Hydrogen production by water electrolysis using TEA.PS-BF₄ ionic liquid and alternative electrocatalysts

Márcia R. Becker[1], Sergio A. Arguello[2], Janine C. Padilha[3]

Latin American Institute of Life and Nature Sciences - Federal University of Latin American Integration, Brazil
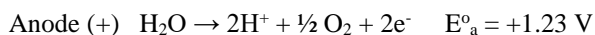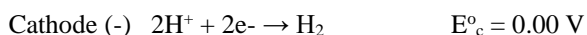Email: [1]marcia.becker@unila.edu.br; [2]sergioarguello2411@gmail.com; [3]janine.padilha@unila.edu.br

Abstract— *Studies on water electrolysis are in permanent development to improve its processes with electrodes and electrolytes that offer lower overpotential values. This work uses an ionic liquid (IL) – tetrafluoroborate of 3-triethylammonium-propane sulfonic acid (TEA-PS.BF₄) – as electrolyte and studies the effect of different electroactive cathode materials on hydrogen production, such as platinum (Pt), nickel (Ni), palladium (Pd), gold (Au) or silver (Ag). Water electrolysis was performed in a Hoffman Cell and analysed by chronoamperometry (CA) and linear sweep voltammetry (LSV) techniques. For the electrodes studied here, in a 0.1 M TEA-PS.BF₄ solution, current density (j) values were 252-404 mA cm⁻²; for 0.3 M TEA-PS.BF₄, values were 406-728 mA cm⁻²; and for 0.7 M, values were 822-1055 mA cm⁻². Low activation energy (Ea) of 5 kJ mol⁻¹ was found for the Au cathode, 9 kJ mol⁻¹ for Pt and Ag, and 24 kJ mol⁻¹ for Ni and Pd. Results show that the Ni electrode is an attractive alternative for hydrogen production by water electrolysis and using IL as electrolyte.*

I. INTRODUCTION

Hydrogen and fuel cells are considered important alternatives for future sustainable energy systems in the stationary power, transportation, industrial and residential sectors. Moreover, hydrogen is used in oil refineries to produce fuels from petroleum hydrocracking, to manufacture fertilizers, [1, 2] in the food industry, in the semiconductor manufacturing process, among others. Hydrogen is a clean energy carrier with high specific energy density [3] that is usually produced by steam methane reforming, coal gasification and a simple process such as water electrolysis. The latter process yields high-purity, carbon dioxide-free hydrogen from renewable sources. [4, 5] Hydrogen produced by water electrolysis combined with other energy generation processes may be a solution to convert long-stored chemical energy back into electricity.

Water electrolysis is an electrochemical process determined by the circulation of an electric current through two electrodes immersed in an electrolyte solution to break water into hydrogen and oxygen. Pure water, although little dissociated, contains ions H^+ and OH^- which, because of electric field action, migrate toward the cathode and the anode to form hydrogen and oxygen gases. The electricity needed for the electrolysis may come from renewable energy sources such as solar, wind, and hydroelectric installations, or excess power from existing generators to produce hydrogen during off-peak times. Due to the low electrical conductivity of pure water, electrolysis should be carried out in the presence of suitable dissolved electrolytes to increase the conductivity of the solution. The electrolytes to be added to water may be acids, bases, or salts. The reaction and standard equilibrium electrode potential (E°) at 298 K can be written as follows:

