

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

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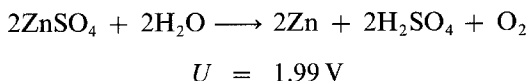
Gas-diffusion electrodes with varying amounts of tungsten carbide catalyst are studied, and their feasibility as suitable anodes for zinc electrowinning is demonstrated. The energy savings achievable with the use of such anodes are evaluated.

1. Introduction

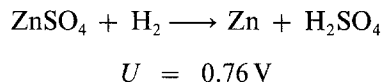
The world production of zinc of about 6.5 million tons a year places it first among the non-ferrous metals. A substantial part (about 90%) of the whole of zinc production is based on the electrolytic method since the zinc produced in this way is of very high purity and meets most of the utilization requirements. 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:



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



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-HgSO₄ electrode was used as reference, and sulphuric acid with varying concentrations of ZnSO₄ 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 (Na_2SO_4) [6]. These electrodes operate without hydrogen overpressure. 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, H_2WO_4 (white modification) (WC-1) and WO_3 (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 m^2g^{-1} , respectively.

The single-layered electrodes (WC-3) were catalysed with tungsten carbide synthesized from H_2WO_4 (yellow modification) at 600–800°C. This carbide (WC-3) had a specific surface area of 9.02 m^2g^{-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 m^2g^{-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 ZnSO_4 . 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 cata-

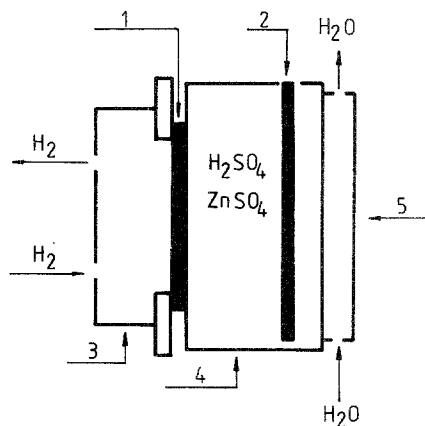


Fig. 1. Diagram of the cell for tungsten carbide hydrogen GDE tests. 1, Tungsten carbide gas diffusion anode; 2, zinc cathode; 3, gas chamber; 4, electrolyte chamber; 5, water jacket for temperature control.

lysed 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; Na_2SO_4); 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 cm^2 and a WC-2 catalyst with 400 mg tungsten carbide per cm^2 . In order to obtain the best characteristics with single-layer electrodes, a substantially larger

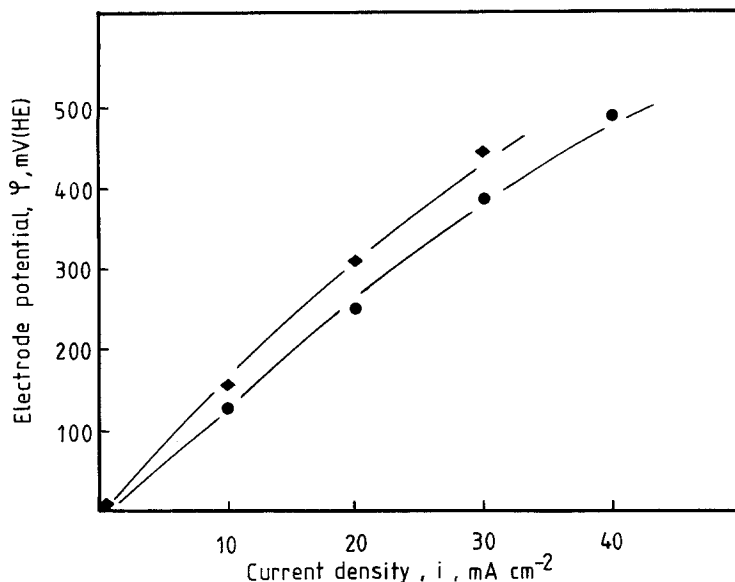


Fig. 2. Current-potential curves for a WC-2 GDE at 60°C. ●, 160 g l⁻¹ H₂SO₄; ◆, 160 g l⁻¹ H₂SO₄ + 80 g l⁻¹ Zn²⁺.

amount of catalyst was necessary, namely 733 mg tungsten carbide per cm².

