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Electrocatalytic hydrogen evolution reaction on carbon paste electrode modified with Ni ferrite nanoparticles

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HIGHLIGHTS

- Ni-ferrite NPs were successfully prepared and evaluated as the HER electrocatalyst.
- The catalytic performance of the ferrite depends upon the Ni substitution level.
- Ni-ferrite NPs MCPE had good stability for the HER.

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ABSTRACT

Nanoparticles of mixed oxides of Fe and Ni are prepared by a low temperature coprecipitation method. The effects of Ni content in synthesized nanoparticles on the electrocatalysts performance for hydrogen evolution reaction are investigated by electrochemical techniques. Scanning electron microscopy and X-ray diffraction spectroscopy are used for studying the morphology and structure of Ni-ferrite nanoparticles (NPs). Electrocatalytic activity of Ni-ferrite NPs for hydrogen evolution reaction is found to increase in the order of $Fe_3O_4 \leqslant Ni_{0.6}Fe_{2.4}O_4 < Ni_{0.2}Fe_{2.8}O_4 \leqslant Ni_{0.8}Fe_{2.8}O_4 < Ni_{0.4}Fe_{2.6}O_4$. The Tafel slopes for the hydrogen evolution reaction are found to be between 97.75 mV dec^{-1} and 122.19 mV dec^{-1} on carbon paste electrodes modified with ferrite NPs and kinetic parameters show that the Volmer step must control the hydrogen evolution reaction. The electrodes are resistive to passivation and they can be renewed easily.

1. Introduction

Hydrogen, as a high-quality clean and renewable energy resource, is increasingly considered as one of the most promising candidates for the fuel of the future [1,2].

There are several methods for hydrogen production; via electrolysis of water, splitting of water by light (photolysis), reforming gas from biomass, and natural gas or any other fossil fuel. Electrochemical water splitting using renewable energy sources such as solar energy has attracted the attention of researchers working on the production of hydrogen [3,4].

Water electrolysis, so far is the simplest method developed to produce high quantities of hydrogen. Nevertheless, this method is too expensive and consumes too much energy, which is directly proportional to the cell voltage used to perform the electrolysis. Therefore, considerable research efforts have been conducted to enhance the electrocatalytic activity of electrodes to reduce the overpotentials for the hydrogen evolution reaction (HER) [5–7]. The most common cathode material for hydrogen evolution in the electrolysis is platinum due to its high electroactivity. Nonetheless, high price and limited source of Pt are other serious barriers for wider use of water electrolysis [8]. Other metallic electrodes are commonly employed for water electrolysis but they are suffering from corrosion effects and consequently having a short life time.

Carbon electrodes are widely used in electrochemistry [9–12]. Contrary to metallic electrodes these electrodes are resistant to corrosion and relatively have a long life time. However the overpotential of HER is high at carbon electrodes. Therefore, considerable research efforts have been made in developing the electrocatalysts for HER that are highly active, stable and inexpensive.

Nowadays, Spinel ferrite $M_xFe_{3-x}O_4$ (M = Ni, Co, Mn, Zn, etc.) nanoparticles have attracted great interests because of their peculiar properties and various important applications. Ferrite (Fe_3O_4) and specially Ni-ferrites ($Ni_xFe_{3-x}O_4$) have been investigated as catalyst for sulfuric acid decomposition [13,14], selective oxidation of CO [15] and thermochemical water splitting [16–18]. To the best of our knowledge, electrocatalytic activity of ferrite and Ni-ferrites for HER are not reported in the literature. In this paper, nanosized $Ni_xFe_{3-x}O_4$ are investigated as electrocatalysts for modifying

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carbon electrode for electrochemical production of hydrogen from water. Carbon paste electrodes (CPE) are homogeneously modified with $Ni_xFe_{3-x}O_4$ nanoparicles (Ni-ferrite NPs) and used for electrocatalytic proton reduction in acidic solution.

The influence of doping of Fe_3O_4 nanoparticles with Ni on its electrocatalytic performance for the HER was examined. The catalytic behaviours of the Ni-substituted Fe_3O_4 nanoparticles modified electrodes were studied by employing electrochemical techniques.

