A voltammetric study of $\alpha$- and $\beta$-hydroxides over nickel alloys

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Abstract

The hydrogen evolution reaction (HER) is one of the most studied electrochemical process due to the alternative energy conversion and the importance in some chemical process. The search for new electrocatalytic materials lead to investigate metals and alloys with particular characteristics/properties. This paper describes aspects of hydrogen adsorption and Ni-hydroxide formation over nickel alloys (SAF2205, INCONEL625 and MONEL400) utilizing cyclic voltammetry. The SAF2205 (6.4% Ni) alloy present behavior analogue to pure Ni electrodes to hydroxide species, and can bring some advantages to HER compared with the carbon steel (SAE1020) electrode commonly utilized in industrial process.

Keywords: Hydrogen evolution; Nickel alloys; Nickel hydride; Nickel (II) hydroxide; HER mechanism

1. Introduction

The electrochemical production method has been pointed as one of the most powerful alternative to chemical process in the primary and secondary industry, being fundamental to produce commodities like alkalis, chlorine and metallic aluminum.

Although the potentiality of electrochemistry in industry, the main restriction for its use is the very high consumption of electric energy, being the aluminum and chlorine plants the higher consumers per weight of final product. Only in Maceió (Alagoas State, Brazil) the energetic consumption of TRIKEM chloralkali plant (Odebrecht Holding) is 110 MW, one-third of the total electricity utilized in the 2.6 million habitants of Alagoas State to produce 420.000 metric ton dry basis NaOH per year [1]. Researches in chlorine-alkali process are conducted in two ways: (a) optimization of dimensionally stable anodes (DSA) used to lower $O_2$ production and reduce the potential to generate $Cl_2$ [2]; or (b) search for alternative electrodes to lower the HER potential, including material composition and also cathode geometry [3].

A classical mechanism is proposed for HER over metallic surfaces in alkali consisting of three steps (see Scheme 1): (i) Volmer—electron transfer with $H$-adsorbed on the metallic surface; (ii) Heyrovsky—$H_2$ production via a new electron transfer; (iii) Tafel—alternatively to Heyrovsky, a chemical recombination of two $H$-adsorbed.

A series of papers reveals fundamental aspects of $H$-adsorption, like metal co-deposits effects [4], influence of hydroxide concentration and roughness [5]. The kinetic aspects of HER are very well reported by Brown et al. [5], evaluating this process over mild steel and also over nickel cathodes. Although emphasizing the electrocatalytic advantage of nickel, the authors pointed for the difficulties to propose a mechanism because the reaction takes place over the nickel oxides or hydroxides, giving irregular Tafel slopes.

A series of new material for water and brine electrolysis in alkaline medium was developed by De Nora Company [6] in 70 and 80 years, focusing on the possibility of reaching currents higher than 300 mA cm$^{-2}$ in a diaphragm cell. This advance was obtained utilizing a ferritic steel coated with a Ni–Mo activate oxide and changes to an expanded steel-base geometry, however, as reported by Ogata et al. [7], the life time of these electrodes were not reported. These last researches
studied hydrogen evolution over carbon steel, nickel and Raney alloys under high temperatures (80–240 °C) and pressures. Nickel was verified to be very resistant to corrosion, but exhibited an overvoltage related to carbon steel. The best potential performance was detected for Raney-Ni alloy, but it was irreversibly degraded. The preparation and characterization of interesting transition metal alloys for hydrogen evolution in alkaline media was also reported [8]. Good electrocatalysts for HER were found in binary mixtures of nickel, cobalt, or iron with molybdenum, tungsten or vanadium. The most potential-advantageous was Ni–Mo, with underpotential of 100 mV, but not stable enough above 200 mA cm$^{-2}$. 

Scheme 1. Generic electrochemical $H_2$ evolution mechanism on an electrocatalytic metal.

The use of electrodeposits was also considered to hydrogen evolution and the surface aspects were observed by X-ray diffraction and electron microscopy [9], where co-deposits of Ni–Zn and Ni–Zn–Mo presented the best electrocatalyst response, being the mechanistic pathway completely different from the above scheme proposed as detected in Tafel slopes (less than 100 mV). This difference was attributed to microcrystalline structure effect. This microcrystalline effect in the electrodeposits was also studied by Stevanovic et al. [10], improving that tetraethylenepentamine (TEPA) buffers give surfaces with better electrocatalytic (100–300 mV) properties for HER compared with citrate–borate medium. The negative aspect of this co-deposit is the highly spongy surface, that has no physical resistance to use in brine and/or water electrolysis.

