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An experimental system to investigate kinetics and isotopic properties of the electrolytic metal hydride formation

F. Leardini*, J. Bodega, J.F. Fernandez, C. Sanchez

Dpto. Física de Materiales, Facultad de Ciencias, Universidad Autónoma de Madrid, Cantoblanco, 28049 Madrid, Spain

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Abstract

We present in this paper an experimental set-up based in a mass spectrometer connected to a closed electrolytic cell. Calibrations accomplished with a Pt cathode and H_2O/D_2O mixtures have shown new kinetics in galvanostatic electrolysis. These findings may be relevant in some important processes such as the hydrogen evolution reaction, isotopic separation factors or the electrolytic formation of metal hydrides.

Keywords: Mass spectrometry; Separation factor; Electrolytic hydrogenation

1. Introduction

Isotopic effects in metal hydrides have received a considerable attention [1] because they can contribute to elucidate the mechanisms of formation of these compounds and to understand some of their properties. In addition, the study of the electrolytic separation factors is an important tool to investigate the hydrogen evolution reaction mechanisms [2,3]. For light–heavy water mixtures the electrolytic separation factor is defined as:

$$S = \frac{(H/D)_{\mathrm{gas}}}{(H/D)_{\mathrm{liq}}}$$

where $(H/D)_{gas}$ and $(H/D)_{liq}$ refers to the fraction of hydrogen and deuterium in the gas and liquid phases, respectively. Usually, the separation factor is determined by doing electrolysis of an electrolyte with a known $(H/D)_{liq}$ ratio and measuring the ratio $(H/D)_{gas}$ in the evolved gases. Different procedures have been used to analyse the evolved gases. However, and as far as we know, in previous papers (see for example [3–5]) gases are accumulated and stored in some reservoir before the $(H/D)_{gas}$ ratio is measured. This procedure excludes the investigation of kinetics phenomena related to the evolved isotopic gas mixtures and, therefore, only allows to measure the separation factor as an average of the whole electrolysis. In this work we describe an experimental setup built to measure the amounts of H_2, HD and D_2 molecules evolved as a function of the time of application of the electrolytic current. Polycrystalline Pt has been selected as a non-absorbing metal to built the cathode and to test the experimental procedure. We have observed transient stages in the evolution of the three molecular hydrogen isotopes evolved from the cathode until they reach a stationary value. In addition, different kinetics for H_2, HD and D_2 molecules evolution have been measured, and some of the obtained results are now reported. The experimental results suggest that the ratio $(H/D)_{gas}$ could change with time of electrolysis and they open a question about the dynamic character of the separation factor.

2. Experimental

The experimental system is depicted in Fig. 1. Electrolysis experiments were done in a glass cell (1) sealed with a rubber top (2) supporting the electrodes and the gas inlet (6) and outlet (8). High purity Ar (99.999%) was passed through

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* Corresponding author. Tel.: +34 91 4974777; fax: +34 91 4978579.
E-mail address: fabrice.leardini@uam.es (F. Leardini).

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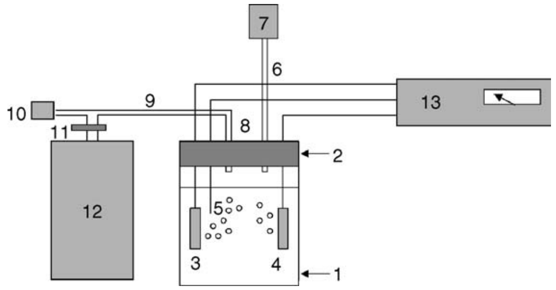

Fig. 1. Scheme of the experimental system used in the electrolysis: (1) glass cell; (2) rubber top; (3) Pt cathode; (4) Pt anode; (5) Pt wire reference electrode; (6) Ar inlet; (7) flowmeter; (8) gas outlet; (9) capillary tube; (10) rotatory pump; (11) needle valve; (12) mass spectrometer and (13) potentiostat.

the cell to carry the evolved gases through a capillary tube (9) (0.1 mm inner diameter and 1 m in length) to the mass spectrometer (MS) (12). A flow meter (7) was used to measure and control the Ar flow to 29.5±0.1 ml/min for all the experiments. Volume of the cell and PVC connectors to the capillary tube of the MS was chosen to minimize the delay time between gas molecules formation at the cathode surface and their detection by the MS. Volume of the electrolyte was 10 ml and the free volume of the cell, the PVC tube and the capillary tube was estimated to be 2 ml.

