Short communication

Study of molybdenum electrodes for hydrogen evolution reaction

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ABSTRACT

The molybdenum electrode, Mo, has been investigated for hydrogen production *via* water electrolysis in 10 vol.% aqueous solutions of 1-butyl-3-methylimidazolium tetrafluoroborate (BMI·BF$_4$) using electrochemical impedance spectroscopy (EIS). The EIS measurements show that the Mo system has much higher interfacial capacitance, and correspondently the electrical double layer formed on this electrode is thicker than those formed on nickel or platinum. The positive displacement of potential of zero charge (PZC) values indicates the specific adsorption of the imidazolium cation on the Mo surface. This study provides an elegant explanation for the better performance of Mo electrodes in the hydrogen evolution reaction (HER): the BMI cation acts as an intermediate for the proton transfer from water to the electrode surface, thereby decreasing the overpotential of HER. This model explains the synergism between Mo and the BMI cation in the HER process.

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1. Introduction

The production of carbon dioxide during fossil fuel combustion is a major drawback in the use of these energy sources and has become a centre of discussion concerning global warming [1–3]. Thus, the substitution of CO$_2$-emitting fuels with renewable and environmentally clean alternatives is object of many research efforts. Fuel cells that employ hydrogen are one of the alternatives considered to be an applicable technology.

Currently, the main industrial production of hydrogen uses the reforming of fossil fuels [4,5]. Using this method, hydrogen is produced as a mixture with CO and CO$_2$, and therefore it must be purified for use in fuel cells to prevent further CO$_2$ pollution. An attractive alternative for the clean production of hydrogen is water electrolysis. However, the practical use of water electrolysis is still limited by the cost of the electrical energy, usually determined by local configurations and availability, and limitations in the performance of the electrolysers, which are intrinsically linked with the materials used for the construction of electrodes and as electrolytes [6,7]. Classic electrolysers use alkaline electrolytes at 330–350 K with noble metal electrodes such as platinum, or alternatively, platinum alloys or nickel, although with poorer performances [8–11]. The research into better and cheaper materials for water electrolysis has been a great challenge in recent years [12,13].

The use of ionic liquids (ILs) as electrolytes for water electrolysis at room temperature opened new possibilities because their physico-chemical properties enable better performances and increase the lifetime of the electrodes [14], which directly affects the overall cost of the process. Using 1-butyl-3-methylimidazolium tetrafluoroborate (BMI·BF$_4$) ionic liquid as the electrolyte, different metals and alloys have been used as electrodes for hydrogen production by water electrolysis at room temperature [15]. A prominent case is the excellent performance of molybdenum (Mo), which has been shown to be better than platinum (Pt). For example, Mo showed current density values that were three times better than Pt and efficiencies of *ca.* 98% [16,17]. This superior performance is due to the reduced activation energy in the hydrogen evolution reaction (HER) with the Mo electrode, but the explanation for the decrease in this activation energy still remains an open question.

Herein, we describe electrochemical impedance spectroscopy (IES) studies of a system using a Mo electrode, thereby providing a more detailed description of the solid/liquid interface and illustrating the reasons for the easy production of hydrogen in the case of the ionic liquid/water system.

2. Experimental

The BMI·BF$_4$ ionic liquid was prepared according to published procedures [18–20]. The electrolyte solutions were prepared by dissolving the ionic liquid or commercial KCl in ultra pure water (conductivity lower than 2 μS cm^{-1}).

The conductivity of the solutions was measured using a Digimed-31 conductimeter using thermostated cells at 298 K.

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The electrochemical analyses with cyclic voltammetry (CV), chronoamperometry (CA) and electrochemical impedance spectroscopy (EIS) were performed with an Autolab PGSTAT30 potentiostat, with GPES and FRA modules, at room temperature (295 K) using a platinum counter electrode and a platinum wire as the quasi-reference electrode (PtQRE). Three kinds of electrodes were studied: molybdenum (99.9 wt.% wiredrawn without heat treatment, purchased from Multialloy), platinum (99.99%, purchased from PlatLab) and nickel (99.99%, purchased from Good-Fellow). The electrode surfaces were polished with sandpaper (1200 grit) and washed with commercial acetone. The electrode areas submerged in the electrolyte solution were determined geometrically.

