

Hydrogen Evolution at Platinum (Pt) and at Platinized Platinum (Ptz) Cathodes

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In this study, the cathodic behaviours of bright platinum (Pt) and at platinized platinum (Ptz) on the platinum anode were investigated in a 1M Na₂SO₄ electrolyte (pH, from 2 to 8) by means of electrolysis. The theoretical (ΔE_{rev}) and experimental (ΔE_{exp}) discharge potentials and the cathodic overpotentials (η_c) of the systems were determined. The amounts of hydrogen gas produced at different times on the cathodes at a constant potential (5V) were measured and the hydrogen yield was calculated. The resulting scheme has been very helpful to obtain modified electrocatalytic coating and electrode structures at Ptz cathode, able to operate for long time with good and stable performances.

Introduction

The hydrogen evolution reaction (HER) is an electrochemical process that has received wide attention because of its importance in both fundamental and technological electrochemistry¹. From a purely technological standpoint, the cost of electrolytic hydrogen is directly dependent on the voltage used to operate the electrolyzer at significant current densities². Meanwhile, the operational voltage depends on the overpotentials for the cathodic and anodic reactions, and on the internal resistance of the cell². Minimizing anodic (η_a) and cathodic (η_c) overpotentials are a problem of electrocatalysis, while the ohmic drop ($\Delta V\Omega$) is in principle a problem of electrolysis, although the two quantities are often interrelated. The minimum value of ΔE_{exp} to obtain electrolysis, the equilibrium ΔE_{rev} , is determined by thermodynamics (Nernst relations) and does not depend on the electrode material. Thus, a more complete equation is in fact the following (1).

$$\Delta E_{exp} = \Delta E_{rev} + \eta_a + \eta_c + \Delta V\Omega + \Delta V(t) \quad (1)$$

where the last term on the right hand-side represents analytically what is called “electrode stability” in practical terms.

Because of cost and stability considerations, very few materials can even be considered for use as anode and cathode in the practical electrolytic cell. Two properties play an important role in selecting catalytically active materials for hydrogen evolution: firstly the actual electrocatalytic effect of the material, and secondly its long-term stability. Apart from the periodicity of the catalytic properties, a useful guide for the choice of suitable electrocatalytically active materials is the volcano-type curves representing a function between the

$\log i_o$ and different properties dependent on the electron configuration of the metal¹⁸. Electrode materials for water electrolysis with catalytic properties have been investigated by several authors, and it was found that platinum is very effective¹⁻¹⁰.

Although platinum is an expensive metal, because it has an electrocatalytic effect on the formation of hydrogen at the cathode, it is the most widely used electrode for electrolysis in industry⁹. The overpotential (η_c) due to H₂ evolution on the platinum cathode in acidic and basic medium is not as high¹⁰.

Pt-metal and Pt-metal oxides are either applied in the form of a thin coating on a less expensive but easily produced and shaped supporting metal-this applies generally to gas evolving electrodes - or they are worked into highly dispersed form into relatively very thin (0.1-0.5mm) porous gas diffusion electrodes⁸. Porous electrodes have a wide range of application, and are commonly used in batteries, fuel cells and electrolysis¹¹.

In this work, the experiments were conducted at bright platinum and platinized platinum (Pt-cover-Pt) cathodes against platinum anode in contact with aqueous solutions composed of 1M Na₂SO₄ covering a pH range of from 2 to 8 by electrolysis. The overpotentials of the cathodes (η_c), and the theoretical (ΔE_{rev}) and experimental (ΔE_{exp}) discharge potentials of the system were determined. The amount of hydrogen gas produced at a constant potential on the cathodes was measured and the hydrogen yield was calculated. With the data obtained, an attempt was made to determine the best cathode for the most economical electrolysis process.

Experimental

The first test electrode consisted of a smooth bright Pt plate of 1cm² apparent area spotwelded to a Pt wire lead sealed in glass tubing. The second test electrode consisted of platinized platinum (Ptz) in which platinum was platinized by cathodizing at room temperature with a current density of 50 mA cm⁻² for 1 min in a solution containing 1mg of H₂PtCl₃ in 100ml of 0.1M HCl (3). The Pt and Ptz working electrodes were connected to a platinum counter electrode in the electrolyte. 1 M Na₂SO₄ solution was used as the electrolyte. The pH of this solution was adjusted with Na₂SO₄ and NaOH. The experiments were carried out in room conditions.

