Al/Cl$_2$ battery with slightly acidic NaCl electrolyte. II. Ti–Ti/Ru oxide chlorine cathodes

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A new version of the Al/Cl$_2$ battery previously described was investigated. Instead of a graphite cylinder, a porous titanium plate was used as a chlorine electrode (cathode). The electrolyte used was a moderately acidic aqueous NaCl solution of pH 2 containing small amounts of In^{3+} and Hg^{2+} as additives. The cell had an open-circuit voltage of 2.6 V and delivered a maximum power of 19.8 W at 1.1 V with a Faradaic efficiency of 69%. The power density was 280 mW cm^{-2}. A module consisting of 4 submodules connected in series, where each submodule contained 4 double-unit cells connected in parallel, had an open-circuit voltage of 10.6 V, a maximum power of 200 W and an energy density of 110 Wh l^{-1}.

1. Introduction

In a previous paper [1] the cell performance of an Al/Cl$_2$ cell was described and found to have some promising features. This cell was operating with cylindrical electrodes. Unfortunately, the battery system had a low maximum power output; the porous graphite chlorine cathode was the limiting element in the cell. The unit individual cells of the battery showed some inhomogeneity in the graphite electrodes. Since the current obtained was limited by the weakest element of the battery, this inhomogeneity affected the performance of the module considerably. Experiments also showed that parasitic H$_2$ evolution was increasing as a function of operation time.

Because of the interesting energy storage aspects of aluminum such as its high energy content (31 MJ kg^{-1}), its abundance, its modest price and its easy transport and storability, the Al/Cl$_2$ cell remains a promising system and therefore a new cell arrangement was tested [2, 3]. In order to improve the cell performance, new chlorine cathodes made from stabilized porous titanium plates were used.

In this paper some performance data of a single unit Al/Cl$_2$ cell with plane-parallel electrode arrangement are described. The parasitic reactions (H$_2$ evolution and the direct corrosion by the dissolved chlorine) were measured.

Finally, using such unit cells, a 200 W Al/Cl$_2$ battery was built, and the voltage, current and power characteristics as well as the long-time performance of this battery were investigated.

2. Experimental details

2.1. Materials

2.1.1. Cathodes. The porous Ti electrodes (BBC) were 1.5 mm thick. They were protected and activated by painting their surfaces with a solution consisting of 1 g RuCl$_3$, 3 ml Ti(BuO)$_4$, 0.4 ml 35% HCl and 20 ml butanol [4]. After this treatment, the electrodes were dried for 15 min at 150° C. Then, a mixed oxide of Ti–Ru was formed on the surface of the electrodes by heating to 420° C for 15 min. After this treatment, the electrodes were washed until the washing water remained clear. Cl$_2$ (> 99.9%, Fluka), RuCl$_3$ (purum, Fluka) and the monomer of tetra-n-butyl ortho-titanate (Ti(BuO)$_4$) (pract., Fluka) were used as received.

2.1.2. Anodes. The Al (99.5%) plates were purchased from Alesa AG. They were 8 mm thick and used as received.

2.1.3. Electrolyte. NaCl (puriss, Siegfried), InCl$_3$ (95%, Fluka) and HgCl$_2$ (puriss, Fluka) were used as received. The electrolyte was a 2 M NaCl solution containing 3 × 10^{-4} M InCl$_3$ + 3 × 10^{-4} M HgCl$_2$ at pH 2 adjusted by addition of HCl. Higher In^{3+} and Hg^{2+} concentrations did not improve the cell performance any more whereas at lower concentrations of these electrolyte additives, the cell performance was not stable and the voltage dropped to the value obtained without additives (OC: 1.9 V).

