Journal of The Electrochemical Society, **154** (6) D334-D338 (2007)
0013-4651/2007/154(6)/D334/5/$20.00 © The Electrochemical Society

Electrowinning Al from Al_2S_3 in Molten Salt

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In order to investigate an alternative process for the production of primary aluminum via a sulfide intermediate, the electrochemical behavior of Al_2S_3 in molten salt has been studied on a laboratory scale. The effects of electrolyte composition, temperature, and cell design on the cell performance have been investigated. Temperature and cryolite addition have positive effects on the current density. Increasing the anode-to-cathode surface area (closer to unity) and shortening the interelectrode distance lead to higher current density. It is concluded that the electrolytic process is governed by the ohmic drop, caused mainly by the sulfur bubbles at the anode.

Manuscript submitted October 9, 2006; revised manuscript received February 9, 2007. Available electronically April 23, 2007.

In terms of primary energy consumption, the Hall–Héroult process requires about 140 MJ energy to produce 1 kg of aluminum metal, which is about four times the theoretical thermodynamic minimum (34 MJ/kg Al). Apart from substantial CO_2 and SO_2 emissions from the production of electrical energy as well as the consumption of carbon anodes, the Hall–Héroult process creates greenhouse gas emissions such as CF_4 and C_2F_6 stemming from the electrolyte that consists mainly of liquid cryolite (Na_3AlF_6). These and other apparent disadvantages of the Hall–Héroult process have led to numerous research efforts to find an alternative route for primary aluminum production throughout the 20th century.

The best investigated alternatives are inert anodes,[1] the use of $AlCl_3$ as an intermediate step,[2] and the carbothermic reduction of alumina.[3] Inert anodes would enable a closed cell concept that is more favorable in terms of environment, energy efficiency, and capital cost. The aluminum chloride process comprises the chlorination of Al_2O_3 to $AlCl_3$ as an intermediate, and subsequent reduction of $AlCl_3$ to aluminum in an electrolysis cell. Due to the lower cell voltage required, the carbon anode remains inert and less electrical energy is required compared to an inert electrode process based on the reduction of alumina. Carbothermic reduction would eliminate the electrolysis step altogether, but high temperatures in excess of 2000°C would be required. Despite the substantial amount of capital spent on these and other processes, no proven and economically feasible alternative to the Hall–Héroult process to date exists.

Another alternative is to use aluminum sulfide as an intermediate step, named the Compact Aluminum Production Process (CAPP™).[4,5] In this process, Al_2S_3 is produced by the reaction of CS_2 and alumina. Subsequently, the aluminum metal can be extracted by electrolysis, producing sulfur gas at the anode, which can be recycled to the production of CS_2. The simplified reactions (assuming no complex ions) of the electrolysis process can be described as follows[6]

$$\text{Cathode} \qquad 2Al^{3+} + 6e^- \rightarrow 2Al \qquad [1]$$

$$\text{Anode} \qquad 2AlS_3^{3-} - 6e^- \rightarrow Al_2S_3 + 1.5S_2(g) \qquad [2]$$

$$\text{Overall} \qquad Al_2S_3 \rightarrow 2Al + 1.5S_2(g) \qquad [3]$$

Due to the lower cell voltage required, the carbon anode remains inert and less electrical energy is required compared with the Hall–Héroult process. As a result of the advantageous electrolysis process, substantial benefits arise in terms of energy efficiency and environment. Figure 1 shows that the electrolysis of Al_2S_3 is very promising with regard to energy consumption,[6] i.e., it has the lowest decomposition potential. The alkali chloride electrolyte permits a relatively low operating temperature of about 700°C, just above the melting point of aluminum. Because of operation with nonconsumable anodes, the interelectrode gap can be reduced and a multipolar cell operation is possible, which increases productivity and reduces energy consumption and capital costs. As Al_2S_3 reacts with air and water, operation under an inert atmosphere is necessary.