During investigation of the cathodic behaviours of Pt and Ptz against the platinum anode by electrolysis, progressively increasing voltage was applied from zero volts up to 3.0V^{12,13} from a direct current source. Current-potential curves were obtained from electrodes arranged this way. With the aid of these curves, the minimum discharge potentials were determined experimentally for each electrode pair.

In the other part of the experimental work, a burette filled with electrolyte was inverted and 5.00V was applied to the system^{12,13}. The volume of hydrogen gas filling the burette and current passing through the circuit was measured at 5-minute intervals for a period of 30 minutes. The yield of hydrogen gas was calculated from the current (I,A) passing from the cell for measured periods of time (t, s) and the volume (V, cm³) of H₂, by the formula shown below^{12,13}:

$$Yield = \frac{2F(V/V_m)}{I.t} = \frac{7.89.V}{I.t} \quad (2)$$

In this equation, the Faraday constant F=96,500 C/mol and the molar volume of hydrogen at 25°C was taken as V_m=24.466 cm³.

Results and Discussion

The experimental results are shown in Figures 1-7. The current-potential curves (Figs. 1a-7a) and the yield of H_2 with time (Figs. 1b-7b) were drawn from the data obtained with Pt-Pt and Pt-Ptz electrodes by electrolysis. The are given for pH=2 in Fig.1, for pH=3 in Fig.2, for pH=4 in Fig.3, for pH=5 in Fig.4, for pH=6 in Fig.5, for pH=7 in Fig.6 and for pH,8 in Fig.7.

As seen Fig.1a-7a, the current-potential curves are similar at the beginning in all solutions and up to a certain potential the current passing through the solution is very small. The flow of steady current from the solution starts after the discharge potential is reached. The experimental discharge potentials (ΔE_{exp}) determined by using the current-potential curves shown in Figs. 1a-7a are given in Table 1. The discharge of hydrogen starts on the Ptz cathode at much lower potentials than on the Pt cathode in acidic solutions (pH from 2 to 4).

Table 1. Experimental discharge potentials (ΔE_{exp})

pH	$\Delta E_{exp}/V$	
	Pt-Pt	Pt-Ptz
2	2.2	1.7
3	2.2	1.7
4	2.2	1.7
5	2.2	2.1
6	2.2	2.1
7	2.2	2.2
8	2.2	2.2

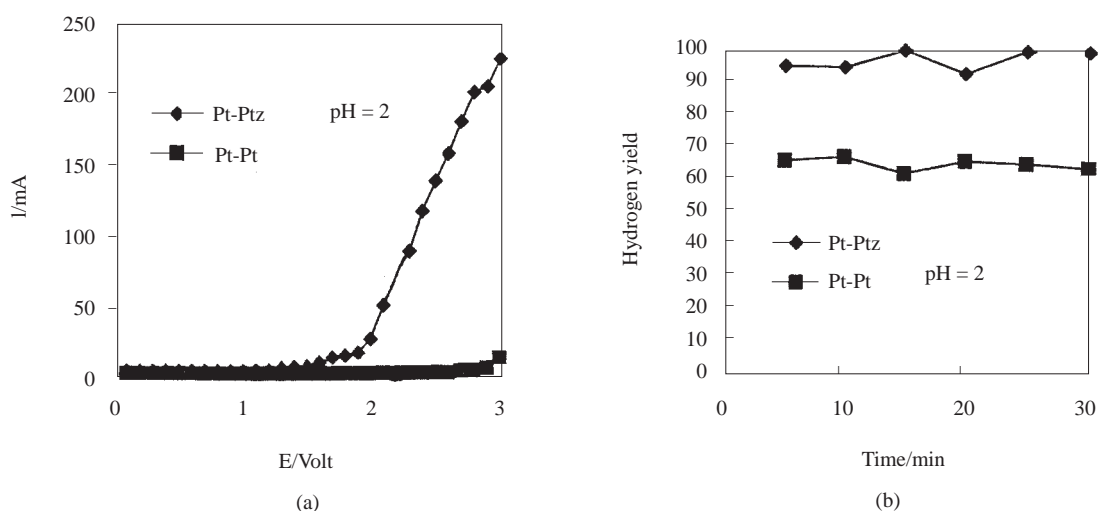


Figure 1. a) The current-potential curves (I-E). b) The yield of hydrogen as a function of time (min) at a constant potential of 5V in 1M Na_2SO_4 at pH=2.

