

Effect of TiO₂ on HER Activity of Electrodeposited Zn–Ni Coatings

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ABSTRACT

This paper demonstrates the improved electrocatalytic behavior of Zn–Ni alloy coatings for alkaline hydrogen evolution reaction (HER), due to addition of TiO₂ nanoparticles into the bath. Zn–Ni alloy coatings have been electrodeposited galvanostatically on copper, with wide compositional range (2.31–7.91 wt. % of Zn) at different current densities (c.d.) between 2.0 and 5.0 A dm⁻². The electrocatalytic behaviors of all coatings have been studied for alkaline HER in 1.0 M KOH solution, through cyclic voltammetry (CV) and chronopotentiometry (CP) techniques. The electrocatalytic activity of Zn–Ni alloy coatings was found to be in close relation with composition, structure and morphology of the coatings, depending on the c.d. used for deposition. The electrocatalytic activity of Zn–Ni alloy deposited at 3.0 A dm⁻² (optimal condition) has been improved further by the addition of TiO₂ nanoparticles into the bath. A drastic improvement in the electrocatalytic activity of Zn–Ni alloy coating was observed, due to the incorporation of TiO₂ nanoparticles in the alloy matrix. The improved electrocatalytic activity of Zn–Ni–TiO₂ coating is attributed to the changed morphology and composition of coatings, confirmed by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) analyses. The highest electrocatalytic character of Zn–Ni–TiO₂ composite coating, under optimal deposition condition, is attributed to the increased porosity and electroactive centers, affected due to TiO₂ nanoparticles addition, and experimental results are discussed.

Keywords: effect of TiO₂, electrocatalysis, improved HER, SEM, Zn–Ni alloy

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INTRODUCTION

The clean and fully recyclable energy carrier, hydrogen is considered as an alternative to fossil fuels [1, 2]. The establishment of an energy infrastructure with hydrogen as a primary energy carrier may enable a secure and clean energy future [3]. Though there are many limitations, the alkaline water electrolysis is an ideal technique for the production of high purity hydrogen to meet our requirements. The high energy consumption due to overpotential for Hydrogen Evolution Reaction (HER)

constrained the widespread practical applications of electrocatalysis [4].

However, the overpotential for electrocatalysis can be reduced to a certain extent by modifying the electrode material. The development of an efficient non-noble electrode material, composed of earth-abundant elements, with good electrical conductivity, low overvoltage, electrochemical stability, low cost and ease of use might be quite attractive for cost-competitive hydrogen production [3].

In this regards, electrodeposition is considered as one of the most effective methods for the development of electroactive coatings [5]. Electrodeposition offers a cheap and efficient route for the synthesis of a wide variety of materials with tailor-made properties [6]. The electrodeposited alloys and composites were reported as efficient electrode materials for alkaline HER. The composite electrodeposition is one of the rapidly growing fields of research which can ensure material characteristics which are otherwise impossible through other methods [6, 7]. The development of composite coatings with homogeneously dispersed nanoparticles can enhance the electrocatalytic activity of its metal/alloy counterparts.

Keeping in view of the appealing appearance, better corrosion resistance and good electrocatalytic activity of Zn–Ni alloy coatings, an effort has been made to enhance its electrocatalytic character through the development of Zn–Ni–TiO₂ composite coating.

EXPERIMENTAL

An aqueous electrolyte contains ZnSO₄·7H₂O, NiSO₄·6H₂O, Na₂SO₄ and H₃BO₃ was optimized as the electroplating bath for the deposition of Zn–Ni alloy coatings using standard Hull cell method. The composition and operating parameters of the optimal plating bath are given in Table 1. The Zn–Ni alloy coatings have been electrodeposited galvanostatically on copper rod (having 1 cm² effective surface area) at different current densities (c.d.'s) from 2.0–5.0 A dm⁻², using DC Power Analyzer (Agilent N6705A, USA) as power source. Further, the Zn–Ni–TiO₂ composite coating was developed from the optimal alloy plating bath by adding nanoparticles in small, but known amount (0.5 g L⁻¹). The co-deposition of the nanoparticles from the plating bath was carried out after achieving a homogeneous dispersion of the suspended TiO₂

nanoparticles by overnight stirring. The c.d. obtained as optimal for alloy deposition (3.0 A dm⁻²) was selected for composite electrodeposition. All other parameters like bath composition, pH, temperature, c.d. *etc.* were kept as same as that for alloy deposition. All depositions were carried out in a homemade electrodeposition glass setup of 400 mL capacity using pre-cleaned copper rod as cathode and Ni as anode. The deposition time (10 min), temperature (303 K) and pH = 2.5 were kept constant for comparison purpose.

Table 1. Composition and operating parameters of the optimal Zn–Ni alloy plating bath.

