

# Evaluation of various steel types for the evolution of hydrogen in KOH

Evaluación de diferentes aceros para la evolución de hidrógeno en KOH

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## Palabras clave

Voltametría; electrólisis; hidrógeno; hidróxido de potasio; acero; acero inoxidable; cronoamperometría.

## Resumen

Se estudió el comportamiento electroquímico de los diferentes tipos de aceros comerciales de bajo costo (A36, 430 y 304) como electrodos para la obtención de hidrógeno.

El propósito de este trabajo fue estudiar la evolución de hidrógeno, para lo cual se utilizaron técnicas electroquímicas como cronoamperometría y curvas voltamperométricas, en diferentes concentraciones de KOH (5% y 25% m/m). El acero inoxidable 304 en una concentración de 25% m/m tuvo el mejor desempeño, pues en estas condiciones el inicio de liberación de hidrógeno disminuyó y presentó el menor requerimiento de potencial para su uso como placa bipolar.

## Key words

Voltammetry; Electrolysis; Hydrogen; Potassium hydroxide; Steel; Stainless steel; Chronoamperometry.

## Abstract

This paper studies the electrochemical behaviour of different types of low-cost commercial steel (A36, 430 and 304) as electrodes to obtain hydrogen.

The aim of this work was to understand hydrogen evolution. The studies were conducted by different electrochemistry techniques like chronoamperometry and voltamperometric curves in different concentrations of KOH (5% and 25% m/m). The 304 stainless steel type in a 25% m/m KOH concentration had the best performance, because in these conditions the potential onset of hydrogen release decreased, demonstrating the lowest potential requirement for use as a bipolar plate.

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## Introduction

The possibility of producing hydrogen by splitting water into hydrogen and oxygen was first discovered in 1789, and from that point on scientifically studied and developed (Rasten, Hagen & Tunold, 2003) (Bičáková & Straka, 2012).

Nowadays, water electrolysis has become a worldwide well established technology to produce hydrogen and many scientists treat this abundant element as energy carrier of the future. At the present day, hydrogen is predominantly used in the refining industry, as well as for the production of methanol and ammonia (Bičáková & Straka, 2012). Furthermore, a lot of applications and ideas are present, such as for example its use in industrial manufacturing processes as a substitute fuel in cars or as a portable energy carrier. The majority of hydrogen production in the world, approximately 96%, is obtained by steam reforming from natural gas. Water electrolysis with a share of 4% represents the second opportunity to obtain hydrogen, whereby several electrolysis

concepts with different systems exist (Rasten et al., 2003) (Bičáková & Straka, 2012).

The alkaline electrolysis is stated to be the most investigated, developed and mature technology, and therefore mostly used for large-scale water electrolysis. The main configuration of an alkaline electrolyzer is made up of a cathode and anode, isolated from one another by semi-permeable membranes or separator submerged in an electrolyte solution. Commercial electrolyzers usually operate under temperatures of between 70-100 °C and pressures in the range of 1-30 bar (Zuttel, A.; Borgschulte, A.; Schlapbach, 2008) (Jensen, O.J.; Bandur, V.; Bjerrum, J.N.; Jensen, H.S. & Ebbsen, S, 2008). In conventional alkaline electrolyzers, KOH aqueous solution electrolyte of 25% to 30% w/w is specified to be widely used due to the high conductivity in this range of concentration. (Mazloomi, Sulaiman & Moayedi, 2012). In addition, increasing the temperature of the KOH solution leads to higher conductivities. A rise of the specific conductivity from 0,6211 S\*cm<sup>-1</sup> to 1,0646 S\*cm<sup>-1</sup> was observed by measuring the

conductivity of a 30% w/w KOH solution at 25 °C and 100 °C, and consequently a higher efficiency was observed by operating the cell at higher temperatures (Gilliam, Graydon, Kirk & Thorpe, 2007).

