

A Kinetic Study of The Hydrogen Evolution Reaction in Phosphoric Acid Solutions with Iron and Manganese Phosphatized Steel Cathodes.

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ABSTRACT

Electrocatalytic hydrogen evolution reaction (HER) on different electrode materials such as Pt, Au and Al has been studied extensively, due to the potential application of molecular hydrogen H_2 as a green fuel as well as the new promising utilization of monoatomic hydrogen species $H\bullet$ (intermediate product of HER) as a powerful reducing agent to carry out the electrocatalytic hydrogenation reactions of minerals and organic materials. However the Pt and Au electrode materials are very expensive. Consequently, knowledge about novel aqueous and electrode catalysts which promote an increase in the HER kinetics is necessary to operate efficiently a Sustainable Hydrogen Generation Electrolytic Cell. In this investigation a kinetic study of the HER was carried out employing a steel rotating disk with different aqueous solutions containing Phosphoric Acid (H_3PO_4) with or without metallic manganese (Mn) and Nitric Acid (HNO_3). Furthermore, the HER was evaluated on iron and manganese phosphate coatings. Analyses of Tafel plots and the charge transfer coefficients, revealed one electrical potential zone where the monoatomic hydrogen can be recombined electrochemically to H_2 as the rate determining step, with charge transfer coefficients similar to an activationless process ($\alpha \rightarrow 0$). On the other hand, an increase in the concentration of H_3PO_4 promotes a higher exchange current for the HER. The Mn in the aqueous solutions has a catalytic effect on the hydrogen generation rate at room temperature. However, the precipitation of $Mn_3(PO_4)_2$ on steel decreases the HER kinetics at high temperatures. The formation of $FePO_4$ on steel promotes the highest rate for the electrochemical recombination of monoatomic hydrogen to H_2 ; actually these observations are also supported with SEM (Scanning Electron Microscopy) characterizations.

1. Introduction

Hydrogen, as a high-quality clean and renewable energy resource, is increasingly considered as one of the most promising candidates for the fuel of the future [1, 2].

Hydrogen evolution reaction (HER) in aqueous solution is one of the most often studied electrode reactions [3, 4].

During the last decades, it has been well established that (HER) occurs via two successive elementary events. The initial discharge of hydrogen ions to adsorbed monoatomic hydrogen (equation 1) [5].



Followed by the chemical (equation 2) or electrochemical (equation 3) recombination of monoatomic hydrogen to molecular hydrogen.



It is well known that water electrolysis is an important technique for hydrogen generation. Although, water electrolysis is not the cheapest method of hydrogen production, it supplies hydrogen of a very high purity in large quantity. Unfortunately, the high energy consumption mainly caused by HER overpotential restrains its application at the present days [6]. One proposed alternative to solve this problem is to use noble metals (such as Pt, Au) as cathode materials for the HER. However, these metals are not only expensive, actually the platinum and gold worldwide reserves are limited [7].

On the other hand, other metallic electrodes such as steels are commonly employed for water electrolysis but these are very susceptible to corrosion effects and consequently their life time is decreased [1]. In this sense, other authors have proposed the use of new and cheap cathode materials resistant to corrosion, for example: the aluminum, Inconel alloys and glassy carbon, however the latter has a very low electrical conductivity, therefore the energy consumption is high. [5]

Another alternative to reduce the corrosion effects relies on the protection of steel cathodes against corrosion employing the iron and zinc phosphatizing process [8]. Therefore, this research studied the effect of iron and manganese phosphate coatings on steel on the HER mechanism and kinetics. It was also evaluated the effect of the manganese ion on the HER.

For that reason, the main objective of this research was to understand the nature of HER on different phosphatizing solutions, to determine the different potential regions and solution conditions for carrying out the HER with different phosphatized cathodes.

2. Experimental Section

Table 1. Chemical composition of the steel disk.

Si 0.247 %	Mn 0.452 %	Cr 1.02 %
Ni 0.075 %	Mo 0.885%	V <0.0004 %
Cu 0.101 %	Al 0.014 %	Ti 0.004 %
Nb 0.035 %	C 0.280 %	S 0.061 %

Steel disk electrodes 10 mm diameter and 0.8 mm thick were prepared with the chemical composition given in Table 1. The sample was mounted in a Teflon support using silver paint connected to a copper wire as an electrical conductor.

2.1. Electrochemical Study

a. Pre-treatment of the substrate surface

The steel samples were conditioned in different ways to be used later in the electrochemical tests: linear polarization (Tafel curves) using the following procedures:

Samples tested were polished to a mirror like finish. Initially, samples were ground on SiC paper of various grain sizes followed by a polishing with Al_2O_3 powder of 0.1 microns and then washed with alcohol. Finally, the samples were glued to a Teflon support using silver paint.

All samples after pre-treatment were immediately phosphatized by immersion in different phosphatizing solutions.

b. Phosphatizing process

Different phosphatizing solutions were tested, varying the concentrations of H_3PO_4 and Mn with and without the presence of catalyst (HNO_3) at temperatures of 25, 50, 80 and 90 °C. Table 2 shows in detail the conditions of the various solutions studied:

Table 2. Phosphatizing solutions.

Solution	H_3PO_4 (mol/L)	Mn (mol/L)	HNO_3 (mol/L)	Temperature (°C)	pH
A	0.47	-	-	25, 50, 80, 90	-
B	0.94	-	-	25, 50, 80, 90	-
C	0.94	0.6	-	25, 90	1
D	0.94	0.6	0.2	90	2.57

It is worth to mention that the phosphatizing solutions A and B were used in order to produce the iron phosphate coating on the steel disk electrode. On the other hand, Solution C was employed to generate an iron phosphate

coating on the steel with the presence of Mn ion in solution. Finally Solution D was used to form the manganese phosphate coating on the steel disk electrode.

