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ORIGINAL PAPER

Effect of dopants on wetting properties and electrochemical behaviour of graphite anodes in molten Al_2O_3-cryolite melts

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Abstract The effects of anode dopants and alumina bath content on the wetting properties of the anode/bath interface in an aluminium electrolysis cell have been investigated in this study. Increasing the wettability of the carbon anode maximises the anode surface area and prevents a sudden increase in current density that polarises the anode leading to the discharge of fluoride ions and the onset of anode effect. From the contact angle measurements presented in this study, it is clear that the presence of carbonate salts inside and at the surface of the substrate greatly increases the wettability of the graphite substrate/cryolitic melt interface. The higher the carbonate salt content of the substrate, up to a dopant levels of 6 wt%, the better the wetting properties. Furthermore, alumina appears to act as a surface-active component when present in the electrolyte in contact with a pure graphite anode, but these properties diminish when carbonate is present in the anode.

Keywords Anode effect · Aluminium reduction · Hall–Heroult process · Anode additives

1 Introduction

Many of the theories relating to the mechanism of the anode effect in the Hall–Heroult Process recognise the importance of the wetting properties of the carbon anode at the anode/bath interface during aluminium electrolysis. Many researchers have viewed the anode/low alumina containing electrolyte interface poor wetting properties as directly responsible for the onset of the anode effect [1–3]. As a consequence, gas bubble detachment from the anode becomes more difficult as the alumina content decreases in the bath. These gas bubbles adhering to the anode at low alumina content block the current path and decrease the effective anode surface area This is turn leads to an increase in current density, increasing the overvoltage and provoking the discharge of fluoride ions, leading to the anode effect. Other researchers have repeatedly disputed this mechanism, however, as they observed the anode effect without any gas bubble evolution at the anode [4].

If anode wetting properties are critical in the onset of anode effect in aluminium electrolysis, any factor that can enhance this wetting would be of important practical significance to the reduction of per fluorocarbon emissions during aluminium smelting.

Liu et al. [5] studied several doping compounds as a possible means to reduce the anodic overvoltage. Amongst all the compounds tested by Liu et al. (including LiF, $Pb(NO_3)_2$, $CrCl_3$, $RuCl_3$, NaCl and $PbCl_2$), some were reported to inhibit the anode effect. In particular, chromium chloride $CrCl_3$ and lead nitrate $Pb(NO_3)_2$ showed positive effects on the critical currently density of the carbon oxidation reaction in molten cryolite. Electrolysis could be performed for as long as half an hour under high current densities with no interfering anode effect in the case of the doped anodes. The authors pointed out a possible mechanism. During the fluoride ions discharge, a ternary compound layer CF_xM_Y ($M = $ Cr, Pb, …) is formed which is more conductive than the normal high resistance CF_X layer. It thus

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enhances the electron transfer at the interface and is then thought to inhibit the anode effect. However, this assumption is not based on any experimental results to identify the presence or nature of any surface layer.

Qiu et al. [6] investigated the effect of lithium as a carbon additive on the wetting properties at the interface carbon/cryolite–alumina melts. Carbon plates made of calcined petroleum coke with addition of 3% Li_2CO_3 were compared with some made without additive. Pure graphite plates were also compared to some graphite plates treated with an aqueous solution of Li_2CO_3. It was found that the angle of wetting of the cryolite +5 wt% alumina melts on carbon plates with the Li_2CO_3 additive reduced by 50–60 degrees compared with that without additive at no polarization. When the carbon plates were anodically polarized, the angle of wetting of carbon plates with the Li_2CO_3 additive reduced by 46–80 degrees compared with that without additive.

The effect of dopants on carbon anode wetting in molten cryolite baths is therefore worthy of further investigation in order to understand the relationship between dopant type, dopant levels and alumina content of the cryolite bath on the observed behaviour.

Wetting involves the interaction of a liquid with a solid. It can be the spreading of a liquid over a surface, the penetration of a liquid into a porous medium, or the displacement of one liquid by another. It can help to characterize surfaces and to determine solid/liquid interactions. Wetting properties are usually estimated by the measurement of the contact angle value. The sessile drop method was used for the contact angle measurement at the graphite substrate/electrolyte interface. A schematic diagram is shown in Fig. 1. The contact angle (θ) is a measure of wettability. A low contact angle means high wettability and a high contact angle means poor wettability [7].

Most models assume that, there is no chemical reaction between any of the phases present, in particular between the solid and the liquid. It also means the liquid cannot penetrate into the solid and that the solid has zero solubility inside the liquid.

Non-equilibrium occurs when

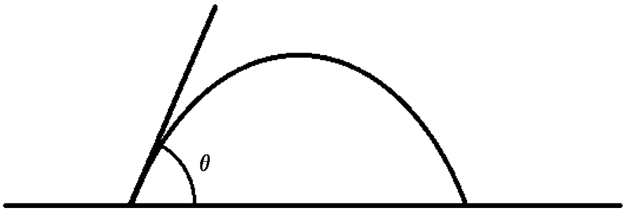


Fig. 1 Sessile drop on an ideal solid surface

- There is a mass transfer between the two phases.
  - Solid soluble into the liquid: mass transfer of solid into the liquid.
  - Solid porous: mass transfer of liquid into the solid.
- There is a chemical reaction between the solid and the liquid, or between any phase involved (reaction solid/gas or reaction liquid/gas)

Wetting under chemical non-equilibrium conditions is significantly different from wetting that occurs under chemical equilibrium conditions, where wetting is only determined by molecular structural differences between the two contacting phases.

In this study, the wetting properties of doped-graphite substrates/cryolite bath interfaces were measured to provide an insight into the mechanism of the inhibition of the anode effect.

2 Experimental

2.1 Electrolyte preparation

The wetting properties between various substrates and different electrolyte compositions were investigated. The different electrolytes analysed included pure cryolite, mixtures of cryolite and 2 wt% alumina, 5 wt% alumina, 10 wt% alumina, or 5 wt% sodium carbonate and finally pure sodium fluoride.

