 1.3 \times 10^{15}}$$

where, i = the steady-state current density at 3500 s of scanning, n = the number of electrons produced by oxidation of 1.0 M ethanol (i.e. 12), F = Faraday constant (96,487 C), 6.023×10^{23} = Avogadro number, and 1.3×10^{15} cm^{-2} = the density of the topmost atoms of an ideal Pt (100) surface **[31,32]**.

TON calculated for ZME was found to be 520 while that for the electrode without ZSM-5 was found to be 480. This established the fact that catalytic ability increased by the introduction of ZSM-5 which again proved the positive role of ZSM-5 in the composite catalyst.

Conclusion

From the investigation, it was found that graphene oxide modified with ZSM-5 increased electrode's resistance towards carbonaceous poisoning confirmed by increase in the ratio of I_F:I_B. The introduction of ZSM-5 into graphene oxide increased the separation and exposure of graphene oxide as well as the platinum sites in the composite matrix which made desorption of CO_2 from adsorbed CO much easier. Moreover, the zeolite modified electrode was found to be more stable than the pure platinum loaded graphene oxide electrodes and also more active in the long run after a time period.

As far as further scope of study is concerned, investigation can be done by modifying the substrate to get higher resolution peaks. More ratios of GO and ZSM-5 composite can be probed to identify the optimum ratio of composite required to catalyze the electro-oxidation of ethanol with best results.

Author's contributions

Conceived the plan: BMD, SG. Performed the expeirments: BMD, DD. Data analysis: BMD, SG. Wrote the paper: BMD, SG. Authors have no competing financial interests.

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