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Citation	北海道大學工學部研究報告, 162, 255-263
Issue Date	1993-01-29
Doc URL	https://hdl.handle.net/2115/42333
Type	departmental bulletin paper
File Information	162_255-264.pdf

Development of Graphite Cathodes for an Aluminum-Chlorine Fuel Cell in High Temperature Chloride Melts

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(Received September 18, 1992)

Abstract

An aluminum-chlorine fuel cell for manufacturing aluminum chloride was proposed as one process of an electrochemical cycle for the production of high-purity aluminum from aluminum scraps. To develop cathodes for the fuel cell, several graphite electrodes with many holes of the same size were tested by changing the hole sizes and numbers, and the performance for the reduction reaction of chlorine was estimated in terms of the discharge characteristics of the cell in a mixture of $MgCl_2$ 25 mol%-NaCl 75 mol% at 750°C. The voltage drops due to the resistance of the reduction reaction decrease with the decrease in the size of the holes, but in small holes such as those 2 mm in diameter hardly all holes worked equally, showing the difficulty of enlarging the reaction zone. To overcome this disadvantage of drilled electrodes, grooved electrodes were developed and an output current of 4 A at an output voltage of 1.5 V was attained using electrodes with a diameter of 68 mm.

1. INTRODUCTION

Manufacturing aluminum with a purity over 99.999% from aluminum scraps is significant from the view-point of saving natural resources and energy. For this production, three stepwise processes should be considered. The processes are described in the flow chart in Fig. 1 : (1) a process for manufacturing aluminum chloride by chlorination of aluminum scraps, (2) a process for refining crude aluminum chloride, and (3) a process for electrowinning high-purity aluminum from the purified aluminum chloride. If, as the first process, an aluminum-chlorine fuel cell is constructed to produce aluminum chloride from aluminum scraps, much electric energy can be produced in contrast to the usual direct chlorination of aluminum, and by applying this energy to step (3) a very advantageous electrochemical cycle for high-purity aluminum production can be constructed in a molten salt system.

In this cycle, (2) and (3) have been investigated in our laboratory for over a decade and most of the problems in these processes have been solved.[1-5] The fuel cell is composed of a chlorine/graphite electrode as the cathode and aluminum scraps as the anode ; chlorine is reduced to chloride ions on the cathode and aluminum is oxidized to aluminum ions on the anode. The chlorine gas can be supplied from step (3), the aluminum electrowinning process, and the electric power generated in the fuel cell, about 1.5 V, can be allotted for the input
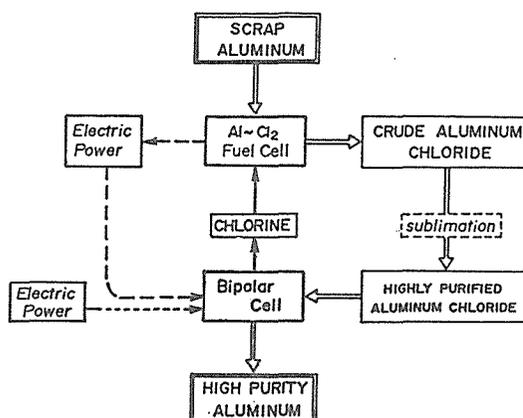
Fig. 1 Flow chart for production of high-purity aluminum from aluminum scraps.

power of the electrolysis process, about 2.5 V. In the fuel cell, the reduction reaction of chlorine gas occurs around a three-phase boundary layer where chlorine gas, fused salts and the graphite electrode coexist. The performance of the cell greatly depends on the cathode characteristics, especially on those of the three-phase boundary layer. The present work is concerned with the development of the cathodes of the fuel cell. Several graphite electrodes with many holes of the same size were tested by changing the hole sizes and numbers. Several grooved electrodes with different reaction-zone areas were also investigated and the results were compared with those from the drilled electrodes.

2. EXPERIMENTAL

The experimental apparatus is schematically described in Fig. 2. A transparent quartz tube with an inner diameter of 95 mm and a length of 500 mm was used as a reaction cell.
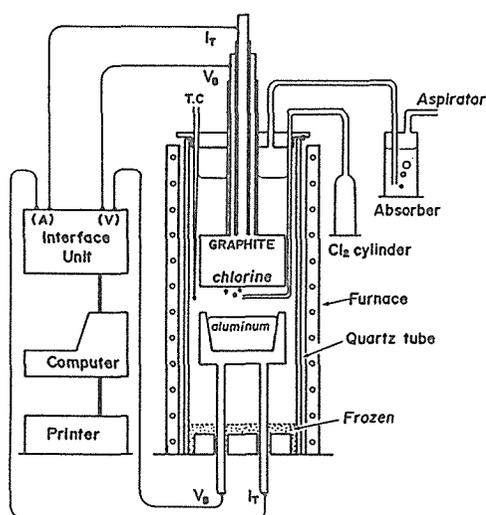

Fig. 2 Schematic diagram of experimental apparatus.

