Hydrogen Generation Characteristics and Efficiency of a Pd80at.%Ni Electrocatalyst in Alkaline Medium

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Abstract

In view of finding an effective electrocatalyst for the hydrogen evolution through water electrolysis, the oxidationreduction behaviours, electrolysis characteristics, surface reaction kinetics and efficiency of a Pd80at.%Ni electrocatalyst was investigated in 30wt.%KOH electrolyte using cyclic voltammetry. Cyclic voltammogram of the electrocatalyst showed three oxidation and two reduction peaks in between the potential range of –1.0 to +0.65 V. Peak potentials and origin of peaks were found to be distinct than those of precursor Pd and Ni electrocatalysts. Addition of Ni with Pd caused to move the hydrogen adsorption potential to the negative potential direction. Tafel plot for the hydrogen evolution reaction (HER) showed two Tafel regions. Kinetic parameters, i.e., exchange current density at zero overpotential (i_o) and slope (b) values for the low and high overpotential (η) regions were found to be 6.91 x 10^{-2} and 4.36 mA/cm^2 and 146.4 and 343.9 mV/dec, respectively. Observed i_o values indicated better efficiency of Pd80at.%Ni electrocatalyst for hydrogen evolution.

Keywords: Pd80at%Ni electrocatalyst, hydrogen evolution, oxidationreduction, tafel plot, kinetic parameters, exchange current density

1. Introduction

Electrolysis is the process of using electricity to split water into hydrogen and oxygen with high purity. This splitting reaction takes place in a scheme called electrolyzer. To devise a costeffective electrolyzer, development of cheap and effective electrocatalyst(s) would be a great advance and is a topic of current hydrogen energy research [14]. Hydrogen emerges to be crucial for fuel cell for generating electricity, combustion engines for running automotive vehicles, fabricating metal hydride battery for light electronic instruments, etc., [2, 5]. Moreover, hydrogen could be used as household fuel in lieu of natural gas [1]. In concern of the depletion and pollution aspects of fossil fuels and ozone depletion trends of conventional refrigerants, hydrogen is believed to be the future fuel and air conditioning medium. Thus, it is explicable that the electrolysis process and the whole hydrogen application processes are carbon neutral and free from any greenhouse gas emissions.

Now a days, it is well known that hydrogen production ability of an electrocatalyst depends on various factors [6]. Still no unique electrocatalyst is discovered that can cover all the requisite criteria's of a standard hydrogen generation electrode. Therefore, worldwide researchers have been working to improvise electrocatalyst for decades. Although a lot of improvements of electrocatalyst materials have been achieved hydrogen production through electrolysis is still expensive and thereby further research is essential [17]. Because of the high cost of noble and precious metals like Pt, Au and Pd, cheaper transition metals like Fe [8], Ni [9] and Co [10] have been extensively studied for water electrolysis. Researchers have also been concentrated on metal composites [11], amorphous metals [12] and bimetallic electrocatalysts. Among the bimetallic electrocatalysts CoCu [13], NiCu [14], NiFe [15], NiCo[16], PdAg [17], PdP [18] and Pd modified Ni foam [19] are remarkable.

The elctrocatalytic behavior and the hydrogen evolution efficiency of Pd [20] and Ni [9, 21] electrocatalysts are well documented. Notable information is that Pd electrocatalyst shows higher capability of hydrogen evolution at lower potentials than the Ni electrocatalyst. It has been reported that Pd based Ni bimetallic electrocatalyts show far better hydrogen evolution efficiency than the pure Ni electrocatalyst [19, 22]. Such an encouraging hydrogen evolution behavior materializes due to the modification of the surface of PdNi electrocatalyst.

Electrocatalysts surface modification could be achieved by alloying. When the alloy components establish a solid solution, it rarely retains the crystallographic structure of its single components. As a result, the potentials of surface reaction steps and the corresponding peak currents of an alloy remarkably differ from those of their components. It is wellknown that Pd and Ni establish a solid solution in all ranges of composition [6, 23]. In such situation, some distinct behavior of PdNi electrocatalyst than those of Pd and Ni electrocatalysts might be expected. Particularly, there may come into sight the predomination of Pd over Ni or vice versa [6]. Such an expected behavior of PdNi electrode may award better electrocatalytic activity for hydrogen generation during electrolysis while being used in an electrolyzer.

