THE EFFECT OF CURRENT DENSITY ON CATHODE EXPANSION DURING START-UP

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Abstract

During start-up of aluminium reduction cells, sodium penetration causes expansion in the carbon cathode, which may influence the lifetime of the cathode lining. Traditionally, the sodium expansion has been measured at cathode current densities up to 0.75 A/cm^2. However, it is well known that the current distribution in the cathode is non-uniform, and high local current densities may be experienced close to the sideledge, which commonly is associated with the W wear pattern. Hence, the sodium expansion may cause both local stresses in the cathode blocks, as well as in the total cell lining. The aim of this study is to determine the sodium expansion over a wider range of current densities. Typically, it is found that the sodium expansion starts to increase again above 0.7 A/cm^2, after the plateau reached at 0.2 A/cm^2. Apparently, this second increase continues outside the range of 1.5 A/cm^2 applied in this work.

Introduction

Aluminium is produced by electrolytic reduction of Al$_2$O$_3$ dissolved in a cryolite-based electrolyte (bath). The electrolysis takes place in a cell containing the electrolyte and produced metal, see Figure 1. The cell is lined with carbon cathode blocks and carbon ramming paste (bottom), and SiC (sides).
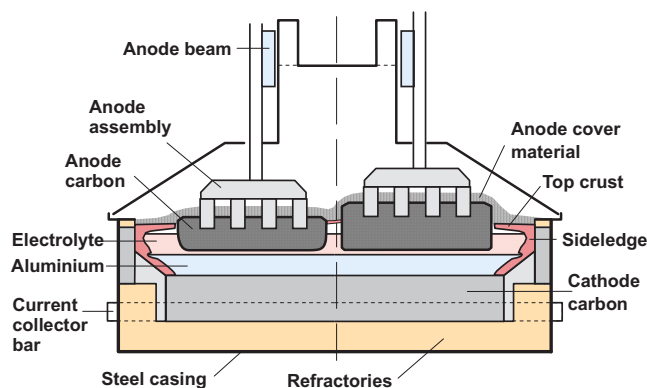

Figure 1. Schematic representation of an aluminium electrolysis cell with prebaked anodes.

The electrolyte, as well as the molten aluminium, contains dissolved sodium metal due to the following equilibrium [1],

$$3NaF \text{ (in bath)} + Al \text{ (l)} = AlF_3 \text{ (in bath)} + 3\underline{Na} \qquad (1)$$

Sodium penetrates into the cathode carbon structure. Besides "opening up the path" for the electrolyte by changing the wetting properties, this causes an expansion of the cathode block. Typically, the sodium penetration and expansion is most noticeable in the early start-up period of a new cell. A method for measuring this sodium expansion was first published in 1957 by Rapoport and Samoilenko [2]. Since that time, the method has been modified several times. One of the modifications is to apply pressure on the sample during the test [3,4].

An important issue for the aluminium industry today is the continuous effort towards increased cell productivity through prolonged cell lifetime and increased potline amperage. A consequence is a more rapid increase in cathodic current density during cell start-up. This will increase the rate of sodium uptake in the cathode blocks and, although it is an efficient way to increase the production capacity, it may have detrimental effects to cell lifetime. In addition, recent studies have indicated increased cathode wear at increasing current densities [5,6]. The aim of this study was to determine the sodium expansion over a wider range of current densities, using a laboratory scale apparatus and different commercial carbon cathode blocks.

Experimental

The following cathode materials were tested:

1. One amorphous block, electrocalcined anthracite with 30 % graphite filler, baked to 1200 °C.
2. One graphitic block, all aggregates graphitized, baked to 1200 °C.
3. One graphitized block, petrol coke filler, whole block calcined above 2300 °C.
4. One graphite reference material.

The sodium expansion measurements were carried out in a RDC-193 apparatus (R&D Carbon Ltd., Switzerland), see the principal drawing in Figure 2. The cathode sample was placed in an anodically polarized graphite crucible containing bath with an initial cryolite ratio (CR) of 4.0. The bath consisted of 71.5 wt% Na$_3$AlF$_6$, 14.5 wt% NaF, 5.0 wt% CaF$_2$, and 9.0 wt% Al$_2$O$_3$. The total amount of bath was 765 g. The anode surface area exposed to the electrolyte was 65.5 cm^2. Since alumina feeding during the experiment was not possible, all the alumina was added at the start of the experiment. For the highest current densities, some excess alumina was added. A constant pressure of 5 MPa was applied to the sample by pressing the graphite extension placed on top of the cathode sample against a stop rod in the top of the furnace by a hydraulic power cylinder. The whole assembly was heated in a tubular furnace to 980 °C and the electrolysis was run until a maximum sodium expansion was reached or for two hours. The cathodic current density was varied between 0.05 and 1.5 A/cm^2. The expansion was measured by an extensometer, which was

