INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2016) 1–15

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he

Electrocatalytic oxidation of ethanol using modified nickel phosphate nanoparticles and multi-walled carbon nanotubes paste electrode in alkaline media for fuel cell

Seyed Karim Hassaninejad-Darzi*, Mojtaba Gholami-Esfidvajani

Research Laboratory of Analytical & Organic Chemistry, Department of Chemistry, Faculty of Science, Babol University of Technology, P.O. Box: 47148-71167, Babol, Iran

ARTICLE INFO

Article history:
Received 8 March 2016
Received in revised form
4 August 2016
Accepted 14 September 2016
Available online xxx

Keywords:
Nanoporous nickel phosphate
MWCNTs
Modified CPE
Ethanol electrooxidation
Fuel cells

ABSTRACT

In this study, nanoporous nickel phosphate molecular sieves was synthesized by conventional heating for 72 h in the presence of triethylamine as template and characterized by X-ray diffraction (XRD), FT-IR spectroscopy and Filed emission scanning electron microscopy (FESEM). FESEM technique showed the presence of rod-like nickel phosphates VSB-5 and nearly spherical particles with diameters between 30 and 80 nm. The carbon paste electrode (CPE) was modified by nanoporous nickel phosphate molecular sieves and multi-walled carbon nanotubes (MWCNTs) and then Ni^{2+} ions incorporated to this electrode to obtain Ni-MW–NP/CPE. Electrochemical techniques such as cyclic voltammetry (CV) and chronoamperometry as well as differential pulsed voltammetry (DPV) were applied in order to investigate the role of nickel phosphate molecular sieves and MWCNTs in the electrocatalytic oxidation of ethanol. The current intensity of ethanol oxidation increases impressively on the surface of Ni-MW–NP/CPE and in comparison with Ni-CPE, Ni-MW/CPE and Ni-NP/CPE that means the catalysts can reduce the overvoltage of ethanol oxidation. Some parameters such as potential scan rates and concentration of ethanol investigated to describe the mechanism of ethanol electrooxidation onto Ni-MW–NP/CPE. The values of electron transfer coefficient and mean value of catalytic rate constant for ethanol and redox sites of electrode were found to be 0.844 and 5.76×10^5 cm^3 mol^{-1} s^{-1}, respectively. The good catalytic activity, high sensitivity, good selectivity and stability and ease of preparation rendered the Ni-MW–NP/CPE to be a capable electrode for ethanol electrooxidation.

Introduction

The electrocatalytic oxidation of alcohols has received a significant amount of interest because of its applications toward energy conversion technologies such as the direct alcohols fuel cell [1–4]. Over the past decade, lots of investigations have been focused upon Pt and Pd-based materials, which were believed to be the best catalysts for low temperature fuel cells. Unfortunately, high cost and limited resource ultimately hinder them use at a commercial level [5]. Since 1970, nickel and nickel-based electrodes in alkaline media have been used for the oxidation of alcohols including methanol, ethanol and isopropanol [3–6]. Direct small organic molecule fuel cells have attracted extensive

* *Corresponding author*. Fax: +98 1132334203.
E-mail address: hassaninejad@nit.ac.ir (S.K. Hassaninejad-Darzi).

http://dx.doi.org/10.1016/j.ijhydene.2016.09.091
0360-3199/

attention for transportation power sources mainly due to their high efficiency, low environmental pollution and high energy density [6]. Generally, methanol is considered the most promising alternative fuel for electrochemical energy conversion [7]. It is known that methanol is a toxic and harmful chemical. Recently, ethanol was also found to be potentially one of the most appropriate fuels for fuel cells. In comparison, ethanol is less toxic, more environmentally friendly and can be easily created in large quantities by fermentation of sugar-containing raw materials [6]. The recent researches demonstrated that the anodic oxidation of ethanol in alkaline media becomes faster than acidic media, which makes it possible to use Pd and Pd-based catalysts as an alternative to Pt-based catalysts for the alcohol oxidation reaction [8–10].

Some materials have been tried for the electrooxidation of ethanol including Pt nanoparticles on carbon nanotubes [11], Pt-based electrode [12], $PdCl_2$/MWCNTs [13], Pt–Ni alloy nanoparticles electrode [14], Pd nanoparticles [15], Pd Nanoparticles/carbon black [16], Pd@Ni_xB/RGO nanocomposite [17], Ni–Nb–Pt–Fe modified carbon paste electrodes [18], Pd-phosphorus nanoparticles on MWCNTs [19], Ni–Pd–Pt nanoparticles MWCNTs [20], Pd–Ni–Sn [21], Ni–Pd–Pt nanoclusters on graphene [22], Au decorated graphene/GCE [23], carbon-supported Pd–Au and Pd–Sn [24], Pt–Au–C electrode [25], PdNPs/SWCNT/carbon electrode [26], Pd–Pt/carbon nanotubes [27], carbon-supported Pt–Pd nanoparticles [28], Pt–Ru–Sn/C [29], Nafion-titanate nanotubes [30], $NiCo_2O_4$-MWCNT nanocomposite aerogels [31], nickel-boron amorphous alloy nanoparticles on nanoporous copper [32], carbon nanotubes–nickel nanoparticles [33], nickel nanoparticles/nafion/graphene [34], polycrystalline nickel electrode [1].