An specific study of HER over nickel polycrystalline electrode was carried out by Lasia and Rami [11] with open circuits relaxation and a.c. impedance methods, where a Volmer–Heyrovsky mechanism was proposed. In this way, the theoretical aspects of Tafel and Heyrovsky steps and its dependence of H-surface coverage was treated by Gennero de Chialvo and Chialvo [12], where fitting curves can give the rate of each step as a potential function.

If the hydride formation over cathodic surface is pointed as the main step to lead Tafel step and give better catalytic properties to the material, the presence of nickel must be emphasized to furnish NiH with low activation energy ($E_a$) (at least in cases where Ni domain the electrochemical behavior). The NiH formation is very well described by Vracar and Conway [13], that attribute to this specie the electrocatalytic behavior of $Ni$–$Mo$–$Cr$–$B$, $Ni$–$Mo$–$Fe$–$B$, $Ti$–$Ni$ and $Ti$–$Ni$–$V$ amorphous and vitreous alloys.

The formation and destruction of nickel hydroxides and its effects in the HER was evidenced over Raney-Ni porous [14], Ni–Co electrodeposits [16] and polycrystalline Ni electrodes [15]. Particular attention is given to $\alpha$- and $\beta$-$Ni(OH)_2$. The $\alpha$-specie is reversibly formed until 400–500 mV more anodic than HER and the $\beta$-$Ni(OH)_2$ formed at 600 mV more anodic than HER, through an irreversible electrochemical process [15,16]. The main problem with the hydroxide species is whether these can be reduced or not, causing troubles to NiH formation and HER suppression [14].

In this paper we will discuss the region of potential formation for the $\alpha$- and $\beta$-$Ni(OH)_2$ and the influence in hydrogen evolution over NICKEL200, SAF2205, INCONEL625 and MONEL400 compared with the carbon steel SAE1020 (presently utilized in the industrial Oxotech® cell).

2. Experimental

The alloys studied in this paper were commercial samples of nickel alloys, transformed into cylinders from rods gently supplied by Sandvik (Sweden/São Paulo Office, Brazil) and Multialloy (São Paulo, Brazil). Non-nickel SAE1020 steel samples were obtained from an old industrial chlorine cell (Oxytech® model, from TRIKEM, Brazil). Cylindrical samples were prepared with 0.7–1.5 cm diameter and 3.0 cm height, with an adequate screw thread to connect in the PAR-RDE rotating disc system. The polishing method performed was from 100 to 1200 mesh to 0.3 μm ζ-alumina suspension. Isopropanol bath was adopted to get grasses out and a final ultrasonic bath was utilized to clean alloy samples. The surface chemical composition of these cathodes was obtained just after polishing/ultrasan bathing) by X-Ray fluorescence (XRF) ‘Alloy Analysers’ model 9266, from Texas Nuclear (USA). Experimental data composition is presented in Table 1.

For all electrochemical studies a suitable technique for investigating the oxidation–reduction behavior of an electrode material is cyclic voltammetry and analogues. The electrochemical equipment was an EG&G PAR Model 273A potentiostat/galvanostat, connected with a 486 IBM-PS microcomputer. PAR Model RDE616 rotating ring disc module at 1000 rpm was eventually used to get an homogeneous convective stirring. The reference electrode was a Hg/HgO/OH$^-$ in 1.0 M NaOH Luggin ($-0.920$ V vs. NHE, 25 °C) and the auxiliary electrode was a Pt wire spiral ($\sim 3.0$ cm$^2$). As
supporting electrolyte was used aqueous 1.0 M NaOH solution standardized by classic volumetry with potassium biphthalate and phenolphthalein as indicator. MILLI-Q® grade water was always used. Cyclic voltammograms were recorded with a 50 mV s⁻¹ potential scan rate (ν) at 25 °C. All the work was carried out in a non-divided EG&G PAR flat cell (stationary experiments) or a home-built cell (~300 ml) with geometry favorable to rotating disc technique, and a Luggin capillary to minimize ohmic drop.

