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High speed zinc electrowinning system using a hydrogen anode and a rotating aluminium disc cathode

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The performance of a novel high speed zinc electrowinning system using a hydrogen anode and an aluminium rotating disc cathode (1 m diam.) was investigated under various experimental conditions. This new type of zinc electrowinning system was continuously operated at a current density of $70\,\mathrm{A\,dm^{-2}}$, which is twelve times higher than that usually employed. Current efficiency is 90% at $50\,\mathrm{A\,dm^{-2}}$ in an electrolyte containing $60\,\mathrm{g\,dm^{-3}}$ Zn + $160\,\mathrm{g\,dm^{-3}}$ H_2SO_4, the zinc purity being at least 99.999%. The energy usage of the system is 1650 kWh per tonne of zinc, $380\,\mathrm{m^3}$ of H_2 gas being required.

1. Introduction

A hydrogen gas diffusion electrode with a platinum catalyst is known to serve as a high performance anode at which hydrogen oxidation takes place at high rate with a low overvoltage in sulfuric acid [1]. Therefore, we have attempted to develop a new type of zinc electrowinning cell [2, 3] using a hydrogen anode.

The conventional zinc electrowinning system is usually operated at a low current density ($5.7\,\mathrm{A\,dm^{-2}}$) and requires a high cell voltage (3.6 V) because of the high anode polarization and the ohmic drop in the electrolyte [4]. The anode is made from a lead–silver (usually 0.5% Ag) alloy. Winand *et al.* have carried out zinc electrowinning at high current densities using a channel cell with conventional anodes in a bath containing $80\,\mathrm{g\,dm^{-3}}$ Zn and $135\,\mathrm{g\,dm^{-3}}$ H_2SO_4, at 50 °C employing an electrolyte velocity of $4\,\mathrm{m\,s^{-1}}$ [5]. Current efficiency was 90% over a wide range of current densities for thicknesses of zinc deposit between 100 and 200 μm.

In an attempt to develop a new zinc electrowinning system with much higher performance we replaced the oxygen evolution reaction at the anode by electrochemical oxidation of hydrogen gas using a hydrogen anode and at the same time reduced the gap between the anode and cathode significantly and were able to operate the cell at a current density of $100\,\mathrm{A\,dm^{-2}}$, which was eighteen times higher than that usually employed in the conventional zinc electrowinning system. Current efficiency was 86% at $50\,\mathrm{A\,dm^{-2}}$ in an electrolyte containing $60\,\mathrm{g\,dm^{-3}}$ Zn and $270\,\mathrm{g\,dm^{-3}}$ H_2SO_4, the purity of the zinc deposit being at least 99.999%. The energy usage of the system was 1400 kWh per tonne of zinc with consumption of $380\,\mathrm{m^3}$ H_2 gas [3]. Furthermore, we found it easy to strip the zinc deposit off an aluminium plate cathode. Therefore, we have investigated the feasibility of a high speed zinc electrowinning system utilizing a small rotating aluminium drum or disc cathode [6]. Ruhr Zinc has also carried out a pilot scale project on zinc electrolysis using a hydrogen diffusion anode [7].

The aim of the present investigation is to study further the feasibility of a high performance zinc electrowinning system using a hydrogen anode and an aluminium rotating disc cathode of 1 m diameter under various operational conditions.

2. Experimental details

2.1. *Apparatus*

The experimental cell system is shown in Fig. 1. An aluminium rotating disc cathode (100 cm diam. × 0.5 cm thickness) of 99.8% purity was driven by a motor via a shaft (10 cm length × 3 cm diam.). The active area of the gas-diffusion electrode loaded with $0.56\,\mathrm{mg\,cm^{-2}}$ Pt was $4\,\mathrm{dm^2}$ ($100\,\mathrm{cm^2} \times 4$). The distance between the cathode and the anode was about 4 mm. The electrolyte was fed to the cell through a metering pump, while hydrogen gas was supplied to the anode through a mass flow controller from a hydrogen cylinder at a rate of 20% in excess of that required by the reaction stoichiometry.