Carbon nanotubes (CNTs) are considered as a novel nano-sized material playing a vital role in the field of nanotechnology. They have captured the attention of researchers worldwide due to their unique nanostructures, remarkable electrical and mechanical properties [35,36]. One of the main potent properties of CNTs is that it can enhance the electron transfer between the electroactive species and the electrodes [37]. With the subtle electronic properties, the CNTs as an electrode material have been studied in detail and can be used in electrochemical sensing. The CNT electrodes display superior performance than other electrodes in terms of promoting electron-transfer and improving reversibility of electrochemical reaction [38]. In the recent years, multi-walled carbon nanotubes (MWCNTs) have received great attention as nanomaterials for the fabrication of electronic devices because of its surprising physical and electrical properties such as highly elastic modules, high tensile strength, good chemical stability, large surface-to-volume ratio and high thermal and electrical conductivity [39].

Research on porous material such as open-framework metal phosphate molecular sieves have attracted considerable attention for applications in catalysis, adsorption, separations, etc [40,41]. The structure of nanoporous nickel phosphates VSB-5 (Versailles Santa Barbara-5) contains a hexagonal array composing of 24-member-ring one dimensional uniform channels with the diameter of about 1.2 nm [42]. In view of the applicative potential of VSB-5 framework, successful modification of VSB-5 with transition metal ions could suggest potential material for application in the area of separation and catalysis. It can be noted that such substitution is reported to occur against Ni^{2+} ions of the VSB-5 framework [43].

It is important to develop a novel electrode that has high sensitivity and stability for the electrooxidation of ethanol [44]. It is mention that zeolites and molecular sieves have utilized for zeolite modified electrodes (ZMEs) and applied in electrocatalytic reaction [45]. Some works were focused to the application of nickel phosphates molecular sieves for the electrochemical oxidation of methanol in the alkaline solution [41,46,47]. With respect to literature survey, no nickel phosphate molecular sieve and MWCNTs were utilized for modification of carbon paste electrode towards electrocatalytic oxidation of ethanol. In the present work, hydrothermally synthesis of nanoporous nickel phosphate molecular sieve has been performed and characterized. Then, this molecular sieve and MWCNTs were used for modification of carbon paste electrode (CPE) and applied for electrocatalytic oxidation of ethanol in the alkaline medium using cyclic voltammetry (CV) and chronoamperometry techniques.

Experimental

Reagents and materials

All chemicals were analytical grade and used without any further purification. Sodium hydroxide, ethanol, $NiCl_2\cdot 6H_2O$, potassium hexacyanoferrate ($K_4Fe(CN)_6$) and potassium chloride were purchased from Merck company that were of analytical reagent grade. Ortho-phosphoric acid (85 wt.%), triethylamine (99 wt.%) and diethyl ether (99 wt.%) were purchased from Fluka, Samchun and Daejung companies, respectively. Graphite powder and paraffin oil ($d = 0.88\ g\ cm^{-3}$) as the binding agent (both from Daejung company) were used for preparing the pastes. Multi-walled carbon nanotubes (MWCNTs) more than 95 wt.% purity was purchased from Iranian nanomaterials pioneers company. Also, deionized water was used throughout the experiment.

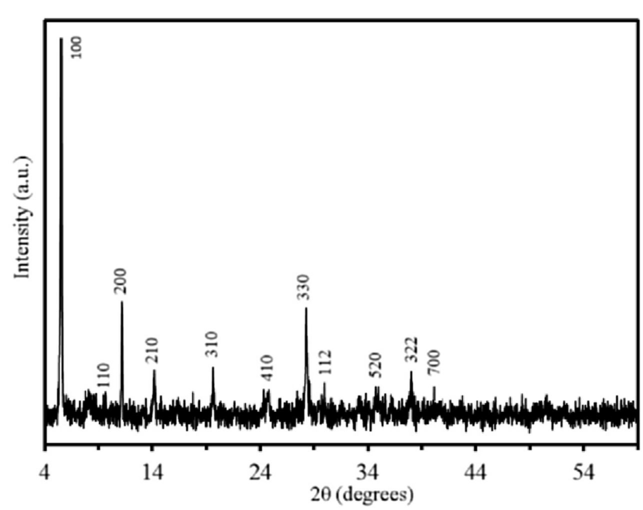

Fig. 1 – The representation XRD pattern of synthesized nanoporous nickel phosphate molecular sieve.

Please cite this article in press as: Hassaninejad-Darzi SK, Gholami-Esfidvajani M, Electrocatalytic oxidation of ethanol using modified nickel phosphate nanoparticles and multi-walled carbon nanotubes paste electrode in alkaline media for fuel cell, International Journal of Hydrogen Energy (2016), http://dx.doi.org/10.1016/j.ijhydene.2016.09.091