The bottom of the tube was stopped up with frozen salts to contain fused salts as a test electrolyte. In the center part of the cell, a graphite electrode as a cathode and a pure aluminum pool in a graphite crucible as an anode were set facing each other. Chlorine gas in a cylinder was led through a pyrolytic carbon tube or a quartz tube to the bottom of the cathode electrode. The anode was prepared from tips of pure aluminum metal which were preliminarily melted down and solidified in a graphite crucible with a diameter of 50 mm.

A mixture of $MgCl_2$ 25 mol% - NaCl 75 mol% was employed as a supporting electrolyte. First, in order to remove impurities contained in the melts, the mixture was pre-electrolyzed at 30 A for 2 hours in the presence of aluminum chloride. Next, electrolysis was carried out and the current-voltage curves were measured to estimate the resistance of the melts. Then the output characteristics of the fuel cell were determined as voltage-current relations by short-circuiting both electrodes with seven kinds of resistances mounted in an outer circuit. The circuit was connected with two graphite leads from the top of the chlorine electrode and with two graphite leads from the bottom of the aluminum electrode ; one was for measurement of output voltage and the other for output current at both electrodes. The experimental temperature was 750°C.
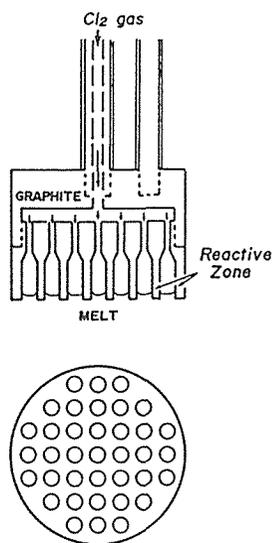

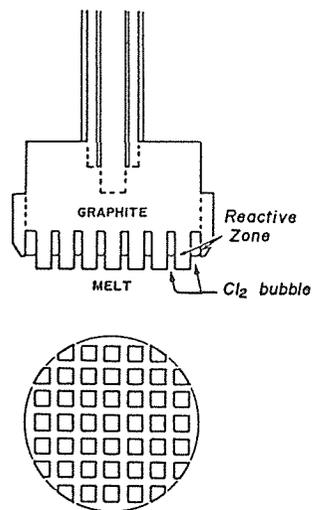Fig. 3 Schematic diagram of cathode with holes. Top : side view, bottom : bottom view.

Fig. 4 Schematic diagram of a grooved cathode. Top : side view, bottom : bottom view.

Both drilled and grooved electrodes were tested by changing the area of the reaction zones around peripheries of holes for the former electrodes and around grooves for the latter electrodes. The side view and the bottom of an electrode with holes are schematically illustrated in Fig. 3 and those of a grooved electrode in Fig. 4. As seen from Fig. 3, chlorine gas led through the pyrolytic carbon tube to the center of the cathode was introduced to the holes at the bottom through branched paths. The hole diameter, d, was changed from 2 to 11 mm and the number, n, from 6 to 186. Now we define the total length of reaction zones

as the total length of the peripheries of the holes, ℓ. Chlorine gas was supplied to the grooved surfaces by a quartz tube, the open end of which was set directly under the center of the bottom surface (the tube is not shown in Fig. 4). The length of the reaction zones, ℓ, that is, the gross length of the circumferences of the square pillars, was changed from 51 to 210 cm.

3. RESULTS AND DISCUSSION

3.1 Electrodes with holes

While changing resistances of the outer circuit, variations in output voltage, V_B, and output current, I_T, were recorded on a chart. One such chart is presented in Fig. 5. As seen from the figure, the output voltage and output current reached steady state values corresponding to the resistances and returned to an open-circuit state within the experimental time duration, 5 minutes. It shows that the reversibility of the reactions of the fuel cell is fairly high.
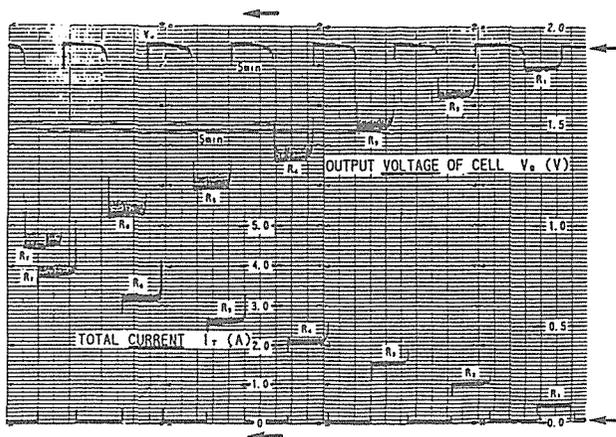

