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ZINC ELECTROWINNING WITH GAS DIFFUSION ANODES: STATE OF THE ART AND FUTURE DEVELOPMENTS

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Abstract — Hydrogen gas diffusion anodes (HGDA) have been considered previously as alternatives to oxygen-evolving lead alloy anodes in metal electrowinning. Despite their higher capital costs, the substantial decrease in electrowinning production costs potentially offered by HGDAs is causing renewed interest in their industrial use. This paper reviews the more recent applications of hydrogen gas diffusion anodes in industrial electrowinning. Using data from the literature, a simplified economical assessment is presented for a zinc electrowinning tank house implementing hydrogen gas diffusion anodes; optimum operating current densities of about 3 kA m^{-2} are predicted.

Résumé — Des anodes de diffusion de gaz hydrogène (ADGH) ont été considérées antérieurement comme remplacement des anodes d'alliage au plomb produisant de l'oxygène pour l'extraction électrolytique du métal. En dépit de leur coût plus élevé en capital, la diminution substantielle des coûts de production par extraction électrolytique offerte potentiellement par les ADGHs suscite un intérêt renouvelé pour leur utilisation industrielle. Cet article révise les applications les plus récentes d'anodes à diffusion de gaz hydrogène dans l'extraction électrolytique industrielle. En utilisant les données de la littérature, on présente une évaluation économique simplifiée d'un ensemble de cellules d'extraction électrolytique de zinc ayant mis en application les anodes à diffusion de gaz hydrogène; on prédit des densités de courant d'opération optimum d'environ 3 kA m^{-2}.

INTRODUCTION

Conventional electrowinning of zinc from aqueous electrolytes involves water decomposition at oxidized lead alloy anodes. This results in the evolution of oxygen, an intrinsically slow and therefore energy intensive process. Increasing environmental and economic pressures have and will continue to heighten pressures to decrease energy consumptions in such processes. In aqueous electrowinning primarily, this involves decreasing the anode thermodynamic and overpotential contributions to the cell voltage, hence decreasing specific electrical energy consumptions [1].

One approach to this objective in conventional zinc electrowinning is to replace the oxygen evolving lead alloy anodes with hydrogen oxidation to hydrogen ions in gas diffusion anodes[1]. These multiphase structures have been developed primarily for use in fuel cells and the engineering is even more challenging in electrowinning processes.

At present, hydrogen is produced from a variety of feedstocks (natural gas, coal, biomass and water) by using several technologies (reforming, gasification and electrolysis). However, steam reforming of methane is the most common and least expensive method for hydrogen production accounting for about 48% of world hydrogen production with a unit cost of $.60 – 1.14 (U.S.)kg^{-1} [2]. Hydrogen is also the main byproduct of the chlor-alkali industry. In 1999, the world chlorine use was estimated as 42.8 million tonnes [3], resulting in co-production of 1.2 million tonnes of hydrogen [4]. In principle, this corresponds to *ca.* 35

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[1] The standard Gibbs free energy change values, at 25 °C, for the reactions $ZnSO_4 + H_2O = Zn + \frac{1}{2}O_2 + H_2SO_4$ and $ZnSO_4 + H_2 = Zn + H_2SO_4$ are, respectively, $\Delta G° = 384.159$ kJ/ξ ($E° = 1.99$ V) and $\Delta G° = 147.018$ kJ/ξ ($E° = 0.76$ V).

million tonnes per annum of zinc that could be produced at a current efficiency of 0.9 with hydrogen diffusion anodes; zinc production in 1999 was 7.7 million tonnes [3,5]. For example, a zinc plant producing 10^5 tonnes per annum would require 4×10^7 Nm^3 hydrogen (see below). Hydrogen can be transported by pipelines or by truck, rail or ship in liquefied or in gaseous form. The primary methods for hydrogen storage are compressed gas, liquefied hydrogen, metal hydride and carbon based systems. Transportation and storage costs must be accounted for in the economical assessment of electrowinning processes using gas diffusion anodes. A survey of the economics of hydrogen technologies can be found in Reference 2.

STRUCTURE OF GAS DIFFUSION ANODES

The structure of a gas diffusion electrode is shown schematically in Figure 1 [6]. Gaseous hydrogen permeates through the porous structure of the electrode, dissolves into the electrolyte and diffuses to the electrocatalyst, when it is oxidised to protons. As the performance of hydrogen diffusion anodes depends mainly on the dissolution of the hydrogen gas in the electrolyte and its diffusion towards reaction sites, higher hydrogen solubilities and higher transport rates improve the performance of such anodes.

