Thermodynamic study of Iridium in HCl: The effect of concentration

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Abstract

In this work, the dissolution of iridium was studied through a thermodynamic theoretic study with different concentrations of hydrochloric acid (HCl) and Iridium (Ir). Three different acid conditions and three different concentrations of iridium were analyzed: 1, 0.1 and 0.01 M HCl and 0.86, 0.021 and 0.002 M of iridium. The system 1 M HCl was the only one that presented soluble species of Ir. Results showed that as the Ir concentration diminished from 0.86 to 0.002 M, the pH range where it is possible to obtain Ir soluble species, increased (from 0-1.2 to 0-2). The presence of two Ir species (valences III and IV) for 0.021M and 0.002 M Ir concentrations was determined from the Pourbaix diagrams; while for the 0.086 M concentration, only the Ir (IV) species was observed. The Pourbaix diagrams showed that it is possible to obtain the species iridium (IV) from a potential range of 0.823 V vs SHE to 1.422 V vs SHE and at a pH between 0 and 1.2 in the 1 M HC1 solution.

Introduction

The elements of the platinum group are: platinum, iridium and osmium. These metals have a crystallographic hexaquisoctahedral cubic structure. The crystals are rare and usually deformed. They are frequently found as small grains and flakes, as irregular masses and as large sizes nuggets. They are magnetic when abundant in iron, they do not melt, they are very stable against ordinary reagents, and they only become soluble in hot aqua regia[1]. They are widely used in industry due to their properties as coatings on metallic pieces to which these metals provide their hardness, high resistance to prolonged exposure to oxidizing agents and corrosion [2], even when their cost is high and their abundance is low.

Iridium is considered a valuable material because of its properties, but its extraction in the world is limited; that is why it is important to recover it from post consumed materials, such as the nozzles of electric arc furnaces. Although the most common refining processes for the metals of platinum group (and therefore including Ir) are *INCO, MRR, MINTEK, LONRHO*[3] processes; they are costly in terms of the employment of multiple stages of leaching and reprecipitation. The need to recycle provokes the production of effluents containing precious metals, whose recovery involves costly materials . A viable alternative to the use of these processes, which implies a major recovery and the minimal environmental impact, is the electrochemical techniques. However, there is a lack of studies to this item[4,5]. Prior to the experimental electrochemical recovery of Ir, it is convenient to perform a thermodynamic study by using the Pourbaix diagrams in order to establish the chemical in solution speciation, since it allows the knowledge of the experimental conditions economizing resources and reagents. From the above, a thermodynamic study performed with the HYDRA-MEDUSA software[6], is presented in this work. This study allowed the elaboration of Pourbaix diagrams for the Ir system in acidic conditions that will be used as a support of the electrochemical study of the iridium recovery.

Methodology

This study began in a previous work[7], with the EDS characterization of the nozzles. Results indicated iridium content of 3.88% and this concentration was used to elaborate the Pourbaix diagrams of the soluble species and insoluble species of iridium in acidic conditions for the system Ir-HCl with the Hydra-Medusa software[6]. The concentrations to elaborate the diagrams are presented in Table 1.

Table 1. Hydrochloric acid and iridium concentration for the elaboration of Pourbaix diagrams.