In acid electrolyte

Cathode (-) $2H^+ + 2e- \rightarrow H_2$ $E^o_c = 0.00$ V

Anode (+) $H_2O \rightarrow 2H^+ + \frac{1}{2}O_2 + 2e^-$ $E^o_a = +1.23$ V

Overall reaction is

$H_2O \rightarrow H_2 + \frac{1}{2}O_2$ $E^o = -1.23$ V

In conventional water electrolysis, corrosive electrolytes such as NaOH, KOH and H_2SO_4 are usually used as conductive materials. Metal electrodes used as catalysts and even the electrolyser may suffer serious damage in these corrosive electrolytes and lose catalytic activity. Ionic liquids (ILs) are low-melting salts that melt at or below 273 K, which are usually composed of a large asymmetric organic cation and an inorganic or organic anion. [6] ILs are materials with many interesting properties that may include low vapor pressure, wide electrochemistry window, solubility in a wide range of organic solvents and water, high conductivity, and thermal and chemical stability. [7] Because of these characteristics, ILs can be used as electrolytes in the electrolysis of water. [8] Fiegenbaum *et al* [9] used tetrafluoroborate of 3-triethylammonium-propane sulfonic acid (TEA-PS.BF$_4$) in different concentrations as a conductive electrolyte to produce hydrogen by water electrolysis. A system using TEA-PS.BF$_4$ in an electrochemical cell with platinum electrodes had current densities up to 1.77 A cm^{-2}, and the activation energy observed was 9.3 kJ mol^{-1} – a low value that can be explained by the facilitation of proton transport in the organized aqueous ionic liquid media. The high efficiency of this system was discussed by considering the high conductivities associated with the Brönsted and Lewis acidity characteristics of the IL.

The water electrolysis process is continually subject to improvement, including, among other features, the use of new and better electrocatalytic materials, which reduce overpotential. [10] The cathodic material that is most active for hydrogen production by water electrolysis is platinum, but high price and limited availability are limiting factors for its extensive use. Several materials have been used to make electrodes, with different effective active areas, catalytic activity, electrical resistance, corrosion resistivity and average lifetime. Lima *et al* [11] investigated vitreous carbon and pyrolytic carbon covered by nickel particles as cathodes in an aqueous solution of tetrafluoroborate of the 3-triethylammonium-propane sulfonic acid (TEA-PS.BF$_4$) ionic liquid for hydrogen production. They observed current density values for the pyrolytic carbon cathode that were higher than those found for the vitreous carbon cathode, indicating that adsorption of H^+ and desorption of H_2 were favoured in the former.

At present, several studies are being conducted on economically viable hydrogen production by water electrolysis, which means finding new materials that can be used as electrodes and electrolytes. This work presents water electrolysis performance using five different electrodes – Pt, Ni, Pd, Au and Ag – and using TEA-PS.BF$_4$ ionic liquid solutions as electrolytes.

II.   METHOD

2.1. Preparation of TEA-PS.BF$_4$

TEA-PS and TEA-PS·BF$_4$ were prepared using procedures available in the literature. [9] In a reaction flask, 51.4 g of 1,3-propanesultone and 42.5 g of triethylamine were mixed with 20 mL of ethyl acetate. The reaction was stirred at 323 K for 2 h and filtered, producing a white solid. The precipitate was dried at 373 K for 2 h, producing 3-triethylammonium-propane sultonate (TEA-PS) as a white powder.

TEA-PS.BF$_4$ was prepared by reacting 56.7 g of TEA-PS dissolved in 5 mL of water and 33.8 mL of tetrafluoroboric acid at room temperature. After 2 h at 363 K, the water was removed under reduced pressure, producing 75.9 g of tetrafluoroborate of the 3-triethylammonium-propane sulfonic acid (TEA-PS.BF$_4$) as a white viscous liquid. [1H NMR (300 MHz, DMSO, ppm): d 1.17 (t, 3H), 1.88 (m, 2H), 3.22 (m, 2H), 3.32 (m, 2H), 4.23 (s, 1H)].

2.2. Electrochemical measurements

The conductivity (σ) of the IL solutions was measured using an MCA 150 conductivity meter calibrated with standard aqueous potassium chloride solutions (491 ± 2.5 mg L^{-1} and 1000 ± 10 μS cm^{-1}, 298 K). The electrochemical experiments used a Hoffmann's Cell with a three-electrode arrangement (Fig. 1), composed of a platinum counter electrode, a platinum wire as the quasi-reference electrode and five types of working electrodes: platinum (Pt), gold (Au), silver (Ag), palladium (Pd) and nickel (Ni) – all the metal electrodes with 99.9% of purity. Electrolysis was performed with 0.1 M, 0.3 M and 0.7 M TEA-PS.BF$_4$ aqueous solution. Chronoamperometry (CA) was performed in a 100 mL Hoffmann's Cell at room temperature at potentials from -1.3 to -2.0 V continuously over 60 min to evaluate the electrodes' stability and H$_2$ production. The residence time of the bubbles on the surface of the electrode was estimated between 15 and 30 min and consists of the average time between two peaks of maximum current. Linear-sweep voltammetry (LSV) measurements were performed in a 30 mL Hoffman's Cell from -2.0 to 0.0 V at a scan rate of 10 mV s^{-1} and range temperature from 288 to 353 K (± 0.1 K). LSV reports the