attached to the frame of the furnace and measured the position of the crucible support.
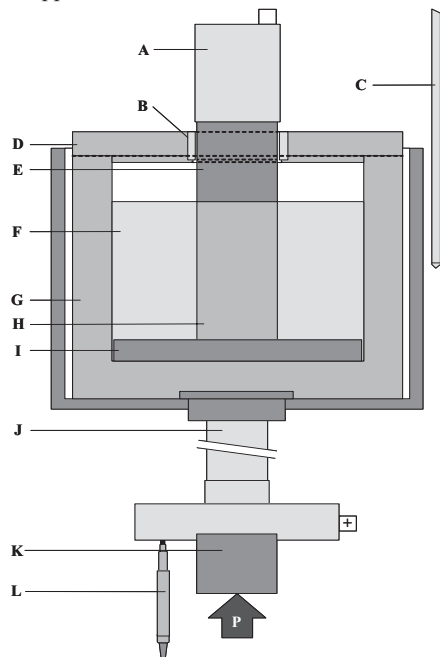

Figure 2.   Principle drawing of the apparatus for measuring sodium expansion. A - heat resistant steel stop rod, B – insulating ring, C – thermocouple (Type K), D – graphite lid, E – graphite cylinder (sample extension), F – cryolitic melt, G – graphite crucible (anode), H – sample (30 mm dia. x 60 mm), I – alumina disk, J – heat resistant steel support, K – Hydraulic power cylinder, L – extensometer (LVD transducer).

Results

Physical Properties of the Materials

The measured physical properties of the cathode blocks are given in Table 1.

Table 1. Average physical properties.

Material	Amorphous	Graphitic	Graphitized
Apparent density (g/cm^3)	1.589	1.650	1.636
Open porosity (%)	14.3	17.8	19.6
Electrical resistivity ($\mu\Omega$m)	24.3	16.7	9.2
Air permeability (nPm)	1.1	6.5	2.3
Compressive strength (MPa)	31.3	23.3	27.0
Young's modulus (GPa)	12.2	7.8	7.3

The Effect of Current Density on the Sodium Expansion

In Figures 3 to 5, the sodium expansion for the different cathode block materials are shown as a function of time for different current densities. Each curve is the average of two to four parallels of each material. The number of parallels can be read from Table 2, showing the sodium expansion as determined from the maximum of the expansion curves of all experiments. The maximum average sodium expansion for the tested materials as function of current density are shown in Table 2 and plotted in Figure 6.
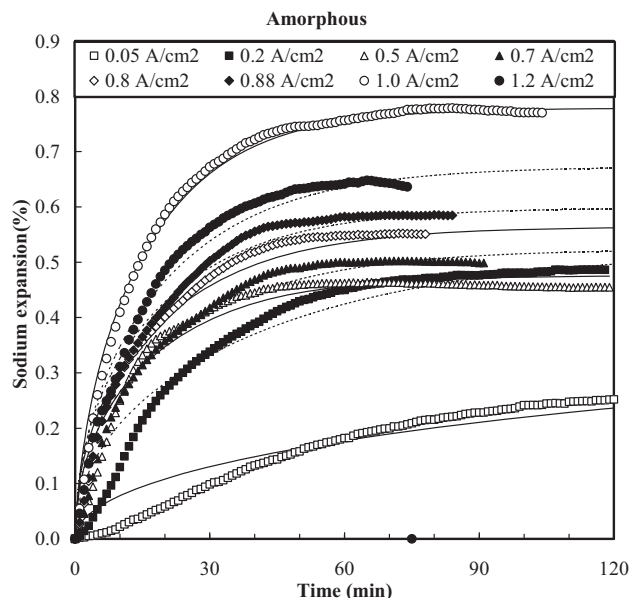

