Water electrolysis using electrodes with modified surface/volume

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Abstract. Steel (12X18H10T) as the real electrode material is investigated to be used for different electrolysis applications, as the parallel plate electrodes for standard electrolysis in alkaline solutions, as well as the coaxial electrodes for high voltage short pulse electrolysis in water. The increase of catalytic activity of steel electrodes for the hydrogen evolution reaction (HER) in different electrolytes could be easy achieved by co-deposition of metal hydride (LaNi₅) particles with electrolytic nickel. The results revealed that Ni + LaNi₅ with high real surface have a very high activity for the HER, due to the high active surface and specific microstructural features determining the electrocatalytic activity of the investigated alloys.

1. Introduction

The efficient production and use of hydrogen as an energy storage medium is a key element in developing clean fossil fuel alternatives. To date, the most cost-effective method of hydrogen production is by steam reforming where steam is used to produce hydrogen from methane, derived from natural gas. Roughly 98% of the hydrogen generated worldwide nowadays is prepared by such method. One of the most promising methods for hydrogen production is water electrolysis using a variety of energy sources such as solar, geothermal, hydroelectric and nuclear [1]. Alkaline water electrolysis represents one of the best choices for the hydrogen production since it is a technically tried-and-tested method and is based on an industrial process reaching back nearly 100 years [2]. However, there have been for about 10 years other electrolysis technologies competing with alkaline electrolysis, including non-traditional methods with high voltage and short pulses.

Conventional alkaline electrolysis works at temperatures below 90 °C and uses steel sheet cathodes and nickel-plated steel anodes. Cathodes sometimes are activated by plating nickel or Raney nickel coatings [3]. In addition, nickel and some of its alloys are amongst the most active electrode materials for the hydrogen evolution reaction (HER) in alkaline solutions [2]. Development of new electrode materials for the HER in alkaline solutions traditionally is directed in following ways: (i) increasing a surface area of electrodes, (ii) improvement of electrocatalytical activity of electrodes, (iii) combination of both previous mentioned effects [4]. Widely investigated nickel exhibits good corrosion resistance in alkaline media and exhibits good catalytic activity for the HER [5]. Several rare earth-based hydrogen storage alloys (mostly LaNi₅) investigated as cathodes for HER exhibit an
improvement of electrocatalytical properties [6]. However the real surface and electrocatalytical activity of the electrode material could be increased for practical application for water electrolysis.

Therefore, a detailed knowledge of the kinetics and mechanism for HER on nickel obtained by electrochemical techniques is an essential starting point for any study involving those materials. Among the important factor that affect the production of hydrogen and the efficiency of the process, is the selection of the electrode materials and cell configuration. The steel (12X18H10T) is chosen as the real electrode material to be used in different electrolysis applications, as the parallel plate electrodes for standard electrolysis in alkaline solutions, as well as the coaxial electrodes for high voltage short pulse electrolysis in water.

2. Experimental
All chemicals used were of reagent grade. The water used for preparing solutions was purified by deionization and distillation. Metallic plates of steel 12X18H10T, nickel and tungsten (cast from pure metals without significant amounts of impurities) were polished by mild abrasion. After that the electrodes were cleaned by immersion in 2M potassium hydroxide solution at the 60°C temperature for 5 min and washed with distilled water. Before use the electrodes were etched for 30 min in 3M HCl solution at the 60°C temperature and repeatedly washed with distilled water.

Thin films of nickel with thickness in the range from 0.5 to 20 μm were electrochemically deposited in the solution of 100 ml containing: 30g NiSO₄•7H₂O, 4.5g NiCl₂•6H₂O, 3.8g H₃BO₃, the current density supplied by DC power was controlled from 15 to 60 mA/cm² and temperature during plating was maintained at 60 °C. Thicknesses of Ni films were determined indirectly by calculation from deposition current and time, considering 90% outcome [7], and their varied from 0.5 to 18 μm (table 1).

Composite electrodes (LaNi₅ powdered particles incorporated in coated Ni layer) were obtained on the steel substrates by a co-deposition method. During the above described nickel deposition process powder of LaNi₅ (from Treibacher Industrie AG (Austria); grains with dimensions 0.2 - 3 μm) were gradually added to the solution during plating, using magnetic stirring. Thickness of Ni+LaNi₅ films was varied by deposition time, immersion time of the electrode substrate in electrolytic solution and/or current (table 1). The nickel plate 20 cm² was used as counter electrode, both for electrochemical deposition of nickel and composite layers.

