

Electrochemical hydrogen production from water electrolysis using ionic liquid as electrolytes: Towards the best device

Roberto F. de Souza^{a,*}, Janine C. Padilha^a, Reinaldo S. Gonçalves^a,
Michele O. de Souza^a, Joëlle Rault-Berthelot^b

^a *Institute of Chemistry, UFRGS, Av. Bento Gonçalves, 9500, Porto Alegre 91501-970, Brazil*

^b *Matière Condensée et Systèmes Electroactifs (MaCSE), UMR CNRS no. 6226, Laboratoire de Sciences Chimiques de Rennes, Université de Rennes 1, Campus Beaulieu, Avenue du Général Leclerc, 35042 Rennes Cédex, France*

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Abstract

Electrodes constructed with different electroactive materials such as platinum (Pt), nickel (Ni), 304 stainless steel (SS) and low carbon steel (LCS) have been tested in water electrolysis using 1-*n*-butyl-3-methylimidazolium tetrafluoroborate (BMI.BF₄). All experiments were performed at room temperature using a classical Hoffman's cell operating at atmospheric pressure and at different cathodic potentials. For the electrodes studied herein, in the presence of a 10 vol.% solution of BMI.BF₄ in water, current densities (*j*) in the range 10–42 mA cm⁻² were observed, with overall hydrogen production efficiencies (experimental/theoretical hydrogen production ratio) between 82 and 98%. The highest *j* values obtained with Pt, Ni, SS and LCS electrodes were 30, 12, 10 and 42 mA cm⁻², respectively, and all efficiencies were in the 85–99% range. These comparative results show that the LCS electrocatalyst constitutes an attractive alternative for the technological production of high purity hydrogen by water electrolysis reaction since the LCS electrode gave *j* and efficiencies as high as those observed with platinum electrodes.

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1. Introduction

Hydrogen is an extremely important energy carrier. It can be produced by different ways, particularly via the processing of hydrocarbons (e.g. steam reforming) or, alternatively, by water electrolysis. In the latter case hydrogen is a clean energy carrier since it can be used to produce energy in fuel cells giving back water, in an environmentally clean process.

Currently several technical debates have discussed the pros and cons of each method of hydrogen production. Large comprehensive texts have been published in this field covering the technical and economical aspects, as elegantly reviewed by Dunn [1].

Among the industrial methods of hydrogen production three have gained prominence: reforming, photoconversion and elec-

trolysis. Nowadays the steam reforming of fossil fuels is largely the most employed method for hydrogen production, but faces the same problems existing for the use of fossil fuels in refining, i.e. the fossil fuels used for reforming are mainly not renewable and, more importantly at this moment, their use produces polluting gases which are the source of dramatic environmental problems. In fact their use leads to indirect costs associated with environmental cleaning. The economical evaluation of hydrogen production processes usually does not include expenses associated with atmospheric air cleaning which, when considered, represents a determining factor in the future technology choice [1].

The cleanest solution for hydrogen production is the use of water electrolysis. Nowadays water electrolysis contributes a low fraction of the world global hydrogen production. This amount was estimated at 4% in 2002, but with a strong increasing tendency. Water electrolysis is an advantageous method for hydrogen production for several reasons: (i) it gives no carbon emissions; (ii) the hydrogen produced by this method is very

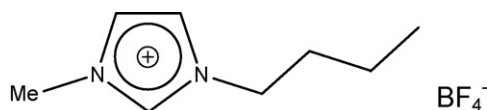
* Corresponding author. Tel.: +55 51 33166303; fax: +55 51 33167304.
E-mail address: rfd@iq.ufrgs.br (R.F. de Souza).

pure, influencing the fuel cell technology, which is dramatically affected by the impurities present in the hydrogen feed; (iii) it is not dependent on fossil hydrocarbon sources; (iv) it can be operated in small scale plants; (v) it can use totally renewable primary energy sources. This technology has some disadvantages such as the need for cheap energy sources to implement the reaction and the need for hydrogen storage [1]. A general agreement is that the technological use of water electrolysis will mainly depend on the equilibrium of a matrix of availability of energy sources, which depend on the location characteristics.