The purest cryolite available for this study was provided by BDH Chemicals and it contained around 0.3 wt% alumina in its as-received condition. For the zero alumina experiments therefore, pre-electrolysis was necessary in order to remove these alumina impurities and be as close as possible to the composition of pure cryolite. A bath of the cryolite was thus placed in a crucible, that was put in the furnace and a pre-electrolysis was performed under inert atmosphere at 2 V for 24 h to achieve very low oxide content in the bath [8]. Samples of the cryolite with or without added alumina were then prepared by placing the required weighed amounts in a vacuum oven and initially heating to 150 °C for 24 h to remove traces of moisture. The crucible was then placed in a high temperature gas-sealed furnace under inert atmosphere; the mixture was melted at around 1,050 °C and left at that temperature for at least 2–3 h to ensure that all the alumina was dissolved. After cooling, solidified blocks were removed from their crucibles and pieces of around 0.10 g were used as specimen for the wetting experiments.

The same procedure as for the alumina/cryolite mixture was used to prepare the mixture of 5 wt% sodium carbonate in cryolite. For the preparation of the pure sodium fluoride specimen, 99.0% AlF_3 (Ajax Chemicals, Australia) was employed in its as-received condition.

2.2 Substrate preparation

Pure graphite as well as doped-graphite substrates for the wettability measurements were prepared by the following cold-mixing doping technique developed by Meunier [8]. After weighing, the desired amount of dopant was added to pure graphite powder in isopropanol and the mixture then placed in a polypropylene bottle with alumina balls for ball-milling overnight in order to ensure homogeneous mixing. After this stage, the solution was poured in a flat beaker, dried first in a fume cupboard for 24 h, then in a vacuum oven for another 24 h. The powders obtained were then pressed into anodes in an 8 mm diameter mould. A list of the different compounds used to dope the graphite samples used in contact area measurements is presented in Table 1 along with the suppliers and other data.

For comparison, undoped-graphite samples were also prepared by the same procedure.

2.3 Wetting measurements

The furnace used for the wettability measurements was a horizontal tube furnace illustrated in Fig. 2 with full details given elsewhere [8].

The furnace atmosphere was a high purity nitrogen atmosphere and the flow rate used was 1 L min^{-1}. The gas was dried in an Alltech moisture trap and deoxygenated in an Alltech oxytrap. This was necessary to avoid oxidation of the graphite substrate at the high temperatures used.

The substrate and the specimen were held in an alumina holder fitted at the top of a steel rod. The specimen was weighed and put on top of the substrate before introduction in the furnace. The wettability measurements were performed at 1,000 °C.

The general experimental procedure consisted of several steps:

- Heating up of the furnace at a rate of 200 °C per hour with no sample present.
- Once the set temperature was reached, the substrate and the specimen were put in the cold zone, at the edge of the alumina tube while the furnace was purged with nitrogen. The alumina holder, the substrate and the specimen were then slowly pushed toward the hot zone at a pace of 5 cm per 5 min to avoid thermal cracking of the alumina holder.
- The recording started just before the melting of the specimen.
- The specimen was left in the hot zone for a certain time of exposure. Its reaction with the substrate sometime brought modification in the contact angle value with time that could be seen on the film.

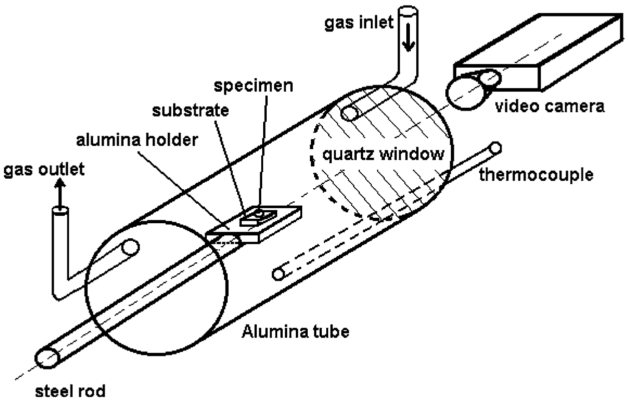


Fig. 2 Schematic of the horizontal tube furnace

The sample was filmed by a high-resolution CCD video camera through a quartz window located on the back of the horizontal alumina tube. The camera was connected to a television monitor and a video tape recorder in order to record, first the melting of the sample on the substrate, and then the spreading of the molten sample across the substrate.

The recorded film was then used to measure the contact angles. Digital images were captured from the film and contact angles were determined from computer analysis of digital images using the mean of the angles determined from each side of the droplet. The experimental method used for contact angle determination was the sessile drop method. Details of the analysis approach are provided elsewhere [9]. The precision of the measurements was ±5°.

Table 1 List of chemical used as dopants

Chemical	Formula	Suppliers	F.W.	Data	Assay (%)
Lithium carbonate	Li_2CO_3	B.P. Townson & Mercer Australia			
Lithium fluoride	LiF	Prepared by S. RAJ in the laboratory			
Sodium carbonate	Na_2CO_3	Aldrich	105.99	m.p. = 851 °C, *d* = 2.532	99.5+
Sodium fluoride	NaF	Ajax	41.99		99.0 min
Potassium carbonate	K_2CO_3	Ajax	138.21		99.5
Lead carbonate	$PbCO_3$	Ajax	267.20		98.0 min
Lead(II) oxide	PbO	Aldrich	223.19	m.p. = 888 °C, *d* = 9.530	

3 Results and discussion

3.1 Wetting properties of pure graphite/cryolitic melts interface

The first measurements were performed with a pure graphite substrate and with cryolite melt containing various alumina contents, as a reference was necessary for comparison with doped substrates further analysed. It was decided to study electrolytes of pure cryolite and cryolite containing 2 wt% Al_2O_3 since anode effect usually occurs within that range of alumina content. To obtain an evolution trend, cryolite containing 10 wt% Al_2O_3 was also studied for all our systems. Moreover, for pure graphite substrates, cryolite with 5 wt% Al_2O_3 was also investigated.