In this context, the present investigation attempt to find out the significant differences in electrochemical surface reaction behaviors, hydrogen evolution characteristics and efficiencies, surface reaction kinetics, etc., of a Pd80at.%Ni alloy electrocatalyst than those of its Pd and Ni components. Higher proportion of Ni than Pd is used to keep the price of the electrocatalyst minimum and economical. Alkaline electrolyte medium has chosen

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because of having corrosion resistance capability of Pd and Ni in this medium than the acidic medium [4, 21].

2. Materials and Methods

Palladium and nickel of purity 99.9 wt.% were purchased from the Tanaka Precious Metal Company, Japan and used to construct Pd80at.%Ni alloy electrocatalyst. At first, an alloy button was prepared by nonconsumable arc melting in an argon atmosphere. The button was then annealed in vacuum of about 1.3×10^4 Pa for 5h at 973 K. It was then rolled into a sheet of 1 mm thickness and cut into square size to construct the working electrocatalyst. The square sheet was reannealed at 1073 K for 2h under vacuum to remove micro cracks as possible as. Then it was spot welded with a nickel wire connector of diameter 0.1 cm. It is essential to mention here that all of the above works were carried out in the Department of Materials Science and Engineering, Nagasaki University, Japan.

After then, the lower end of the connecting wire was insulated by a pyrex glass pipe and epoxy resin (Merk, Germany). The geometric area of the electrode was 0.79 cm^2. A nickel sheet of area 9.25 cm^2 was used as the counter electrode. To remove any oxides present on the surface of the electrocatalysts, these were chemically etched with 2:2:1 H_2SO_4:HNO_3:H_2O standard etching solution. The electrocatalysts surfaces were then polished with 0.3μm Al_2O_3 paste and subsequently rinsed with distilled water. The used electrolyte was 30wt.%KOH solution. This solution was prepared from reagent grade KOH pellets (Merk, Germany).

A three electrode cylindrical electrochemical cell designed and developed in the electrochemistry laboratory, Atomic Energy Centre, Dhaka, and was used for the experimental investigations. The indigenously prepared working electrode, counter electrode and the Hg/HgO.OH reference electrode were immersed in 100 ml electrolyte in triangular way. The luggin capillary end of the reference electrode was placed approximately 2 mm apart from the surface of the working electrocatalyst in order to minimize the internal resistance (IR).

The electrolyte was freed from dissolved oxygen by bubbling N_2 gas for 0.5h. Cyclic voltammetric (CV) measurements of the electrocatalyst were carried out by EG&G PARC Model 362 potentiostat/Galvanostat and currentpotential (I vs. V) responses were drawn by EG & G PARC Model RE 0089 XY recorder. Initially, the electrode was activated by selecting a cathodic potential 1.0 V for 0.5h. The anodiccathodic (redox) transformations and the hydrogen evolution characteristics of the alloy electrocatalyst were investigated in between the potential range of -1.0 to +0.65 V by applying a potential sweep rate of 50 mV/s. For the determination of the kinetic parameters, i.e., Tafel slope (b) and exchange current density at zero over potential (i_o) of the hydrogen evolution reaction (HER), continuous potential sweep method was used. Potential sweeps were carried out by varying the cathodic potential 0.02 V in each scan towards positive potential direction from –1.50 V with a sweep rate of 10 mV/s. The final negative terminal potential was –1.0 V. The experiments were carried out at 298 K.

3. Results and Discussion

Fig. 1a shows the Scanning Electron Microscope (SEM) image of the surface of the prepared PdNi electrocatalyst. It may be seen that the surface of the electrocatalyst is almost free from metal agglomeration but consists of narrow cracks and voids of ranging 1-6 μm. Fig. 1b represents an Energy dispersive Xray (EDX) pattern of a small fraction of the electrocatalyst surface. It may be seen that four remarkable peaks are appeared in the EDX pattern among them three are identified to be for Ni and the rest one is for Pd. It is notable that both the SEM and EDX studies of the catalyst surface were carried out in the Materials Science Division, Atomic Energy Centre, Dhaka. Nonexistence of any other peak for any other metal in the EDX pattern can be taken as an indication that the electrocatalyst is free from impurity. A number of similar EDX studies carried out on different portions of the surface of the electrocatalyst and obtained comparable results supported to conclude that the average composition of the electrocatalyst is Pd80.12at.%Ni.

