Chemical Engineering Journal 303 (2016) 167–181

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Nickel and nickel phosphide nanoparticles embedded in electrospun carbon fibers as favourable electrocatalysts for hydrogen evolution

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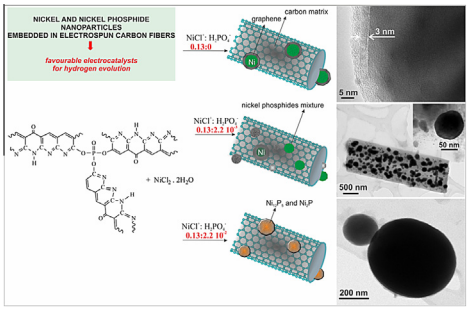
HIGHLIGHTS

- Nickel phosphide nanoparticles were incorporated into carbon fibers by electrospinning method.
- Designed composite fibers afford perspective electrocatalytic materials for hydrogen evolution.
- Defectless composite fibers were obtained by thermal treatment set according to TG/DSC analysis.
- Composite carbon fibers display the highest HER when designed in hydrogen atmosphere.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 22 March 2016
Received in revised form 23 May 2016
Accepted 31 May 2016
Available online 1 June 2016

Keywords:
Electrospinning
Fibers
Carbon fibers
Nanoparticles
Electrocatalysis

ABSTRACT

The needle-less electrospinning method is used for a preparation of carbon, carbon/nickel, carbon/nickel/nickel phosphides and carbon/nickel phosphides fibers of a continual length and a high specific surface area. The prepared fibers were produced in a large scale as a potential electrode material for electrocatalytic hydrogen evolution reaction (HER). The polyacrylonitrile (PAN) was used for a preparation of spun solution and subsequent precursor fibers formation. The phosphoric acid of 0.5 or 5 wt% was added to the spun solution in order to increase conductivity of the spun solution as well as to provide a source of phosphorus in the final fibers. The exactly defined temperature schedules of calcinations and atmosphere were suggested according to the results obtained from TG/DSC analysis. The phosphoric acid in the electrospun PAN precursor fibers is responsible for the cyclization and aromatization during stabilization of the electrospun precursor fibers. The XRD analysis confirmed the formation of phosphides at different molar ratio of $NiCl_2$:H_3PO_4. The final morphology, porosity and position of the incorporated nickel or nickel phosphides nanoparticles can be designed by the calcinations temperature and used atmosphere. A possible mechanism for a formation of nickel, nickel/nickel phosphide and nickel phosphide nanoparticles was suggested. The linear sweep voltammetry, impedance spectroscopy and Tafel slopes measured in 0.5 M H_2SO_4 solution confirmed that the highest HER activity exhibit carbon fibers containing the nickel and nickel phosphide nanoparticles after the heat treatment in the hydrogen reduction atmosphere.

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http://dx.doi.org/10.1016/j.cej.2016.05.147
1385-8947/

1. Introduction

The growing demand for energy and the depletion of primary fossil energy resources causes an increasing pressure on the use of alternative energy sources in larger scale. The environmental pollution due to the fossil energy resources represents another important aspect in favour of this effort. It is assumed that in the following decades the energy industry will enhance the usage of "green technologies" and try to loose its dependence on fossil fuels with the aim to avoid negative impacts on environmental assets and enhance the quality of life. Nowadays it is necessary to ensure sustainable development and fundamental change in the energy system [1]. One of the most perspective sources of energy is hydrogen fuel. The principal advantage of hydrogen is its easy availability and high calorific value (three times higher in comparison with petrol or diesel oil). A significant source of hydrogen is water and several organic compounds, but the simple, efficient and secure methods of hydrogen retrieval must be developed before it will become economically significant resource with the exceptional energy potential [2,3].

