

The Behavior of Additives LiF, MgF₂ and KF on Current Efficiency in Aluminium Electrolysis

Peng Cui,¹ Bo Qin,^{1,z} and Geir Martin Haarberg²

¹Kunming University of Science and Technology, Kunming 650093, China

²Norwegian University of Science and Technology, Trondheim NO-7491, Norway

The effects of LiF, MgF₂ and KF additions to the electrolyte on current efficiency were investigated during aluminium electrolysis using base NaF–AlF₃–Al₂O₃ system with a cryolite ratio of 2.5, 4% Al₂O₃ and 5% CaF₂ at 980°C in laboratory scale. The duration of each electrolysis experiment was 4 h with a graphite anode and a cathodic current density of 0.85 Acm⁻². The influences of various additives on the current efficiency of the aluminium electrolysis are compared. Additions of LiF up to 5 wt % were found to improve the current efficiency of aluminium deposition. Additions of MgF₂ had a positive effect on current efficiency and KF addition was harmful for the current efficiency. Current efficiencies for aluminium deposition were obtained when the additions of LiF mixed together with the additions of KF and MgF₂. The concentration of the alkali metals including K, Na and Li in deposited aluminium were analyzed as a function of the additives. Results are presented from a study of the influence of the additions on the cathode process. Correlations between the sodium content in aluminium with different additions and the current efficiency are discussed. © 2019 The Electrochemical Society. [DOI: 10.1149/2.0431913jes]

Manuscript submitted May 21, 2019; revised manuscript received July 18, 2019. Published August 13, 2019. This was Paper 1446 presented at the Cancun, Mexico, Meeting of the Society, October 5–9, 2014.

Industrial aluminium production is mainly based on the Hall-Héroult process. The main electrolyte system is Na₃AlF₆–Al₂O₃–AlF₃ for aluminium electrolysis. Current efficiency is an important parameter to describe the performance of aluminium production. It is ratio of the amount of aluminium actually produced as compared to the theoretical amount predicted from Faraday's laws. It also knows how efficiently the cell uses electric current to reduce alumina to aluminium. The current efficiency of the modern potlines today can reach above 95%. The electrolyte can be regarded as the core of the electrolysis process. Besides the main components (Na₃AlF₆, AlF₃, Al₂O₃), the electrolyte may contain some additives such as CaF₂, LiF and MgF₂.¹ The current efficiency of the process can increase by using additives that improve the physicochemical properties of the electrolyte.

Additions of LiF and MgF₂ have been reported to be beneficial for current efficiency in industrial cells.^{2–4} Grjotheim⁵ reviewed the effects of the contents of LiF and MgF₂ on the current efficiency. Lithium fluoride and magnesium fluoride are good additives and are very effective in improving current efficiency. Grjotheim⁶ found that each 10°C reduction in temperature in the range from 890 to 940°C gave 1.2% increase in current efficiency in an electrolyte composition of 20 wt % AlF₃ and 3 wt % LiF. Sterten⁷ found that low-melting electrolytes gave higher current efficiency than conventional electrolytes. Maximum current efficiency was found for the composition Na₃AlF₆–Li₃AlF₆. Dewing⁸ found the following expression for the loss in current efficiency (CE):

$$\log(\% \text{ loss in CE}) = \text{constant} - 0.019(\text{wt}\% \text{ AlF}_3) + 0.060(\text{wt}\% \text{ LiF}) + 0.0095(\text{Superheat}) \quad [1]$$

MgF₂ has been shown to have a positive effect on current efficiency in laboratory electrolysis cells.⁹ Stevens¹⁰ reported a very high value of 4.8% improvement in current efficiency for each wt % MgF₂ added.