HCl Concentration [M]	Ir Concentration [M]
1.0	0.086
0.10	0.021
0.01	0.002

Results

The main objective for elaborating Pourbaix diagrams is to obtain the theoretical electrochemical potential of the iridium dissolution that can be used with electrochemical techniques. Figures 1 to 5 show the diagrams obtained for the conditions pointed out in Table 1. For the acidic concentrations 0.10 and 0.01 M HCl the diagrams showed that there are not iridium dissolved species.
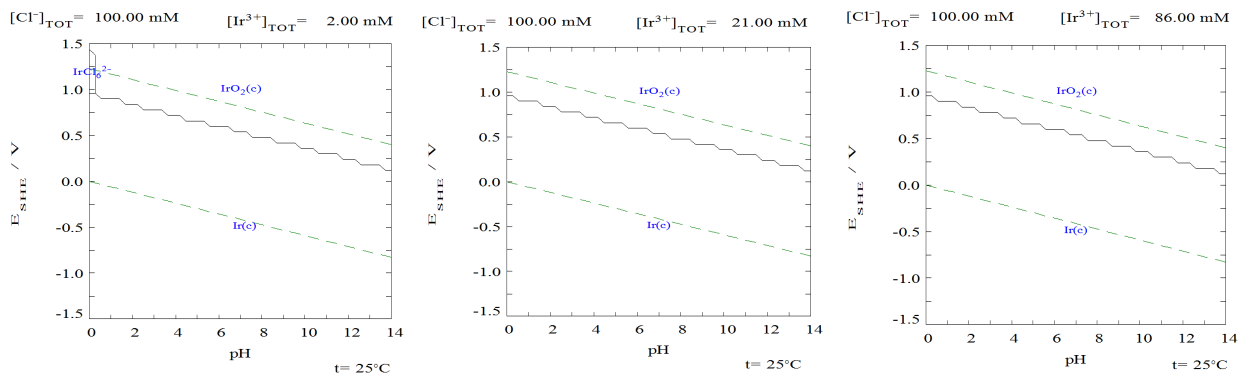

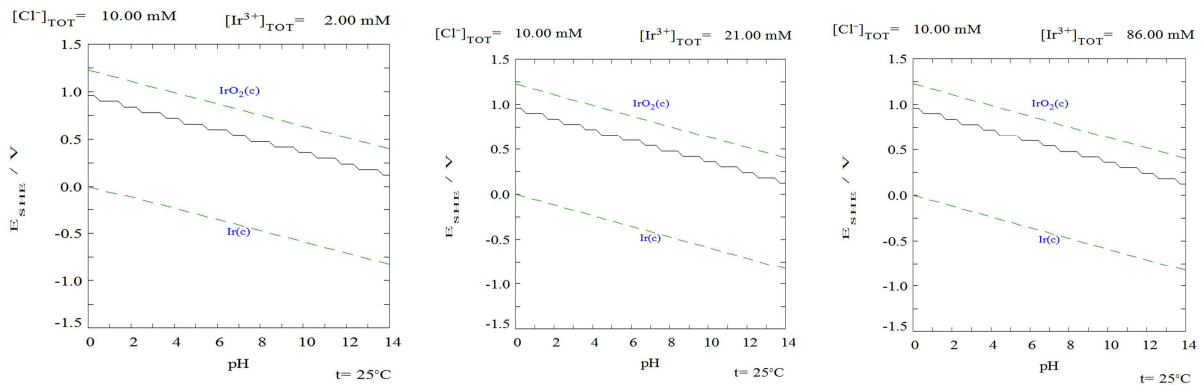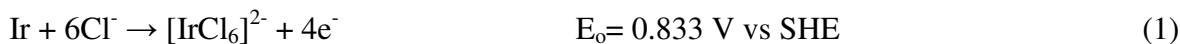Figure 1. Pourbaix diagrams elaborated for 0.1 M HCl and 0.86, 0.21, 0.02 M Ir at 25° C.

Figure 2. Pourbaix diagrams elaborated for 0.01 M HCl and 0.86, 0.21 0.02 M Ir at 25° C.

From Fig. 3 and 4, it was observed the presence of two iridium species, valences (III) and (IV), for the acidic concentration 1 M HCl y 0.21 y 0.02 M de Ir.

However, Fig. 5 (1M HCl and 0.86 M Ir) only shows the iridium (IV) species. Also, it is possible to observe an increase of the pH range where iridium can be dissolved with the decrease of iridium concentration.

The suggested processes for the mechanism of iridium dissolution under the conditions exposed in the thermodynamic analysis are the following:
The dissolution of the Ir (IV) specie to 0.86 M of Ir and 1 M of HC1 in solution is indicated in the equation (1)

$$Ir + 6Cl^- \rightarrow [IrCl_6]^{2-} + 4e^- \qquad\qquad E_o= 0.833 \text{ V vs SHE} \qquad\qquad (1)$$

