Influence of Pb^{2+} ions in the H_2 oxidation on Pt catalyzed hydrogen diffusion anodes in sulfuric acid: presence of oscillatory phenomena

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Abstract

The influence of Pb^{2+} ions in sulfuric acid medium on the behavior of a platinum catalyzed hydrogen diffusion electrode (HDE) in a filter press reactor has been studied. A voltammetric study of the H_2 oxidation reaction on a polyoriented platinum electrode and a platinum rotating disk electrode (RDE) in presence of lead ions in solution has also been carried out. Potential oscillations were found in galvanostatic experiments of H_2 oxidation using a HDE catalyzed with platinum when Pb^{2+} ions are present in solution. This oscillatory phenomenon was also observed when hydrogen oxidation was carried out in presence of Pb^{2+} ions using a platinum RDE. The oscillatory behavior observed has been attributed to an adsorption–oxidation–desorption process of lead on the platinum surface. Due to the low solubility of Pb^{2+} in sulfuric acid, at high values of coverage, lead is oxidised to insoluble lead sulfate that blocks the Pt surface. The coupling of the dissolution of lead sulfate and the Pb electrochemical adsorption–oxidation processes cause the oscillatory phenomenon.
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Keywords: Sulfuric acid medium; Hydrogen diffusion anode; Potential oscillations; Platinum; Lead

1. Introduction

The first report about oscillatory phenomena in electrochemical processes is related to the dissolution of iron in an acidic silver nitrate solution [1]. Since then, oscillatory behavior of potential or current have been reported and studied in many electrochemical reactions. Different works focused on metal corrosion systems [1–3], metallic electrodeposit processes [4,5], electrocatalytic reduction of hydrogen peroxide [6,7], electroxidation of small organic molecules [8–12], etc. have been reported.

The first study of oscillations in the oxidation of H_2 on Pt was made by Thalinger and Volmer [13] in 1930. Afterwards, this oscillatory behavior has been observed in many experimental conditions [14–20]. Horányi and Visy [16] observed that the presence of different electrosorbing metal ions induces an oscillatory behavior of this reaction under galvanostatic conditions. To explain this oscillatory behavior a mechanism based on the adsorption–desorption of metal cations on the active electrode sites was proposed.

Wolf and coworkers [18–20] studied the oxidation of H_2 in different electrolytes in the presence of Cu^{2+} ions. They proposed a model concerning the influence of the anion in solution on the potential oscillations.

The oxidation of H_2 on Pt is the anodic reaction in fuel cells and for this reason is of technological interest. Hydrogen diffusion electrodes (HDEs) were developed as electrodes for fuel cells [21–23]. This type of electrodes is usually made up of a semihydrophobic composite of catalyzed high surface area carbon and a fluorocarbon binder that are termally sintered onto a planar substrate. The substrate materials of choice are normally carbon cloth, carbon paper, metallic mesh or expanded metal. In order to form a three-phase interface of very high surface area it is desirable to achieve very fine porosity. HDE have also been previously employed as counter-electrodes in Zn [24,25], Ni [26] and Pb [27,28] electrowinning processes in Pb removal from wastewater [29] and in organic electrosynthesis processes [30].

In this work, the influence of the presence of Pb^{2+} ions in solution on the behavior of a platinum catalyzed HDE in sulfuric acid medium has been studied. Firstly, a voltammetric study of the H_2 oxidation reaction on a polyoriented platinum electrode and a rotating disk electrode in presence of lead ions in solution was carried out. This study was

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followed by a more applied one in which a HDE was used in a filter press reactor.

2. Experimental

2.1. Voltammetric experiments

Electrochemical experiments were made with a Voltalab-32 Radiometer system and a PGSTAT30 AUTOLAB from Eco Chemie. The RDE was a Tachyprocesseur EDI 10000 of Radiometer. Solutions were prepared with ultrapure water from a Millipore Milli-Q system. Ar, N_2 and H_2 were from L'Air Liquide all of them of quality N-50. The working electrodes were polyoriented platinum and a platinum RDE (area: 3.14 mm^2). The counter electrode was a Pt wire and the reference electrodes were a reversible hydrogen electrode (RHE) or a Tacussel TR-100 saturated calomel electrode (SCE). Unless otherwise stated, all potentials are referred to RHE. The products employed for the different solutions, sulfuric acid and lead sulfate, were all p.a. reactives from Merck and were used without additional purification.