Although KF can increase the solubility of alumina in the melts, little attention has been paid to the addition of KF because it lowers the cell lifetime due to its corrosion of carbon materials. However, there are many papers about the KF–AlF₃ system that seems to be a promising candidate as low temperature electrolyte due to its lower eutectic temperature.^{11–13} Low temperature aluminium electrolysis contributes not only to energy saving but also to the application of inert anodes in the Hall-Héroult process. Meanwhile, it also reduces material corrosion, electrolyte evaporation, aluminium solubility (which can raise current efficiency), and alkali metal content in the aluminium product.

The alkali metals are not reduced at the cathode because they are less noble than aluminium. However, it has been found that some reduction of these metals does take place as an equilibrium concentration of lithium, magnesium, and calcium in the aluminium metal pool in cells relative to the concentration of these metals present in the cryolite electrolyte. Sodium is produced at the bath–metal interface to form an alloy with aluminium due to the chemical reaction occurring when reaching thermodynamic equilibrium and sodium partitioning into the two phases (cryolite-based melts and aluminium cathode) based upon equilibrium constant for the following reaction:



The standard state in this reaction is considered at normal bath temperature (960°C–980°C) and normal pressure (the standard atmospheric pressure).

When LiF and KF is added to the melts, the equilibrium contents of lithium and potassium in aluminium are related to the composition of the melt at the aluminium/melt interface and can be described by the following reaction



where M is either Li or K

Alumina produced from deposits in China contains high proportion of K₂O and Li₂O at the present so that LiF and KF are formed and accumulate in the electrolyte during the electrolysis process. In recent years, many aluminium smelters in China have to face this type of situation during the production process. The normal content of LiF in electrolyte are over 3% in most of smelters, the highest is up to 8%. The content of KF in electrolyte is usually around 2%, some plants can reach 4%. In the future, their contents will remain in an uptrend with growth of cell life. The complex electrolyte containing relatively high content of LiF and KF can make the cell operation quite difficult and sometimes unstable. Scientists and engineers have been trying to look for innovative technologies for aluminium production in order to reduce the energy consumption and the emission of greenhouse gases. There will be further improvements in the electrolyte composition and its stability in the cell based on the traditional electrolytes, aiming at increasing current efficiency and decreasing energy consumption. Efforts need to be tried to find an optimal electrolyte composition on the modification of the conventional electrolyte by the addition of LiF, KF and some other additives, and to perform aluminium electrolysis at temperature below 900°C. For another, there has been quite a large amount of work done concerning low temperature electrolytes for the alumina reduction process. Therefore, the new research should be studied on the complex electrolyte, especially the effects of LiF and KF

on current efficiency in aluminium electrolysis.

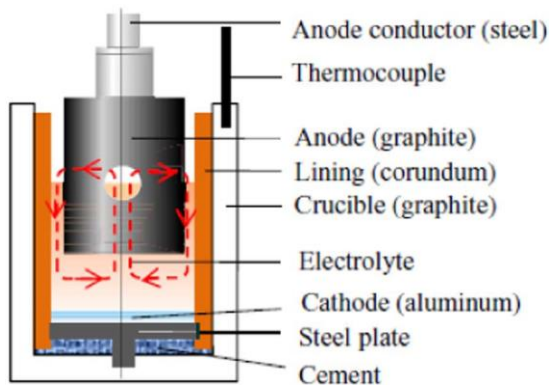


Figure 1. The cell design for laboratory study. The circulation pattern of the electrolyte is shown by arrows.

In this work, the effects of LiF, MgF₂ and KF on current efficiency were studied in conventional electrolytes in which sodium cryolite is a basic component of electrolyte. The predetermined amounts of additives were mixed with electrolyte contents before the start of the experiment to get a quantitative understanding of the influences of various additives on the current efficiency of the aluminium electrolysis. Results are given of the content of additives as a function of current efficiency. Correlations between sodium content in the aluminium with different additions and current efficiency are discussed.