The phosphatizing and the HER tests were carried out in a conventional three electrodes electrochemical cell (see Figure 1). The cell consisted of a 250 mL round-bottomed flask, instrumented with a thermometer, a Ag/AgCl reference electrode (ThermoScientific Orion) in contact with the solution through a Luggin capillary, a high purity graphite rod (Alfa Aesar) as a counter electrode and a port to place the working electrode (steel sample). The electrochemical cell was placed in a heating mantle.

The procedure used to study the phosphatizing process along with the HER was as follows: the prepared phosphatizing solution was placed (200 mL) in the electrochemical cell (Figure 1), then the solution was heated to the desired temperature (since 25 to 90 °C), once the thermal equilibrium was reached, the working electrode was introduced (steel sample) and connected to the potentiostat PGZ301 (VoltaLab). The polarization curves were recorded in the cathode direction every four minutes during the immersion process. At the end, the phosphatized steel sample was withdrawn (working electrode), rinsed with distilled water and then it was characterized by microscopy. The following sections describe the technique of linear polarization and microstructural characterization used.

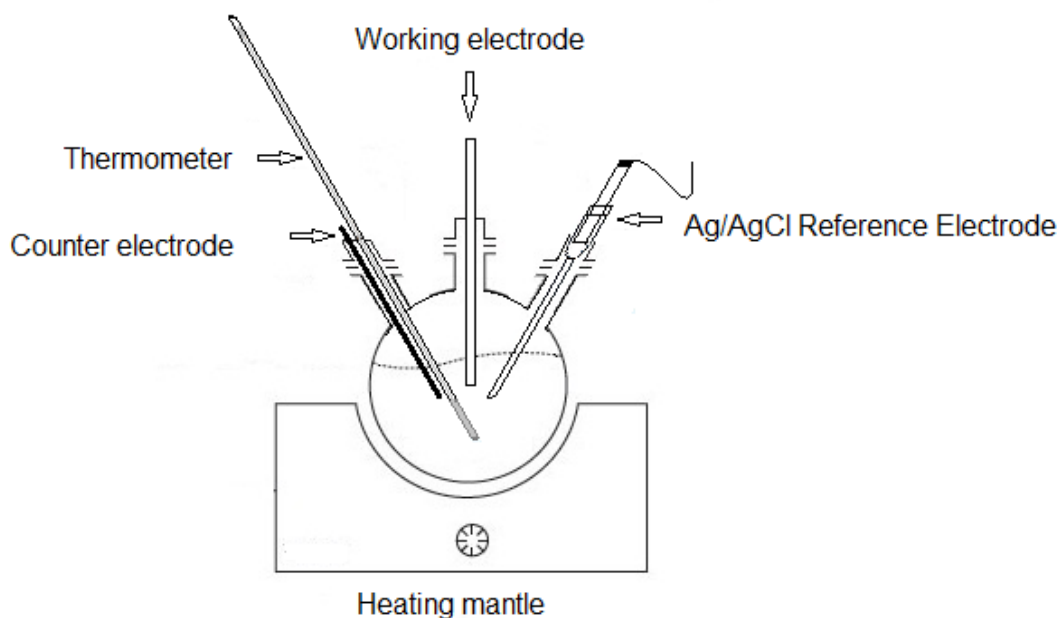


Figure 1. Single-Chamber, three-electrode electrochemical cell for the phosphatizing experiments.

c. Measurement of corrosion potential (E_{corr}) during the phosphatizing process

The measurements of E_{corr} of steel during the phosphating process were performed at various temperatures using the experimental setup described in the previous section. For accomplishing this, the following electrochemical technique was used:

E_{corr} measurement technique: Polarization curves were performed, sweeping the potential linearly at 10mV/s from -700 mV to 50 mV vs Ag/AgCl at different temperatures. The polarization curves were carried out every 4 min during 24 min of experimentation. In order to study the HER kinetics, data obtained from E vs. i (current vs. potential) curves in the cathode direction were converted to E vs $\log i$, better known as Tafel curves. The E_{corr} was also calculated in the different acid solutions H_3PO_4 using the VoltaMaster software.

2.2. Morphological characterization of the resulting coatings

The morphology of the coatings were examined by SEM (Phillips, Model: XL30ESEM) taking secondary electron images.

3. Results and Discussion

The polarization behavior of hydrogen evolution on all cathodes was studied at a microelectrolysis level, varying acidity, temperature and component in the phosphatizing solution. The polarization behavior on the steel cathodes in presence of manganese ion is shown.

Before presenting the results it is important to show the shape of the polarization curves resulting. The Figure 2 shows a typical polarization curve, or complete Tafel plot with the Tafel lines and slopes.

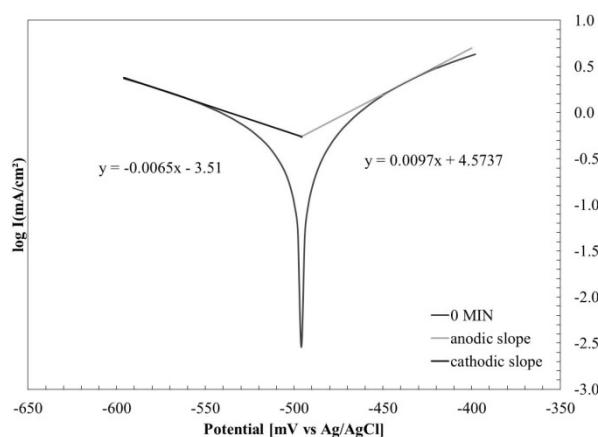


Figure 2. Typical polarization curve or Tafel plot, representing the Tafel lines for an anodic and cathodic process.