The process optimization for water electrolysis using alkaline electrolytes has been the subject of intense research. Many conditions and materials have been tested [2–6] in order to enable hydrogen production for use as an alternative fuel for applications such as in automotive transport [7]. Indeed there is intense research on the best operational conditions for hydrogen production including aspects such as methods, materials, temperature and pressure. Many electrocatalysts have been tested in an attempt to operate at ambient temperature and atmospheric pressure with a high current density [8] and operating with solar energy sources [9]. Currently most of the industrial production of hydrogen is performed through water electrolysis using aqueous KOH (30 wt.%) at 353 K [10] applying a cathodic potential of -1.47 V to overcome the enthalpy change. Classical electrolyzers, using a KOH aqueous solution at -2.0 V give current densities of ca. 100 mA cm^{-2} . For this system nickel alloys as electrode materials with several depositions on the electrode surface have been successfully used as electrocatalysts in order to increase the current density and to enhance its life span [11,12].

In a previous communication [13], we reported that ILs such as BMI.BF₄ (Scheme 1) can be used as efficient electrolytes for water electrolysis. This system showed high efficiency and high current densities at low temperatures (298 and 333 K) in ILs solutions containing up to 30 vol.% of water. BMI.BF₄ has been shown to be an ionic liquid with interesting properties such as high conductivity, chemical and electrochemical stability [14,15], used in many catalytic reactions [16] and as an electrolyte in fuel cell [17]. The electrolysis system operating at 298 K and -1.7 V (platinum quasi-reference electrode (PtQRE)), produces hydrogen gas with evolution of heat and efficiencies around 95%. For comparison, a similar system, described by Viswanath [18] operating at -1.75 V, gives a current density of 1 A cm^{-2} and 70% energy efficiency.

The aim of this work is to demonstrate the potential use of low concentration ILs in aqueous solution for hydrogen production through water electrolysis using different electrode materials, i.e. platinum, 304 stainless steel, nickel and low carbon steel. For these experiments a Hofmann's cell (Fig. 1) was used which



Scheme 1. Structure of the 1-*n*-butyl-3-methylimidazolium tetrafluoroborate (BMI.BF₄) ionic liquid used in this study.

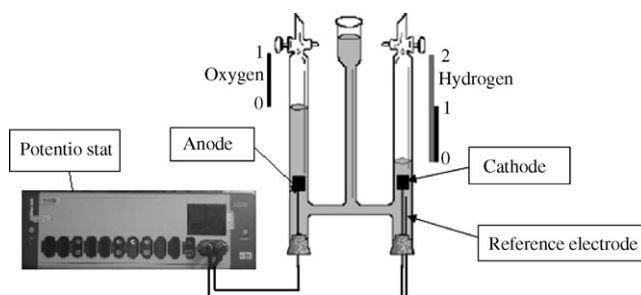


Fig. 1. Hofmann's cell used for the HER runs.

enables a convenient comparison of the electrocatalytical performances of these electrodes observing the current densities (j) and the hydrogen production efficiencies (η).

2. Experimental

The BMI.BF₄ ionic liquid (IL) was prepared according to previously published procedures [19–21]. All other reagents were purchased from Aldrich and used as received. The purity of the IL was determined by spectrometric methods. The electrolysis solutions were prepared by dissolving the IL in ultra pure water, varying from 1 to 30 vol.%.

The production of hydrogen from water electrolysis was performed using a Hofmann's cell, shown in Fig. 1, equipped with a working electrode, platinum as quasi-reference electrode and platinum wire as an auxiliary electrode.

Different electrocatalysts for water electrolysis were tested as working electrodes: pure platinum wire, nickel 99.5 wt.%, 304 stainless steel (C: 0.08; Cr: 18–20; Ni: 8–10; Mn: 2.0; Si: 1.0; S: 0.03; P: 0.04 wt.%) and low carbon steel (C: 0.05; Mn: 0.227; S: 0.0005; Cr: 2.34 wt.%).

