



A KINETIC-MECHANISTIC STUDY OF THE HYDROGEN EVOLUTION REACTION IN SULFURIC ACID SOLUTIONS WITH DIFFERENT ELECTRODE MATERIALS

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ABSTRACT

The hydrogen evolution reaction (HER) has been studied extensively due to the potential application of molecular hydrogen H_2 as a green fuel. Recently this particular reaction attracted the attention of several electrometallurgical researchers because of another promising application, in which the monoatomic hydrogen species H^\bullet (intermediate product of HER) is employed as a reducing agent for copper-sulfide minerals. Consequently, knowledge about the kinetics, mechanisms and rate determining step (rds) of HER in sulfuric acid solutions employing aluminum, copper, Inconel® or glassy carbon(GC) cathodes is necessary to determine the under and overpotential domains where H_2 and H^\bullet can be generated in a selective manner. To accomplish this, cathode polarization curves with the different electrode materials were carried out using the rotating disk electrode technique at several conditions of acidity, temperature, and applied potential, with or without ferrous ion (mineral phase reduction product). Analyses of the Tafel slopes and the charge transfer coefficients, revealed two electrical potential zones for



copper, Inconel and GC, where the monoatomic hydrogen can be recombined chemically or electrochemically to H₂ as the rds. On the other hand, with aluminum, only the electrochemical recombination to H₂ occurs as the rds. A catalytic effect on the hydrogen recombination reaction was also found when ferrous ion is contained in the solution. The results of the exchange current densities for each of the tested cathode materials showed that aluminum is the most efficient electrocatalyst for producing H• and H₂, followed by inconel, copper and GC.

Key words: Polarization, Tafel, monoatomic hydrogen, HER.

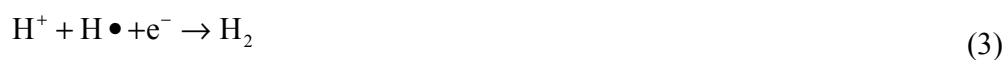
1. INTRODUCTION

Electrocatalytic hydrogen evolution reaction (HER) on different electrode materials such as Pt and Au has been studied extensively^[1,2,3,4], since it is one of the most fundamental electrochemical reactions. During the last decades, it has been well established that (HER) occurs via two successive elementary events^[5,6,7]:

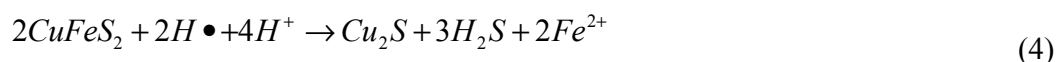
The initial discharge of hydrogen ions to adsorbed monoatomic hydrogen.



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



It also has been found that monoatomic hydrogen (equation 1) can be generated on Pt at positive potentials to the thermodynamic reversible potential of HER, the so-called under-potential deposition (UPD).^[1] This implies that either monoatomic hydrogen or molecular hydrogen can be produced in a selective manner, which could have practical implications. For example: the molecular hydrogen produced in high over-potential regions can be employed as a reactant of a green fuel cell. On the other hand, the monoatomic hydrogen formed in under and over-potential domains can be used as a powerful reducing agent of copper sulfide minerals^[8,9]. A novel application of monoatomic hydrogen in the field of electro and hydrometallurgy, basically consists of reducing the chalcopyrite (CuFeS_2), which is the most abundant copper reserve in the world, to a less refractory mineral such as chalcocite (Cu_2S), as shown in the following equation:



It is important to mention, particularly in this process, molecular hydrogen generation should be minimized, because it would decrease the efficiency of reaction (4). For that reason in this research, a study is presented of the kinetics and mechanisms of HER employing less expensive cathode materials, such as: aluminum, copper, Inconel® or glassy carbon (GC) than platinum and gold. The main objective of this research is to understand the nature of HER on different substrates, to determine the different potential regions where monoatomic hydrogen can be selectively produced, and to find the most suitable cathode material for carrying out the HER.

2. EXPERIMENTAL PROCEDURE

In order to understand the nature of HER in this system, its mechanisms and kinetics were investigated on different cathode materials using the rotating disk electrode technique, varying the rotation velocity, solution acidity, temperature and ferrous ion concentration. The cathode materials employed were a polished rotating disk electrode of aluminum (99%), inconel, pure

copper or pure glassy carbon, with a geometrical area of 19.6 mm^2 , supplied by Energy Research and Generation, Inc. All chemicals employed in this study were reagent grade and the water was deionized. The surface of the electrodes was prepared by first sanding with 1200-grit carbide paper for ten minutes, then polishing with a cloth and wetted $0.05\mu\text{m}$ alumina powder for 50 minutes, and finally rinsing with deionized water.

The polished rotating disk electrode was placed in the rotator (Pine), as the working electrode (WE) in the 70 mL single-chamber, three-electrode electrochemical cell (Figure 1). The reference and counter electrodes were saturated sulfate (Radiometer Analytical) $\text{Hg}/\text{Hg}_2\text{SO}_4/\text{K}_2\text{SO}_4$ (SSE, which is $+0.645\text{V}$ vs SHE) and graphite (Alfa Aesar, 99.99%), respectively. The electrolyte was 50 mL of 0.5, 1 or 2M aqueous H_2SO_4 at 25 or 40°C , with 0 or 750ppm Fe^{+2} ; which had previously been sparged with nitrogen for 30 minutes to eliminate O_2 and CO_2 . It is important to mention that in all experiments, an inert atmosphere was maintained by blowing nitrogen above the surface of the electrolyte solution.

