# ADDITION OF LITHIUM CARBONATE TO THE ANODE PASTE USED IN SÖDERBERG CELLS①

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**ABSTRACT** Laboratory studies showed that addition of about 0.5%(in mass) $Li_2CO_3$ to the anode used in an aluminium electrolysis cell gave increased wetting of the anode by the cryolite-alumina melt, increased critical current density and reduced anodic overvoltage. The lithium carbonate then acted as a catalyst for the oxidation reaction between the anode carbon and the oxide-containing ions in the melt. Anode paste containing lithium carbonate has been employed in Chinese aluminium smelters with 62 kA HSS cells. This lead to improved current efficiency, reduced cell voltage and energy consumption, as well as fewer anode effects per day.

**Key words** lithium carbonate anode paste Söderberg cell

## 1 INTRODUCTION

In the industrial aluminium electrolysis process, addition of $Li_2CO_3$ to the electrolyte is presently used by a number of smelters world-wide. $Li_2CO_3$ is superior to all other additives with respect to the physico-chemical properties of cryolite-alumina melts. The main practical effects are lower electrolyte temperature and higher electrical conductivity, which in turn may improve the current efficiency and reduced the energy consumption of the cells.

The common way of supplying $Li_2CO_3$ is in the form of a powder added directly into the molten electrolyte. Some years ago extensive research work was done to study the possibility for addition of $Li_2CO_3$ to the anode paste used in Söderberg cells[1-3]. The purpose of the present work has been to report some further studies on this subject, both in the laboratory and in industrial scale.

One may say that the purpose of using $Li_2CO_3$ mixed into the anode paste is twofold. First, lithium carbonate may act as a catalyst of the anodic oxidation reaction in the process, and secondly, the carbon anode then may act as a more or less continuous supply of $Li_2CO_3$ to the electrolyte when the carbon is gradually consumed by the anode reaction.

## 2 LABORATORY MEASUREMENTS

### 2.1 *Anode Sample Preparation*

Petroleum coke and pitch were used to make the anode samples. 0.5%(in mass) $Li_2CO_3$ was then mixed with the green anode paste, and the anode samples were then pressed and baked at 950 ℃.

### 2.2 *Wettability Studies*

Anode plates were made from samples with and without $Li_2CO_3$ added. Fig. 1 illustrates the time dependence of the wetting of a cryolite-alumina melt sample on a $Li_2CO_3$-containing carbon anode plate. It took only 2 min

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before the melt wetted the carbon plate completely. If the anode plate contained no $Li_2CO_3$ the melt could stay for 7 to 10 min before the wetting was complete.

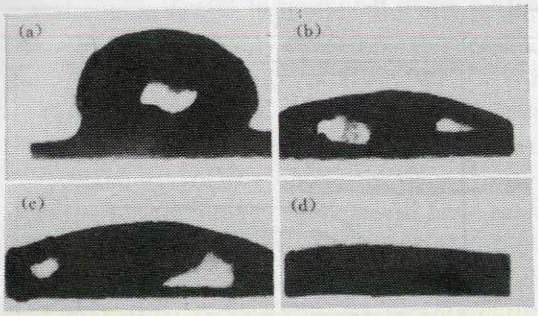


**Fig. 1 Wetting of a sample of a cryolite-alumina melt on a plate made of anode carbon with addition of 1% (in mass) $Li_2CO_3$**

(a)—Just after melting; (b)—1 min after melting; (c)—2 min after melting; (d)—3 min after melting

If a direct current was passed through the melt, the situation changed. Current densities of 1.76 and 3.52 A/cm$^2$ were employed. In these cases the melt could stay for 4 min on a carbon plate with no $Li_2CO_3$ content, but only for one minute on a plate with 1% (in mass) $Li_2CO_3$ addition. Thus, addition of $Li_2CO_3$ to the anode improves its wettability, and also if it is anodically polarized. Fig. 2 shows the wetting conditions when current was passed through the melt.

## 2.3 *Critical Current Density Measurement*

Critical current density is defined as the maximum current density which may be attained before an anode effect occurs in the cell. It is an expression of the ability of a given molten salt mixture to cause an anode effect. The critical current density is usually measured by gradually increassing the cell potential, whereby the current then increases until a maximum value is reached. Then it falls off, signalling the approach of an anode effect.