The current densities ($j = I/A$) were calculated from the measured intensity (I) and the surface (S) of the electrode exposed to the medium. The area of the electrodes were geometrically calculated (304 stainless steel: 0.96 cm^2 , nickel: 0.78 cm^2 and low carbon steel: 0.61 cm^2) and, in the case of the platinum electrode the observed value (1.29 cm^2) was confirmed by calculation from the monolayer formed from hydrogen adsorption according to methods published elsewhere [22].

With the Hofmann's cell the gas volumes were measured directly and their values used to calculate the efficiency of the electrolytic system. The electrolysis potential was controlled with an Autolab potentiostat model PGSTAT30.

Two electrochemical methods were employed. Cyclic voltammetry (scanning the region -2.0 to 2.0 V (PtQRE) at sweep rates of 100 mV s^{-1}) was used to study the electrode behavior in the medium electrolyte, and the chronoamperometry (imposing a potential of -1.5 to -2.0 V (PtQRE) continuously over 60 min) was used to study the stability of the electrodes.

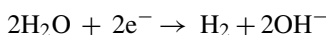
The reproducibility of the data in the electrolysis runs was determined from the repetition of at least three independent runs. The system was tested with different concentrations of ionic liquid in water and at different electrolysis potentials. All experiments were carried out at room temperature.

Analysis of the LCS electrode surface was observed by scanning electronic microscopy (SEM) (JEOL-JSM 6060) with 20 kV voltage acceleration and a 120 magnitude. Chemical surface analysis was performed through electronic diffraction spectroscopy (EDS) coupled to the SEM equipment.

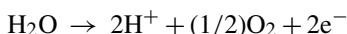
3. Results and discussion

Water electrolyses were performed in a Hofmann's cell (Fig. 1) equipped with different working electrode materials such as platinum (Pt), nickel (Ni), 304 stainless steel (SS) and low carbon steel (LCS) using aqueous solutions of ILs at different concentrations and operating at different imposed cathodic potentials.

In the cathodic compartment of the cell water is reduced at the working electrode leading to the production of hydrogen:



whereas in the anodic compartment oxygen is produced through water oxidation:



The performance of the system was determined from the consumed charge data (Q) and from the volume of hydrogen produced measured in the cathodic compartment of the cell during the electrochemical reaction.

The performance of the system depends on the electrocatalyst used to perform HER. The efficiency of the process (η) was calculated as the ratio between the amount of hydrogen produced and the amount of hydrogen theoretically produced, calculated from the consumed charge during the experiment, as shown by:

$$\eta\% = \frac{V_{\text{H}_2}^{\text{R}}}{V_{\text{H}_2}^{\text{T}}} \times 100 \quad (1)$$

where $V_{\text{H}_2}^{\text{R}}$ is the volume of hydrogen measured directly and $V_{\text{H}_2}^{\text{T}}$ is the volume of hydrogen theoretically calculated from the charge value by $V_{\text{H}_2}^{\text{T}} = (Q/2F)(RT/P)$.

3.1. Electrochemical behavior of the electrodes in pure IL and at low concentration IL aqueous solutions

Preliminary experiments were made in order to confirm the potential range where the hydrogen evolution reaction (HER) occurs. This strategy was previously used for the platinum electrode [13] and has been employed herein for all electrodes studied in this investigation.

Fig. 2 shows the cyclic voltammograms obtained using the nickel electrode in pure IL and in the presence of 10 vol.% of BMI.BF₄ aqueous solutions. The HER is observed in the potential range of -1.5 to -2.0 V (PtQRE). Similar results have been obtained with the SS electrode (shown in Fig. 3) and with the LCS electrode.

Although the highest current densities have always been observed at -2.0 V (PtQRE), the efficiency under these conditions tends to decrease because the reactive species compete for the active sites of the electrode and this slows down the HER.