Electrochemical impedance measurements were carried out in an electrolytic cell with a sinusoidal voltage perturbation of 10 mV amplitude under different *cc* potentials over a frequency range from 100 kHz to 0.01 Hz with 10 measurement points per frequency decade. The electrochemical experiments were performed in a three-electrode cell under an argon atmosphere.

The current density values, j, were calculated from $j = IS^{-1}$, where I is the measured current intensity and S is the area of the electrode exposed to solution. All measurements were repeated at least three times.

3. Results and discussion

The molybdenum electrodes showed outstanding performance for hydrogen evolution reactions (HERs) using ionic liquid (IL) electrolytes [16,17]. The activation energies, E_a, of the HER using Mo and Pt electrocatalysts with IL as the electrolyte have been reported to be 9.22 and 23.40 kJ mol^{-1}, respectively. The remarkably low E_a observed with Mo in this medium makes it an attractive choice. However, it is surprising that Pt electrodes behave better than Mo when using KCl as the electrolyte. The synergism between the Mo and the IL electrolyte has attracted much attention and still demands an explanation.

The difference in the behaviour of the electrocatalysts in the HER using an IL electrolyte can be understood from the EIS studies. The Nyquist diagrams obtained with Mo, Pt and Ni in the presence of IL electrolytes, as presented in Fig. 1, show the difference in polarization resistance of such electrodes.

These data enable the calculation of the values of R_s (solution resistance), R_p (polarization resistance) and C_d (capacitance of elec-
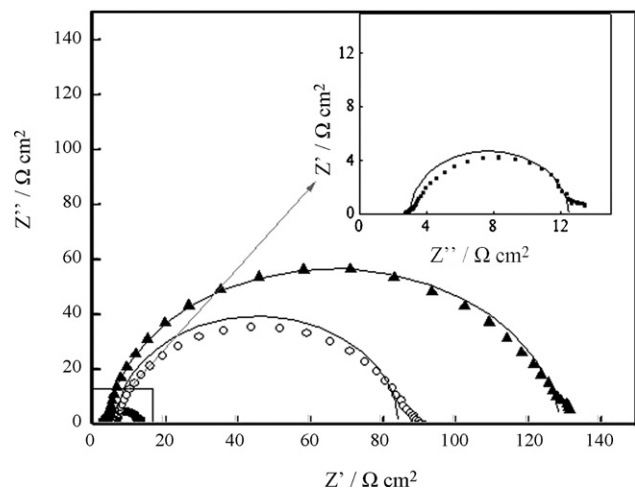
Table 1
R_s, R_p and C_d values obtained by fitting the experimental results of water electrolysis in different electrodic systems at −1.7 V (PtQRE).

Entry	System	R_s (Ω cm^2)	R_p (Ω cm^2)	C_d (μF cm^{-2})
1	Mo in IL$_{(aq)}$	2.9	9.5	2100
2	Ni in IL$_{(aq)}$	7.4	77.3	19
3	Pt in IL$_{(aq)}$	3.8	120.0	16
4	Mo in KCl$_{(aq)}$	1.7	1970	432

tric double layer) using a simulation of an equivalent circuit [21]. Table 1 shows the values obtained for the systems described in Fig. 1 and, for comparison, the Mo/KCl system with the same conductivity as the IL solution.

The values for the R_s were similar. The Ni electrode gave somewhat higher solution resistance, probably due to the hydration of an air formed oxide film that has a gel-like consistency close to the metal surface [22].

On the other hand, the R_p values were vastly different. In the presence of IL, the Mo electrode showed a remarkably lower R_p than Ni and Pt, entries 1–3. Surprisingly, the R_p for Mo in KCl, entry 4, for the same conditions was extremely high. These results indicate that the best performance of the Mo electrode in an IL electrolyte is associated with the aptitude for polarization of the electrode specifically in the presence of an IL, a phenomenon that is not observed when the electrolyte is KCl.

Still more impressive is the high differential capacitance of the electrical double layer values, C_d, obtained for Mo compared with the values measured for Pt and Ni. The values obtained for Pt and Ni, entries 2 and 3, are typical of bare metals [21,23]. Meanwhile, the values obtained for Mo/KCl, entry 4, and Mo/IL, entry 1, were one order and, more surprisingly, two orders of magnitude higher than those values for Pt and Ni, respectively.