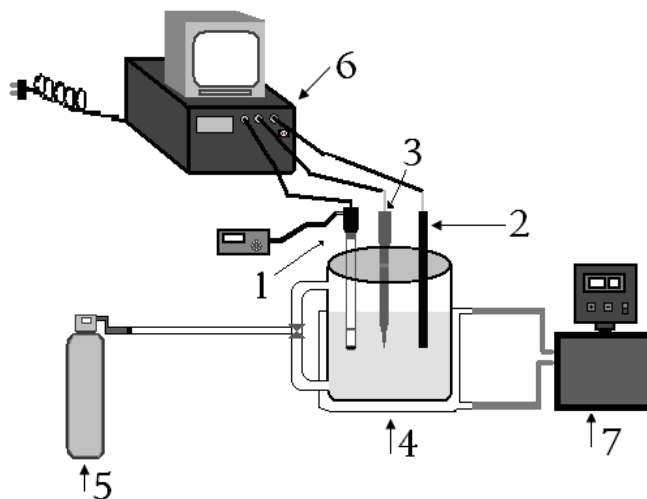


Figure 1. Schematic diagram of the equipment used for studying the electrochemical generation of hydrogen on different cathode materials, where: (1) rotating disk electrode of aluminum, inconel copper or glassy carbon, (2) graphite counter-electrode, (3) SSE reference electrode, (4) single-chamber cell, (5) nitrogen, (6) potentiostat and (7) constant temperature bath

Since one of the objectives of this research is to elucidate the mechanisms and kinetics of HER, polarization experiments were performed in the single-chamber cell, which was connected to a PAR 2273 potentiostat/galvanostat to carry out sampled current experiments (chronoamperometry) at 1200, 1600, 2000 or 2500 rpm. In order to obtain a constant reading, potential pulses were applied for 5 seconds, after which time the current was recorded. The potential pulses were scanned in the negative direction from the open circuit potential (OCP).

3. RESULTS AND DISCUSSION

First, the polarization behavior of hydrogen evolution on the four cathode materials (aluminum, inconel, copper and glassy carbon) was studied using microelectrolysis, varying the agitation velocity, acidity and temperature. Finally, the polarization behavior on the same cathode materials in presence of ferrous ion is shown.

According to several authors (Vijh et al., 1985; Krishtalik et al., 1986; Greef et al., 1993; Elhamid et al., 2000)^[6,7,10,11], the hydrogen evolution reaction (HER) can be studied by constructing polarization curves on different cathode materials. Before presenting the results, it is important to explain the shape of the polarization curves that are theoretically expected. Figure 2 shows a typical polarization curve, or Tafel plot, for a particular electrochemical reaction (or elementary event). It is constructed by plotting the natural logarithm of the current density ($\ln i$) vs the polarization potential (π), where the polarization potential is given by $\pi = E_{\text{applied}} - E_{\text{OCP}}$, namely the difference between the cathode applied potential (E_{applied}) and the open circuit potential (E_{OCP}). An increase in the polarization potential causes the same effect in the current density, only for the processes with charge transfer coefficients, α , of 1 and 0.5. The three lines represent the Tafel equation ($\pi = -b' \ln i - a$), not considering any reverse reaction, where the slope and the origin ordinate terms are defined by:

$$b' = \frac{RT}{\alpha nF} \quad (5)$$

$$a = \frac{RT}{\alpha nF} \ln i_0 \quad (6)$$

where R is the universal gas constant, T the temperature, n the number of electrons transferred in an electrochemical reaction, F the Faraday constant and i_0 the exchange current.

According to Krishtalik et al. (1986)^[6], the Tafel lines obtained in a polarization curve (Figure 2) correspond basically to three types of processes, which represent a controlling discharge reaction: barrierless discharge with ($b' = -0.025\text{V/decade}$ and $\alpha = 1$), ordinary discharge with ($b' = -0.051\text{V/decade}$ and $\alpha = 0.5$) and activationless discharge with ($b' = -\infty\text{V/decade}$ and $\alpha = 0$). The physical meaning of these types of processes relies on the magnitude of the activation energy in the discharge reaction. In other words, for each discharge process with a $\alpha = 1, 0.5$ and

0, the height of the activation energy barrier is high, modest or negligible, respectively. The same figure shows that as the polarization potential is increased, the Tafel slope begins to decrease from -0.025V/decade to $-\infty$ and the charge transfer coefficient becomes 0, which corresponds to an activationless discharge process. If the polarization potential is increased from this point, the Tafel slope and the charge transfer coefficient remain constant for this particular reaction, this means that its rate is constant. However, if the Tafel slope and the charge transfer coefficient increase again, behaving either as a barrierless or as an ordinary discharge process (Krishtalik et al., 1986)^[6], this implies a change in the rate determining step and therefore a different reaction controls the process kinetics.