The Tafel slope (b') obtained in a polarization curve corresponds basically to three types of processes, which represent a controlling discharge reaction: barrierless with ($\alpha=1$), ordinary discharge with ($\alpha=0.5$) and activationless

discharge with ($\alpha = 0$). The physical meaning of these types of processes relies on the magnitude of the activation energy in the discharge reaction [5].

3.1. Effect of the acidity at different temperatures without Mn in solution

Figure 3 presents the charge transfer coefficients for a 0.47 M H_3PO_4 solution at different temperatures (25, 50, 80, 90°C), these charge transfer coefficients were obtained from a Tafel analysis of Figure 4, employing the next equation, which represents the slope term in the Tafel equation:

$$b' = \frac{RT}{\alpha nF} \quad (4)$$

It is interesting to note, that the charge transfer coefficients remain almost constant during the 24 min of the phosphatizing process in a range from 0.16 to 0.26. These charge transfer coefficients are representative of an activationless process ($\alpha \rightarrow 0$), suggesting a low activation energy for the HER.

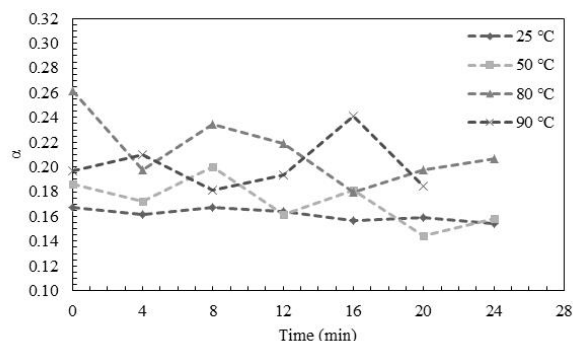


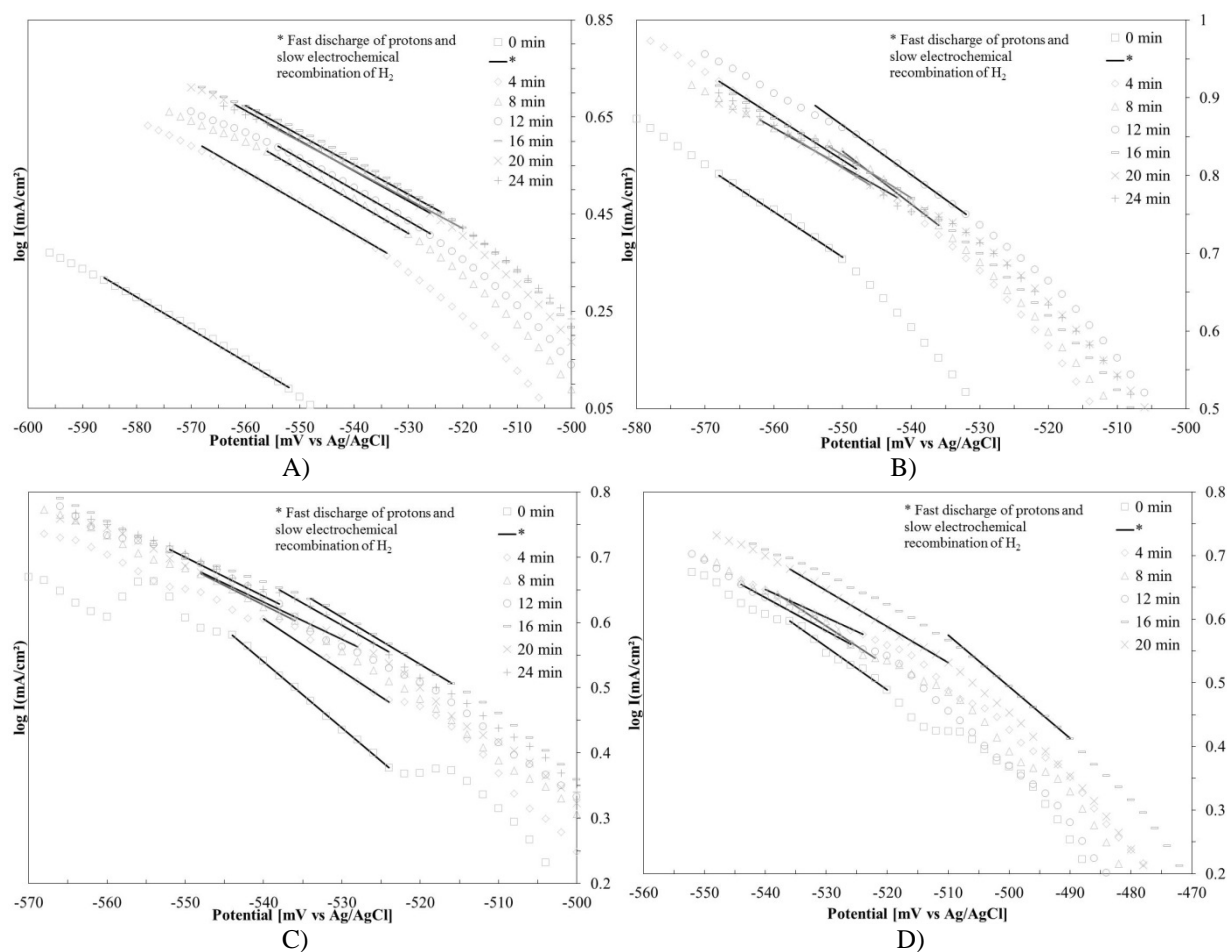
Figure 3. Comparison of charge transfer coefficient (α) at different temperatures and times in an aqueous 0.47 M H_3PO_4 solution.