The eutectic of a $MgCl_2$–NaCl–KCl mixture (50–30–20 mol %) has been selected as an appropriate electrolyte for the electrolysis of Al_2S_3. Electrochemical studies of Al_2S_3 in a chloride melt showed that the reduction of Al ions at a graphite electrode is a diffusion-controlled process and proceeds via a reversible three-electron charge transfer.[7,8] Minh et al.[8] reported a limiting current density of $0.3\ A\ cm^{-2}$ at the saturation solubility of Al_2S_3 (~ 3 wt %) and $0.2\ A\ cm^{-2}$ in the $MgCl_2$–NaCl–KCl eutectic containing 2 wt % Al_2S_3. The current efficiency was about 80% at a current density of $0.2\ A\ cm^{-2}$, a cell potential of about 1.5 V, and interelectrode gap of 3 cm. By adding 10 wt % $AlCl_3$ to increase the solubility of Al_2S_3 to 5 wt % and to increase the concentration of Al ions, current densities of up to $2\ A\ cm^{-2}$ were obtained. In this situation, the current density was limited by the anodic reaction.

In the present work, the behavior of electrowinning Al from Al_2S_3 under different conditions is investigated in order to validate and improve the operating conditions described in the above.

Experimental

Raw materials.— Al_2S_3 with 98% purity was used for the experiment. The NaCl, KCl, Na_3AlF_6, and $MgCl_2$ were of laboratory grade with minor impurities. The chemicals were stored and handled in a glove box in an argon atmosphere.

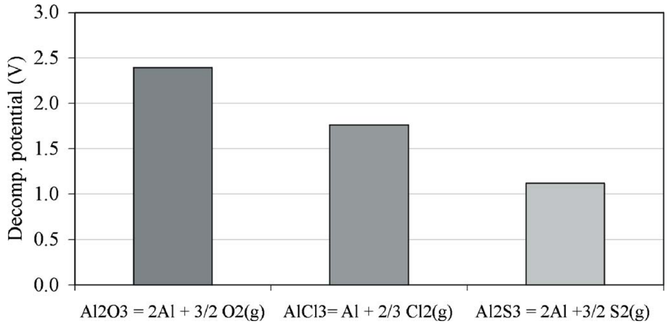

Figure 1. Decomposition potential of aluminum species for aluminum production.

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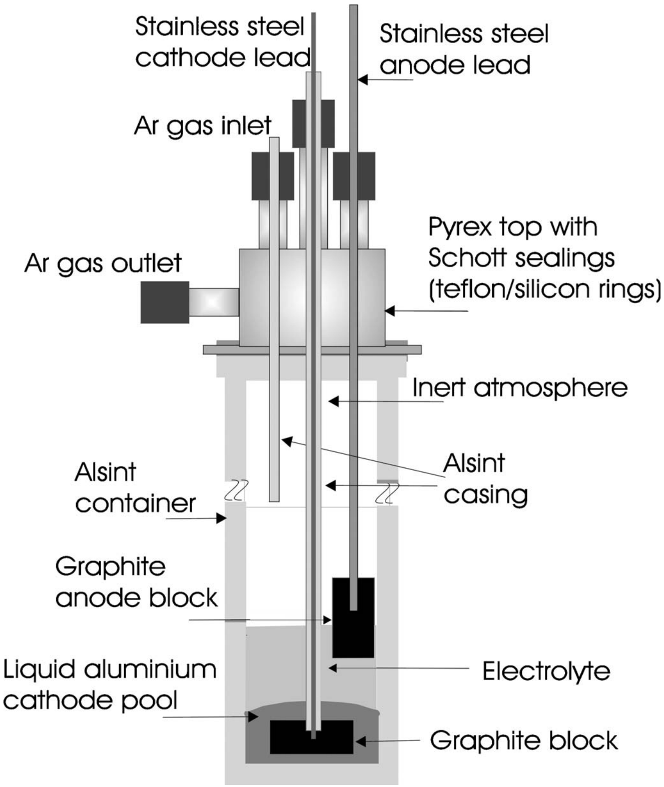

Figure 2. Experimental setup.