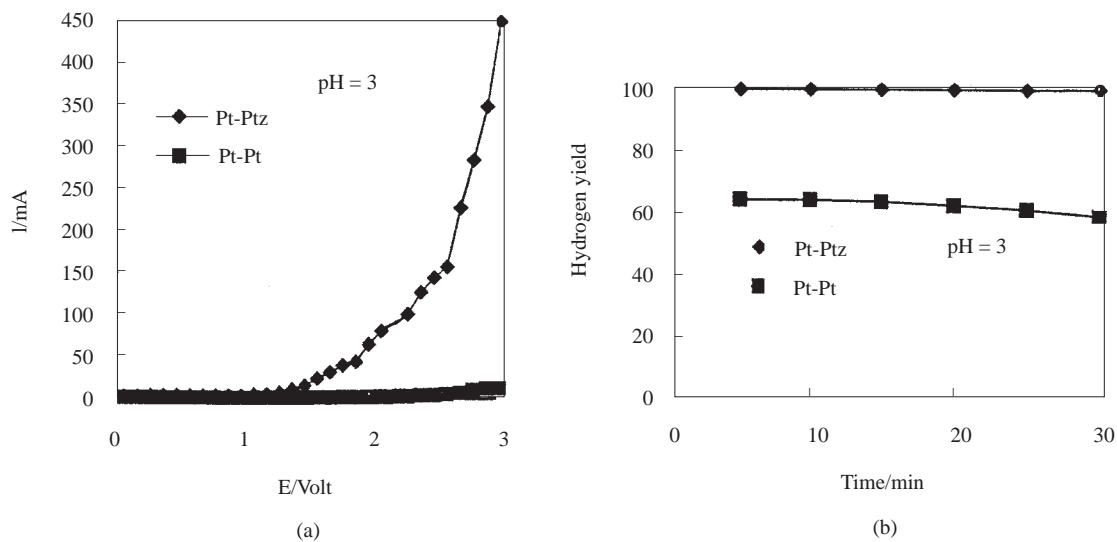


Figure 2. a) The current-potential curves (I-E). b) The yield of hydrogen as a function of time (min) at a constant potential of 5V in 1M Na₂SO₄ at pH=3.

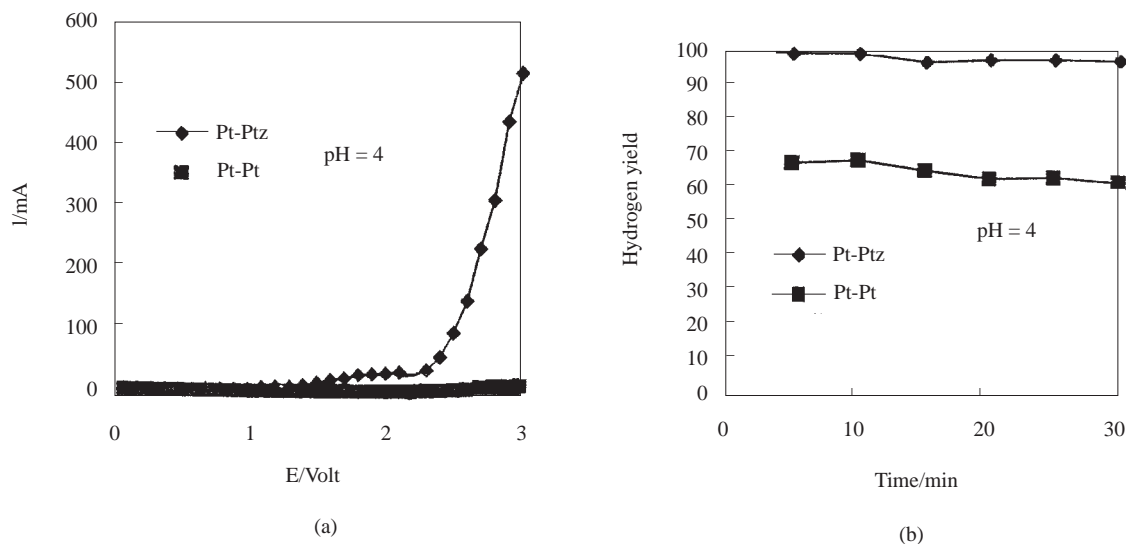


Figure 3. a) The current-potential curves (I-E). b) The yield of hydrogen as a function of time (min) at a constant potential of 5V in 1M Na₂SO₄ at pH=4.