Figure 3a shows the images obtained for different alumina contents of the melt on a pure graphite substrate, while the trend in the measured contact angle versus alumina content is presented in Fig. 3b.

The contact angle value of 135° measured here for the system graphite/pure cryolite was very similar to previous literature results, while the general trend was also very similar to what was presented in previous literature findings. Most authors found a decrease in contact angle with the alumina content in the electrolyte. Metson et al. [10] found a linear decrease over the range from 0 wt% to 6 wt%, but most authors [1, 11–13] presented a decrease trend that could be fitted by an equation of the type

$$\theta = \frac{\theta(0\,\mathrm{wt\%}\ \mathrm{Al_2O_3})}{10^{Kw}} \tag{1}$$

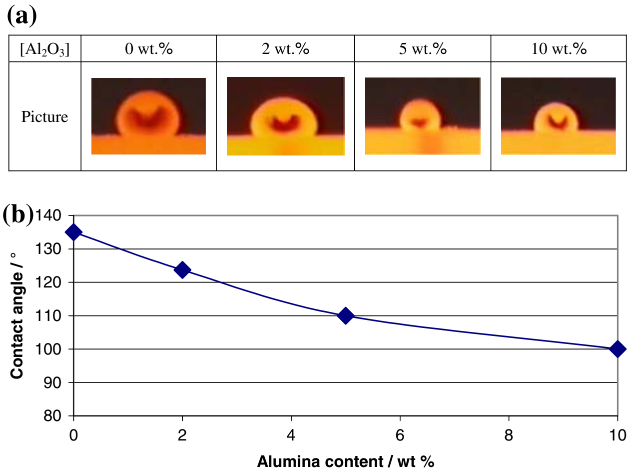


Fig. 3 **a** Images of droplets of molten cryolite, containing various alumina content, resting on graphite substrates. **b** Influence of the alumina content on the contact angle at the interface pure graphite/cryolite

where w is the alumina mass fraction and K a numerical factor that varies between 0.5 and 5 according to authors. Vogt [3] attributed the disagreement between literature results (especially as observed for larger alumina contents) to the action of exposure time and electrode material on wettability, which can vary greatly between investigations. Parameters such as micro-roughness, surface polishness, carbon quality, graphite ash content and so on, can greatly affect the wetting properties at the interface graphite/cryolite. It is therefore not surprising to see results obtained in this work differing in absolute values from previous values published in the literature. Contact angle values obtained in this work, however, followed the general trend observed in the literature and described by Eq. (1).

3.2 Wetting properties of doped-graphite/cryolitic melts interface

In this study, the wetting properties of different carbonate salt-doped substrates/cryolite electrolytes were measured, amongst which were Li_2CO_3, K_2CO_3, Na_2CO_3 and $PbCO_3$. Carbonate salts were chosen since no undesirable foreign anions would be introduced into the cryolite bath. Wetting properties were compared with both undoped and corresponding fluoride salt-doped substrates/cryolite electrolytes. Cryolites containing various alumina contents were tested, as well as substrates containing various dopant concentrations.

Lithium carbonate-doped substrates were studied in detail in order to understand the wetting property improvements observed with the dopants containing carbonate salts. Since it was found that the main effect of dopants on the wetting properties of each system were better observed in pure cryolite, other dopants were only investigated with pure cryolite. It should be mentioned that throughout this study, although not all experiments were repeated to establish reproducibility, those that gave extreme or unusual results were repeated, and the increased wetting of the anode with certain dopants and alumina concentrations was confirmed.

Table 2 presents a summary of the contact angle numerical values obtained in this work for various substrates and electrolytes. These results are discussed in the next section.

3.2.1 Influence of the carbonate molar ratio in the substrate on the wettability at the interface carbonate-doped substrate/pure cryolite

The influence of the carbonate molar ratio in the substrate on the contact angle at the carbonate-doped-graphite/pure cryolite interface was plotted for all carbonate dopants

Table 2 Contact angle values for measurements involving carbonate and fluoride salts as dopants

	Dopant		Electrolyte			
		Additive Content (wt%)	[Al_2O_3] 0 wt%	[Al_2O_3] 2 wt%	[Al_2O_3] 10 wt%	[Na_2CO_3] 5 wt%
Substrate	None	0	134	123	100	119
	Li_2CO_3	1	113	128→81[a]	130	–
	Li_2CO_3	3	59	94	94	–
	Li_2CO_3	6	23	53	48[b]	57
	LiF	6	100	–	–	–
	Na_2CO_3	6	47[c]	–	–	–
	NaF	10	126	–	–	–
	K_2CO_3	6	71	–	–	–
	$PbCO_3$	6	114	–	–	–
	PbO	6	145	–	–	–

Notes: [a] There was a gradual dynamic evolution of the contact angle with time

[b] In a first experiment, there was a sudden transition from 103° to 45° one minute after melting. The droplet went suddenly from a non-wetting behavior to a good wetting shape in a fraction of a second. In a second experiment the contact angle value was found 53° without any sudden transition. The value of 48° was then calculated as the average between 45° and 53°. It was assumed the first value of 103° was an unstable equilibrium

[c] This value was calculated as an average of contact angles measured when observing the cryolite droplet from different orientations

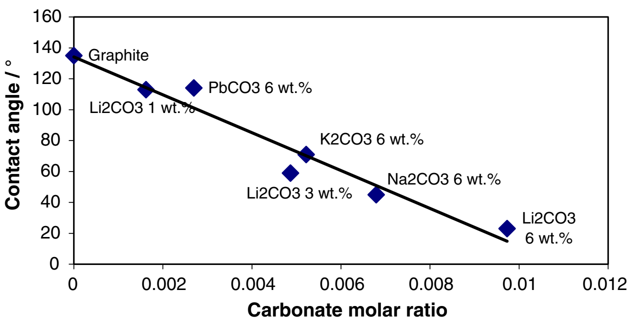


Fig. 4 Influence of the carbonate molar ratio in the substrate on the contact angle at the interface doped substrate/pure cryolite