3. Results and discussion

3.1. Electrocatalytic study

The preliminary electrolytic comparison between SAE1020 commercial electrode and studied alloys was carried out in the flat cell (electrode area = 0.73 cm²). A cathodic current of 233 mA cm⁻² was passed through the electrodes for at least 65 h. Cathodic potential was measured against the Hg/HgO, OH⁻ (1.0 M) electrode. The current density applied was chosen on a basis of industrial diaphragm cell. The results for extensive electrolysis are shown in Fig. 1.

We realized that the cathode potentials vary randomly in the first 2–4 h, until a surface stabilization in the electrolyte, except for SAF2205, that performed very stable since the beginning of the experiment. Although INCONEL625 gave H₂ in potentials near those carbon steel in the first 20 h, the potential shifted to 300 mV more cathodic than SAE1020 at the end of the experiment. SAF2205 always presented potential below the carbon steel one, sometimes more than 200 mV less cathodic. These results pointed out to a very possibly competitive use of SAF2205 to produce electrolytical H₂ in alkaline media. MONEL400 presented an initial potential compared to SAF2205 (~2.000 V) but grown linearly to ~2.450 V after 5 h, remaining constant thereafter. The possibility of copper segregation to surface, inhibiting Ni electrochemistry, was previously described in Ref. [18] and could be used to justify this behavior.

3.2. Voltammetric experiments

The voltammetric experiments for nickel selected alloys was carried out in three blocks.

3.2.1. Effect of the successive scans

After the polishing process the electrode was polarized at −1.600 ≤ Eₚ𝑜𝑙 ≤ −1.100 V for 5 min under rotation (1000 rpm). As soon as the rotation stopped, cyclic voltammograms were obtained in the range (variable) between −1.100 V and Eₗ, (Eₗ varying from −0.900 to −0.300 V vs. Hg/HgO, OH⁻ (1.0 M) in steps of 25–50 mV). Scan rate was 50 mV s⁻¹.

As obtained by Machado and Avaca [16] for Ni foil (99.95%) electrode, NICKEL200 presented a well-defined wave, not reversible, in the region corresponding to the β-Ni(OH)₂ formation until −0.600 V (Fig. 2). The α-Ni(OH)₂ only converts to β-Ni(OH)₂ form in potential more anodic than −0.600 V. The proof is the NiH wave formation at −0.900 V in the backward scan (cathodic), when Eₗ > −0.500 V. The integrated charge was obtained under all potential scan (software M270 from EG&G) spotting for the −0.650 V barrier of conversion from α- to β-Ni(OH)₂ form, as presented in Fig. 3(A), revealing the possibility of forming NiH over

![Fig. 1](image-url)
Fig. 2. Cyclic voltammograms of NICKEL200 in 1.0 M NaOH. $E_{\text{pol}} = -1.100 \text{ V (5 min, } \omega = 1000 \text{ rpm); } \nu = 50 \text{ mV s}^{-1}; 25 \text{ °C.}$

Fig. 4. Cyclic voltammograms of SAF2205 in 1.0 M NaOH. $E_{\text{pol}} = -1.300 \text{ V (5 min, } \omega = 1000 \text{ rpm); } \nu = 50 \text{ mV s}^{-1}; 25 \text{ °C.}$

Fig. 3. Integrated voltammetric charge, $\nu = 50 \text{ mV s}^{-1}; 25 \text{ °C; polarization for 5 min, } \omega = 1000 \text{ rpm.}$ (A) NI200, $E_{\text{pol}} = 1.100 \text{ V, anodic potential effect;}$ (B) SAF2205, polarization potential effect ($-1.500 \leq E_{\text{pol}} \leq -1.100\text{V});$ (C) SAF2205, $E_{\text{pol}} = 1.500 \text{ V, anodic potential effect;}$ (D) INCONEL625, $E_{\text{pol}} = 1.300 \text{ V, anodic potential effect.
NICKEL200, favored by β face. This result is very near those published for pure Ni [16], except by the fact that we advanced to the more cathodic potential region, obtaining a higher charge (H₂ evolution).

