Use of hydrogen diffusion anodes during lead electrowinning in a chloride medium

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Abstract

The results of an investigation on the use of a hydrogen diffusion anode (HDE) for electrowinning of lead in chloride medium are reported. Given that lead ions may poison the platinum electrocatalyst of the HDE, the H_2 oxidation reaction in the presence of lead ions on a platinum rotating disk electrode (RDE) was studied. Finally, the influence on the lead electric cost of the substitution of the traditionally used O_2-dimensionally stable anode (DSA-O_2) by an HDE was studied. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Within the next few years, the percentage of recycled lead acid batteries in the European Union must increase to almost 100%, in agreement with new regulations. At the moment, the recovering of lead from batteries is carried out by pyrometallurgical processes [1]. However, these processes have important drawbacks. First, emissions of lead and SO_2 fumes during pyrometallurgical smelting are very hard to control being difficult and expensive to meet the emission standards promulgated by environmental organisations. Second, the lead obtained should be of high purity to be suitable for manufacturing maintenance free batteries [2].

For these reasons, in the last two decades there has been an increasing effort on the research of new electrolytic methods for recycling lead from scrap batteries [3–9]. These processes generally consist in a three-step treatment. After the first step of breaking the batteries and separating the plastic compounds and grids, the next one is the leaching and hydrometallurgical processing of these scrap batteries. At the end of this stage a solution with a high concentration of Pb^{2+} ions is obtained. Fluoboric, fluosilicic and hydrochloric acids together with ammonium sulphate have been used as electrolytes. The last step is the electrowinning of lead in order to obtain it in metallic form.

In a previous paper [10] lead electrowinning in an acid highly concentrated chloride medium has been studied. The reaction of lead electrodeposition was studied by voltammetric methods. Afterwards, in order to maximise the current efficiency of the lead deposition, the influence of different electrochemical experimental variables were investigated.

The usually employed anodes for lead electrowinning are oxygen dimensionally stable anodes (DSA-O_2) or Pb–Ag alloys. On these anodes, the anodic reaction is the oxidation of water

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-, \quad E^0 = 1.23\,V$$
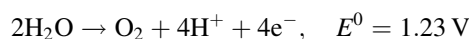
One of the main problems when using DSA-O_2 in lead containing solutions is its poisoning by deposition of lead dioxide according to the reaction

$$Pb^{2+} + 2H_2O \rightarrow PbO_2 + 4H^+ + 4e^-$$

that not only decreases the amount of lead recovered but also diminishes the lifetime of the DSA-O_2 anode. These problems can partially be prevented by adding small amounts of arsenic [4] or phosphoric acid [11] or totally eliminated using a divided cell.

Another possibility to avoid the problem caused by lead dioxide formation and, at the same time, to diminish the energetic cost of the process is to replace the DSA-O_2 anode by a hydrogen diffusion electrode (HDE). The low working potential of a HDE anode avoids PbO_2 formation allowing the use of an undivided cell. In a previous paper [12], the use of this anode in lead electrowinning in fluorborate medium has been studied.

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Hydrogen and oxygen diffusion electrodes were developed as electrodes for fuel cells [13–15]. These electrodes are usually made up of a semihydrophobic composite of catalysed high surface area carbon and a fluorocarbon binder that are thermally sintered onto or into a planar substrate. The substrate materials of choice are normally carbon cloth, carbon paper, metallic mesh or expanded metal. It is desirable to achieve very fine porosity in order to form a three-phase interface of very high surface area. HDE have also been previously employed in Zn [16,17], Ni [18] and Pb [12] electrowinning processes and in Pb removal from waste-water [19].

The anodic reaction that takes place at a HDE is the oxidation of H_2

$$H_2 \rightarrow 2H^+ + 2e^-, \quad E^0 = 0.00\,V$$
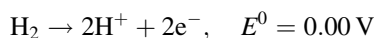
Thus, the change of the oxygen evolution reaction by the hydrogen oxidation reaction decreases the thermodynamic cell voltage of the lead electrowinning cell by 1.23 V at standard temperature and pressure. Taking into account that the oxygen evolution reaction is more sluggish than hydrogen oxidation, the real voltage saving should in fact be greater. In order to translate this voltage saving to cost saving, the price of the hydrogen employed to feed the HDE must obviously also be taken into account.