Experimental equipment and procedure.— A schematic view of the experimental cell is shown in Fig. 2. The electrochemical cell is assembled in a corundum alumina tube under inert Ar atmosphere in a glove box. The cathode is a pool of molten aluminum with effective area of 8.1 cm^2, which is polarized by a graphite block connected by a rod of stainless steel shielded by a quartz tube. The anode is constructed of a graphite block of 1×1 cm and 5 cm high, which is immersed 2 cm into the electrolyte and is connected by a stainless steel rod. The surface area ratio of anode to cathode is 0.12. The interelectrode gap is 2 cm. The anode acts also as the reference electrode; thus, the cell potential is measured during the electrolysis.

In the experiment, the cell is externally heated by a 2100 W cylindrical furnace equipped with Kanthal Super heating elements, with maximum operating temperature of 1400°C. The temperature is measured with Pt–PtRh10 thermocouples. In the off-gas line, two water bottles were installed to wash the off-gas and to remove the sulfur before gas release to the atmosphere. A buffer bottle was installed before the water bottles to prevent a backflow in the system.

During the experiment, a continuous flow of argon (0.5 L/min) was led through the cell to protect it from contact with air. The furnace was first heated and remained at 200°C for 45 min to remove the moisture in the system. Then the furnace was further heated to the experimental temperature and was equilibrated at that temperature for 1 h before the measurement. To investigate the electrochemical behavior of the cell, linear sweep voltammetry and amperometry experiments were performed. At the end of the measurement the electrolyte was taken out and the aluminum metal was collected to determine the current efficiency.

Results

The effects of various experimental parameters on the electrowinning behavior have been investigated, including cryolite addition, amounts of added aluminum sulfide, temperature, anode-cathode distance, and the ratio of the anode-to-cathode surface area.

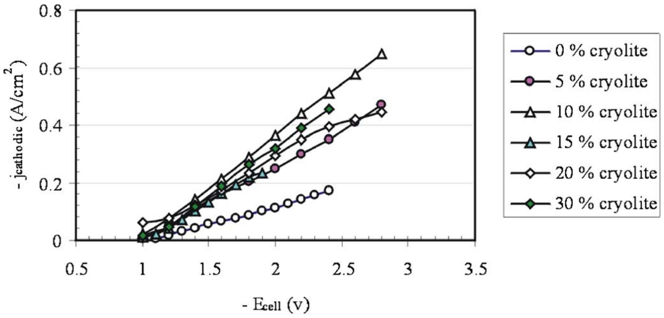

Figure 3. (Color online) Electrowinning of Al from Al_2S_3 in $MgCl_2$–NaCl–KCl based electrolyte of 50–30–20 mol % with cryolite addition at 725°C.

Electrolysis of Al_2S_3 in $MgCl_2$–NaCl–KCl eutectic-based system.— In order to saturate the electrolyte with aluminum sulfide, 4 wt % of Al_2S_3 was added into the eutectic $MgCl_2$–NaCl–KCl of 50–30–20 mol %. Figure 3 shows the results of the electrolysis of Al_2S_3 with the ternary eutectic at an operating temperature of 725°C. A linear relationship between the cell potential and the current density is observed. The kick off of the reaction was determined by extrapolation of the *j-E* relationship to the intercept with the *x* axis. The apparent decomposition potential is $E = -1.1$ V, which is close to the theoretical value of -0.98 V at 725°C.

The results from the experiment with no cryolite addition indicate a limiting current density at approximately 0.17 A/cm^2, occurring at -2.4 V. The effective electrode area of the cathode was assumed to be the cross-sectional area of the cell. This is somewhat less than the limiting current density of 0.3 A/cm^2 as reported by Minh et al.[8] In both cases, the limiting current density in the $MgCl_2$–NaCl–KCl eutectic electrolyte is too low to compete with that of 0.7–1.2 A/cm^2 in the Hall–Héroult process.

In order to increase the current density, cryolite was added to the electrolyte to increase the solubility of Al_2S_3 and to increase the activity of aluminum ion in the melt. Linear extrapolation of the *j-E* curve gives a decomposition potential of -0.98 V, which equals the theoretical value. The amount of cryolite added was varied between 5 and 30 wt %. The highest current density was achieved with 10 wt % of added cryolite. In this case the current density increased by more than a factor of three. This is most probably due to both the increased Al_2S_3 solubility and the increased conductivity. From solubility experiments it was observed that the solubility of Al_2S_3 in the electrolyte increases by a factor of four when adding 10 wt % of cryolite to the electrolyte.[9] In addition, the specific conductivity of cryolite ($2.79\ \Omega^{-1}\ cm^{-1}$ at 1000°C[10]) is higher than that of the ternary eutectic (estimated to be about $1.6\ \Omega^{-1}\ cm^{-1}$ [6]). However, when further increasing cryolite from 10 to 30%, the current density is lowered. This is most probably due to the increased viscosity of the electrolyte. In general, it is demonstrated that the addition of fluoride contributes to a positive effect on the electrowinning process to a certain extent.