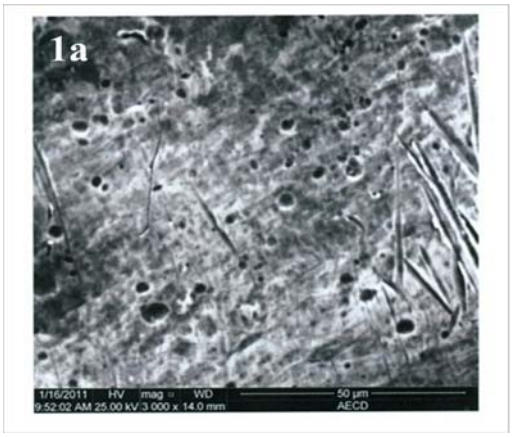

Fig. 1a SEM image of the surface of the PdNi Electrocatalyst

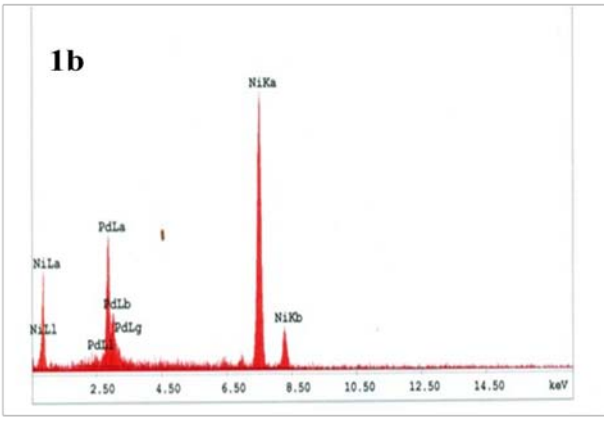

Fig. 1b EDX pattern of the surface of the PdNi electrocatalyst.

It is notable that in view to omitting the writing complexity, the electrocatalyst is named as Pd80at.%Ni electrocatalyst in the text. However, small variation of the atomic compositions of Pd and Ni may be taken as an indication that both the metals were mixed nicely and homogeneously during the arc melting process.

Fig. 2 represents the cyclic voltammogram appeared for the Pd80at.%Ni electrocatalyst in 30wt.%KOH electrolyte in between the potential range of –1.0 V to +0.65 V at 298 K at the sweep rate of 50 mV/s. From the voltammogram, it is clear that the electrocatalyst surface materials suffered from a number oxidation and reduction steps. It may be seen that two small oxidation peaks designed as P_{a1} and P_{a2} which are more clearly shown in the inset Fig. and a large one named P_{a3} and two reduction peaks designed as P_{c1} and P_{c2} are appeared in the voltammogram. Potentials of the oxidation peaks are –0.93 V, –0.82 V and 0.45 V, and those of reduction peaks are –0.42 V and 0.33 V, respectively.

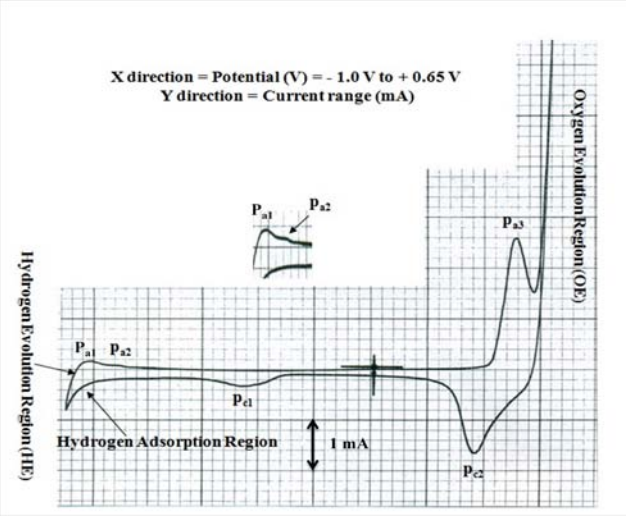

Fig. 2 Cyclic voltammogram appeared for the Pd80at.%Ni electrocatalyst in 30wt.%KOH electrolyte at 298 K [Potential range –1.0 V to +0.65 V; Sweep rate 50 mV/s]

