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Electrodeposited Ni-P alloy thin films for alkaline water splitting reaction

Liju Elias¹, Vinayaka H. Damle² and A. Chitharanjan Hegde^{1*}

¹Electrochemistry Research Lab, Department of Chemistry

²Department of Metallurgical and Materials Engineering
National Institute of Technology Karnataka, Surathkal
Srinivasnagar- 575 025, India

*acrhegde@gmail.com

Abstract. Ni-P alloy thin films was developed as a robust electrode material for alkaline water splitting for hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), through electrodeposition technique. The influence of alloy composition, achieved through induced codeposition of the reluctant non-metal, i.e. phosphorous (P) on its electrocatalytic activity was studied, and arrived at the best composition of alloy for HER and OER. The water splitting efficacy of the alloy films was tested in 1.0 M KOH using electrochemical methods such as cyclic voltammetry and chronopotentiometry. The experimental observation shows that the alloy thin film with 9.0 wt. % of P and 4.2 wt. % of P are the best electrode materials for HER and OER, respectively. The electrocatalytic performance of alloy films towards HER and OER were related to its surface topography, composition and crystal structure through field emission scanning electron microscopy (FESEM), energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD) analyses, respectively.

Keywords: Electrodeposition; Ni-P alloy; water splitting reaction; SEM; XRD

1. Introduction

Hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) are the most frequently investigated reactions because of the importance of water splitting reaction for the future clean energy source [1]. Water electrolysis industry is mainly focusing on improving the efficiency of HER and OER to overcome the limitations due to overvoltage, leading to high energy consumption [2]. To a certain extent, this could be improved by the proper selection of electrode materials with electrocatalytic activity [3,4]. This challenge in developing a good electrode material with high catalytic activity and low cost for future clean energy source making it as a research area of great interest. Apart from the noble metals, Nickel is more electrocatalytically active and hence much research works have already been reported on Ni-based electrode materials [1-3]. From the literature, it is clear that the electrocatalytic efficiency of Ni can be enhanced either by proper alloying with transition metal elements or by incorporating some foreign nanomaterials into the metal matrix [3-7]. Alloying Ni with transition metal can modify the overall electrode kinetics and therefore change the activation energy of HER and OER [2,4]. The effect of alloying on electrode activity very much depends on composition, structure, morphology etc. [5-7]. In this regards, electrodeposition is an efficient method for developing alloys or composites with excellent properties and low cost [8,9]. Moreover, the physical and chemical nature of the alloy electrodes and thereby the electrocatalytic activity towards HER and OER can be controlled by proper



selection of alloying metals and the operating conditions for electrodeposition [3-7]. Another important factor related to electrocatalytic efficiency is the stability of the electrode materials under working conditions in terms of corrosion. Most of the electrocatalytically active materials may not have the preferred stability in terms of corrosion resistance in practice [5-7]. This is another serious problem which makes the industrialization of electrocatalytic water splitting technology for hydrogen production far from reality [1,4,7]. Thus, in the present study, we are intended to develop a corrosion resistant and electrocatalytically active Ni-P alloy electrodes for alkaline water splitting reaction.

2. Experimental

2.1 Electrodeposition of Ni-P alloy thin films

Ni-P alloy thin films were electrodeposited on copper substrate from a Hull cell optimized bath with glycerol as an additive. All the chemicals used in the present study are of analytical grade and were sourced from Merck Mumbai. The electrolyte for plating was prepared using double distilled water and contains $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (28.2 g L^{-1}), $\text{NaPO}_2\text{H}_2 \cdot \text{H}_2\text{O}$ (51.0 g L^{-1}), $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ (56.2 g L^{-1}), H_3BO_3 (10.2 g L^{-1}), NH_4Cl (20.5 g L^{-1}) and $\text{C}_3\text{H}_8\text{O}_3$ (20.0 mL L^{-1}). The optimal deposition conditions within a c.d. range of 1.0 to 6.0 A dm^{-2} at room temperature was arrived using conventional Hull cell method [6]. The pH of the plating bath was maintained at 8.0 to ensure the stability and complete solubility of the constituents. The alloy thin films were developed on a pre-cleaned copper substrate using Ni as an anode. The duration for all the plating process was kept constant for comparison purpose. The obtained alloy films were characterized using field emission scanning electron microscopy (FESEM), energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD) analyzes.