steady-state current densities dependence on a variety of overpotential, obtained from Tafel plots according to (1):

$$\eta = a + b\, log j \tag{1}$$

where b (V dec-1) is the Tafel coefficient, which indicates the rate of change in current density, j (mA cm^{-2}), with the applied overpotential, η (V). CA and LSV were performed with an AUTOLAB model PGSTAT302N and its associated NOVA software to control the experiments and data acquisition.
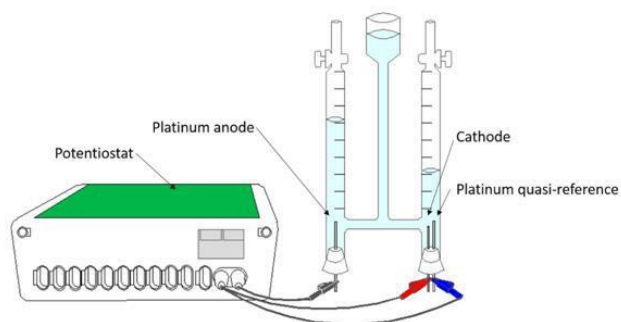

Fig 1. Hoffmann's Cell used for water electrolysis.

III. RESULTS AND DISCUSSION

The nature of electrolytes and electrodes influences the electrolysis process. TEA-PS.BF$_4$ had its conductivities in aqueous solutions measured, and the results are shown in Fig. 2. Specific conductivity values increased with higher IL concentration, which may be attributed to its higher dissociation degree in water. At these concentrations – 0.1 M, 0.3 M and 0.7 M – water is in the TEA-PS.BF$_4$ network, breaking the strong Coulombic interactions, resulting in solvation and increase in the dissociation of the TEA-PS$^+$ and BF$_4^-$ ions. In this concentration range, the electric force attributed to the presence of the ions dissociated and subjected to the electric field seems to prevail over the frictional forces attributed to the increase in the viscosity of the medium due to IL concentration. This indicates that ionic conductivity is not only related to the viscosity but also to the ion-ion, ion-solvent, and solvent-solvent interactions.
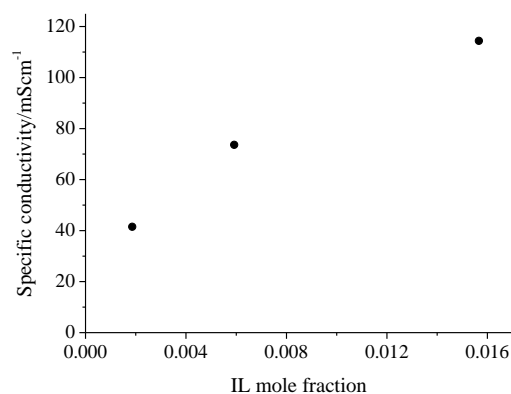

