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Double metal oxide based nickel hybrid nanocatalyst for electrooxidation and alkaline fuel cell device fabrication

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ABSTRACT

Dual metal oxides immobilized on amine functionalized fly ash coated conducting co-polymer composite as the catalyst supporting material has been prepared. Here, a facile method has been employed to prepare nickel nanoparticles deposited hybrid nano-composite with unique morphology (Ni/Poly(Py-co-O-Anis)/ZnO/CuO/AFA). The resulted composite material has been characterized by different analytical techniques like scanning electron microscopy, transmission electron microscopy, X-ray diffraction, BET, EDX, elemental dot color mapping and infrared spectroscopy. Further, electrochemical performance of Ni/Poly(Py-co-O-Anis)/ZnO/CuO/AFA modified graphite electrode has been investigated for methanol and sodium sulphide electrooxidation by cyclic voltammetry, linear sweep voltammetry and chronoamperometric measurements. From electrocatalytic studies, it was found that the hybrid Ni/Poly(Py-co-O-Anis)/ZnO/CuO/AFA electrode shows superior catalytic activity compared with Ni/Poly(Py-co-O-Anis) catalyst. In addition, nanorods/nanosheets structure were obtained for hybrid composite through a simple room temperature reaction. In order to generate energy, the single stack test alkaline fuel cell has been carried out and results show the maximum power density of 103.24 and 44.75 mWcm^{-2} for methanol and Na_2S, respectively. From the overall results, it has been concluded that the prepared Ni/Poly(Py-co-O-Anis)/ZnO/CuO/AFA is a potent, non-precious and low cost catalyst with an improved catalytic activity in direct alkaline fuel cells.

Introduction

Developing potential anode catalysts and catalyst supporting matrices for application in direct alkaline methanol (DAMFC) and direct alkaline sulfide fuel cell (DASFC) are an open challenge for the researchers. At present, the oxidation of cheap, renewable and low molecular weight alcohols as well as an environmental pollutant like sulfide ions has received great attention due to their importance in commercialization aspects of DAMFC and DASFC [1–3]. In this aspect, non-precious metals along with organic-inorganic hybrid composites have been progressed as anode material to electro catalytically oxidize the methanol and sodium sulphide. The kinetics of methanol oxidation reaction is slow and incomplete on existing catalyst. Hence, developing a new catalyst is

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required to increase its oxidation efficacy and to undergo complete oxidation of alcohol fuels. Platinum based electrocatalysts have been employed as the anode material to oxidize methanol. However, the use of platinum was limited due to its high cost, and electrode poisoning as a result of CO formation. These reasons persuaded many researchers to develop novel catalysts towards fuel cell applications [4–6]. Innovative attempts have been made to prepare a cheaper and active catalyst, which is less prone to poison. In this regards, nickel metal has been found to be a good replacement for platinum in promoting oxidation of organic compounds in alkaline solution due to its less expense and more stable nature [7–9].

In addition, metal oxide based nanocomposites have shown enormous application in number of fields due to its good catalytic activity and strong interaction with the nickel nanoparticles. In this context, ZnO has been added as promoter to the supporting material due to its promising rich resource, diverse morphology, eco-friendliness and high theoretical capacity. ZnO also acts as conducting scaffolds to support electrochemically active material with effective electron flow channels. Along with zinc oxide semiconductor (ZnO), CuO also possess unique properties like low cost, nontoxic, ease of synthesis and chemical stability [10,11]. Generally, coupling of one semiconductor material (ZnO/CuO) with another semiconductor material (CuS, ZnS, SnO_2, Ag_2O, etc.) or supporting material (like CNT, conductive polymers, fly ash, graphene, Vulcan carbon, etc.) will improve the total surface area, conductivity, and kinetics of electron flow along with reduced band gap energy that favors enhanced catalytic activity. Therefore, coupling of CuO with ZnO semiconductor is expected to reduce the band gap energy and thereby it increases the conductivity of the resultant material with improved surface area, which can boost the catalytic activity by fast flow of electrons with reduced ohmicloss. Further, mixed metal oxides of CuO and ZnO based catalysts were found to be selective and active in some industrially important chemical process along with CO oxidation, ethanol synthesis by hydrogenation of CO/CO_2, the water gas shift reaction, etc. Hence, this combination is used to reform H_2 from alcohol in fuel cells. In this present work, mixed metal oxides like ZnO–CuO were immobilized on the support material to reduce the agglomeration, and to increase surface area. It is then further modified with conductive copolymer to get improved conductivity, porous structures and more anchoring sites for metal deposition with improved electron flow by shortening the electron path ways [12–24].