Thus the aim of this paper is to investigate the use of a HDE as anode during lead electrowinning in a chloride medium. Given that lead ions may poison the platinum electrocatalyst of the HDE, the first step in our work was to investigate the H_2 oxidation reaction on a platinum rotating disk electrode (RDE) in presence of lead ions in solution. This study was followed by a more applied one in which a HDE was used during lead electrowinning in a filter press reactor. Although filter press type reactors are not appropriated for electrowinning processes, this reactor was chosen because it has very uniform potential and current distributions and defined flow patterns. In this way, it allowed us to obtain great reproducibility of the results being very convenient if HDE anodes are used. Finally, the multielectrode cells developed in the LEREFLEOS European Project [8] have flow patterns very similar to those of a filter press.

2. Experimental

2.1. RDE experiments

Electrochemical experiments were made with a Voltalab-32 Radiometer system. The RDE was a Tachyprocesseur EDI 10000 of Radiometer. Solutions were prepared with ultrapure water from a Millipore Milli-Q system. N_2 and H_2 were from L'Air Liquide both of quality N-50. The platinum RDE had an area of 3.14 mm^2. The counter electrode was a spiral of Pt and the reference electrode

was a Tacussel TR-100 saturated calomel electrode (SCE). The products employed for the different solutions, hydro-chloric acid, sodium chloride and lead chloride 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 were shown in a previous paper [12]. The cathode was a Ti mesh. Metakem supplied the DSA-O$_2$ and the HDE was home-made as follows. A fixed amount of 10% in weight platinum catalysed Vulcan XC-72 carbon (supplied by Etek Inc.) was 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 (10 kg cm^{-2}) and sintered at a maximum temperature of 350°C.

3. Results and discussion

3.1. RDE experiments

The first step was to study the influence of Pb^{2+} ions on the H_2 oxidation reaction on Pt.

To simulate the HDE operation the procedure employed during the RDE experiments (in presence and absence of Pb^{2+} ions) was the following. Firstly, the solution was saturated with H_2. Next, a series of current density (j) versus E_{RDE} curves at different rotation speeds (w) were registered. After that, experiments at constant current and constant rotation speed were carried out and the E_{RDE} versus t curves were registered. The current density and the rotation speed in these experiments were chosen in such a way that the H_2 oxidation reaction was not mass transport controlled.

3.1.1. Experiments with a lead free solution

Fig. 1a shows the steady state voltammogram of a Pt static RDE in a 0.1 M HCl solution previously deaerated by N_2 bubbling. The potential limits were −0.325 and 1.050 V. Next, the solution was saturated with H_2 and a series of j versus E_{RDE} curves were registered for different rotation rate. The results obtained are shown in Fig. 2. The hydrogen oxidation limiting current is controlled by mass transport as shown by the linear dependence of limiting current with the square root of rotation rate, Levich equation.

For the constant current experiments in a 0.1 M HCl solution the experimental conditions were $j = 0.64$ mA cm^{-2} and $w = 2000$ rpm. The value of the E_{RDE} potential was measured during 5000 s. The potential remained constant at approximately −0.35 V showing that H_2 oxidation on Pt in these experimental conditions (hydrochloric acid medium without Pb^{2+} ions in solution) was not poisoned.
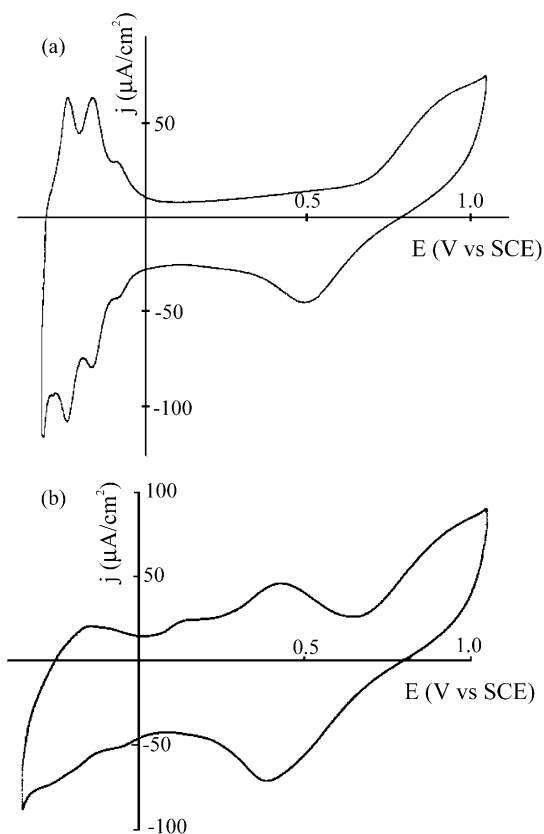
Fig. 1. Voltammetric curves of Pt in (a) 0.1 M HCl, (b) 0.1 M HCl + 5 × 10^{-4} M PbCl$_2$; $v = 50$ mV s^{-1}.