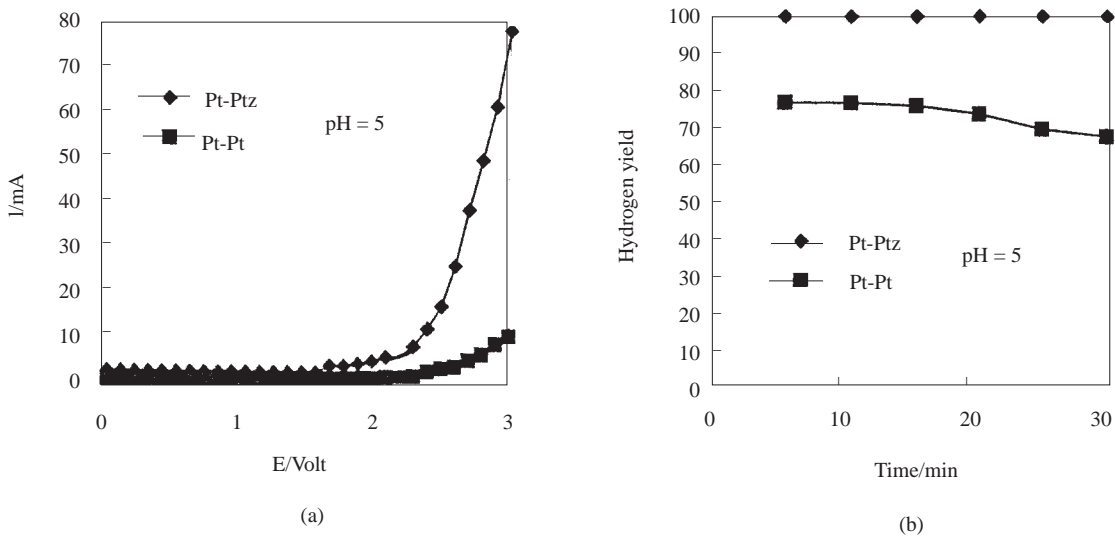


Figure 4. a) The current-potential curves (I-E). b) The yield of hydrogen as a function of time (min) at a constant potential of 5V in 1M Na₂SO₄ at pH=5.

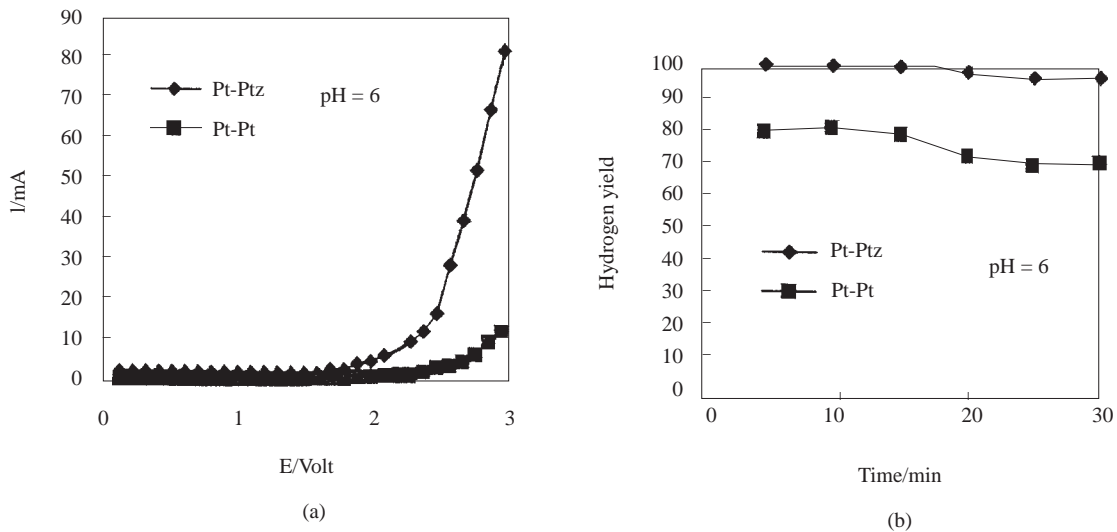


Figure 5. a) The current-potential curves (I-E). b) The yield of hydrogen as a function of time (min) at a constant potential of 5V in 1M Na₂SO₄ at pH=6.