Bath composition	Amount (g L ⁻¹)	Operating parameters
ZnSO ₄ ·7H ₂ O	130.0	Temperature: 303K (30°C)
NiSO ₄ ·6H ₂ O	15.0	pH = 2.5
Na ₂ SO ₄	40.21	Anode: Nickel Cathode: Copper
H ₃ BO ₃	15.31	c.d. range: 2.0–5.0 A dm ⁻²

Characterization

The surface morphology and composition of the alloy and composite coatings were carried out using scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS) analysis respectively. The electrocatalytic behavior of the alloy and composite coatings were studied by depositing them on one end of a copper rod (having 1.0 cm² cross sectional area), using a specially designed three-electrode tubular glass assembly as reported elsewhere [5]. The electrocatalytic study was carried out in 1.0 M KOH medium using the developed coatings on copper rod as working electrode, platinum as counter electrode and saturated calomel electrode (SCE) as reference. The HER activity of the alloy and composite coatings were examined using cyclic voltammetry study (CV), within a potential range of 0.0–1.6 V. Further, the stability and the amount of H₂ gas evolved during the analysis were monitored

through chronopotentiometry analysis (CP) at a constant cathodic c.d. of -300 mA cm^{-2} .

RESULTS AND DISCUSSION

Electrodeposited Zn–Ni alloy coatings

The alloy coatings developed at lower c.d.'s such as 2.0 and 3.0 A dm^{-2} were found to be bright, and observed to become semi-bright at higher c.d.'s. The surface morphologies of the coatings observed through SEM is was also found to be varied from granular to flaky

pyramidal structures and further to smooth porous structures at high deposition c.d. The representative SEM images of Zn–Ni alloy coatings deposited at 3.0 and 5.0 A dm^{-2} are shown in Figure 1. The SEM images in Figure 1 clearly depict the transformation of uniform crystalline coating obtained at 3.0 A dm^{-2} to a porous structure at 5.0 A dm^{-2} . Further, the compositional analysis of the developed alloy coatings showed an increase in Ni content with deposition c.d. as shown in Table 2.

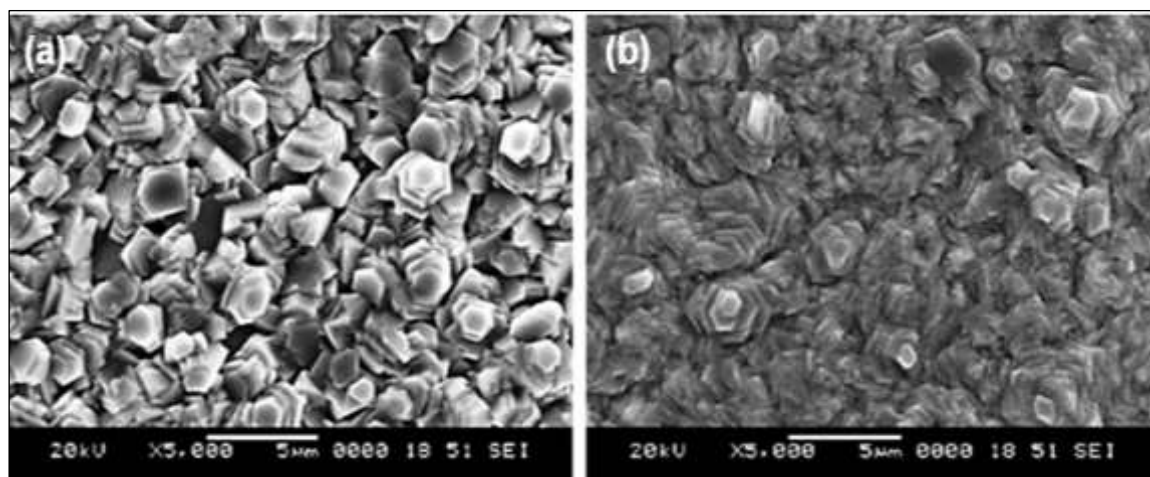


Fig. 1. The representative SEM images of Zn–Ni alloy coatings deposited at different c.d.'s from optimal bath; (a) 3.0 A dm^{-2} , and (b) 5.0 A dm^{-2} .

Table 2. The composition and appearance of Zn–Ni alloy coatings developed at different c.d.'s from optimal bath.

Deposition c.d. (A dm^{-2})	wt.% of Ni	Appearance
2.0	2.31	Bright
3.0	4.62	Bright
4.0	6.86	Semi-bright
5.0	7.91	Semi-bright

Electrodeposited Zn–Ni–TiO₂ Composite Coating

The initial studies on the electrocatalytic activity of Zn–Ni alloy coatings deposited at different c.d.'s showed that the alloy coating obtained at 3.0 A dm^{-2} as the best for alkaline HER. Even though it is active for alkaline water splitting reactions, its activity is very much limited due to the

less Ni content and the powdery appearance of the coating. Further, to enhance its electrocatalytic activity for HER, Zn–Ni–TiO₂ composite electrode was developed at the optimal deposition c.d. by adding TiO₂ nanoparticles into the plating bath.