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

Fig. 1b shows the voltammetric curve obtained for a 0.1 M HCl + 5 × 10^{-4} M Pb^{2+} solution. The sweep rate was 50 mV s^{-1}. The comparison between Fig. 1a and b makes evident that the presence of Pb^{2+} ions give rise to important changes in the voltammetric profile. Thus, the voltammetric peaks traditionally assigned to hydrogen adsorption–desorption decrease and two new peaks at approximately 0.125 and 0.43 V appeared. These peaks are attributed to an underpotential deposition (upd) process of lead on platinum.
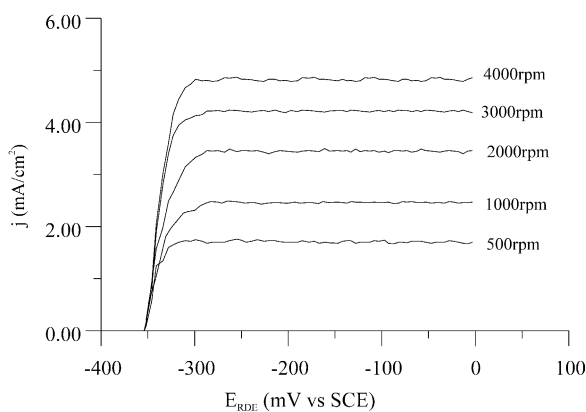

Fig. 2. j vs. E_{RDE} curves in 0.1 M HCl during H$_2$ oxidation on platinum at different rotation speeds; $v = 5$ mV s^{-1}.

Next, H$_2$ was bubbled and a series of constant current experiments at different rotation speeds was made. The experimental conditions were $j = 0.64$ mA cm^{-2} and $w = 1000$, 2000 and 4000 rpm. The results obtained are shown in Fig. 3. After some seconds the potential increases very fast and starts to oscillate. The potential oscillations are composed by a primary wave of high amplitude modulated by high frequency perturbations. The oscillation starts at shorter times on increasing rotation frequency and the frequency of the primary wave increases with the frequency of rotation. This behaviour makes evident the influence of Pb^{2+} transport to Pt surface on potential oscillations. The increase of the stirring increases the transport of Pb^{2+}, speeding up the poisoning of the electrode and shorting the time of apparition of the potential oscillations.

Oscillations during the oxidation of hydrogen at Pt electrodes have been known since 1930. In presence of different adsorbed metal ions there exist different experimental conditions have been found that produce oscillatory behaviour of the hydrogen oxidation reaction under galvanostatic conditions [20–23]. The proposed mechanism to explain the oscillations is based on an adsorption–desorption process on the platinum surface. In presence of chloride ions and at low potential values, lead is adsorbed on the surface blocking the hydrogen adsorption sites in such a way that the hydrogen oxidation is unable to support the imposed current. At this moment, the potential shifts to more positive values. At these positive potential values lead is eliminated from the surface by oxidation increasing the number of free sites for hydrogen adsorption. 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. The inhibition caused by lead adsorption is strongly dependent on the anion present in the solution. If Cl$^-$ anions are substituted by fluoboric anions, a bigger anion, the oscillation did not appeared [12].

3.2. Filter press cell experiments

As we stated previously, for saving energy, the O$_2$ evolution reaction can be replaced by the H$_2$ oxidation that takes place at much more positive potentials, decreasing the cell voltage and, therefore, the energy consumption of the lead electrowinning process.

The influence of Pb^{2+} concentration on the HDE potential at constant current was studied. The results obtained are shown in Fig. 4. The experimental conditions are indicated in Table 1. To maintain constant the Pb^{2+} concentration during the experiments in the catholyte, an anionic membrane was used as separator to avoid Pb^{2+} transport from anolyte to catholyte.