With the same procedure above, after a pre-conditioning of 5 min at $E_{\text{pol}} = -1.300$ V, SAF2205 showed a clear increase of peak current in $-0.650$ V when the $E_a$ is displaced to more anodic potentials (Fig. 4). Although SAF2205 has only 6.4% in Ni content, the surface electrochemistry is determined by Ni, except when some metal like Cu can mask this behavior [17].

Based on the Ni dominating electrochemistry in SAF2205, we can relate between the peak obtained in $-0.650$ V and the $\alpha$-Ni(OH)₂ formation when scanning potential more anodic than $-0.700$ V. The more anodic the $E_a$ scanned the more intensive peak/shoulder current is revealed at $-0.750$ V in the cathodic scan. This peak can be attributed to the NiH formation on SAF2205 once other components of this alloy (Mo, Nb and Cr) did not present detached waves in this region [17] and iron only present a strong peak in amorphous structure [18]. The only problem detected concerns the initial forward scan: there is no overlap between the curves, in despite of the initial polarization at $-1.300$ V as pre-treatment for a complete cleanup of Ni-hydroxides over alloy surface. This result induced a particular study to discover the potential range of Ni-hydroxides species existence (see below).

With the same procedure above an INCONEL625 electrode was polarized at $E_{\text{pol}} = -1.400$ V, resulting in a $-0.650$ V peak, that could be attributed to $\alpha$-hydroxide, with the respective β-formation in potential more anodic than $-0.500$ V (see Fig. 5). This conversion potential was supposed on a basis of the slightly cathodic corresponding shoulder, shown in the $-0.850$ V region. A very bad overlap is obtained when scan begins ($-1.100$ V), like for SAF2205 cv’s.

The SAF2205 electrodes showed a pronounced catalytic effect compared with INCONEL625. We attributed this effect to the higher concentration of Ni(OH)$_x$ species on the surface of SAF2205. An evidence is presented in the cathodic scan ( $\sim -0.8$ V vs. ref.), where current is increased the more positive is the potential reach in the initial anodic scan.

Although the greater Ni content of MONEL400 (67%), the electrochemical behavior in the same Ni(OH)$_x$ (for NICKEL200 and SAF2205) region never remembers a typical Ni dominance. Fig. 6 presents a series of MONEL400 cv’s where the initial scans (anodic) showed higher cathodic currents than the backward scan until $E_a = -0.650$ V. The crossing confirms the non-Ni electrochemistry domain. The same behavior was detected by Carvalho [17] in studies of metal co-deposition where electrochemical domain was attributed to copper. In fact, MONEL400 composi-
tion has at least 31% in Cu, leading to confirm its domain.

3.2.2. Effect of polarization in the HER potential on Ni-hydroxides

This experiment was carried out to verify the effect of cathodic potential in the destruction of Ni-hydroxide species formed during the anodic scan. The methodology utilized here was physical polishing followed by 10 consecutive scan cycles between $-1.100$ and $-0.200$ V. This pre-cycling method was utilized to guarantee the same amount of Ni-hydroxide species before apply the polarization potential. Immediately we proceeded polarization for 5 min under rotation (1000 rpm) in a variable $E_{pol}$ ($-1.500 \leq E_{pol} \leq -1.100$ V; steps of 50 mV). The activation of Raney-Ni composite-coated electrodes for HER (in the same medium) was very well related by Choquette et al. [19], improving that activation can occur after destruction of the Ni-oxide or $\beta$-Ni(OH)$_2$, after long polarization time ($10^3$–$10^5$ s). Searching for an adequate, but shorter conditioning time, we tested polarization in cathodic potentials added to rotating electrode procedure. The same results were obtained for 120, 60 and 5 min of conditioning polarization (tested for SAF2205), thus the last value was chosen as good enough.

As soon as the rotation stopped, cv’s were obtained in the range from $-1.100$ to $-0.700$ V. Scan rate was always 50 mV s$^{-1}$. This region was chosen not to reach the $\beta$-specie region (more anodic than $-0.600$ V) that is supposed to be irreversible [16]. The polishing process was repeated before each change of $E_{pol}$.

NICKEL200 gave very good cv’s overlays till $E_{pol} = -1.100$ and $-1.200$ V, but SAF2205 gave it only for $E_{pol} < -1.400$ V, as shown in Fig. 7.