Effect of temperature.— The operating temperature in an electrolytic cell used for the winning of aluminum is an important parameter that influences many of the properties of the electrolyte, for example density, viscosity, conductivity, and vapor pressure. All these properties have more or less influence on the electrochemical behavior in the cell and further on the current efficiency. However, none of these properties are known for the $MgCl_2$–NaCl–KCl eutectic with cryolite and Al_2S_3 additions. Voltammograms and linear sweeps were performed at the temperatures of 725, 775, 785, and 825°C. The results are shown in Fig. 4. The temperature has a slightly positive effect on the cathodic current density.

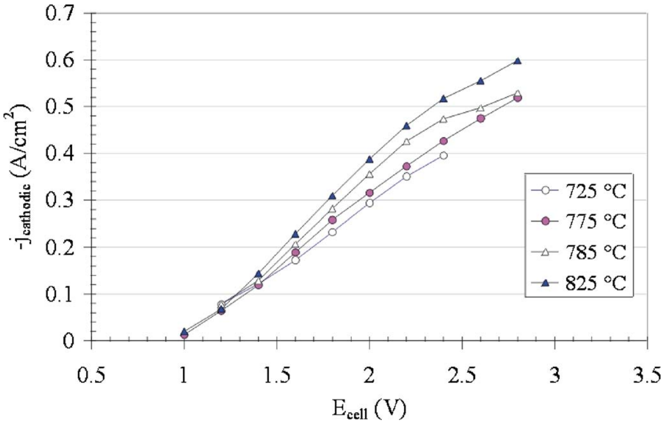

Figure 4. (Color online) Effect of temperature on the electrowinning of Al from 4 wt % Al_2S_3 in $MgCl_2$–NaCl–KCl eutectic based electrolyte with 20 wt % cryolite addition.

Effect of cell design.— In the electrolysis process, both interpolar distance and surface area ratio of anode to cathode are important for the cell performance. The left side of Fig. 5 illustrates the original layout of the cathode and anode in the cell. The anode is not symmetrically located above the middle of the cathode. In addition, the anode surface opposing the cathode is much smaller than the cathode surface. These geometrical constraints reduce the effective cathode surface area to a value much smaller than the cross section of the alsint cell tube. As this cross section was used in calculating the limiting current density, the real limiting current density for a more favorable geometry would be substantially higher. This was investigated by changing the cell layout and using the graphite block as the cathode, as illustrated on the right side of Fig. 5.

The electrolysis results under different arrangements are depicted in Fig. 6. The experiment with surface area ratio of 0.12 was carried out with an aluminum pool as cathode. The other experiments were performed with a graphite cathode without Al pool. When using the graphite block as the cathode, the cathodic current density increased significantly, in comparison to that with the Al pool as the cathode. Increasing the anode-to-cathode surface area ratio to a value closer to unity has positive effect on the cathodic current density. The cathodic graphite block is 2.2 cm in diameter and 2 cm in height. If the 3.80 cm^2 top surface of the graphite block is considered as the effective surface area of the cathode, the anode-to-cathode surface area ratio increases to 0.26. This is more than twice the original value of 0.12 based on the surface area of the aluminum cathode pool, which equals the cross section of the cell, 8.04 cm^2. In both cases, the same anode was used with an assumed effective surface area of 1 cm^2.