Fig. 4a shows that without Pb^{2+} in the anolyte, the potential of the HDE remains constant. However, in presence of Pb^{2+} (Fig. 4b–d), the potential increases up to approximately 0.4 V and starts to oscillate. The shape of the potential oscillations is quite similar to those registered for
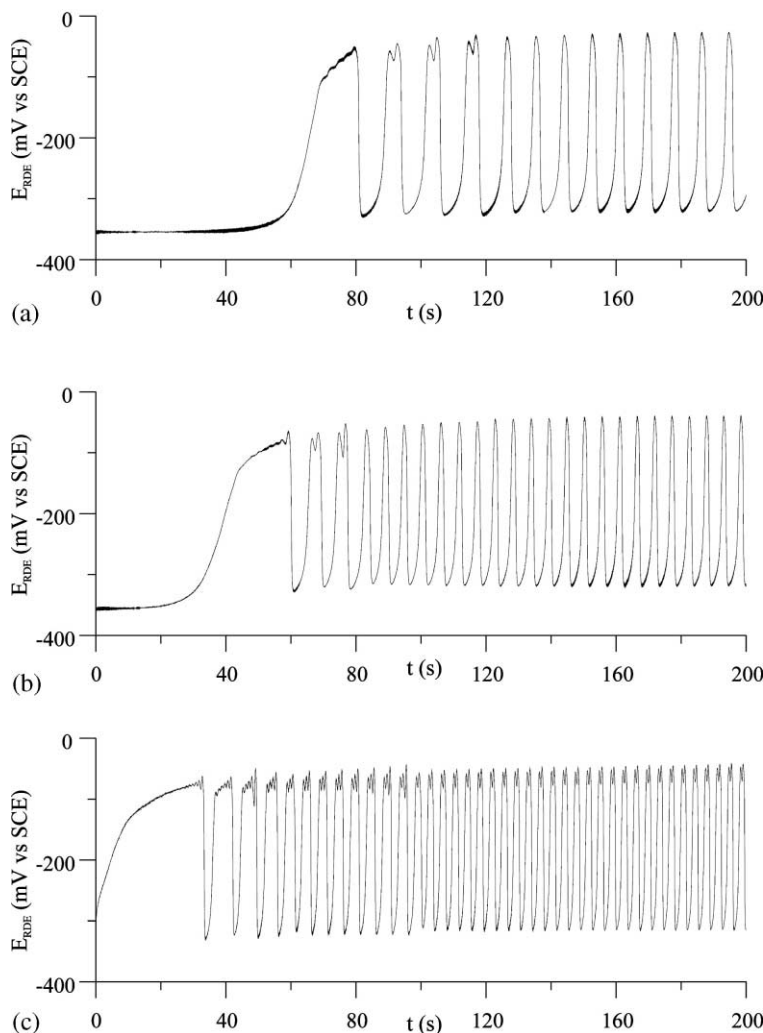
Fig. 3. Variation of E_{RDE} vs. t for galvanostatic H_2 oxidation experiments at different rotation speeds. Electrolyte composition: 0.1 M HCl + 5×10^{-6} M Pb^{2+}; $j = 0.64$ mA cm^{-2}; (a) $w = 1000$ rpm; (b) $w = 2000$ rpm; (c) $w = 4000$ rpm.

RDE. Thus, there is a primary oscillation, characterised by a high amplitude and a low frequency, modulated by a secondary oscillation, with low amplitude and high frequency. On the other hand, both amplitude and frequency of the primary oscillations are very constant (Fig. 5).

As we have said before the origin of the potential oscillations could be an adsorption–desorption process of Pb^{2+} and Cl^- ions on the HDE platinum electrocatalyst.

The fast poisoning of platinum electrocatalyst makes very difficult the use of HDEs as anodes in lead electrowinning in chloride medium in a non-divided cell. So a divided filter press was used. Two experiments of lead electrowinning using DSA-O$_2$ and HDE anodes were carried out. The experimental conditions are shown in Table 2. The catholyte composition of these experiments was the same than the catholyte employed in the LEREFLEOS process [8]. Fig. 6a

Table 1
Experimental conditions for the galvanostatic H_2 oxidation experiments

Geometric area	20 cm^2 (4 × 5)
Cathode	Ti plate
Anode	HDE
Catholyte	NaOH 1 M
Anolyte	NaCl 4.3 M + HCl 0.1 M + different $c_{Pb^{2+}}$
Current density	100 mA cm^{-2}
Anolyte flow	100 l h^{-1}
Temperature	60°C

Table 2
Experimental conditions of the lead deposition experiments using a DSA-O$_2$ and a HDE anode