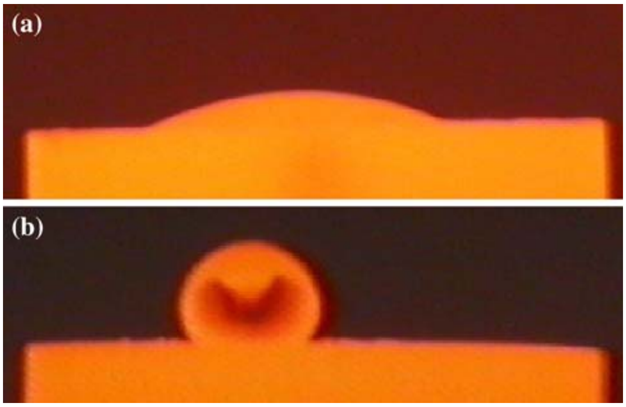


Fig. 5 **a** Drop of molten pure cryolite resting on a 6 wt% Li_2CO_3 doped substrate. **b** Drop of molten pure cryolite resting on a pure graphite substrate

studied. Figure 4 shows the curve obtained. A general trend was observed for all dopants. The higher the carbonate molar ratio inside the substrate was, the better the wettability. The carbonate molar ratio seemed to be the main parameter governing the wettability. However, the nature of the cation (Li^+, Na^+, K^+, Pb^{2+}) also seemed to have a small influence on the wettability. Lithium and sodium carbonate-doped substrates exhibited lower contact angle compare to potassium and lead carbonate-doped substrates. These variations were, however, within experimental error.

The smallest contact angle value, 23°, was found for the system 6 wt% Li_2CO_3 doped substrate/pure cryolite. An image of the molten cryolite resting on this substrate is shown in Fig. 5 to illustrate the high wettability compare to the pure graphite/pure cryolite system.

3.2.2 *Influence of the alumina melt content on the wettability at the interface carbonate-doped substrates/cryolite melts*

Figure 6 shows the influence of the alumina content of the melt on the contact angle at the anode/melt interface for a pure graphite substrate and for various contents of lithium carbonate in the doped substrates. The use of the carbonate-doped substrate significantly increased the wettability, and this increase was much more pronounced at lower alumina content. Results obtained with the substrate containing 1 wt% lithium carbonate were not consistent with results obtained with other lithium carbonate contents.

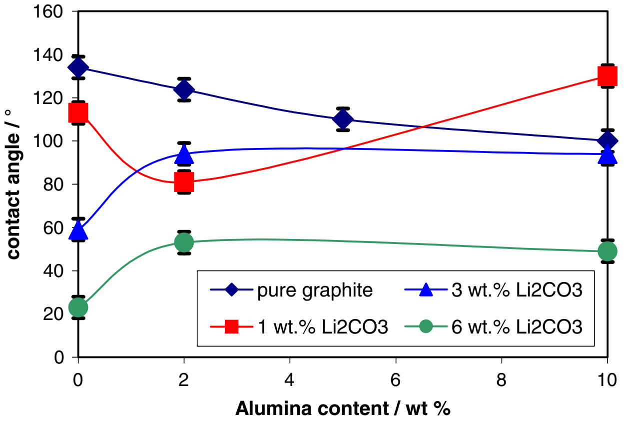


Fig. 6 Influence of the alumina content of the melt on the contact angle at the interface anode/melt. (◇) Pure graphite substrate (■) 1 wt% Li_2CO_3 doped substrate (▲) 3 wt% Li_2CO_3 doped substrate (●) 6 wt% Li_2CO_3 doped substrate

In the first analysis, two parameters were greatly influencing wettability: the carbonate content inside the substrate and the alumina content inside the bath.

The best improvement in the wetting properties was observed for pure cryolite. For example, in cryolite, the contact angle decreased from 135° on pure graphite to 23° on the 6 wt% Li_2CO_3 doped substrate, i.e. a 112° decrease compare to only a 52° decrease with a melt containing 10 wt% alumina. The presence of alumina at a level higher than 2 wt% in the cryolite seemed to somehow decrease the ability of lithium carbonate to improve the wetting properties of the interface.

3.2.3 Dynamic evolution of the contact angle

There were two systems that presented transition regimes where the contact angle was varying with time. In the first case, the substrate was a 1 wt% Li_2CO_3-doped substrate and the melt contained 2 wt% Al_2O_3. Immediately after melting the contact angle was 128° and that value was observed for around 1 min. The contact angle then changed rapidly and decreased down to 81° after 3 min, as shown in Fig. 7. This contact angle value was then stable at longer times.

This dynamic evolution was accompanied by gas evolution inside the droplet. There was a continual gas bubble growth inside the droplet and when the bubble became too large, it was expelled out of the droplet and a distortion of the bubble shape was observed. After one bubble expulsion, another bubble started growing until an explosion occurred, and so on. It was difficult to determine the reaction involved, since it did not appear on other similar systems. This phenomenon might, however, have caused the dynamic evolution in the contact angle. The phenomena of bubble growth and bubble expulsion are shown in Fig. 8.

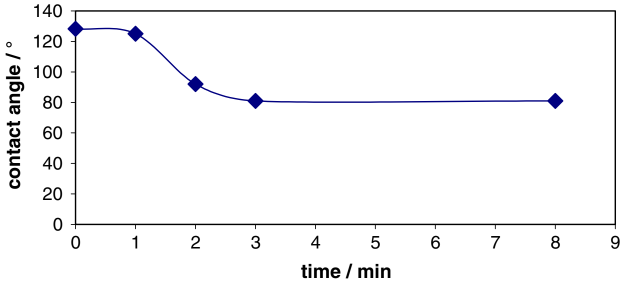


Fig. 7 Evolution of the contact angle with time for the system 1 wt% Li_2CO_3 doped substrate/cryolite +2 wt% Al_2O_3

The dynamic evolution of contact angle found in the system 1 wt% Li_2CO_3 doped substrate/cryolite + 2 wt% Al_2O_3 was hard to explain. A possible explanation was that there was a slow dissolution of carbonate inside the melt that essentially increased the melt alumina content and decreased the carbonate substrate content, which in turn affected the free energies at the surface and/or brought the

