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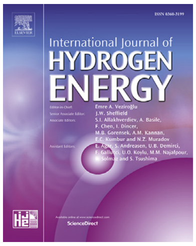

Polyrhodanine/$NiFe_2$ O_4 nanocomposite: A novel electrocatalyst for hydrazine oxidation reaction

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ABSTRACT

This study reports a facile fabrication of magnetic polyrhodanine/nickel-ferrite (PR/$NiFe_2O_4$) nanoparticles as a novel electrocatalyst for oxidation of hydrazine. Several technique were utilized to indicate the properties of the synthesized nanocomposite including the X-ray diffractometry (XRD), scanning electron microscopy (SEM), and fourier transform infrared spectroscopy (FT-IR). The electrocatalytic activity of the PR/$NiFe_2O_4$ modified carbon paste electrode was examined for hydrazine oxidation in alkaline solution by cyclic voltametry (CV) and chronoamperometry (ChA) methods. According to the obtained results, the modified electrode showed a suitable catalytic activity for hydrazine electro-oxidation at lower overpotential and a significant high response for hydrazine oxidation. Moreover, the findings indicate that the reaction follows a Cottrell in behaviour during CA experimentand the diffusion coefficient of hydrazine is determined to be 3.56×10^{-9} cm^2 s^{-1}.

Introduction

Fuel cells are seen by many researchers as key solution in the current century for application in the energy source, which is clean and renewable [1–3]. Accordingly, there has been a great number of studies working on direct liquid fuel cells such as direct alcohol fuel cells [4–6], direct formic acid fuel cells [7], direct dimethylether fuel cells [8,9], and direct hydrazine fuel cells [10–13]. Hydrazine is the simplest inorganic compound which is famous for having a high reactive base, and a reducing agent through losing electrons. These features made hydrazine an ideal substance for usage in fuel cells, catalysts, blowing agents, corrosion inhibitors, antioxidants, pharmaceutical ingredients, pesticides and insecticide, plant regulators for intercellular communications, and the materials used in photography [14,15]. Furthermore, the excessive energy stored inside the hydrazine can be used in the explosives [16].

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Some other characteristics of hydrazine sch as nonexplosive and less toxic in dilute solution make it a appropriate candidate for application in direct hydrazine fuel cells [17]. When hydrazine is utilized as the fuel, it is referred as direct hydrazine fuel cell (DHFC), which produces the gas and liquid without any toxic intermediates that are detrimental to electrocatalysts, compared with the conventional fuel cells [18].

The electrocatalytic oxidation of hydrazine have been widely studied by electrochemists at many electrodes such as platinum (Pt) [19], gold (Au) [20], nickel (Ni) [21], palladium (Pd) [22], silver (Ag) [23], cobalt (Co) [24,25] and carbon materials [26]. The electrode materials are essential towards hydrazine electro-oxidation [27]. Due to the high cost of Pt, Au and Ag, using of these metals as the anode in DHFCs is not practical.

Ni is an earth-abundant first row transitional metal with corrosion-resistance and ductility [28]. Ni and its oxide were discovered to exhibit high catalytic activity towards oxygen evolution reaction in alkaline media [29–31]. Nickel-ferrite ($NiFe_2O_4$) is apliable spinel compound as one of the few ferromagnetic materials with high electrochemical stability. The term spinel is generally applied for composition with the formula of MFe_2O_4 ($M = Ni$, Co, Mn, Zn, etc.). Considering the conducting nature of $NiFe_2O_4$ for its electronic function, it is anticipated to be used as an electrocatalyst [32]. Based on the previous findings, $NiFe_2O_4$ exhibits good electrochemical stability, therefore it can be used as a material for hybrid supercapacitors, Li ion batteries, and electrocatalysts [33]. The new trend in the related research is based on improving the electrocatalytic activity for hydrazine oxidation while Ni based ternary alloy is present. Furthermore, the modified electrode with lower cost and high activity for hydrazine oxidation have been explored [34–37].