Figure 3.   Sodium expansion versus time for an amorphous cathode block at different current densities. Symbols are experimental data based on 2-4 parallels, lines are modeled data. Applied pressure: 5 MPa.
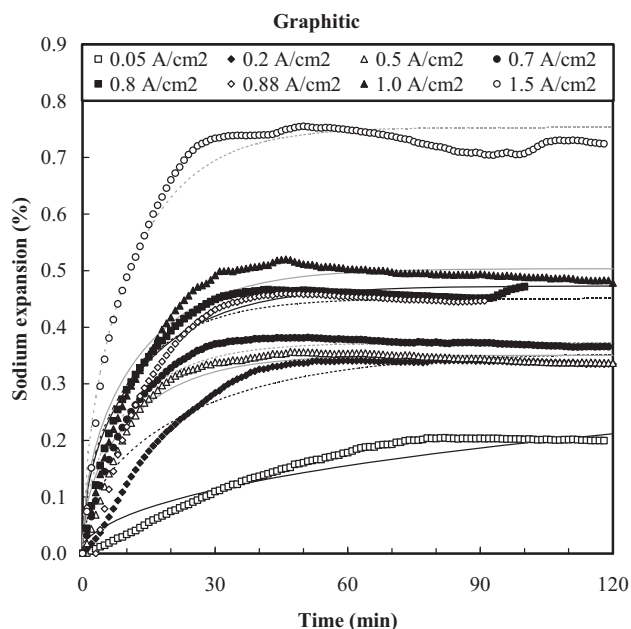

Figure 4. Sodium expansion versus time for a graphitic block material at different current densities. Symbols are experimental data based on 2-4 parallels, lines are modeled data. Applied pressure: 5 MPa.
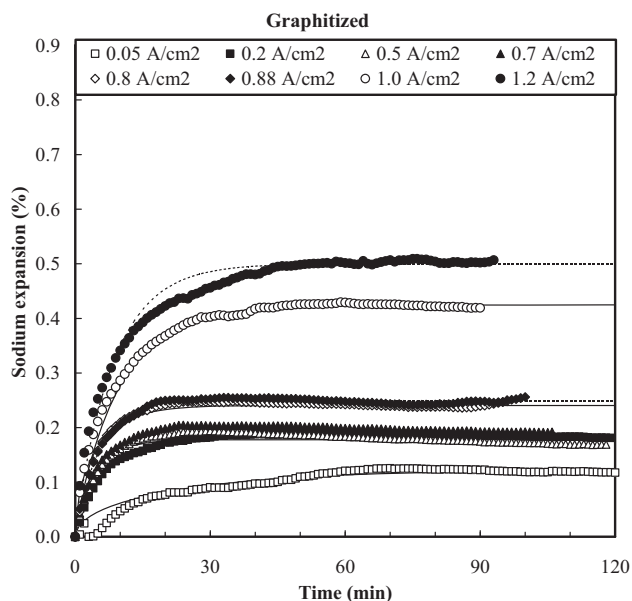
Graphitized

Figure 5.   Sodium expansion versus time for a graphitized cathode block at different current densities. Symbols are experimental data based on 2-3 parallels, lines are modeled data. Applied pressure: 5 MPa.
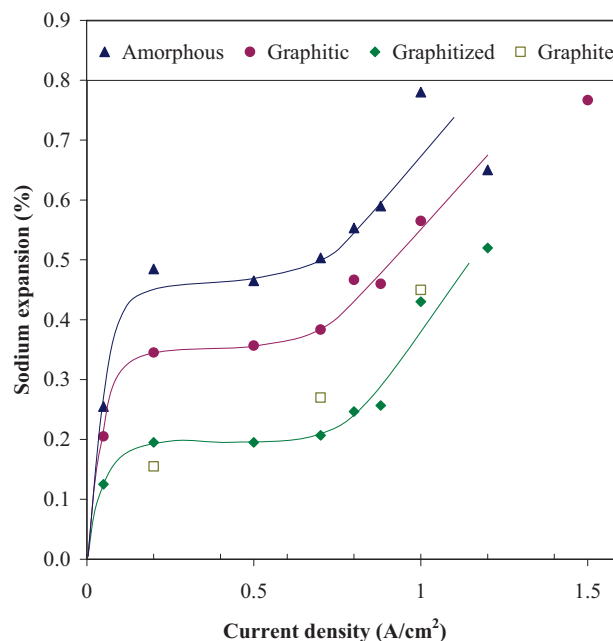
Table 2. Maximum sodium expansion (percent) of cathode blocks at different current densities.