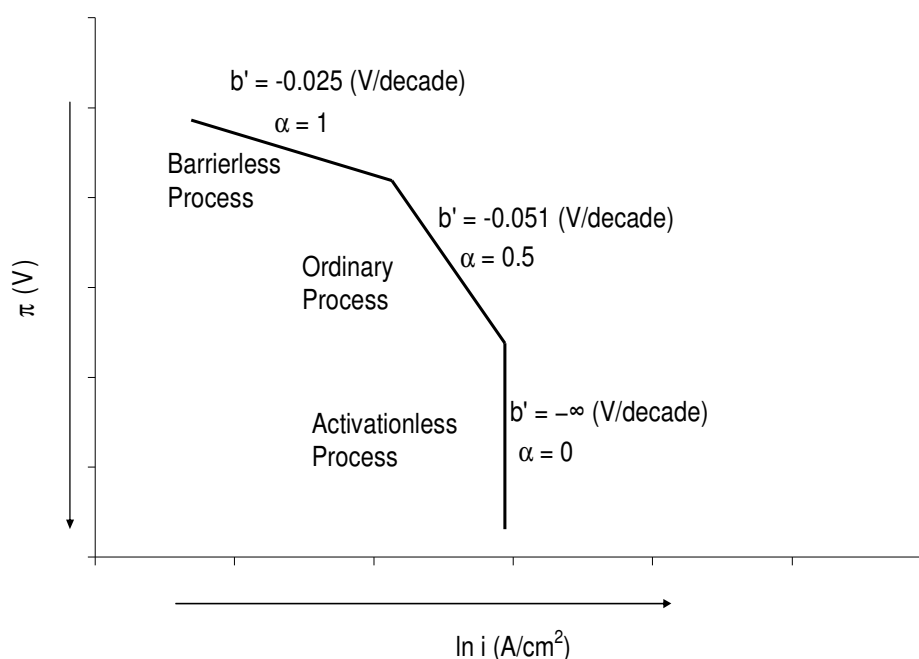


Figure 2. Typical polarization curve for a particular electrochemical reaction (or elementary event) over a wide range of potentials at 25°C

However, there are two other possibilities for describing the behavior obtained in the so-called activationless process, the first one is related with mass transfer control^[7] and the second, associated to a process controlled by a chemical reaction^[12]. In the next section, evidence is

presented regarding the different types of processes that occurs in the polarization of HER.

3.1. Effect of the acidity with different cathode materials.

Having established the theoretical shape of the polarization curves, the experimental polarization curves for the hydrogen evolution reaction on different cathode materials at different acidity and temperature are shown in Figures 3 and 4. In order to insure that the polarization curves represent only the electrochemical or chemical reactions occurring in the cathode surface, it was important to eliminate any mass transfer effects of protons in the solution. To accomplish this, polarization experiments were carried out with each of the rotating disk electrodes (aluminum, inconel, copper and glassy carbon) at different rotation speeds. A rotation velocity of 2500 rpm was found adequate to eliminate mass transfer effects for all four cathode materials, before reaching the highest polarization potential with each material at different conditions of acidity and temperature (data not shown here).

Figure 3 shows cathodic polarization curves for aluminum, copper, inconel and glassy carbon (Figure 3-A, 3-B, 3-C and 3-D respectively) at three different acid concentrations (0.5, 1 and 2M of H_2SO_4). When the Tafel lines are traced over the polarization curves for the aluminum in 0.5 and 1 M H_2SO_4 , several changes in slopes are perceivable. At low polarizations, between -0.1 and -0.3V (Figure 3-A, lines a_1 and a_2), two slopes are detected; the dashed line a_1 corresponds to the discharge of protons to monoatomic hydrogen (equation 1), when the polarization potential was decreased the Tafel slopes became more negative and the charge transfer coefficient decreases to nearly 0, (gray line a_2 , Figure 3-A); according to Krishtalik^[6], the latter condition is representative of an activationless discharge process. However, if this were true, the activationless condition would correspond to the highest rate of production of monoatomic hydrogen, due to the absence of the activation energy barrier. Analyzing the behavior of line a_2 , the current density is nearly independent of the polarization potential. Since at the rotation speed employed (2500 rpm), mass transfer effects were proven to be negligible,

another possible explanation for this behavior could be that a chemical reaction is controlling the process in this polarization potential region. The only chemical reaction that occurs is the recombination of two monoatomic hydrogen to molecular hydrogen (equation 2). This behavior has been reported by Shreir^[12] and suggests a mechanism where the monoatomic hydrogen generation (equation 1) is fast and the chemical recombination to molecular hydrogen (equation 2) is the rate determining step.