2.2. Apparatus

The current–potential curves were obtained using an Amel potentiostat Model 555B, and an Amel function generator Model 568 and a Linseis LY1800 X–Y recorder. A saturated calomel reference electrode (SCE) with an agar-filled capillary was introduced between the anode and cathode in order to make potentiostatic measurements. The cell voltage and the corresponding cell current, obtained when different resistors were used as external load, were recorded by an Olivetti PC M24.
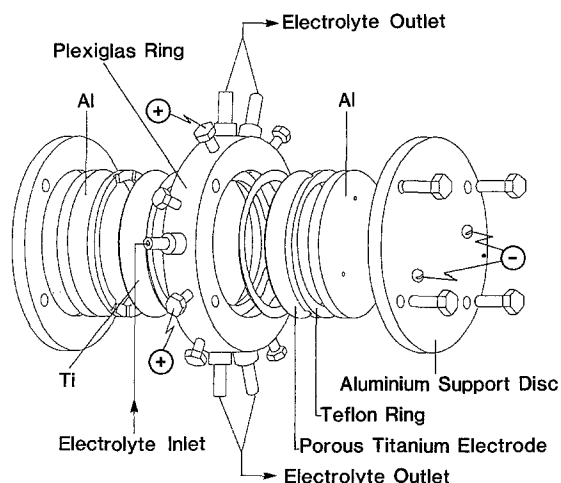
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Fig. 1. AlCl$_2$ double-unit cell with parallel porous titanium plates as chlorine cathodes and two circular Al plates as anodes (ϕ_{ext}: 10.5 cm, ϕ_{activ}: 9.5 cm). Surface area of a single electrode: 70.9 cm^2.

2.3. Cell design

The cell configuration is presented in Fig. 1. Two circular porous titanium cathode plates arranged back to back were inserted vertically in the middle of the polymethyl methacrylate (plexiglas) ring, which served to support all elements of the double-cell unit. Two circular Al electrode plates were placed parallel to the cathodes. The interelectrode distance was adjusted to 2 mm with a Teflon^R ring. The double-unit cell was held together by two external support discs tightened with four screws.

The electric connection of each cathode was ensured by four silver wires (1.5 mm diameter) which were pressed against the periphery of the Ti plate edge by screws. The electric contacts to the Al anodes were made directly at the Al anode plates with two screws penetrating the support disc.

The electrolyte was circulated through the cell by an external peristaltic pump with a flow rate of 8.5 ml cm^{-2} min^{-1}. An electrolyte inlet hole was pierced radially in the middle of the plexiglas ring, in order to feed the electrolyte solution into the gap between the two Ti electrodes. Two outlet holes were made between the cathode and the anode at the top and bottom of
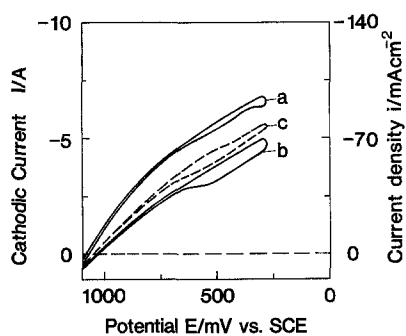

Fig. 2. Current–potential curve of the chlorine electrode described in Fig. 1. Reference electrode: SCE. Auxiliary electrode: Al electrode. Sweep rate: 10 mV s^{-1}. Electrolyte: 2 M NaCl + 3 × 10^{-4} M HgCl$_2$ + 3 × 10^{-4} M InCl$_3$, pH 2. (a) At the beginning (electrolyte volume: 3 l). (b) After 6.5 h operation time at a current of 5 A. (c) After 6.5 h operation time but with fresh electrolyte.
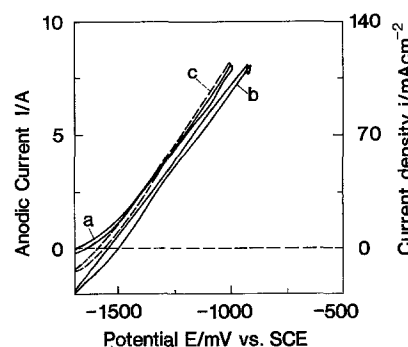

Fig. 3. Current–potential curve of the aluminum electrode depicted in Fig. 1. Reference electrode: SCE. Auxiliary electrode: chlorine electrode (porous titanium plate). Sweep rate: 10 mV s^{-1}. Electrolyte: 2 M NaCl + 3 × 10^{-4} M HgCl$_2$ + 3 × 10^{-4} M InCl$_3$, pH 2. (a) At the beginning (new electrolyte, 3 l). (b) After 6.5 h operation time at 5 A. (c) After 6.5 h operation time but with fresh electrolyte.

the ring to drain off the solution to the 3 l electrolyte reservoir where the electrolyte was continuously saturated with chlorine. The hydrogen produced was separated via a bubble trap and measured as described in the previous paper [1].