It is common knowledge that the elements from group 8 (Fe, Ru, Os), group 9 (Co, Rh, Ir), group 10 (Ni, Pd, Pt) and their alloys are conventionally used as electrode, even if not all of these elements are suitable for their application in the water electrolysis process. Metals like platinum, iridium and gold are known to be the most efficient choices for the use of electrodes due to their high catalytic activity (Grimes C.A.; Varghese, O.K. & Ranjan, 2008). However, these noble metals are highly expensive, and therefore electrodes in commercial alkaline electrolyzers are typically made of nickel-plated steel and steel to bring down the material cost. The elements nickel, cobalt and iron have relatively low over potentials in KOH solution, and Ni additionally features high corrosion stability and seems to be one of the best choices as electrode material. The use of different commercial metals, covered with Ni, Co, Mo or other materials with electro-catalytic effects, as well as the treatment and modification of the electrode surface in order to obtain a large surface area to improve the reaction kinetics, is a general trend today. In addition, many experiments with advanced electrolyzers were performed, using different kinds of Ni, for example, Raney nickel, Ni foam substrate and Ni mesh. (Grimes, C.A.; Varghese, O.K. & Ranjan, 2008) (Bidault, B.; Middleton, Abson & Brandon, 2009) However, electrodes with a high percentage of Ni are more expensive in comparison to conventional kinds of steel, and frequently not affordable and economical for various electrolyzer projects.

Therefore, it became necessary to find commercial low costs metals, and to investigate them with respect to their properties during the electrolysis process by different types of measurement techniques

such as voltammetry and spectroscopy. Parameters affecting the total efficiency of an electrolyzer are the durability of the electrode material and the overvoltage in the electrolysis process. A further important basic parameter is the choice of a suitable metal for the electrodes, which was in our case predominantly limited by the material cost with the aim to keep this factor that is related to the total efficiency of an electrolyzer, as low as possible.

In view of these considerations, the goal of this paper is a study concerning the oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) of three conventional low cost metals and to evaluate them by means of typical electrochemical methods.

## Experimental

### Electrodes

The electrodes were prepared with stainless steel 430 (SS 430), stainless steel 304 (SS 304) and standard steel (ASTM A36), and controlled with a spectrometer, type GDS 500A, LECO, according to the respective norm. The specifications of the respective kinds of steel are depicted in Table I. These electrodes were immersed in polyethylene resin in order to protect the junctions between the metal parts and the wires from the caustic solution.

All steels before start measures are polished with increased sand paper into 120 to 240 mesh.

### Solutions

Solutions of 25% and 5% KOH where prepared by using KOH pellets, manufactured by Panreac, with a purity of 85%. To dissolve the solid KOH, distilled water with a grade of IV was used, subject to the regulations ASTM 1193-2001 with a conductivity of less than 5  $\mu\text{S}\cdot\text{cm}^{-1}$ , a pH between 5 and 8, as well as concentrations of Na and Cl short of 50  $\text{mg}\cdot\text{l}^{-1}$ .

Table I. Chemical composition for steel ASTM A36, stainless steel 304 and stainless steel 430 in % w/w (Davis, J.R., 1998).

Material	C %	Si %	Mn %	P %	S %	Cr %	Ni %
SS 430	0,05	1,0	1,0			16,0-18,0	
SS 304	0,08	1,0	2,0	0,05	0,03	18,0-20,0	8,0-10,5
A36	0,25	0,40	0,80	0,04	0,05		

## Electrochemistry experiments

### Equipment

For the current and voltage measurements a Gamry potentiostat galvanostat, model Reference 600, was used. It served to perform the different electrochemistry techniques to record the open circuit potential ( $E_{oc}$ ), as well as to obtain cyclic voltammetry (CV) and chronoamperometric (CA) curves. A common measure system was used, consisting of the working electrode with a geometrical area of 1 cm<sup>2</sup>, a large area Pt auxiliary electrode and an AgCl/Ag reference electrode. All the measured potentials have reference to AgCl/Ag.

All experiments were carried out at room temperature.

### Cyclic Voltammetry

Referring to the CV experiments, a number of cycles were applied between the limits of stability of the solution for the evolution of H<sub>2</sub> and O<sub>2</sub> in order to obtain potential ranges and various redox peaks for each material, in solutions of 5 % KOH and 25 %, with a scan rate of 50 mV\*s<sup>-1</sup>, and with influence of air.

### Cronoamperometry

CA was performed in the region of H<sub>2</sub> evolution to assess the stability of the currents by applying poten-

tial jump from  $E_{oc}$ . Paying attention not to exceed the limits of the equipment that was operating in an open system because the potential exceeds the limits where the HER starts. This process served to estimate the quantity of hydrogen evolution at the same potential employing different steels.