Recently, oxidation of low molecular weight alcohol fuels using non-precious metal deposited hybrid materials [22,25,26] has received more attention owing to its commercialization aspects. Although CNT, graphene, graphene oxides, zeolites, etc., are used as supporting materials for catalyst particles [27–36], expensive and complicated synthetic procedures, restrict their usage for commercialization. According to our previous reports [12–14], fly ash waste residue obtained from thermal electric power station during the coal combustion process, which is an alumino-silicate rich byproduct was used as substrate material for the preparation of semiconductor materials for catalysis applications [37–40]. The addition of fly ash along with the metal oxide doped conducting polymer increase the electrocatalytic activity of the prepared composite due to its enhanced electrical conductivity [25,41] and improved surface area. Further, the direct methanol oxidation fuel cell has limitation in acidic medium because of its low stability, more corrosive nature and high cost of the membranes. In addition to that the sodium sulphide is commonly used as source in processing techniques for many leather industries to transform animal hide into leather. Hence, there is a possible risk of producing poisonous H_2S while mixing sulphide ions with acid wastewater or diluting it. So, the present work is attempted to remove the sulphide ions from the environment along with the generation of energy.

From the above point of view, the present study is focused on to develop a fresh and advanced material as support for nickel nanoparticles. The support material composed of mixed ZnO/CuO metal oxide immobilized on amine functionalized fly ash coated conductive poly(Py-co-O-Anis) co-polymer composite (Ni/Poly(Py-co-O-Anis)/ZnO/CuO/AFA). The catalytic performance of the Ni/Poly(Py-co-O-Anis)/ZnO/CuO/AFA catalyst was checked for 0.5 M alcohol and 0.5 M sulphide ions in alkaline medium. Further, nickel nanoparticles anchored on Poly(Py-co-O-Anis)/ZnO/CuO/AFA substrate shows enhanced activity in catalysis due to its porous bucky ball interconnected nanorod shaped morphology and high electrical conductivity than that of the Ni/Poly(Py-co-O-Anis) catalyst. In addition, the use of fly ash, bio-fuel, Na_2S and nickel reduce the overall fuel cell cost. Moreover, the processes involved here also easy, renewable, eco-friendly and waste management along with improved catalytic performance.

Materials and methods

Chemicals and reagents

Analyticalgrade nickel(II) chloride hexahydrate ($NiCl_2.6H_2O$), $Zn(CH_3CO_2)_2$, NaOH, $Cu(NO_3)_2.3H_2O$, toluene, methanol, pyrrole, *ortho*-anisidine, sodium borohydride ($NaBH_4$), and ammonium persulphate were purchased from SRL India. 3-aminopropyltriethoxysilane (APTES) was purchased from Sigma–Aldrich, India. Nafion was purchased from Alfa Aesar, India. Aqueous solutions were prepared with Milli-Q water (18.2 MΩ cm) and fly ash was obtained from thermal power station located at Neyveli, Tamil Nadu, India. In addition, Ni/Poly(Py-co-O-Anis)/ZnO/CuO/AFA catalyst was prepared according to the following Scheme 1. The detail step wise preparation methods were given in the forth coming sections.

Preparation of amine functionalised fly ash material (AFA)

The obtained coal fly ash particles were heated in a furnace at 600 °C for about 2 hrs to remove the dust particles. Then, the fly ash particles (4 gm) were mixed with 100 ml of 1.0 mol hydrochloric acid solution and the reaction mixture was stirred at 80 °C for 3 hrs to remove iron particle and to activate its surface hydroxyl group. The acid activated fly ash particles were washed with water until it becomes neutral and dried for the further use.

After acid activation, fly ash particles were surface functionalized with 3-aminopropyltriethoxysilane (APTES).

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