At high polarizations (black continuous lines a_3 , b_2 and c_1 , Figure 3-A), the Tafel slope becomes less negative (approximately -0.06 V) and, consequently, also the charge transfer coefficient, behaving as an ordinary discharge process with a charge transfer coefficient of nearly 0.5. According to Krishtalik^[6], this change in the Tafel slope, is not possible for the same controlling reaction, therefore this modification in the Tafel slope and the charge transfer coefficient is due to a different controlling reaction. Since the black continuous lines show that the polarization potential is again dependent on the current density, an electrochemical reaction is occurring. Therefore, in these potential domains, a change in the type of recombination to molecular hydrogen is implied; in other words, the HER mechanism consists of a fast discharge of protons (equation 1) with an electrochemical recombination to molecular hydrogen as the rate determining step. On the other hand, for a concentration of 2M, only one type of mechanism is observed, where the generation of monoatomic hydrogen is the fast process and the electrochemical recombination to molecular hydrogen is rate determining step. An important characteristic is that at any polarization potential π between -0.2 and -0.5 V, the current is larger at higher acid concentrations. The current is related by Faraday's law to the quantity of the species that is being generated; therefore, an increase in the acid concentration causes an increase in the production rate of monoatomic hydrogen as well as molecular hydrogen.

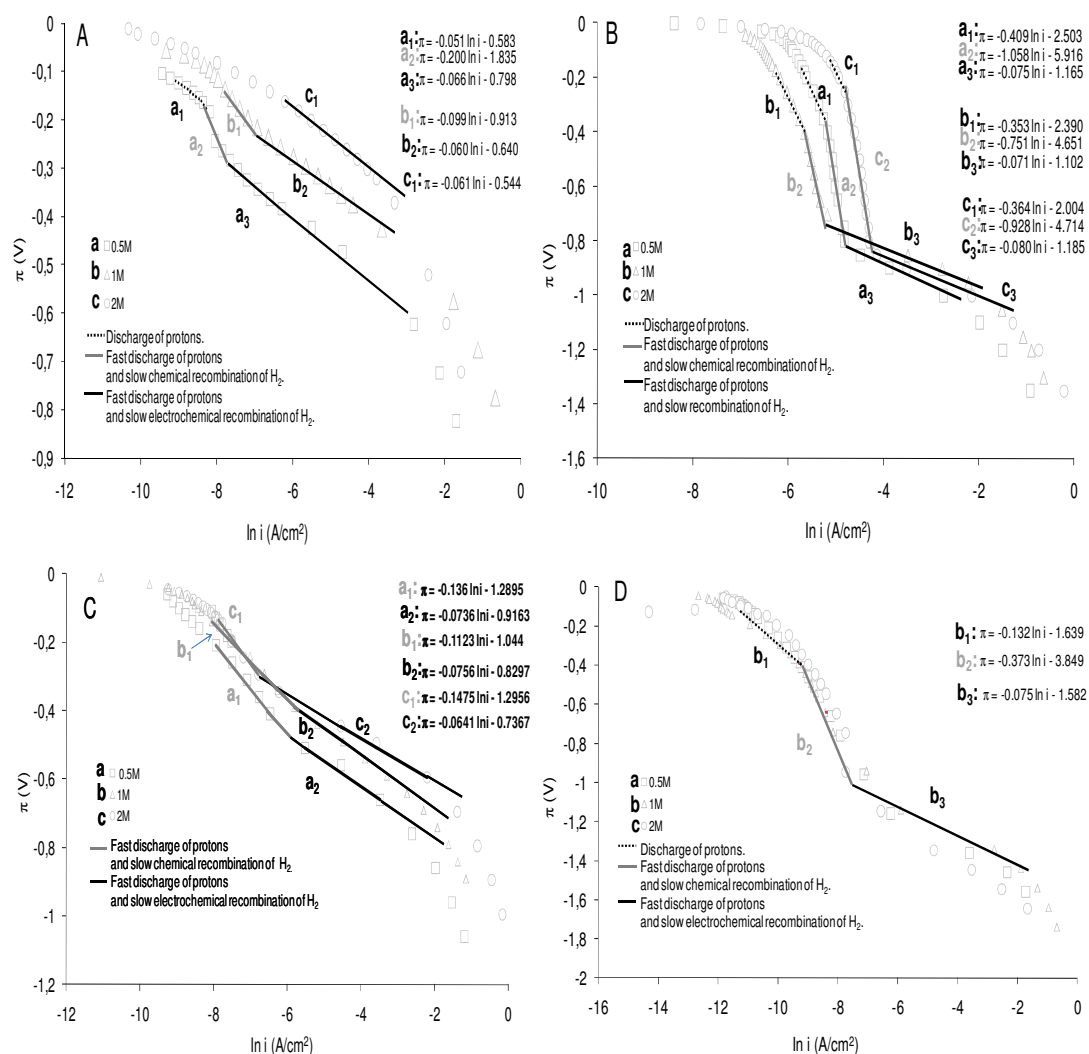


Figure 3. Cathodic polarization curves (where $\pi = E_{\text{applied}} - E_{\text{OCP}}$) in different concentrations of H_2SO_4 for four rotating disk electrodes: (A) aluminum, (B) copper, (C) inonel and (D) glassy carbon. All experiments employed a temperature of 25°C and a rotation velocity of 2500 rpm. Potential pulses were applied for 5 seconds, in order to obtain stable current readings. Potentials were applied, starting from the OCP, in the negative direction

