

PRODUCT ANALYSIS FROM  $D_2O$  ELECTROLYSIS WITH PALLADIUM  
AND TITANIUM CATHODES

E. Brillas\*, G. Sardin\*, J. Casado, X. Doménech and J. Sánchez  
Departament de Química Universitat Autònoma Barcelona.  
Bellaterra (Barcelona) Spain.

\*Departament de Química Física. Universitat de Barcelona.

ABSTRACT

The possible generation of tritium in the electrolyte and the incorporation of species such as tritium, lithium and platinum to cathodes during the electrolysis of 0.1M LiOD solutions with Pd and Ti cathodes and Pt anodes at low and high current densities have been studied by means of different techniques.

INTRODUCTION

During  $D_2O$  electrolysis, large amounts of deuterium are absorbed by Pd and Ti cathodes to yield the respective Pd+D and Ti+D phases. However, less is known about other species either incorporated or possibly generated in cathodes. In this way, Chêne and Brass<sup>1</sup> reported a small tritium production into Pd during the electrolysis of 0.1M LiOD in open cells at high current densities. Several authors<sup>2,3</sup> have proposed a slow diffusion of  $Li^+$  ions into the bulk of Pd.

In this communication, we present results of a study on the electrolysis products of 0.1M LiOD solutions with Pd and Ti cathodes or produced in them, such as tritium, lithium and platinum, as well as to investigate the tritium enrichment of the electrolyte.

## EXPERIMENTAL

0.1M LiOD solutions were prepared by addition of Li metal to 99.95% D<sub>2</sub>O and 0.1 M LiOH solutions by adding LiOH to bidistilled light water. All chemicals were of analytical grade. A 0.1M LiOD solution with a tritium content 3 times higher than that of pure D<sub>2</sub>O was prepared by addition of standardized tritium labelled water, supplied by Amersham.

Pd and Pt sheets of 99.9% purity (SEMP) with respective dimensions of 0.1cmx1.5cm and 0.25mm x 1.5cm x 3cm, and 1.4 cm diameter x 3cm Ti rods of 99.9% purity (Inagasa), were employed as cathodes in the electrolyses at low current density. In the experiments at high current density, Pd and electrolytic Ti (99.9% purity) sheet cathodes of 0.1cm x 0.5 cm were used.

D<sub>2</sub>O electrolyses were carried out either at a low current density of 5 mA cm<sup>-2</sup> for periods up to 30 days or at high current densities of 100 and 300 mA cm<sup>-2</sup> for 15 to 16 days. Experiments were conducted in thermostatted cylindrical glass cells containing 20 ml of electrolyte. The cathodes were placed in the center of cells, being surrounded by spiral anodes (Pt) of 4 cm diameter x 4cm height. The volume of the electrolyte was maintained constant by addition of controlled amounts of solution after sampling for tritium analysis. The temperature was always kept constant at 25 °C. Gases evolved during electrolyses were vented through a glass rod placed in the top of the cells.

Tritium specific activity on samples of the electrolyte was determined using a Wallac Quantulus 1220 liquid scintillation. A 1 ml aliquot was periodically withdrawn from the cell and thoroughly mixed with 9 ml of a high efficiency water soluble scintillation cocktail (Optiphase Hisafe 3, LKB). Samples were left to stabilize in the chamber for at least 24h and counted for a 60 min period. The tritium efficiency of the system was found to be 0.38. No chemiluminescence nor significant quenching was observed in any of the samples.

The products accumulated near to the surface of cathodes used in D<sub>2</sub>O and H<sub>2</sub>O electrolysis experiments were analy-

sed from SIMS spectra obtained with an Atomika A-DIDA 3000 secondary ion microscope, using  $O_2^+$  with 6kV energy as primary ion beam. A Jeol JSM 840 scanning electron microscope (SEM) with 20kV accelerating voltage was used to determine the depth of the  $O_2^+$  attack by SIMS. The overall Li and Pt contents for Pd and Ti sheets of  $0.25 \text{ cm}^2$  area and for Ti rods of 0.5 cm height, before and after electrolysis, were respectively obtained with a Varian 875 atomic absorption spectroscope and a Jobin Yvon JY38VHR inductively coupled argon plasma spectroscope, after solving the metals with HCl acid.