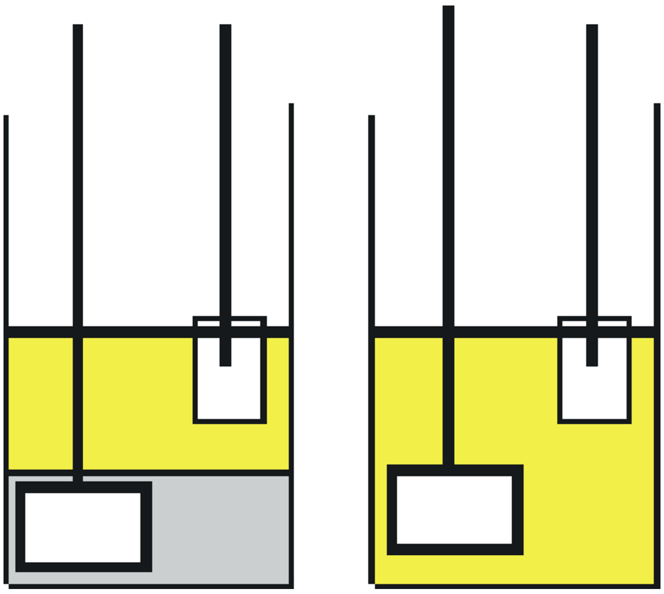

Figure 5. (Color online) Cell layout: (left) Al pool as cathode and (right) graphite block as the cathode.

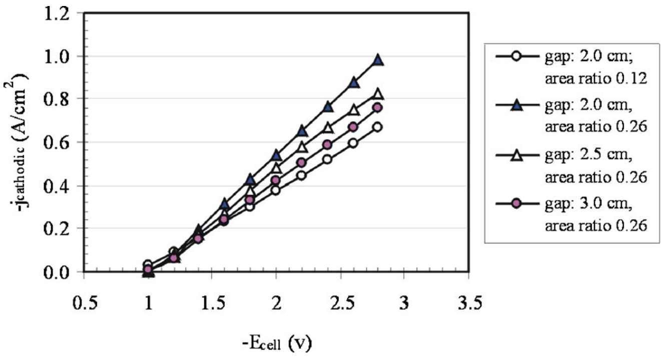

Figure 6. (Color online) Effect of interpolar distance (gap) and the surface area ratio of anode to cathode on the electrowinning of Al from 4 wt % Al_2S_3 in $MgCl_2$–NaCl–KCl-based electrolyte with 10 wt % cryolite addition at 725°C.

To investigate the effects of an increased distance on the current density, experiments were carried out with the graphite block cathode, using a vertical interpolar distance of 2.0, 2.5, and 3.0 cm, respectively. The shorter the distance, the higher the cathodic current density.

Current efficiency.— The current efficiency (CE) of aluminum electrolysis is an important factor in both technical and economical aspects. CE is defined as the percentage of the metal amount actually produced divided by the theoretical metal output. The theoretical metal output is calculated as below

$$W_{\mathrm{Al}}^{\mathrm{theoretical}} = \frac{Q}{nF} M_{\mathrm{Al}} \quad [4]$$

where Q is the electric charge that passes through the cell, n is the valence of aluminum ion in the electrolyte, F is Faraday's constant, and M_{Al} is the mole mass of aluminum metal.

The current efficiency is influenced by a number of variables including temperature, composition of the electrolyte, and cell design. In the present study, in order to determine the current efficiency, a fixed potential of 2.2 V was supplied to the cell with graphite cathode at 725°C to prevent codecomposition of other species like $MgCl_2$. The electrolyte contains $MgCl_2$–NaCl–KCl eutectic with 10 wt % cryolite and 4 wt % Al_2S_3. The result is shown in Fig. 7. From the linear scan it was indicated that after 1300 s the concentration of aluminum ion in the electrolyte is very low. The total amount of current passed through the electrolyte is 7000 C at this stage. This equals 0.66 g of theoretical aluminum output. As no aluminum pool was used in this experiment, the metal produced was dispersed into the electrolyte as fine droplets. After the experiment, the electrolyte was dissolved in the distilled water. The aluminum metal was collected and further dissolved in HCl. The actually produced amount of aluminum from electrolysis was determined by analyzing the HCl solution with atomic absorption spectrophotometry (AAS). The total amount of actually produced aluminum is 0.39 g, which is equivalent to the consumption of 1.08 g of Al_2S_3. The Al_2S_3 added is 2.6 g; thus, about 42% of Al_2S_3 has been converted into aluminum metal during the electrowinning process. The current efficiency for this experiment was determined to be about