2.2. *Preparation of gas-diffusion electrode*

A gas-diffusion electrode of conventional structure with a reaction and a gas supplying layers was prepared as follows. The reaction layer was made from hydrophobic carbon black (45%), hydrophilic carbon black (35%), PTFE (20%) and a platinum catalyst ($0.56\,\mathrm{mg\,cm^{-2}}$). The gas supply layer was made from hydrophobic carbon black (70%) and PTFE (30%). A gas diffusion electrode with an active area of $100\,\mathrm{cm^2}$ loaded with $0.56\,\mathrm{mg\,cm^{-2}}$ Pt was finally prepared by hot-pressing the reaction and the gas

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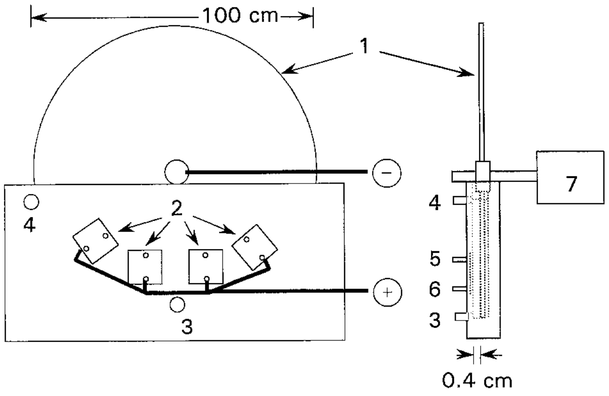

Fig. 1. Configuration of the test cell system: (1) Rotating aluminium disc cathode: 1 m diam.; (2) hydrogen anodes, active area: $100\,cm^2 \times 4$; (3) electrolyte inlet; (4) electrolyte outlet; (5) hydrogen inlet; (6) hydrogen outlet; (7) electric motor.

supplying layers at $600\,kg\,cm^{-2}$ and 380 °C. The thickness of the reaction and gas supplying layers were 0.1 mm and 0.5 mm, respectively [8].

2.3. *Experimental conditions*

The electrolytes were prepared from reagent grade $ZnSO_4 \cdot 7H_2O$ and H_2SO_4 (Kanto Chemical Industry) and 18 MΩ water (Organo Puric Model-R) to contain $60\,g\,dm^{-3}$ Zn and 120 to $250\,g\,dm^{-3}$ H_2SO_4. They were purified using Zn powder (Mitsui Mining and Smelting Co.). The electrolyte was fed to the cell at a constant flow rate proportional to the current density. The content of zinc in the electrolyte was reduced to about $10\,g\,dm^{-3}$ or less after electrolysis, which was usually conducted at room temperature, $21 \pm 4\,°C$. The electrolysis current density at the Al cathode was varied between 15 and $70\,A\,dm^{-2}$, the total cell current of 60 to 280 A being supplied by a Kikusui Electronics Co. Pak6. The rate of disc rotation was varied from 0.5 to 2.0 revolutions per hour.

3. Results and discussion

3.1. *Operation of the system*

Figure 2 shows the typical time dependence of the cell voltage. Figure 3 shows the rotating aluminium disc cathode with the zinc deposit after 6 h operation. It is clear that the zinc deposit can be obtained as a continuous strip (about 13 cm wide and about 0.17 mm thickness) on the rotating aluminium disc.

The thickness of the zinc deposit depends both on the current density and the rotation speed of the aluminium disc cathode. In order to maintain the constant thickness of the zinc deposit during electrowinning the rotation speed should be increased in proportion to the increase in current density. For the present system, the proportionality constant for maintaining constant film thickness of about 0.17 mm was 0.3 cathode rotation per $10\,A\,dm^{-2}$ (i.e. 1.5 rotation at $50\,A\,dm^{-2}$). We have found that the surface morphology and the current efficiency were not affected by the current density between 10 and $70\,A\,dm^{-2}$ as shown in Fig. 5; this is equivalent to between 0.3 and 2.1 in terms of cathode rotation per hour.

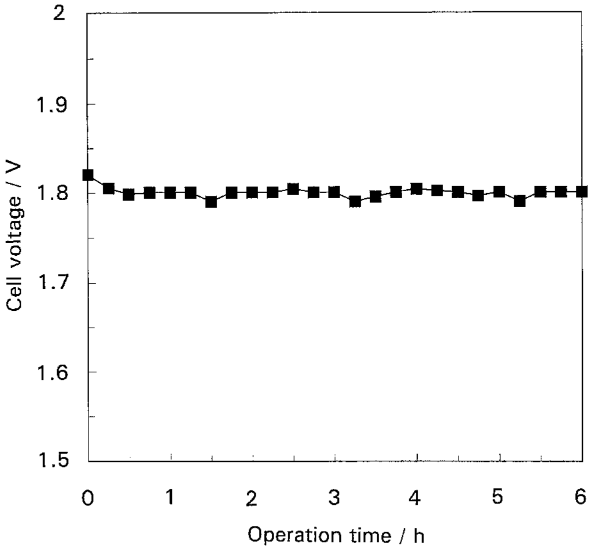

Fig. 2. The time dependence of the cell voltage at $50\,A\,cm^{-2}$. Electrolyte: $60\,g\,dm^{-3}$ Zn + $160\,g\,dm^{-3}$ H_2SO_4. The rotation rate of aluminium disc is 1.25 revolutions per hour.