The double-unit cell was composed of two cathodes and two anodes each having the same surface area (2 × 70.9 cm^2). Each pair of cathode and anode formed a single-unit cell which could also be operated independently. Figure 1 shows the three-dimensional view of a double-unit cell.

The battery module was composed of 16 double-unit cells. It was divided in four submodules, each of them with four double unit cells. The cells in the submodules were electrically connected in parallel, whereas the submodules were connected in series. This system formed the 200 W Al/Cl$_2$ battery, each submodule having its own electrolyte supply. The total surface area of the cathodes and anodes was 2268 cm^2.

3. Results and discussion

The Al and Cl$_2$ electrodes were electrochemically studied by measuring their potentiostatic current–potential curves (Figs 2 and 3). An aqueous 2 M NaCl solution containing 3 × 10^{-4} M HgCl$_2$ and 3 × 10^{-4} M InCl$_3$ at pH 2 was used as an electrolyte.

Figure 2a shows that the cathodic current of the titaneous chlorine electrode started at +1070 mV (SCE). At an overpotential of 570 mV, a current of 5 A was reached (current density of 70 mA cm^{-2}) with this electrode. Curve b (Fig. 2) was obtained after the cell was used for 6.5 h. At this time, the electrolyte contained 0.15 M Al^{3+}. Replacement of the electrolyte finally yielded curve c.

Figure 3 shows the analogous current–potential curves obtained with the Al electrode. The anodic current of the Al electrode starts at −1650 mV vs SCE and a current of 5 A (current density of 70 mA cm^{-2}) flows at a potential −1200 mV vs SCE. There were only minor changes after 6.5 h (curve b) and after replacing the electrolyte (curve c).
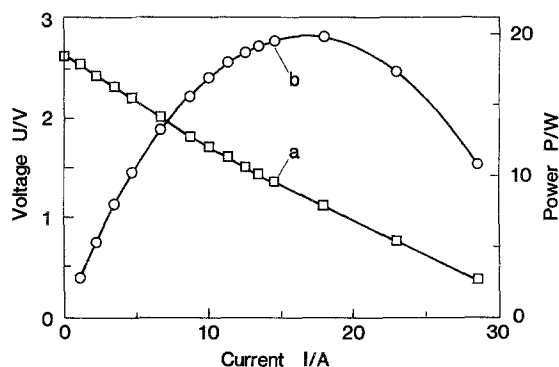
Fig. 4. Voltage (curve a) and power (curve b) each as a function of the current obtained from a single-unit cell (one cathode and one anode). Electrode surface: 70.9 cm² each. Electrolyte: 2 M NaCl + 3 × 10⁻⁴ M HgCl₂ + 3 × 10⁻⁴ M InCl₃, pH 2.

Fig. 6. Voltage and current each as a function of time during the first 20 h for a single-unit cell (half of the double cell depicted in Fig. 1). The arrows indicate when the electrolyte was replaced. Electrolyte: 2 M NaCl + 3 × 10⁻⁴ M HgCl₂ + 3 × 10⁻⁴ M InCl₃, pH 2, electrolyte volume: 1.5 l.

From the current–potential curves (Figs 2a and 3a), we would expect an open-circuit voltage of 2.72 V and 1.7 V at 5 A. Measurements of the voltage and power at the terminals of the two electrodes (one cathode and one anode) using a series of external resistors are shown as functions of current in Fig. 4 (a and b). These values were taken only after the cell voltage and current were invariant. An open-circuit voltage of 2.62 V was measured. The maximum power obtained was 19.8 W, and the cell voltage at maximum power was 1.1 V. This corresponds to a maximum power density of 280 mW cm⁻² and a current density of 255 mA cm⁻². The maximum current density was about 400 mA cm⁻² at 0.4 V. The specific values were obtained in experiments using anodes and cathodes having an area of 70.9 cm² each. From the slope of the current voltage curve 80 mΩ can be estimated as an internal resistance of a single-unit cell.