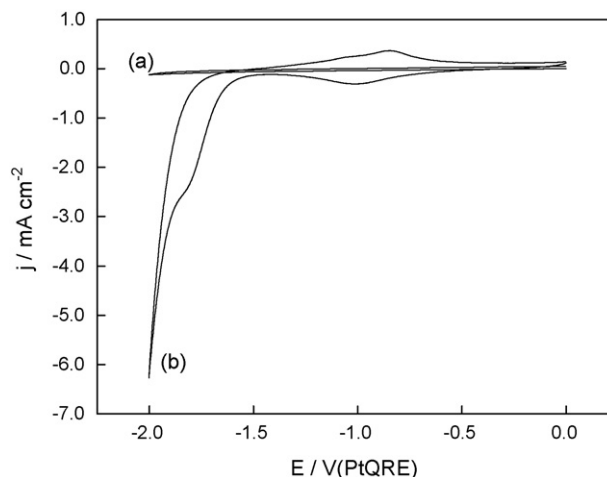


Fig. 2. Cyclic voltammograms taken from the nickel electrode in: (a) pure BMI.BF₄ and (b) with BMI.BF₄ solution 10 vol.% in water at room temperature, recorded at 100 mV s^{-1} under static conditions.

For all studied electrodes, i.e. platinum [13], Ni, SS, and LCS, the HER started at the same potential value, -1.5 V (PtQRE). In this work the performance of each electrode through efficiency, current density and exchange current density is evaluated.

3.2. Chronoamperometric evidences of the metal influence on the HER

Chronoamperometric experiments were performed with the working electrode polarized cathodically during 60 min at different potentials. The electrolyte concentrations were selected in the range 1–30 vol.% of BMI.BF₄ in water, and the reduction potential employed was varied from -1.5 to -2.0 V (PtQRE). The electrolysis time was kept constant at 60 min. The results presented Table 1 show that the cathodic current density varies with the reduction potential, the electrode and with the IL concentration.

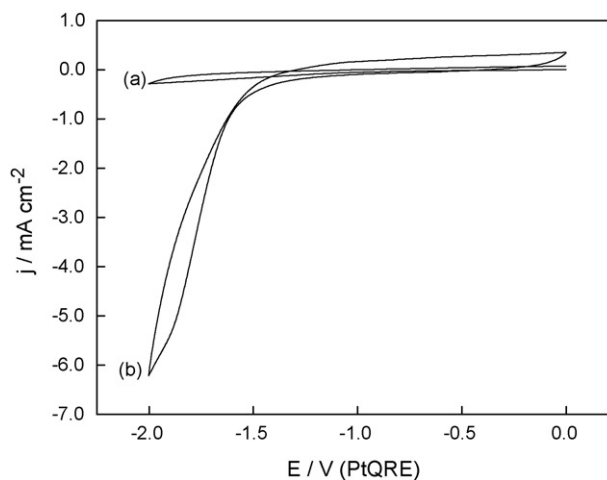


Fig. 3. Cyclic voltammograms taken from a 304 stainless steel electrode in: (a) pure BMI.BF₄ and (b) with BMI.BF₄ solution 10 vol.% in water at room temperature, recorded at 100 mV s^{-1} under static conditions.

Table 1

Cathodic current densities values for water electrolysis at different BMI.BF₄ concentrations, electrocatalyst and cathodic potentials recorded at room temperature

<i>E</i> (PtQRE, V)	<i>C</i> _{IL} ^a (vol.%)	<i>j</i> (mA cm ⁻²)			
		Pt	LCS	SS	Ni
-1.5	1	9	6.5	2.3	2
	10	19	20	4	7
	30	5	5	3	2
-1.7	1	13	8.5	3	3.5
	10	30	44	10	12
	30	7	10	11	8
-1.9	1	19	10	3.5	5
	10	55	55	17	20
	30	13	22	23	20
-2	1	23	12	4	6
	10	70	65	20	33
	30	18	28	37	26

^a BMI.BF₄ concentration in water, expressed as vol.%; Pt: platinum; LCS: low carbon steel; SS: 304 stainless steel; Ni: nickel. Ambient temperature between 293 and 300 K.