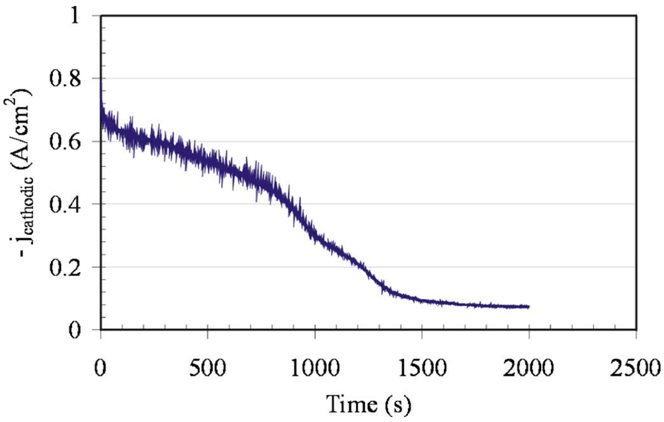

Figure 7. (Color online) Plot of cathodic current density at 2.2 V in the electrolyte of $MgCl_2$–NaCl–KCl eutectic with 10 wt % cryolite and 4 wt % Al_2S_3 at 725°C.

60%. The maximum current efficiency achieved under the present conditions was 62% when potential of 2 V was applied for 5700 s.

Discussion

Current efficiency.— The current efficiency of 60% obtained during the experiment is rather low compared to the average values of 90-95% in the modern Hall–Héroult process for the Al production process. This may be explained by various factors to be discussed below.

Considering the low solubility of Al_2S_3 (~0.32 wt %) in the $MgCl_2$–NaCl–KCl eutectic with 10 wt % cryolite at 850°C,[9] initially only a small fraction of the total 4 wt % of Al_2S_3 is dissolved in the melt. As the initially dissolved Al_2S_3 is reduced, more Al_2S_3 may dissolve. The dissolution of Al_2S_3 in the electrolyte may be as fast as the reduction of Al_2S_3. However, the total time of the experiment is about 90 min, which is substantially lower than the equilibrium time of 5 h derived from solubility experiments.[9] Therefore it is possible that the reduction process is faster than the dissolution process, and the melt becomes gradually depleted of Al_2S_3. This may explain the gradual reduction of the current density in Fig. 7. If this happens, the conditions gradually become less favorable as the experiment proceeds, and Al_2S_3 may have not dissolved into the electrolyte at the end of the experiment, as indicated by the low Al_2S_3 conversion of 42% in the experiment.

In addition, due to the use of a graphite cathode, which is not wetted by aluminum metal, the formed aluminum droplets are dispersed in the electrolyte. This combined with the sulfur gas evolution at the anode can result in a convection flow inside the electrolyte whereby the aluminum droplets come into contact with sulfur and form aluminum sulfide again. Besides, the possible codeposition of sodium and potassium and dissolution of reduced metal in the electrolyte may also lower the current efficiency. Using a liquid aluminum pool as a cathode can avoid this problem.

It must be kept in mind that the cell geometry differs substantially from the industrial design and should be regarded as less favorable. Using an aluminum pool as a cathode would have counteracted the formation of fine aluminum droplets in the molten salt. Furthermore, the presence of high electrical current densities affects the flow pattern in an industrial cell, which in turn influences the behavior of gas bubbles and the stability of the metal/salt interface. As a consequence, current efficiencies derived from small-scale experiments should be treated with some caution.

Current density.— The addition of cryolite in the electrolyte has two distinct positive effects on the electrochemical behavior of the cell, as seen in Fig. 3. First, the limiting current density is markedly increased, by at least a factor of four. Secondly, the current density at a given cell potential increases by about a factor of three. These effects may be attributed to different reasons.