For copper (Figure 3-B), as with aluminum, polarization curves show the three types of mechanisms: dashed lines, which correspond to the generation of monoatomic hydrogen; gray continuous lines, associated with the fast generation of monoatomic hydrogen and slow chemical recombination to molecular hydrogen; and the black continuous lines, associated with the fast

generation of monoatomic hydrogen and slow electrochemical recombination to molecular hydrogen. However, there are significant differences between copper and aluminum: in the zone where the chemical recombination of monoatomic hydrogen is rate-controlling, (gray continuous lines a_2 and b_2 , Figure 3-B) with monoatomic hydrogen and molecular hydrogen being formed faster for 0.5M than for 1M H_2SO_4 . A possible explanation for this phenomenon may be the adsorption of anions, such as sulfate, on the copper surface. Krishtalik^[6] found that the adsorption of anions on the cathode surface alters the polarization potentials and generation rates of hydrogen in the polarization curves. This implies that the sulfate ion adsorption on the copper surface may be responsible for these discrepancies in the polarization curves with 0.5 and 1M H_2SO_4 .

At a polarization potential of -0.8V in the case of copper, for all acid concentrations (black continuous lines a_3 , b_3 and c_3 , Figure 3-B), the process passed from a chemical recombination step to an ordinary discharge (with charge transfer coefficient near to 0.5 and Tafel slope of -0.07 V/decade, approximately). As was mentioned for the case of aluminum, this process modification is associated directly with a change in the rate determining step where the electrochemical recombination to molecular hydrogen is now controlling the HER. Another characteristic is that the rate of hydrogen production in this polarization potential region was insensitive to the acid concentration.

For inconel (see Figure 3-C), there are two mechanisms: for low polarization potentials, the fast production of monoatomic hydrogen and slow chemical recombination to molecular hydrogen occurs (gray continuous line a_1 , b_1 and c_1 , Figure 3-C); at high polarization potentials, only a change in the rate determining step is observed, from a chemical to an electrochemical recombination reaction (black continuous lines a_2 , b_2 and c_2 , Figure 3-C). A behavior similar to aluminum is noted, where an increase in acid concentration promotes higher rates for HER.

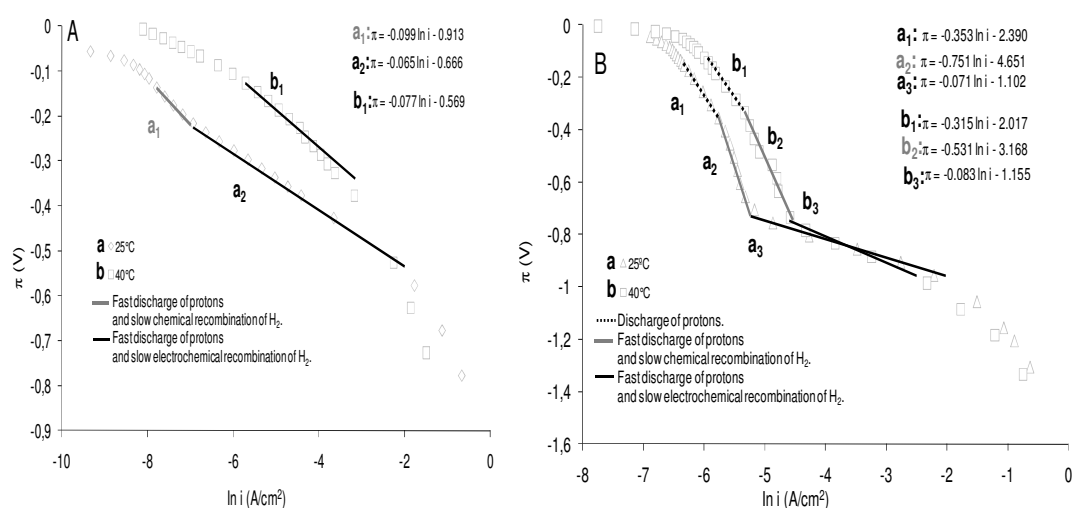
Finally, for glassy carbon (see Figure 3-D); as with the aluminum and copper cathodes, there are three mechanisms: the generation of monoatomic hydrogen (dashed line b_1 , Figure 3-D), the fast generation of monoatomic hydrogen and slow chemical recombination to molecular hydrogen (gray continuous line b_2 , Figure 3-D), and the fast generation of monoatomic hydrogen and slow electrochemical recombination to molecular hydrogen (black continuous line b_3 , Figure 3-D). The polarization curves are very similar at each acid concentration, indicating that the generation of monoatomic and molecular hydrogen on this material is independent of the acid concentration.

3.2 Effect of the temperature with different cathode materials.

Another important variable for the HER process is temperature. Cathodic polarization experiments were performed at 25 and 40°C using 1 M H_2SO_4 , employing the same cathode materials: aluminum, copper, inonel and glassy carbon. Figure 4-A shows the cathodic polarization curves for the aluminum at both temperatures. As discussed above, two zones are evident at 25°C, corresponding to the rate being controlled by chemical recombination to molecular hydrogen (gray continuous line a_1 , Figure 4-A), and electrochemical discharge of molecular hydrogen (black continuous line a_2 , Figure 4-A). In contrast, at 40°C the kinetics are controlled over the entire polarization potential range by the electrochemical discharge of molecular hydrogen (black continuous line b_1 , Figure 4-A). At any polarization potential π between approximately -0.1 and -0.5 V, the current is larger for 40°C than 25°C; this indicates greater rates of hydrogen evolution at 40°C than at 25°C. In addition, it suggests a greater availability of monoatomic hydrogen at the higher temperature, since the generation of this intermediate is not rate controlling.

