High speed zinc electrowinning using a hydrogen gas-diffusion electrode

N. FURUYA, N. MINEO

Department of Applied Chemistry, Faculty of Engineering, Yamanashi University, 4-3-11 Takeda, Kofu, 400, Japan

The feasibility of a high speed zinc electrowinning cell using a Pt catalyzed hydrogen gas-diffusion electrode as an anode is investigated. This new type of zinc-winning cell is operated at a current density of $1.0\,A\,cm^{-2}$, which is 20 times higher than usually employed in conventional methods. Current efficiency is 86% at $0.5\,A\,cm^{-2}$ in an electrolyte containing $60\,g\,l^{-1}$ Zn $+ 270\,g\,l^{-1}$ H_2SO_4, the zinc purity being at least 99.999%. The energy usage of the system is 1400 kWh and $380\,m^3$ H_2 gas per ton of zinc.

1. Introduction

Gas-diffusion electrodes with platinum catalyst have been developed for hydrogen-oxygen fuel cells. The hydrogen oxidation reaction takes place at high rate with low overvoltage on such gas-diffusion electrodes [1]. Therefore, we have attempted to develop a new type of zinc electrowinning cell [2] by using such an electrode as the anode.

Electrowinning is the most important method by which zinc is produced; currently some 90% of the world's total zinc production is by this method, and this percentage is still increasing. This process uses a low current density ($57\,mA\,cm^{-2}$) and a high cell voltage (3.6 V), because the anode polarization and the ohmic drop in the electrolyte are large [3]. The anode is made from a lead-silver alloy which usually contains 0.5% Ag.

Oxygen evolution on the lead electrode in zinc electrowinning cells is accompanied by high overpotential even at a current density of $57\,mA\,cm^{-2}$, as currently used in industrial cells. But oxygen evolved in the cell is an unnecessary product. When the lead-silver anode is replaced by a gas diffusion electrode and hydrogen is fed to the gas diffusion electrode, hydrogen oxidation instead of oxygen evolution occurs at the anode. This reduces the cell voltage by more than 1.23 V and enables use of higher current densities. Taking into account the lower overvoltage at a hydrogen gas-diffusion electrode compared to that at a lead-silver anode, it may be expected that the overall cell voltage with a hydrogen gas-diffusion electrode will be about 1.8 V lower. Actually, the decrease of the anode potential depends on the performance of the gas-diffusion electrode [4]. Furthermore the gap between the electrodes (9–7.5 cm) in conventional cells is too wide. Consequently in hydrogen gas-diffusion electrode-type anodes, gas bubbles are not formed on the electrode, and so the ohmic drop is not increased at higher current densities.

The aim of the present investigation, therefore, is to study further the feasibility of the low overvoltage and high speed zinc-electrowinning system utilizing such a hydrogen gas-diffusion electrode as anode.

2. Experimental details

Figure 1 shows the test cell used for this work; the distance between the cathode and the anode varied between 1.5 to 4 mm. The active area of the gas-diffusion electrode loaded with $0.56\,mg\,cm^{-2}$ Pt was $50\,cm^2$. The cathode material was either an aluminium or a zinc plate.

The electrolyte solutions used for electrolysis were prepared from $ZnSO_4 \cdot 7H_2O$ and H_2SO_4 of GR grade. The electrolyte solution, containing $60\,g\,l^{-1}$ Zn and $270\,g\,l^{-1}$ H_2SO_4 was purified by Zn powder. The electrolyte was supplied to the cell at a constant flow rate, for which the current density has been found to be proportional. The content of zinc in the electrolyte decreased to about $10\,g\,l^{-1}$ or less after electrolysis, which was usually conducted at 27° C.

The gas-diffusion electrode consisted of a reaction layer and a gas supplying layer [1]. 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 supplying layer was made from hydrophobic carbon black (70%) and PTFE (30%). The gas diffusion electrode was made by hot-pressing at $600\,kg\,cm^{-2}$ and 380° C. The thicknesses of the reaction layer and the gas supplying layer was 0.1 mm and 0.5 mm, respectively [5].