From the Fig. 2 it is almost clear that the hydrogen adsorption region begins from about –0.77 V and ends at the set negative terminal potential –1.0 V. It is notable that the commencement of hydrogen adsorption over this electrocatalyst surface occurred at about 0.24 V negative potentials than that of Pd electrocatalyst [22]. Maximum current for the hydrogen evolution appeared at the terminal potential and the value is around 1 mA. It is mentionable here that this hydrogen evolution current value is about 5 times lower than that of Pd electrocatalyst but 100% higher than that of Ni electrocatalyst. For the Ni electrocatalyst, no hydrogen evolution peak was observed at the chosen potential range of –1.0 V to +0.65 V [22]. Current for the hydrogen evolution gradually decreased with decreasing the negative potential value and became minimal just after reaching the potential of the peak P_{a1}.

It is understandable that hydrogen evolution occurred by abiding the necessary and successive reaction steps such as hydrogen adsorption over the electrode surface, desorption of adsorped hydrogen and their combinations [9, 20]. Considering the rational reaction steps, it is possible to articulate the mechanism of hydrogen evaluation reactions (HER) over the electrocatalyst surface. It provides the idea that HER proceeds via the preliminary step involving atomic hydrogen adsorped on the Pd80at.%Ni electrocatalyst surface namely water reduction with hydrogen adsorption known as Volmer step. The Volmer step then followed by two parallel competitive steps electrochemical known as Heyrovsky step and chemical known as Tafel step which can be represented as:

Volmer step : $[PdNi] + H_2O + e = [PdNi]H_{ads} + OH^-$ (1)

Heyrovsky step : $[PdNi]H_{ads} + H_2O + e = H_2 + [PdNi] + OH^-$ (2)

Tafel step : $2[PdNi]H_{ads} = 2[PdNi] + H_2$ (3)

The reaction steps (1-3) may be taken as an important indication that pure electrocalyst surface means zero valent electrocatalyst surface is essential for obtaining HER. Presence of any oxide layer on the surface is an unnecessary layer and HER hindering entity.

Table 1 summarizes the surface characteristic peaks and their corresponding potentials observed for the pure Pd and Ni electrocatalysts [22] accompanying with those presently observed for the Pd80at.%Ni electrocatalyst. Comparing the peaks and their corresponding potentials observed for the Pd80at.%Ni electrocatalyst with those of pure Pd and Ni electrocatalysts, it can be said that the peaks P_{a1} and P_{a2} in fact are not oxidation peaks. These peaks are appeared due to the successive desorption of diffusional hydrogen absorped in the PdNi lattice [20, 22]. Initial desorption of the diffusional hydrogen from its lattice interstices occurred at about 0.52 V negative potentials than that of Pd electrocatalyst. It occurred probably due to the smaller volume of its lattice interstices which is less suitable to occlude more hydrogen atoms than that of Pd. Ni is lattice contracted metal. Therefore, addition of Ni with Pd causes PdNi lattice contracted alloy with smaller volume of lattice interstices.

Taking into account the locations of the peaks and almost equal peak heights, it can be envisaged that the peaks P_{a3} and P_{c2} are couple of oxidationreduction peaks and they are generated due to the transformations of M(II) oxides ↔ M(III) oxides, respectively. Here the symbol M represents both the Pd and Ni metals. The remarkable feature is that both the redox transformations are appeared at least 0.03 V and 0.06 V negative potentials than those obtained for the Ni(II) ↔ Ni(III) and Pd(II) ↔ Pd(III) oxides transformations [22].

