Abstract

Among various energy conversion devices, fuel cells have been regarded as the promising and sustainable energy conversion system, where fuels are not burnt making it clean energy resource. Direct methanol fuel cells (DMFCs) have attained much attention as a potential alternative over conventional hydrogen fuel cell in mobile electronics and electric vehicles, owing to the abundance of methanol, low cost with high energy density, easy handling and storage of methanol and low operating temperature. Presently, platinum (Pt)-based catalysts have been used in pre-commercial fuel cells due to its high electrocatalytic activity. However, high price and catalytic poisoning over Pt surface due to formation of poisonous intermediates such as formaldehyde (CHO), carbon monoxide (CO) etc. hinder the commercialization of DMFC. The performance of fuel cells basically depends upon the activity, stability, durability and abundance of the electrocatalyst material. Therefore, development of efficient, durable and affordable electrocatalyst is an urgent need for practical applications of DMFC. The successful design of non-noble metal based electrocatalyst is still a challenge because of low conductivity, less stability and catalytic performance of other metal based electrocatalysts.

In comparison to noble metals, the transition metals are abundant in nature and therefore affordable which make them use as efficient alternative to noble metals. The morphology and size of the transition metal based materials have direct effect on electrocatalytic activity of the catalysts. The transition metal oxides (TMO) have drawn tremendous attention due to its excellent redox activity, high capacity and low price. Mixed transition metal oxides (MTMO) have also been studied in recent years due to presence of two different redox active centres, where faradaic reaction occurs. Recently, composites of transition metal oxides and conducting polymers have attracted great interest, since synergetic effects of both the components in such composites enhance the physical, chemical and electrocatalytic properties of the materials. Conducting polymers such as polypyrrole, polyaniline and poly(3,4- ethylenedioxythiophene) etc. are conjugated π bonded materials having good electrical conductivity (10^{-6} S cm^{-1}), high electrochemical stability. Among different conducting polymers, poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) doesn't easily get oxidized due to the presence of ethylenedioxy group at the 3- and 4- positions of the thiophene ring. Moreover, the use of PEDOT:PSS in the nanocomposite allows edges and corners of it for storage of charge and also protects the binary material from dissolution into the electrolyte. Reduced

graphene oxide (rGO) is a physical analogue of graphene which can be prepared by removing the oxygen containing functional groups present at the edges and basal plane of graphene oxide (GO) by reduction method. rGO nanosheets have gained huge attention of the researchers owing to its high electrical conductivity, large surface area and good mechanical strength. Incorporation of rGO with conducting polymer and metal oxide can improve the catalytic activity of the material. In addition, the incorporation of PEDOT:PSS and rGO in the nanocomposite systems prevents agglomeration of the metal nanostructures. Previous reports depict the application of graphene derivatives, conducting polymer and metal oxide based ternary nanocomposites in supercapacitors [1-4], sensors [5, 6], dye degradation [7] etc. However, the application of this ternary nanocomposite as anode catalyst for methanol oxidation was probably a maiden attempt. In the present thesis, ternary nanocomposite of a mixed transition metal oxide having two redox centres has been synthesized and composited with PEDOT:PSS and rGO. The presence of two redox centres is likely to significantly improve the electrocatalytic activity in comparison to that of a single transition metal oxide. The present thesis also includes the application of electrocatalytic activities of NiO consisting both nanoplate and nanorods structure and composited with PEDOT:PSS and rGO nanosheets. The presence of two dimensional NiO nanoplate provides large surface area with remarkable electroactive sites for adsorption of methanol molecules. Moreover, one dimensional NiO nanorods consist of plenty of open pores facilitating easy path for electronic and ionic transport and hence decreasing the electrical resistance. In addition, two dimensional nanoplates having large number of electroactive sites at the surface after conjugation with one dimensional nanorods provides additional active sites for electrocatalysis. Thus, probably it is the novel approach to develop rGO, conducting polymer PEDOT:PSS and transition metal oxide based ternary nanocomposites as anode catalyst for methanol oxidation.

In the present thesis, three different systems, rGO/PEDOT:PSS/MnO_2, rGO/PEDOT:PSS/NiO and rGO/PEDOT:PSS/$NiMn_2O_4$ ternary nanocomposites, have been synthesized and their morphological, physical and electrocatalytic properties toward methanol oxidation have been studied. All these systems have been characterized using sophisticated analytical instruments. Morphological and structural properties of all the prepared samples have been investigated using Scanning electron microscopy (JEOL model JSM 6390 LV), high resolution transmission electron microscopy (model JEOL

JEM 2100), X-ray diffraction (Rigaku miniflex X-ray diffractometer using monochromatic Cu Kα radiation) and Raman spectroscopy (Renishaw in via spectrometer equipped with 514.5 nm argon ion laser). The specific surface area of the prepared samples has been calculated by Brunauer-Emmett-Teller (BET) method while the pore volume and pore size distribution are determined using Barrett-Joyner-Halenda (BJH) methods. X-ray photoelectron spectroscopy (XPS) measurements have been done with an ESCALAB Xi + (Thermo Fisher Scientific Pvt. Ltd., UK) system using a monochromatic aluminium Kα radiation in a vacuum of 10^{-10} mbar with pass energy of 20 eV. The electron transfer kinetics and electrocatalytic properties toward methanol oxidation have been studied using cyclic voltammetry (CV). Linear sweep voltammetry (LSV) has also been done to investigate the electrocatalytic activities towards methanol oxidation. The electrochemical impedance spectroscopy (EIS) has been performed to understand the resistances appear at the electrode and electrolyte interface during charge transfer process. The stability of the catalysts has been observed using chronoamperometry (CA) and cyclic stability test.