The surface morphology of the obtained Zn–Ni–TiO₂ composite coating is shown in Figure 2. A remarkable variation in surface morphology was evident in the composite coating as compared with the alloy coating, deposited from the same bath at same c.d.

The presence of nodular growths on the surface as a result of TiO₂ nanoparticles incorporation is clear in Figure 2.

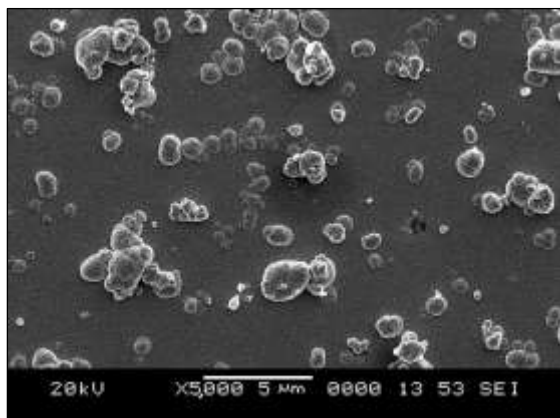


Fig. 2. SEM image of Zn–Ni– TiO_2 composite coating, deposited at 3.0 A dm^{-2} .

Electrocatalytic Activity for Alkaline Hydrogen Evolution Reaction

The alkaline HER activity of the alloy and composite coatings were tested using CV and CP methods in 1.0 M KOH medium and to establish the efficiency and long-term stability.

Cyclic Voltammetry Study

The electrocatalytic behavior for HER of electrodeposited Zn–Ni alloy and Zn–Ni– TiO_2 composite coatings were analyzed using CV technique, in a potential window 0.0–1.6 V, at a scan rate of 50 mV s^{-1} for 50 cycles. The current responses of the CV pattern at -1.6 V were found to be decreased sequentially with increase in the number of cycles and then reached a constant value. The Zn–Ni– TiO_2 composite coating was obtained as electrocatalytically more active towards HER with a high cathodic peak c.d. and a low onset potential for H_2 evolution. The CV responses showing the variation in peak c.d. and onset potential for HER of the Zn–Ni alloy and Zn–Ni– TiO_2 composite coatings, developed at 3.0 A dm^{-2} are shown in Figure 3, and the corresponding data are given in Table 3.

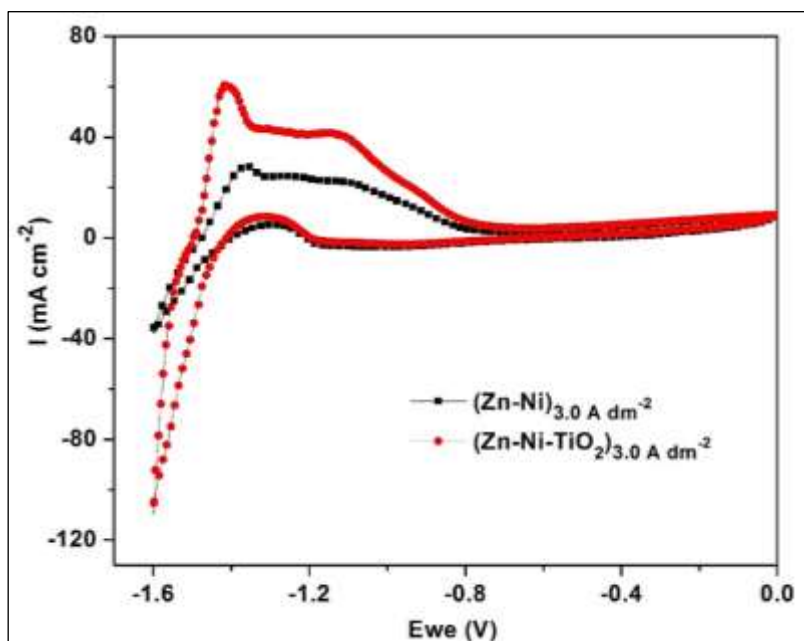


Fig. 3. The variation in CV pattern of Zn–Ni alloy and Zn–Ni– TiO_2 composite coatings.

The obtained results showed a significant variation in HER activity of Zn–Ni alloy coatings after the incorporation of TiO_2 nanoparticles and the improvement in electrocatalytic activity are attributed to increase in the number of active sites and the increased surface area due to the incorporation of TiO_2 nanoparticles [8].