Experimental

A laboratory cell developed by Solli^{14,15} was used to determine the current efficiency for aluminium during electrolysis. The laboratory cell is shown in Fig. 1.¹⁶ Anode, cathode and electrolyte are contained in a graphite crucible with a sintered alumina cylinder side lining. The anode material is graphite, cylindrically shaped with a vertical hole through the center. Most of the anode gas bubbles run out through the central vertical hole, and make electrolyte flow out through the horizontal holes. The electrolyte reaches half way up to the horizontal holes of the anode. The cathode is aluminium wetted on a steel plate in order to ensure a close to flat aluminium surface, and consequently an even current distribution on the cathode surface. A steel pin is glued by carbon glue and used to contact between the steel cathode plate and the graphite crucible. The steel plate is placed on the layer which is cemented with cast alumina cement on the bottom of the crucible, to prevent contact of aluminum metal with the graphite crucible. The disadvantage of the layer can result in aluminum loss and aluminum carbide formation. The laboratory cell is designed specifically to obtain good and reproducible convective conditions, and to give an almost flat metal surface during electrolysis.

The cell was placed in a vertical tube furnace and positioned to avoid temperature gradients in the electrolyte. The furnace was flushed with nitrogen gas and a small gas flow was maintained through the furnace to prevent air burn of the cell during the experiments. The current is supplied by a DC power supply. The thermocouple (Pt/Pt10Rh) is placed inside a slot beside the crucible to read the temperature during the electrolysis. Standard experimental conditions are Na₃AlF₆-Al₂O₃ with excess AlF₃ corresponding to a molar ratio of NaF/AlF₃ of 2.5, 4 wt% Al₂O₃ and 5 wt% CaF₂ at 980°C and a constant current density of 0.85 A/cm². The additions of LiF, MgF₂ and KF are added in the electrolyte respectively before the start of the experiment. Alumina powder (Merck, 99.0%, Anhydrous γ-alumina) are supplemented manually every 15 minutes through a central steel tube screwed into the hollow anode during the experiments. The duration of each elec-

Table I. Current efficiency values and deviation in measured points.

Number	CE%	Average	Deviation
1	91.2	91.4	0.4
2	91.8		
3	91.3		

cleaned mechanically and left in an aqueous solution of AlCl₃ · 6H₂O at 25°C for 30 minutes. CE is obtained from the relation:

$$CE/\% = 100 m_a/m_t \quad [4]$$

where m_a is the actual produced aluminium and the m_t is the theoretical production of aluminium given by Faraday's laws. m_t can be expressed by the equation:

trolysis experiment is 4 h.

The influence of on the current efficiency was studied. The current efficiency was calculated from the ratio of metal produced and the theoretical amount given by Faraday's law of electrolysis. The crucible is broken after termination of electrolysis, then and the aluminium is

$$m_t = (MIt) / (zF) \quad [5]$$

where I is the cell current, t is the electrolysis time, M is the molar mass of aluminium, and F is the Faraday constant.

The contents of lithium and potassium in aluminium pad with additives of LiF and KF were measured. The metal samples drilling and weighing around 0.5 g was dissolved in 10 ml of an acidic mixture with one part HNO_3 (65%) and 3 parts HCl (30%). The dissolved samples were diluted in deionized water and kept in a plastic container for analysis by ICP-MS.

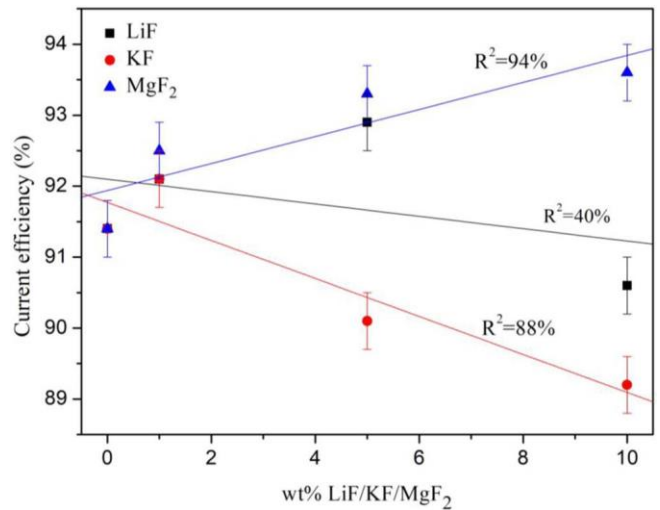
Results and Discussion

Some experiments were performed without addition at the current density of 0.85 A/cm^2 and at 980°C , with a NaF/AlF_3 molar ratio of 2.5, in order to study the reproducibility of the determined CE. The values are shown in Table I. The results indicate that the deviation is

$\pm 0.4\%$.