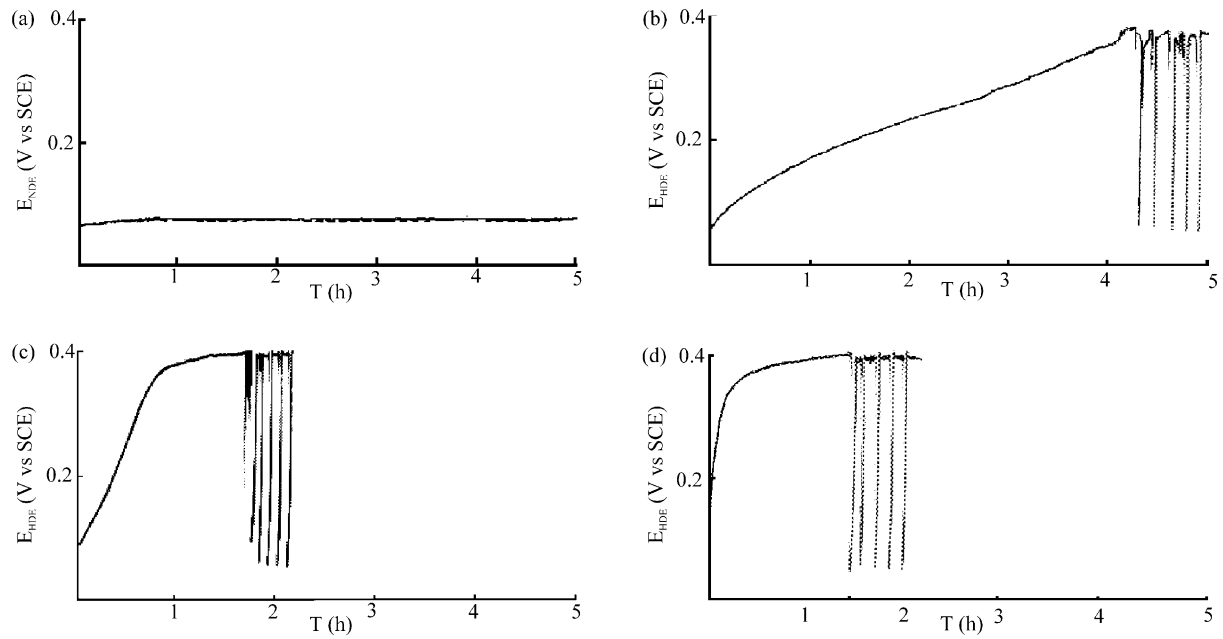|	
Geometric area	20 cm^2 (4 × 5)
Cathode	Ti mesh
Catholyte	NaCl 4.3 M + HCl 0.1 M + 0.05 M Pb^{2+}
Anolyte	H$_2$SO$_4$ 1 M
Current density	100 mA cm^{-2}
Catholyte and anolyte flow	100 l h^{-1}
Temperature	60°C

Fig. 4. Variation of E_{HDE} vs. t during galvanostatic H_2 oxidation experiments at different Pb^{2+} concentrations. Electrolyte composition: 4.3 M NaCl + 0.1 M HCl; $j = 100$ mA cm^{-2}; (a) without Pb^{2+}; (b) 0.01 M Pb^{2+}; (c) 0.03 M Pb^{2+}; (d) 0.05 M Pb^{2+}.
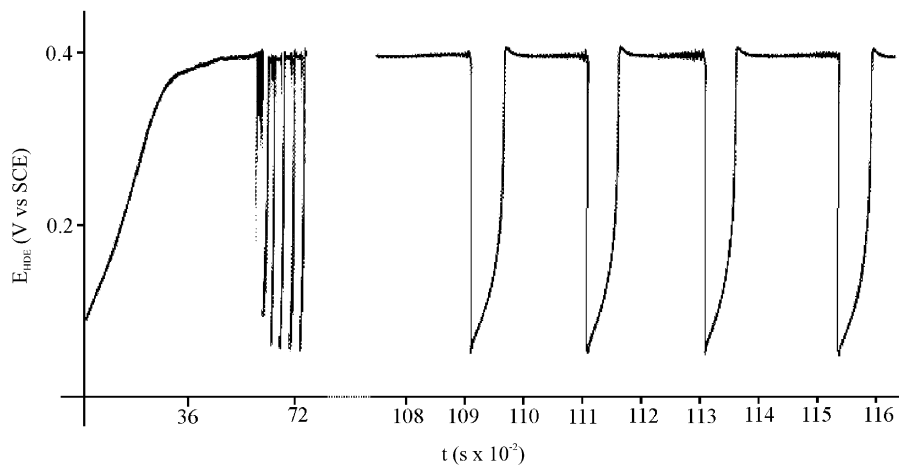