The integrated charge of cv’s gives a better view of this behavior. The line break in Fig. 3(B) suggests that $E_{pol} = -1.45$ V is enough to completely destroy the Ni-hydroxide layer. The presence of these species in very cathodic potential may be attributed to the low Ni composition (6.4%) and to the crystal structure, although the surface’s electrochemistry is yet controlled by Ni atoms.

INCONEL625 showed the same behavior as SAF2205, with cv’s overlays for $E_{pol} < -1.60$ V.

3.2.3. Effect of anodic potential on Ni-hydroxides formation

This experiment was carried out to evaluate how anodic the potential can get to form the irreversible $\beta$-Ni(OH)$_2$ in the cv’s experiments. Bearing in mind that the results of the experiment above, an $E_{pol} = -1.500$ V is enough to break the Ni(OH)$_2$ layer, we applied this polarization potential for 5 min before obtaining the cv

![Fig. 7](image1.png)  
Fig. 7. Effect of pre-polarization potential on cyclic voltammetry of the SAF2205. $E_{pol} = -1.500$ (1); $-1.400$ (2); $1.350$ (3); $1.300$ (4); $1.200$ (5); $1.100$ V (6) versus Hg/HgO (1.0 M NaOH) (after 5 min, $\omega = 1000$ rpm); $v = 50$ mV s$^{-1}$; 25 °C.

![Fig. 8](image2.png)  
Fig. 8. Cyclic voltammograms of SAF2205 in 1.0 M NaOH. $E_{pol} = -1.500$ V (5 min, $\omega = 1000$ rpm); $v = 50$ mV s$^{-1}$; 25 °C.
from $-1.100$ V to a variable $E_2$. The $E_2$ was varied from $-0.900$ to $-0.300$ V in steps of 25 mV. The actual cv of SAF2205 gave a much better overlay of cv’s (Fig. 8) in contrast against the obtained with $E_{pol}$ less cathodic (Fig. 4). When the scan reaches potentials more anodic than $-0.600$ V, the cv reverse scan reveals an ill-defined cathodic wave in the $-0.700$ to $-0.900$ V range. The current of this wave grows with the anodic displacement of $E$, being attributed to the change of the irreversibly formed $\beta$-Ni(OH)$_2$ into NiH.

The anodic and cathodic voltammetric scans were integrated, giving the data plotted in Fig. 3(C). The dashed line in Fig. 3 represents the limit region where $\alpha$-Ni(OH)$_2$ begins to be formed, in potentials more anodic than $-0.600$ V.

The INCONEL625 behavior is to be interpreted as easy as the SAF2205 one, as shown in cv’s (Fig. 9). Bearing in mind that Ni is the electrochemically dominating metal in this region, the presence of Ni-hydroxide species is justified with the anodic wave with peak in $-0.600$ V ($\alpha$-formation) and its corresponding cathodic one at $-0.900$ V. The more anodic the potential scanned, the more visible is the cathodic shoulder at $-0.700$ V, attributed to $\beta$-specie conversion to NiH. The NiH region for this alloy goes from $-0.600$ V to the foot of HER in $-1.100$ V, as revealed by charge plot in Fig. 3(D).

4. Conclusion

The results above showed that the SAF2205 presented an overpotential 100–200 mV more favorable for $\text{H}_2$ evolution in 1.0 M NaOH, compared with the industrially utilized SAE1020. Although the low Ni-content composition, SAF2205 has shown NiH and Ni(OH)$_2$ electrochemistry analogous to the pure Ni electrode previously described in Ref. [16] to which is attributed the electrocatalytic behavior. The $\alpha$-Ni(OH)$_2$ is reversibly formed in the $-0.900$ V and $\beta$-Ni(OH)$_2$ is irreversibly generated above $-0.600$ V. Both hydroxides are completely destroyed at $-1.450$ V giving NiH.

The INCONEL625 also gives a typical Ni electrochemistry, but with the $\beta$-Ni(OH)$_2$ being reduced to NiH in potential less cathodic than verified for SAF2205. MONEL400 alloy showed non-Ni electrochemistry.

The low composition of Ni associated to the corrosion resistance character and good electrocatalytic effect for HER may induce to consider SAF2205 as a good alternative for $\text{H}_2$ production studies incoming.

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