

**REDUCED GRAPHENE OXIDE-POLY(3,4
ETHYLENEDIOXYTHIOPHENE):POLY(STYRENE
SULFONATE)-TRANSITION METAL OXIDE BASED
TERNARY NANOCOMPOSITES AS ANODE CATALYST
FOR METHANOL OXIDATION**

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CHAPTER VII

Conclusions and Future Prospects

The present thesis deals with the synthesis, morphological and structural characterizations and electrochemical and electrocatalytic studies of reduced graphene oxide, poly(3,4-ethylenedioxythiophene):polystyrene sulfonate and transition metal oxide (MnO₂, NiO and NiMn₂O₄) based ternary nanocomposite toward methanol oxidation. The major conclusions drawn from the three chapters in the present thesis and future prospects of this work are summarized in the following two sections:

7.1 Conclusions

1. The first work deals with the development of a ternary nanocomposite rGO/PEDOT:PSS/MnO₂ by *in situ* oxidative polymerization method. TEM image of rGO/PEDOT:PSS/MnO₂ nanocomposite confirms that the morphology of MnO₂ nanorods are well maintained even after polymer coating and incorporation of rGO. rGO/PEDOT:PSS/MnO₂/ITO electrode exhibits a pair of redox peak within the range from -0.35 V to +0.35 V in the cyclic voltammetry curve in presence of 0.5 M NaOH due to Mn³⁺/Mn⁴⁺ redox couple. rGO/PEDOT:PSS/MnO₂/ITO exhibits anodic oxidation current density of 56.3 mA cm⁻² at an onset voltage of 0.32 V. The higher electrochemical performance of rGO/PEDOT:PSS/MnO₂/ITO electrode can be attributed to fine dispersion of PEDOT:PSS coated MnO₂ nanorods over rGO sheets. Moreover, the presence of highly porous MnO₂ nanorods makes it accessible for the electrolyte ions and electrons to penetrate deep into the pores of the nanocomposite modified electrode. Again the wrapped rGO nanosheets in ternary nanocomposite enhance the electron transfer rate and number of reaction sites due to its high conductivity and large surface area. Chronoamperometric analysis shows that rGO/PEDOT:PSS/MnO₂/ITO electrode holds current density of 50 mA cm⁻² with current retention factor 70.3% of initial current and cyclic stability upto 1000 cycles with current retention factor 74% of initial current at a scan rate of 50 mV s⁻¹. The decrement of current is observed due to consumption of methanol and formation of

intermediate products. The TEM micrographs of rGO/PEDOT:PSS/MnO₂ nanocomposite reveal that MnO₂ nanorods appear even after 1000 CV cycles however diameter and length of the nanorods reduce. The changes in XPS core spectra of Mn 2p, C 1s, O 1s and S 2p peak after 1000 CV cycling suggest the consumption of Manganese species, carbon content and degradation of PEDOT:PSS film, respectively.