Current density (A/cm²)	Maximum sodium expansion (%)			
	Amorphous	Graphitic	Graphitized	Graphite (ref)
0.05	0.24	0.21	0.13	
	0.27	0.20	0.12	
0.2	0.50	0.31	0.20	0.17
	0.47	0.38	0.19	0.14
0.5	0.44	0.39	0.18	
	0.49	0.33	0.21	
		0.35		
0.7	0.44	0.38	0.24	0.21
	0.54	0.41	0.20	0.33
	0.53	0.36	0.18	
0.8	0.55	0.43	0.23	
	0.54	0.49	0.27	
	0.57	0.48	0.24	
0.88	0.51	0.44	0.23	
	0.66	0.46	0.31	
	0.54	0.47	0.23	
	0.65	0.47		
1.0	0.79	0.52	0.46	0.45
	0.77	0.61	0.40	0.45
1.2	0.63		0.50	
	0.67		0.54	
1.5		0.66		
		0.80		
		0.84		

Figure 6. The maximum average sodium expansion of 2-4 parallels of tested cathodes versus current density. Applied pressure: 5 MPa.

Modeling of the Diffusion of Sodium into the Carbon

Zolochevsky *et al.* [7,8,9] have presented several models for the sodium expansion based on radial diffusion into a cylinder. The model that was found to give the best fit of the experimental data was:

$$\varepsilon_s = AC_0\left[1 - 4\sum_{n=1}^{\infty}\frac{L^2}{\beta_n^2(\beta_n^2 + L^2)}\exp(-D\beta_n^2 t/b^2)\right] \quad (2)$$

where ε_s is the sodium expansion, A is a material parameter describing the sodium expansion, C_0 is the bulk concentration of sodium in the melt, t is the time, b is the radius of the cylinder, D is the apparent diffusion coefficient, L=ba/D, where a is the surface exchange coefficient, β_n (n=1,2, …,∞) are roots of $\beta J_1(\beta)$-$LJ_0(\beta)$=0. $J_0(x)$ is the Bessel function of the first kind of order zero and $J_1(y)$ is the Bessel function of the first kind of the first order.

The sodium expansion after infinite time is defined as ε_s^{∞}=AC_0. The A coefficient is given as a material constant, but may also be regarded as the Na expansion coefficient for the given material. In this perspective, C_0 is in reality a representation of the sodium activity, a_{Na}. Since it is well known that the sodium expansion is reversible, considering C_0 as the Na concentration in the bulk melt is at best misleading. In reality, the factor that determines the measured maximum sodium expansion of a cathode material is a_{Na} at the melt/electrolyte-cathode interface and the sodium expansion coefficient of the material.

To determine the sodium expansion coefficient or material constant A, we assumed that the activity of sodium at maximum sodium expansion (steady state) is independent of the tested

material, *i.e.*, the sodium activity for a given current density is material independent. Using this approach, the material constant may be deduced from the observed differences between the maximum sodium expansion for the individual materials.

In the first approximation of the material constants, we assumed that the activity of sodium at current densities above 0.7 A/cm^2 is linearly proportional to the current density with intercept through origo. This is not an exact approach as current efficiency models show that there is a slight nonlinearity between current density and the activity. However, considering the scatter in the experimental data, this approximation was considered satisfactorily to deduce the material constants for the tested materials. When the sodium expansion coefficient, A, is determined, C$_0$ can be calculated from the maximum of the expansion curves. The deduced materials constants are included at the bottom of Table 3.

The model based apparent diffusion coefficients based on fitting Eq. 2 to the expansion curves are given in

Table 3. The apparent diffusion coefficient increases rapidly from low current densities and levels out for higher current densities (above 0.2 A/cm^2). As expected, the apparent diffusion coefficients increase inversely proportional to the Na content (or the sodium expansion) of the tested materials, Figure 7.

Table 3. Diffusion coefficient (cm^2/s) determined from sodium expansion measurements of cathode block materials at different current densities using Equation (2). Bulk CR = 4.0.