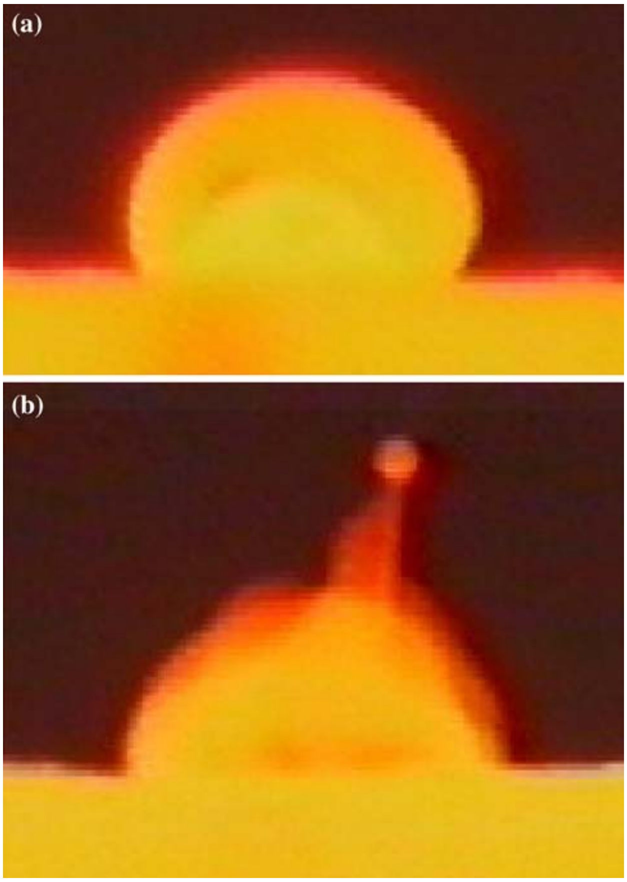


Fig. 8 **a** A gas bubble growing inside the cryolite droplet (The bubble can be detected by the brighter yellow colour at the center of the droplet). **b** Expulsion/explosion of a gas bubble from inside the droplet

system to a different state. The intensity of the observed contact angle decrease, $\Delta\theta = -50°$, was, however, surprisingly large for such a mechanism.

A time transition was also observed in a second system involving a 6 wt% Li_2CO_3-doped substrate and a melt containing 10 wt% Al_2O_3. This transition was not as gradual as the first one observed, but was instead very abrupt. Immediately after melting, the contact angle seemed stable at 103°. Around one minute after melting, the droplet suddenly wetted and adopted a 45° contact angle configuration on the substrate. This value was then stable with time. In another separate experiment, a value of 53° was found to be stable with time from immediately after melting and for longer times. It was then concluded that the first transition observed must have arisen from an initial unstable equilibrium due to surface roughness or heterogeneity that moved into a stable configuration.

3.2.4 *Influence of the dopant content on the wettability at the interface Li_2CO_3 doped substrate/cryolitic melt*

The results presented in Fig. 6 were plotted in another way in order to show the influence of the substrate lithium carbonate content on the contact angle for various alumina melt contents. Figure 9 shows the contact angles immediately after melting as function of Li_2CO_3 content.

From these graphs, the following trends are observed:

- For pure cryolite, the trend was uniform and the contact angle decreased with the lithium carbonate content inside the substrate. The wettability simply increased with lithium carbonate content.
- For melts containing 2 wt% and 10 wt% alumina, the wettability appeared to decrease from a pure graphite substrate to a 1 wt% lithium carbonate content substrate, but then increased at higher lithium carbonate contents.

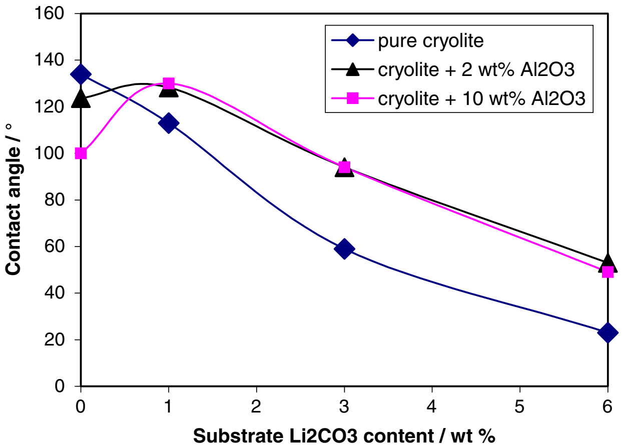


Fig. 9 Influence of the substrate Li_2CO_3 content on the contact angle at the interface doped-anode/melt measured immediately after melting. (◇) Pure cryolite (▲) cryolite + 2 wt% Al_2O_3 (■) cryolite + 10 wt% Al_2O_3

It appeared that the introduction of even a minor amount of lithium carbonate inside the substrate radically changed the surface properties and wettability. With a pure graphite substrate containing no carbonate, the addition of alumina in the melt increased wettability. Alumina thus acts as a surface-active component. When lithium carbonate was inserted inside the graphite substrate, the addition of alumina in the melt decreased wettability. In this case, alumina thus acts as a “surface-inactive” component, in the sense that addition of alumina decreased wettability.

For substrates containing lithium carbonate, melt alumina contents above 2 wt% did not seem to significantly affect the contact angle. Contact angle values with a 2 wt% Al_2O_3 melt were similar to the ones with a 10 wt% Al_2O_3 melt.

3.2.5 *Comparison between carbonates and fluorides*

A comparison between carbonates and fluorides dopants was made by examining the behaviour of lithium carbonate and lithium fluoride doped substrates The pictures of droplets of pure cryolite resting on top of fluoride and carbonate-doped substrates are shown in Fig. 10.

Corresponding contact angle values are represented in Fig. 11 and a much more pronounced decrease in contact angle is seen when carbonate dopants were used instead of the corresponding fluoride dopants.

