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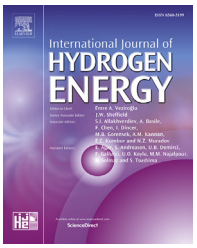

Fabrication of Mo-modified carbon felt as candidate substrate for electrolysis: Optimization of pH, current and metal amount☆

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ABSTRACT

Mo was electrochemically deposited over a carbon felt (C) support in order to enhance hydrogen evolution activity of the support and make it a candidate for further modifications. For this aim, the effects of pH of deposition bath solution, deposition current and amount of deposited Mo were studied and optimized. Hydrogen evolution activity of the electrodes was evaluated in 1 M KOH solution with the help of electrochemical techniques. Surface structures of the electrodes were examined by scanning electron microscopy (SEM). It was found that 1 g Mo/g C modified electrode at pH 6 and 50 mA current exhibits the best hydrogen releasing performance. The enhanced current density at this electrode under −1.60 V(Ag/AgCl) was 59.6% with respect to the bare support, which demonstrates that modifying the support by a thin Mo layer favors the hydrogen evolution reaction (HER) and reduces the energy requirement. The high hydrogen evolution performance of this modified substrate was assigned to its excellent structure, large surface area as well as high intrinsic catalytic activity of Mo. According to experimental findings, the Mo-modified C substrate was suggested for preparation of further modified electrode materials, especially with trace amounts of precious metals.

Introduction

The HER has been one of the most studied electrochemical processes since hydrogen gas is the cleanest and considered to be one of the most promising future green energy carriers for replacing petroleum fuels [1–4]. Hydrogen gas is produced using various production methods. Electrochemically splitting of water is one of the candidate methods among them since renewable hydrogen gas can be produced in large scale and high purity by industrial water electrolysis. Unfortunately, the cost of hydrogen gas produced by this technique is currently high due to the low electrode efficiency, high anodic and cathodic overpotentials and high energy requirement, which is directly proportional to the cell voltage applied to operate the electrolyzer [5–8]. In order to overcome these disadvantages, new and cheap electrodes with high electrochemical activity, large surface area, low hydrogen onset potential as well as good stability and corrosion resistance should be improved.

The electrocatalytic activity of electrodes toward the HER could be enhanced by enlarging electrochemically active real surface area of electrodes and/or increasing their intrinsic electrocatalytic activity [5,9–11]. The intrinsic

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activity depends on crystallite size, electronic properties and chemical nature of electrode materials. Pt group precious metals are promising for this aim. But, their usage is limited due to high cost and low abundance. Enlarged real surface areas are also very suitable as supporting material for deposition of platinum-group metals. The use of porous electrodes having large real surface area as a supporting material will reduce the loaded amount of precious metals to fabricate HER electrodes [5]. There are some ways to enlarge porosity/surface area of supporting materials. Fabrication of Raney-type electrodes, which were developed by Murray Raney [12,13], where a porous surface structure is obtained by a controlled leaching process of specific phases, e.g. $NiAl_3$ and Ni_2Al_3 [11] have been widely used for this aim [14–27].

Due to their unique properties, carbon nanomaterials, *i.e.* carbon nanotubes, carbon nanofibers, graphene [9,28–30] have been widely used as supporting materials for electrocatalysts to be used in electrolysis system. However, these materials are expensive. The C felt could be a candidate for fabrication of electrode materials since this material is cheap, heavy and has large spaces as well as relatively good physical stability. Although this material has such unique advantages, electrocatalytic activity of this support is not sufficient [31–33]. By comparing with pure C felt, Mo has promising hydrogen evolution performance [7,34–39]. Therefore, modification of the C felt by this metal may make it a candidate electroactive substrate. Deposition of trace amount of precious metal over the supporting material enhances catalytic activity of the electrode [31,33,40]. However, only active sites of precious metal deposits provide high performance, whereas remaining un-covered zones of carbon are still inactive. Therefore, before precious metal deposition, modifying carbon support by an active metal provides further activation of electrocatalysts [31–33,41,42].

In this study, the C felt support was modified by Mo and effects of some deposition parameters were optimized. Their hydrogen evolution activity was studied in 1 M KOH solution using electrochemical measurements. The main aim of the study was improving surface area and electroactive sites of the C felt and fabricating a suitable supporting material, *i.e.* to be used for deposition of expensive noble metals with trace amounts. In the next part of this study, the optimized substrate improved in this section will be reported for trace amount of Pd or MoPd binary deposits with various metal ratios and tested as cathode material in alkaline solution.

Materials and methods

Preparation of C supports

The C felt samples with 3 mm thickness and 5 mm × 10 mm dimensions were used as supporting material for Mo-modification. The average weight of the samples was 0.0139 g. After cutting with a lancet, the felt samples were washed with distilled water properly, exposed to distilled water for a certain time, dried in an oven at 105 °C for 1 h and stored in a desiccator before measurements. The C samples were connected to a stainless steel wire having 0.5 mm radius and used as working electrode.

Fabrication of Mo-modified C/Mo substrates

The cleaned C felt samples were modified by electrochemical deposition of Mo at room temperature to improve its electrochemical activity for the HER applications. Deposition bath solution consisted of 1.0 M $Na_2MoO_4{\cdot}2H_2O$ + 0.2 M $Na_3C_6H_5O_7{\cdot}2H_2O$. The bath solution with almost 80 mL volume was stirred with a magnetic stirrer during the deposition. The modification process was performed at room temperature. The deposition was performed galvanostatically with the help of a DC power supply. The average loaded amount of Mo over the C samples was calculated theoretically from deposition charge according to Faraday's laws taking into account the current efficiency was 100%. During the deposition, the C samples were used as working electrodes and a Pt electrode having 2 cm^2 total surface area was used as counter electrode in the electrolysis system.

Because surface structure as well as electrochemical activity of the deposits depends on preparation conditions, the effects of pH of deposition bath solution, deposition current and loaded amount of Mo were optimized. To do this, following procedures were followed:

(i) *Optimization of pH*: Initially, pH of the deposition bath was optimized. Fort his aim, pH was adjusted to 3, 4, 5, 6 and 7 using a concentrated (37%) HCl. In each case, a constant 10 mA current was applied to the electrolysis system until 1 g Mo/g C was theoretically deposited. The bath solution with the best pH (herein pH = 6) was used for further studies.
(ii) *Optimization of deposition current*: By using the deposition bath with the best pH, different currents (10, 50 and 100 mA) were applied to the electrolysis system until 1 g Mo/g C was theoretically deposited, and more suitable deposition current (herein 50 mA) was determined.
(iii) *Optimization of amount of deposited metal*: Finally, various amounts of Mo were deposited over the C samples at a constant pH (pH = 6) and current (I = 50 mA). After hydrogen activity tests, the amount of deposited Mo suitable for hydrogen production was determined.

After the deposition of Mo, the modified electrodes were sufficiently rinsed with distilled water in order to remove possible residues of bath chemicals and unattached particles, dried in an oven and stored in a desiccator before the measurements.

Characterization of deposits

The surfaces of Mo-modified substrates were examined using a SEM instrument (Jeol 6510). (We also attempt to perform X-Ray diffraction analysis. However we could not obtain related patterns most probably due to the structure of the C felt).

Electrochemical measurements

The hydrogen evolution performance of the modified substrates was tested in 1 M KOH solution at ~298 K. The test solutions were opened to atmosphere. For this aim, electrochemical impedance spectroscopy (EIS) and cathodic current-

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