Table 1. Conditions for electrochemical deposition of thin metallic layers.

| Coating       | i (mA/cm²) | t (s) | Thickness (μm) |
|---------------|------------|-------|----------------|
| Ni (0.5)      | 16         | 10    | 0.50           |
| Ni (2)        | 60         | 10    | 1.86           |
| Ni (11)       | 60         | 60    | 11.2           |
| Ni+LaNi₅ (6+) | 60         | 60    | 6-8            |
| Ni+LaNi₅ (15+) | 60       | 150   | 15-18          |

All investigations of the electrochemical properties of the electrodes were conducted in a conventional three-electrode glass cell at room temperature using VoltaLab PGZ 301 Dynamic – EIS Voltammetric (Radiometer Analytical Ltd.). Cyclic voltammetry measurements of single and composite electrodes were performed in electrolytes which are under the investigation for water electrolysis: distilled water and 6M potassium hydroxide solution. The potential of the working electrode was measured against a saturated calomel electrode (SCE) connected with a Lutin capillary. The surface area of all electrodes investigated was 1 cm². Voltammetric curves were obtained at a scan rate100 mV/s in the potential interval from 0.5 V up to -2.5 V against SCE.

Composite electrodes were produced from electroplated nickel and LaNi₅. Structural and morphological analyses were made to determine the composition of steel and photos of plated films
onto steel substrate using Scanning Electron Microscope EVO 50 XVP (Carl Zeiss) with EDX facility and Optical microscope ECLIPSE L150 equipped with Color Matrix CCD.

3. Results and discussion

3.1. Structural and morphological studies
Micro XRF analysis revealed that the steel 12X18H10T (GOST 5632-72) used for investigation of hydrogen evolution reaction (HER) has the composition listed in the Table 2.

| Element | C    | Si   | P    | S    | Ti   | Cr   | Mn   | Fe   | Ni   | Cu  |
|---------|------|------|------|------|------|------|------|------|------|-----|
| Composition (wt%) | 0.12 | 0.83 | 0.04 | 0.02 | 0.67 | 17.88| 2.02 | 68.36| 9.77 | 0.29|

Optical inspection revealed that sample Ni(0.5) has island-type coating from electroplated nickel (Figure 1a), when Ni(2) and Ni(11) are characterised with thick film homogenous coating (Figure 1b). Addition of powdered LaNi5 alloy during plating gives rough coating (Figure 1c and d), where LaNi5 grains are clearly visible Figure 1d).

![Figure 1](image_url)

**Figure 1.** Optical images of steel electrode samples coated with Ni and Ni+LaNi5: a- sample Ni (0.5); b- sample Ni(2); c- and d- sample Ni+LaNi5(6+) in different magnifications.

3.2. Cyclic voltammetry studies
Voltammetric curves were recorded in water and 6 M KOH solution for the composite Ni and NiLa5 electrodes on the steel substrate and compared with the smooth metallic electrodes (Figures 2 and 3).

There are two quite different types of voltammetric curves obtained in water. Almost linear current – voltage dependence is obtained for smooth metallic electrodes which characterizes resistive behaviour of the electrode – water interface. At the same much higher currents and hysteresis loop at the current – voltage dependence is obtained for thin film Ni electrodes and composite Ni+LaNi5 electrodes which indicates on presence of capacitor element on the interface due to the more developed surface of the electrode.

Voltammetric curves obtained in 6M KOH solution for metallic electrodes, thin film nickel electrodes and composite electrodes exhibit similar behaviour. Tungsten and steel electrodes have higher hydrogen evolution potential than nickel electrode, thin film Ni electrodes and composite Ni + LaNi5 electrodes (Figure 3).
As seen from the Figure 3, the current densities on composite nickel electrodes are remarkably higher than that for smooth metallic electrodes which represents higher rates of hydrogen evolution. Current densities for investigated electrodes at the potential -2V against SCE are summarized in the Table 3.

![Voltammetric curves of steel electrode samples coated with Ni+LaNi₅ in water (a) and 6M KOH (b).](image)

**Figure 2.** Voltammetric curves of steel electrode samples coated with Ni+LaNi₅ in water (a) and 6M KOH (b).

![Voltammetric curves of steel electrode samples coated with Ni and Ni+LaNi₅ in alkali.](image)

**Figure 3.** Voltammetric curves of steel electrode samples coated with Ni and Ni+LaNi₅ in alkali.
Table 3. Current densities of metallic and composite electrodes at voltage -2V against SCE.