2.2 Electrochemical Characterization

The electrocatalytic activity of the developed alloy films (test electrodes) towards alkaline HER and OER was studied in 1.0 M KOH medium, using cyclic voltammetry (CV) and chronopotentiometry (CP) methods. All the electrochemical study was carried out in a home-made three-electrode glass setup as discussed in our earlier work [7]. The setup is having the provision to collect the amount of gases evolved from the cathode and anode, during analysis. An electrochemical workstation Biologic SP-150 (Biologic Science Instruments, France) was utilized in the present investigation for all electrochemical characterizations.

3. Results and Discussion

3.1 Morphological and structural characterization

The morphological characteristics of the developed alloy films were examined using FESEM analysis and the corresponding images of the thin films obtained at different c.d.'s are given in Figure 1(A). The composition of the films gathered through EDS analysis showed that the P content in the deposits is increasing with c.d. The thin films developed at 2.0 A dm^{-2} , 4.0 A dm^{-2} and 6.0 A dm^{-2} were found to contain 4.2, 9.0 and 13.5 wt.% of P respectively. The incorporation of P in the deposit resulted in the formation of micro-cracks on the surface of the developed thin films due to the brittle nature of P and also due to the hydrogen evolution during deposition. Apart from the micro-cracks, the roughness of the thin films was found to increase with deposition c.d., i.e., with an increase in P content.

The crystal structure determination of the alloy films was achieved by the XRD analysis. The obtained XRD patterns for the thin films developed at different c.d.'s are given in Figure 1(B). The phase structural changes of the films with deposition c.d. is evident from the peak intensity variation in the XRD pattern. The P-rich phases were found to appear at higher deposition c.d. than Ni-rich phases [8].

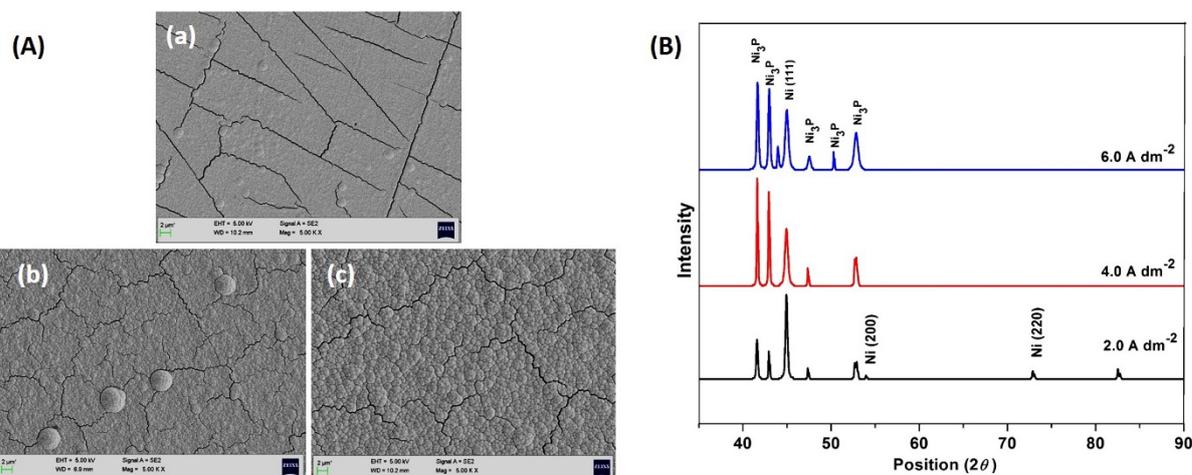


Figure 1. The morphological and structural characterization of the developed Ni-P alloy thin films: A) FESEM images of the thin films developed at different c.d.'s a) 2.0 A dm⁻², b) 4.0 A dm⁻² and c) 6.0 A dm⁻², and B) XRD patterns of the alloy films achieved at different deposition c.d.'s.

3.2 Hydrogen evolution reaction

The stability and activity of the test electrodes towards alkaline HER was studied using electrochemical methods such as CV and CP in 1.0 M KOH medium. The response in current density of the test electrodes while cycling within a fixed potential window can give the electrochemical stability and robustness. Accordingly, a CV study was performed in a potential range of 0 to -1.6 V at a scan rate of 50 mV s⁻¹ for 50 cycles. The reduction peak c.d. (*i*_{pc}) and the onset potential for the evolution of hydrogen was found to vary initially and became stabilized eventually with an increase in the number of cycles. The initial perturbations in the CV responses were attributed to the non-equilibrium conditions of the surface reactions and later on it attains equilibrium to give stable cycles. The obtained CV curves show almost same HER parameters of the developed thin films at different c.d.'s with respect to *i*_{pc} and onset potential. Whereas, the coating developed at 4.0 A dm⁻², having 9.0 wt.% of P, was found to be the best with large *i*_{pc} value and least onset potential as shown in Figure 2(A).