The relation between the current density and the cell voltage is shown in Fig. 4 for electrolyte containing $60\,g\,dm^{-3}$ Zn and $160\,g\,dm^{-3}$ H_2SO_4. This graph shows that a substantial improvement in the performance of zinc electrowinning cells is achieved by utilizing a gas-diffusion type anode. The cell voltage of 1.8 V at $50\,A\,dm^{-2}$ using a rotating aluminium disc cathode is as low as that for a small stationary aluminium cathode of $50\,cm^2$ [3]. This low cell voltage is remarkable when it is compared with a typical cell voltage of 3.5 V at a much lower current density of $5.7\,A\,dm^{-2}$ in a conventional zinc-winning cell with a lead anode.

Figure 5 shows the dependence of the current efficiency on current density in an electrolyte containing $60\,g\,dm^{-3}$ Zn and $160\,g\,dm^{-3}$ H_2SO_4. The current efficiency is as high as 90% even at $70\,A\,dm^{-2}$, while a comparable efficiency can only be obtained at a much lower current density of $5.7\,A\,dm^{-2}$ in a conventional zinc electrowinning cell.

Fig. 3. Photograph of the aluminium disc cathode and zinc deposit coil.

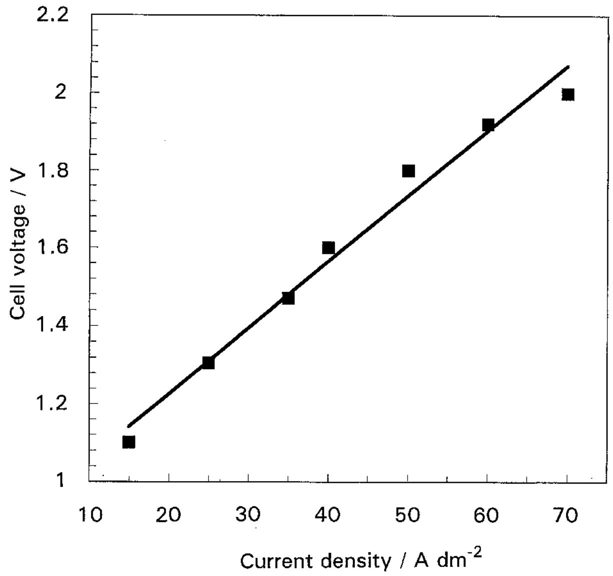

Fig. 4. Effect of current density on cell voltage. Electrolyte: 60 g dm^{-3} Zn + 160 g dm^{-3} H_2SO_4.

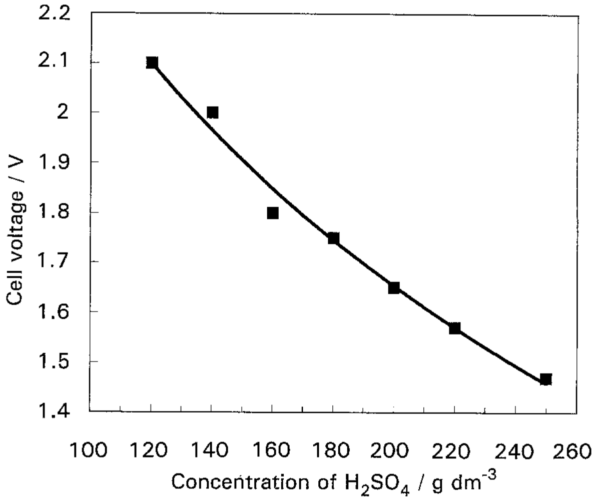

Fig. 6. Effect of sulfuric acid concentration on cell voltage at 50 A dm^{-2}. Electrolyte: 60 g dm^{-3} Zn + X g dm^{-3} H_2SO_4.

3.2. *Effect of sulfuric acid concentration*

The relation between the cell voltage and the sulfuric acid concentration of the electrolyte is shown in Fig. 6 at 50 A dm^{-2} (200 A). The cell voltage decreases with increasing sulfuric acid concentration. For an electrolyte containing 60 g dm^{-3} Zn and 250 g dm^{-3} H_2SO_4, the cell voltage is only 1.47 V.