| Electrode          | i, mA cm⁻² in water | i, mA cm⁻² in 6M KOH |
|--------------------|---------------------|---------------------|
| Ni                 | -0.06               | -517                |
| Anodized Ni        | -0.34               | -551                |
| W                  | -0.09               | -299                |
| Steel              | -0.07               | -320                |
| Ni (0.5)           | -0.35               | -580                |
| Ni (2)             | -0.40               | -620                |
| Ni (11)            | -0.29               | -564                |
| Ni + LaNi₅ (6+)    | -0.32               | -678                |
| Ni + LaNi₅ (15+)   | -0.52               | -879                |

Higher values of current density for nickel electrode, than for tungsten and steel electrodes, indicate on the catalytic properties of nickel for HER. However, obtained current densities for thin nickel layers on steel are higher than for smooth nickel electrode or anodized nickel (anodized Ni is nickel electrode previously used as an anode for nickel deposition on cathode). An explanation for that could be attributed to more developed surface of composite electrodes. Therefore for hydrogen evolution reaction in alkaline electrolyte the nickel electrode could be replaced with more available steel electrodes coated with an electroplated catalytic nickel film.

An addition of LaNi₅ to nickel films during the electrochemical co-deposition noticeably increases obtained current densities. Due to the fact that HER mainly involves surface process, the surface composition and microstructure are very important factors for the electrode reactions. Obtained results indicate that a presence of LaN₅ even in small amounts in nickel films plays a very important role in an improvement of electrocatalitical activity of electrodes for HER. Similar increases of electrocatalytical activity of nickel electrodes by adding mischmetals on steel are reported [4].

Tafel analysis was based on the validity of Butler – Volmer equation [8]:

\[ i = -i_0 \exp(2.303 \eta / b) \]

which was applied for determination the kinetic parameters of HER, where i - the current density, \( i_0 \) - the exchange current density, \( \eta \) - the overpotential \( \eta = E - E_{eq} \), \( b \) - the Tafel slope. The electrochemical activity of the electrodes was evaluated from the kinetic parameters derived from the linear part of the Tafel plots in co-ordinates \( \eta - \lg i \). Kinetic parameters \( b, i_0 \) and \( \eta \) for different electrodes are presented in Table 4 together with those of steel substrate for comparison.

Table 4. Kinetic parameters of the HER for thin film electrodes on steel substrate in 6M KOH.

| Electrode          | \( E_{eq} \), mV | \( i_0 \), µA cm⁻² | \( b \), mV/dec | \( \eta \), mV |
|--------------------|------------------|-------------------|----------------|---------------|
| Steel              | -890             | 1.2               | -152           | -598          |
| Ni (0.5)           | -825             | 52.9              | -218           | -575          |
| Ni (2)             | -712             | 48.1              | -208           | -588          |
| Ni (11)            | -656             | 18.3              | -198           | -644          |
| Ni + LaNi₅ (6+)    | -849             | 134.4             | -204           | -451          |
| Ni + LaNi₅ (15+)   | -807             | 202.6             | -224           | -493          |

For both types of thin film electrodes (with or without LaNi₅ addition) the Tafel slopes shows higher values than those for smooth steel electrode. These values also are higher than for smooth nickel electrode (-118 to -122 mV/decade) presented by other researchers [4,5,9]. An explanation for
the noticeable increasing of Tafel slopes is based on the mathematical models for porous electrodes which predict an increase or even doubling of the Tafel slope for semi-infinite pore length [10].

Regardless of higher Tafel slopes the electrodeposited Ni and Ni+LaNi₅ alloy electrodes show high activity for HER explained in terms of real exchange current density. Obtained current densities 134 and 203 µA/cm² for composite electrodes are comparable with i₀ obtained both for Fe-mischmetal crystalline alloys [4] and for skeleton Ni electrodes obtained by thermal arc spraying technique [5]. Obtained results indicate that the presence of LaNi₅ leads to the remarkable increase of the intrinsic activity of the electrodes.

4. Conclusions
From the results obtained it was found that electrodes produced from conventional steel 12X18H10T with high nickel and chromium content are useful for different electrolyzers, as well for classic alkali, as well as for non-traditional high voltage electrolyzers working with deionised water as electrolyte. The increase of catalytic activity of steel electrodes for the HER in different electrolytes could be easy achieved by co-deposition of metal hydride (LaNi₅) particles with electrolytic nickel. The results revealed that Ni + LaNi₅ with high real surface have a very high activity for the HER, due the high active surface and specific microstructural features determining the electrocatalytic activity of the investigated alloys. Investigation on the long term performance of the Ni+LaNi₅ thin film alloys is the subject of future studies.

5. References
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