Fig. 5 Output voltage and output current responses to changes of resistances of the outer circuit. Electrode: $d=6$ mm and $n=40$.

Typical relations between output voltage, V_B and output current, I_T, (characteristic curves of the fuel cell) are shown in Fig. 6. Both curves in the figure show linear relations in the region of relatively small currents, and the extrapolation of the curves to the output voltage axis give the same value, the open-circuit voltage, V_d, of 1.91 V.

The output voltage-current relation for the fuel cell is presented in Fig. 7 with the voltage-current relation under electrolysis in the same system. The dashed, dotted line in the figure indicates the open-circuit voltage which corresponds to the electromotive force of the cell. As the circuit is connected with a certain resistance, some output current flows and
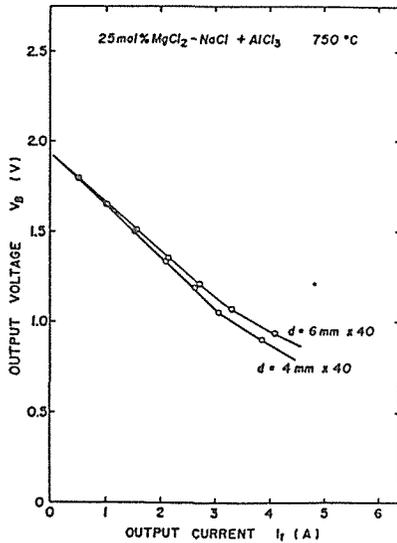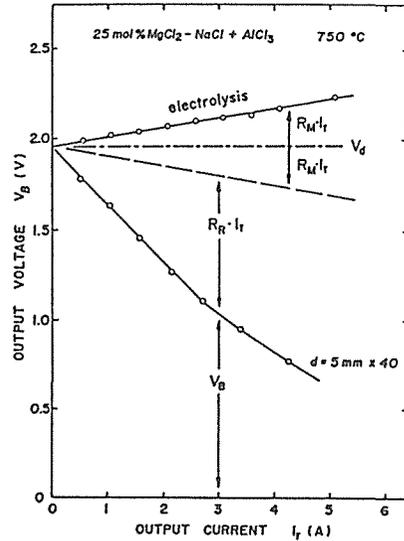
Fig. 6 Output voltage-current relation.

Fig. 7 Output voltage-current relation for the fuel
cell in a short-circuiting cathode and anode
for certain resistance and voltage-current
relations in electrolyzing.

the output voltage changes to V_B. Since the voltage drop due to anodic dissolution of the
aluminum is negligible in the present experimental conditions, the difference between V_d and
V_B is the voltage drop caused by the resistance of the melts, R_M, and some resistance
attributed to chlorine reduction. We refer to the resistance as the reaction resistance of the
chlorine electrode, R_R, though its origin is not yet clear. The relation between them is
written as $V_B = V_d - (R_M + R_R) \cdot I_T$. An investigation on the electrowinning of aluminum
using the same melt composition as in this work showed that the cell voltage for electrolysis
was composed only of Ohmic drop in the melts and that the resistance of melts could be
calculated from the gradient of voltage-current relations obtained under electrolysis.[6] If
the resistance of the melts obtained in this manner is nearly the same as R_M, the voltage drop
due to the resistance of the melts, $R_M I_T$, can be estimated as shown by the broken line in the
figure and, as a result, the voltage drop due to R_R, $R_R I_T$, can be obtained. To create a high-
quality fuel cell the voltage drop caused by R_R should be lowered as little as possible.

The relations of output voltage-current were determined at several electrodes by
changing their diameters and the numbers of holes. The voltage drops for reaction resis-
tance estimated from the above relations are presented as a function of output current in Fig.
8. The hole diameters and numbers of electrodes were changed from 4 to 9.6 mm, from 7 to
40, respectively, and they are shown with the total length of the circumference of the holes,
ℓ, in the figure. The figure shows that the voltage drops decrease with increases in ℓ.