Current efficiency.—Current efficiencies were obtained at different additions of lithium fluoride, magnesium fluoride and potassium fluoride in Figure 2. There is no obvious effect of additions of 1 wt% LiF because small amounts of LiF have a limited effect on current efficiency. However, LiF up to 5 wt% is beneficial for current efficiency, followed by a considerable decrease of the current efficiency at 10 wt% LiF. Wang¹⁷ found that the total metal solubility decreased with increasing LiF concentration. The impact of LiF on the total metal solubility is not known in detail, but it is likely that additions of LiF

Figure 2. Current efficiency for aluminium deposition as a function of additions of LiF, MgF_2 and KF.



lead to decreased activities of NaF and AlF_3 , so that the metal solubility decreases and the current efficiency increases by adding LiF. The activity is a measure of the effective concentration of a species in a mixture. Although metal solubility decreased with increasing LiF concentration, the solidified metal after the experiment was found to form a distinct sphere at the cathode instead of spreading out on the steel plate at 10 wt% LiF. That must be caused by some kind of dewetting at the cathode. The possible reason is that the addition of LiF decrease the rate of dissolution of alumina in cryolite melts leading to sludge formation at the cathode. Sludge formation may raise serious technological problems. 10 wt% LiF addition can affect some experimental conditions and parameters, such as actual cryolite ratio, superheat and so on. It is hard to judge what the primary reason leads to decreasing current efficiency. Short circuit is the possible circumstance because metal can touch directly the anode due to unbalances in the cathode current distribution. In this case the electrical current passes directly from the anode to the metal pad without producing electrolysis of the alumina and hence reducing the current efficiency. However, most of study about LiF addition reported that small amount of LiF has a positive effect on current efficiency in laboratory cells and industrial cells. This might be explained by the contribution of lithium cations to the transport of electrical charge in the cell.

Current efficiencies with additions of MgF_2 were obtained ranging from 92.5% to 93.5%. Current efficiencies were found to increase with increasing addition of MgF_2 . MgF_2 has a positive effect on current efficiency. In this study, the same trend was also observed. Higher MgF_2 addition reduces the metal solubility in the electrolyte. The effect appears to be attributable to physicochemical properties of aluminium electrolyte changes that increase the interfacial tension at the electrolyte/aluminium phase boundary, which affects the rate of dissolution of aluminium in the electrolysis process. The disadvantage of MgF_2 addition is that it can reduce the solubility of alumina in the electrolyte. However, the negative influence of MgF_2 on the solubility of alumina may be compensated for by its positive effect on the interfacial tension at the electrolyte/aluminium phase boundary. Although MgF_2 addition is beneficial for current efficiency, it is limited by its price and side effects. Usually a higher concentration of additives may cause contamination of the aluminium.

Small amount of KF additions also has no obvious effect on current efficiency. KF additions above 5 wt % were found to reduce the current efficiency considerably. The addition of potassium fluoride exhibits some negative effects on the rate of alumina dissolution, the electrical conductivity and the interfacial tension in the electrolyte. When the KF concentration went up to 10 wt %, high unstable voltage fluctuations were recorded during the experiment. The reduction of alumina dissolution in the electrolyte may contribute to formation of alumina sludge, the current distribution will deteriorate, and current efficiency will thereby decrease due to anode effect because of the low concentration of the alumina in the electrolyte. The alumina reduction reactions are interrupted during an anode effect. The electrical current flows without producing aluminum. Therefore, KF additions are harmful for the current efficiency.