The shape of the M(II) oxides ↔ M(III) oxides transformation peaks looks alike to that of Ni(II) ↔ Ni(III) oxides transformations. It means that in the Ni80at.%Pd electrocatalyst, the Ni(II) ↔ Ni(III) oxides transformations predominates over the Pd(II) ↔ Pd(III) oxides transformations. The single reduction peak P_{c1} seems appeared for the M(II) oxide → M(0) transformation which is the resultant and overlapping transformations of both the Pd(II) oxide → Pd(0) and Ni(II) oxide → Ni(0) transformations. Compared to the relevant peak of Pd, this peak positioned to about 0.15 V negative potential.

Table 1. Surface characteristic peaks and corresponding potentials of Pd and Ni [22] and Pd80at.%Ni electrocatalysts

Pd [reference 22]	Ni [reference 22]	Pd80at.%Ni [present study]
$Pd_{diff.}$	$Ni_{diff.}$	$(PdNi)_{diff.1}$
– 0.41 V	x	– 0.93 V (E_{Pa1})
		$(PdNi)_{diff.2}$
x	x	– 0.82 V (E_{Pa2})
Pd(II) → Pd(III)	Ni(II) → Ni(III)	(PdNi)(II) → (PdNi)(III)
+ 0.51 V	+ 0.48 V	+ 0.45 V (E_{Pa3})
	Ni(III) → Ni(II)	(PdNi)(III) → (PdNi)(II)
x	+ 0.40 V	+ 0.33 V (E_{Pc1})
Pd(III) → Pd(IV)	Ni(III) → Ni(IV)	(PdNi)(III) → (PdNi)(IV)
+ 0.57 V	+ 0.55 V	+ 0.51 V
Pd(II) → Pd(0)		(PdNi)(II) → (PdNi)(0)
– 0.27 V	x	– 0.42 V (E_{Pc2})

Thus, it is clear that the Pd80at.%Ni electrocatalyst surface shows distinct oxidationreduction characteristics and different peak potentials than those of its precursor electrocatalysts Pd and Ni. It may be taken as an evident that alloying of Pd with Ni changes the surface characteristics of Pd and Ni electrocatalysts remarkably.

From the observed oxidationreduction peaks of Pd80at.%Ni electrocatalyst, the consecutive oxidation reaction steps and reaction paths can be represented as follows:

$$\text{Oxidation step : } M(II)O \rightarrow M(III)_2O_3 + e \quad (4)$$

$$\text{Oxidation step : } M(III)_2O_3 \rightarrow M(IV)_2O_4 + e \quad (5)$$

The next reaction step is the decomposition and simultaneous reduction of $M(IV)_2O_4$ to $M(III)_2O_3$. An oxygen atom/half molecule of oxygen is produced through this reaction step which then combines with other oxygen atom and produces oxygen molecule to evolve in gaseous form. This combination step of oxygen atoms is known as Tafel step. The steps can be represented as:

$$\text{Decomposition and reduction step : } M(IV)_2O_4 + e \rightarrow M(III)_2O_3 + 1/2O_2 \quad (6)$$

$$\text{Tafel step : } 1/2O_2 + 1/2O_2 \rightarrow O_2 \quad (7)$$

$$\text{The next reduction steps are : (i) } M(III)_2O_3 + e \rightarrow M(II)O \quad (8)$$

$$\text{: (ii) } M(II)O + 2e \rightarrow M(0) \quad (9)$$

Hydrogen atom adsorps on this M(0) surface means zero valent surface of the Pd80at%Ni electrocatalyst.

Fig. 3 represents the cyclic voltammograms observed at various potential ranges starting from –1.50 V to 0.0 V. Potential sweeps were carried out by varying the cathodic potential 0.02 V in each scan towards positive potential direction. The final potential range was –1.0 V to 0.0 V. Various current ranges was used to obtain better response and better voltammograms. From the Fig., it may be seen that appreciable amount of hydrogen evolution is observed at all the investigated potential ranges. At the potential – 1.50 V, the observed hydrogen evolution current is 133 mA which is equivalent to the current density (i) of 168.4 mA/cm^2. It is notable that the surface area of the electrode is 0.79 cm^2. Current density value gradually decreases with decreasing the terminal negative potential value. At the potential values of 1.40 V and 1.30 V, the i values decreased to 86.1 and 25.3 mA/cm^2, respectively. Finally, the i value reached to 0.21 mA/cm^2 at the terminal potential –1.0 V.