Meanwhile, to obtain the Ir(III) and Ir (IV) species under the conditions of 0.002 or 0.21 M of Ir in HC1 1M. The mechanism is indicated in the equation (2 and 3)
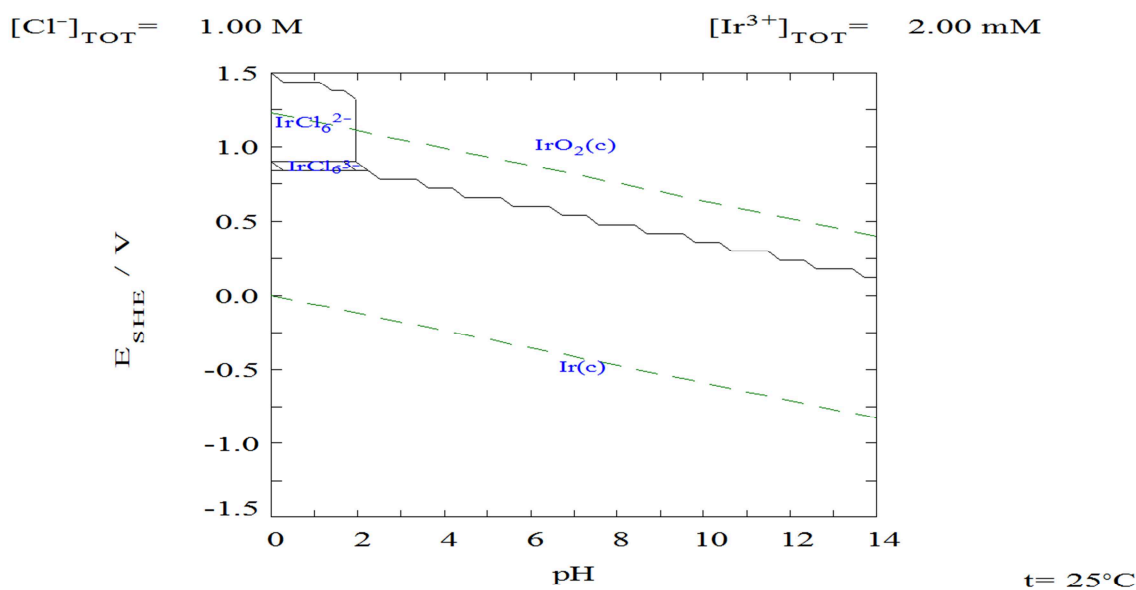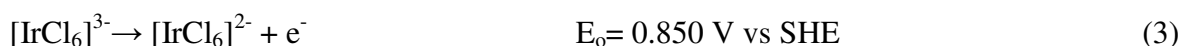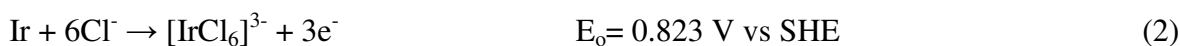
$$Ir + 6Cl^- \rightarrow [IrCl_6]^{3-} + 3e^- \qquad\qquad E_o= 0.823 \text{ V vs SHE} \qquad\qquad (2)$$

$$[IrCl_6]^{3-} \rightarrow [IrCl_6]^{2-} + e^- \qquad\qquad E_o= 0.850 \text{ V vs SHE} \qquad\qquad (3)$$

Figure 3. Pourbaix diagram elaborated for 1 M HCl and 0.002 M Ir at 25° C.

$[Cl^-]_{TOT}=$ 1.00 M $[Ir^{3+}]_{TOT}=$ 21.00 mM

Figure 4. Pourbaix diagram elaborated for 1 M HCl and 0.021 M Ir at 25° C.

