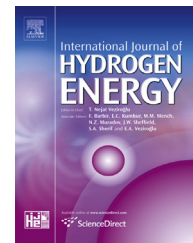




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Pt/Fe-NF electrode with high double-layer capacitance for efficient hydrogen evolution reaction in alkaline media

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ABSTRACT

The electrode with high catalytic activity, low hydrogen overpotential and low cost is desired for hydrogen evolution reaction (HER) via electrocatalytic water splitting. In this study, Pt/Fe-Ni foam (Pt/Fe-NF) electrode was synthesized via cathodic electrodeposition followed by impregnation deposition. Physical and electrochemical properties of Pt/Fe-NF, NF and Pt/NF electrodes were characterized by various techniques. The Pt/Fe-NF electrode exhibited better electrochemical activity for HER under alkaline condition than those of Pt/NF and NF electrodes, owing to the introduction of zero valences Pt and Fe onto the NF, and synergetic effect resulted from the formation of Fe-Ni alloy. Furthermore, Pt/Fe-NF electrode showed extremely high double-layer capacitance (69.1 mFcm^{-2}), suggesting high active sites for the Pt/Fe-NF. Tafel slope of Pt/Fe-NF was 59.9 mV dec^{-1} , indicating that the Volmer-Heyrovsky HER mechanism was the rate-limiting step. The Pt/Fe-NF electrode with great electrocatalytic activity is a promising electro-catalyst for industrial hydrogen production from alkaline electrolyte.

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Introduction

Hydrogen, as a renewable and clean fuel, represents one of the most promising new energy sources [1,2]. Water electrolysis is an important method for the production of highly pure hydrogen [3]. At present, the most commonly used catalyst for HER is platinum (Pt), since it has high catalytic activity and very low over-potential for HER [4,5]. However, as a noble metal, its depletion and high cost hinders its practical application. Hence, efficient alternatives or reducing the usage of Pt are of great importance. It was found that the

earth-abundant metals or their compounds, such as Ni, Co, Fe, Mo, Mo-P and Mo_2C , could be used as electro-catalysts [4,6–8]. Among these materials, Ni and its alloys, for example, Ni-Fe, Ni-Cu, Ni-Mo, Ni-Zn, and Ni-Co-Zn [9–12] have exhibited high chemical stability and excellent catalytic properties towards HER. It has been demonstrated that the effective catalytic activity of some transition-metals (such as Fe, Ni) for HER could be attributed to Brewer-Engel valence bond theory [13]. That is, whenever metals of the left half of the transition series in the periodic table with empty or less-filled d-orbitals are alloyed with metals of the

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right half of the series with more filled d-bands, a maximum in bond strength and stability of the intermetallic alloy phases is expected, and there is a well-pronounced synergism in the electrocatalysis, resulting in good electron-transport properties as well as the efficient absorption and desorption of hydrogen in the process of hydrogen evolution [13]. In other words, the composite catalyst forms the synergetic effect, which is advantageous to HER. Therefore, transition-metals are promising materials for HER.

Despite of the HER catalysts, conductive supporting are also essential in electrochemical systems. The supporting material is a crucial factor in determining the particle size and distribution of the metal particles located on its surface, which has a great influence on the amount of active sites, catalytic performance and stability of the supported catalyst [14,15]. The reported supporting materials include multi-walled carbon nanotubes [16], reduced graphene oxide [17], glassy carbon [18], stainless steels [19], and NF [20] and so on. Among these conductive substrates, NF is an ideal cathode substrate since it possesses good electrical conductivity, high specific surface area, uniform pores, high H₂ uptake capacity and good mechanical strength [21–25].