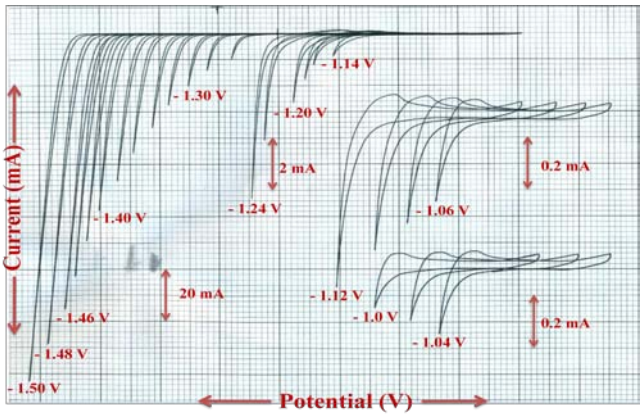

Fig. 3 Cyclic voltammograms observed for the Pd80at.%Ni electrocatalyst at various potential ranges in 30wt.%KOH electrolyte at the sweep rate of 10 mV/s at 298 K

Fig. 4 shows the Tafel plot [Overpotential (η) vs. $\log_{Current\ density}(\log i)$ plot] for the hydrogen evaluation reaction (HER) over the Pd80at.%Ni electrocatalyst. This plot is essential to find out the reaction kinetic parameters i.e., the exchange current density value at zero overpotential (i_o) and Tafel slope (b) value and the efficiency of an electrocatalyst for the hydrogen evolution through electrolysis. The overpotential (η) value is obtained by deducing the Hg/HgO.OH reference electrode potential (– 0.95 V) from the working potentials [9].

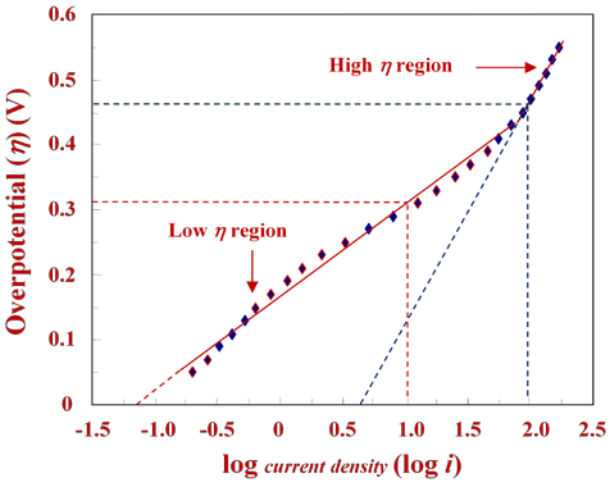

Fig. 4 Tafel plot for the hydrogen evaluation reaction (HER) over the Pd80at.%Ni electrocatalyst in 30wt%KOH electrolyte at 298 K

It may be seen that the Tafel plot shows two well defined Tafel regions as that observed for Ni [9], Pd [24] and PdNi based alloy [25]. The region at low overpotentials is known as low η region. For the low η region, i_o and b values are found to be 6.91 x 10^{-2} mA/cm^2 and 146.4 mV/dec, respectively. The region at high overpotentials is known as high η region. For this region, i_o and b values are found to be 4.36 mA/cm^2 and 343.9 mV/dec, respectively. b values are calculated from the slopes of the Tafel lines and these are usually known as experimental values. In view to justifying the obtained experimental values, it was essential to check them by some alternative ways. The possibility to calculate η value at a i value is by putting the experimental values of i_o and b in the well known equation: $\eta_i = b \log_{10}(i/i_o)$ [9]. For the high η region, η value is calculated at the i value of 100 mA/cm^2 and for the low η region, η value is calculated at the i value of 10 mA/cm^2. The calculated η values are found to be 316 mV and 467 mV, respectively. It is mentionable that the experimental values are 312 mV and 469 mV, respectively.