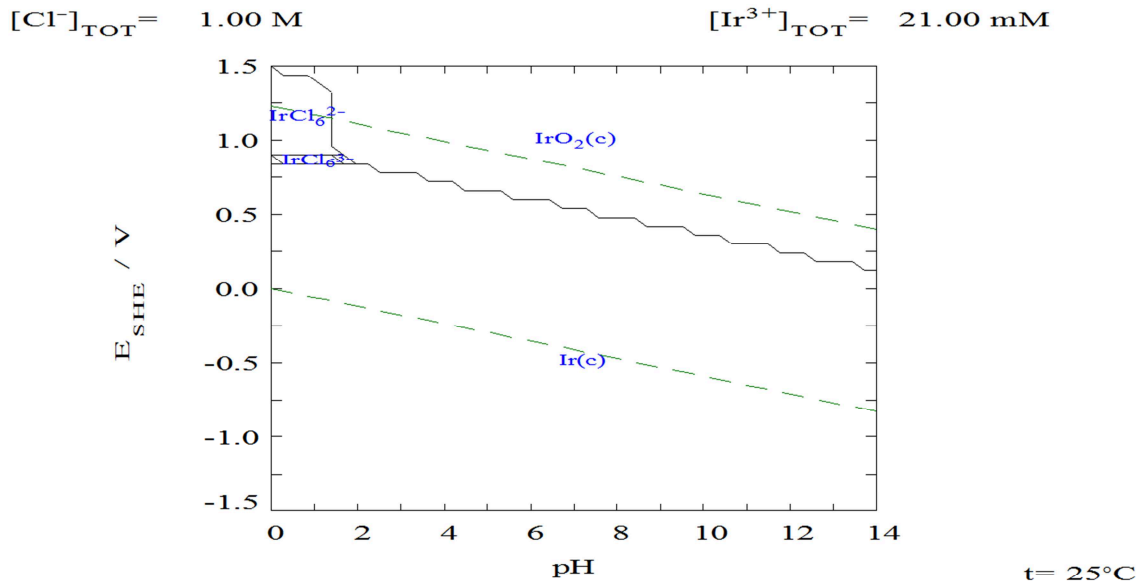$[Cl^-]_{TOT}=$ 1.00 M $[Ir^{3+}]_{TOT}=$ 86.00 mM
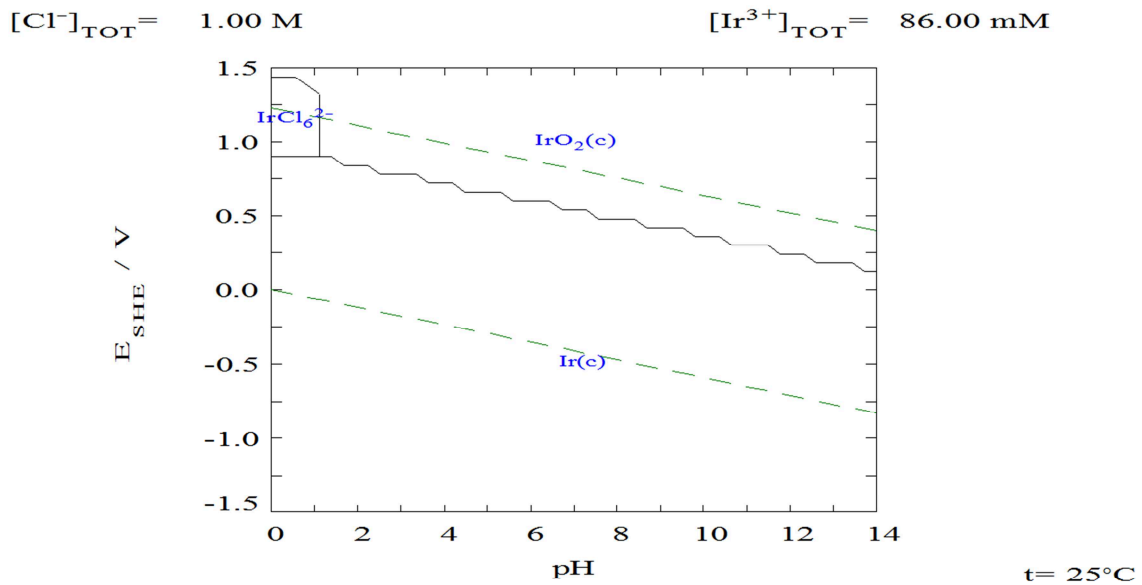

Figure 5. Pourbaix diagram elaborated for the 1 M HCl and 0.086 M Ir at 25° C.

Conclusions

It was observed that the 1M HCl acidic medium is the best way to obtain soluble species of iridium at all concentrations; therefore it is the best way of obtaining iridium dissolution using electrochemical techniques.
It is possible to obtain in solution the Ir (IV) species to a potential range between 0.833 and 1.5 V vs SHE and the Ir (III) species in from 0.823 to 0.833 V vs SHE

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