## RESULTS AND DISCUSSION

A mean tritium specific activity of  $0.077 \pm 0.008 \text{ Bq ml}^{-1}$  was obtained for all  $H_2O$  solutions before and during their electrolyses with Pd, Ti and Pt cathodes at  $5 \text{ mA cm}^{-2}$ . The mean tritium specific activity,  $a_o$ , for the two 0.1M LiOD solutions studied was of  $280 \pm 5$  and  $817 \pm 12$  (after addition of tritium)  $\text{Bq ml}^{-1}$ . In all  $D_2O$  electrolyses carried out with Pd, Ti and Pt cathodes, at low and high current densities, a gradual increase of the tritium specific activity of the electrolyte at constant volume,  $a_{i,v}$ , was always found. The increase in this parameter with time for all cathodes was explained from the expected tritium enrichment in open cell, according to the equation,<sup>4</sup>

$$a_{i,v}/a_o = 1/S \{1 - (1-S) \exp[-Srt/N]\}$$

where S denotes the observed tritium-deuterium separation factor of the cathode, r the rate of electrolysis, t the electrolysis time and N the number of deuterium atoms in the solution. Using this equation, S values of 0.4 to 0.6 for Pd and Ti and 0.55 to 0.75 for Pt were obtained from experimental data.

Several Pd and Ti cathodes previously charged either at low or at high current densities were thoroughly rinsed with bidistilled water and further introduced in cells containing 20 ml of 0.1 M LiOH, which were then run at  $100 \text{ mA cm}^{-2}$  for 24h. After this, all species (D and T) previously contained in cathodes were completely displaced by hydrogen and trans-

ferred to the electrolyte, as confirmed by SIMS. Electrolytes proceeding from Ti cells did not show any increase in tritium activity, as expected if this species is not accumulated into Ti during D<sub>2</sub>O electrolysis. Electrolytes of Pd cells, however showed increases of 40 to 60 Bq in tritium activity, indicating the presence of small amount of T into Pd cathodes.

From comparison with blank determinations, it can be established that small quantities of Li are incorporated into both Pd and Ti cathodes after prolonged electrolyses. The Li accumulated in Ti cathodes is higher than the accumulated in Pd cathodes. Also small amounts of Pt from anode are electrodeposited on both Pd and Ti cathodes.

SIMS depth profiles in the form intensity (counts s<sup>-1</sup>) vs. sputter time (proportional to the depth) were simultaneously recorded for the positive and negative secondary ions generated until a m/e ratio of 7 from the O<sub>2</sub><sup>+</sup> attack on Pd and Ti cathodes. Positive and negative secondary ions with m/e ratio of 1 (H<sup>+</sup> and H<sup>-</sup>) were always detected. Positive m/e=6 and 7 ions (Li isotopes 6 and 7) were also recorded. High increases of ca. 20 and 500 times in intensity with respect to that of virgin electrodes were found for spectra of Li<sup>+</sup> ions recorded for Pd and Ti cathodes, respectively. This indicates that a preferential accumulation of Li near to the electrode surface takes place in electrolyses of both D<sub>2</sub>O and H<sub>2</sub>O. All cathodes used in D<sub>2</sub>O electrolysis showed SIMS spectra for positive and negative secondary ions with m/e values of 2, which can be ascribed to D<sup>+</sup> and D<sup>-</sup> ions.

Inspection of the data obtained from SIMS analysis confirms that tritium is not accumulated into Ti. All Pd cathodes after D<sub>2</sub>O electrolysis showed positive ions with m/e values of 3, 4 and 5. Since T is absorbed by Pd and H<sub>2</sub><sup>+</sup> and H<sub>3</sub><sup>+</sup> ions are detected for Pd cathodes saturated with hydrogen, T<sup>+</sup> and DH<sup>+</sup> ions can be ascribed to m/e=3, TH<sup>+</sup>, D<sub>2</sub><sup>+</sup> and DH<sub>2</sub><sup>+</sup> ions to m/e=4 and TD<sup>+</sup>, D<sub>2</sub>H<sup>+</sup> and TH<sub>2</sub><sup>+</sup> ions to m/e=5.

Pd and Ti cathodes previously charged with deuterium and further electrolysed in 0.1M LiOH solutions at 100 mA cm<sup>-2</sup> for 24h showed the same SIMS spectra obtained for cathodes only used in H<sub>2</sub>O electrolysis, as expected if all species pre-

viously contained in them are displaced by hydrogen and transferred to the electrolyte.

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