The next stage in the present investigation was to determine the most suitable operating conditions of these hydrogen GDEs with respect to the concentration of sulphuric acid and zinc sulphate in the operating electrolyte, the temperature and the current density. All these parameters also affect the current efficiency of zinc

deposition; for this reason this dependence was investigated. From a practical and theoretical point of view it is known that at sulphuric acid concentrations between 40 and 200 g l⁻¹ and zinc ion concentrations between 40 and 100 g l⁻¹, the current efficiency of the zinc deposition is at its greatest. The change in the current efficiency of zinc deposition with increase in sulphuric acid concentration at two different

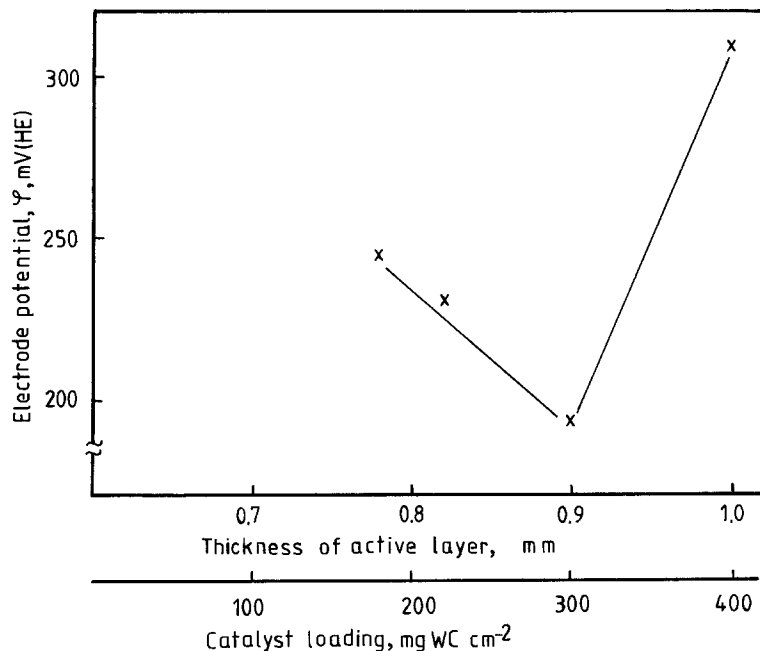


Fig. 3. Dependence of the potential of a WC-2 GDE on the thickness of the active layer at constant ratio of the components in this layer: 89.3% tungsten carbide; 5.5% PTFE; 3.7% C; 1.5% Na₂SO₄; 160 g l⁻¹ H₂SO₄; 54.3 g l⁻¹ Zn²⁺. Temperature = 40°C; $i = 20 \text{ mA cm}^{-2}$.

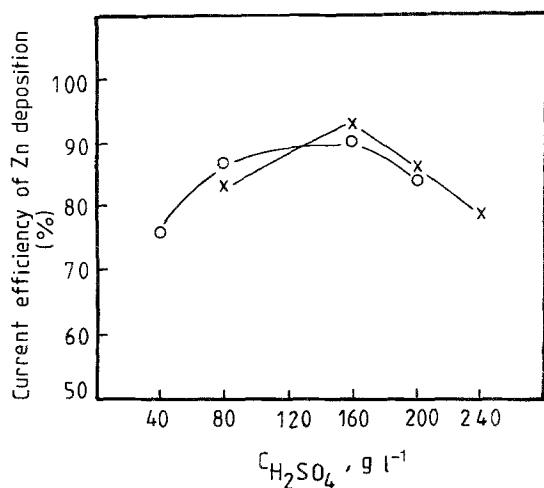


Fig. 4. Dependence of the current efficiency of zinc deposition on the H_2SO_4 concentration. \times , $54.3 \text{ g l}^{-1} \text{ Zn}^{2+}$; \circ , $90 \text{ g l}^{-1} \text{ Zn}^{2+}$; $i = 36 \text{ mA cm}^{-2}$; temperature = 40°C .

zinc ion concentrations is shown in Fig. 4. It is seen that this efficiency reaches 90–93% at $160 \text{ g l}^{-1} \text{ H}_2\text{SO}_4$. Fig. 5 demonstrates the influence of current density on the current efficiency of zinc deposition. From Fig. 6 it can be seen that, with tungsten carbide anodes, the highest efficiency is obtained at 40°C .