2.2. Laboratory scale plant

Schematic diagrams of the laboratory plant and the filter press reactor are shown in Figs. 1 and 2. The cathode was a Ti sheet. Metakem supplied the DSA-O_2 anode and the HDE was home made. The separator was an anionic membrane
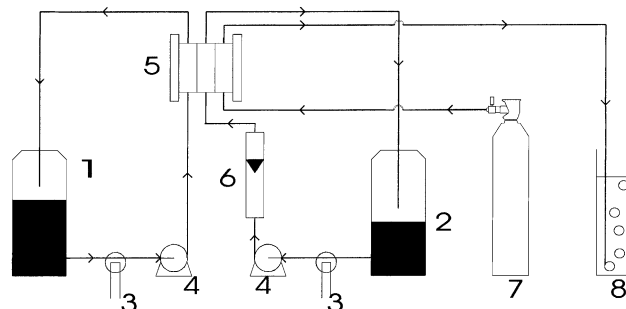

Fig. 1. Schematic illustration of the experimental assembly. 1—Catholyte reservoir. 2—Anolyte reservoir. 3—Heat exchanger. 4—Pump. 5—Filter press reactor. 6—Flowmeter. 7—Hydrogen feed. 8—Water column for hydrogen overpressure.
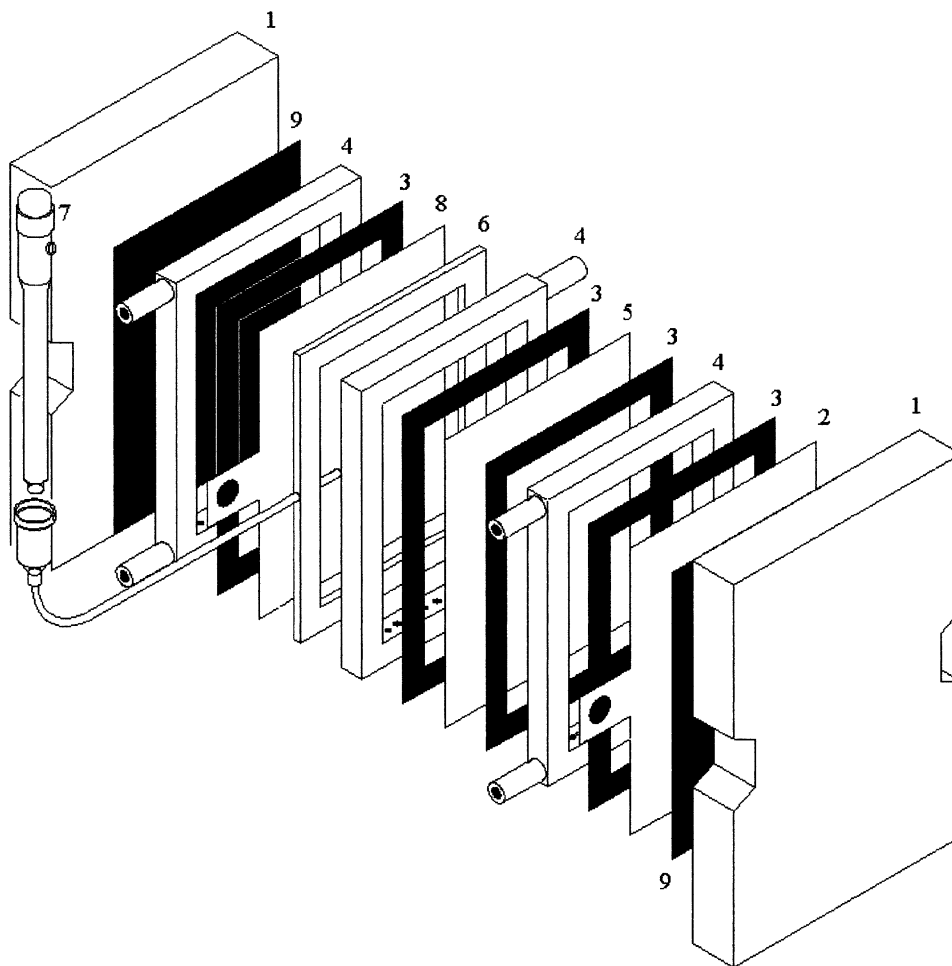

Fig. 2. Scheme of the filter press reactor. 1—End plates. 2—Cathode. 3—Rubber gasket 4—Compartment frame. 5—Anionic membrane. 6—Silicon gasket. 7—Reference electrode. 8—HDE anode. 9—Insulator gasket.