Since it is difficult to specify the real reaction areas around the peripheries of menisci,
we introduce an output current per length of the reaction zone, I_T / ℓ, to estimate the
effectiveness of the holes for chlorine reduction (the value is equal to current density at a unit

width of the reaction zone).   The voltage drops in Fig. 8 are re-plotted against I_T/ℓ in Fig. 9.   The figure shows that the voltage drops against I_T/ℓ only slightly depend on hole diameter and the number of holes.   It is suggested that the width of reaction zones is not much different for all holes focused in the figure.
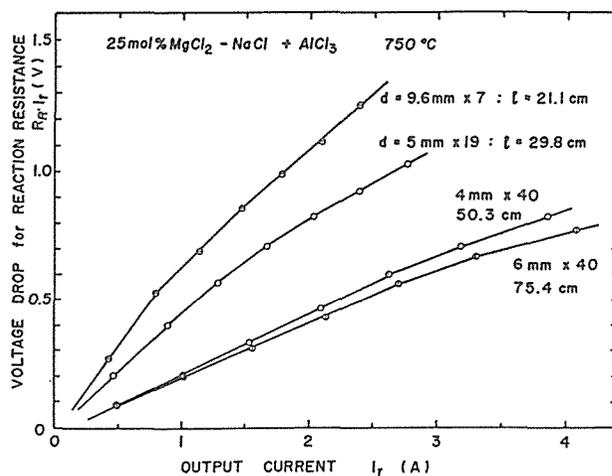

Fig. 8 Output voltage-current relations of various drilled cathodes.
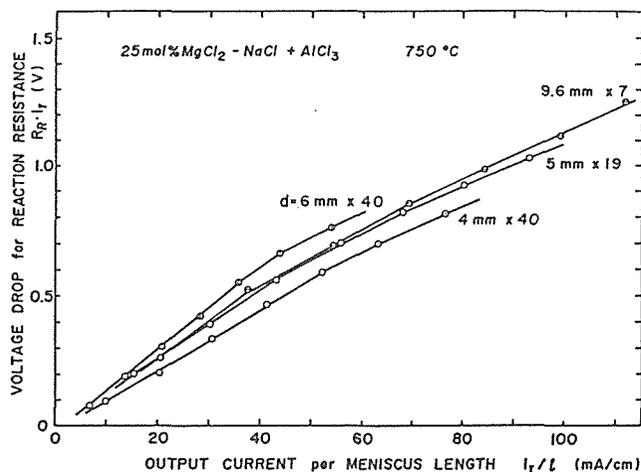

Fig. 9 Voltage drops as a function of output current per length of reaction zone. Electrode : drilled type.

The gradient of the $R_R I_T - I_T/\ell$ curve, R_R, indicates a special value such as specific resistance of the reaction zone ; the unit of the gradient is ohm·cm.   The value is a function of the specific resistance for chlorine reduction and the width and thickness of the reaction

zone : both width and thickness cannot be constant throughout the reaction zone and we suppose here an average width and thickness for the effective reaction area. The chlorine gas dissolution into the melts or the diffusion of dissolved chlorine to graphite surfaces must control the rate of the reduction reaction. Supplementary experiments showed that the voltage drops due to reaction resistances did not change with the flow rates of chlorine gas and the vibration of the chlorine electrodes so that effective agitation against the diffusion layer might not be produced.[7] It is, in any case, reasonable to consider that the thickness of the reaction zones was nearly equal for all kinds of holes in our experimental conditions, and that R_R became a parameter for the width of the reaction zone.
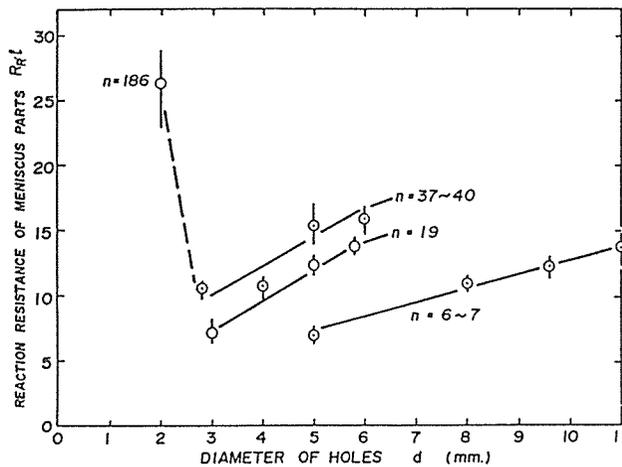

Fig. 10 Dependency of reaction resistance on the diameter of chlorine-supply holes.