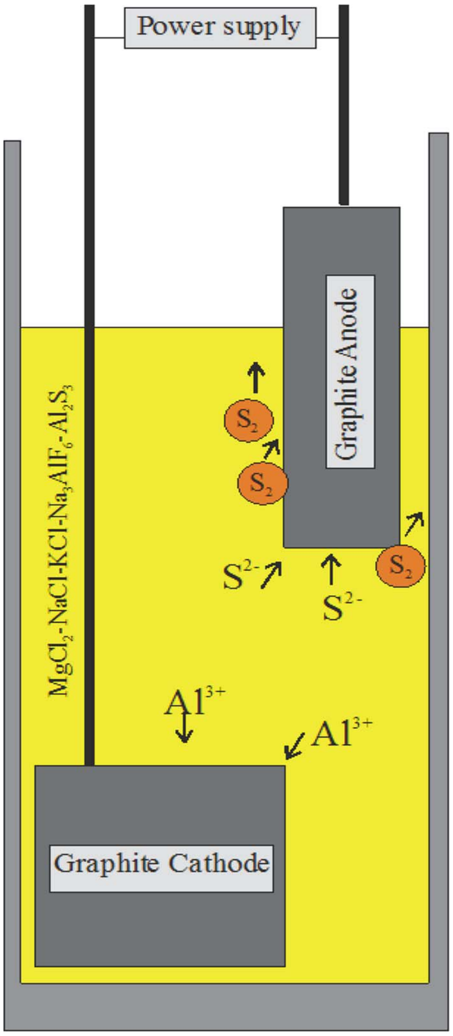

Figure 8. (Color online) Schematic illustration of mass and current flow in the electrowinning process.

The increase in limiting current density can be caused mainly by the increased solubility of Al_2S_3. It can also be argued that the amount of fluoride contributes to the positive effect on the electrowinning process, resulting from a higher activity of AlF_n^{m-} than AlS_3^{3-} species. When complexing of Al with F is more preferred, the concentration of S ions would be higher, thus favoring the anodic reaction.

As long as the *j*-*E* relationship is almost linear, its slope is determined by an ohmic drop, rather than a depletion of ionic species. Thus, the increase of the slope of the *j*-*E* curve should be ascribed merely to a reduction of the resistivity between anode and cathode. The slope increases by almost a factor of three on the addition of cryolite to the $MgCl_2$–NaCl–KCl eutectic, which is much more than expected only from the increased melt conductivity. A hypothetical explanation is that upon the addition of cryolite, a complex ion is formed, changing interfacial tension at the anode. This may result in different characteristics of the sulfur bubble layer at the anode and reduce the ohmic drop. Further research is needed to understand these phenomena completely.

In general, the cell potential consists of thermodynamic, kinetic (activation potential and mass-transfer limitations), and ohmic contributions. Figure 8 shows the schematic diagram of the experimental setup. The cell potential involving gas evolution is contributed by the items in the following equation

$$E_{\mathrm{cell}} = E^{\mathrm{rev}} + \eta_{\mathrm{anode}} + \eta_{\mathrm{cathode}} + E_{\mathrm{electrolyte}} + E_{\mathrm{electriclead}} \qquad [5]$$

E^{rev} is the reversible decomposition potential of Al_2S_3; η_{anode} and η_{cathode} are the overvoltages of the anode and cathode, and $E_{\mathrm{electriclead}}$ is the voltage from outside of the reaction system including the electrical leads. The $E_{\mathrm{electrolyte}}$ $(=IR_{\mathrm{electrolyte}})$ contains voltages from inside of the reaction system, including the voltage drop across the electrolyte, cathode, and anode. Due to gas evolution at the anode, the resistance of the electrolyte $(R_{\mathrm{electrolyte}})$ is for an important part determined by the bubble formation in the melt, because these bubbles have virtually zero conductivity and can reduce the available anode surface. $E_{\mathrm{electriclead}}$ can be ignored as the same materials were used as cathodic and anodic electric leads. Disregarding η_{anode} and η_{cathode}, the overvoltage can be written as follows

$$E_{\mathrm{over}} = j\rho \qquad [6]$$

where E_{over} is the overvoltage $(E_{\mathrm{cell}}\text{-}E^{\mathrm{rev}})$ (V), E_{cell} is measured cell voltage (V), E^{rev} is the reversible decomposition potential of 0.98 V at 725°C, ρ is the resistivity in the system (Ω cm^2), and j represents the current density (A/cm^2), assuming ρ consists of the resistivity of both the bubble layer and the melt. The Eq. 6 can then be rewritten as