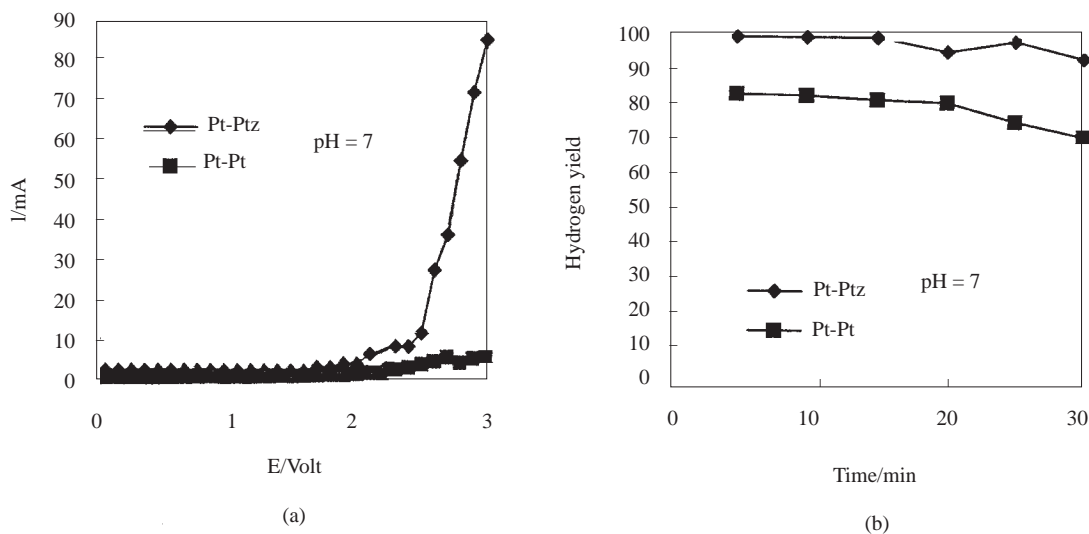


Figure 6. a) The current-potential curves (I-E). b) The yield of hydrogen as a function of time (min) at a constant potential of 5V in 1M Na₂SO₄ at pH=7.

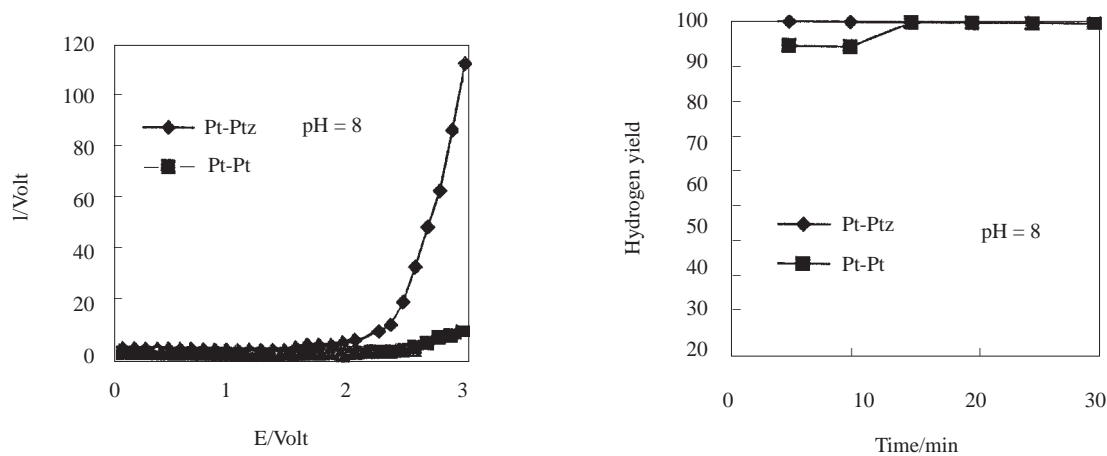


Figure 7. a) The current-potential curves (I-E). b) The yield of hydrogen as a function of time (min) at a constant potential of 5V in 1M Na₂SO₄ at pH=8.

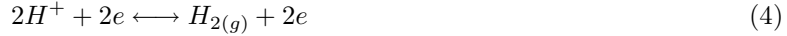
Under these conditions the only factor affecting the discharge potential is the type of cathode used. After the discharge potential is exceeded, the current passing through the solution is larger with Pt-Ptz electrodes than with other Pt-Pt electrodes at all potentials and at all pH values (Figs.1a-7a).