The experimental data shows that the Mo/IL system for the HER is less resistive and more capacitive than the corresponding systems using classical electrolytes.
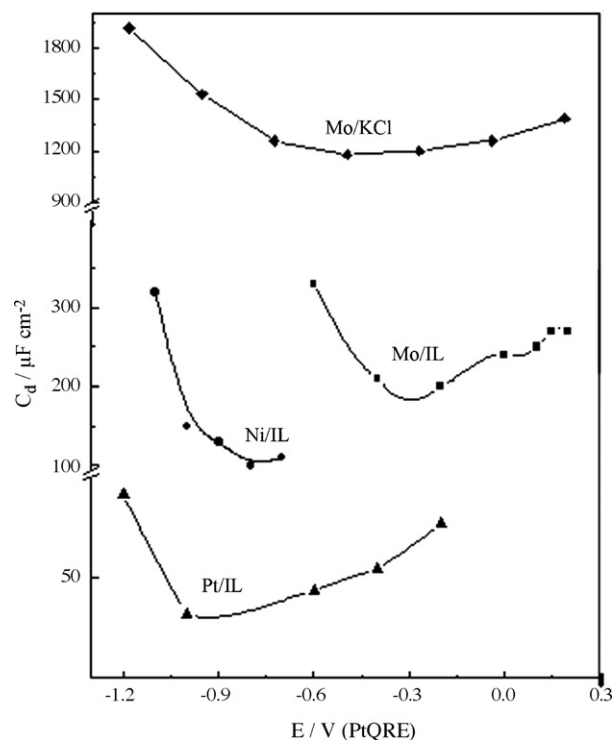

Fig. 1. Electrochemical impedance spectra of 10 vol.% of BMI·BF$_4$ in water with Mo (■), Ni (○) and Pt (▲) electrocatalysts at −1.7 V (PtQRE). The continuous lines in the spectra are the simulated calculations.

Fig. 2. Interfacial capacitance (C_d) versus potential (E) for Mo, Ni and Pt/IL systems and for Mo/KCl at room temperature.

An analysis of these results leads to the conclusion that there are great differences in the electrical double layer formed between Mo/IL and all other studied electrodes. In order to explain the structure of the electrical double layer, the potential of zero charge (PZC) for all of the electrocatalysts was determined.

The PZC potential is the minimum in the C_d versus E curve and represents the potential value where the discharge of the electrical double layer at the metal/electrolyte occurs, thereby eliminating the adsorbed ions. Specific, the adsorption of cations shifts the desorption potential to more positive values, and the specific adsorption of anions shifts the PZC value to higher negative potentials [21,23] compared to capillary inactive electrolytes. Fig. 2 shows the variation of the interfacial capacitance (C_d) with the potential plots for Pt, Ni and Mo in IL and Mo in KCl systems. The capacitance values were obtained by EIS at the potential corresponding to the electrochemical window of each metal/solution system, as deter-

mined by cyclic voltammetry, in the range of potentials without faradaic processes.