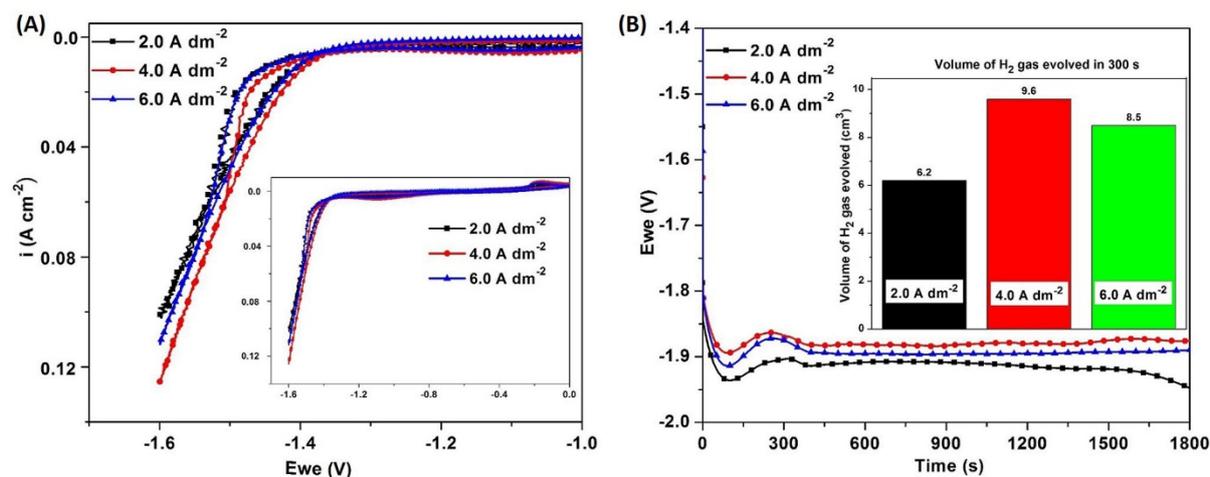


Figure 2. Electrocatalytic activity study results for alkaline HER; A) CV responses of the thin films deposited at different c.d.'s, and B) CP responses of the thin films achieved at different deposition c.d.'s.

The practical applicability of the test electrodes for alkaline HER was investigated using CP technique by passing a constant current of -300 mA cm⁻², for a duration of 1800 s. The amount of H₂ hydrogen evolved during the analysis (for 300 s) was also quantified to distinguish the electrocatalytic

activity of the test electrodes effectively. The obtained CP responses are shown in Figure 2(B) and the corresponding HER parameters are given in Table 1. The results further confirm the Ni-P alloy coating developed at 4.0 A dm⁻² as the best electrode for alkaline HER.

Table 1. The alkaline HER parameters of the Ni-P alloy films deposited at different c.d.'s along with the corresponding amount of H₂ gas evolved during the analysis.

Deposition parameters	Cathodic peak c.d. at -1.6 V (A cm ⁻²)	Onset potential for H ₂ evolution (V vs SCE)	Volume of H ₂ evolved in 300 s (cm ³)
2.0 A dm ⁻²	-0.10	-1.39	6.2
4.0 A dm ⁻²	-0.13	-1.30	9.6
6.0 A dm ⁻²	-0.11	-1.34	8.5

3.3 Oxygen evolution reaction

The electrocatalytic activity of the Ni-P alloy test electrodes towards alkaline OER was also examined using CV and CP analysis under a different set of adjusted parameters. The CV analysis was performed in a potential window of 0 to 0.75 V at a scan rate of 50 mV s⁻¹, for 50 cycles. The obtained CV responses are shown in Figure 3(A) and it clearly shows the distinct variation in the activity towards OER irrespective of the HER activity. The anodic peak current density (*i*_{pa}) values and the onset potential for oxygen evolution obtained from the CV responses are given in Table 2. The obtained results show that the alloy film deposited at 2.0 A dm⁻², with 4.2 wt.% of P, as the best electrode material for OER with large *i*_{pa} value and least onset potential.