The conducting polymer (CP) have been subject of many studies focusing on polymer for their function in technological fields. Several advances have been reported for the use of prepared polymer on the surface of different metals for application in electrochromic devices, electrocatalysis, biosensors, and rechargeable batteries [38]. It was reported that, rhodanine and its derivatives have features such as being antibacterial [39], antidiabetic [40], anticonvulsant and antiviral [41,42]. Three types of electronegative atoms were reported for rhodanine molecules namely nitrogen, sulfur and oxygen as the main part of its functionality. This functional group in polyrhodanine (PR), prepare the good active site for metal, where the electron-accepting ability of nitrogen species enhanced the catalytic activity, stability and durability of electrocatalysts [43]. The current study reports investigation of the PR/$NiFe_2O_4$ modified carbon paste electrodes for the electrocatalytic oxidation of hydrazine in alkaline media.

Experimental methods

Reagent

Iron (III) nitrate hexahydrate (purity > 99%), nickel nitrate (purity > 99%), rhodanine (97%), citric acid, sodium hydroxide (NaOH) that all obtained from Merck, Germany. Potassium permanganate ($KMnO_4$) (99%) was purchased from Chadwell Heath Essex England. Distilled water was the main tool for preparation of entire aqueous solutions.

Synthesis of the PR/$NiFe_2O_4$ nanocomposite

Polyrhodanine nanoparticles were synthesized by the chemical oxidative polymerization method [44]. $NiFe_2O_4$ nanoparticles were also prepared according to the procedures described in the literature [45].

For preparation of PR/$NiFe_2O_4$ nanocomposite, 0.15 g of rhodanine monomer was added to 50 mL of deionized water and was stirred. The mixture was heated slowly until rhodanine monomers completely dissolve (usually occurs between 60 and 70 °C). 0.15 g $NiFe_2O_4$ was sonicated in 20 mL deionized water for 30 min. The prepared solution was added to the solution containing rhodanine. Then, the oxidant solution consisting of 0.4 g KMnO4 dissolved in 30 mL deionized water was added drop wise. The in-situ-oxidative polymerization of rhodanine with $NiFe_2O_4$ was carried out at room temperature for 20 h under constant stirring on a magnetic stirrer. The product was washed thoroughly with deionized water several times to remove the traces of reactants and polyrhodanine oligomers. Finally, after washing the product thoroughly with deionized water several times to remove the traces of reactants and polyrhodanine oligomers, the prepared nanocomposites was dried in an oven at 50 °C for 24 h.

Electrochemical measurements

Cyclic voltametry (CV) and chronoamperometry (ChA) were used to evaluate the electrochemical properties of the samples in a standard three-electrode cell by PSGSTAT-204 Autolab (Metrohm, the Netherlands) electrochemical workstation at 21 °C. A carbon paste electrode (4.6 mm in diameter) was used as the working electrode. A Pt wire was used as the counter electrode and an Ag/AgCl (3 M KCl) electrode was used as the reference electrode. Hydrazine electro-oxidation activity was studied by CV measurements from 0 to 1.5 V with the identical scan rate in a solution of hydrazine (0.05) and KOH (0.1 M). On the other side, ChA was evaluated in the same solution at 0.90 V for 2000 s.

Electrode preparation

To obtain the modified carbon paste electrodes, the graphite powder was combined with PR/$NiFe_2O_4$ powder and paraffin oil with ingradient of 66.6, 7.4, 26 (w/w%), respectively. The prepared paste was packed into one side of a glass tube (6 mm o.d, 4.6 mm i.d. and 120 mm in length) in that there was anelectrical contact with a copper rod going through the electrode body. To obtain the working surfaces again, a butter paper was used to polish the electrode surface.

Characterization

Fourier transform infrared spectra (FT-IR) was used for the structural characterization of PR/$NiFe_2O_4$ using a shimadzu 4100 (Shimadzu, Kyoto, Japan). To obtain FT-IR, the PR/$NiFe_2O_4$ powder was combined with KBr and then tablet was

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