Experimental polarization curves for the hydrogen evolution reaction at different acidity and temperature are shown in Figure 4 and 6. Figure 4 shows the cathodic polarization curves for a 0.47 M H_3PO_4 solution at 25°C, 50°C, 80°C, 90°C (Figures 4A, 4B, 4C, and 4D, respectively) this polarization curves were registered every 4 min during 24 min of immersion.

The Figure 4A shows that the production of HER is slow when the experiment was commenced due to at time 0 the steel surface was clean (without any layer on it) and when the immersion time is increased, the hydrogen production rate raises due to the formation of an iron phosphate coating on the steel and this type of coating favors the HER kinetics. For example this behavior can be observed in Figure 4A at a potential of -560mV vs Ag/AgCl where the

current density is increased at higher processing times than 0 min. Furthermore the exchange current density (i_0) is increased while the phosphatizing process proceeds (see Table 3). The Tafel slopes (b') in all cases are very similar (see Table 3A), suggesting the same type of HER mechanism, according to Fuentes-Aceituno and Lapidus (2012) [5], the most probable mechanism that is occurring in these type of systems can be a slow electrochemical recombination of monoatomic hydrogen to H_2 , representing the rate determining step of HER.

On other hand, the temperature promotes an increase in the HER kinetics, this result was expected from the viewpoint of electrochemical reactions kinetics theory, however it is worth to mention that the formation of the iron phosphate coating is accelerated at higher temperatures than 25°C , for this reason, it is probable that the iron phosphate coating can accelerate the HER kinetics, as was shown at 90°C (Fig. 4D). Actually it requires low energy to carry out the HER, for example the potential at this temperature was $-500\text{ mV vs Ag/AgCl}$, while at 25°C the potential corresponded to $-560\text{ mV vs Ag/AgCl}$.



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Figure 4. Comparison of the cathodic polarization curves for immersion of steel in an aqueous H_3PO_4 solution at A)25°C, B)50°C, C)80°C, D)90°C. All experiments employed 0.47 M H_3PO_4 . The polarization curves were recorded every 4 minutes during the immersion process.

When the solution temperature was controlled at 50°C, the same phenomena were observed. However, some differences in the current density were elucidated, basically it was observed that the current incremented significantly in comparison with the others tested temperatures. Moreover, the exchange current density at this temperature was the highest ($1.44 \text{ mA}\cdot\text{cm}^{-2}$), which means that the HER kinetics at this condition is favored (Table 3B). It was mentioned before, that iron phosphate coatings are favored when the temperature is increased, and therefore this phenomenon at 50 °C may be related to a different coating morphology obtained under this particular condition.

Table 3. Kinetic parameters for the electrochemical recombination rate-controlling step, employing an aqueous 0.47M H_3PO_4 solution. A) 25°C, B) 50°C, C) 80°C, D) 90°C.

A)				B)			
Time (min)	b' (V/decade)	i_0 ($\text{mA}\cdot\text{cm}^{-2}$)	a	Time (min)	b' (V/decade)	i_0 ($\text{mA}\cdot\text{cm}^{-2}$)	a
0	-0.154	0.771	-3.510	0	-0.149	1.350	-2.986
4	-0.159	1.000	-2.993	4	-0.161	1.448	-2.582
8	-0.154	1.062	-3.030	8	-0.139	1.350	-3.150
12	-0.156	1.062	-2.976	12	-0.172	1.448	-2.325
16	-0.164	1.133	-2.724	16	-0.154	1.350	-2.764
20	-0.161	1.133	-2.795	20	-0.192	1.448	-2.070
24	-0.167	1.133	-2.670	24	-0.175	1.448	-2.334

C)				D)			
Time (min)	b' (V/decade)	i_0 ($\text{mA}\cdot\text{cm}^{-2}$)	a	Time (min)	b' (V/decade)	i_0 ($\text{mA}\cdot\text{cm}^{-2}$)	a
0	-0.116	0.882	-4.092	0	-0.159	1.020	-2.788
4	-0.154	1.133	-2.936	4	-0.149	1.020	-2.943
8	-0.130	1.133	-3.512	8	-0.172	1.133	-2.473
12	-0.139	1.139	-3.249	12	-0.161	1.127	-2.718
16	-0.169	1.221	-2.532	16	-0.130	1.064	-3.339
20	-0.154	1.221	-2.894	20	-0.169	1.139	-2.490
24	-0.147	1.133	-3.025				