2. Another work focuses on the synthesis of ternary nanocomposite of rGO/PEDOT:PSS/NiO, where coexistence of both NiO nanorods and nanoplates has been observed in TEM image. The cyclic voltammogram of rGO/PEDOT:PSS/NiO/ITO electrode in presence of 0.5 M NaOH shows oxidation and reduction peaks around 0.45 and 0.3 V, respectively, attributing to the conversion between Ni⁺²/Ni⁺³ binary redox states. rGO/PEDOT:PSS/NiO/ITO electrode exhibits oxidation peak current density 62.6 mA cm⁻² at an onset voltage 0.34 V in presence of 0.5 M methanol containing in 0.5 M NaOH. The enhanced electrocatalytic activity is due to the conversion of NiO into NiOOH that acts as electroactive media during methanol oxidation, presence of numerous pores in the nanocomposite, high specific surface area owing to the coexistence of nanoplate and nanorod structures in NiO, enhanced electron transport along the one-dimensional NiO nanorod and large surface area of rGO nanosheets. Chronoamperometric analysis shows that rGO/PEDOT:PSS/NiO/ITO electrode holds a current density of 50.7 mA cm⁻² with current retention factor 62% of initial current for 1 h. Moreover the electrode exhibits 71% current retention after 1000 CV cycles. The TEM images of rGO/PEDOT:PSS/NiO nanocomposite reveal the coexistence of NiO nanorod and nanoplate structure even after 1000 CV cycles. After continuous CV cycling, aggregation of nanoplates occurs and the lengths of NiO nanorods are shortened. The decrease in intensities of XPS core level spectra of Ni 2p, C 1s, O 1s and S 2p peak after continuous 1000 CV cycles implies consumption of nickel species, depletion of carbon and disintegration of PEDOT:PSS film, respectively.
3. A mesoporous ternary nanocomposite based on NiMn₂O₄, poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) and reduced graphene oxide (rGO) has been synthesized via *in situ* polymerization method. The TEM micrographs of rGO/PEDOT:PSS/NiMn₂O₄ nanocomposite display a porous structure, where PEDOT:PSS coated NiMn₂O₄ particles are embedded within interconnected network of rGO sheets. The cyclic voltammograms of rGO/PEDOT:PSS/NiMn₂O₄

electrode exhibits oxidation peak at 0.21 V and reduction peak at 0.12 V in presence of 0.5 M NaOH solution due to the charge transfer mechanism in redox couples of $\text{Mn}^{2+}/\text{Mn}^{3+}$ and $\text{Ni}^{2+}/\text{Ni}^{3+}$ in NiMn_2O_4 . The onset voltage at rGO/PEDOT:PSS/ NiMn_2O_4 /ITO electrode is less (0.21 V) while the oxidation peak current density is higher (70.4 mA cm^{-2}) in comparison to PEDOT:PSS/ NiMn_2O_4 /ITO and NiMn_2O_4 /ITO electrodes. The excellent catalytic performance of rGO/PEDOT:PSS/ NiMn_2O_4 /ITO electrode is due to the homogeneous distribution of NiMn_2O_4 nanoparticles within PEDOT:PSS matrix preventing aggregation of NiMn_2O_4 nanoparticles and thereby increasing the surface area, porous structure of rGO/PEDOT:PSS/ NiMn_2O_4 nanocomposite enhancing the migration and penetration of ions into the electrode surface and high electrical conductivity of rGO nanosheets. Chronoamperometry curves show that rGO/PEDOT:PSS/ NiMn_2O_4 /ITO electrode can hold a current density of 38 mA cm^{-2} and current retention factor 65.2% for 1 h indicating better stability of rGO/PEDOT:PSS/ NiMn_2O_4 /ITO electrode as compared to PEDOT:PSS/ NiMn_2O_4 /ITO and NiMn_2O_4 /ITO electrodes. Moreover, rGO/PEDOT:PSS/ NiMn_2O_4 /ITO electrode maintains a current retention factor 77.4% of initial cycle after 1000 CV cycles. TEM micrographs of rGO/PEDOT:PSS/ NiMn_2O_4 nanocomposite show slight agglomeration of NiMn_2O_4 nanoparticles and increase in diameter after cyclic stability test for 1000 CV cycles. The decrease in intensity of deconvoluted peaks of Mn 2p and Ni 2p after cyclic stability test indicates consumption of Mn and Ni species during methanol oxidation. Moreover, the decrease in intensity of C 1s peak suggests the consumption of carbon content and disappearance S 2p_{3/2} and S 2p_{1/2} electronic states of PEDOT in S 2p spectrum confirms degradation of PEDOT due to continuous CV cycles.