The PZC value obtained for Mo was -0.50 V (PtQRE) in the KCl solution and -0.30 V (PtQRE) in the IL solution. The PZC for Mo in KCl represents a reference for a nonadsorbed K^+ cation [21–24]. Since the PZC value obtained for Mo in the presence of IL showed higher values than in KCl electrolytes, one can conclude that the imidazolium cation (BMI^+) is specifically adsorbed onto the Mo surface. The specific adsorption of the imidazolium moiety both determines the decrease in thickness of the double layer and increases the corresponding C_p values. The thickness of the electrical double layer can be easily calculated using the relationship $d = \varepsilon \varepsilon_o / C_d$, where d is the thickness of the electrical double layer, ε_o is the permittivity of vacuum (8.85×10^{-12} F m^{-1}), ε is the dielectric constant of the medium (78.55 F m^{-1} for pure water), and C_d is the interfacial capacitance [21,23,24]. Table 2 shows the values for the potential of
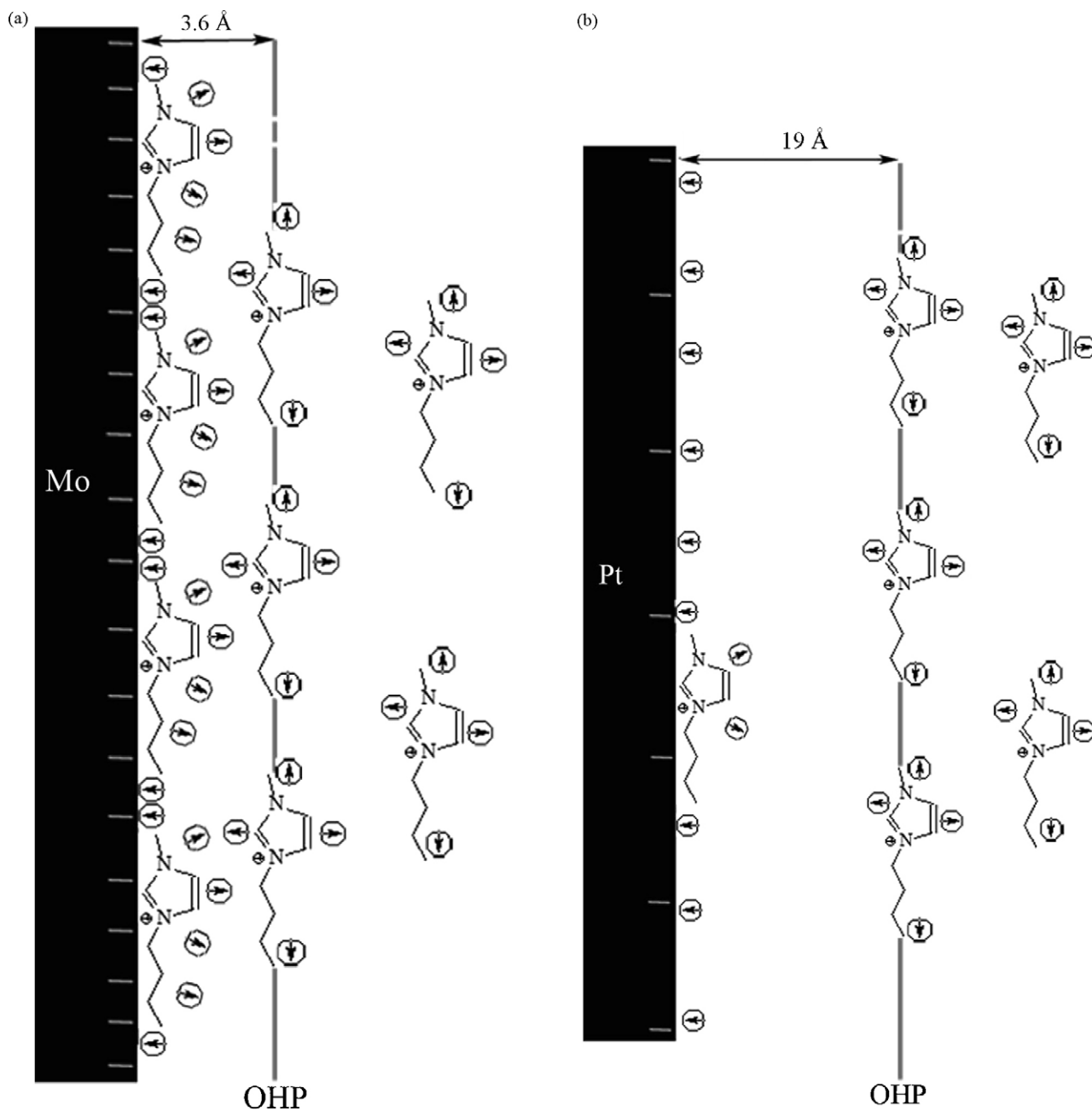

Fig. 3. Gouy–Chapman–Stern model representation of the electric double layer on the surface of the Mo and Pt electrodes in IL solution, with the corresponding Outside Helmholtz Planes (OHP). The arrows represent salvation water.

Table 2
Potential of zero charge (PZC), interfacial capacitance at the PZC (C_d (PZC)), thickness of electrical double layer at the PZC (d_{PZC}), and the interfacial capacitance at -1.7 V (C_d (-1.7 V)).

System	PZC (V)	C_d (PZC) (μF cm^{-2})	d_{PZC} (Å)	C_d (-1.7 V) (μF cm^{-2})
Mo in IL$_{(aq)}$	-0.30	191	3.6	2100
Ni in IL$_{(aq)}$	-0.78	100	6.9	19
Pt in IL$_{(aq)}$	-0.88	36	19	16

zero charge, the differential capacitance and thickness of the electrical double layer at the PZC, and the differential capacitance at -1.7 V (PtQRE). Pt and Ni showed more negative values for PZC and lower C_d values than those obtained for Mo, indicating once again that there is a lower specific adsorption in Pt and Ni than in Mo.