3. Results and discussion

3.1. Performance of the gas-diffusion electrode

Figure 2 shows the typical performance of a gas-diffusion electrode for hydrogen oxidation in various
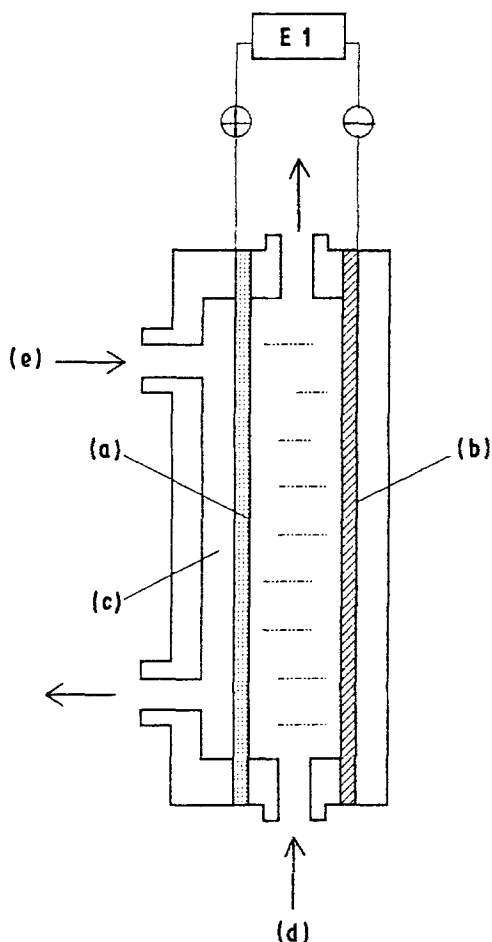
Fig. 1. Configuration of test cell: (a) Hydrogen gas-diffusion electrode, (b) aluminium or zinc cathodes, (c) gas chamber, (d) electrolyte inlet, (e) hydrogen inlet. Active area = 50 cm².

electrolyte solutions. A current density of 1000 mA cm⁻², which is 20 times higher than that used in industrial zinc-winning cells, was obtained at an overpotential of only 75–120 mV. Such an overpotential is negligibly small when compared with that needed in industrial zinc-winning cells using a Pb anode. Thus, replacing the Pb anode by the gas-diffusion electrode, leads to an attainable reduction of
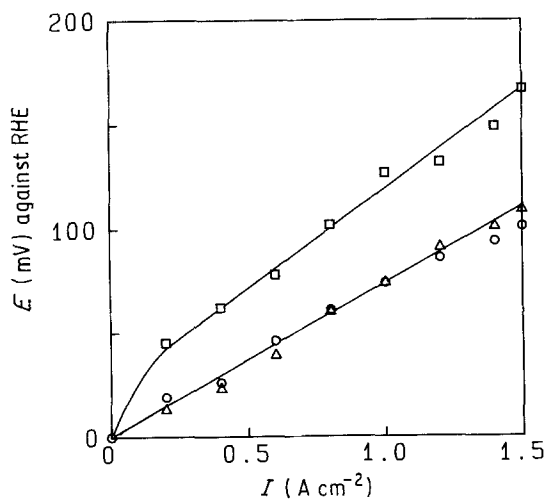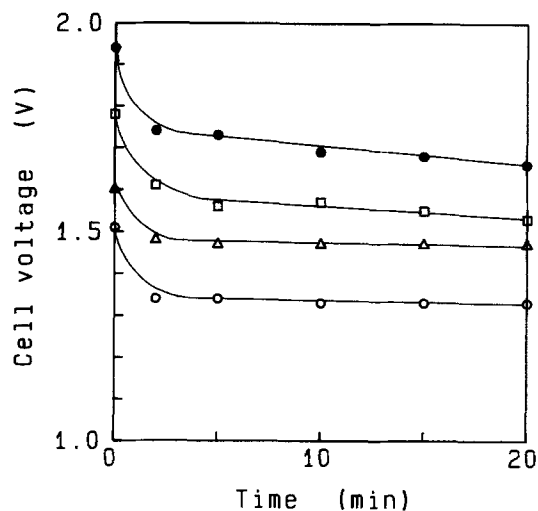

Fig. 3. Effect of time and current density on cell voltage. Initial gap = 3 mm. Temperature = 25° C. Electrolyte: $60 \text{g} \text{l}^{-1}$ Zn + $270 \text{g} \text{l}^{-1}$ H₂SO₄. Current density (A cm⁻²): (O) 0.4, (△) 0.5, (□) 0.6, (●) 0.7. Cathode: Zn.

the cell voltage of about 1.8 V (that is, 1.2 V + 0.6 V) whilst the cell voltage may be only 0.93 V, regardless of any ohmic potential drops.