*Fig. 2. TEA-PS.BF$_4$ molar fraction dependence on specific conductivity.*

The rate of the electrode reaction, characterized by current density, depends on the nature of the electrode surfaces and on the composition of the electrolytic solution adjacent to the electrodes. The ions that are close to the electrodes in the solution and therefore under the effect of electrode form double layers, and the rate of the reaction depends on electrode potential characterized by the reaction's overpotential. The mechanism of the hydrogen evolution reaction is widely accepted [12] to be a step involving the formation of adsorbed hydrogen

$$H^+ + e^- \rightarrow H_{ads} \tag{R1}$$

which is followed by either chemical desorption

$$2H_{ads} \rightarrow H_2 \tag{R2}$$
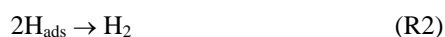
or electrochemical desorption

$$H^+ + e^- + H_{ads} \rightarrow H_2 \tag{R3}$$
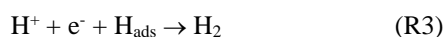
where the subscript *ads* represent the adsorbed status. Increasing overpotential could lead to a change in the mechanism rate. The rate-determining step will change at different potential ranges. When the potential is low, electron transfer (R1) is not as fast as desorption and hydrogen adsorption will be the rate-determining step. On the other hand, when the potential is high enough for the hydrogen adsorption rate to be higher than the desorption rate, hydrogen desorption will be the rate-determining step (R2 and R3). Fig. 3 shows increasing current density values with increasing potential for the electrodes tested, indicating that larger electric power is consumed by the electrolyser and therefore hydrogen production is higher. Pt with the IL presented the best performance at any potential range. Its current density increases from 200 to 400 mA cm^{-2}. Similarly, Ni presented variation of 130 to 350 mA cm^{-2}. Pd and Au, with small differences especially at lower potentials, presented behaviour similar to Ni. Ag presents the smallest current density variation, being subject to low or high overpotentials. Its variation was

only 140-250 mA cm^{-2}, showing that working at smaller overpotentials (-1.3 V) may be more advantageous for Ag.
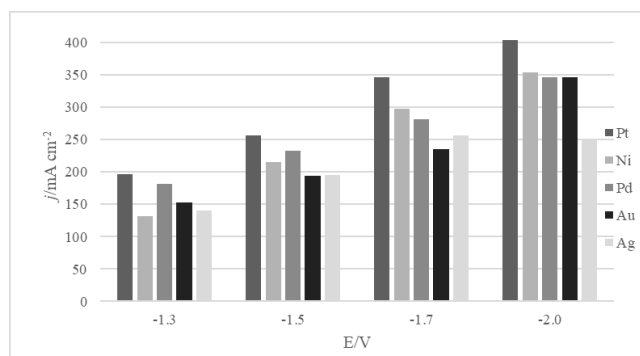

Fig 3. Potential effect on the current density for 0.1 M TEA-PS.BF$_4$ solution.

In addition to the overpotential imposed on the system, which is known to favour electrolysis, the system is affected by bubble formation on the work electrode's surface. The hydrogen bubbles produced tend to electrically insulate the active sites in the electrode surface, reducing its activity and consequently the current densities values. Fig. 4 and Table 1 show longer release time for bubbles produced at higher potential (-1.3 V) (Fig. 4a) than at lower potential (-2.0 V) (Fig. 4b). When several bubbles, represented by the circles, are produced, they adhered to the electrode, which remains with its active area unavailable for the reactions, and current values decrease. As soon as the bubbles are released, the reaction resumes and current increase again. Systems with higher amounts of bubbles tend to leave the electrode less exposed; therefore, those with higher potentials are privileged and present better performances. [13]
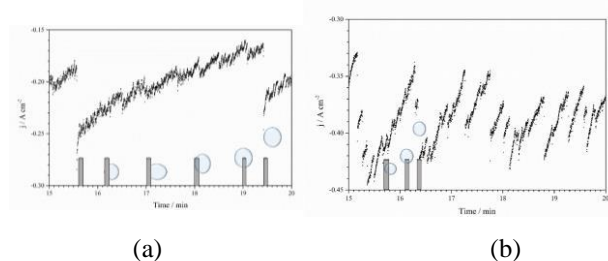

(a)   (b)

Fig. 4. Bubble release time to (a) -1.3 V or to (b) -2.0 V on Pt electrode with 0.1 M TEA-PS.BF$_4$ solution.

Interestingly, for the systems proposed here, the time during which the bubbles remain on the surface of the electrodes does not seem to vary significantly within the range of potentials studied. However, it can be inferred that on the Ag surface, the bubbles remain longer at -1.3 and -2.0 V potentials than on the surface of the other electrodes. This may contribute to their poor performance in electrolysis compared to other electrodes.