As a general trend, displacing the reduction potential to more cathodic values (from -1.5 to -2.0 V (PtQRE)) increases the current densities for all IL solutions irrespective of the electrode. However, it is noticeable that these values depend strongly on the electrode material. The data set clearly provides evidence that, for Pt, LCS and Ni electrodes and at any given potential, the highest current density values were obtained with 10 vol.% IL solutions. The presence of other metals such as Ni, Cr and Mn in the composition of SS should be responsible for the low catalytic activity of this electrode in HER. This low catalytic activity is probably associated with the well known passivation of SS in aqueous solutions [23].

Fig. 4 shows the current density dependency on the IL concentrations in water obtained at -1.7 V (PtQRE) comparatively for all electrocatalysts.

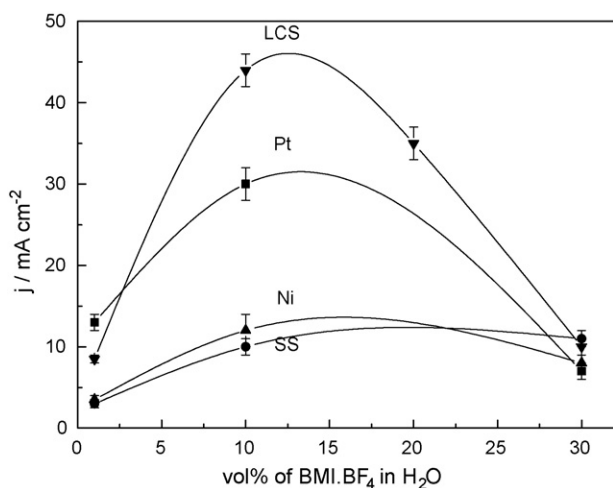


Fig. 4. Cathodic current densities of platinum (■); 304 stainless steel (●); low carbon steel (▼); nickel (▲) working electrodes at different concentrations of BMI.BF₄ in water taken at -1.7 V (PtQRE).

Table 2

Tafel parameters for the hydrogen electroreduction reaction with different electrocatalyst

Electrode	<i>j</i> ₀ (A cm ⁻²)	<i>β</i> _c (V dec ⁻¹)	<i>β</i> _a (V dec ⁻¹)
LCS	3.5 × 10 ⁻⁵	0.029	0.030
Pt	1.6 × 10 ⁻⁶	0.122	0.122
SS	3.1 × 10 ⁻⁶	0.069	0.079
Ni	3.3 × 10 ⁻⁷	0.092	0.103

Conditions: 10 vol.% BMI.BF₄ aqueous solution; room temperature.

The observed points fit to a bell shaped curve for Ni, Pt and LCS electrodes. The maximum current density value observed for the LCS is higher than the observed with Pt under the same conditions. It is expected that *j* increases with the electrolyte concentration, due to the higher availability of conducting species at a higher concentration of electrolyte. The decrease of *j* at IL concentrations higher than 13 vol.%, observed in Fig. 4, was surprising. This effect can be explained in different ways: (i) the formation of H₂ bubbles on the surface of the electrode, depleting the actual electrolysis area [24] and, by consequence, decreasing the observed *j* and (ii) the formation of aggregates of ionic pairs at higher concentrations as already proposed by different authors in the case of ionic liquids [25].

Tafel experiments are enlightening in this field since they enable the determination of important parameters such as the exchange current densities (*j*₀), the cathodic slope (*β*_c) and the anodic slope (*β*_a). This linear sweep voltammetry affords a linear free energy relation between the current and the potential. By plotting the ln |*j*| versus *E*, the slopes and the intercept at *E* = *E*_{eq} gives the exchange current density for the electrode reaction [26], the hydrogen evolution reaction, in this case.

Table 2 shows the data obtained from Tafel plots for different electrocatalysts in 10 vol.% ionic liquid.

It is worth noting that the highest exchange current density and lowest cathodic slope were observed for LCS in this medium and at this temperature.