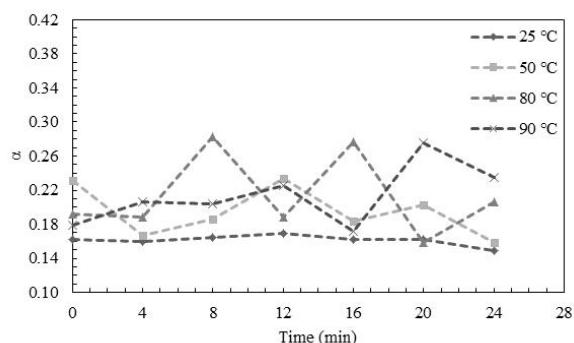
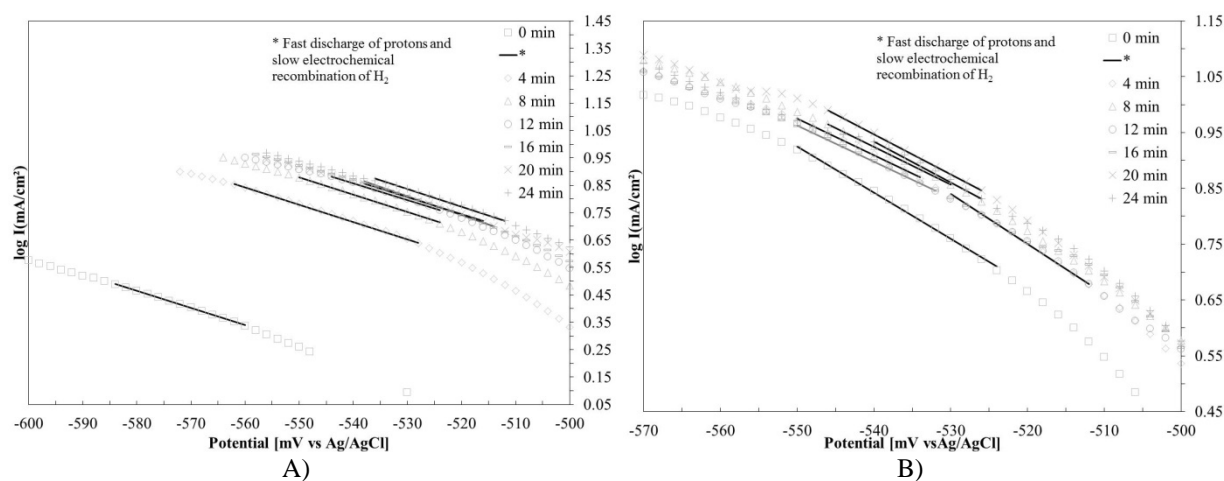


Figure 5. Comparison of charge transfer coefficient (α) at different temperatures and time in an aqueous 0.94 M H_3PO_4 solution.

On the other hand, when the acidity is increased to 0.94M, the charge transfer coefficient remains similar to an activationless process as can be seen in Figure 5. Furthermore the Tafel slopes b' (see Table 4) are very similar to the 0.47M condition (Table 3), therefore the electrochemical recombination of monoatomic hydrogen to H_2 is the rate determining step for the HER.

However, an increase in the H_3PO_4 concentration promotes a high current density for the HER as can be seen in Figure 6A at -560 mV vs Ag/AgCl. For example, the current density increased around $0.25\text{mA}/\text{cm}^2$ since the beginning of the phosphatizing process, in comparison with the Figure 4A at -560 mV, where the current density was around $0.10\text{mA}/\text{cm}^2$. Furthermore the exchange current densities for this acid concentration at different temperatures were higher (see Table 4) than the 0.47M concentration (see Table 3). It was also observed that the current density was favored when the temperature was raised up to 90°C .



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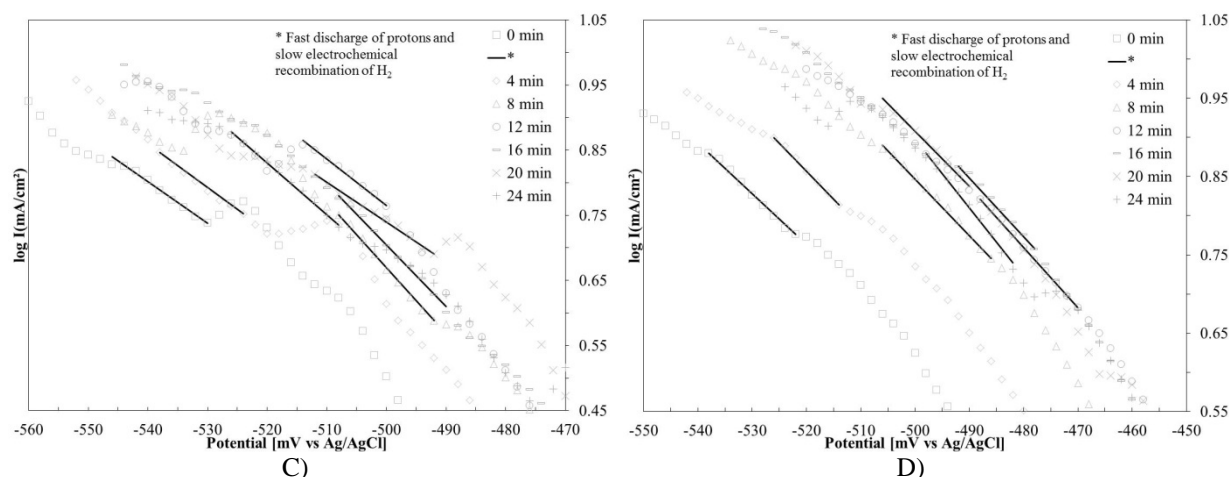


Figure 6. Comparison of the cathodic polarization curves for immersion of steel in an aqueous H_3PO_4 solution at A) 25°C, B) 50°C, C) 80°C, D) 90°C. All experiments employed 0.94 M H_3PO_4 . The polarization curves were recorded every 4 minutes during the immersion process.