3.2. Deposit on the zinc plate

Figure 3 shows variation of the cell voltage with time using a zinc cathode. The initial gap between the anode and cathode is 3 mm. The cell voltage decreases with time when the current density is high, because the gap between the electrodes becomes smaller as the deposition of zinc proceeds on the cathode. The relation between the current density and the initial cell voltage is depicted in Fig. 4. This result shows that a substantial improvement in performance of zinc-winning cells is achieved by utilizing a gas-diffusion type anode. The cell voltage is 1.5 V at 0.5 A cm⁻², using a zinc cathode. This compares with a cell voltage of 3.5 V at the much lower current density of 0.057 A cm⁻² in a conventional zinc-winning cell with a lead anode.
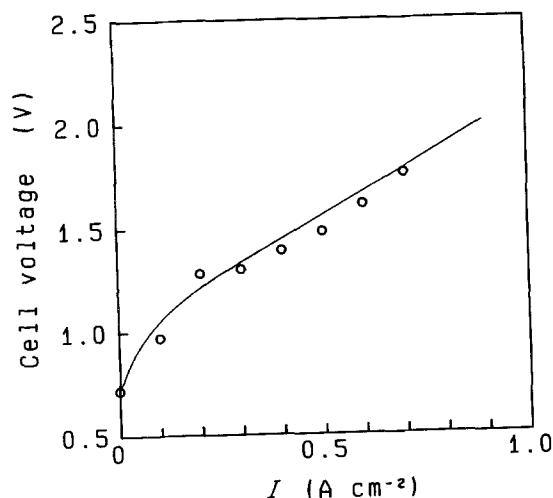

Fig. 2. Anodic performance of the hydrogen diffusion electrode loaded 0.56 mg cm⁻² Pt catalyst. Temperature = 25° C. Electrolyte: (□) $60 \text{g} \text{l}^{-1}$ Zn + $100 \text{g} \text{l}^{-1}$ H₂SO₄; (△) $60 \text{g} \text{l}^{-1}$ Zn + $180 \text{g} \text{l}^{-1}$ H₂SO₄; (O) $60 \text{g} \text{l}^{-1}$ Zn + $270 \text{g} \text{l}^{-1}$ H₂SO₄.

Fig. 4. Effect of current density on cell voltage. Inital gap: 3 mm. Temperature: 25° C. Electrolyte: $60 \text{g} \text{l}^{-1}$ Zn + $270 \text{g} \text{l}^{-1}$ H₂SO₄. Cathode: Zn.
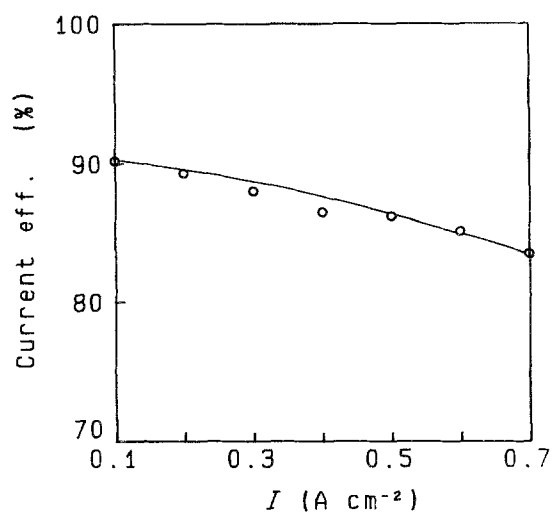
Fig. 5. Effect of current density on current efficiency. Inital gap: 3 mm. Temperature: 25°C. Electrolyte: $60 g l^{-1}$ Zn + $270 g l^{-1}$ H_2SO_4. Cathode: Zn.

Fig. 7. Effect of current density on cell voltage. Inital gap: 3 mm. Temperature: 28°C. Electrolyte: $60 g l^{-1}$ Zn + $270 g l^{-1}$ H_2SO_4. Cathode: Al.

Figure 5 shows the dependence of the current efficiency on current density for the zinc electro-winning cell using a Zn cathode. The current efficiency for zinc deposition is as high as 86% at $0.5 A cm^{-2}$. This compared with an efficiency of 90% at the lower current density of $0.057 A cm^{-2}$ in a conventional cell.