Chronopotentiometry Study

The CP study for HER on Zn–Ni alloy and Zn–Ni– TiO_2 nanocomposite coatings were made at a constant applied c.d. of -300 mA cm^{-2} for duration of 900s. The electrocatalytic behavior of the coatings was evaluated by measuring the amount of H_2 liberated for first 300s. The CP

responses for the Zn–Ni alloy and Zn–Ni–TiO₂ composite coatings are shown in Figure 4, along with the volume of hydrogen liberated on each test electrodes

for first 300s in the inset. There is a marked difference in the potential and the amount of H₂ gas evolved as evident from Figure 4.

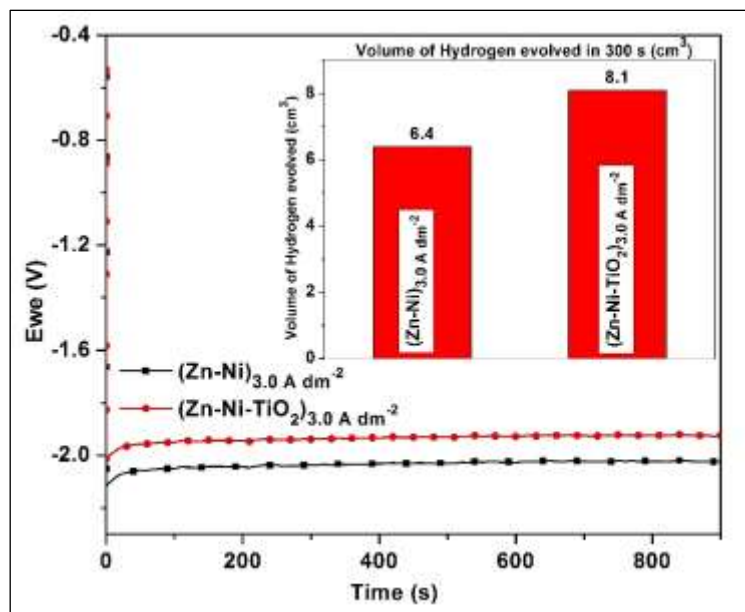


Fig. 4. Chronopotentiometry curves for Zn–Ni alloy and Zn–Ni–TiO₂ composite coatings under an impressed cathodic current of thyroid disorders 300 mA cm⁻², along with the volume of H₂ evolved in 300s on each test electrodes are shown in the inset.

Table 3. The HER parameters of the optimal Zn–Ni alloy coating in comparison with Zn–Ni–TiO₂ composite coating.

Coatings developed at an applied c.d. of 3.0 A dm ⁻²	Cathodic peak c.d. at – 1.6 V (mA cm ⁻²)	Onset potential of H ₂ evolution (V vs SCE)	Volume of H ₂ evolved in 300s (cm ³)
Zn–Ni alloy	35	–1.21	6.4
Zn–Ni–TiO ₂ composite	108	–1.16	8.1

CONCLUSION

The following conclusions were made after analyzing the experimental results on the electrocatalytic efficiency of Zn–Ni alloy and Zn–Ni–TiO₂ composite coatings, developed using electrodeposition technique:

- A stable bath for the electrodeposition of bright Zn–Ni alloy has been optimized using conventional Hull cell method.
- Zn–Ni alloy coating deposited at 3.0 A dm⁻² was found to be the electrode materials for HER, demonstrated by CV and CP studies.
- The electrocatalytic efficiency of Zn–

Ni alloy coatings has been improved by the incorporation of TiO₂ nanoparticles into the Zn–Ni alloy matrix through composite electrodeposition technique.

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REFERENCES

1. T.N. Veziro, F. Barbir. Hydrogen: the wonder fuel, *Int J Hydrogen Energy*. 1992; 17(6): 391–404p.

2. T.N. Veziroğlu, S. Şahi. 21st Century's energy: hydrogen energy system, *Energy Convers Manage*. 2008; 49(7): 1820–31p.
3. X. Zou, Y. Zhang. Noble metal-free hydrogen evolution catalysts for water splitting, *Chem Soc Rev*. 2015; 44(15): 5148–80p.
4. D. Pletcher, X. Li. Prospects for alkaline zero gap water electrolyzers for hydrogen production, *Int J Hydrogen Energy*. 2011; 36(23): 15089–104p.
5. L. Elias, K. Scott, A.C. Hegde. Electrolytic synthesis and characterization of electrocatalytic Ni–W alloy, *J Mater Eng Perform*. 2015; 24(11): 4182–91p.
6. N. Kanani. *Electroplating: Basic Principles, Processes and Practice*. Elsevier; 2004.
7. L. Elias, A.C. Hegde. Synthesis and characterization of Ni–P–Ag composite coating as efficient electrocatalyst for alkaline hydrogen evolution reaction, *Electrochim Acta*. 2016; 219: 377–85p.
8. L. Elias, A.C. Hegde. Electrodeposition of TiO₂/Ni–P composite electrodes for efficient water electrolysis, In: *Recent Advances in Chemical Engineering*. Singapore: Springer; 2016, 203–9p.