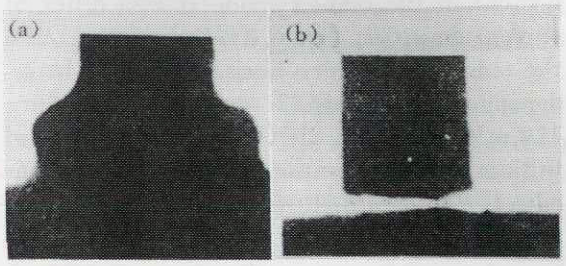


**Fig. 2 Wetting of a drop of a cryolite-alumina melt on a plate made of anode carbon containing 1% (in mass) $Li_2CO_3$, when the carbon plate was anodically polarized**

(a)—Just after melting

(b)—Just after current was passed through the melt

In the present work critical current density measurements were carried out with the $Li_2CO_3$-containing anode material. The results are shown in Fig. 3, where the critical current density is plotted as a function of the alumina content in the melt. It is seen that increasing content of alumina in all measured cases gave a considerable increase in critical current density. The higher values were found when the graphite anode was impregnated with molten LiF. Impregnation with molten cryolite gave lower values, which in turn were found to be higher than for anode samples with no previous melt impregnation.

## 2.4 *Anodic Overvoltage Measurements*

A three-electrode arrangement was used to measure the anodic overvoltage. The working electrode consisted of carbon containing 0%～2.0% (in mass) $Li_2CO_3$. The reference electrode was made of aluminium, while the counter electrode consisted of aluminium contained in a graphite crucible, which also contained the cryolite-alumina melt.

The measurements were carried out by the steady-state polarization method. Fig. 4 shows the general form of the anodic polarization curves. It is seen that addition of $Li_2CO_3$ decreased the anodic overvoltage.

Fig. 5 shows the measured decreases in anodic overvoltage as a function of the $Li_2CO_3$

content in the carbon anode at two different current densities. For 0.8%(in mass) $Li_2CO_3$ the reduction in overvoltage appeared to be independent of the $Li_2CO_3$ content, being 120—150 mV. For a 0.4%(in mass) addition of lithium carbonate to the carbon anode, the anodic overvoltage then was reduced by 40 to 80 mV.

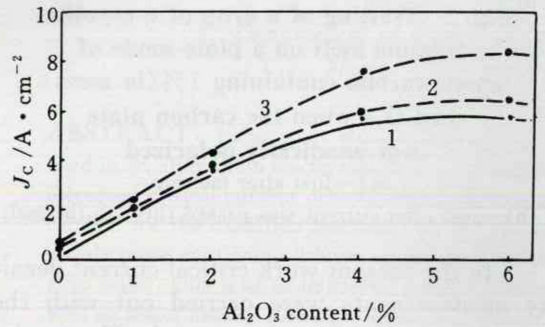


**Fig. 3 Critical current density as a function of alumina content in the cryolite melt**

1—Graphite anode with no previous melt impregnation;
2—Graphite anode impregnated with molten cryolite;
3—Graphite anode impregnated with molten LiF

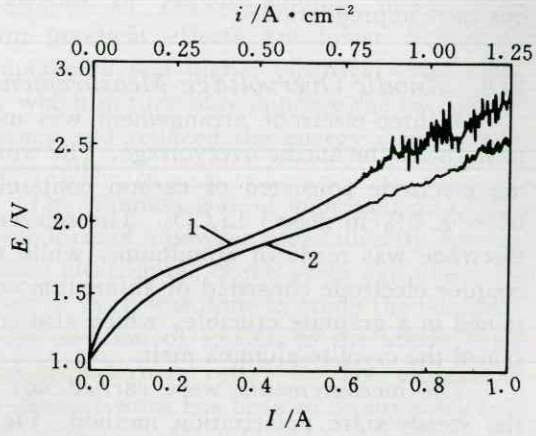


**Fig. 4 The general form of anodic polarization curves**

1—without $Li_2CO_3$ addition;
2—with $Li_2CO_3$ addition

Fig. 6 shows two anodic overvoltage curves of the same lithium-containing carbon anode during the first sweeping (curve 1) and the second sweeping (curve 2) within an interval of 0.5h. These two curves are parallel but with a small deviation of 20mV. This fact il-