Table 1: Release time of the H$_2$ bubbles on the electrodes surface.

	Release time (min)			
	-1.3 V	-1.5 V	-1.7 V	-2.0 V
Pt	2 ± 1	1.2 ± 0.6	1.0 ± 0.4	0.6 ± 0.2
Ag	4 ± 1	0.9 ± 0.5	1.2 ± 0.6	3.0 ± 2
Au	1.2 ± 0.6	1.4 ± 0.8	1.2 ± 0.2	1.4 ± 0.7
Ni	1.6 ± 0.6	2.2 ± 0.9	1.0 ± 0.5	2 ± 2
Pd	3 ± 2	1.1 ± 0.6	1.2 ± 0.6	1.0 ± 0.4

Fig. 5 shows the influence of TEA-PS.BF$_4$ concentration on current density at different potentials and with different electrodes. The results show an increase in current density values with increasing concentration of the IL. This behaviour agrees with those found in conductivity measurements where conductivity increases with higher concentration of the LI solution. The results also indicate strong dependence of water electrolysis on the electrode's material.

The data on Ni electrode showed efficiency only 10% lower than Pt, indicating Ni as a promising material to be used as a catalyst in water electrolysis with TEA-PS.BF$_4$. In addition, systems using Pd, Au and especially Ag appear to be strongly influenced by the concentration of the IL, at least more than those using Pt and Ni. Electrodes made of Pt, Ni, Pd, Au and Ag were stable during the electrolysis process.
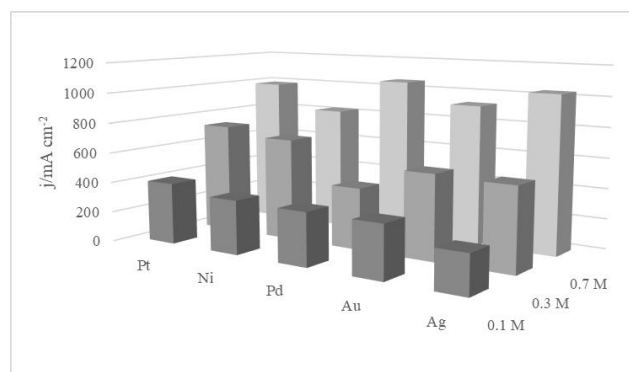

Fig. 5. Effect of TEA-PS.BF$_4$ concentration on current density at -2.0 V and 298 K.

Kinetic parameters for hydrogen production were evaluated by exchange current density at the open-circuit potential (j_o) and cathodic slope (b_c); both are shown in Table 2. Hydrogen production on the electrode is given by the slopes and intercept at E = E$_{eq}$ by plotting ln|j| versus E.

Table 2. Tafel parameters of the HER to different cathodes and TEA-PS.BF$_4$ solutions.

	j_o (µA cm^{-2})			b_c (mV dec^{-1})			E_{eq} (V)		
	0.1 M	0.3 M	0.7 M	0.1 M	0.3 M	0.7 M	0.1 M	0.3 M	0.7 M
Pt	1.2	2.8	6.5	104	97	83	0.70	-0.11	-0.20
Ni	5.2	3.0	0.8	120	106	79	-0.20	-0.09	-0.06
Pd	367	320	324	61	110	116	-0.35	-0.55	-0.26
Au	4.9	3.6	3.6	63	125	44	-0.35	-0.21	-0.03
Ag	1.2	2.5	5.1	96	66	6	-0.20	-0.04	0.28

It is worth noting that the highest exchange current density (j_o) values were observed for Pd. Pt and Ag show increase in current density with increasing IL concentration. Ni and Au, in turn, present lower jo with higher IL concentration. The lowest cathodic slope was observed for Ag with 0.7 M TEA-PS.BF$_4$ solution, followed by Au at the same concentration and Pd with 0.1 M solution. For Ag electrocatalyst, lower electrode polarization is needed for proton adsorption/desorption, and the reaction occurs faster (kinetic factor). It indicates that IL concentration influences electrode activity, and the best solution seems to be 0.7 M TEA-PS.BF$_4$ with Au, Ag, Ni and 0.1 M TEA-PS.BF$_4$ with Au and Pd.