For both the copper and glassy carbon cathodes, the hydrogen evolution reaction mechanism was also influenced by the temperature. In Figures 4-B and 4-D, the polarization

curves at 25 and 40°C show regions where the generation of monoatomic hydrogen, chemical recombination of molecular hydrogen and electrochemical discharge of molecular hydrogen are rate-controlling, these occur at low, moderate and high polarization potentials, respectively. In the same manner, for polarization potentials π up to -0.8 V for copper and -1.4 V for glassy carbon at 40°C; the current responses are always larger than those at 25°C. This behavior is observed only in the regions where the monoatomic hydrogen and chemical recombination of molecular hydrogen are rate-controlling.



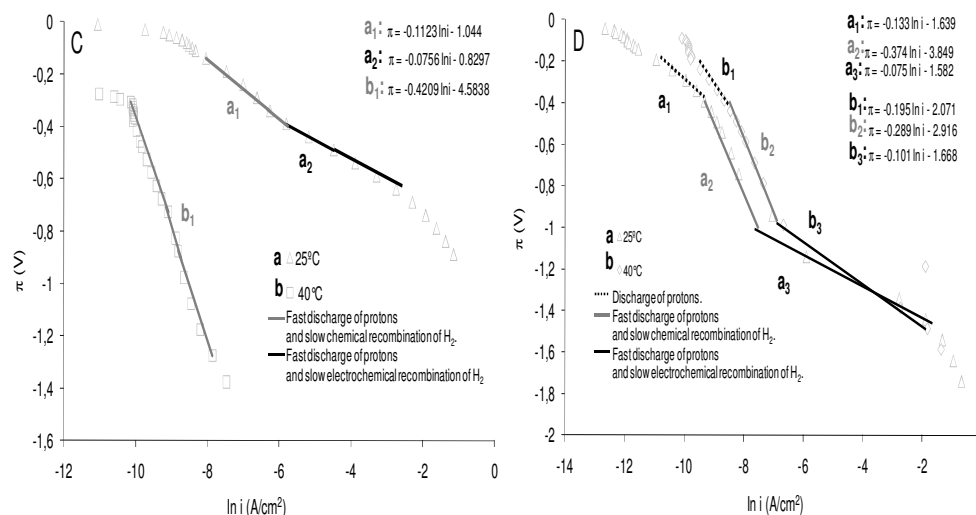


Figure 4. Cathodic polarization curves (where $\pi = E_{\text{applied}} - E_{\text{OCP}}$) at different temperatures for four rotating disk electrode materials: (A) aluminum, (B) copper (C) inonel and (D) glassy carbon. All experiments employed 1M H_2SO_4 and a rotating velocity of 2500 rpm. Potential pulses were applied for 5 seconds, to obtain stable current readings, starting from the OCP and scanning in the negative direction

Finally, for inonel (Figure 4-C), for 25°C the two mechanisms, already described above, are observed, where the chemical and electrochemical recombination of molecular hydrogen are rate determining steps. However when the temperature is increased up to 40°C, the rate determining step is the chemical recombination of molecular hydrogen in the entire polarization potential range.

3.3 Comparison of the HER kinetics with different cathode materials.

Figure 5 directly compares the polarization behavior of the four different cathode materials in 1 M H_2SO_4 at 25°C. Although all of the cathode materials had regions where the rate was controlled by the generation of monoatomic hydrogen (reaction 1) (dashed lines G-C₁ and Cu₁, Figure 5), chemical recombination of molecular hydrogen (reaction 2) (gray continuous lines Al₁, Inc₁, Cu₂ and G-C₂, Figure 5) and electrochemical discharge of molecular hydrogen (reaction

3) (black continuous lines Al_2 , InC_2 , Cu_3 and G-C_3 , Figure 5), there are dramatic differences in the polarization behavior of the distinct substrates. Glassy carbon was clearly the most polarizable cathode, with very low currents passing even at high overpotentials or polarization potentials, and the generation of monoatomic hydrogen and chemical recombination of molecular hydrogen was rate-controlling for overvoltages of 0 to -1.05 V. Although copper had the highest exchange current density, the evolution of monoatomic hydrogen was more strongly polarized on copper than on aluminum. The overall current on copper only exceeded that on aluminum for overvoltages between 0 and -0.3V. The generation of monoatomic hydrogen and chemical recombination of molecular hydrogen were rate-controlling on copper for a polarization potential from 0 to -0.8 V. Although aluminum has a lower exchange current density than copper, the evolution of hydrogen on aluminum is not strongly polarized; the chemical recombination of molecular hydrogen was rate-controlling over a very small potential range (overpotentials of -0.15 to -0.25V), and by overpotentials of -0.3V, the overall cathodic current on aluminum exceeded that of copper at the same overvoltage, albeit with a different rate-controlling process (for aluminum this is electrochemical discharge of molecular hydrogen).