In order to attain high current densities, porous electrodes must satisfy some basic requirements:

1) Catalysts must have high activities.

2) Pores must neither fill with electrolyte because of capillary action ("flooding", "percolation") nor must the gas pressure become so large that electrolyte is completely expelled from the pores.

3) The shorter the distance from gas dissolution sites to catalyst sites, the higher the gas feed rate and consequently, the higher the sustainable current densities.

The main parts of a gas diffusion electrode are the gas supplying layer and the reaction layer. The current collector is imbedded in the structure so as to be in electrical contact with the electrocatalyst region. To prevent electrolyte percolation, the side of the electrode exposed to the electrolyte is made hydrophobic by a layer that constitutes a barrier for the electrolyte; electrode performance also depends on the characteristics of that hydrophobic layer.

Furuya [27] performed zinc electrowinning experiments using gas diffusion electrodes prepared by hot pressing together the reaction and the gas supplying layers at 600 kg cm^{-2} and 380 °C. The reaction layer was made from hydrophobic carbon black (45%), hydrophilic carbon black (35%), PTFE (20%) and a platinum catalyst (0.56 mg cm^{-2}). The gas supply layer was made from hydrophobic carbon black (70%) and PTFE (30%). The thickness of the reaction and gas supplying layers was 0.1 mm and 0.5 mm, respectively. A similar structure was fabricated by Nikolova *et al.* [7,8] for their experiments on zinc and nickel electrowinning using a gas supplying layer coupled with an active layer containing PTFE coated carbon black and tungsten
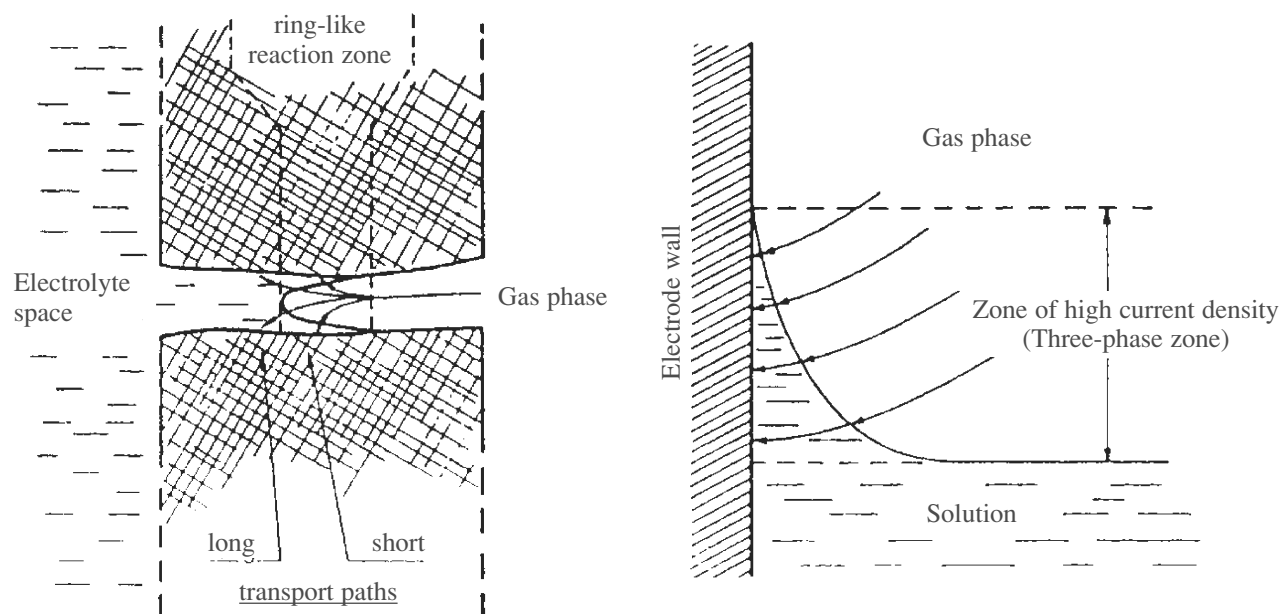