The anode and cathode were Pt foils (Goodfellow) of 99.95% purity with a thickness of 0.25 mm and geometrical area equal to 1 cm^2. The reference electrode was a Pt wire (Johnson Matthey, grade 1) 0.50 mm in diameter, placed near the cathode. All the electrodes were etched in hot sulfuric acid during 1 h and then washed with distilled water (18.2 MΩ cm) before the first experiment. They were subsequently kept in distilled water during the time before the experiments.

LiOH and LiOD electrolytes were independently prepared in an Ar atmosphere by dissolving granulated metallic Lithium in light (18.2 MΩ cm) and heavy water (99.7%). Analysis of the electrolytes by means of inductively coupled plasma (ICP) spectrometry gave a Lithium concentration of 672±17 and 676±16 mg/l, respectively. The prepared electrolytes were mixed in order to have an electrolyte with a deuterium molar fraction of 0.7. Lithium concentration of the electrolyte after the experiments was the same as before them within the error bars.

The electrolysis was galvanostatically controlled by using a potentiostat Princeton Model 362. Current densities up to 40 mA/cm^2 were applied. This potentiostat was also used to measure the cathode potential vs. the reference Pt wire.

Gases evolved from the electrodes were analysed by using a quadrupole mass spectrometer Balzers Mod. Prisma. A rotatory pump, located at the end of the capillary tube, pumped the gases into the mass spectrometer. The ionization current was 2 mA and the ionization voltage was selected at 100 V during all the measurements. Before each experiment m/q values of the current peaks appearing in the mass spectra were calibrated. We measure the current at the maximum of each peak of the mass spectra, denoted as $i_{m/q}$, as a function of electrolysis time. The dwell time for data acquisition was ~5 s.

3. Results and discussion

3.1. Determination of the ions associated to each m/q value

Due to the fact that different ions have the same m/q value it is necessary to know the relative contribution of each ion to a given current peak appearing in the mass spectra. To this purpose detailed calibrations were done by using high purity (99.999%) H_2–Ar and D_2–Ar mixtures. As a result we have concluded that i_2, i_3 and i_4 current peaks are due to H_2^+, HD^+ and D_2^+ ions, respectively, with an uncertainty less than 1%. A detailed discussion of the different molecular ions (and their formation mechanisms) that can contribute to each $i_{m/q}$ current peak can be seen in [6]. Furthermore, we have verified that the measured i_2, i_3 and i_4 current peaks were always proportional to the H_2, HD and D_2 molar fractions of the analysed gas mixtures.

3.2. Kinetics of hydrogen (deuterium) evolution in LiOH/LiOD mixtures at a Pt cathode

The experiments were controlled galvanostatically by applying a given current density up to 40 mA/cm^2 during ~10 min. Currents were applied without a determinate increasing or decreasing sequence to avoid systematic errors in the measurements. Time intervals (~10 min) of zero applied current were kept between two successive measurements in order to allow the cathode to reach an stationary potential value (~100 mV respect to the Pt reference electrode).

Fig. 2a–c shows current peaks corresponding to H_2, HD and D_2 evolved from the cathode when applying an electrolytic current (5 mA/cm^2) through the cell, as a function of time. Dotted lines in these figures represent the background signals ($i^0_{m/q}$) of each current, corresponding to the residual atmosphere present in the system. The dispersion in the experimental points is mainly due to hydrogen bubbles evolved from the cathode time by time. The evolution of the cathode potential is also shown (Fig. 2d), in order to clarify any possible correlation between the amount of evolved gases and the changes in the cathode potential.