From the perspective of selecting a cathode material for the most energy-efficient production of monoatomic and molecular hydrogen, aluminum seems to be the most attractive of the four materials studied based on the following two criteria. First, lower overvoltages are needed to achieve a given current density, and hence rate. Second, over most of the potential range, and specifically at potentials that yield reasonably high current densities, the overall rate of hydrogen discharge is determined by the rate at which monoatomic hydrogen combines electrochemically with hydrogen ions. This suggests that the aluminum surface has a high concentration of monoatomic hydrogen, which would be available to participate in a competing electroreductive reaction such as that provided by chalcopyrite (reaction 4).

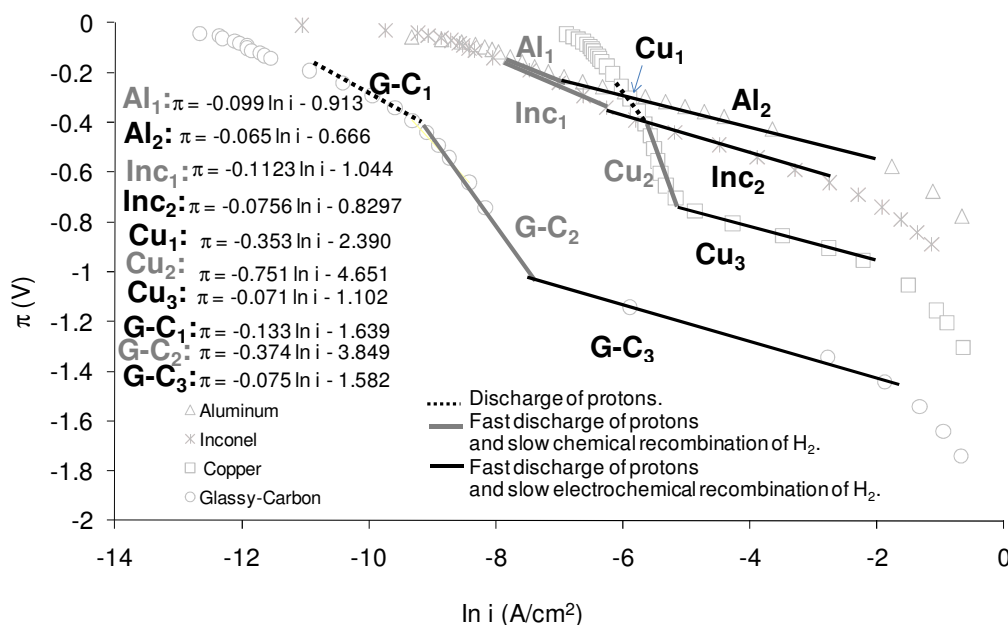


Figure 5. Comparison of the cathodic polarization curves (where $\pi = E_{\text{applied}} - E_{\text{OCP}}$) for four rotating disk electrode materials: Aluminum (Al), Copper (Cu), Inconel (Inc) and Glassy-Carbon (G-C). All experiments employed 1M H₂SO₄ at 25°C and a rotating velocity of 2500 rpm. Potential pulses were applied for 5 seconds, to obtain a stable current reading, originating from the OCP in the negative direction

Finally, the last statement can be validated with the calculated current exchange i_0 for the electrochemical recombination rate-controlling step in each cathode material. In Table 1, it is shown the following kinetic parameters for this rate determining step reaction: b' Tafel slope, α charge transfer coefficient, i_0 exchange current density and a , ordinate of Tafel equation. This table confirms that aluminum is the most efficient electrocatalyst for carrying out HER, because it has the highest exchange current density (3.133×10^{-5} A/cm²), followed by inconel, copper and glassy carbon.

Table 1. Kinetic parameters for the electrochemical recombination rate-controlling step, employing four cathode materials at 25°C

<i>Cathode Material</i>	<i>b' (V/decade)</i>	<i>α</i>	<i>i₀ (A/cm²)</i>	<i>a</i>
Aluminum	-0.065	0.4	3.133x10 ⁻⁵	-0.666
Inconel	-0.075	0.34	1.7x10 ⁻⁵	-0.829
Copper	-0.071	0.36	1.962x10 ⁻⁷	-1.102
Glassy-Carbon	-0.075	0.34	8.054x10 ⁻¹⁰	-1.582

3.4 Ferrous ion effect on the HER.

When the aluminum cathode is polarized in the presence of ferrous ion, two differences are observed (Figure 6-A). First, there is only one mechanism: the electrochemical recombination of molecular hydrogen is controlling (black continuous line *a*₁, Figure 6-A), contrary to the behavior in the absence of ferrous ion (lines *b*₁ and *b*₂, Figure 6-A). Second, a catalytic effect is evident in the electrochemical recombination of molecular hydrogen, indicated by a higher current, in a polarization potential range from -0.2 to -0.5V (line *a*₁, Figure 6-A).