Fig. 1. Single pore of a gas diffusion electrode (left) and three-phase zone in a gas diffusion electrode (right). Reproduced by permission of Wiley-VCH.

carbide as a catalyst. In both cases, the gas was supplied to the diffusion electrode from a gas chamber structure in an arrangement similar to that shown schematically in Figure 2.
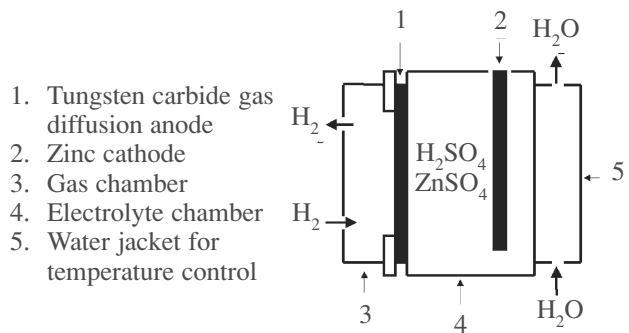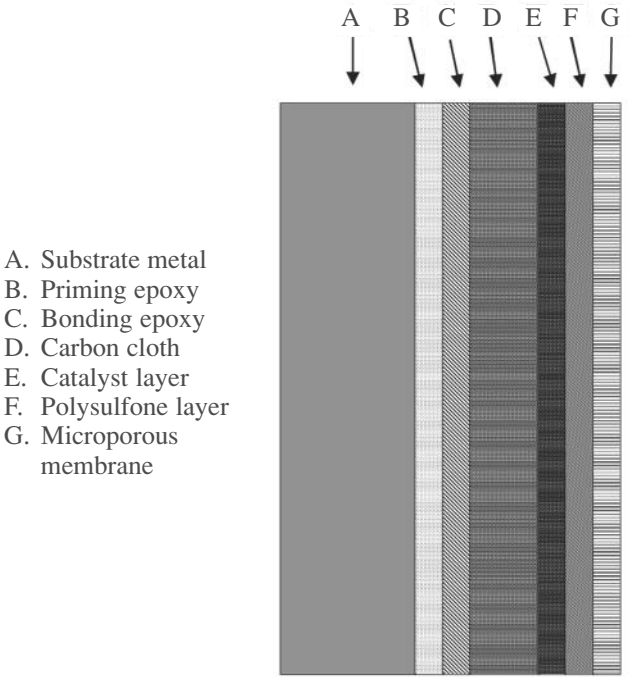
in preference to tungsten carbide because of their higher catalytic activity. Hydrogen was supplied to the carbon cloth layer through grooves in the substrate (Figure 4). Such anodes are no longer produced by E-TEK.

1. Tungsten carbide gas diffusion anode
2. Zinc cathode
3. Gas chamber
4. Electrolyte chamber
5. Water jacket for temperature control

Fig. 2.   Schematic arrangement of the cell with a gas diffusion electrode [7,8].

Instead of using a separate gas plenum structure, it is actually more convenient to flow hydrogen over a large electrode surface area through a carbon cloth electrode substrate. Figure 3 represents the laminated structure of an anode used in metal electrowinning by Allen *et al*. [9,11]. A thick catalysed carbon cloth coated with an anti-percolation layer is epoxy bonded to a solid substrate material. Lead was generally used as metal substrate in sulfuric acid electrolytes and platinum group metals catalysts were used

LABORATORY, PILOT AND INDUSTRIAL TESTS

Prototech (U.S.A.) investigated the influence of zinc sulfate and sulfuric acid concentrations, and of current density on cell voltage and energy consumption for zinc elec-

A. Substrate metal
B. Priming epoxy
C. Bonding epoxy
D. Carbon cloth
E. Catalyst layer
F. Polysulfone layer
G. Microporous membrane