From these values the best electrocatalyst for HER is LCS, in agreement with the results presented in Fig. 4 and explain that the observed effects are due to a charge transfer process involved in the electroreduction of the proton.

The cathodic slope (*β*_c) values obtained in these Tafel plots can also be extremely elucidative. Fig. 5 shows the dependence of the *β*_c with the IL concentration. The lower polarization energy is observed at 10 vol.% and this is an elegant explanation as to why this is the optimal IL concentration for HER.

The mechanism of the reaction of hydrogen production depends on the nature of the metal. Bockris considers the Pt electrode as a "soft" metal in acid solution, and then a Volmer's mechanism becomes the main hydrogen evolution pathway. By this mechanism, the hydrogen production has two pathways. At first, there is a proton discharge onto the surface sites, a chemical reaction follows in which adsorbed H atoms diffuse to each other across the electrode surface and undergo a chemical reaction to form H_{2(g)} [27].

Bockris and Khan studied the rate of the HER in H⁺-containing solutions (H₂SO₄ 1.0 mol L⁻¹) and concluded that

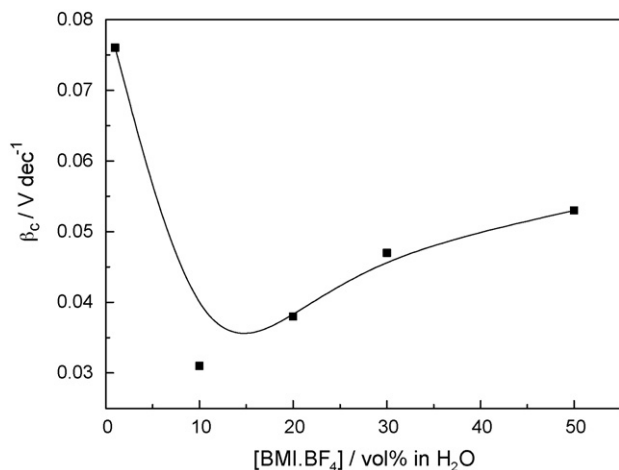


Fig. 5. The cathodic slope (β_c) values of different IL concentrations with a low carbon steel electrode obtained by Tafel plots. Conditions: sweep linear voltammetry at 1 mV s^{-1} under static conditions (PtQRE).

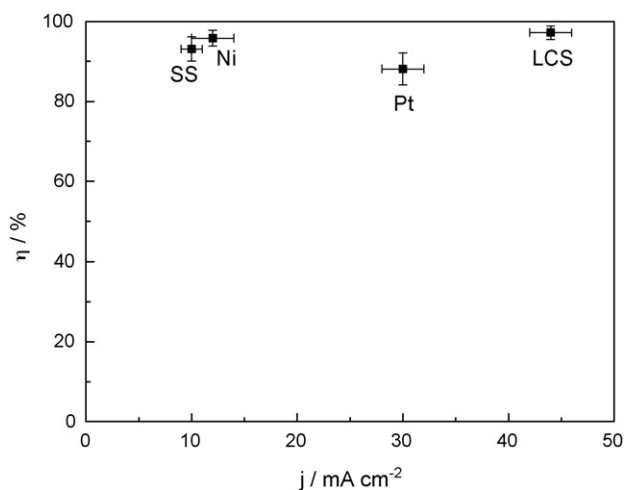
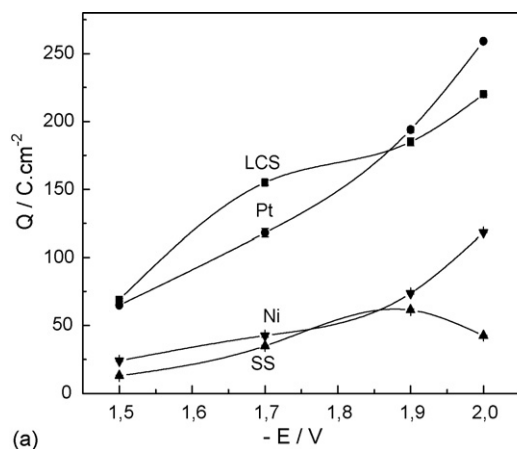
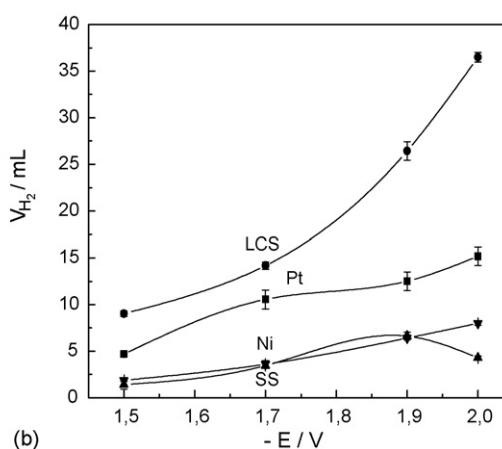