Figure 5 shows the behavior of the cell voltage and cell current measured over a long period of time (200 h). Constant operating conditions were maintained by renewing the electrolyte every 6.5 h and replacing the Al anodes every 40 h. The voltage and the current were rather stable. The variations were not more than 5%. This indicates that the porous Ti cathode material was stable against Cl₂ corrosion and
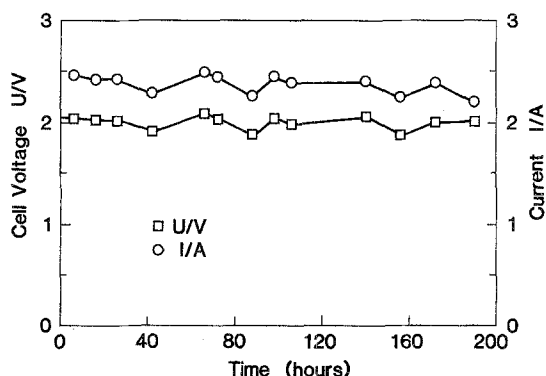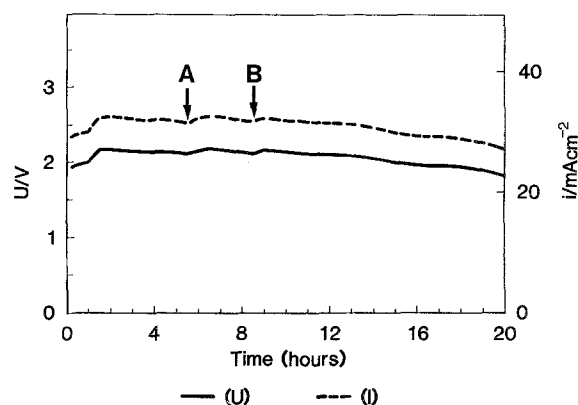
that within 200 h no passivation of the electrode surface occurred (which would be expected if the Ru/Ti oxide protecting layer on the electrode was lost).

The cell voltage and current for a single cell operated over a period of 20 h are plotted in Fig. 6. The arrows (A, B) indicate the time when the electrolyte was renewed. Figure 6 shows that the cell performance was very stable after a short transition period at the beginning. This induction time was probably due to the fact that the Al electrode was not pretreated with the In³⁺- and Hg²⁺-containing electrolyte. After renewal of the solution, a small improvement of the voltage and current was observed. The voltage decay seems mainly due to the increase of Al³⁺ concentration in the solution.

The voltage–time, current–time and power–time curves are reported in Fig. 7. These curves show the behavior of the cell over a period of 18 h without changing the electrolyte. In the beginning the power output was 8.8 W. The power curve indicates a decrease of 14% after 5 h at an average current of about 4 A. After 10 h, the power decreased by 38% to 5.4 W, while the cell was still producing an average current of 3.8 A. After 18 h, the delivered power output was
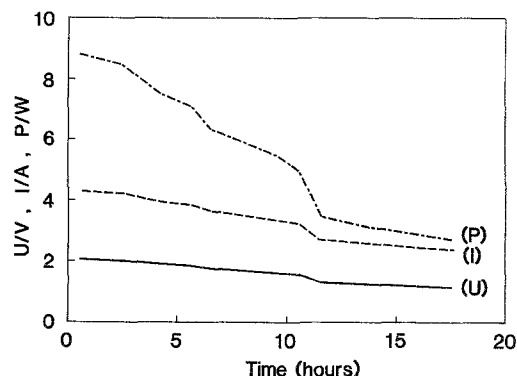

Fig. 5. Long-time behavior of the voltage (□) and current (○) of a single-unit cell. Electrolyte: 2 M NaCl + 3 × 10⁻⁴ M HgCl₂ + 3 × 10⁻⁴ M InCl₃, pH 2, electrolyte volume: 0.8 l, renewed after about 6.5 h; the Al electrodes were replaced every 40 h.