Electrodes' catalytic performance was measured by activation energies (E$_a$) for the HER. Arrhenius-type dependence predicts that the exponential increases with the reciprocal of the temperature, which, in a logarithmic form, is as (2):

$$\ln j = \ln A - E_a / RT \qquad (2)$$

Where A is the pre-exponential factor (cm s^{-1}), E$_a$ is the activation energy, R is the universal gas constant (8.31 J K^{-1} mol^{-1}), and T (K) is the absolute temperature.

The effect of temperature on the system with 0.1 M TEA-PS.BF$_4$ solution at 288-353 K with applied potential of -2.0 V is shown in Fig. 7.
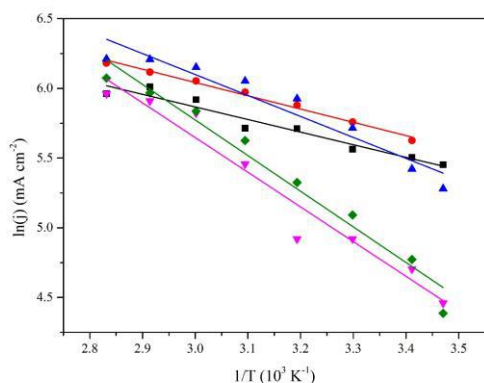

Fig. 7. Temperature effect on the current density for the system using 0.1 M TEA-PS.BF$_4$ at -2.0 V with Pt (■), Ni (•), Pd (◆), Au (▲) and Ag (▼).

Linear increase of the density current with temperature can be observed for all cathodes and between 298 and 318 K. Table 3 reports E$_a$ values for each cathode studied. The adjusted R-square is shown to demonstrate the good approximation of the Arrhenius plots.

Table 3. Activation energy for the system with 0.1 M TEA-PS.BF$_4$ solution.

Cathode	E$_a$/kJ mol^{-1}	R^2
Platinum	9	0.94
Nickel	24	0.94
Gold	5	0.96
Silver	9	0.98
Palladium	25	0.96

E$_a$ values are low for all electrodes, and Au, Ag and Pt have good performances and are promising materials to be used as working electrodes in water electrolysis with this IL. However, E$_a$ values were higher for nickel and palladium than for those materials previously mentioned. Increase in temperature in the system may lead to higher density and diameter of the bubbles adsorbed on their surface. This increase in the surface area covered reduces the electrocatalytic area and therefore current density. This behaviour seems to be linear with increasing temperature but is more pronounced for Ni and Pd, making the slope of the line smaller. These values are comparable to those found in the literature when the electrolyte used is 30% KOH solution, that is, 16 kJ mol^{-1}. [9]

IV. CONCLUSIONS

Water electrolysis was performed with Pt, Ni, Pd, Au or Ag electrodes using TEA-PS.BF$_4$ as electrolyte. The Ni electrode's efficiency was only 10% lower than Pt, pointing to it as a promising material to be used use as a catalyst in water electrolysis. Pt, Ni, Pd, Au and Ag electrodes were stable during the electrolysis process.

The best IL/cathode combination was obtained at 0.7 M TEA-PS.BF$_4$ for Au, Ag, Ni and at 0.1 M TEA-PS.BF$_4$ for Au and Pd, with high hydrogen production.

The major point of these studies is the economical attractiveness of performing water electrolysis using an inexpensive electrode such as Ni and a very stable IL. The system constituted by these elements must be considered

as an alternative to the currently employed to produce high-purity hydrogen through electrolysis.