The electrodes are usually prepared by loading the catalysts onto the supporting materials, for instance, Pt/Ni [26] and Cu-Pt/NPCC [27]. However, preparation of the advanced Pt/Ni electrode not only required a large amount of Pt but also fairly long reaction time [26]. Introduction of Cu into the catalyst could substantially reduce the amount of Pt; whereas, the standard potential of Cu (0.337 V vs. NHE) was relatively high, resulting in high hydrogen evolution overpotential and impeding HER on the electrode surface. Thus, the transition metal with lower standard potential would be more satisfied as doping material. As mentioned above, Fe, which has been used as electro-catalyst material, has a low standard potential of –0.440 V vs. NHE; furthermore, the less-filled 3d-orbitals of Fe (the electronic track arrangement of 3d⁶4s²) would be paired with the 1s hydrogen atom to form Fe-H during HER. Meanwhile, as it is well known that the M–H bond energy (where M represents various metal elements) exhibits a ‘volcano’-shaped curve on heterogeneous catalysis [28]. Hydrogen adsorption energy that is too high would prevent the release of H₂ at the surface of catalyst. In contrast, hydrogen adsorption energy that is too low would result in slow electron-transfer rates. According to the ‘volcano’-shaped curve, the Fe-H bond energy is moderate [28], which is favorable to HER. Hence, it is hypothesized that the combination of Pt, Fe and NF could be a promising cathode material for HER.

Herein, in this report, we attempted to synthesize Pt/Fe-NF electrode using the electrodeposition technique and impregnation deposition method. The Pt/Fe-NF electrode was expected to have the following superiorities: (a) catalytic activity could be enhanced since both efficient Pt with low overpotential and promising transition-metal Fe were loaded onto the 3D porous, dendritic structured NF; (b) the addition of Fe is beneficial to the Pt loading on NF electrode; (c) the original usage amount of Pt could be significantly reduced as composite material was prepared, which decreased the overall cost of the electrode for HER. The performance of the as-prepared electrodes were determined in terms of onset

potential, double-layer capacitance, charge-transfer resistance, Tafel slopes and stability, and so on.

Experimental

Reagents and materials

Chloroplatinic acid (H₂PtCl₆), Na₂SO₄ and ethanol (C₂H₅OH) were purchased from Guangzhou Jinhua Chemical Reagent Co. Ltd. (Guangzhou, China); NaBH₄, H₂SO₄, KOH, and FeSO₄·7H₂O were purchased from Shantou Xilong Chemical Factory (Shantou, China); Hexadecyl trimethyl ammonium bromide (CTAB) were purchased from Aladdin Ltd; NF (pores per linear inch: 120 ppi, apparent density: 0.1–0.8 g cm⁻³, void volume of the alloy: 60%–98%) were purchased from Suzhou Jialongde Foam Metals Co. Ltd. (Suzhou, China). All chemicals were of analytical grade and directly used without further purification. The Ultra-pure water (18.25 MΩ cm) was used for solution preparation.

Preparation of Pt/Fe-NF electrode

Pt/Fe-NF electrode was prepared by a two-step procedure, including: (a) cathodic electrodeposition preparation of Fe deposited NF (Fe/NF) electrode, (b) impregnation deposition preparation of Pt/Fe-NF electrode.

- (a) Cathodic electrodeposition. Fe/NF electrode was synthesized using the electrodeposition technique [29]. This method could not only remove the use of polymer binders but also result in smoother surface and better nanoparticles dispersion on the electrode [29,30]. Briefly, prior to the electrodeposition, NF electrode (5.0 cm × 3.0 cm × 0.17 cm) was firstly steeped with H₂SO₄ (1 M) for 5 min to the remove surface native oxides; then, NF electrode was washed respectively with C₂H₅OH and Ultra-pure water for 15 min under ultrasonic condition to remove the surface impurities. After that, the pretreated NF electrode was used as the cathode and graphite (5.0 cm × 3.0 cm × 0.4 cm) electrode was served as the anode, and the electrodeposition was carried out for 30 min under a constant current of 10 mA condition, and with a solution of 15 mM FeSO₄·7H₂O, 10 mM Na₂SO₄ and 1 mM CTAB as the electrodeposition electrolyte. The addition of Na₂SO₄ was to improve the conductivity of the solution, while adding CTAB was to reduce the agglomeration of nanoparticles [31]. Then, the Fe/NF electrode was obtained. Fe was deposited on the surface of NF electrode according to Eq (1).



- (b) Impregnation deposition. The as-prepared Fe/NF electrode was submerged in 50 mL of 0.6 mM aqueous H₂PtCl₆ solution in a beaker and stirred with 120 r min⁻¹ for 4 h at 30 °C. After soaking for 4 h in the Pt salt solution, the electrode was then soaking in 10 mL of 0.918 M NaBH₄ solution (initial pH was adjusted to 12

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