Utilization of gas-diffusion electrodes catalysed with tungsten carbide as anodes for zinc electrowinning

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Gas-diffusion electrodes with varying amounts of tungsten carbide catalyst are studied, and their feasibility as suitable anodes for zinc electrowinning is demonstrated. The energy savings achievable with the use of such anodes are evaluated.

1. Introduction

The world production of zinc of about 6.5 million tons a year places it first among the non-ferrous metals. A substantial part (about 90%) of the whole of zinc production is based on the electrolytic method since the zinc produced in this way is of very high purity and meets most of the utilization requirements. Insoluble lead–silver alloys are used for anodes during electrolysis. These alloys may, in addition, be doped with other additives such as strontium, calcium, cobalt, etc.

Recently, as a result of the world energy crisis, new technical solutions for the electrochemical production of zinc are being attempted, aiming at economy in electroenergy consumption [1–3]. One of these is a better utilization of the hydrogen obtained during chlor-alkali electrolysis [4]. At present this hydrogen is frequently inadequately used in industry. Its utilization in a hydrogen gas-diffusion electrode (GDE) operating as the anode during zinc electrowinning may be of interest.

During conventional electrowinning with insoluble lead–silver anodes the following general reaction occurs:

$$2\text{ZnSO}_4 + 2\text{H}_2\text{O} \rightarrow 2\text{Zn} + 2\text{H}_2\text{SO}_4 + \text{O}_2$$

$$U = 1.99 \text{V}$$

With a hydrogen GDE as the anode the following reaction could take place:

$$\text{ZnSO}_4 + \text{H}_2 \rightarrow \text{Zn} + \text{H}_2\text{SO}_4$$

$$U = 0.76 \text{V}$$

From thermodynamic considerations, the second reaction requires a voltage 1.23 V lower. Bearing in mind the lower overvoltage at a hydrogen electrode compared to that at an oxygen electrode, it can be expected that the overall cell voltage with a hydrogen GDE will be about 1.5 V lower.

The aim of the present investigation is to study the feasibility of using a hydrogen GDE, catalysed with tungsten carbide, as an anode in zinc electrowinning conditions.

2. Experimental conditions

The tungsten carbide hydrogen GDE tests were carried out galvanostatically in a cell with a zinc plate as the cathode and a water jacket for temperature control (Fig. 1). The Hg–HgSO_4 electrode was used as reference, and sulphuric acid with varying concentrations of ZnSO_4 was used as the operating electrolyte. The current efficiency of zinc deposition was measured by weight gain of the cathode.

The galvanostatic current–voltage curves were traced with a RADELKIS OH 405 (Budapest)
potentiostat with a built-in resistance so that it could be used as a galvanostat. The long-term tests were carried out with a custom-built galvanostat (0.5 A, 5 V) designed at the laboratory.

The tungsten carbide anodes were of two types. The first was double-layered, consisting of a gas-supplying layer developed by Iliev et al. [5] for oxygen GDEs and an active layer containing tungsten carbide. Teflonized carbon (PTFE-C) and a pore-forming agent (Na2SO4) [6]. These electrodes operate without hydrogen over-pressure. The second type was single-layered and consisted of tungsten carbide, active carbon, carbon black and a Teflon dispersion (60%) [7]. Investigations with these electrodes were made at a hydrogen pressure of 40–50 mm Hg.

The carbides used for the catalysis of double-layered electrodes were synthesized from two initial starting materials, H2WO4 (white modification) (WC-1) and WO3 (WC-2), fired at 800–850 °C, a temperature assuring a good corrosion resistance of the carbide [8]. The carbides obtained had almost equal specific surface areas, according to BET, of 8.4 and 9.3 m² g⁻¹, respectively.

The single-layered electrodes (WC-3) were catalysed with tungsten carbide synthesized from H2WO4 (yellow modification) at 600–800 °C. This carbide (WC-3) had a specific surface area of 9.02 m² g⁻¹.

These carbides had a smaller specific surface and a correspondingly smaller catalytic activity than those of a previous investigation [8]. The smaller specific surface areas were necessary because previous investigations had shown that, under the conditions of zinc electrowinning, the carbides with a specific surface above 13 m² g⁻¹ were prone to corrosion.

3. Results

It was first necessary to check whether the presence of zinc ions in the solution leads to a considerable decrease of the catalytic activity of the tungsten carbide. For this purpose current-potential curves for the same tungsten carbide GDE were taken in a sulphuric acid solution and in the same solution containing ZnSO4. As seen from Fig. 2, the addition of zinc ions to the electrolyte does not lead to any significant increase in the polarization of the GDEs catalysed with tungsten carbide. At the same time, a comparison of the curve from Fig. 2, taken in a sulphuric acid solution, with the current-potential curves of electrodes from a previous study [6] shows that the polarization of the electrode under study substantially surpasses that of the electrodes previously developed. This increase in polarization is probably due not only to the smaller catalytic activity of the carbide employed, but also to the non-optimal structure of the GDE active layer. Therefore, we undertook an optimization of the GDE active layer.

It is known from studies carried out by Iliev and co-workers [9] that the main parameters determining the GDE characteristics are the thickness and porosity of the active layer. Optimization of the structure of this layer with respect to these parameters was carried out in two stages. First, its thickness was varied at a constant ratio of components (tungsten carbide; PTFE-C; Na2SO4); Fig. 3 presents the way in which the potential of the electrodes, catalysed with WC-2, changes as a function of this parameter. Second, the amount of Teflonized carbon was varied for each different amount of carbide.

As a result of this optimization it was established that electrodes with the best characteristics contained a WC-1 catalyst with a loading of 300 mg tungsten carbide per cm² and a WC-2 catalyst with 400 mg tungsten carbide per cm². In order to obtain the best characteristics with single-layer electrodes, a substantially larger