Once again, it appeared that carbonate group presence was a pre-requisite for a good wettability. The LiF-doped substrate, however, presented a better wettability compare to the pure graphite substrate.

3.2.6 *Comparison between oxide (PbO) and carbonate ($PbCO_3$) doped substrates*

Earlier studies showed that lead dopants can provide good anode effect inhibiting behaviour when inserted inside the anode [5]. The wetting properties of two lead-doped

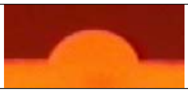
	Fluoride	Carbonate
	NaF – 10 wt.% (0.028 molar ratio)	Na_2CO_3 – 6 wt.% (0.007 molar ratio)
Sodium		
	LiF – 6 wt.% (0.027 molar ratio)	Li_2CO_3 – 6 wt.% (0.007 molar ratio)
Lithium		

Fig. 10 Images of droplets of pure molten cryolite resting on various doped substrates

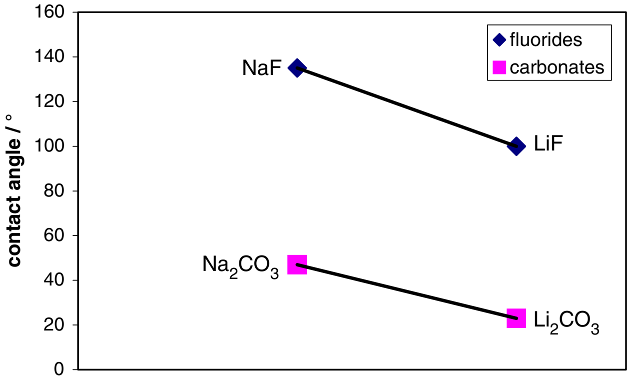


Fig. 11 Contact angle values at various doped-graphite/pure cryolite interfaces. Dopant content = 6 wt% (except for NaF, 10 wt%)

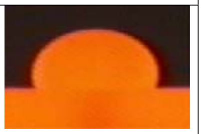
Substrate doped with	PbO – 6 wt.%	$PbCO_3$ – 6 wt.%
Molar ratio	0.0032	0.0027
Picture of molten cryolite		
Contact angle (°)	145	114

Fig. 12 Sessile drops of cryolite resting on lead-doped substrate and corresponding contact angles

substrate/cryolite interfaces (for PbO and $PbCO_3$) were therefore studied to determine any difference between an oxide or carbonate anode additive. Since $PbCO_3$ was expected to decompose into PbO and CO_2 on contact with cryolite, it was thus interesting to establish a comparison between these two lead dopants. Figure 12 shows the sessile drop images for cryolite on both PbO and $PbCO_3$ doped-graphite substrates.

A significant difference in contact angle is observed. These results will be later discussed together with other carbonate-doped substrates results.

3.2.7 *Introduction of Na_2CO_3 inside the electrolyte*

Since carbonate salts used as dopants inside the substrate were proved to bring great improvements to the wetting properties of graphite substrate/cryolitic melts interfaces, it was thought interesting to study the effect of such carbonate salts when added to the electrolyte. Wetting properties of graphite anode/Na_2CO_3-containing cryolite interfaces were studied for a pure graphite substrate and for a 6 wt% Li_2CO_3 doped substrate. About 5 wt% Na_2CO_3 was added to a melt of pure cryolite and this electrolyte was used for the two measurements. The results are presented in Table 3.

It is generally accepted in the literature [14, 15] that when Na_2CO_3 is introduced in a cryolitic bath, it decomposes into Na_2O and CO_2. Evidence for this mechanism is that sodium carbonate has been used to quench anode effect [Welch BJ, *Unpublished data*] since its introduction in the bath during an anode effect is followed by a strong gas evolution that can break the gas layer underneath the anode. It has also been used to increase the NaF/AlF_3 ratio. Indeed, when Na_2CO_3 is introduced into the bath, it liberates CO_2 and the remaining sodium oxide reacts with AlF_3 to produce alumina, thus increasing the NaF/AlF_3 ratio. Mergault et al. [16] also indirectly showed that dissolution of Na_2CO_3 inside cryolite gives dissolved oxides and carbon dioxide.

Results shown in Table 3 can be simply interpreted by such a dissolution mechanism.

$$\begin{aligned} Na_2CO_3 &= Na_2O + CO_2 \text{ followed by } Na_2O + 2/3AlF_3 \\ &= 2NaF + 1/3Al_2O_3 \end{aligned}$$

Knowing that M (Na_2CO_3) = 106 g mol^{-1} and M (Al_2O_3) = 102 g mol^{-1}, adding 5 wt% Na_2CO_3 in a pure cryolite is equivalent to add 1.6 wt% Al_2O_3.

The introduction of 5 wt% sodium carbonate does not have a different effect than adding the equivalent amount of 1.6 wt% alumina, at least within the measurement error. What is important is that it does not have more effect than the equivalent addition of alumina in the system. It does not improve the wetting properties because of the presence of any possible carbonate groups in the bath, but simply because it brings sodium oxide into the bath. This explains why carbonate salts significantly affect wetting properties only when present inside the substrate.

3.3 Electrochemical performance

The effect of doping on the electrochemical behaviour of the graphite anodes was studied using cyclic voltammetry. Figure 13 compares a cyclic voltamogram obtained in on the graphite anode with that obtained with that doped with 3 wt% in a purified cryolite bath containing 0.2 wt%

Table 3 Contact angle values measured for various substrates and various composition electrolytes

Additives		Electrolytes				
		5 wt% Na_2CO_3	Cryolite	2 wt% Al_2O_3	5 wt% Al_2O_3	10 wt% Al_2O_3
Substrates	Graphite	119	134	123	110	100
	6 wt% Li_2CO_3	57	23	53	–	49

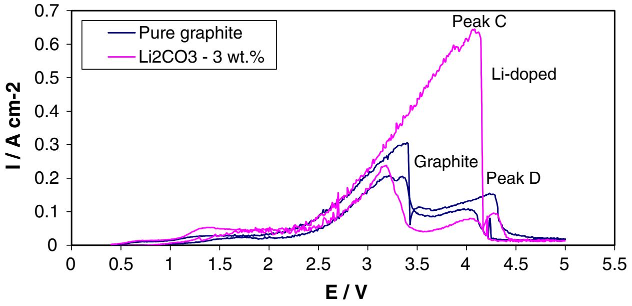


Fig. 13 Cyclic voltammograms obtained in purified cryolite (E = 2 V, t = 10 h) containing. About 0.2 wt% alumina at a pure graphite anode and at a 3 wt% Li_2CO_3-doped anode. T = 1,030 °C, v = 0.1 V s^{-1}

alumina. Prior to addition of alumina, the cryolite was purified by pre-electrolysis at a voltage of 2 V for 10 h to remove impurities.