Fig. 5. Enlargement of the potential oscillations shown in Fig. 4c.

shows $E_{cathode}$, E_{anode}, E_{cell} values for the experiment with the DSA-O$_2$. Fig. 6b shows the same parameters when a HDE was used. The decrease in cell potential when the HDE was used was approximately 1.4 V. This means that 40% of energy saving is obtained. Table 3 shows E_{anode}, E_{cell},

current efficiency (CE%) and energy consumption (EC) values at various % of the theoretical charge passed for both anodes. CE% is defined as the percentage of electrical charge used for the desired reaction (lead electrodeposition) to the total charge passed. EC is the energy to obtain a given

Table 3
E_{anode}, E_{cell}, CE% and EC values for the experiments shown in Fig. 6

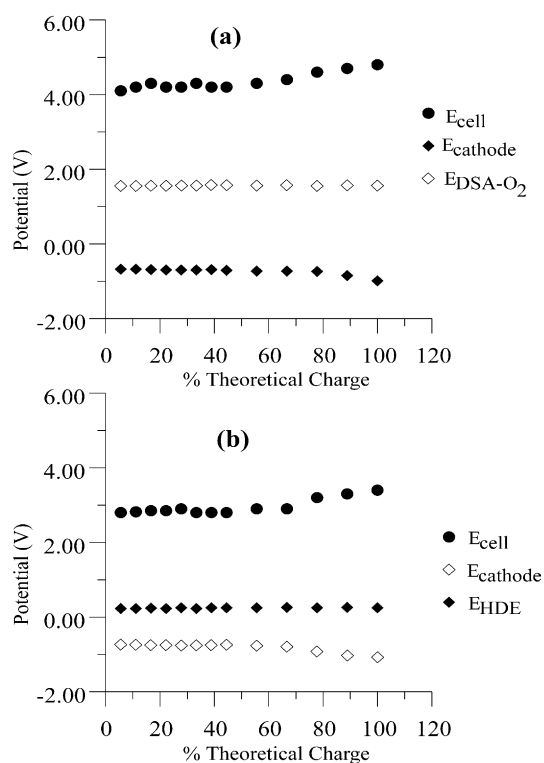| Theoretical charge (%)	DSA-O$_2$ anode				HDE anode			
	E_{cell} (V)	E_{DSA-O_2} (V)	CE% Pb	EC (kWh/kg$_{Pb}$)	E_{cell} (V)	E_{HDE} (V)	CE% Pb	EC (kWh/kg$_{Pb}$)
25	4.2	1.56	94	1.16	2.8	0.23	92	0.79
50	4.3	1.56	96	1.16	2.9	0.23	94	0.80
75	4.6	1.57	89	1.25	3.2	0.25	88	0.87
100	4.8	1.56	81	1.41	3.4	0.23	79	1.01

Fig. 6. Representation of $E_{cathode}$, E_{anode} and E_{cell} vs. % theoretical charge circulated (a) DSA-O$_2$ anode (b) HDE anode. Experimental conditions are shown in Table 2.

amount of product. Normally, it is expressed in kWh per kg of the product obtained. The theoretical charge is the necessary charge to deposit all the lead in solution supposing 100% of current efficiency [10].

As it was expected, the use of a HDE does not affect the current efficiency of the lead electrodeposition. However, its use decreases approximately 40% of the energy consumption due to an important diminution of the anode potential.

4. Conclusions

Lead electrowinning in chloride medium can be carried out employing an HDE anode instead of the classical DSA-O$_2$. The cell employed was a divided filter press cell (Nafion 117 exchange membrane was used as separator). A diminution of approximately 40% in the electric cost of lead was obtained. The use of a non-divided cell was not possible due to the poisoning of the platinum electrocatalyst of the HDE anode. This poisoning caused the apparition of potential oscillations during galvanostatic operation. This oscillatory phenomenon is also observed when hydrogen oxidation was carried out in presence of Pb^{2+} and Cl$^-$ ions and using a platinum RDE. The origin of this oscillatory behaviour was the existence of a Pb^{2+} and Cl$^-$ co-adsorption–desorption process on the platinum surface.

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