Figure 7 shows the dependence of the current efficiency on the sulfuric acid concentration at 50 A dm^{-2} (200 A in terms of total electrolysis current). The current efficiency is almost 90% below a sulfuric acid concentration of about 160 g dm^{-3} H_2SO_4, above which, however, the efficiency decreases sharply with increasing sulfuric acid concentration and drops to 84% in electrolyte containing 60 g dm^{-3} Zn and 250 g dm^{-3} H_2SO_4. The sharp reduction in the current efficiency suggests that this is closely related to increasing dissolution of the aluminium disc at higher sulfuric acid concentrations.

Figure 8 shows the calculated electrical energy requirement of the system as a function of the acid concentration at 50 A dm^{-2}, the total current being 200 A. The energy requirement decreases almost linearly with increasing concentration of sulfuric acid and is as low as 1650 kW per tonne in the electrolyte containing 60 g dm^{-3} Zn and 160 g dm^{-3} H_2SO_4.

3.3. *Zinc deposit purity*

The surface morphology of the zinc deposit was investigated at several current densities, but no dendritic growth was observed until the current density exceeded 70 A dm^{-2}. In addition, it was easy to strip the zinc deposit off the rotating aluminium disk cathode.

Table 1 shows the analysis for various impurities in the zinc deposit obtained at various current densities. The purity of the zinc deposit at higher current

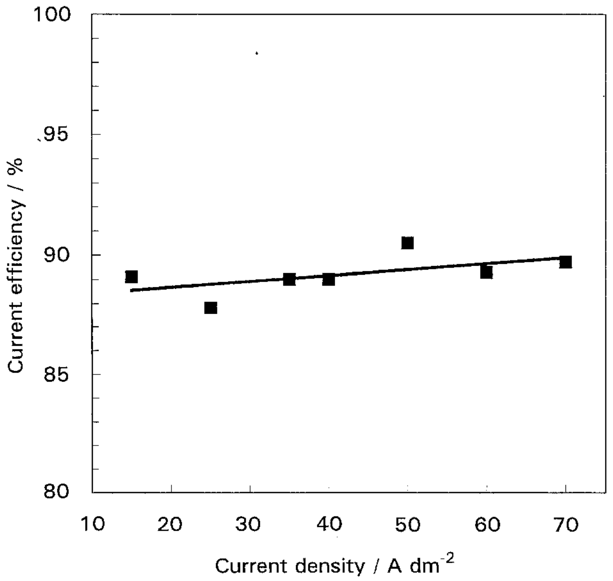

Fig. 5. Effect of current density on current efficiency. Electrolyte: 60 g dm^{-3} Zn + 160g dm^{-3} H_2SO_4.

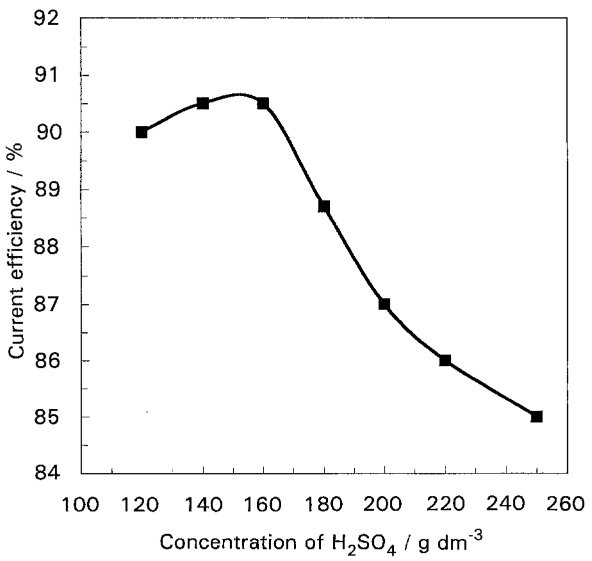

Fig. 7. Dependence of current efficiency on the concentration of sulfuric acid.