In many cases R_R showed a linear relation with I_T/ℓ in the small output current range as seen in Fig. 9, and the gradients of $R_R I_T - I_T/\ell$ relations are calculated and plotted against diameters of holes in Fig. 10. As seen from the figure, R_R decreased with the decrease in the diameter of the holes and had a minimum value at about 3 mm. This suggests that small holes have wide reaction zones which should depend on the shapes of the menisci. In small holes with a diameter such as 2 mm, hardly all holes work in the same way, because even small differences in the shapes and sizes of the holes can bring about large differences in the contact angle of chlorine gas with the electrode. It was also confirmed from experiments that the fuel cell could work steadily for a long time as long as excess chlorine gas was supplied.

3. 2 Grooved electrode

As explained above, to create a homogeneous flow of chlorine gas through all holes of small sizes is difficult and it leads to a limitation of the area of the reaction zone for drilled electrodes. In order to enlarge the area in a particular electrode, electrode surfaces were grooved and a length of 210 cm for the reaction zone was attained. The same experiments as at the drilled electrodes were carried out using grooved electrodes and the obtained

relations between voltage drop and output current per length of reaction zone are presented in Fig. 11. The voltage drops for reaction zones with different lengths were not much different from each other as those of the drilled electrodes shown in Fig. 9. The values were slightly larger and, as a result, the R_R became a little larger than with the drilled electrodes, but the gross drop of the output voltage became smaller than that of the drilled electrode, because of its large reaction area.
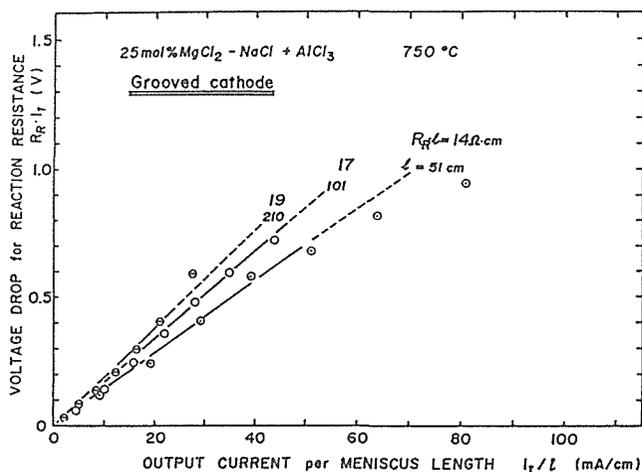

Fig. 11 Voltage drops as a function of output current per length of reaction zone. Electrode: grooved type.

Figure 12 shows the output voltage for a grooved cathode with a reaction zone of 210 cm in comparison with that for a drilled cathode with a reaction zone of 117 cm. As shown in the figure, the grooved electrode was superior to the drilled electrode and the former could supply 4.0 A at 1.5 V for the electrowinning process, in contrast to 1.4 A at 1.5 V for the latter.
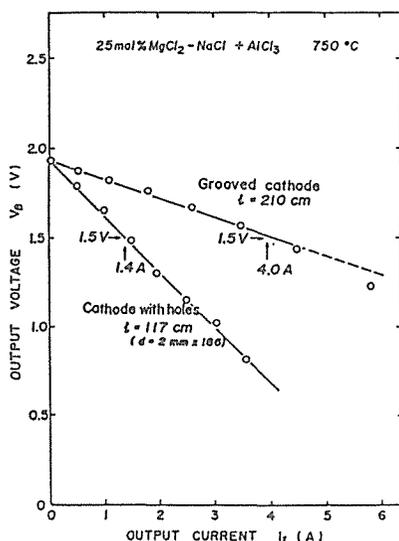

Fig. 12 Comparison of output voltage of the grooved cathode to that of the drilled cathode.

4. CONCLUSIONS

In order to develop cathode electrodes for an aluminum-chlorine fuel cell, electrodes with chlorine-supply holes were tested by changing the hole sizes and numbers. The discharge characteristics showed that the voltage drops due to resistance of the reduction reaction decreased with the increase in the length of the reaction zone and with the decrease in the size of holes. However, when the hole became as small as 2 mm, the holes did not function evenly. The grooved electrodes made it possible to enlarge the length of the reaction zone to 210 cm and to produce 4 A at 1.5 V.

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