On the basis of these results, the behaviour of a GDE catalysed with tungsten carbide was investigated. From Figs 7 and 8 it is seen that,

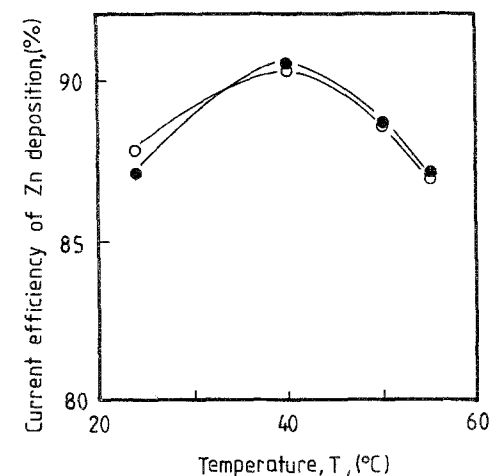
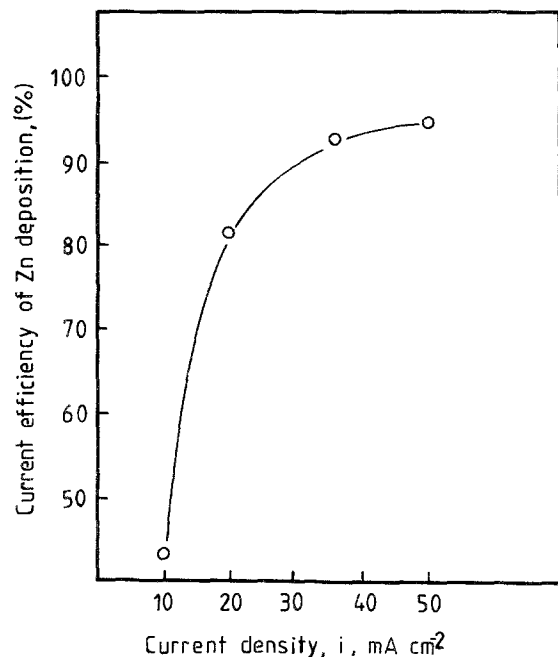


Fig. 6. Dependence of the current efficiency of zinc deposition on temperature at $i = 60 \text{ mA cm}^{-2}$; $54.3 \text{ g l}^{-1} \text{ Zn}^{2+}$; $160 \text{ g l}^{-1} \text{ H}_2\text{SO}_4$. \bullet , WC-3 anode; \circ , Tainton anode.

for the concentrations investigated, double-layered tungsten carbide GDEs with the optimum structure display the best potential–current density characteristics at a sulphuric acid concentration of 160 g l^{-1} and a zinc content of 54.3 g l^{-1} .

The use of single-layer electrodes (tungsten carbide = 733 mg cm^{-2}) in an electrolysis cell results in behaviour similar to that obtained with double-layer electrodes. Fig. 9 confirms this: a

Fig. 5. Dependence of the current efficiency of zinc deposition on the current density at $160 \text{ g l}^{-1} \text{ H}_2\text{SO}_4$; $54.3 \text{ g l}^{-1} \text{ Zn}^{2+}$; 40°C .

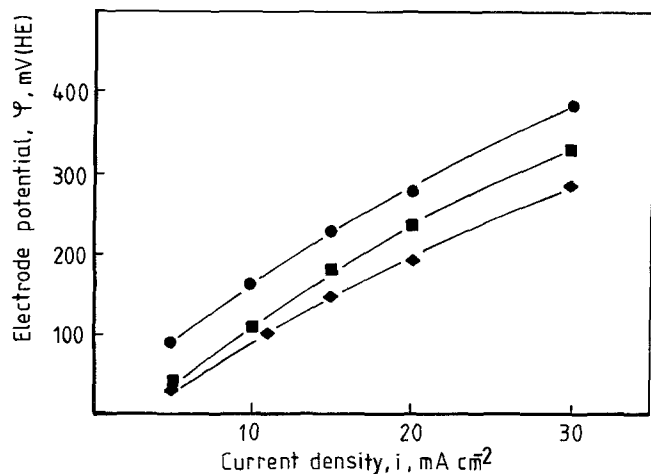


Fig. 7. Current-potential curves of a WC-1 GDE measured at different zinc ion concentrations: ●, $120 \text{ g l}^{-1} \text{ Zn}^{2+}$; ■, $90 \text{ g l}^{-1} \text{ Zn}^{2+}$; ◆, $54.3 \text{ g l}^{-1} \text{ Zn}^{2+}$, with $160 \text{ g l}^{-1} \text{ H}_2\text{SO}_4$ at 40°C .

Fig. 8. Current-potential curves of a WC-1 GDE measured at different sulphuric acid concentrations: ●, $40 \text{ g l}^{-1} \text{ H}_2\text{SO}_4$; ■, $80 \text{ g l}^{-1} \text{ H}_2\text{SO}_4$; ◆, $160 \text{ g l}^{-1} \text{ H}_2\text{SO}_4$; with $54.3 \text{ g l}^{-1} \text{ Zn}^{2+}$ at 40°C .