Figure 6 shows the cathodic polarization curves for the four tested temperatures, it is possible to see that at 50°C in all immersion times the highest current density recorded at -570 mV vs Ag/AgCl was around 1.00 mA/cm^2 , for that reason this temperature could be a good condition for improving the HER kinetics. However, when the temperature was increased to 90°C, the potential or energy required to carry out the H_2 production is lowered (Fig 6D).

Table 4. Kinetic parameters for the electrochemical recombination rate-controlling step, employing an aqueous 0.94 M H_3PO_4 solution. A) 25°C, B) 50°C, C) 80°C, D) 90°C.

A)				B)			
Time (min)	b' (V/decade)	i_0 (mA*cm ⁻²)	a	Time (min)	b' (V/decade)	i_0 (mA*cm ⁻²)	a
0	-0.159	1.051	-3.183	0	-0.120	1.455	-3.632
4	-0.161	1.419	-2.655	4	-0.167	1.649	-2.312
8	-0.156	1.419	-2.647	8	-0.149	1.568	-2.717
12	-0.152	1.419	-2.675	12	-0.119	1.455	-3.639
16	-0.159	1.455	-2.518	16	-0.152	1.462	-2.672
20	-0.159	1.455	-2.521	20	-0.137	1.568	-2.901
24	-0.172	1.462	-2.216	24	-0.175	1.649	-2.132

C)				D)			
Time (min)	b' (V/decade)	i_0 (mA*cm ⁻²)	a	Time (min)	b' (V/decade)	i_0 (mA*cm ⁻²)	a
0	-0.159	1.455	-2.578	0	-0.175	1.455	-2.194
4	-0.161	1.350	-2.456	4	-0.152	1.455	-2.551
8	-0.108	1.221	-3.986	8	-0.154	1.492	-2.385

12	-0.161	1.455	-2.337	12	-0.139	1.455	-2.688
16	-0.110	1.221	-3.850	16	-0.182	1.649	-1.878
20	-0.192	1.492	-1.840	20	-0.114	1.284	-3.480
24	-0.147	1.350	-2.685	24	-0.133	1.350	-2.877

Until this moment, it has been showed the effect of employing different phosphatizing solutions on the HER, and it was proposed the iron phosphate coatings as a detrimental factor to increase the hydrogen evolution kinetics. Furthermore in the last Figures it was mentioned that the coating morphology plays an important role in the HER kinetics. Actually, Alvarado-Macías et al (2013) revealed a continuous change of the coating morphology during the immersion time, i.e. the layer nature can be porous or even uniform. [8]

As can be seen in Figure 7, the morphology of the iron phosphate coating on steel presents craters in the entire surface, which can be associated to the continuous evolution of hydrogen bubbles. Therefore, this micrograph can show that hydrogen can be produced on iron phosphate surfaces. Actually these results are in good agreement with the findings reported by Alvarado-Macías et.al. [8]

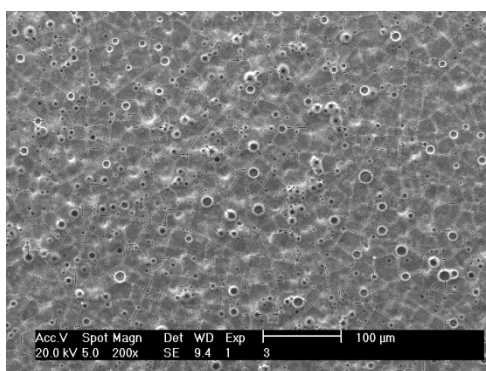


Figure 7. Microstructural characterization of the iron phosphate coating employing a phosphatizing solution with 0.94 M H_3PO_4 at 90°C

3.2. Effect of the temperature and Mn in solution on the H_2 evolution kinetics

On the other hand, the effect of Mn ions in solution were tested on the HER kinetics, using the same acidity 0.94 M H_3PO_4 at pH 1 and 25 or 90°C. Figure 8, revealed similar charge transfer coefficients behaving as an activationless process, which suggests low activation energy for the HER. The Tafel plots presented in Table 5 are characteristic for the same mechanism: the fast discharge of monoatomic hydrogen and a slow electrochemical recombination of H_2 . Figure 9, shows the polarization curves for this manganese solution, the results shows that Mn in solution had a catalytic effect on the hydrogen generation rate at room temperature and the coating formed on the steel was iron phosphate, actually when the temperature was increased up to 90°C the generation rate was favored. Furthermore the

exchange current densities for these experiments (Table 5) were the highest when they are compared with that of Table 4, i.e. without the presence of Mn in solution.

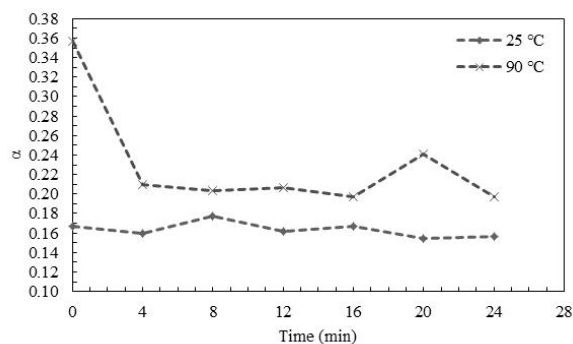


Figure 8. Comparison of charge transfer coefficient (α) at different temperatures and times in an aqueous H_3PO_4 -Mn solution; 0.94 M, pH=1.