3.3. Deposit on the aluminium plate

The variation of the cell voltage with time for an aluminium cathode, with a 3 mm initial gap between the anode and cathode, is shown in Fig. 6. As with the cell containing zinc cathode, the cell voltage decreases with time as the deposition of zinc proceeds and the inter-electrode distance is reduced at high current density.

The relation between the current density and the cell voltage is depicted in Fig. 7. This shows performance characteristic of the zinc electrowinning cell using an aluminium cathode at the inter-electrode distance of
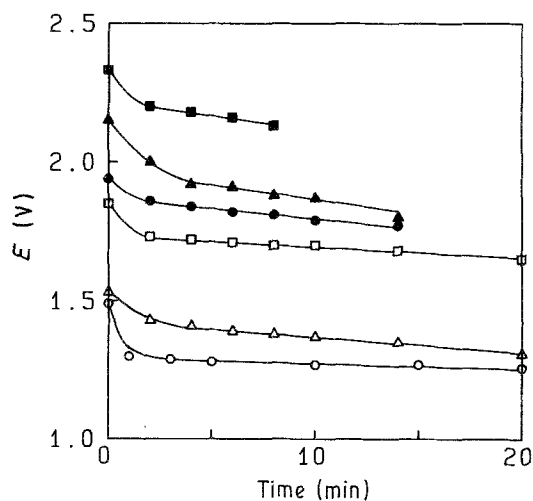
2.5 mm. The cell voltage is 1.4 V at $0.5 A cm^{-2}$ and 2.2 V at $1.0 A cm^{-2}$ respectively.

The current efficiency for zinc deposition on the aluminium cathode is shown in Fig. 8 as a function of current density. The current efficiency is as high as 75% at $1.0 A cm^{-2}$ and 86% at $0.5 A cm^{-2}$ respectively. This compares with an efficiency of 90% at the current density of $0.057 A cm^{-2}$ in a conventional zinc-winning cell.

The perfomance of the cell using an aluminium cathode is almost the same as a cell with a zinc cathode.

3.4. Nature of the zinc deposit

The surface morphology of the zinc deposit was investigated at several current densities, but no dendritic growth was observed until the thickness of the deposit exceeded ca. 0.5 mm at $1.0 A cm^{-2}$. In addition, it was easy to strip the zinc deposit layer off the aluminium cathode. Therefore, it would be better to produce zinc

Fig. 6. Effect of current density on cell voltage. Inital gap: 3 mm. Temperature: 28°C. Electrolyte: $60 g l^{-1}$ Zn + $270 g l^{-1}$ H_2SO_4. Current density: ($A cm^{-2}$): (O) 0.4, (△) 0.5, (□) 0.6, (●) 0.7, (▲) 0.8, (■) 1.0. Cathode: Al.
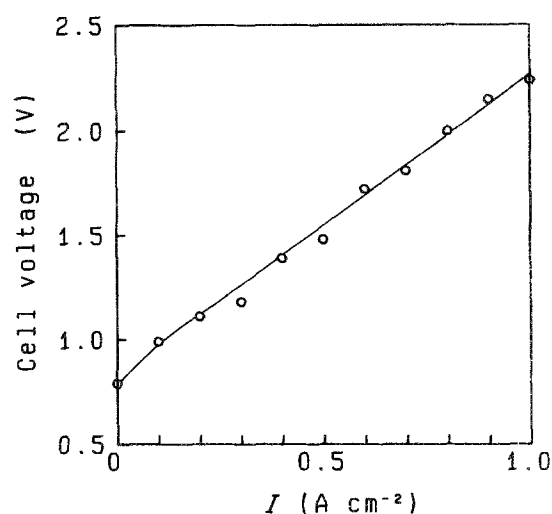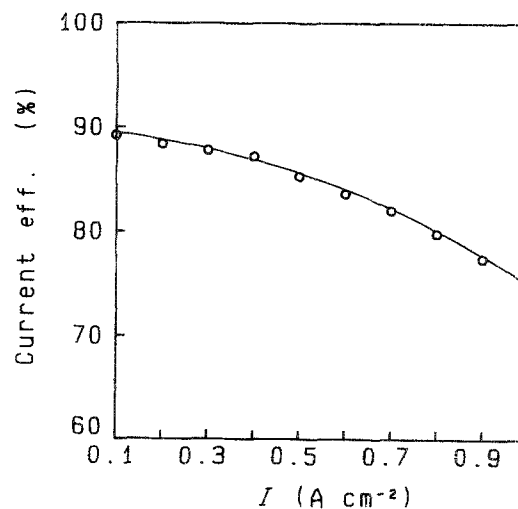