## Results and discussion

### Cyclic voltammetry for several kinds of steel under different conditions

A variety of CV were performed between the limits of stability of the solution for the evolution of H<sub>2</sub> and O<sub>2</sub>, demonstrating the various redox peaks for each material in a solution of 5% KOH with a scan rate of 50 mV\*s<sup>-1</sup> these are depicted in figure 1.

The value of  $E_{oc}$  oscillates in a range of (-200 to -400) mV for all steels in both solutions.

In the case of SS 430, an oxidation peak of Fe (A1) is identified at a value near to (-675) mV and another one at the potential of (+350) mV associated to the oxidation of Cr (A2), whereas the reduction of Fe (C1) in (-1050) mV.

With respect to the CV of SS 304, the oxidation peaks were obtained at values of (-700) mV (A1) and (+350) mV (A2), similar to the results of SS 430. Referring to the reduction peaks, an additional peak associated to Ni appears at (+370) mV (C2), and

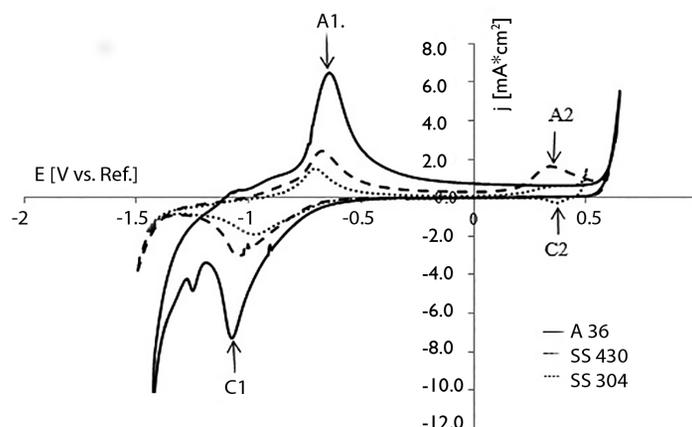


Figure 1: Cyclic Voltammetry of the different steels samples: 430 (dashed line), 304 (dotted line) and A36 (solid line) in a KOH 5% solution with at a velocity of 50 mV\*s<sup>-1</sup>, illustrating the different oxidation and reduction peaks, as well as the initial potential for the OER and HER.

the reduction peak of Fe appears at a potential of (-975) mV (C1).

For Steel A36 the main peak of the Fe oxidation (A1) was observed at (-635) mV, and in addition two reduction peaks for the iron at a potential of (-1050) mV (C1) and (-1200) mV were recognized, representing different reduction stages of Fe (Rebouillat, Lyons, Brandon & Doyle, 2011) (Freire et al., 2012) (Wieckowski & Ghali, 1985) (Song, Gervasio & Reserve, 1996).

CV were performed at concentrations of 5 and 25% KOH, to see differences. These showed slight variations in potential of the peaks, as well as at the highest peak increase in their intensities, by increasing the concentration of KOH, associated with the increased conductivity of the solution (see Table 4).

The CV experiments, carried out with different concentrations of KOH (5% and 25%), featured the effect of a displacement of the HER's and OER's initial potential, relative to the different materials, which can be seen in Table 2.

The increase of the KOH concentration led to a reduction of around 100 mV in the range of potential. The potential where the H<sub>2</sub> was released moved to a slightly lower value, while it was observed that the O<sub>2</sub> evolution potential decrease was higher.

Steel A36 exhibited the lowest initial potential for the H<sub>2</sub> evolution, whereas sample of SS 304 attained the lowest potential at the side where the evolution of O<sub>2</sub> occurs.

The initial slopes, calculated for each of the systems, showed increases in the KOH concentration and decreases in the values of electrode steel 304. An

enhancement of the concentration led to a rise of the slopes, for H<sub>2</sub> and O<sub>2</sub> by using electrode Steel A36. For sample of steel 430 the results differed and an increase for the H<sub>2</sub> side was noticed, while the contrary took place for O<sub>2</sub>.

### Measurement of H<sub>2</sub> evolution at a fixed potential

CA was performed to ascertain the H<sub>2</sub> production of the different metals in KOH solutions of 5 and 25% with respect to time. After adapting the E<sub>oc</sub> to the samples for a short initial period of 100 s, a defined and stable voltage of -1,8V was applied for 600 s, the respective charge measured and converted into amount of substance, applying a geometrical area of 1 cm<sup>2</sup>.