Fig. 6. Efficiency and current density of different electrodes used in HER. Conditions: BMI.BF₄ 10 vol.% in water and -1.7 V (PtQRE).



(a)



(b)

Fig. 7. Effect of the applied cathodic potentials on the: (a) charge recorded and (b) hydrogen volume production during water electrolysis using as electrolyte 10 vol.% of BMI.BF₄ in water observed with the platinum (●); 304 stainless steel (▲); low carbon steel (■); nickel (▼) working electrodes in 1 h.

Table 3

Hydrogen production efficiencies ($\eta\%$) determined at -1.7 V (PtQRE) during 60 min at room temperature, for all electrocatalyst using a 10 vol.% BMI.BF₄ aqueous solution

Electrode	HER efficiency (η , %)
Pt	88.5
LCS	95.5
Ni	97.1
SS	96.1

the observed rate was characteristic of a rate-determining discharge rather than that of desorption [27]. The value of the exchange current density for the platinum electrode observed by these authors was $7.9 \times 10^{-4} \text{ A cm}^{-2}$ [28]. In our case, with Pt electrodes the exchange current value was $1.6 \times 10^{-6} \text{ A cm}^{-2}$, which means that the HER occurs more slowly in the system BMI.BF₄ than H₂SO₄. In opposition, using a LCS electrode the exchange current density was $3.5 \times 10^{-5} \text{ A cm}^{-2}$, which is a rate similar to the observed with H₂SO₄.

3.3. Efficiency of the HER with different electrocatalysts

Table 3 shows the HER efficiency (η) for all electrocatalysts studied at -1.7 V (PtQRE) in 10 vol.% IL at room temperature.

It is worth noting that the HER efficiency depends on the potential and concentration of the IL solution. At more cathodic potential ranges and using more dilute IL solutions the efficiency of platinum increases up to 100%.

Fig. 6 shows that different electrodes give similar efficiencies but different current densities. These data have been obtained from the chronoamperometric curves.

As observed in Fig. 6 the highest current density values were obtained with the LCS electrode. This effect confirms that LCS electrode is the best electrocatalyst for water electrolysis in this medium.

Fig. 7 shows the dependence of the charge (Q) and the volume of hydrogen produced (V_{H_2}) with the potential. The platinum electrocatalyst, which is a very stable and efficient material, experienced a drawback at -2.0 V (PtQRE) for water electrol-

