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SHORT COMMUNICATION

Insoluble anode of α-lead dioxide coated on titanium for electrosynthesis of sodium perchlorate

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1. Introduction

Lead dioxide is an important electrode material due to its stability under aggressive conditions (such as acidity of the electrolyte and high anode potentials), high electronic conductivity and low cost of material. Two major areas of applications of lead dioxide are lead-acid batteries and electrosynthesis. Lead dioxide exhibits different morphological forms of which the orthorhombic α-form and the tetragonal β-form have been extensively studied. Methods of preparation of these two forms of lead dioxide as well as their characteristics have been reviewed [1, 2].

Generally, the preferred form of this electrode material in lead-acid batteries, as well as for electrosynthesis applications, is the β-form. In spite of the fact that α-PbO_2 is superior to β-PbO_2 both in electronic conductivity [1] as well as electrochemical stability [3], no study appears to have been made to evaluate the suitability of α-PbO_2 as an electrode material. In this paper we report our results on the preparation of an α-PbO_2 electrode coated onto a titanium substrate (α-PbO_2 (Ti)) and its use as an insoluble anode for the electro-oxidation of sodium chlorate to sodium perchlorate.

2. Experimental details

Both α-PbO_2(Ti) electrodes and β-PbO_2(Ti) electrodes were prepared for comparative studies. The β-PbO_2 was electrolytically deposited on a platinized titanium surface as reported earlier [4] from an acidic lead nitrate and copper nitrate bath in the absence of any surface active agent. The α-PbO_2(Ti) electrode was prepared by anodic electrodeposition under the following conditions: (i) electrolyte, potassium hydroxide solution (4 M) saturated with lead acetate and filtered; (ii) bath temperature, ambient (25 ± 5° C); (iii) cathode material, low-carbon steel (area about 20 times larger than that of the anode); (iv) anode, platinized titanium strip (area about 8 cm^2); (v) stirring, mild stirring using a magnetic stirrer; (vi) anode current density, initially 50 $mA\,cm^{-2}$ for two minutes, then decreased to 10 $mA\,cm^{-2}$ for a few hours until the required thickness was obtained.

In order to characterize and evaluate the performance of the α-PbO_2(Ti) electrode in comparison with the β-PbO_2(Ti) electrode, powder X-ray diffraction studies, steady-state galvanostatic anodic polarization curves in sodium chlorate solutions and instantaneous current efficiency measurements for perchlorate production by a gas analysis technique were carried out.

The analytical procedures, electrochemical cell, electrical circuit and the procedure for recording steady-state galvanostatic anodic polarization curves and current efficiency measurements were as reported previously [5].

3. Results and discussion

3.1. *Preparation of α-PbO_2(Ti) electrode*

The conditions for preparation of the α-PbO_2(Ti) electrode (see Section 2, Experimental details) were arrived at as a result of deposition of α-PbO_2 on platinized titanium substrates from alkaline plumbite solutions of different compositions with different current densities and bath temperatures etc. The α-PbO_2(Ti) electrode consisting of a 1.5 mm thick PbO_2 layer prepared under these favourable conditions was similar in appearance to the β-PbO_2(Ti) electrode and the adherence to the substrate, as well as the coherence within the coating, were good. The α-lead dioxide layer did not peel off when the electrodes were used for anodic perchlorate synthesis, in contrast to reports in the literature [6]. A mild stirring of the alkaline plumbite solution was found to be essential during the PbO_2 coating process, since, in the absence of such a stirring formation took place of a loosely bound reddish brown oxide of lead which subsequently became detached from the anode. As the solubility of lead acetate in potassium hydroxide (4 M) is only about 40 $g\,l^{-1}$ a fairly large quantity of the electrolyte (one liter for 8 cm^2 of electrode) was required to deposit a 1.5 mm thick α-PbO_2 coating to minimize the depletion of plumbite ions during the coating operation. When the electrolysis was prolonged to almost complete depletion of plumbite ion in solution, the α-PbO_2 coating, already present on the anode, was found to be partially converted to reddish brown oxide, rendering the electrode unsuitable for electrosynthetic applications.