Applying low potentials shows that the evolution of H<sub>2</sub> is relatively stable over time (Freire et al., 2012) (Wieckowski & Ghali, 1985) (Song et al., 1996) (Olivares-Ramírez, Campos-Cornelio, Uribe Godínez, Borja-Arco & Castellanos, 2007). The amount depends on -1,8V generated from the electrode and the concentration of KOH, finding that increasing the concentration of 5% to 25%, H<sub>2</sub> production in SS 430 and A36 is doubled, whereas SS304 is approximately 1,5. This is shown in Figure 2.

During the evolution of hydrogen, the electrode behavior of SS 430 and steel A36 was similar, and the SS 304 featured the highest evolution of H<sub>2</sub> compared to the other samples in both KOH solutions. This behavior can be associated with the Ni content and its electro-catalytic effect in respect to the other materials (Bidault et al., 2009) (Freire et al., 2012) (Wieckowski & Ghali, 1985) (Song et al., 1996) (Olivares-Ramírez et al., 2007).

Table 2: Potential of H<sub>2</sub> and O<sub>2</sub> evolution (mV) for different materials tested at their global range, as well as the initial slopes of detachment (V\*A<sup>-1</sup>).

Material	KOH (%)	Evol. H <sub>2</sub> (mV)	Evol. O <sub>2</sub> (mV)	Range (mV)	Slope H <sub>2</sub> (V*A <sup>-1</sup> )	slope O <sub>2</sub> (V*A <sup>-1</sup> )
SS 430	5	-1500	600	2100	25,5	31,8
SS 430	25	-1550	500	2050	48,7	8,6
SS 304	5	-1500	600	2100	70,2	27,5
SS 304	25	-1550	400	1950	19,4	4,0
A36	5	-1450	650	2100	7,1	12,5
A36	25	-1450	560	2010	18,3	20,2

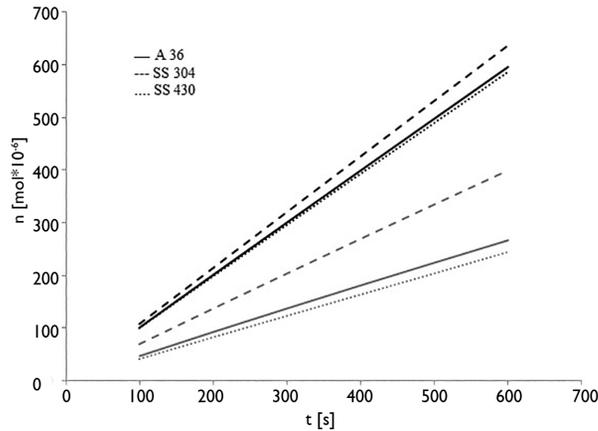


Figure 2. Amount of H<sub>2</sub> evolved at a fixed potential of -1800 mV in KOH solutions of 5% (grey) and 25% (black) with the time, for A36 (solid line), SS 304 (dashed line) and SS 430 (dotted line).

It was observed that increasing the concentration of the solution led to a higher increase of the H<sub>2</sub> production rate using electrodes SS 430 and A 36 compared to SS 304, which can be seen in the difference of the slopes presented in table 3.

### Effects of the HER on the distinct kinds of steel

CV was carried out before and after the HER to obtain voltammograms showing the effects of the HER on the materials, where the HER was conducted by applying a fixed potential similar to the experiment of 2.3 using the CA-method to perform the detachment of H<sub>2</sub>.

Table 3: Different slopes for evolution of H<sub>2</sub> for SS 430, SS 304 and steel A36 in KOH solution of 5% and 25%.

Material	KOH	Slope [mol*10 <sup>-6</sup> *s <sup>-1</sup> ]
SS 430	5%	0,405
SS 430	25%	0,989
SS 304	5%	0,661
SS 304	25%	1,058
A 36	5%	0,439
A 36	25%	0,974

The evolution of H<sub>2</sub> affects the peaks of the electrodes, mainly modifying the oxidation and reduction peaks of Fe, while the other peaks kept stable or became more defined after the HER as depicted in figure 3 for SS 304 (Olivares-Ramírez et al., 2007).

It was observed that the height of the peaks increased in both solutions after the HER was carried out, as represented in table 4. The differences of the rise in the peaks were not significantly different in respect to the distinct concentrations of KOH.