The electrolysis of water is the most promising technology for hydrogen production. However, the hydrogen production from the electrolysis of water is still at least three times more expensive than steam reforming [4]. The hydrogen evolution reaction (HER) acquired by the electrocatalytic reduction of water may provide a sustainable energy supply for the future, but this technique is currently limited due to a high price and resource scarcity of the used noble metals such as Pt. A lot of activities were therefore focused on the fabrication of electrodes enabling the effective and economically viable HER. The hydrogen production by HER is rather complicated, because it is manufactured on a relatively small scale what is the main limitation for an application in industrial processes. An improvement of electrode material plays the crucial role in developing of the cost effective HER, which will generate large cathodic current densities at low overpotentials. At present, the electrodes from noble metals are preferentially replaced with various cheaper electrode materials with a comparable efficiency such as MoB [5], Mo_2C [6], MoS_2 nanoparticles [7] and nanosheets [8], $MoSe_x$/Mo thin films [9], Ni/Mo nanorods [10], Mo-base composites such as multi-walled carbon nanotubes-Cu-MoS_2 [11], three-dimensional MoS_2/reduced graphene oxide [12] and Cu–MoS_2/reduced graphene oxide hybrides [13], CoP/MoS_2-CNTs hybrid catalyst [14]. The other promising class for electrocatalytic materials are Ni and Ni-based alloys, for example, Ni/NiO core/shell nanosheets [15] or NiS_2 [16], which display the current density approximately of 5 mA cm^{-2} at an overpotential of 110 mV. A lot of investigations on the influence of in-situ ionic activation using the combination of three different metals on HER mechanism and kinetics were performed [17–19]. Recently, it has been found that solid structures designed from monodispersed nickel phosphides (Ni_xP_y) exhibit superior catalytic activity due to the higher positive charge of Ni and stronger ensemble effect of P in Ni_xP_y structures [20–22]. Pan et al. have designed efficient, stable and inexpensive electrocatalysts for HER aimed at replacing Pt, which are either based on nickel phosphide nanoparticles decorating multiwall carbon nanotubes Ni_2P/CNT [23], nanostructured nickel phosphides on carbon nanospheres [24], the hybrid compounds composed of Ni_2P nanoparticles and N-doped reduced graphene oxide [25] or cobalt phosphide electrocatalysts including Co_2P, CoP, Co_2P/CNTs, CoP/CNTs, Co_2P/NCNTs or CoP/NCNTs [26] with superior electrocatalytic activity. Carbon nanotubes and fibers (CNFs) with diameters in the submicron and nanometer range exhibit high specific surface area, hierarchically porous structure, flexibility, thermal conductivity, excellent chemical resistance and high strength, which allow to use them as electrode materials or energy storage devices [27–31]. Moreover, it has been found that the combination of CNFs with nanoparticles facilitates the electrochemical process. Introducing of metallic nanoparticles to the carbonaceous fibers can improve power and energy density of the electrochemical capacitors [32,33].

One of the most suitable, cost-effective and versatile techniques for a preparation of carbonaceous fibers is electrospinning [34,35]. The most of researchers pay their attention to the study of the fibers formation from liquid polymer jet reservoir in a longitudinal electric field. However, the limitation of the mass yield from electrospinning process using the jet often does not comply requirement for today industrial-level production. Therefore, the free liquid surface technology was used in the present work as economically viable to produce fibers in a mass of industrial scale [36]. Unfortunately, the needle-less electrospinning also has unique characteristics like any other technology, which must be necessarily fulfilled in order to produce the high-quality and low-cost fibers.

The present work is focused on the process of preparation of the modified carbonaceous fibers via needle-less electrospinning method for the effective hydrogen generation. Ni or Ni/NiP nanoparticles were homogenously incorporated in the carbonaceous fiber matrix in-situ during the processing of fibers. The exactly defined thermal treatments and atmospheres for a preparation of individual types of the composite fibers will be thoroughly described. The relative concentration of H_3PO_4 in the spun solution basically influences formation and abundance probability of nickel and nickel phosphides nanoparticles incorporated in the carbon fiber matrix. The microstructure of fibers was investigated in detail depending on a composition of the spun solution, electrospinning process and thermal treatment steps. The structural characterization of the final composite fibers was visualized and evaluated by XRD, SEM and TEM analysis. The XPS analysis was performed for the chemical composition of individual prepared catalysts. The possible mechanism of nickel or nickel phosphides formation was suggested. The electrocatalytic activity of individual fibrous samples for HER was evaluated.

2. Experimental

2.1. Materials

Polyacrylonitrile (PAN, Aldrich, Mw = 150,000 g mol^{-1}), N,N-dimetylformamide (DMF, Acros Organic, 99.8%) and hexahydrate of nickel chloride $NiCl_2{\cdot}6H_2O$ (p.a. Central Chem) were used without further purification for a preparation of the solution used for the electrospinning. The initial molar ratio of $NiCl_2{\cdot}6H_2O$/DMF/PAN was set to 3/30/3. Two different molar ratios of $NiCl_2$:H_3PO_4 (H_3PO_4, Merck 85%) were used to set the molar amount of the phosphoric acid either to 2.2×10^{-3} mol or 2.2×10^{-2} mol, what is equivalent to 0.5 or 5 wt% of phosphoric acid in the spun solution. For a study of the electrocatalytic activity, 2.5 mg of the sample and 2.5 ml of DMF was ultrasonically irradiated for 6 h in order to deagglomerate and disperse fibrous material into the solution. Thereafter, 5 μl of the sample suspension was dried off on a surface of the paraffin impregnated graphite electrode (PIGE) at 60 °C for 10 min. This procedure was repeated 6 times. The prepared electrodes were partially activated in 0.5 mol/l H_2SO_4 by applying potential −500 mV for 5 min before each measurement of the catalytic activity.

2.2. Fibers preparation

Carbon fibers (C), carbon fibers with nickel (C/Ni) and carbon fibers with nickel and nickel phosphides nanoparticles (C/Ni/NiP)