In the case of copper, the presence of ferrous ion also produces a catalytic effect in HER for a polarization potential range from -0.2 to -0.8V (lines *a*₁ and *a*₂, Figure 6-B), where the generation of monoatomic hydrogen and chemical recombination of molecular hydrogen are rate determining steps, respectively. It is interesting to note that in contrast to aluminum, the catalytic effect does not produce any change in the mechanisms (lines *b*₁, *b*₂ and *b*₃, Figure 6-B).

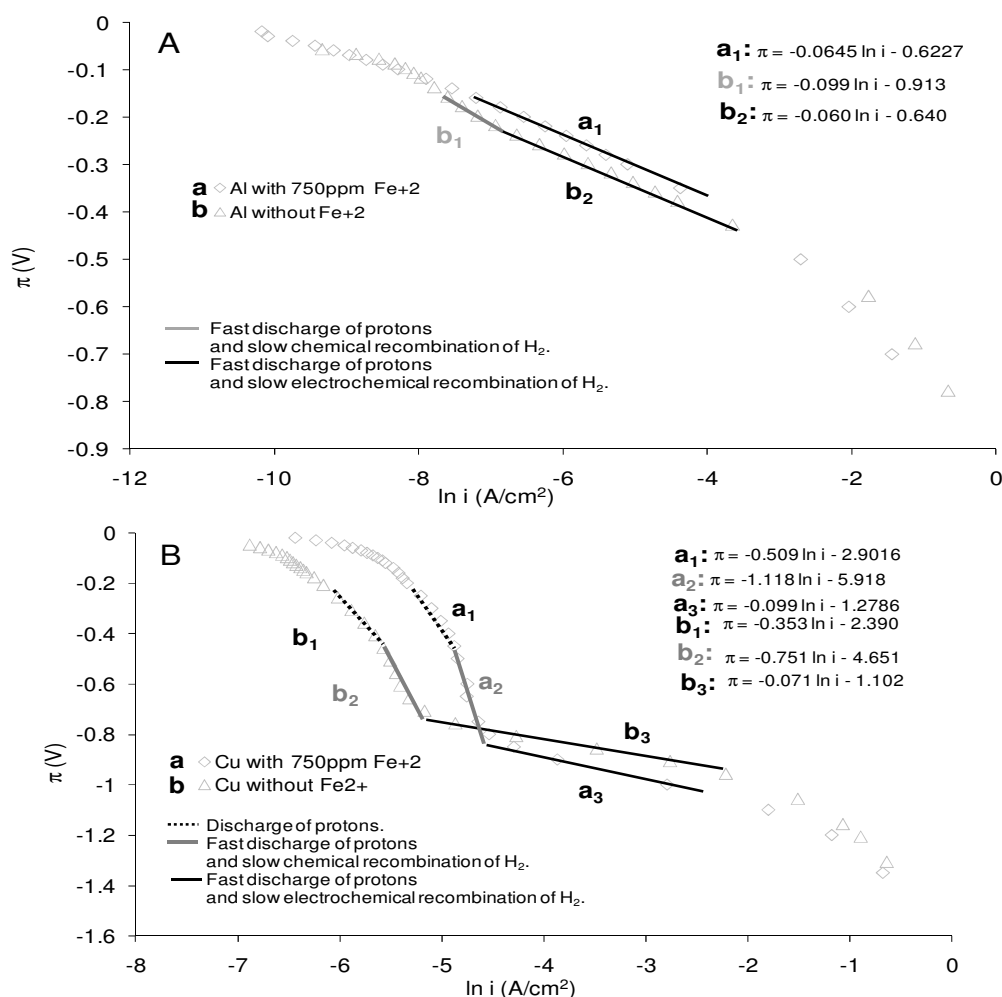


Figure 6. Cathodic polarization curves (where $\pi = E_{\text{applied}} - E_{\text{OCP}}$) with and without Fe⁺² for two rotating disk electrode materials: (A) aluminum and (B) copper. All experiments employed 1M H₂SO₄ at 25°C and a rotating velocity of 2500 rpm. Potential pulses were applied for 5 seconds, to obtain stable current readings, starting from the OCP and scanning in the negative direction

4. CONCLUSIONS

In this research, cathodic polarization experiments were performed, in order to study the nature of the hydrogen evolution reaction mechanism on different cathode materials (aluminum,

copper, inconel and glassy carbon), varying the sulfuric acid concentration (0.5, 1 and 2M) and the temperature (25 and 40°C). For aluminum, both chemical and electrochemical recombination mechanisms for molecular hydrogen formation were found at different polarization potentials. However, it was found only the electrochemical recombination of molecular hydrogen as well as a catalytic effect at 40°C, 2M or 750ppm Fe^{2+} . For copper, inconel and glassy carbon three controlling mechanisms exist under different conditions: monoatomic hydrogen generation, chemical and electrochemical recombination to form molecular hydrogen. However, with inconel at 40°C, only the chemical recombination to molecular hydrogen was controlling. The generation of monoatomic hydrogen, and molecular hydrogen strongly depended on the acidity, temperature and concentration of ferrous ion. The aluminum cathode was the best producer of monoatomic and molecular hydrogen, followed by the inconel, copper and glassy carbon.

5. ACKNOWLEDGEMENTS

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