Current efficiencies for aluminium deposition were obtained when additions of 1% LiF and 5% LiF together with different the contents of KF and MgF_2 in Figure 3. When 1% LiF or 5% LiF was added, the current efficiencies decreased with increasing KF additions. Single addition of LiF is better than the combination LiF and KF additions. The additions of 5 wt % LiF and 1 wt % KF were found to increase current efficiency compared to the others with additions of LiF and KF, but it is slightly lower than 5 wt% LiF additions. Due to the presence of KF addition in the electrolyte, it offsets the positive effect of LiF addition. Qin¹⁸ reported that this complex system may lead to reducing the current efficiency because of some reasons such as temperature fluctuation, unsubstantial ledge due to the poor stability of superheat, an increase of anode effect frequency owing to the poor

alumina solubility, and formation of sludge at the bottom of cell.

5% LiF and 5% MgF_2 additions were found to increase current efficiency compared to the others with additions of LiF and MgF_2 . It is just slightly higher than 5% MgF_2 addition. The combination of LiF

with lithium fluoride additions increased. The equilibrium contents of

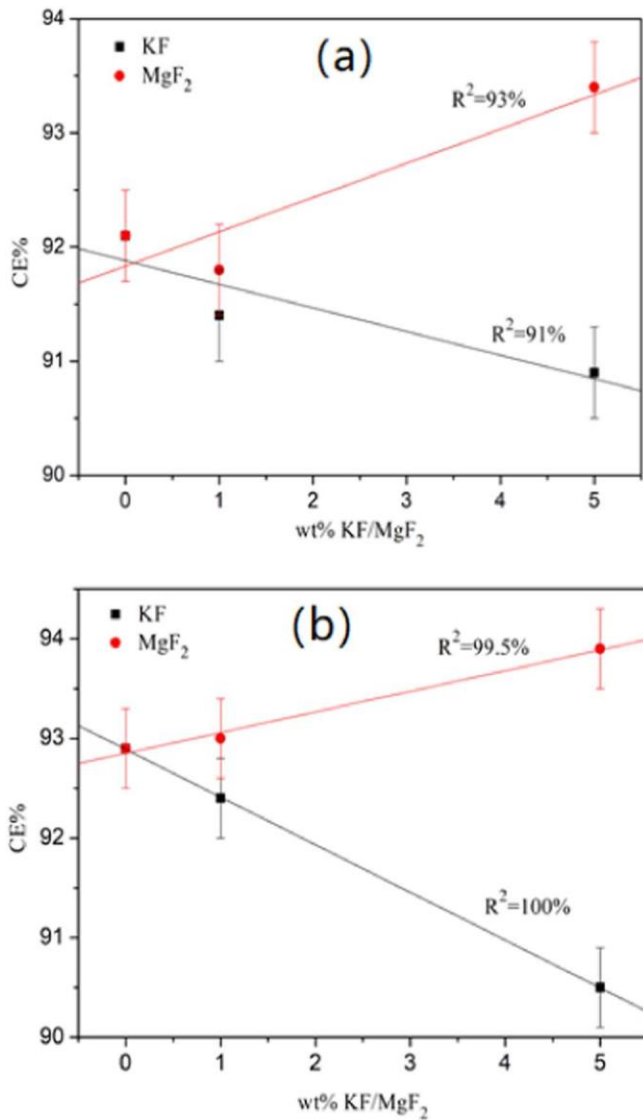


Figure 3. Current efficiency for aluminium deposition as a function of additions of 1% LiF (a) and 5% LiF (b) together with different the contents of KF and MgF₂.

and MgF₂ wasn't found to raise the current efficiency significantly as expected in this work.