The current efficiency for the deposition of the α-PbO_2 is lower than that for the deposition of the β-PbO_2 (60% for the α-PbO_2 and 95% for the β-PbO_2). As a result, it requires a longer time to deposit the α-PbO_2 than the time required for depositing the β-PbO_2 of comparable thickness. Nervertheless, this is not a major disadvantage since the electrode is prepared only once for use as an insoluble anode, for a duration of several months.

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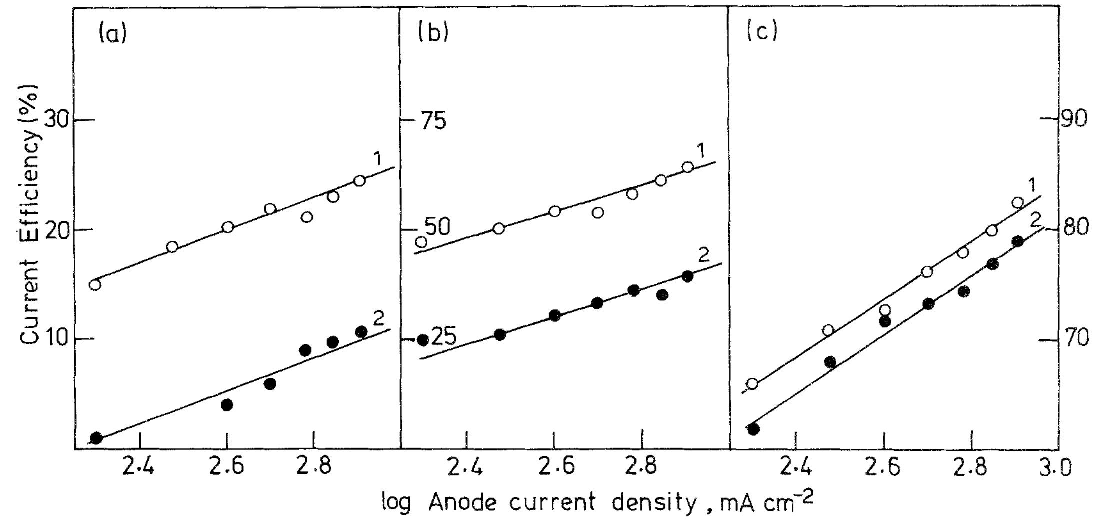

Fig. 1. Instantaneous current efficiency for anodic chlorate oxidation on (1) α-PbO_2(Ti) electrode; (2) β-PbO_2(Ti) electrode as a function of anode current density in a solution of (a) 1 M sodium chlorate; (b) 3.2 M sodium chlorate; (c) 6.5 M sodium chlorate at 60 ± 2° C and pH 6.5 ± 0.2.

The use of low carbon steel as cathode material on which the overvoltage for the hydrogen evolution reaction is low, is expected to reduce the losses of plumbite ion due to cathodic reduction, in addition to a reduction in cell voltage during electrolysis.

3.2. *Characterization of α-PbO_2(Ti) electrode*

X-ray diffractograms of powdered samples of α-PbO_2 (freshly prepared as well as from an electrode used as an insoluble anode) revealed that the samples did not contain any form of PbO_2 other than the α-form. This is in contrast to β-PbO_2 prepared from an acidic nitrate bath which contains the α-form as a minor component [4, 7].

Current efficiency data obtained with an α-PbO_2(Ti) anode and a β-PbO_2(Ti) anode in sodium chlorate solutions of 1 M, 3.2 M and 6.5 M concentrations are presented in Fig. 1. The corresponding steady-state galvanostatic anodic polarization curves are shown in Fig. 2.