Sibron 3475 and the reference electrode was a saturated calomel electrode model TR-100 from Tacussel.

The HDE anode was fabricated in the following manner: A fixed amount of 10% in weight platinum catalyzed Vulcan XC-72 carbon (supplied by ETEK Inc.) is dispersed with a PTFE emulsion 50% w/w and applied onto a thin sheet of Toray Paper TGPH-090 (supplied by ETEK Inc.). Next, the composite structure was dried at 110 °C under pressure $(98.1 \times 10^4 \, \text{Pa})$ and sintered at a maximum temperature of 350 °C.

3. Results and discussion

3.1. Voltammetric experiments

Fig. 3 shows the steady state voltammograms of poly-oriented platinum in 1 M H_2SO_4 and 1 M H_2SO_4 + saturated $PbSO_4$. The presence of Pb^{2+} produces important changes in the voltammetric profile of Pt. Thus, the voltammetric peaks traditionally so-called hydrogen adsorption–desorption decrease and a new oxidation peak at approximately 0.7 V appears. This peak is attributed to the oxidation of underpotential deposited lead. These results are in agreement with those obtained by Beden et al. [30].

In order to study the maximum coverage of adsorbed lead on the platinum surface the experimental procedure was the following. Firstly, the Pt electrode is immersed in a 1 M H_2SO_4 + saturated $PbSO_4$ solution at a controlled potential of 0.08 V (lead adsorption takes place) during a time period between 30 s and 600 s. After that, a voltammogram between 0.06 V and 1.46 V is registered. Fig. 4 shows the obtained results. The increase of the lead adsorption time causes a higher poisoning of Pt surface. After 600 s of immersion at 0.08 V a maximum coverage of lead is attained. It is interesting to note that two new lead oxidation peaks at 0.41 V and 0.52 V, respectively, appear when the adsorption time is increased. The presence of these two new peaks is related with the oxidation of underpotentially
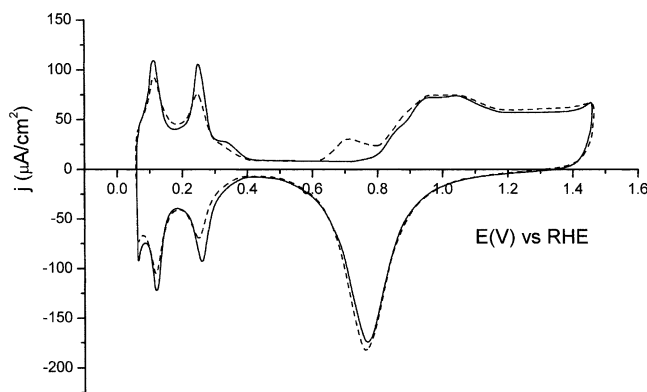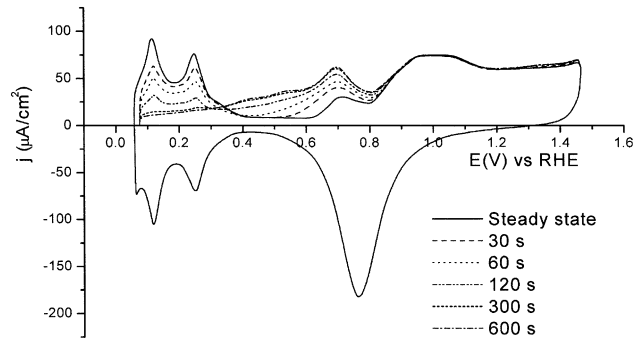

Fig. 4. Voltammetric curves of lead adsorption on polyoriented Pt. Solution composition: 1 M H_2SO_4 + saturated $PbSO_4$. Sweep rate: 50 mV/s.

deposited lead onto platinum to insoluble compounds of Pb^{2+} at high values of lead coverage [31].