Further, the CP analysis also performed to study the electrocatalytic activity of the test electrode for OER. The obtained CP responses of the alloy films developed at different c.d.'s are shown in Figure 2(B). The obtained OER parameters and the corresponding amount of O₂ evolved during the analysis confirms the test electrode developed at 2.0 A dm⁻² as the best for OER.

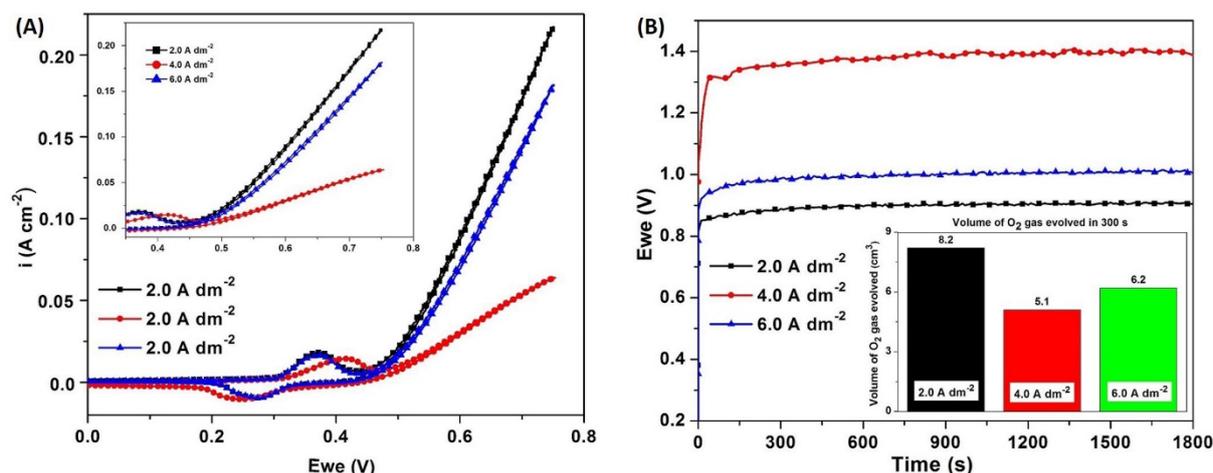


Figure 3. The electrocatalytic activity study results for alkaline OER: A) CV responses of the thin films deposited at different c.d.'s, and B) CP responses of the thin films developed at different deposition c.d.'s.

The overall the electrocatalytic activity study results for HER and OER shows the existence of a synergistic effect of composition on the electrocatalytic activity. The material which was found to show maximum activity towards HER is least active for OER and vice versa. Further, the HER activity was found to increase with P content only up to an optimal level and then decreased, this shows that the deposited thin film with a certain amount of P can only provide ideal hydrogen adsorption characteristics

for maximum activity [10]. Whereas the OER efficiency of the electrode materials was found to be decreased with P content, and the alloy material with least P content showed the best activity for OER. Thus, it can be concluded that the Ni-rich alloy films show more activity towards OER and least activity towards HER. Whereas, its HER activity can be enhanced by the incorporation of a certain amount of P. These enhancement in electrocatalytic activity of Ni with certain amount of P is attributed to the synergism in composition of the alloy coatings for electrocatalytic water splitting.

Table 2. The alkaline OER parameters of the Ni-P alloy thin films deposited at different c.d.'s along with the corresponding amount of O₂ gas evolved during the analysis.

Deposition parameters	Cathodic peak c.d. at 0.75 V (A cm ⁻²)	Onset potential for O ₂ evolution (V vs SCE)	Volume of O ₂ evolved in 300 s (cm ³)
2.0 A dm ⁻²	0.22	0.43	8.2
4.0 A dm ⁻²	0.06	0.47	5.1
6.0 A dm ⁻²	0.18	0.45	6.2

4. Conclusions

1. Electrocatalytically active Ni-P alloy thin films with varying amount of P were developed successfully from an aqueous electrolyte using electrodeposition technique.
2. The Ni-P alloy thin films deposited respectively, at 4.0 A dm⁻² and 2.0 A dm⁻² was found to be the best electrode materials for HER and OER.
3. The material which was found to show maximum activity towards HER is least active for OER and vice versa.
4. The Ni-rich alloy films showed more activity towards OER (least activity towards HER) and its HER activity was found to be enhanced with the incorporation of P in a definite amount.

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