It may be seen from Fig. 1, that the current efficiency for perchlorate synthesis is higher on the α-PbO_2(Ti) electrode than on the β-PbO_2(Ti) electrode in all the three electrolyte concentrations studied. The polarization curves (Fig. 2) are non-linear due to the interference by the oxygen evolution reaction and by ohmic drop in the electrolyte [5]. It may be seen from the polarization curves that the anode potential is less at the α-PbO_2(Ti) electrode than at the β-PbO_2(Ti) electrode, which is an additional advantage with α-PbO_2(Ti) insoluble anodes when used in perchlorate cells. A study of the literature on the subject reveals that the oxygen evolution reaction takes place at lower anode potentials than the anodic oxidation of chlorate ion to perchlorate ion [8] while the overpotential for oxygen evolution is less on α-PbO_2 than on β-PbO_2 [3]. These facts explain the present results, *viz.* the increase in current efficiency and the decrease in anode potentials for anodic oxidation of chlorate ion to perchlorate ion on α-PbO_2(Ti) electrodes as compared to β-PbO_2(Ti) electrodes, as due to either an electrocatalysis of the anodic oxidation of chlorate and/or electro-retardation of anodic oxygen evolution on α-PbO_2(Ti) electrode.

Continuous electrolysis of sodium chlorate starting

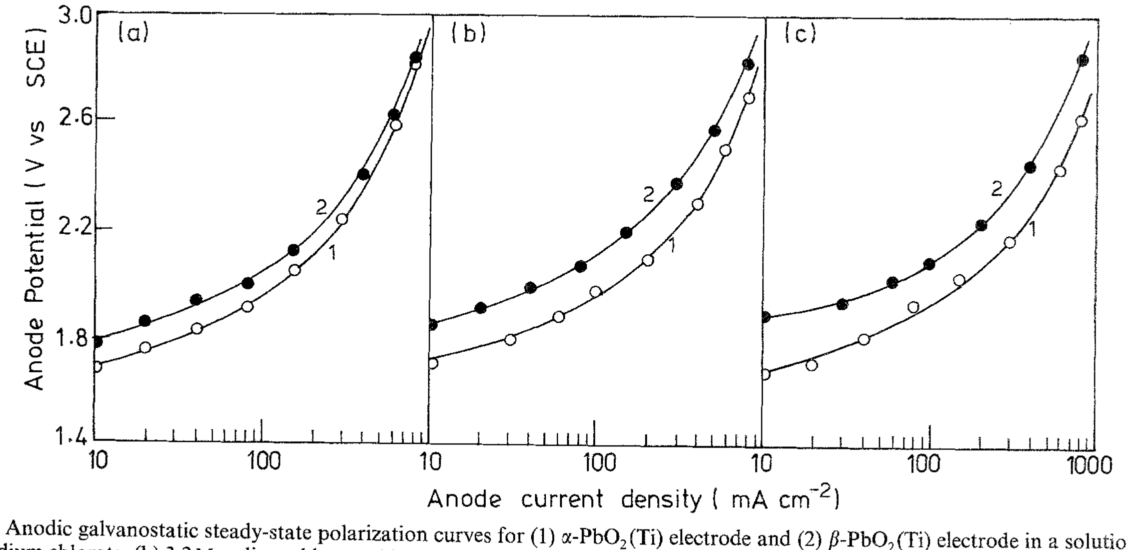

Fig. 2. Anodic galvanostatic steady-state polarization curves for (1) α-PbO_2(Ti) electrode and (2) β-PbO_2(Ti) electrode in a solution of (a) 1 M sodium chlorate; (b) 3.2 M sodium chlorate; (c) 6.5 M sodium chlorate, at 60 ± 2°C and pH 6.5 ± 0.2. 'SSCE', Calomel electrode with saturated sodium chloride.