There exists a transient stage before the amount of evolved gases reaches the equilibrium. Experimental points of Fig. 2a–c can be well fitted by simple exponential functions of the form:

$$i_{m/q}(t) - i^0_{m/q} = i^*_{m/q}(1 - e^{-t/\tau_{m/q}})$$

Fig. 3 represents the average stationary values i^*_2, i^*_3 and i^*_4 as a function of the electrolytic current densities applied in different experiments. Due to the fact that evolved molecules

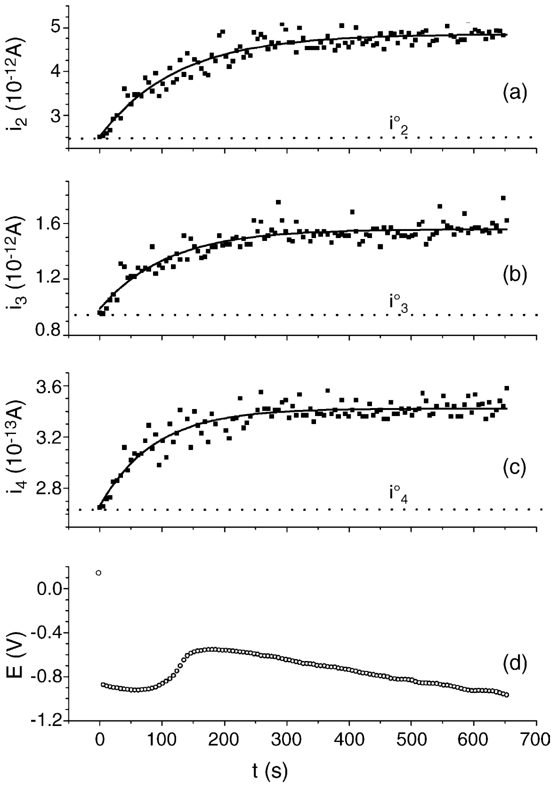

Fig. 2. Evolution of: (a) i_2 current peak corresponding to H_2; (b) i_3 current peak corresponding to HD; (c) i_4 current peak corresponding to D_2 and (d) cathode potential when applying in $t = 0$ a current density of 5 mA/cm^2 through the cell. Dotted lines shows the background signals ($i^0_{m/q}$) corresponding to the residual atmosphere present in the system. The solid lines in Fig. 2a–c represent the fits of the $i_{m/q}$ currents by exponential functions $i_{m/q}(t) - i^0_{m/q} = i^*_{m/q}(1 - e^{-t/\tau_{m/q}})$.

are dissolved in an Ar flow, their concentrations are proportional to their molar fraction within a good approximation. Therefore, the measured i^*_2, i^*_3 and i^*_4 current peaks are proportional to the amount of H_2, HD and D_2 evolved from the cathode. In consequence, Fig. 3 shows that the stationary values of hydrogen molecular isotopes evolved from the cathode are proportional to the electrolytic current according to Faraday's law. This implies that the fraction of isotopes in the gas phase reach an stationary value independently of the current density, what agrees well with published data [5].

Fig. 4 shows the time constants ($\tau_{m/q}$) of H_2, HD and D_2 evolution, obtained from the fits of Fig. 2a–c, as a function of the electrolytic current density. They decrease on increasing the applied current density and change between 162±25 and 4±1 s. Time constant error bars are also obtained from the fits of Fig. 2a–c. Here we have to point out that the variation of time constants for the gases evolution with the electrolytic current density is not due to the time required by the transport of gases from the cathode surface to the MS. Due to the small volume of the system and to the value of the Ar flow used to carry the evolved molecules, the time for mass transport is estimated to be less than 5 s.