ACKNOWLEDGEMENTS

REFERENCES

[1] Yue, M., Lambert, H., Pahon, E., Roche, R., Jemei, S., Hissel, D. (2021). Hydrogen energy systems: A critical review of technologies, applications, trends and challenges. Renewable and Sustainable Energy Reviews, 146, 111180. https://doi.org/10.1016/j.rser.2021.111180

[2] Hashmi, M. H., & Dubey, N. (2018). Experimental Investigation of the Effects of Hydrogen Addition with Diesel on Performance and Emission of a Single Cylinder Diesel Engine. International Journal of Advanced Engineering Research and Science, 5(4), 135-145. https://dx.doi.org/10.22161/ijaers.5.4.19

[3] Lui, J., Chen, W. H., Tsang, D. C.W., You, S. (2020). A critical review on the principles, applications, and challenges of waste-to-hydrogen technologies. Renewable and Sustainable Energy Reviews, 134, 110365. https://doi.org/10.1016/j.rser.2020.110365

[4] Haverkort, J. W., Rajaei, H. (2021). Voltage losses in zero-gap alkaline water electrolysis. Journal of Power Sources 497, 229864. https://doi.org/10.1016/j.jpowsour.2021.229864

[5] Anwar, S., Khan, F., Zhang, Y., Djire, A. (2021). Recent development in electrocatalysts for hydrogen production through water electrolysis. International Journal of Hydrogen Energy, 46(63), 32284–32317. https://doi.org/10.1016/j.ijhydene.2021.06.191

[6] Thimmappa, R., Walsh, D., Scott, K., Mamlouk, M. (2020). Journal of Power Sources 449, 227602. https://doi.org/10.1016/j.jpowsour.2019.227602

[7] Nordness, O. & Brennecke, J. F. (2020). Ion Dissociation in Ionic Liquids and Ionic Liquid Solutions. Chem. Rev. 120, 23, 12873–12902. https://doi.org/10.1021/acs.chemrev.0c00373

[8] Amaral, L., D.S.P. Cardoso, D.S.P., Šljukić, B, Santos, D.M.F., Sequeira, C.A.C. (2019). Electrochemistry of hydrogen evolution in RTILs aqueous mixtures. Materials Research Bulletin, 112, 407-412. https://doi.org/10.1016/j.materresbull.2018.04.041

[9] Fiegenbaum, F., Martini, E. M., Souza, M. O., Becker, M. R., Souza, R. F. (2013) Hydrogen production by water electrolysis using tetra-alkyl-ammonium-sulfonic acid ionic liquid electrolytes. Journal of Power Sources, 243, 822-825. https://doi.org/10.1016/j.jpowsour.2013.06.077

[10] Fiegenbaum, F., Souza, M. O., Becker, M. R., Martini, E. M., Souza, R. F. (2015). Electrocatalytic activities of cathode electrodes for water electrolysis using tetra-alkyl-ammonium-sulfonic acid ionic liquid as electrolyte. Journal of Power Sources, 280, 12-17. https://doi.org/10.1016/j.jpowsour.2015.01.082

[11] Lima D. W., Trombetta, F., Benvenutti, P. P., Teixeira, S. R., Martini, E. M. A. (2019) Effect of different carbon supports for Ni particles for the HER in tetra-alkylammonium-sulfonic acid media. Int J Energy Res. 1–12. https://doi.org/10.1002/er.4765

[12] Zeng, K. & Zhang, D. (2010) Recent progress in alkaline water electrolysis for hydrogen production and applications. Progress in Energy and Combustion Science, 36, 307-326. https://doi.org/10.1016/j.pecs.2009.11.002

[13] Zeradjanin, A. R., Narangoda, P., Spanos, I., Masa, J., Schlögl, R. (2021). How to minimise destabilising effect of gas bubbles on water splitting electrocatalysts? Current Opinion in Electrochemistry, 30, 100797. https://doi.org/10.1016/j.coelec.2021.100797

[14] Bae, M., Kang, Y., Lee, D. W., Jeon, D., Ryu, J. (2022). Superaerophobic Polyethyleneimine Hydrogels for Improving Electrochemical Hydrogen Production by Promoting Bubble Detachment. Adv. Energy Mater., 12, 2201452, 1-9. https://doi.org/10.1002/aenm.202201452