The mixture of additions which have the positive effect is not an efficient path to improve the current efficiency of aluminium deposition. The additives play an important but limited role. It should be noted that additives of up to 5 mass % are beneficial for CE, a higher concentration of additives may cause unacceptable contamination of the aluminium. Although it seems worthwhile considering the possibility of the simultaneous application of both additives using LiF as the major additive, the problem which must be taken into account is the influences of various additives on the physicochemical properties of the electrolyte. Some parameters, such as alumina solubility in the electrolyte, the density, the electrical conductivity and the interfacial tension of the electrolyte, will result in the operating conditions of the cell change.

Metal content in aluminium.—The concentrations of sodium, lithium and potassium in aluminium are plotted as a function of the concentrations of LiF and KF in the melt in Fig. 4. Both the concentrations of sodium and lithium in aluminium were found to increase

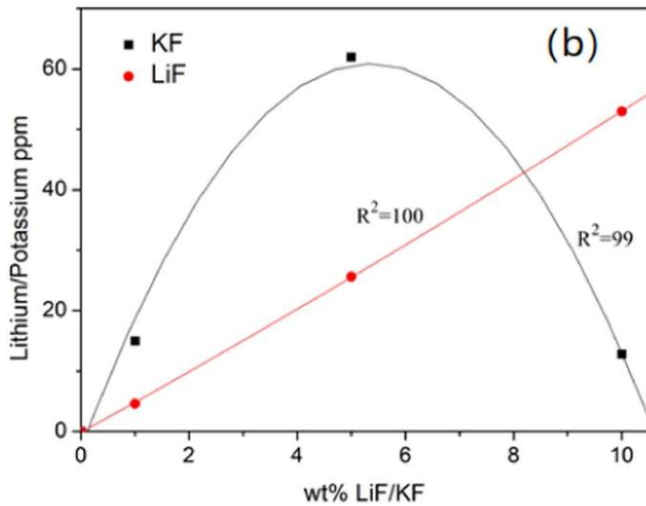
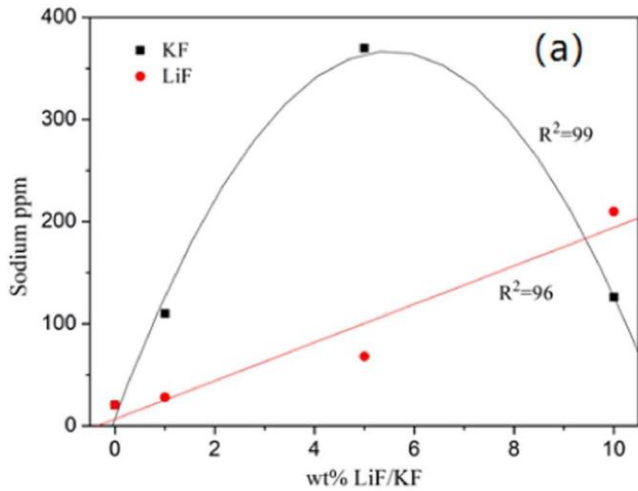
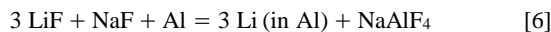


Figure 4. The concentrations of sodium (a), lithium and potassium (b) in aluminium as a function of the concentrations of LiF and KF in the melt.

sodium and lithium in aluminium are related to the composition of the melt at the aluminium/melt interface by the reactions



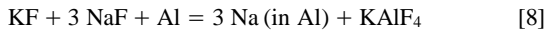
From Fig. 4a, it can be seen that the content of sodium in aluminium increases slowly at LiF addition up to 5 wt %, which is beneficial for the current efficiency of aluminium deposition. However, the content of sodium in aluminium increases rapidly and the current efficiency decrease when 10 wt % LiF was added during the experiment.