As seen in Fig. 13, the critical current density, as measured by Peak C height, was much higher with lithium carbonate than without. The anode effect potential was also shifted towards more anodic potentials when the lithium was present in the anode. Reactions in the potential range below 2.5 V did not seem affected by the presence of Li_2CO_3.

Results obtained with a graphite anode doped with 6 wt% Li_2CO_3 showed a critical current density, as measured by Peak C height, of 0.86 Amp cm^{-2} for the graphite electrode, and 2.66 Amp cm^{-2} for the Li_2CO_3 doped electrode. This represented a factor 3 increase in the critical current density and confirms the results obtained from the wetting studies.

3.4 Interpretation

From the contact angle results presented above, it is clear that the presence of carbonate salts inside and at the surface of the substrate greatly increases the wettability of the graphite substrate/cryolitic melt interface. The more carbonate salt presents inside the substrate, the better the wetting properties. Moreover, it seems that carbonate salts only significantly affect wetting properties when present inside the anode, and not when present in the melt. It seems also that alumina acts as a surface-active component when present in an electrolyte in contact with pure graphite anode and that these properties disappear when carbonate is present in the anode.

It is therefore, important to understand one main fact in particular: why do carbonate salts present inside the anode increase the wettability? Some tentative interpretations for the improvement of the wetting properties by carbonate salt doping will be given below.

Consistent with the ionic nature of molten salts, if they dissolve in the molten bead, they could provide an interacting carbonate anion, $CO_3{}^{2-}$. However, the carbonates can also decompose to varying extents in the melt because of their limited stability as is illustrated by the following reactions

$$Li_2CO_3 = Li_2O + CO_2(g) \qquad \Delta G_{1,000^\circ C} = +49\ kJ\ mol^{-1} \tag{2}$$

$$Na_2CO_3 = Na_2O + CO_2(g) \qquad \Delta G_{1000^\circ C} = +146\ kJ\ mol^{-1} \tag{3}$$

$$K_2CO_3 = K_2O + CO_2(g) \qquad \Delta G_{1000^\circ C} = +203\ kJ\ mol^{-1} \tag{4}$$

$$PbCO_3 = PbO + CO_2(g) \qquad \Delta G_{1000^\circ C} = -89\ kJ\ mol^{-1} \tag{5}$$

The situation can be further complicated by exchange reactions to form fluorides of the newly introduced anion as illustrated by the following reactions for Lithium carbonate.

$$Li_2CO_3 = Li_2O + CO_2(g) \qquad \Delta G_{1000^\circ C} = +47\ kJ\ mol^{-1} \tag{2}$$

$$3Li_2O + 2AlF_3 = Al_2O_3 + 6LiF \quad \Delta G_{1000^\circ C} = -204\ kJ\ mol^{-1} \tag{6}$$

$$3Li_2CO_3 + 2AlF_3 = Al_2O_3 + 6LiF + 3CO_2(g) \quad \Delta G_{1000^\circ C} = -156\ kJ\ mol^{-1} \tag{7}$$

$$3Li_2CO_3 + 2Na_3AlF_6 = Al_2O_3 + 6LiF + 3CO_2(g) + 6NaF \quad \Delta G_{1000^\circ C} = -85\ kJ\ mol^{-1} \tag{8}$$

3.4.1 *Dissolution of the dopant at the interface and modification of the electrolyte*

An interpretation for the increase of wettability observed with carbonate dopant could be the following. As can be seen in the reactions written above, the dissolution of the dopant in the bath would modify the bath composition at the interface. Al_2O_3 and NaF are by-products of the dissolution of both Li_2CO_3 and Na_2CO_3. Alumina has been proven to be a surface-active species, so its introduction in the bath at the interface would increase the wettability. Sodium fluoride has also been postulated as being a strong surface-active species [17]. The sodium fluoride bath enrichment at the interface would therefore result in an increase in wettability.

However, the increased wettability observed with carbonate salt doping cannot be fully explained by these mechanisms, since the previous explanation does not fit some of the results obtained in this work. When the alumina content of the bath is increased to the saturation limit, around 10 wt%, the contact angle is only 100°. If the observed improvement of wettability was due to alumina bath enrichment at the interface, the contact angle should not decrease more than this value of 100°. The contact angle was, however, much lower than 100° in many experiments with carbonate dopant. The case of sodium fluoride is more complex since the influence of the cryolite ratio on the wettability was not studied in this work. The contact angle at the interface pure graphite/sodium fluoride only was determined and was found to be 110°. It is therefore postulated that the NaF-enrichment mechanism itself is not sufficient to explain the observed increase in wettability with the use of carbonate dopants.

To be perfectly rigorous and to be able to verify the above theory, the influence of the alumina electrolyte content on the wetting properties should be studied for many different cryolite ratios, particularly at high cryolite ratios (CR > 3). However, this investigation was beyond the scope of the present work.

Another observation that tends to invalid this mechanism is that the wetting properties were better improved by the lead carbonate $PbCO_3$ dopant than by the lead oxide PbO dopant. If the effect of $PbCO_3$ was simply to dissolve and to bring NaF and Al_2O_3 to the interface, then PbO should have the same effect.