Fig. 8. Effect of current density on current efficiency. Inital gap: 3 mm. Temperature: 28°C. Electrolyte: $60 g l^{-1}$ Zn + $270 g l^{-1}$ H_2SO_4. Cathode: Al.
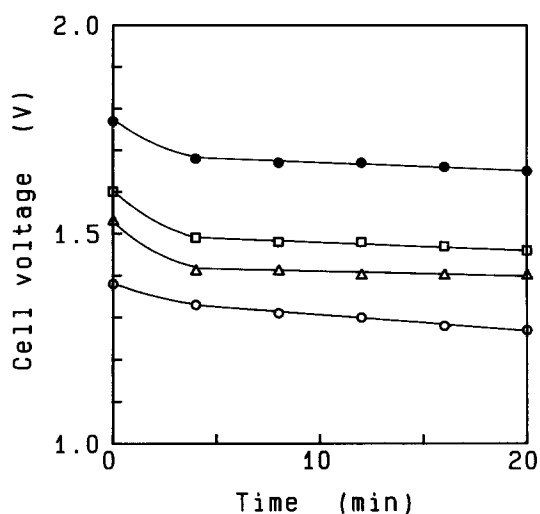
Fig. 9. Effect of initial gap on cell voltage. Temperature: 27°C. Electrolyte: $60\,g\,l^{-1}$ Zn + $270\,g\,l^{-1}$ H_2SO_4. Initial gap (mm): (●) 4.0, (□) 3.0, (△) 2.5, (○) 2.0. Current density: $0.5\,A\,cm^{-2}$. Cathode: Al.

continuously on a rotating drum or a disc cathode in order to achieve a high production rate [6].

3.5. Purity of the zinc deposit

Another merit of this new type zinc-winning cell is the high purity of the deposited zinc. This is a result of the replacement of the lead anode, which is the source of the lead impurity in the zinc deposit by the gas-diffusion electrode. The various impurities in the deposit are given in Table 1. The lead content is only 3 ppm, and the purity of the zinc was over 99.999% at $0.5\,A\,cm^{-2}$.

3.6. Electrolytic potential drop

Figure 9 shows the effect of the inital gap between the cathode and the anode on the cell voltage. The cell voltage is reduced by 0.2 V when the gap decreases by 1.0 mm at $0.5\,A\,cm^{-2}$. The gap can be made smaller than that of industrial cells. The heat evolved was calculated based on the overpotential data and ohmic drop in both cases.

The heat evolved in the cell using a gas-diffusion electrode is only a quarter of that in industrial cells. This is again a favourable condition for zinc-winning

Table 1. Impurities in the zinc deposit

	Impurity (ppm)					
	Al	Cd	Cu	Pb	Fe	Pt
This work (0.5 A cm⁻²)	1 <	1 <	1 <	1 <	0	0
Conventional cell (0.05 A cm⁻²)	1 <	3	3	24	5	0

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

	Using a Pb anode	Using a hydrogen gas diffusion electrode
Current density	$570\,A\,m^{-2}$	$5000\,A\,m^{-2}$
Current efficiency	90%	86%
Cell voltage	3.5 V	1.4 V
Electrical energy requirement	$3300\,kWh\,tonne^{-1}$	$1400\,kWh\,tonne^{-1}$
Hydrogen gas requirement	–	$380\,m^3\,tonne^{-1}$

because the current efficiency of the zinc deposition is higher at lower temperatures.

3.7. Life of the hydrogen gas-diffusion electrode

The hydrogen gas-diffusion electrode was operated for 100 hours at $0.5\,A\,cm^{-2}$ without any noticeable decrease of activity: the overpotential of the hydrogen oxidation on the gas-diffusion electrode did not change even beyond this duration, as shown in Fig. 2.

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 gas-diffusiuon electrode. Utilizing a hydrogen gas-diffusion electrode, zinc-electrowinning can be conducted at current densities about ten times higher than those employed in the conventional zinc-electrowinning cell and at almost the same current efficiency. The cell voltage and the electrical requirement are reduced by more than 50%. The purity of the zinc is better than that obtained by the conventional method.

The economic balance will, of course, depend on the cost of hydrogen and the electric 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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