In A36 the change in the peaks is not significant, but for SS 430 if concentration of KOH increases, the change in the peaks decreases. For SS 304 if concentration of KOH increases affect the different form the peaks, the A1 peak increases, while the C2 peak decreases, and for the others, the effect on the peak is not significant.

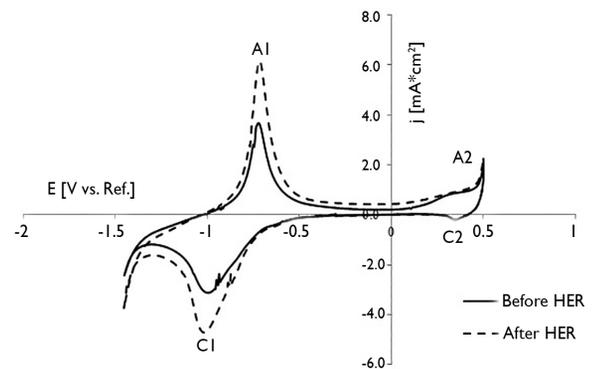


Figure 3. A graphic illustrating the CV for SS 304 in the diluted solution of 5% KOH before (solid line) and after (dashed line) the HER.

Table 4: Relation of the height between the different occurring peaks before (b) and after (a) the HER in KOH 5% (see Figure 3).

Material	KOH [%]	A1 a. / A1 b.	A2 a. / A2 b.	C1 a. / C1 b.	C2 a. / C2 b.
SS 430	5	3,21	1,23	2,75	-
SS 430	25	1,21	1,28	1,42	-
SS 304	5	1,68	1,07	1,51	2,82
SS 304	25	2,80	1,14	1,88	1,49
A36	5	1,57	-	1,49	-
A36	25	1,64	-	1,60	-

### Estimation of use in bipolar cell for the distinct kinds of steel

Applying CV beyond HER and OER can estimate the necessary potential for a given current in a bipolar cell (same electrode where anode and cathode).

The figure 4 presents the relationship DE vs I obtained in each type of steel. You can see that it takes less of DE for the same intensity with SS304, with respect to SS430 or A36.

### Conclusions

the stainless steel shows more peak in a CV about normal steel (A36) and with low current.

It was observed that all materials are generally located in the same range of potential in view of the potential necessary to start the HER and OER, respectively.

Furthermore, it was found that the use of a 25% KOH solution serves to reduce the initial potential of the HER and OER and is therefore recommended as an electrolyte.

In general, steel A36 featured the lowest initial potential for the evolution of H<sub>2</sub>, while the different kinds of stainless steel showed similar potentials that were a shade higher.

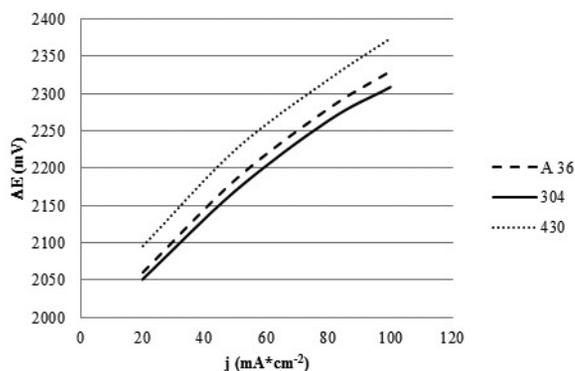


Figure 4. DE vs j for different steel: 430 (dotted line), 304 (solid line) and A36 (dashed line) in a KOH 25% solution, CV with at a velocity of 50 mV\*s<sup>-1</sup>

The initial slope for H<sub>2</sub> and O<sub>2</sub> evolution decreases only for 304 when there is an increase in the KOH concentration.

In terms of the evolution of hydrogen at a fixed potential (-1800 mV), electrode SS 304 exhibited the highest production of H<sub>2</sub>, qualifying that there is a most efficient option for the use as cathode in the materials evaluated.

The KOH concentration of the electrolyte turned out to have an important influence on the production rate, where an increased 5% to 25% KOH concentration approximately doubles the H<sub>2</sub> production.

Necessary potential for use this steels where bipolar plate, show what SS 304 is the best material of the samples.

The effect of the HER on the electrodes, investigated by the voltammetry measurements before and after the evolution of H<sub>2</sub>, present high differences in peaks associated to Fe, and did not show an important modification in other peaks.

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