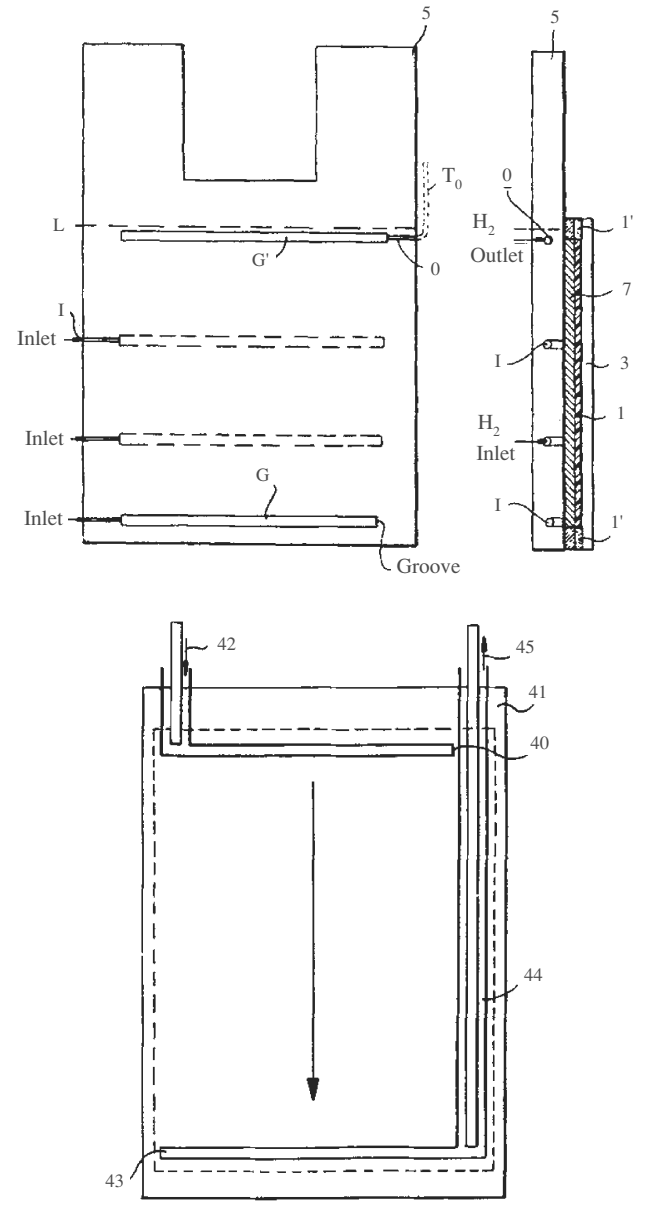Fig. 3.   The sequence of laminations applied to the anode substrate (E-TEK).

Fig. 4.   Examples of gas distribution in plenum-free gas diffusion electrodes (Allen, Metallgesellschaft AG).

trowinning using hydrogen diffusion anodes which resulted in a patented process [12]. For 100 g dm^{-3} H$_2$SO$_4$ at 55 °C and a current density of 388 A m^{-2}, increasing the Zn(II) concentration in the range 0 - 100 g dm^{-3} increased current efficiencies from 0 to 96%, whereas above 100 - 120 g Zn(II) dm^{-3}, current efficiencies were 95 - 96% (Figure 5). Cell voltages increased with increasing Zn(II) concentration due to sulfate ions forming hydrogen sulfate ions, decreasing proton activities and so increasing electrolyte resistances. Under such experimental conditions, specific electrical energy consumptions were insensitive to Zn(II) concentration in the range of 50 - 120 g dm^{-3}.
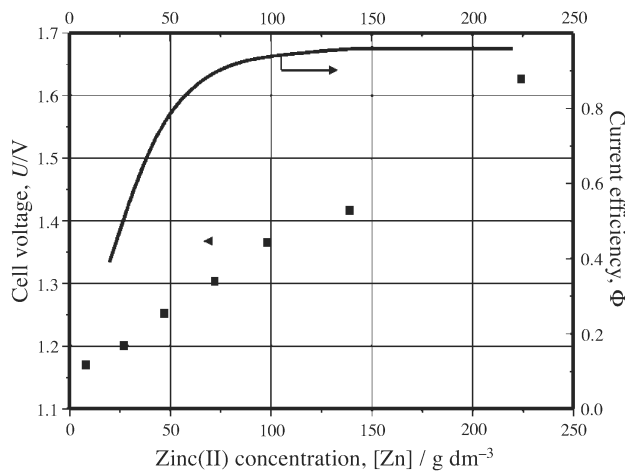

Fig. 5. Effect of Zn(II) concentration on reactor performance at 100 g H$_2$SO$_4$ dm^{-3} and 388 A m^{-2} (Prototech).