Fig. 7. Voltage, current and power for a single-unit cell as functions of time without electrolyte exchange. Electrolyte: 2 M NaCl + 3 × 10⁻⁴ M HgCl₂ + 3 × 10⁻⁴ M InCl₃, pH 2, electrolyte volume: 0.75 l. Final Al³⁺ concentration: 1.9 M.
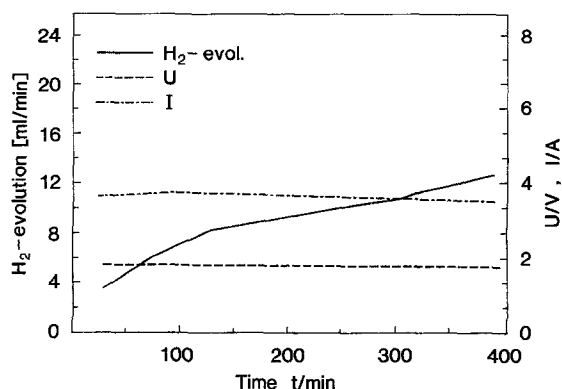
Fig. 8. Voltage, current and rate of the H_2 production as functions of time for a single-unit cell. Total operating time 375 min. Electrolyte 2 M NaCl + 10^{-4} M HgCl$_2$ + 10^{-4} M InCl$_3$, pH 2, electrolyte volume: 1.5 l.

2.9 W. The final electrolyte concentration of Al^{3+} was 1.9 M with pH 2.7 ± 0.2. The electrolyte was a rather viscous fluid at this stage.

Figure 8 shows the rate of parasitic H_2 evolution as well as the cell voltage and the cell current as functions of time. The production of hydrogen was continuously increasing, even though the voltage and the current were constant during this period. The H_2 volume developed in the cell was measured after elimination of Cl$_2$ by washing the gas with a 4 M NaOH aqueous solution as described in Ref. [1].

The fractions of the three processes, i.e. Faradaic current for the aluminium oxidation (I_{elec}), hydrogen evolution (I_{H_2}) and chlorine corrosion (I_{corr}) which account for the weight loss of the aluminum electrode are depicted in Fig. 9. This shows a rather strong dependency on the power output. These values were obtained as average values over a period of 375 min. The Faradaic efficiencies, which correspond to the I_{elec} values, were between 37 and 69%. The energy efficiencies calculated from these data were between 33 and 49%. The chlorine corrosion decreased from 32.7 to 9.2% when the power output was increased from 3.3 to 10.1 W. The H_2 evolution varies somewhat less. The H_2 evolution also varies with time, as can be seen in Fig. 8 therefore every measurement was made with
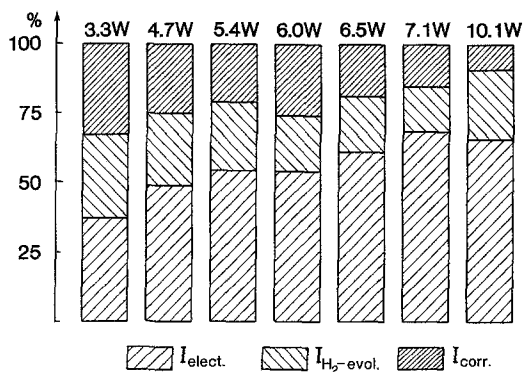

Fig. 9. Relative current densities associated with electrochemical Al oxidation (I_{elec}), hydrogen evolution (I_{H_2-evol}) and chlorine corrosion (I_{corr}). Average values for 375 min. Electrode areas (Al or Cl$_2$): 70.9 cm^2 each. Electrolyte: 2 M NaCl + 3 × 10^{-4} M HgCl$_2$ + 3 × 10^{-4} M InCl$_3$, pH 2, electrolyte volume: 1.5 l.
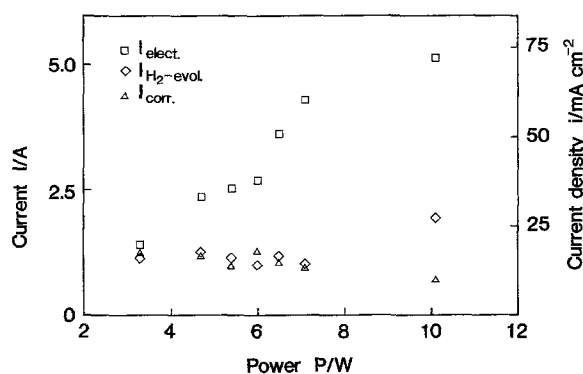