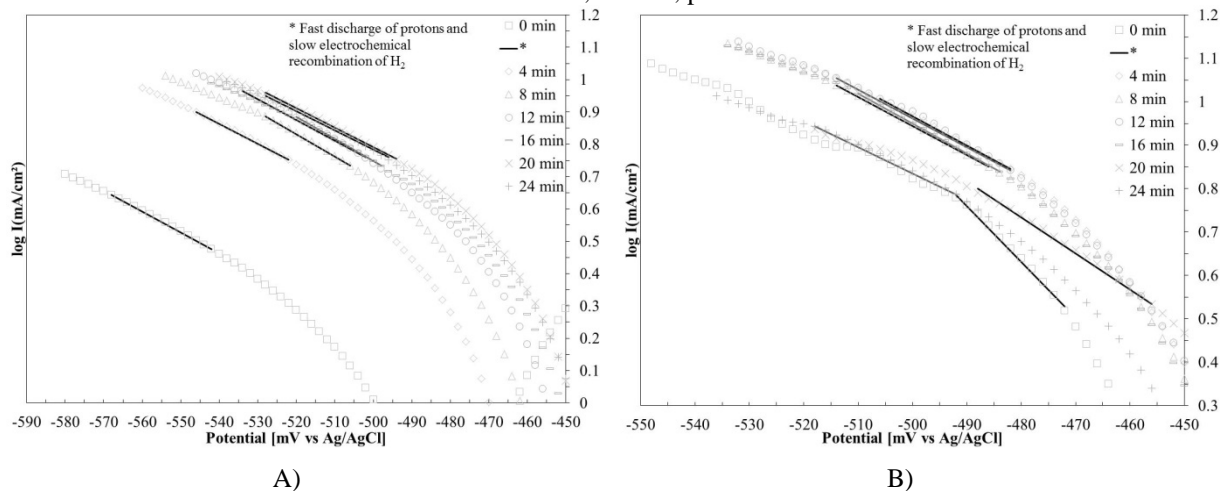


Figure 9. Comparison of the cathodic polarization curves for immersion of steel in an aqueous H_3PO_4 -Mn solution at A) 25°C, B) 90°C. All experiments employed 0.94 M H_3PO_4 and Mn. The polarization curves were recorded every 4 minutes during the immersion process.

This catalytic effect can be clearly observed by comparing the cathodic polarization curves of the solution C at 25°C (Figure 9A) with the curves of the solution B at the same temperature (Figure 6A). For example, if the cathode potential is fixed at -520 mV vs Ag/AgCl, it can be observed an increment in the current density at 24 min, i.e. the Figure 6A has 0.75mA/cm² approximately; however the current density was increased to 0.95mA/cm² (Figure 9A). It can be also observed in the end of the immersion time (Figure 6A), that the potential became more negative in comparison with that of Figure 9A and this represents a higher energy consumption to produce H_2 without

manganese than with the presence of manganese ions. On the other hand, the catalytic effect of manganese ions on the HER kinetics can be also observed at 90°C (Figure 9B). Actually, the current density recorded for a solution without manganese was higher than with a solution containing manganese, for example with a fixed potential of -520 mV vs Ag/AgCl the current density was 0.95mA*cm⁻² (see Figure 6D), on the other hand, the presence of manganese promotes an increase in the current value around 1.05mA/cm² (see Figure 9B).

Table 5. Kinetic parameters for the electrochemical recombination rate-controlling step, employing an aqueous H₃PO₄-Mn solution; 0.94 M. A) 25°C, B) 90°C.

A)				B)			
Time (min)	b' (V/decade)	i ₀ (mA*cm ⁻²)	a	Time (min)	b' (V/decade)	i ₀ (mA*cm ⁻²)	a
0	-0.154	1.127	-3.048	0	-0.088	1.284	-4.852
4	-0.161	1.455	-2.460	4	-0.149	1.649	-2.403
8	-0.145	1.455	-2.764	8	-0.154	1.649	-2.302
12	-0.159	1.462	-2.394	12	-0.152	1.649	-2.332
16	-0.154	1.455	-2.474	16	-0.159	1.665	-2.207
20	-0.167	1.568	-2.208	20	-0.130	1.284	-2.982
24	-0.164	1.568	-2.249	24	-0.159	1.492	-2.304

Figure 10 displays the microstructural characterization of the iron phosphate coating during the hydrogen evolution experiments. The iron phosphate coating presented more craters than that of Figure 7, it is important to remember that the craters were related to the generation of hydrogen bubbles on the coating surface. Therefore, this Figure 10, shows an increase in the number of craters or holes, so it is indicative the HER is promoted under this condition. In addition to the last, two different types of morphology are shown; 1) a porous layer and 2) a less porous uniform layer, probably these differences can be associated to the different composition of the iron phosphate layers.

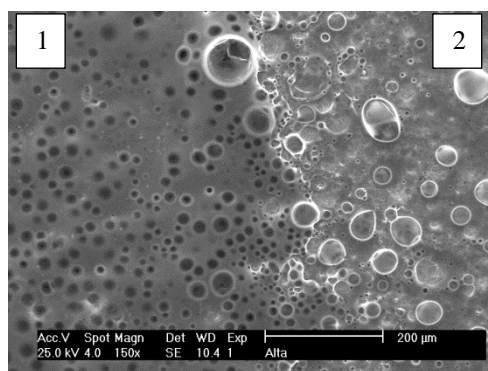


Figure 10. Microstructural characterization of the iron phosphate coating employing a phosphatizing solution with 0.94 M H_3PO_4 and Mn in solution at 90°C. 1) Porous Layer, 2) Less Porous Uniform Layer.