When a potential of -1.7 V (PtQRE) is applied, the differential capacitance increases for Mo in IL solution and decreases for Ni and Pt. The system behaviour is not only capacitive, since, at this potential, a faradaic contribution due to HER is observed. The cathodic reaction modifies the electrical double layer structure. Probably the electrical double layer of Ni and Pt in IL solutions enlarges taking to lower C_d. This shows that interaction between Mo and the IL gives rise to a very particular arrangement of the ions in its surface, which is closely packed. This arrangement leads to very low d_{PZC} values, which can correspond to a single layer of imidazolium cations occupying the surface of the Mo electrode.

These results are in agreement with those published by Baldelli [25], who recently described how BMI·BF$_4$ covers the platinum electrodes with the imidazolium ring arranged as a parallel layer on the metallic surface, at lower potentials than the PZC, in a situation that maximizes the attractive interaction. These authors reported PZC values of -0.55 V (AgQRE) for pure BMI·BF$_4$ IL/Pt, a capacitance value of 12 μF cm^{-2} and a double layer thickness of 5 Å.

The Gouy–Chapmann–Stern model [21,23,24] can account for most of the measured properties described herein. This model describes the system with the surface of the electrodes and two regions, one compact with ions adsorbed on the surface electrode and the other as a diffused layer in the solution adjacent to the electrode. The imaginary plane between these two regions is the Outside Helmholtz Plane (OHP), which crosses the centre of the hydrated positive ions in the negatively polarized electrode surface, as depicted in Fig. 3, which represents an imidazolium cation on the Pt and Mo electrode surfaces.

This model gives an explanation for the outstanding performance of the Mo electrocatalyst in the BMI·BF$_4$ aqueous solution. The hydrogen of the imidazolium ring is very close to the Mo surface, due to its adsorption. It should be emphasized that it is known that the hydrogen attached to C2 of the imidazolium ring is extremely acidic, yielding a proton donor capacity for the BMI$^+$ moiety. As a result, at a proper distance to the surface, the hydrogen production can be facilitated by the decrease in the overpotential for proton reduction on Mo, which is, in turn, due to the decrease of the activation energy.

The mechanism for the HER can be seen as following a reaction sequence similar to the Brdicka model [21]. In the case of the BMI·BF$_4$ solution, the BMI$^+$ cation is adsorbed and activated on the metallic surface according to

$$[R - CH]^+ + e^- \rightarrow [R - C] + H_{ads}$$

$$[R - C] + H_2O \rightarrow [R - CH]^+ + OH^-$$

$$H_2O + e^- \rightarrow H_{ads} + OH^-$$
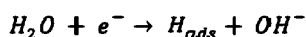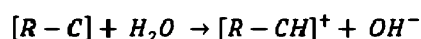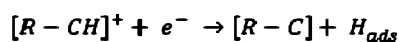
where R—CH$^+$ represents the imidazolium cation, and C is C2 with the linked H. In the case of BMI, the cation is adsorbed and activated on the metallic surface. In the case of KCl, water is adsorbed on the Mo surface, where it is reduced and produces H adsorbed (H$_{ads}$) on the metal [24]. Subsequently, these adsorbed species recombine and produce hydrogen gas. The results described herein explain the synergic effect of Mo, with the imidazolium cation easily adsorbed, serving as intermediates for proton activation on the metal surface with the corresponding decrease in the overpotential of the HER.

4. Conclusion

Pt, Ni and Mo electrodes have been tested for hydrogen production in 10 vol.% aqueous solutions of BMI·BF$_4$ ionic liquid. The highest current values were obtained with Mo in IL solution, which showed the excellence of this system for water electrolysis.

The EIS measurements give an elegant explanation for the electrical double layer nature where the charge transfer occurs. The positive displacement of the potential of zero charge indicates the specific adsorption of the imidazolium cation on the Mo surface. The highest differential capacitance value and the lower electric double layer thickness for Mo–IL system suggest that the imidazolium ring is strongly adsorbed on the electrode surface. In this situation, the BMI$^+$ cation mediates the proton transfer from water to the surface, decreasing the overpotential of the HER. This model explains the synergism between Mo and the BMI$^+$ cation in the HER process.

Acknowledgements

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