Figure 6 shows that increasing H$_2$SO$_4$ concentrations decreased current efficiencies because of the enhancement of the hydrogen evolution reaction rate. However, their effect in decreasing the electrolyte resistance, decreasing ohmic potential drops and cell voltages led to a corresponding decrease in specific electrical energy consumption which exhibited a minimum at *ca.* 100 g H$_2$SO$_4$ dm^{-3}. Increasing current densities to 776 A m^{-2} then 967 A m^{-2} produced minima at *ca.* 125 g H$_2$SO$_4$ dm^{-3} and 150 g H$_2$SO$_4$ dm^{-3}, respectively. The hydrogen diffusion anodes performed well in even more concentrated sulfuric acid solutions with the optimum concentration being about 4 molar [13]. Moreover, the decrease in current efficiencies with increasing acid concentration is less of a drawback than in conventional zinc electrowinning, as hydrogen evolved at the cathode is reusable at the anode. The value of the cathodically by-product hydrogen, $e_{H_2,by\text{-}prod.}$' (US$ kg^{-1}) is given by:

$$e_{H_2,by-prod.} = \left(\frac{2F}{M_{H_2}}\right)\frac{Ue}{3600} = 26.8Ue \qquad (1)$$

This value must be compared with the cost of hydrogen produced, for example, by steam reforming of methane. If the electrolyte contains 300 g H$_2$SO$_4$ dm^{-3}, according to Figure 6, the current efficiency of the zinc deposition process at 388 A m^{-2} is 60 % and the cell voltage is *ca.* 1.1 V when the energy requirement for Zn electrowinning is still low (Figure 7). By comparison, hydrogen production in conventional water electrolysis cells requires cell voltages of 1.8 - 2 V [14,15].

Table I lists contributions to the cell voltage (*U*) for zinc electrowinning, conventionally and using a hydrogen gas diffusion anode at 450 A m^{-2} and pH = 1 [16]. Assuming a current efficiency (Φ) of 0.90 for both processes, then Equation 2 gives

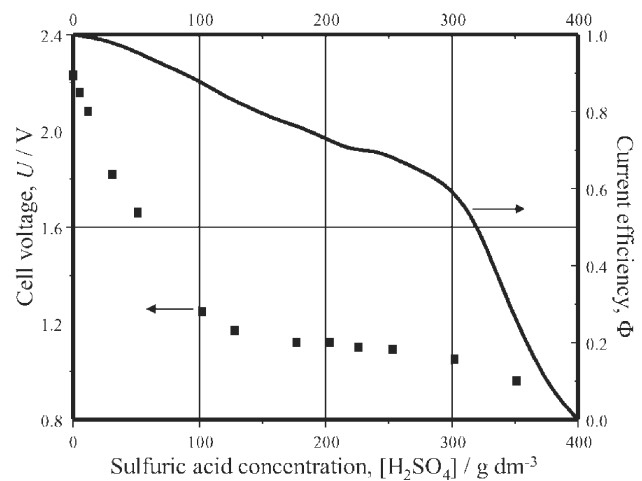$$\text{SEEC/kWh}\left(\text{tonne } Zn\right)^{-1} = \frac{2F|U|}{3.6M_{Zn}\Phi} \qquad (2)$$

Fig. 6. Effect of H$_2$SO$_4$ concentration on reactor performance at 50 g Zn(II) dm^{-3} and 388 A m^{-2} (Prototech).
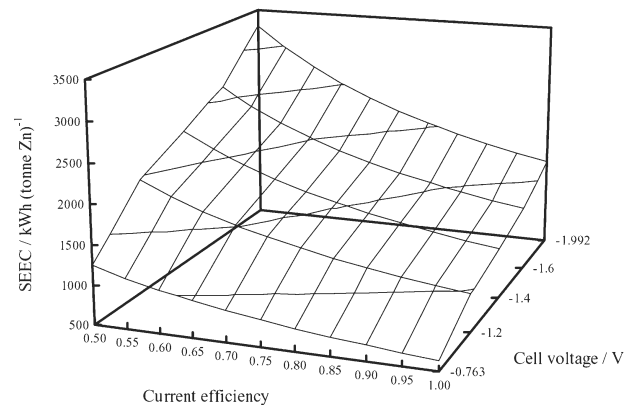

Fig. 7. Effect of current efficiency and cell voltage on specific electrical energy consumption.

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