The next step was to study the influence of Pb^{2+} ions on the H_2 oxidation reaction on a Pt RDE. To simulate the HDE operation, the methodology employed was the following. Firstly, the solution with and without lead was saturated in H_2. Next, a series of current density (j) versus E_{RDE} curves at different rotation speeds (ω) were registered. After that, galvanostatic experiments were carried out and E_{RDE} versus t curves were registered. The working current density and rotation speed in these experiments both were chosen in such a way that H_2 oxidation reaction was not mass transport controlled.

3.1.1. Experiments with a lead-free solution

Taking into account the above-mentioned procedure, 1 M H_2SO_4 solution was saturated with H_2 and a series of j versus E_{RDE} curves were registered. The results obtained are shown in Fig. 5. A linear dependence of limiting current with the square root of rotation rate as predicted for a mass transport controlled processes by Levich equation was found [32].

In the galvanostatic experiments E_{RDE} versus t was monitored. The experimental conditions were $j = 0.64 \, \text{mA/cm}^2$ and $\omega = 2000 \, \text{rpm}$. Solution composition was 1 M H_2SO_4.

Fig. 3. Voltammetric curves of polyoriented Pt in 1 M H_2SO_4 (—) and 1 M H_2SO_4 + saturated $PbSO_4$ (- - -).Sweep rate: 50 mV/s.
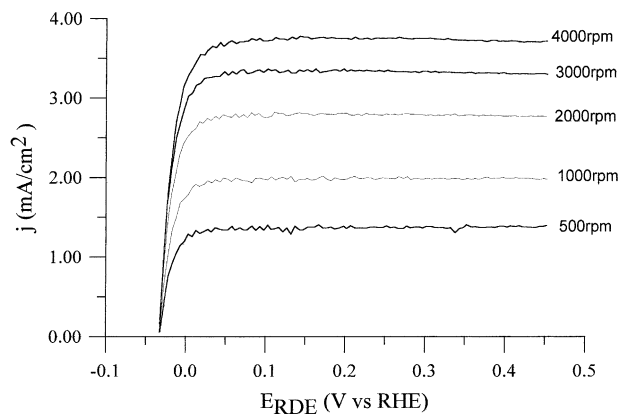

Fig. 5. j vs. E_{RDE} curves in 1 M H_2SO_4 during H_2 oxidation on a Pt RDE at different rotation speeds. Sweep rate: 5 mV/s.
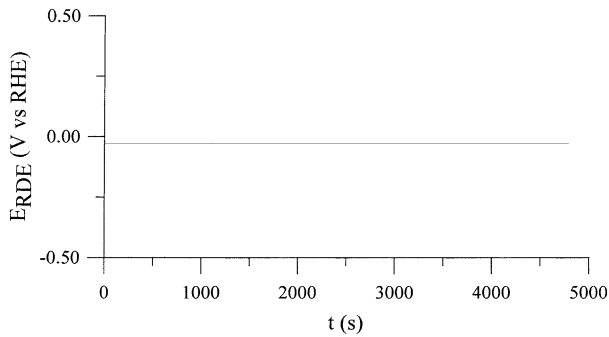
Fig. 6. Variation of E_{RDE} vs. t for galvanostatic H_2 oxidation experiments. Solution composition: 1 M H_2SO_4. $j = 0.64$ mA/cm^2. $\omega = 2000$ rpm.

The results obtained are shown in Fig. 6. The experiment continued for 5000 s, and E_{RDE} remained constant at approximately 0 V showing that, as expected, H_2 oxidation on Pt in these experimental conditions (sulfuric acid medium without Pb^{2+} ions in solution) is not inhibited.

3.1.2. Experiments with Pb^{2+} in solution

A lead saturated 1 M H_2SO_4 solution was employed. Several j versus E_{RDE} curves at different rotation speed were registered Fig. 7. A comparison between Figs. 5 and 7 shows that the presence of Pb^{2+} ions decreases the limit
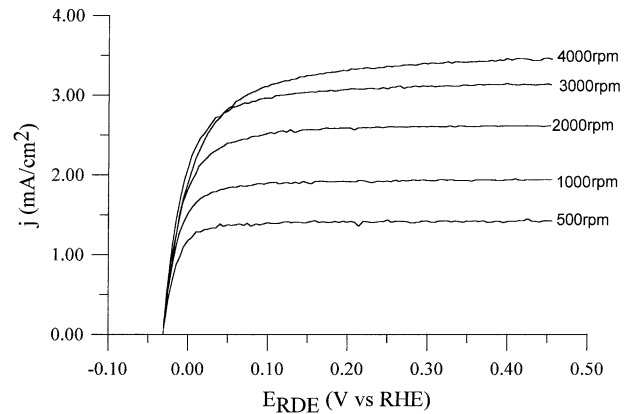