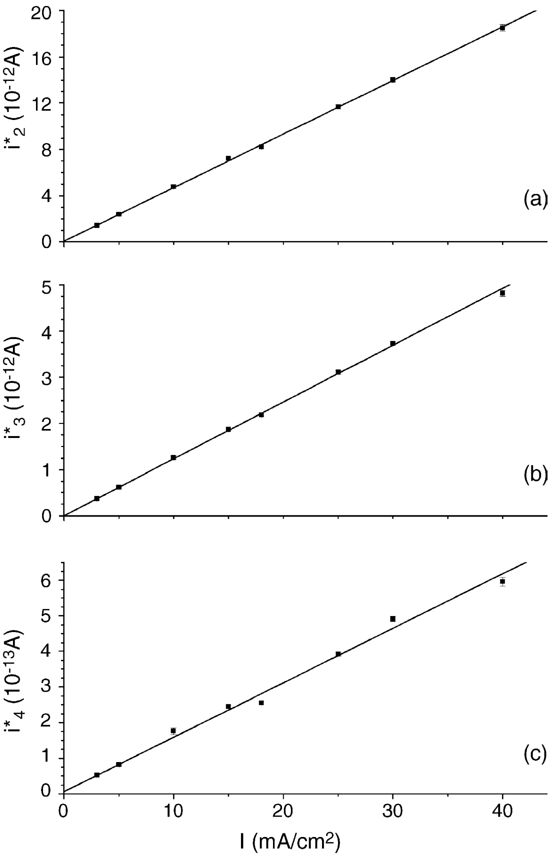

Fig. 3. Faraday's plots relating the stationary values of the amount of evolved molecules to the electrolytic current density. (a) i^*_2 current peak corresponding to H_2; (b) i^*_3 current peak corresponding to HD; (c) i^*_4 current peak corresponding to D_2.

We feel that the existence of transient responses of evolved gases and the increase of the transient time on decreasing the current density, are due to the adsorption of discharged hydrogen–deuterium at the Pt cathode surface [7]. In other words, the amount of evolved molecules would reach the stationary value when the cathode surface would be fully

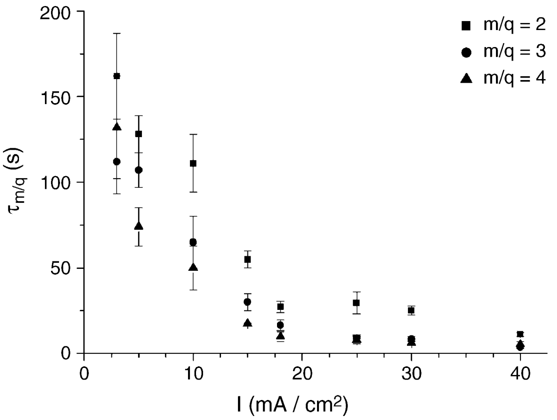

Fig. 4. Time constants for evolved molecules evolution as a function of the electrolytic current density. Squares stand for H_2, circles for HD and triangles for D_2. These times are obtained from the fits shown in Fig. 2.

covered. Several facts support this view. In the first place, the changes of the cathode potential (Fig. 2d) during the transient times of $i_{m/q}$. In fact, before the amount of evolved gases reaches the stationary value, the cathode potential presented a minimum and a maximum for all the studied current densities. On the other hand, the kinetics of the three molecular hydrogen isotopes evolution is different, being faster for D_2 and slower for H_2, as can be seen in Fig. 4. This result also indicates that the fractions of isotopes in the gas phase change with time of electrolysis. As a consequence the separation factor will have changing values before the stationary state is attained. As it has been stated above, when the evolved gases are stored before the $(H/D)_{gas}$ ratio is measured, an average separation factor of the whole electrolytic process is obtained and the mentioned transitory evolution can not be detected. Certainly that, for high current densities or long times of electrolysis, the contribution of the transitory process to the total amount of evolved molecules can be neglected. In these conditions, both the measure of the stationary values of the separation factor in a dynamic Ar flow and by storing the gases before analyse them should give the same results.

4. Conclusions

In this work we have presented an experimental procedure that allows to measure, as a function of electrolysis time, the amount of H_2, HD and D_2 evolved from the electrolysis of light and heavy water mixtures. To demonstrate the possibilities of this technique we present the results obtained for the electrolysis of a mixture of LiOH and LiOD with a Pt cathode. When applying a constant electrolytic current through the cell, the amount of evolved molecules reaches a stationary value after passing through a transitory state. Faraday's plots relating the amount of evolved molecular hydrogen isotopes to electrolytic current density has been obtained for the stationary state. The time evolution of the evolved H_2, HD and D_2 has been also considered. Time constants necessaries to reach the stationary value increase on decreasing the electrolytic current density. This effect can be related to the formation of a hydrogen-deuterium adsorbed layer at the cathode surface during the initial stages of the electrolysis. In addition, different time constants have been measured for the three molecular hydrogen isotopes investigated. This implies a variation of the separation factor during the transitory state that cannot be observed by means of the traditional procedures to measure the separation factor. The results also suggest the possibility to employ this technique to measure 'in situ' the amount of absorbed hydrogen in a metallic cathode, by comparing the curves of evolved gases with those obtained from a non-absorbing electrode, such as Pt.

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