A comparative analysis of all the synthesized ternary nanocomposites has been presented in Table 7.1. rGO/PEDOT:PSS/NiO nanocomposite exhibits higher BET specific area of $270 \text{ m}^2 \text{ g}^{-1}$ and larger pore volume of $0.79 \text{ cm}^3 \text{ g}^{-1}$ as compared to rGO/PEDOT:PSS/ MnO_2 and rGO/PEDOT:PSS/ NiMn_2O_4 nanocomposites due to the coexistence of both NiO nanorods and nanoplates. However, rGO/PEDOT:PSS/ NiMn_2O_4 /ITO electrode exhibits lower onset voltage of 0.21 V and higher oxidation peak current density of 70.4 mA cm^{-2} owing to the presence of rich binary redox active species $\text{Mn}^{2+}/\text{Mn}^{3+}$ and $\text{Ni}^{2+}/\text{Ni}^{3+}$ in NiMn_2O_4 and highly conductive rGO nanosheets. Lower Tafel slope of 67 mV dec^{-1} suggests slower

Table 7.1: Comparative analysis of the major findings of three synthesized systems.

Parameters	rGO/PEDOT:PSS/ MnO ₂ /ITO	rGO/PEDOT:PSS /NiO/ITO	rGO/PEDOT:PSS /NiMn ₂ O ₄ /ITO
BET specific surface area (m ² g ⁻¹)	190	270	212
Pore volume (cm ³ g ⁻¹)	0.55	0.79	0.69
peak to peak separation (ΔE_p) (mV)	170	136	87
Surface coverage of redox couples (mol cm ⁻²)	3.34×10^{-8}	4.07×10^{-8}	4.60×10^{-8}
Heterogeneous rate constant (k_s) (cm s ⁻¹)	0.055	0.089	0.150
Onset voltage of methanol oxidation (V)	0.32	0.34	0.21
Oxidation peak current density (mA cm ⁻²)	56.3	62.6	70.4
Tafel slope (β) (mV dec ⁻¹)	69	73	67
Electron transfer coefficient (α)	0.86	0.81	0.88
Exchange current density (i_0) (mA cm ⁻²)	2.29×10^{-2}	2.86×10^{-2}	5.61×10^{-2}
Current retention factor from Chronoamperometric analysis	70.3%	62%	65.2%
Current retention factor after 1000 CV cycles	74%	71%	77.4%

increase in overvoltage with increase in current density while higher exchange current density of 5.61×10^{-2} mA cm⁻² implies fast electron transfer kinetics and stability of rGO/PEDOT:PSS/NiMn₂O₄/ITO electrode towards external causes. The higher cyclic

stability of 77.4% after 1000 CV cycles than that of the other two nanocomposite modified electrodes indicates better stability of the synthesized electrode. Hence the results depicted in Table 7.1 ensure that rGO/PEDOT:PSS/NiMn₂O₄/ITO electrode is the most suitable one to be used in devices.

7.2 Future prospects

Direct methanol fuel cells have gained much interest of the researchers as an alternative energy source due to high energy density (5.04 kWhL⁻¹), easy handling and transportation of methanol, low emission and low operating temperature (60 °C-120 °C). However, methanol crossover, CO poisoning and high cost of platinum catalyst impede its practical application. Hence extensive research work is going on to develop non noble metal based anode catalyst for methanol oxidation. In this work, transition metal oxide, poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) and rGO based ternary nanocomposites have been developed as an anode catalyst for methanol oxidation. The future prospects of this work to improve the activity of the electrodes are discussed below:

1. In present work, transition metal oxide and PEDOT:PSS have been composited with rGO nanosheets. This work can be further extended for other two dimensional materials such as MXenes, transition metal dichalcogenides etc. Moreover, nanostructures of PEDOT:PSS such as nanoparticle, nanofibre, nanotube, nanorods etc. can be composited with carbon nanotube, carbon quantum dot, carbon aerogel etc. to improve the electrocatalytic activity of the catalyst. Further studies can also be carried out on nanocomposites of perovskites and metal organic frameworks.
2. Swift heavy ion (SHI) irradiation is an efficient technique to enhance the structural, morphological and electrochemical properties of the materials in a controlled manner. Similarly, plasma irradiation, low energy ion irradiation etc. can be carried out in order to investigate the modifications in structural, morphological and electrochemical properties of the nanocomposite modified electrodes.
3. DMFC device performance can also be investigated using the modified electrodes.