Sodium is produced at the bath–metal interface. Tabereaux¹⁹ found the sodium concentration in the metal pad is directly related to the movement at the bath-metal interface. There is a strong relation between the sodium content of the aluminium and CE% in industrial reduction cells. Modern reduction cells have superior magnetic compensation and stable operating conditions, which leads to a low rate of interface movements near the bath/metal interface. Thus, the high sodium level in aluminium means high current efficiency. In this study, the laboratory cell was designed that convection of the electrolyte didn't influence the current efficiency. However, dissolved al-

kali metals often give rise to the existence of electronic conductivity, which may reduce the current efficiency for aluminium deposition process. The excess electrons attributed to dissolved sodium are likely to cause electronic conduction, which may decrease the current effi-

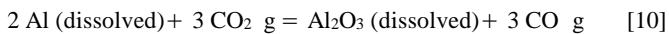
ciency. Therefore, it has the reverse trend compared with the industry cells.

The concentrations of sodium and potassium in aluminium increases with increasing potassium fluoride additions up to 5 wt%. Compared to lithium addition, there is a higher sodium content in aluminium due to the existence of potassium fluoride. The equilibrium content of sodium and potassium in aluminium can be described by the following reactions



The high sodium level in aluminium means low current efficiency in this work. Although 10 wt% KF addition has a lower sodium level in aluminium, it was found to reduce the current efficiency.

The empirical model for the liquidus temperatures of Na_3AlF_6 - AlF_3 - CaF_2 - KF - LiF - Al_2O_3 melts was derived.²⁰ Both KF and LiF can reduce the liquidus temperature of cryolite melts, LiF especially leads to the strongest decrease of the liquidus temperature. The reduction of the liquidus temperatures of the electrolyte is 2.8°C to 4.0°C by 1% KF and 8°C to 9°C by 1% LiF, respectively, dependent on other components.²¹ The use of additives (LiF, KF) as well as an increase of the AlF_3 excess allows decreasing the liquidus temperature of the cryolite melts dramatically. Some metal diffuses from the aluminum pad into the molten bath. The dissolved metal may react with the CO_2 (g) that is formed on the anode, and it is then oxidized in the back reaction:



The back reaction takes place outside the diffusion layer near the cathode/electrolyte interface. The rate of the back reaction is controlled by diffusion of dissolved metal through diffusion layer.²² Thus, the concentration of dissolved metal at the cathode/electrolyte interface and the thickness of diffusion layer are important for the loss in current efficiency.

Conclusion

s

Current efficiencies were obtained at different additions of lithium fluoride, magnesium fluoride and potassium fluoride. LiF up to 5 wt% is beneficial for current efficiency, followed by a considerable decrease of the current efficiency at 10 wt% LiF. Current efficiencies were found to increase with increasing addition of MgF_2 . KF additions above 5 wt% were found to reduce the current efficiency considerably. High unstable voltage fluctuations were recorded at KF additions up to 10 wt% during the experiment. Additions of LiF and MgF_2 can't raise the current efficiency apparently. The presence of KF addition in the electrolyte even can offset the positive effect of LiF addition to decrease the current efficiency. The additives play an important but limited role. The concentrations of sodium and lithium in aluminium were found to increase with increasing lithium fluoride additions. There is a higher sodium content in aluminium at potassium fluoride additions up to 5 wt%. The loss in current efficiency caused by increasing aluminium solubility. That is because LiF and KF additions change the electrolyte composition so that superheat increases. The metal diffuses from the aluminum pad into the molten bath and oxidizes in the back reaction.

Acknowledgments

Funding for this work was provided by Norwegian University of Science and Technology.