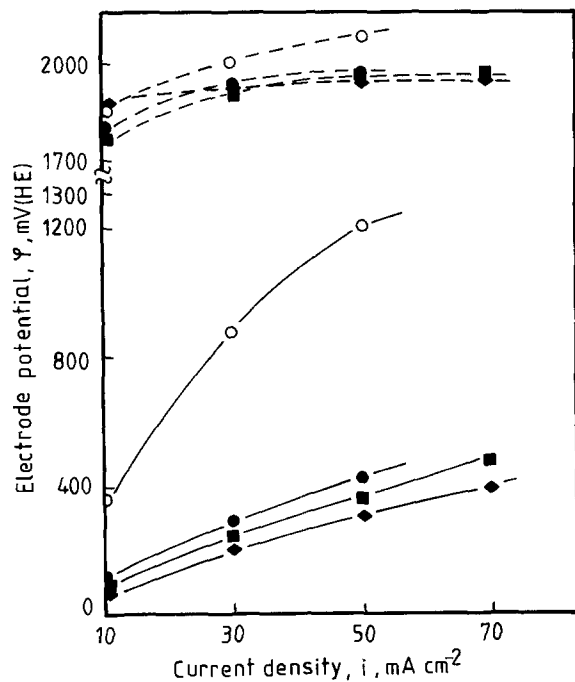
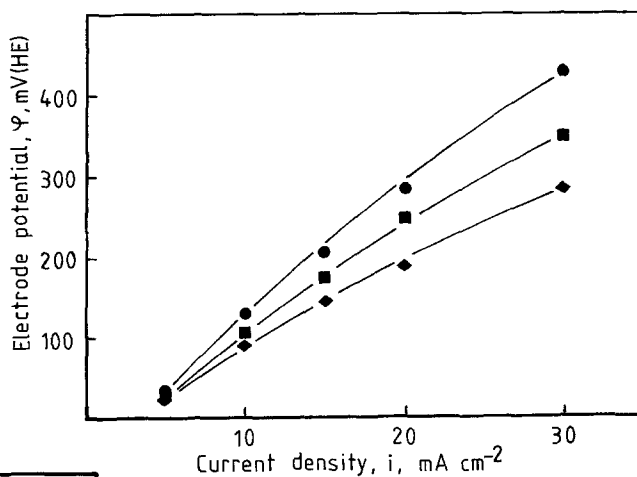


Fig. 9. Current-potential curves of a WC-3 GDE (full lines) and a Tainton anode (dotted lines) at different sulphuric acid concentrations: ○, $0.2 \text{ g l}^{-1} \text{ H}_2\text{SO}_4$; ●, $40 \text{ g l}^{-1} \text{ H}_2\text{SO}_4$; ■, $80 \text{ g l}^{-1} \text{ H}_2\text{SO}_4$; ◆, $160 \text{ g l}^{-1} \text{ H}_2\text{SO}_4$, with $54.3 \text{ g l}^{-1} \text{ Zn}^{2+}$; temperature = 40°C ; $P_{\text{H}_2} = 40\text{--}50 \text{ mm Hg}$.

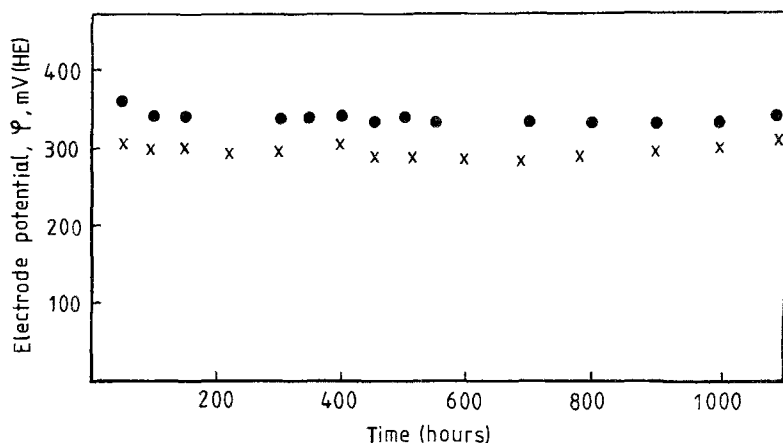


Fig. 10. Long-term tests of a WC-2 GDE. ●, $S = 2 \text{ cm}^2$; ×, $S = 10 \text{ cm}^2$; $160 \text{ g l}^{-1} \text{ H}_2\text{SO}_4$; $54.3 \text{ g l}^{-1} \text{ Zn}^{2+}$; 40°C ; $i = 36 \text{ mA cm}^{-2}$.

change of the sulphuric acid concentration in the electrolyte changes the polarization of the tungsten carbide anodes. In this case, the best results were obtained with a sulphuric acid concentration of 160 g l^{-1} . This figure also includes, for comparison, the performance of Tainton anodes.

