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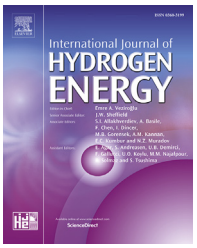

Efficient and stable electrocatalyst for hydrogen evolution reaction prepared by hybrid technique in surface engineering: Electrochemical and magnetron sputtering methods

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ABSTRACT

Developing low-cost, stable, and robust electrocatalysts is significant for high effective hydrogen evolution reaction (HER). In this work, a coating system with Cu_2O/NiMoCu on stainless steel (SS) is employed as a highly active and stable catalyst for HER in acidic solutions. Electrochemical measurements for as-designed system on SS show a low onset overpotential, small Tafel slope of ~32 mV/decade and long-term durability over 7 days of HER operation. To further inspections of electrocatalytic behavior of as-prepared system in HER, the EIS measurements are performed at several overpotentials and temperatures. It is found that high hydrogen evolution activity and stability of Cu_2O/NiMoCu hybrid is likely due to special morphology of Cu_2O which result in large number of active sites for hydrogen adsorption, and a synergetic effect giving electronic structure suitable for the HER.

Introduction

Since precious metal electrocatalysts such as platinum (Pt) and Pt-based nanomaterials suffer from the scarcity and high cost, there is tremendous endeavor to find an efficient, cheap and environmentally friendly catalysts for water-splitting systems [1–3]. The hydrogen evolution reaction (HER; $2H^+ + 2e = H_2$) at the cathode is one of two half-reactions occurred during the water splitting process [4,5] and discovering the efficient material with low overpotential and high current density for HER remains a key challenges in pursuit of researches [6,7]. Nickel–molybdenum, NiMo, based alloy is one of the cost-effective candidates as electrocatalysts for HER because of the Mo and Ni electronic structure mixture. Despite of extensively studies for Ni–Mo binary or ternary

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compounds, the improvement is rather limited compared to that of Pt based HER catalysts. To reduce the overpotential, extensive efforts have been made to develop the efficiency, employing metal–organic frameworks (MOFs) [8], changing in surface morphology [9,10] or electrode composition [11,12]. Although a number of HER studies have been done on NiMo based alloys, the majority of them have been performed in alkaline media [13].

In the HER, acidic electrolytes are more favorable than alkaline electrolytes because these units are more compact and could potentially run in reverse mode to produce electricity [14]. Moreover, there are enough H ions in the electrolyte to react on the electrode surface [1]. However, non-noble metal alloys such as Ni–Mo chemically corrode under acidic conditions, limiting the stability of these cathodes [15]. Considering the corrosive nature of the strongly acidic environment, major improvements in several areas, including lowering overpotentials, increasing catalyst durability, and using earth abundant elements, are needed [16–18].

In 1994, one of the earliest reports is related to characterization of electrodeposited NiMo alloys for HER in alkaline media [19]. Wang et al. [10] in 2015 reported that porous NiMo film prepared by one-step electrodeposition under super gravity field exhibited high catalytic activity for HER in alkaline media. Recently, a porous Ni–Mo alloy films with microsphere structure prepared by electrochemical method on copper foils [9]. The results show that the prepared alloy acts as a highly efficient and durable catalyst for both HER and oxygen evolution reaction (OER) in 1.0 M KOH.

So far, a few research groups reported on the electrochemistry of these or similar compounds in acidic media. A recent survey research on a NiMo nanostructures by Wang et al. [20] suggested that the biphasic nanocrystalline Ni–Mo–N catalyst synthesized by heat treatment method shows very low overpotential in both acid and alkaline electrolytes with 24 h stability.

The synthesis of NiMo based alloys usually involve preparation of alloys from metallurgy methods, physical-vapor deposition (PVD), or electrodeposition techniques. PVD techniques, such as thermal or electron-beam evaporation, magnetron sputtering, and pulsed-laser deposition, allow for precise control over the composition and thickness of the coatings, well control over chemical composition, and also good adhesion. Magnetron sputtering is one of the most popular PVD systems for the industrial-scale production of thin films [21,22].

Inspired by the above considerations, herein, electrochemical and magnetron sputtering methods have been used to prepare Cu_2O/NiMoCu catalysts on SS substrate.

Due to the unique combination of high corrosion resistance, excellent mechanical strength and low price [23], 316L SS has been selected as a substrate. Hierarchical flower-like structures of copper-oxide, Cu_2O, with large surface area for the nucleation of alloy catalyst, was synthesized by electrochemical method and following that NiMoCu was deposited by PVD. Our results demonstrated that high HER efficiency and excellent acid stability (at least 7days) were achieved.

Experimental details

Synthesis of Cu_2O hierarchical flower-like structures

All reagents used were purchased from the commercial sources and were used directly without further purification. Electrodeposition of Cu_2O hierarchical flower-like structures was carried out on 316L SS sheets via cathodic electrodeposition using Autolab PGSTAT30 Potentiostat/Galvanostat (Netherland Instruments). The electrochemical experiments were carried out in a conventional three-electrode cell consisted of Pt grid and saturated calomel electrode (SCE) as counter and reference electrodes, respectively. The working electrode was the SS substrate. Prior to each deposition, the SS samples were cleaned ultrasonically in ionized water and ethanol for 10 min, washed with ionized water, and finally dried. The linear sweep voltammogram was employed to deposit Cu_2O from electrolytic bath solution containing $[Cu(NO_3)] = 0.01$ M and 0.1 M NH_4NO_3. The potential sweep started at an open-circuit potential and was scanned cathodically to 1.5 V vs. SCE at a scan rate = 2 mV/s.

Deposition of NiMoCu coating by PVD

NiMoCu coatings on the SS substrates were prepared by a direct current (DC) magnetron sputtering method. Before loading the substrates into the vacuum chamber, they were ultrasonically cleaned in ethanol and distilled water, then dried in air, respectively. A base pressure of 1.0×10^{-3} Pa was attained by pumping down the sputtering chamber. Subsequently, the substrates were cleaned by Ar ion beam from two end-Hall ion guns. Highly pure (≥99.99%) source targets of Ni, Mo and Cu were used in the sputtering experiments. All the targets were also cleaned in situ with Ar for 15 min to remove the impurities by pre-sputtering them on the shutters.

During sputtering, the substrate holders were kept rotating to form homogeneous coatings. All the targets were simultaneously sputtered in Ar plasma atmosphere at a working pressure of 1.0×10^{-1} Pa. The Ar flow rate was set as 40 sccm.

Initially experiments demonstrated that as-prepared NiMoCu coating was easy to delaminate during the electrochemical tests. Therefore, to solve this problem, the deposition conditions have been changed. The Ni and Mo targets were sputtered at a constant power mode while the Cu target was sputtered at constant voltage mode. The detailed deposition parameters are presented in Table 1. Thickness of each

Table 1 – Process parameters for the deposition of NiMoCu electrode.

No.	Ar flow rate (sccm)	Operating pressure (Pa)	Power density ($W.cm^{-2}$) Ni	Mo	Cu	Thickness (nm)
1	40	1.0×10^{-1}	4.1	3.6	5.6	1316.9
2	40	1.0×10^{-1}	4.1	3.6	5.1	1093.2
3	40	1.0×10^{-1}	4.1	3.6	4.6	1691.3
4	40	1.0×10^{-1}	4.1	3.6	4.1	1455.4
5	40	1.0×10^{-1}	4.1	3.6	3.6	1596.1