$$E_{\mathrm{over}} = j(\rho_b + d/\sigma) \qquad [7]$$

where ρ_b is the resistivity of the bubble layer (Ω cm^2), d is the thickness of the electrolyte (cm), and σ is the conductivity of the electrolyte (Ω^{-1} cm^{-1}). If the thickness of the bubble layer is supposed to be negligible, d equals the anode-cathode distance. Assuming ρ_b and σ are constant, the conductivity of the electrolyte σ and resistivity of the bubble layer ρ_b can be approximated from Fig. 4. On average, the conductivity of the electrolyte was 1.63 Ω^{-1} cm^{-1}, which compares quite well to the estimated value of 1.6 Ω^{-1} cm^{-1} in the ternary eutectic system. Aaberg et al.[11] measured bubble-layer characteristics in Hall–Héroult cells and found the maximum resistance of the anodic bubble layer varied between 0.50 and 1.50 Ω cm^2. The present calculated resistivity of the bubble layer of 0.792 Ω cm^2 is in the reported range.

The results show that for $d = 2$ cm and a 10% cryolite addition, the melt resistivity and the resistivity of the bubble layer are of the same magnitude. This justifies the assumption that the nature of the bubble layer is important in determining the ohmic drop across the cell. It must be kept in mind that due to the cell geometry, the figures should be treaded as indicative. The bubble evolution mechanism in the Hall–Héroult process is different because the anode is consumed. The evolution of sulfur may be of the same nature as the evolution of chlorine in chloride melts at graphite anodes, i.e., bubbles tend to grow at the anode and stick to the anode, causing the buildup of high resistance at the surface of the anode.[12,13]

It can be argued that addition of fluoride in the form of cryolite is not desirable because this results in fluoride emissions. However, compared to the Hall–Héroult process, the required amount of cryolite is relatively small and the operating temperature is lower. Cryolite has melting point of 1012°C, and its volatilization potential at 700–750°C is much lower than that in the Hall–Héroult process operating at 950°C.

Based on the results obtained so far with cell potential of 2.8 V and 62% current efficiency, an energy consumption of 13.4 kWh/kg aluminum is calculated, which is at the same level of the Hall–Héroult process. However, when the current efficiency is improved (e.g., by increasing the solubility of Al_2S_3) and ohmic drops are further reduced, which should be possible with an optimized cell design and an optimized electrolyte, a lower energy consumption of near the theoretical value of 8.4 kWh/kg can be achieved for aluminum electrolysis from Al_2S_3. The current density is expected to increase with a larger anode-to-cathode surface area ratio (i.e., closer to unity), and with a symmetrical cell design. In an industrial electrolysis process, the electrodes are normally aligned as parallel surfaces with about the same cathode and anode area. This arrangement would result in a higher current density.

Conclusions

Electrowinning of Al from Al_2S_3 is technically feasible. The influence of various operational parameters on the cell performance has been investigated including electrolyte composition, temperature, surface area ratio of anode to cathode, and anode-cathode distance. It can be concluded that the electrolytic process is governed by its ohmic drop, resulting in a linear relationship between I and E. It appears that sulfur bubbles at the anode contribute very significantly to the ohmic drop. Increasing the temperature results in a higher current density. The addition of cryolite in the $MgCl_2$–NaCl–KCl eutectic electrolyte decreases the ohmic drop and increases the (limiting) current density. The former is for an important part ascribed to a change in the sulfur bubble layer, while the increase in limiting current density is attributed to the increased solubility of Al_2S_3. Higher surface area ratio of anode to cathode and shorter interpolar distance lead to higher cathodic current density. The maximum current efficiency achieved was 62%, and the energy consumption was determined to be 13.4 kWh. By improving the cell design and electrolyte composition, the theoretical energy consumption needed for 1 kg of aluminum of 8.4 kWh could be approached, which is considerably lower than the value of 14 kWh/kg aluminum in the Hall–Héroult process.

Delft University of Technology assisted in meeting the publication costs of this article.

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