The present thesis consists of seven chapters. **Chapter 1** begins with the overview of fuel cell as energy conversion device and its different classifications. Details of direct methanol fuel cell (DMFC), operating principle, half-cell reactions, methanol oxidation mechanism, applications, components of DMFC and its limitations have been described. This chapter also emphasizes on the development of non-noble metal based anode catalysts including transition metals, carbon nanomaterials, conducting polymers and their nanocomposite systems. At the end of this chapter, scope of the thesis and statement of the thesis problem have been discussed.

The various theoretical models and mechanisms related to the experimental measurements have been reviewed in **Chapter 2**. Different theories related to the electron and charge transfer kinetics using CV and LSV measurements have been discussed in detail. Different impedance parameters in an electrochemical system including charge transfer resistance (R_{ct}), equivalent series resistance (R_s) and Warburg impedance (W) have been also discussed. The theory for CA to measure stability of the electrocatalysts has been described. The theories employed for the calculations of specific surface area, pore volume and pore size distribution have also been included in this chapter.

Chapter 3 discusses the materials and methods used for the synthesis of MnO_2, NiO, $NiMn_2O_4$, rGO and their nanocomposites. The synthesis processes and formation

mechanisms of all the synthesized nanocomposites have been discussed in detail. The principles of various characterization techniques viz. SEM, TEM, XRD, Raman spectroscopy, XPS, N_2 adsorption-desorption measurements, CV, LSV, EIS and CA used in the present thesis work have been described briefly.

Chapter 4 presents the synthesis and characterization of rGO/PEDOT:PSS/MnO_2 nanocomposite that has been synthesized via *in situ* polymerization technique. From the morphological investigations of the ternary nanocomposite, it is confirmed that PEDOT:PSS coated MnO_2 nanorods are wrapped in rGO nanosheets. Brunauer-Emmett-Teller (BET) measurements confirm the porous structure and high surface area (190 $m^2 g^{-1}$) of the ternary nanocomposites. rGO/PEDOT:PSS/MnO_2/ITO electrode exhibits higher anodic current density of 56.3 mA cm^{-2} at an onset voltage of 0.32 V indicating the synergetic effects of excellent conductivity of rGO nanosheets and porous nanostructure of PEDOT:PSS coated MnO_2 nanorods. rGO/PEDOT:PSS/MnO_2/ITO electrode shows current retention factor 70.3% of initial current for 1 h and cyclic stability upto 1000 CV cycles with current retention factor 74% of initial current.

In **Chapter 5**, a ternary nanocomposite of reduced graphene oxide (rGO), Poly (3,4-ethylenedioxythiophene) (PEDOT): poly (styrene sulfonic acid) (PSS) and nickel oxide (NiO) nanoplate-nanorod structures has been developed to use as electrocatalyst for methanol oxidation. Two dimensional nanostructures have large number of electroactive sites at the surface and conjugation with one dimensional nanostructure provides additional active sites at the interface. The synergetic effect of conducting polymer of PEDOT:PSS, large surface area of rGO and metal oxide enhances electrical conductivity and also facilitates contact between electrolyte ions and the nanocomposite for methanol oxidation. An anodic current density of 62.6 mA cm^{-2} has been obtained with an onset voltage of 0.34 V at a 50 mV s^{-1} scan rate for 0.5 M of methanol oxidation. Chronoamperometry analysis shows that rGO/PEDOT:PSS/NiO/ITO electrode exhibits current retention factor 62% of initial current for 1 h and cyclic stability 71% of initial cycle after 1000 CV cycles.

Chapter 6 deals with the development of a mesoporous ternary nanocomposite based on $NiMn_2O_4$, poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) and reduced graphene oxide (rGO) as anode catalyst for methanol oxidation. Initially, $NiMn_2O_4$ nanoparticles have been synthesized using solvothermal-assisted calcination and then polymerization of EDOT monomer has been done in presence of rGO

nanosheets and $NiMn_2O_4$ nanoparticles to form rGO/PEDOT:PSS/$NiMn_2O_4$ nanocomposite. rGO/PEDOT:PSS/$NiMn_2O_4$/ITO electrode exhibits peak current density of 70.4 mA cm^{-2} at an onset voltage of 0.21 V towards oxidation of 0.5 M methanol. Chronoamperometry curves show that rGO/PEDOT:PSS/$NiMn_2O_4$/ITO electrode shows a current retention factor 65.2% for 1 h and it maintains a cyclic stability of 77.4% of initial cycle after 1000 CV cycles. The improved electrocatalytic activity and cyclic stability of rGO/PEDOT:PSS/$NiMn_2O_4$ nanocomposite can be attributed to the presence of rich binary active sites of Ni and Mn species, large surface area and high electrical conductivity of rGO and uniform dispersion of $NiMn_2O_4$ nanoparticles over PEDOT:PSS.

In Chapter 7, the major conclusions drawn from the present thesis work have been summarized. At the end of this chapter, the future scope of research in the area of nanocomposite as anode catalyst for DMFC has also been briefly discussed. The as-synthesized ternary nanocomposite modified electrodes can be treated with high energy ion irradiation, low energy ion implantation, plasma irradiation to modify the structural, morphological and electrochemical properties of the electrodes. DMFC device performance can be observed using the synthesized electrodes. Moreover, ternary nanocomposites can be prepared using MXenes, transition metal dichalcogenides, conducting polymer nanostructures and other carbon allotropes such as carbon nanotube, carbon quantum dot, carbon aerogel, graphene nanoribbon etc.

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