Fig. 7. j vs. E_{RDE} curves in 1 M H_2SO_4 + saturated $PbSO_4$ during H_2 oxidation on a Pt RDE at different rotation speeds. Sweep rate: 5 mV/s.

current density of H_2 oxidation. Fig. 8 shows E_{RDE} versus t curves registered at two different current densities (0.64 and 1.28 mA/cm^2)in the galvanostatic experiments of H_2 oxidation with Pb^{2+} ions in solution. Rotation speed was 2000 rpm in both experiments.

Analysis of Fig. 8a ($j = 1.28$ mA/cm^2) shows three zones. First, an increase of E_{RDE} until 0.64 V is observed. This E_{RDE} value is reached approximately after 6500 s. Second, E_{RDE} starts to oscillate. The oscillations are not constant. Both, the
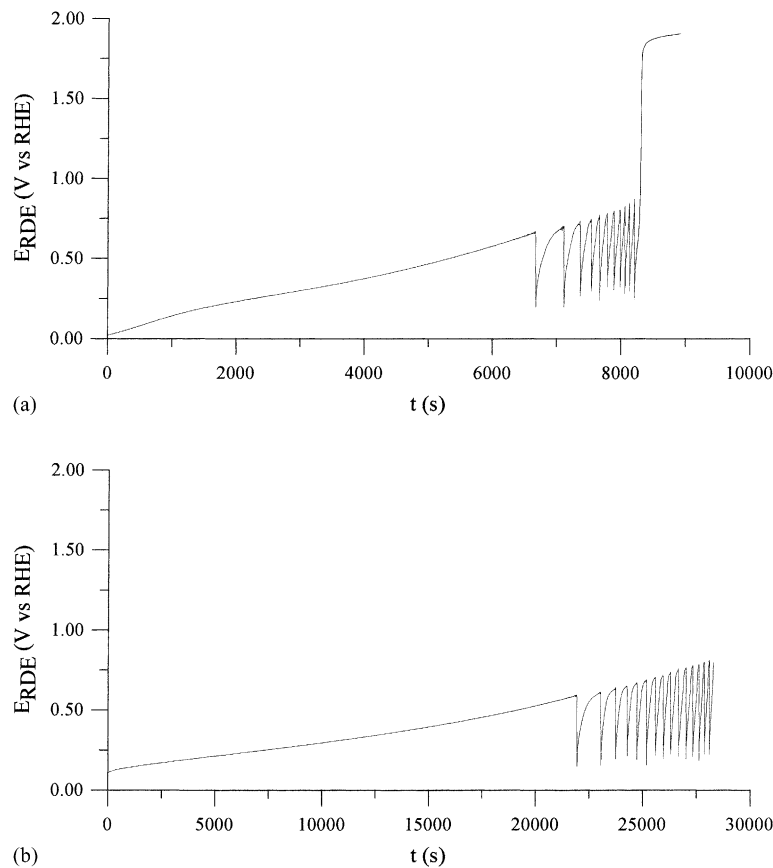

(a)

(b)

Fig. 8. t vs. E_{RDE} curves in 1 M H_2SO_4 + saturated $PbSO_4$ during H_2 oxidation on a Pt RDE at different current densities. Sweep rate: 5 mV/s. (a) $j = 1.28$ mA/cm^2. (b) $j = 0.64$ mA/cm^2.

frequency and the maximum potential of each oscillatory period increases with time. Finally, E_{RDE} quickly increases up to 1.84 V approximately, where it remains constant. This E_{RDE} corresponds to the O_2 evolution reaction.

The initial E_{RDE} increase in Fig. 8a and 8b is explained by the adsorption of lead on the platinum surface. This adsorption decreases the active area of platinum available for the oxidation of H_2 and gives rise to the registered E_{RDE} increase. On the other hand, as it was expected, the higher the current density, the faster the E_{RDE} increases.