The electrochemical cells (Pt-Pt, Pt-Ptz) are used as the electrolysis system. In the electrolysis of 1M Na₂SO₄ at all pH values, the possible anodic reactions and the reversible electrode potential can be indicated as shown below:



$$e_{O_2/H_2O} = 1.23 - 0.059pH(P_{O_2} = 1atm)$$

In the electrolysis, the possible cathodic reaction at the cathode (Pt, Ptz) and the reversible electrode potential are as shown below:



$$e_{H^+/H_2} = -0.059pH(P_{H_2} = 1atm)$$

Consequently, the reversible discharge potential for the system ($\Delta E_{rev} = e_{O_2/H_2O} - e_{H^+/H_2}$) is 1.230 V under these conditions. Because of the existing overpotentials in the system, the experimental discharge potentials (ΔE_{exp}) shown in Figs. 1a-7a and Table 1 are greater than the reversible discharge potentials. Related to the anodic reactions, it is reported in the literature that the overpotential (η_a) of the oxygen on platinum is around 0.47 V (12-16). According to the literature, the hydrogen overpotential (η_c) on the platinum cathode is very small¹²⁻¹⁶. Therefore, the reversible discharge potential measured in electrolysis systems where the gases are discharged at the anode and cathode O_2 and H_2 , respectively, is around 1.7V ($\Delta E_{rev} + \eta_a$). As seen in Table 1, this value is in good agreement with the E_{exp} on Pt-Ptz when pH values are 2, 3 and 4. But for other conditions, the E_{exp} shown in Figs 1a-7a and Table 1 is greater than $E_{rev} + \eta_a$. In the equation 1, $\Delta V(t)$ may be related to the deterioration of the outer surface of the electrocatalyst and/or of the support/active layer interface in the case of coatings¹. Under these conditions, the electrode stability of the Pt and Ptz cathodes is fixed and the electrolyte is the same solution, and thus $\Delta V(\Omega)$ and $\Delta V(t)$ are neglected in Equation 1. In these systems, the difference between the measured and theoretically calculated values [$\Delta E_{exp} - (\Delta E_{rev} + \eta_a)$] can be taken to be cathode overpotential (η_c) or hydrogen overpotential. In Table 2, the variation of the overpotentials with different cathodes and pH is given. It is seen in Table 2 that the cathode overpotentials of Ptz are zero in acidic solutions (pH=2.3 and 4). Literature studies indicate^{9,17,18} that the Ptz cathode will be great surface catalysts for reaction 4 and reduce the hydrogen overpotential. This property of Ptz has not been observed in bright platinum (Figs. 1a-7a, Tables 1 and 2). In neutral and slightly basic solutions (pH=7 and 8), the same cathode overpotentials were observed in these cathodes (Pt and Ptz).

Table 2. The cathodic over potentials (η_c)

pH	Pt-Pt	Pt-Ptz
	$\eta_c(V)$	$\eta_c(V)$
2	0.5	0.0
3	0.5	0.0
4	0.5	0.0
5	0.5	0.4
6	0.5	0.4
7	0.5	0.5
8	0.5	0.5

In Figs 1b-7b, the variation of hydrogen yield with time is given. Platinum was used as the anode and a constant voltage of 5.00V was applied to the electrodes while the cathode changed from Pt to Ptz and the pH from 2 to 8. As seen in Figs 1b-6b, at a constant pH, the hydrogen yields obtained in electrolysis cells using Ptz cathodes are greater than those of Pt cathodes. At pH 8, the hydrogen yields of Pt and Ptz

cathodes have the same values (Fig. 7b). As pH increases, the highest yields of H₂ are obtained when a Pt cathode is used (Figs. 1b-7b). At all pH values, the Pt-Ptz electrode couple which produces the largest amount of H₂ is the most efficient electrode couple (Figs. 1b-7b). The H₂ yield does not vary much with time when the Pt cathode is used at all pH values. The yield of H₂ shows some variation with time when a Pt cathode is used at pH from 2 to 7 and at a constant pH, as time increases, the yields of H₂ decrease (Figs. 1b-7b). But, at pH=8, the yield of H₂ produced by a Pt cathode does not change much with time. It also was recently mentioned in the literature that the coadsorption of hydrogen on Pt in acid solutions decreases with poisoning¹⁹, which reduces the rate of evolution of hydrogen gas. Thus, the Pt-Pt system which has the highest overpotential with time (Figs. 1b-7b). In all solutions, Pt cathodes provide a porous electrode for cathodic hydrogen evolution and reduction of charge transfer overpotentials.

Conclusions

The choice of catalyst materials for HER is the subject matter of electrochemical catalysis. Maintenance of the catalyst properties under real working conditions is strongly influenced by engineering considerations.

From the data obtained, it is suggested that Pt anode and Ptz cathode couples should be employed for the best electrolysis system in Na₂SO₄ solutions at pH levels from 2 to 8. The resulting scheme has been very helpful in obtaining modified electrocatalytic coating and electrode structures at the Ptz cathode capable of operating for a long time with good and stable performances.

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