3.3. Effect of the manganese phosphate coating on the H_2 evolution kinetics

Finally when the manganese phosphate coating was tested on steel, the results showed that the hydrogen generation was decreased considerably in comparison with the iron phosphate coatings. Figure 11, displays the charge transfer coefficients for a phosphatizing solution containing 0.94M H_3PO_4 , 0.6M Mn and 0.2M HNO_3 (as a catalyst for the manganese phosphate generation), it is interesting to note that the charge transfer coefficients were very similar to that of Figure 3, 5 and 8, which are related to an activationless process. Actually the Tafel slopes recorded at different immersion times (Table 6) showed that a different HER mechanism is occurring at lower generation rates than with the iron phosphate coatings. Furthermore, it is possible to observe the current density decreased drastically during the immersion time (see Figure 12), i.e. the current density was $0.6\text{mA}/\text{cm}^2$ at -670 mV vs Ag/AgCl and 0 min, while in the end the current reached a value of $-0.1\text{mA}/\text{cm}^2$ at -620 mV vs Ag/AgCl, this suggests that HER was inhibited. Actually the exchange current density at 12 and 20 minutes decreased (Table 6) in comparison with any condition tested in this research. On the other hand, Figure 12 shows the necessity to apply a more negative potential to activate the HER than the other conditions showed in Figure 9B, indicating an increase in the energy consumption.

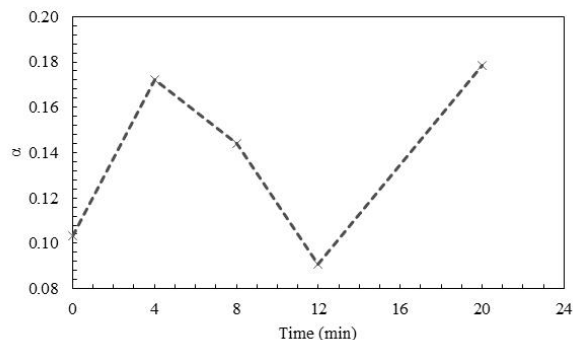


Figure 11. Comparison of charge transfer coefficient (α) at different times on a manganese phosphate coating at 90°C.

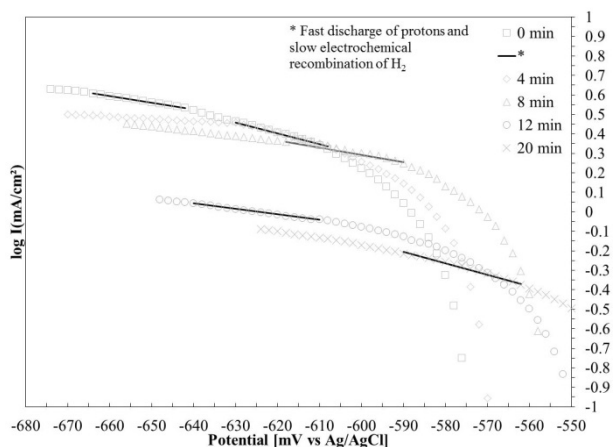


Figure 12. Comparison of the cathodic polarization curves for immersion of steel in manganese phosphate coating at 90°C. The experiment employed 0.94 M H₃PO₄. The polarization curves were recorded every 4 minutes during the immersion process.

Table 6. Kinetic parameters for the electrochemical recombination rate-controlling step, employing a manganese phosphate coating at 90°C.

Time (min)	b' (V/decade)	i ₀ (mA*cm ⁻²)	a
0	-0.303	1.363	-1.607
4	-0.182	1.116	-2.980
8	-0.217	1.116	-2.488
12	-0.345	0.795	-1.820
20	-0.175	0.560	-3.593

4. Conclusions.

In this research, cathodic polarization experiments were performed in order to study the nature of the hydrogen evolution reaction mechanism on steel with different types of phosphatizing solutions by varying the acidity, temperature, immersion time, coating (iron or manganese phosphate) with or without Mn ion in solution.

The Tafel plots of the phosphatizing process revealed one electrical potential zone where the monoatomic hydrogen is recombined electrochemically to H₂ as the rate determining step, with charge transfer coefficients similar to an activationless process.

Another important factor in the HER kinetics is the temperature; it was found that an increase in temperature up to 90°C helps to produce more hydrogen than at 25°C. On the other hand, a temperature of 50°C employing either 0.47 or 0.94M H₃PO₄ at pH 1 promotes an increase in the current density due to the formation of an iron phosphate coating on the steel cathode. The formation of FePO₄ on steel promotes the highest rate for the electrochemical recombination of monoatomic hydrogen to H₂.

Furthermore an increase in the acidity causes a higher exchange current density that benefits the hydrogen generation rate. The microstructural characterizations revealed that the coating morphology is an important factor in the hydrogen generation, i.e. the HER is favored on the porous iron phosphate coatings.

On the other hand, it was found a catalytic effect on the hydrogen generation rate at room temperature, when Mn ions were incorporated to the solution at pH 1. This catalytic effect is more efficient when the temperature was increased up to 90°C. Finally it was also observed that the manganese phosphate coating decreases the HER kinetics at pH 2.57 and 90°C.

5. Acknowledgements.

Gabriela Alvarado Macías is grateful to CONACyT (México) for the postgraduate scholarship received. Also, the collaboration of Felipe Márquez, Socorro García and Teodoro Caballero in this investigation is duly recognized.

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