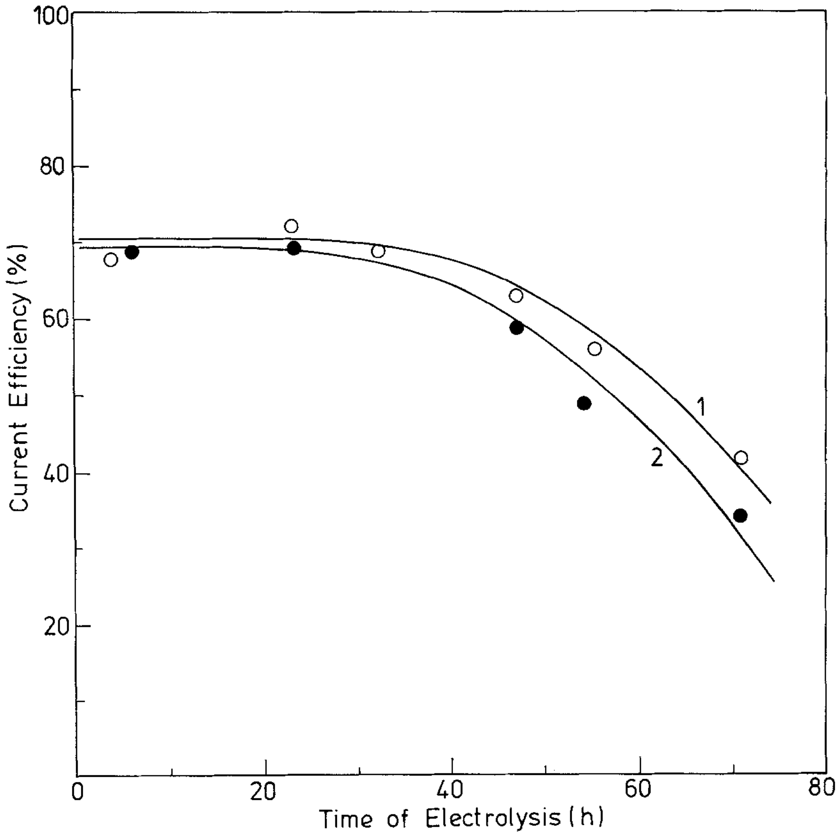

Fig. 3. Instantaneous current efficiency for anodic chlorate oxidation during continuous electrolysis of a solution of sodium chlorate (initial concentration 6.5 M; concentration at the end of electrolysis 1 M) at 60 ± 2°C, pH 6.5 ± 0.2 and anode current density 0.5 A cm^{-2} on (1) α-PbO_2(Ti) electrode and (2) β-PbO_2(Ti) electrode.

with 6.5 M solution and reaching about 1 M concentration at the end of the electrolysis (Fig. 3) revealed that the α-PbO_2(Ti) electrode performed marginally better than the β-PbO_2(Ti) electrode with regard to cumulative current efficiency. Thus the average cumulative current efficiency obtained by estimating the initial and final concentrations of chlorate ion for two electrolytic runs with each type of anode was 63.5% at the α-PbO_2(Ti) electrode and 58.8% at the β-PbO_2(Ti) electrode.

The rate of anodic oxidation of chlorate ion to perchlorate ion increases with an increase in ionic strength of the electrolyte at a constant concentration of chlorate ion [5]. Therefore, the current efficiency, when the chlorate concentration dropped to 1 M during continuous electrolysis in the electrolyte of ionic strength of 6.5 M, was higher (Fig. 3) compared to the current efficiency in 1 M sodium chlorate (Fig. 1(a)). The difference in current efficiencies for the α-PbO_2(Ti) electrode and the β-PbO_2(Ti) electrode was also not substantial in the electrolyte of high ionic strength (Fig. 3).

In conclusion it may be stated that chemical, mechanical and electrochemical stability of an α-PbO_2(Ti) electrode is as good as that of a β-PbO_2(Ti) electrode. Additional advantages in using an α-PbO_2(Ti) electrode are increased current efficiency and decreased overpotential for anodic oxidation of chlorate ion to perchlorate ion.

Acknowledgement

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