3.4.2 *Dissolution of carbonate salt into the bath—presence of CO_3^{2-} ions*

Another consequence of the dissolution of carbonate salt in the melt is to bring CO_3^{2-} ions to the interface. Indeed, reactions corresponding to Eqs. 2–8 above are all expected to produce CO_2 (g), but no gas evolution was usually observed inside the droplet. It is therefore, thought that the dissolution of carbonate salt in the cryolite will bring CO_3^{2-} ions to the interface. CO_2 (g) evolution can then occur with a nucleation and bubble growth process but if no nucleation site is favourable, no gas evolution will occur. One possibility is that these CO_3^{2-} ions act as surface-active species. The more carbonate ions in the bath, the better the wettability.

This mechanism is not supported by results obtained in this work concerning the wetting properties of pure graphite/$Na_3AlF_6 + Na_2CO_3$ melt interfaces. However, it is unclear whether the direct dissolution of sodium carbonate in the cryolite will have the same effect as a gradual dissolution from the substrate. Moreover, supportive results for this theory have been found in the literature.

Fontana and Winand [18] studied the wettability of graphite by $NaF–ZrF_4–ZrO_2$ mixtures. The wettability of a ZrO_2 free mixture was low in an argon atmosphere and increased on replacement with a CO_2 atmosphere. For samples containing ZrO_2 the change to a CO_2 atmosphere had little effect. A change to a CO or CF_4 atmosphere appeared to have no effect on any sample. In Argon, CO, or CF_4, the angle of contact did not vary with time. In O_2 or CO_2, after sufficient time, the graphite was completely wetted. Burnakin et al. [19] also studied the contact angle between an anode and an industrial electrolyte at 980°C under atmospheres of argon and CO_2. The contact angle in a CO_2 atmosphere was markedly smaller, decreasing from 140° under argon to 69°–112° under CO_2, depending on the sulphur content of the anode used.

In both works, the use of a CO_2 atmosphere instead of an argon atmosphere greatly improved the wetting properties. These large modifications could be due to surface tensions modification. Indeed, $\gamma_{\mathrm{graphite}/CO_2}$ might be different from $\gamma_{\mathrm{graphite/argon}}$, and $\gamma_{\mathrm{cryolite}/CO_2}$ might be different from $\gamma_{\mathrm{cryolite/argon}}$. It was difficult to find precise literature data for these surface tensions. But modifications could also arise from the dissolution of CO_2 inside the droplet resting on the substrate, following Henry's law, and subsequent formation of CO_3^{2-} that could in turn act as a surface-active component.

Rey [20] pointed out carbon dioxide was soluble in cryolite-alumina melts at 1,300 °K, and the author proposed CO_3^{2-} as a product of dissolution. Dissolution of CO_2 into cryolite was studied quantitatively by Numata and Bockris [21]. A value of 7.73×10^{-4} Mol L^{-1} atm^{-1} was found for CO_2 at 1,285 K in cryolite.

3.4.3 *Functional groups surface modification*

Another consequence of the carbonate doping is the presence at the substrate surface of carbonate $–O–CO_2$ functional groups. Even if there is partial dissolution of the carbonate dopant and a transfer into the cryolite, some groups would remain at the substrate surface. Those groups can be considered as Lewis base since they possess non bonded electron pairs. AlF_3 is a Lewis acid since the aluminium does not fulfil the octet rule and possesses an electron deficiency in its electronic orbital. There is therefore, an acid–base interaction at the interface between AlF_3 and $–CO_3$ and this Lewis acid–base interaction might play a role in the wetting properties of the interface. The affinity of AlF_3 for these electron-rich groups at the surface is translatable into a chemical potential that could induce the observed wetting improvement.

3.5 Effect of carbon matrix

In the above analysis, the presence of the carbon matrix was ignored and it was assumed that there was no interaction between the additives and the anode carbon within the time-frame of the experiments. Lead carbonate is expected to be very unstable, however, and the carbon matrix will thermodynamically reduce lead oxide even at a temperature below 200 °C. Accordingly the net formation of lead fluoride may not actually occur in that instance, although slow kinetics may change this situation over the relatively short time-frame of these experiments. Furthermore, carbon dioxide is converted to carbon monoxide in the presence of the carbon.

Thermodynamics would thus suggest that there would not be much carbonate present at all in some of these systems although slow kinetics may change these predictions. A reaction mechanism is likely therefore to be responsible for the wetting behaviour of the cryolite baths at the doped carbon surfaced examined in this study.

4 Conclusions

In this study, the effect of dopants on the wettability of carbon anodes by molten cryolite was studied with quite dramatic effects observed as a function of dopant type, content and alumina concentration in the bath. Although not all experiments were repeated to establish reproducibility, those that gave extreme or unusual results were repeated, and the increased wetting of the anode with certain dopants and alumina concentrations was confirmed.

Increased anode wetting, particularly at low alumina contents, may assist in delaying the onset of anode effect in the aluminium reduction cell by preventing an increase in current density due to surface area reduction. Any dopants used for this purpose should not introduce undesirable impurities into the molten cryolite bath that will lead to metal contamination and lithium carbonate meets this criterion. Although no definite conclusion could be drawn concerning the exact mechanism by which the wetting properties increase when a carbonate dopant is used inside the substrate, the results of this study have demonstrated that it is possible to drastically increase the wetting properties at the graphite/melt interface by adding reasonable amounts (for example 6 wt%) of dopant into the graphite. The wetting of carbonaceous materials by a melt is greatly affected by the electrode potential imposed. However, if the carbon is charged positively, with a potential lower than that required for oxidation of the oxy-anion, the wetting of carbon is diminished [22]. Imposed potential is therefore expected to influence the wetting behaviour of the doped and undoped anodes in aluminium electrolysis. Preliminary electrochemical studies have shown that, the electrochemical behaviour of the doped anodes is enhanced with a dramatic increase in the critical current density observed before anode passivation. Further electrochemical studies of doped anodes in alumina/cryolite baths have been conducted and results from cyclic voltametric and galvanostatic studies will be presented in a separate paper.

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