The proposed mechanism to explain the oscillations is based on an adsorption–desorption process on the platinum surface. At low potential values, lead is adsorbed on the platinum surface blocking the adsorption sites in such a way that the hydrogen oxidation is unable to support the imposed current. At this moment, E_{RDE} shifts to more positive values. At these positive potential values lead is eliminated by oxidation from the surface increasing the number of free adsorption sites. Now the hydrogen oxidation reaction is able to support the imposed current and the potential decreases. At this point, lead adsorption starts again and the cycle is repeated. However, the complexity of the registered potential oscillation Fig. 8 points out that the model based on a simple process of lead adsorption–desorption is only qualitatively valid.

The dissolution of the insoluble Pb^{2+} compounds is a chemical process and it is independent of electrode potential. On the other hand, the adsorption–desorption of Pb is a potential dependent electrochemical process. The coupling of these two processes causes the complexity of the registered oscillatory behavior.

3.2. Filter press cell experiments

Next, the influence of Pb^{2+} ions on the HDE potential at constant current was studied. The experimental conditions are indicated in Table 1. To maintain constant the Pb^{2+} concentration in the anolyte during the experiments, an anionic membrane was used as separator to avoid Pb^{2+} transport from anolyte to catholyte.

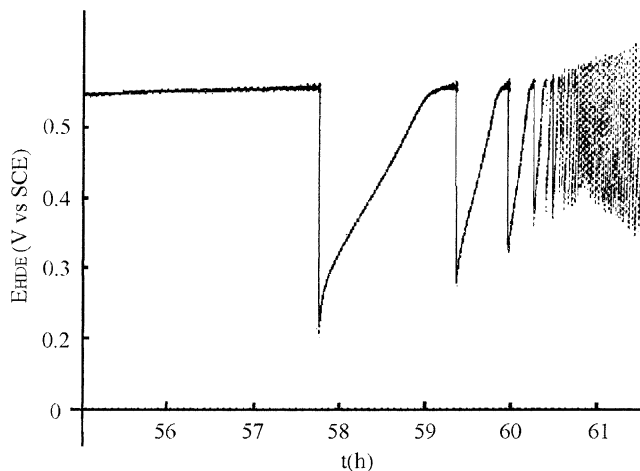In the experiments without Pb^{2+} in the anolyte, the potential of the HDE remains constant. However, in

Fig. 9. Variation of E_{HDE} vs. t during galvanostatic H_2 oxidation experiments. Anolyte composition: 1 M H_2SO_4 and, 1 M H_2SO_4 + Pb^{2+} saturated. j: 100 mA/cm^2.

presence of Pb^{2+}, E_{HDE} increases up to approximately 0.55 V versus SCE and starts to oscillate Fig. 9. The shape of the potential oscillations is quite similar to those registered for RDE, which indicates a reproducible oscillatory behavior for both RDE and HDE electrodes.

4. Conclusions

Potential oscillations appear in galvanostatic experiments of H_2 oxidation using a HDE catalyzed with platinum in a sulfuric acid medium when Pb^{2+} ions are present in solution. This oscillatory phenomenon is also observed when hydrogen oxidation is carried out in presence of Pb^{2+} ions using a platinum RDE.

This oscillatory behavior is attributed to an adsorption–oxidation–desorption process of lead on the platinum surface. Due to the low solubility of Pb^{2+} in sulfuric acid, lead at high values of coverage is oxidized to insoluble lead sulfate that blocks the Pt surface. The coupling of the dissolution of lead sulfate and the Pb electrochemical adsorption–oxidation processes causes the oscillatory phenomenon. A kinetic analysis is now in progress and will be reported in a separate paper.

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Table 1
Experimental conditions for the galvanostatic H_2 oxidation experiments

Reactor	Filter press (area 20 cm^2)
Cathode	Ti sheet
Anode	HDE
Catholyte	1 M NaOH
Anolyte	1 M H_2SO_4 and, 1 M H_2SO_4 + Pb^{2+} (saturated)
Separator	Sibron 3475 anionic membrane
Current density	100 mA/cm^2
Anolyte flow	100 l/h
Temperature	30 °C
H_2 overpressure	40 mmHg
H_2 flow	3 l/h

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