The double-layered electrodes with optimum current density–potential characteristics, containing tungsten carbide synthesized from tungsten oxide, were put to long-term test at $I = 36 \text{ mA cm}^{-2}$ (Fig. 10). These electrodes operated for 1000 h without a noticeable decrease of activity. After each 240-h period, X-ray diffractograms of the electrodes were taken. There

was no evidence of catalyst corrosion during this period of operation.

Figs 11 and 12 show the cell voltage at different zinc ion and sulphuric acid concentrations in the electrolytic bath. The best results were obtained at 160 g l^{-1} sulphuric acid and 54.3 g l^{-1} zinc ions. The difference between the voltage curves of the cells with Tainton and tungsten carbide–GDE anodes demonstrates the different polarizations of oxygen and hydrogen electrodes. As can be seen, this difference is

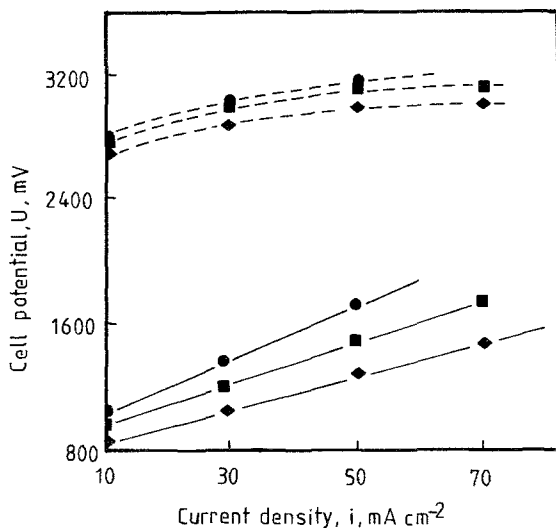


Fig. 11. Potential versus current density characteristics of an electrolysis cell with a WC-3 GDE (full lines) and a Tainton anode (dotted lines) at different zinc ion concentrations: ●, $120 \text{ g l}^{-1} \text{ Zn}^{2+}$; ■, $90 \text{ g l}^{-1} \text{ Zn}^{2+}$; ◆, $54.3 \text{ g l}^{-1} \text{ Zn}^{2+}$, with $160 \text{ g l}^{-1} \text{ H}_2\text{SO}_4$; temperature = 40°C ; $P_{\text{H}_2} = 40\text{--}50 \text{ mm Hg}$.

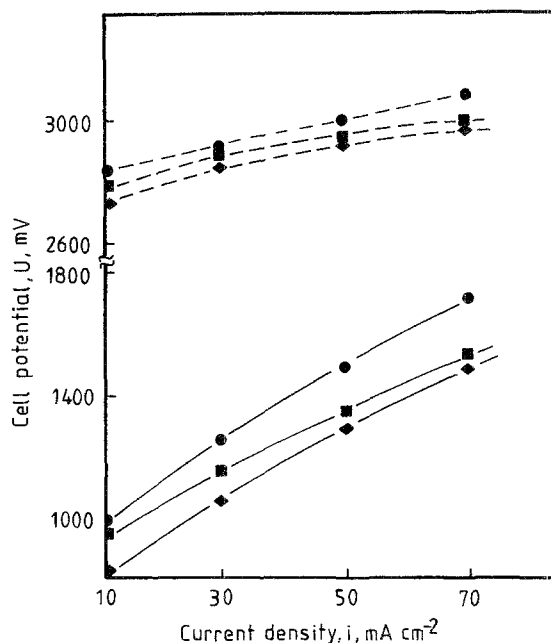


Fig. 12. Potential versus current density characteristics of an electrolysis cell with a WC-3 GDE (full lines) and a Tainton anode (dotted lines) at different sulphuric acid concentrations: ●, $40 \text{ g l}^{-1} \text{ H}_2\text{SO}_4$; ■, $80 \text{ g l}^{-1} \text{ H}_2\text{SO}_4$; ◆, $160 \text{ g l}^{-1} \text{ H}_2\text{SO}_4$, with $54.3 \text{ g l}^{-1} \text{ Zn}^{2+}$; temperature = 40°C ; $P_{\text{H}_2} = 40\text{--}50 \text{ mm Hg}$.

always higher than the 1.23 V difference theoretically expected from the standard potentials, and amounts to 1.50–1.85 V since polarization of the tungsten carbide hydrogen GDE is much lower than that of the Tainton oxygen electrode. With a current efficiency of about 90% the electric energy consumption can be reduced from 3100–3300 to 1500–1800 kWh per ton of zinc.

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