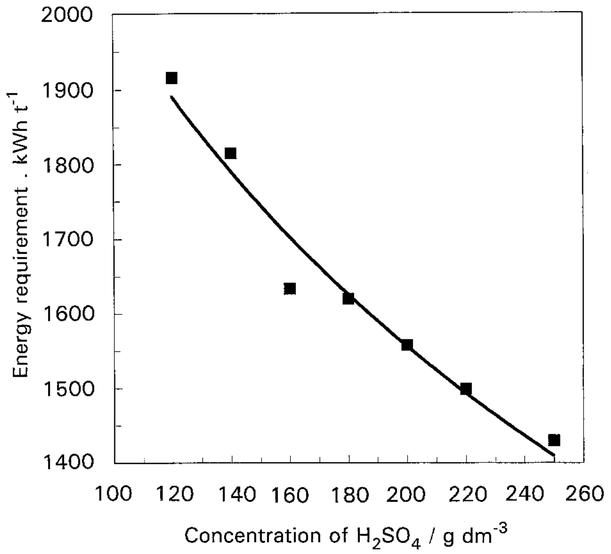

Fig. 8. Requirement of electrical energy at 50 A dm^{-2} for various concentrations of sulfuric acid in an electrolyte containing Zn = 60 g dm^{-3}.

densities is better than that at lower current densities and reaches over 99.999% at 70 A dm^{-2}, the lead content being only 2 ppm. The marked reduction in lead content is a result of replacement of the conventional lead anode by the hydrogen anode.

3.4. *Life of the hydrogen anode*

The performance of the system was assessed based on experiments which typically ran for six hours. It is necessary, however, to test the long term durability of the hydrogen anode under actual zinc electrowinning conditions for practical applications of the new system. The long term durability of the hydrogen gas diffusion electrode was tested by operating the new system for 200 h continuously under various conditions. The long term operation was completed successfully without any noticeable decrease in activity of the hydrogen anode; the overpotential of the hydrogen oxidation reaction at the gas diffusion electrode did not change during this experiment.

One aspect related to the long term durability of the new system is the possible formation of thick nodular or dendritic zinc deposits on the aluminium disc cathode which could lead to short-circuiting of the anode and the cathode, the separation between which is only 4 mm. It was found, however, that this is not the case for the new system; the zinc deposit formed on the aluminium disc cathode was uniform and no nodular or dendritic phase formation was observed.

Table 1. Impurities in the zinc deposits at various current densities

Current density A dm^{-2}	*Impurity*/ppm					*Zinc purity*
	Cu	*Cd*	*Fe*	*Al*	*Pb*	
Conventional cell						
5	3	3	5	1<	24	99.995%
This work						
15	1.00	0.12	0.13	23	2.0	99.9972%
25	2.30	0.14	0.08	96	2.0	99.9989%
35	0.94	0.08	0.07	4	3.0	99.9991%
50	0.70	0.10	0.11	3	2.0	99.9993%
60	0.56	0.08	0.17	2	2.0	99.9994%
70	0.42	0.08	0.18	2	2.0	99.9994%

Table 2. Operating characteristics and requirements of energy in zinc electrowinning

	Operating energy requirement	
	Using a Pb anode	*Using a hydrogen anode*
Current density	580 A m^{-2}	5000 A m^{-2}
Current efficiency	90%	90%
Cell voltage	3.6 V	1.8 V
Electrical energy requirement	3300 kWh tonne^{-1}	1640 kWh tonne^{-1}
Hydrogen requirement	–	380 m^3 tonne^{-1}

Another aspect during prolonged electrolysis is the possible deactivation of the hydrogen anode by impurities in the electrolyte. The effect of both organic and inorganic impurities could be more serious for the hydrogen anode than for the conventional oxygen evolving anode, due to the much lower working potential of the former anode associated with the hydrogen ionization. In other words, the oxygen evolving anode would suffer much less from both inorganic (metallic) and organic impurities because of its high working potentials at which most of the impurities would be anodically oxidized. Purification of the electrolyte could become a serious problem in long term electrolysis when using a hydrogen anode, in view of its low working potential.

4. Conclusion

A comparison of the operating characteristics is made in Table 2 between a conventional zinc-winning cell and the cell with a hydrogen anode using a gas diffusion electrode. Using a hydrogen anode, zinc electrowinning can be conducted at current densities about ten times higher than those employed in the conventional zinc electrowinning cell at almost the same current efficiency. The cell voltage and the electrical energy requirement are reduced by more than 50% and the purity of the zinc deposit is better than that obtained by the conventional method.

The economic balance will, of course, depend on the cost of hydrogen and the electrical energy thus saved by the replacement of the anode. One way of improving the cost performance of the new type zinc electrowinning cell will be by better utilization of hydrogen obtained from chlor-alkali electrolysis.

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