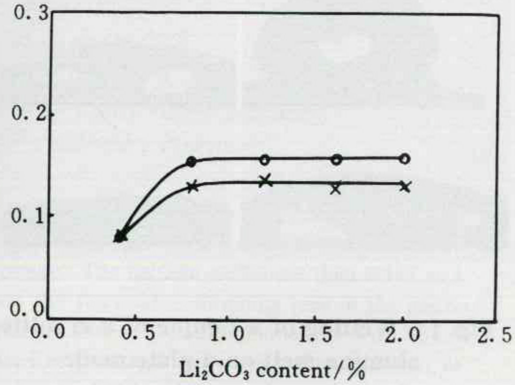


**Fig. 5 The measured decrease in anodic overvoltage as a function of the $Li_2CO_3$ content in the carbon anode at various current densities**

×—0.4 A/cm$^2$;
○—0.6 A/cm$^2$

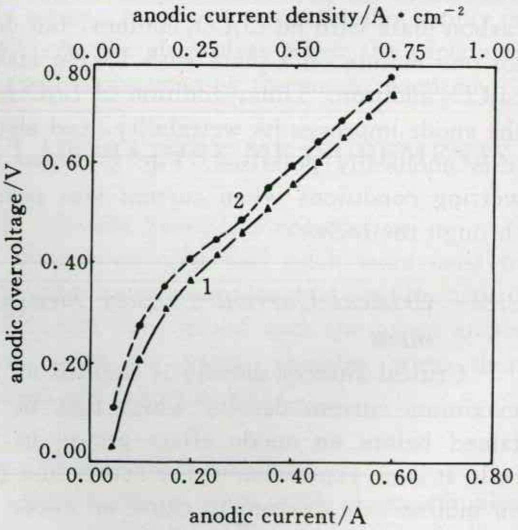


**Fig. 6 Anodic overvoltage curves of the same lithium salt-containing carbon anode during the first sweeping (curve 1) and the second sweeping (curve 2) at an interval of 0.5 h**

lustrates the reliability of the experimental results.

## 3 DISCUSSION

The observed reduction in the anodic overvoltage is probably caused by the presence of $Li_2CO_3$, which may catalyze the carbon-oxygen reaction at the anode. As we have reported earlier in this paper, $Li_2CO_3$ improved the wettability of the anode by the cryolite-alumina melt. Thus, the melt will have easier access to the boundary surface of the anode gas bubbles. The "sweeping" action of the melt may then reduce the gas retention time underneath the anode. The anodic overvoltage caused by the presence of the gas film under the anode may then be reduced considerably.

## 4 INDUSTRIAL APPLICATION

From 1988 the Shandong Aluminium Smelter in Zibo, China, carried out extensive test with anode paste containing $Li_2CO_3$. There were 62 kA Horizontal Stud Söderberg (HSS) cells. First, 6 cells were selected, and then the whole plant was operated with this anode paste. The main operational data were:

Current efficiency: 89.2%

Energy consumption: 14.2 kW·h/kg Al

Carbon consumption: 543 kg/t Al

$Li_2CO_3$ consumption: 2.2 kg/t Al

Furthermore, the cell voltage was only 4.2 V at an interpolar distance of 4.1 cm. The bath temperature was 950 ℃ and the metal and bath heights were 30 and 18 cm respectively. The anode effect frequency was low at 0.18 per day.

Compared to the operational results of a group of reference cells, the current efficiency increased by 0.5% and the energy consumption decreased by 0.26 kW·h/kg Al. These are small, but are significant improvements to an aluminium smelter.

It is interesting to note that by the beginning of 1992, about two thousand Söderberg cells in sixteen Chinese aluminium smelters used anode paste with addition of lithium carbonate[3].

## 5 CONCLUSIONS

The main advantages of carbon anodes containing 0.5% (in mass) $Li_2CO_3$ have been shown to be as follows:

(1) Increased wetting of the anode by the cryolite-alumina melt, increased critical current density, and reduced anodic overvoltage in laboratory experiments;

(2) Improved current efficiency, reduced energy consumption and fewer anode effects were achieved in plant trials with 62 kA HSS cells in China.

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