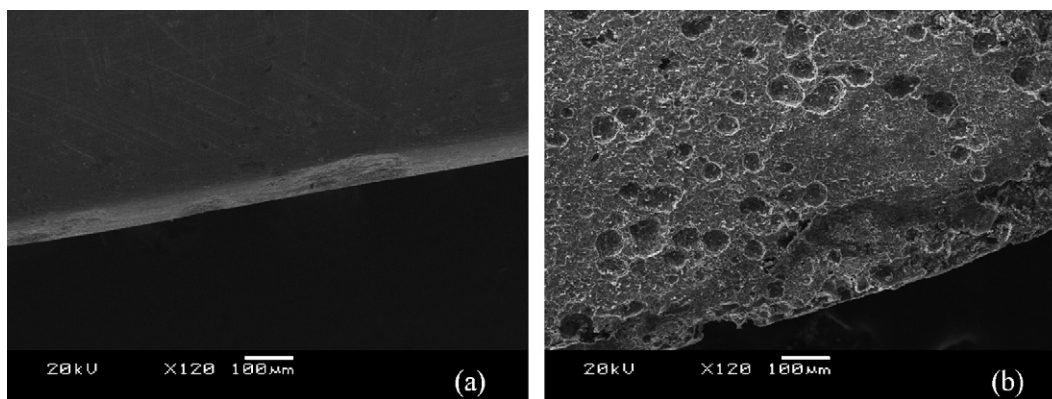


Fig. 8. SEM evidences of the corrosiveness of the low IL concentration solution on low carbon steel electrode: (a) without immersion in the electrolyte solution and (b) after 5 days immersed in 1 vol.% of IL in aqueous solution.

ysis, evidenced by a loss of efficiency. Comparing this behavior with that of the LCS electrode, the latter showed the highest charge value and the highest hydrogen production with an increase in the applied potential. Taking this into account these results, the LCS electrode, a cheap electrode, represents an interesting alternative material for the production of hydrogen by water electrolysis.

The low carbon steel electrocatalyst showed the highest values of charge (Q) regarding to the HER over almost all of the potential range as well as the highest hydrogen volume evolution (V_{H_2}). The LCS electrocatalyst gave very high efficiencies, between 95 and 99%. These results are in agreement with the j_0 values observed for this metal in this medium.

The charge and hydrogen volume associated with the HER obtained with the SS electrocatalyst were lower than LCS, over the full potential range. This phenomenon is probably associated with the known capacity of stainless steel to form a protecting film originating from the chromium in its composition [23]. The efficiency observed with SS is in the range 87–96%. The same comments can be made from the nickel electrocatalyst. Active metals such LCS in aqueous solutions are susceptible to corrosion processes. It should be pointed out that the pH of aqueous IL solutions decreases slowly with storage time. For example, the pH measured in a 10 vol.% BMI.BF₄ solution immediately after preparation was 6.54 and after 3 h at room temperature the pH dropped to 3.95. This effect was previously described by other authors and is due to the hydrolysis of the imidazolium cation [29] which causes deprotonation of the imidazolium ring. Surprisingly, the expected corrosion of the LCS was observed only with the 1 vol.% IL solution. Fig. 8 shows the micrographies of the LCS electrode before contact with the electrolyte solution (a) and the electrode corroded after 30 h of HER operation (b).

The corrosion of LCS in these aqueous solutions of imidazolium ionic liquids was expected since it is known that these compounds produce acids by deprotonation of the carbon 2 of the imidazolium ring in water, producing HBF₄. This acidity leads to the corrosion of the electrode. Otherwise, it is worth noting that the corrosion phenomenon is not observed during electrolysis performed with more concentrated solutions. The absence of corrosion under such conditions was unexpected and

should be ascribed to an inhibitor effect, as has been described for many imidazolium derivatives [30].

4. Conclusion

It has been shown that hydrogen production can occur efficiently from the reduction of water in the presence of low concentrations of IL using different electrode materials. The judicious combination of an electrolyte and electrocatalyst, solution concentration and electrode materials should lead to a high efficiency system with low cost, in order to enable technological applications. The high efficiency and current density observed at low concentrations of the 1-*n*-butyl-3-methylimidazolium tetrafluoroborate (BMI.BF₄) ionic liquid in water makes this system extremely attractive.

The best combination of IL and electrocatalyst was obtained at 10 vol.% IL in water, giving current densities (j) as high as 42 mA cm⁻² for LCS, with hydrogen efficiencies between 95 and 99% and high stability.

The major point of these studies is the economical attractiveness of performing water electrolysis using an inexpensive electrode such as low carbon steel and a very stable IL. The system constituted by these elements has to be considered as an alternative to the currently employed technology for the production of high purity hydrogen through HER.

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