Fig. 10. Absolute current values of the electrochemical Al oxidation (I_{elec}), hydrogen evolution (I_{H_2-evol}) and chlorine corrosion (I_{corr}).

new Al electrodes and with a new electrolyte solution to get comparable results. The volumetric determination of H_2 evolution had an uncertainty of about 10%. The absolute current values of these processes are given in Fig. 10.

The performance of the whole module with 16 double-unit cells had an open-circuit voltage of 10.6 V. The maximum power density obtained with such a system was about 90 mW cm^{-2}. A maximum power of about 200 W was reached at a voltage of 7.7 V, and the current density at this voltage was 48 mA cm^{-2}.

Although the porous chlorine electrode had a rather uniform structure, it was not easy to contact these electrodes. Some differences in contact resistance between different electrodes led to some irregularity in cell performance.

The volume of the whole battery including 60 l of electrolyte, 10 l of chlorine and 2.43 kg of usable Al was approximately 90 l. With such a battery about 10 kWh of electrical energy can be produced. If the module is working at its maximum energy efficiency point (η = 47%) this would lead to an energy density of 110 Wh l^{-1}. As mentioned before the battery can work with a maximum power of 200 W, which corresponds to a power density of 2.2 W l^{-1} when the discharge occurs in 50 h. Three times higher power density can be achieved when the electrolyte and chlorine volume are reduced to 10 and 2 l, respectively. Higher energy densities can be attained when an electrolyte exchange or regeneration is allowed while the battery is in operation.

4. Conclusion

The Al/Cl$_2$ cell with porous stabilized Ti plates had a somewhat better performance than the cell with porous graphite chlorine electrodes described in the previous paper [1]. The performance of a single cell was best when 2 M aqueous NaCl with 3 × 10^{-4} M HgCl$_2$ + 3 × 10^{-4} M InCl$_3$ at pH 2 was used as an electrolyte [5]. The open-circuit voltage was 2.6 V. The power density reached 280 mW cm^{-2} at 1.1 V. The maximum current density was 400 mA cm^{-2}. The current density and power density obtained were about 5 times higher than in the previous cell. Hydrogen

evolution, however, did not cease to increase as a function of operation time. The Ru-stabilized porous Ti electrode was very stable against corrosion and no decrease of performance was observed after 200 h of operation. However, we could not rule out that small amounts of Ru were dissolved by the electrolyte and deposited on the Al electrode catalyzing the H_2 production. The maximum Faradaic efficiency (69%) was obtained at a power density of $90 \, mW \, cm^{-2}$ and a voltage of 1.55 V. The best energy efficiency was 49%. The power also depended on the Al^{3+} concentration in the electrolyte. It decreased by 30% when the Al^{3+} concentration rose to 1 M. At an $AlCl_3$ concentration of 1.9 M the power output was still one-third of its original value.

The power delivered by a battery composed of four submodules with four double cells reached 200 W at 7.7 V. This corresponded to a power density of $48 \, mW \, cm^{-2}$. Improvements of the battery performance would be possible especially if the contact to the chlorine electrodes could be improved.

From the point of view of energy density per volume, the system is interesting. Although it was not optimized for this purpose, energy density of $110 \, Wh \, l^{-1}$ could easily be achieved. It can be increased considerably if the electrolyte is exchanged or regenerated while the battery is in operation (the energy density of the battery was calculated including 60 l of electrolyte and 10 l of chlorine). The power density, however, was only $2.2 \, W \, l^{-1}$. Higher power densities can be achieved at the expense of operating time using smaller electrolyte and chlorine volumes.

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