Thus, it is clear that the calculated values are almost equal to that of the experimental values. Such good coincidence between the calculated and experimental values is implying that the experimental observations are excellent. However, in view to understanding the difference in kinetic behaviors of Pd80at.%Ni catalysts observed presently with those of Pd, Ni and PdNi electrocatalysts, their reported Tafel parameters, i_o and b values, are summarized in the Table 2.

Table 2. Tafel parameters for the hydrogen evolution reactions (HER) of Pd, Ni, Pd50at.%Ni and Pd80at.%Ni electrocatalysts in 30wt.%KOH electrolyte

Electrocatalyst	Tafel parameters	Low η region value	High η region value
Pd	i_o value (mA/cm^2)	0.19	4.07
[Reference 24]	b value (mV/dec)	151.0	312.0
Ni	i_o value (mA/cm^2)	0.06	2.11
[Reference [9]	b value (mV/dec)	80.0	160.0
Pd50at.%Ni	i_o value (mA/cm^2)	~ 0.02	1.52
[Reference 25]	b value (mV/dec)	127.0	273.0
Pd80at.%Ni	i_o value (mA/cm^2)	~ 0.07	4.36
[Present study]	b value (mV/dec)	146.4	343.9

From the Table 2, it is understandable that the i_o value observed for the low η region of the Pd80at.%Ni electrode is 2.8 times smaller and the b value is 4.6 mV lower than that of the Pd electrocatalyst, but conversely 1.1 times higher and 66.6 mV higher than that of the Ni electrocatalyst. For the high η region, the i_o value is 1.1 times higher and the b value is 31.9 mV higher than that of the Pd electrocatalyst but concurrently 2.1 times higher and 183.9 mV higher than that of the Ni electrocatalyst. Compared to the findings for Pd50at.%Ni electrocatalyst, the observed i_o value for the low η region is 3.5 times higher and b value is 19.4 mV higher and for the high η region i_o value is 2.8 times higher and 70.9 mV higher.

The findings are indicating that addition of 80at%Ni with Pd decreases the i_o value for the low η region but keeps b value almost comparable to that of Pd electrocatalyst. On the other hand, i_o value slightly increased but b value highly increased compared to that of the Ni electrocatalyst. Then again, for the high η region, the i_o value slightly increased and the b value moderately increased compared to that of Pd electrocatalyst whereas both the i_o and b value doubly increased compared to that of Ni electrocatalyst. It is wellknown that in the field of electrolysis, the performance of an electrocatalyst mainly counted by considering the i_o value. Higher i_o value implies higher activity of the electrocatalyst for the hydrogen evolution [6, 17, 20]. In this sense, presently tested Pd80at.%Ni electrocatalyst can be considered to be an efficient electrocatalyst for the hydrogen production through electrolysis.

4. Conclusion

A Pd80at.%Ni electrocatalyst was prepared indigenously by arc melting of Pd and Ni, after that it is rolling, cutting, spot welding and packing. Then the oxidationreduction behaviours, electrolysis characteristics, surface reaction kinetics and efficiency of the electrocatalyst were investigated in a three electrode cell using 30wt.%KOH electrolyte by applying cyclic voltammetric technique at room temperature. Cyclic voltammogram of the electrocatalyst showed three oxidation and two reduction transformations in between the potential range of -1.0 to +0.65 V. Peak potentials and the origin of the peaks were found by taking help of the available and reliable earlier reports. It was found out that addition of Ni with Pd and vice versa caused to alteration of the hydrogen adsorption potential. Sufficient number of cyclic voltammograms were collected by applying various potential ranges starting from -1.50 V to 0.0 V in view to drawing a Tafel plot [Overpotential (η) vs. $\log_{Current\ density}$ (log$i$) plot] to find out the hydrogen evolution reaction (HER) kinetics. From the Tafel plot, the kinetic parameters i.e., the exchange current density at zero overpotential (i_o) and the slope (b) values were found. Attempt was made to justify the obtained experimental b values. A nice coincidence was observed between the experimental and calculated values. The observed kinetic parameters were compared with the available reported data's of Pd, Ni and PdNi electrocatalysts. The comparison helped to come in a conclusion that the constructed Pd80at.%Ni electrocatalyst has better efficiency for the hydrogen evolution through electrolysis in alkaline medium.

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