ORCID

Peng Cui <https://orcid.org/0000-0002-9500-4412>

Bo Qin <https://orcid.org/0000-0002-9832-6206>

References

1. J. Thonstad, P. Fellner, and G. M. Haarberg, *Aluminium electrolysis: fundamentals of the Hall-Héroult process*, p. 248, Aluminium-Verlag GmbH, Düsseldorf, Germany (2001).
2. D. R. Shirley, in *Light Metals 1985*, H. O. Bohner, Editor, p. 471, *The Minerals, Metals & Materials Society (TMS)*, Warrendale, PA (1985).
3. L. Vujasinovic and S. Gulin, in *Light Metals 1990*, C. Bickert, Editor, p. 341, *The Minerals, Metals & Materials Society (TMS)*, Warrendale, PA (1990).
4. H. Kvande, *JOM*, **46**(11), 22 (1994).
5. K. Grjotheim, K. H. Kvande, and K. Matiasovsky, in *Light Metals 1983*, E. M. Adkins, Editor, p. 397, *The Minerals, Metals & Materials Society (TMS)*, Warrendale, PA (1983).
6. K. Grjotheim, F. N. Xiang, B. Haugsdal, and H. Kvande, *Canadian Metallurgical Quarterly*, **26**(3), 185 (1987).
7. Å. Sterten, S. Rolseth, A. Solheim, and J. Thonstad, in *Light Metals 1988*, L. G. Boxall, Editor, p. 663, *The Minerals, Metals & Materials Society (TMS)*, Warrendale, PA (1988).
8. E. W. Dewing, *Metall Mater Trans B*, **22**(2), 177 (1991).
9. K. Grjotheim, C. Krohn, M. Malinovsky, K. Matiasovsky, and J. Thonstad, *Aluminium electrolysis - Fundamentals of the Hall-Héroult process, 2nd edition*, Aluminium-Verlag GmbH, Düsseldorf, Germany (1982).
10. F. J. Stevens, W. Zhang, M. P. Taylor, and J. Chen, in *Light Metals 1992*, E. Cutshall, Editor, p. 541, *The Minerals, Metals & Materials Society (TMS)*, Warrendale, PA (1992).
11. J. Yang, J. N. Hryn, B. R. Davis, A. Roy, G. K. Krumdick, and J. A. Pomykala, in *Light Metals 2004*, A. T. Tabereaux, Editor, p. 321, *The Minerals, Metals & Materials Society (TMS)*, Warrendale, PA (2004).
12. T. R. Beck, C. M. Macrae, and N. C. Wilson, *Metall. Mater. Trans B*, **42**(4), 807 (2011).
13. O. Tkacheva, J. Hryn, J. Spangenberg, B. Davis, and T. Alcorn, in *Light Metals 2012*, C. E. Suarez, Editor, p. 675, *The Minerals, Metals & Materials Society (TMS)*, Warrendale, PA (2012).
14. P. A. Solli, T. Eggen, S. Rolseth, E. Skybakmoen, and Å. Sterten, *J. Appl. Electrochem.*, **26**, 1019 (1996).
15. P. A. Solli, T. Eggen, E. Skybakmoen, and Å. Sterten, *J. Appl. Electrochem.*, **27**, 939 (1997).
16. R. Meirbekova, G. M. Haarberg, J. Thonstad, and G. Saevarsdotir, *J. Electrochem. Soc.*, **164**, 161 (2017).
17. X. Wang, R. Peterson, and N. Richards, Dissolved metals in cryolitic melts, in *Light Metals 1991*, E. Rooy, Editor, p. 323, *The Minerals, Metals & Materials Society (TMS)*, Warrendale, PA (1991).
18. H. Qin, in 10th International Conference on Molten Salt Chemistry and Technology, p. 444 (2015).
19. A. T. Tabereaux, in *Light Metals 1996*, W. Hale, Editor, p. 319, *The Minerals, Metals & Materials Society (TMS)*, Warrendale, PA (1996).
20. Y. Z. Di, J. P. Peng, Y. B. Bai, and N. X. Feng, in *Light Metals 2013*, B. Sadler, Editor, p. 681, *The Minerals, Metals & Materials Society (TMS)*, Warrendale, PA (2013).
21. J. P. Peng, Y. Z. Di, Y. W. Wang, Y. B. Bai, and N. X. Feng, *J. Min. Metall. Sect. B-Metall.*, **50**(1), 23 (2014).
22. J. Thonstad, P. Fellner, and G. M. Haarberg, *Aluminium electrolysis: fundamentals of the Hall-Héroult process*, p. 228, Aluminium-Verlag GmbH, Düsseldorf, Germany (2001).