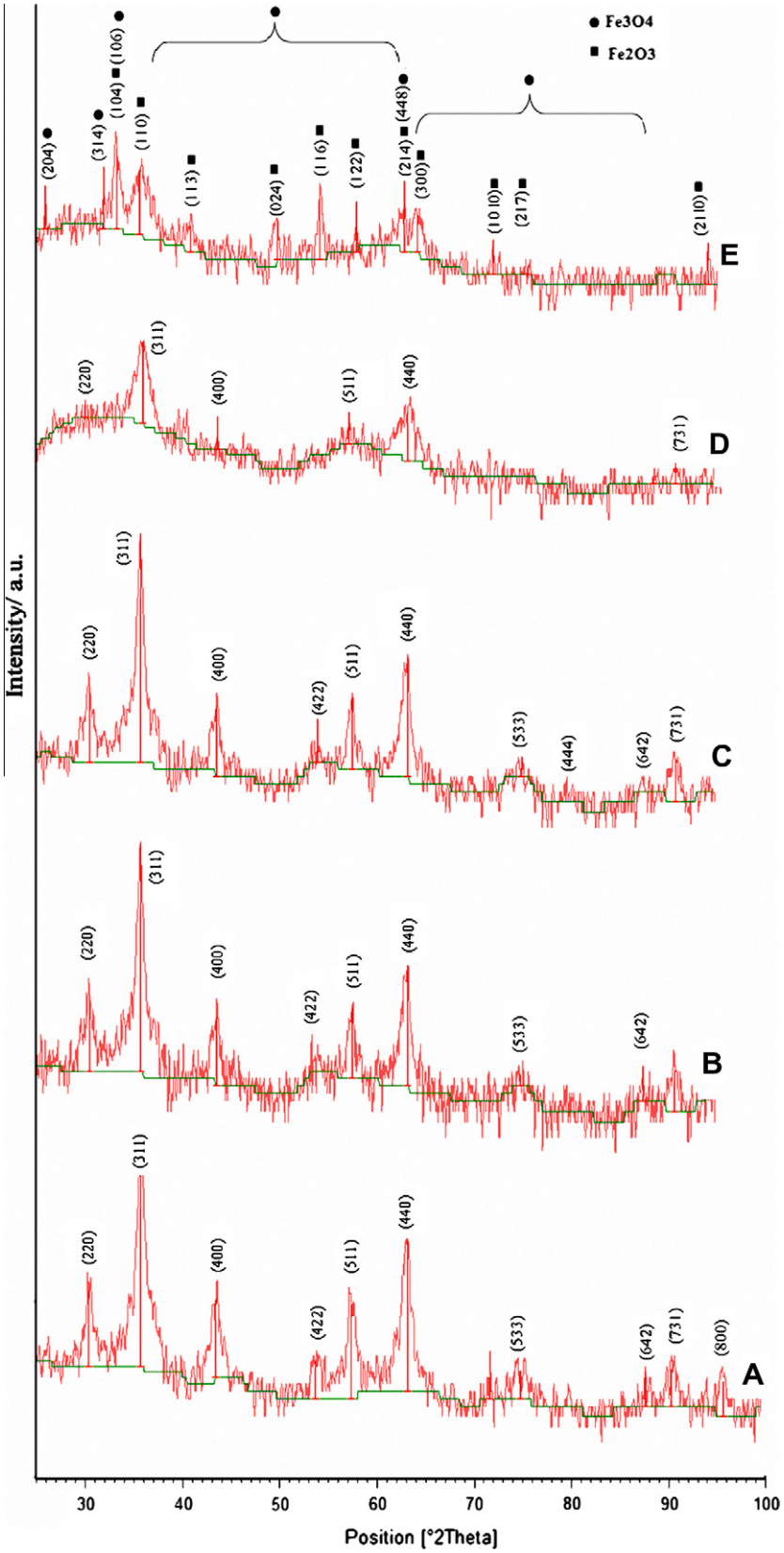

Fig. 1. Powder X-ray diffraction spectra (XRD) of $Ni_xFe_{3-x}O_4$ NPs. (A) $Ni_{0.8}Fe_{2.8}O_4$ (B) $Ni_{0.6}Fe_{2.4}O_4$ (C) $Ni_{0.4}Fe_{2.6}O_4$ (D) $Ni_{0.2}Fe_{2.8}O_4$ (E) Fe3O4.