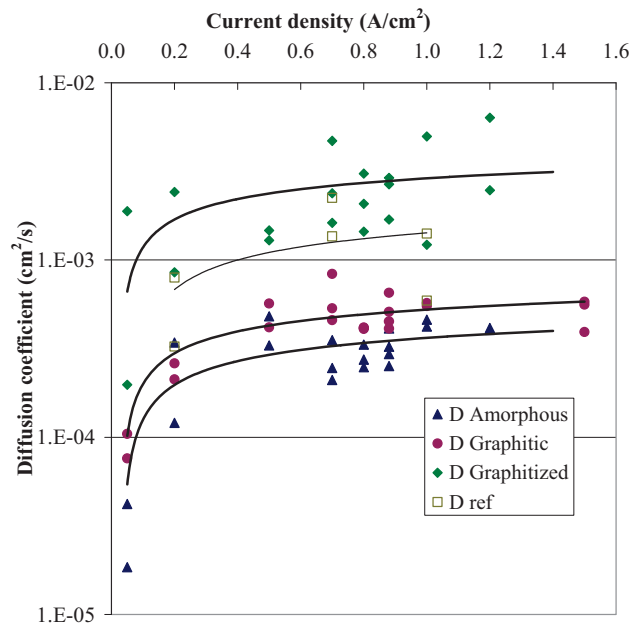| Current density (A/cm^2)	D*10^4 Amorphous	D*10^4 Graphitic	D*10^4 Graphitized	D*10^4 Graphite ref
0.05	0.4 0.2	0.8 1.0	2.0 19	
0.2	3.4 1.2	2.1 2.6	9 24	3.2 8.0
0.5	3.3 4.8	5.7 4.2	15 13	
0.7	2.5 3.5 2.1	4.6 5.3 8.4	24 47 16	14 22
0.8	3.3 2.5 2.7	4.1 4.2 4.1	15 31 21	
0.88	2.5 3.2 2.9 4.1	5.1 4.1 6.5 4.5	29 27 17	
1	4.2 4.6	5.7 5.5	12 50	5.9 14
1.2	4.1 4.0		25 64	
1.5		3.9 5.6 5.8		
A (Na expansion coefficient)	0.68	0.55	0.37	

Figure 7. Apparent diffusion coefficients of Na into different cathode block materials as a function of the current density. Determined from model fitting of sodium expansion measurements.

Discussion

Tested Materials

In line with previous results, the amorphous material has a higher sodium expansion than the more graphitic materials. The graphite reference material has the same sodium expansion as the graphitized material. Normally, graphite materials show even lower sodium expansion, but the type of graphite and how it is heat treated will influence its sodium expansion.

The amorphous material contains more than 60 % anthracite. Even so, the difference between the amorphous material and the graphitic material is small compared to the difference between the graphitic material and the graphitized material. This indicates that the binder phase may be more important for the sodium expansion than the heat treatment of the aggregates used in the materials.

Cathodic Current Density

The investigation of Na expansion at higher current densities is motivated both by the drive towards higher cell productivity through increased current density and the inherent variations in current density across the cathode. The higher current densities at the circumference of the cells, which is especially pronounced for graphitized blocks, may also cause unwanted effects during cell start-up; effects that may affect the long time stability of the cathode block.

From measurements and modeling, it is known that the current density at the cathode varies across the cell, see for instance [10], possibly by a factor of 100 or more, *i.e.*, from very low current

densities in the middle of the cell to values exceeding 10 A/cm^2 along the sides. Two calculated current distributions, based on electrical conductivities typical for amorphous and graphite cathode blocks, are shown in Figure 8.
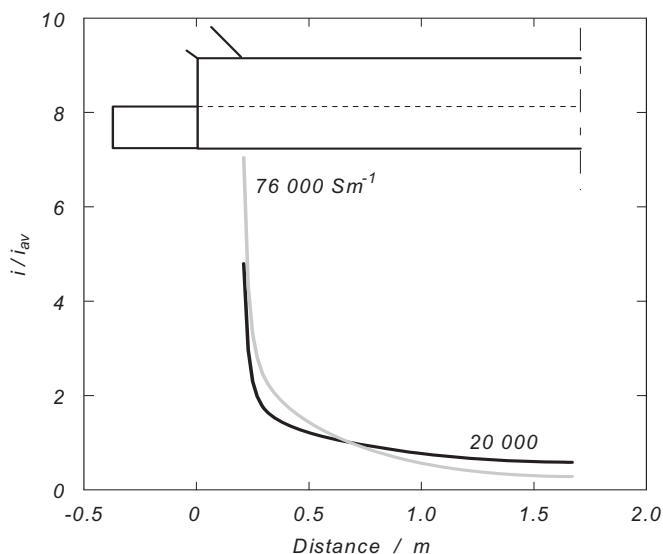

Figure 8.   Example of calculated current distribution across the cathode assuming two different electrical conductivities of the carbon. The bottom ledge extends 0.2 m onto the carbon block.

Also, it is known that the sodium activity increases with increasing cryolite ratio, CR, which also is evident from Eq. 1. Hence, higher sodium expansion is experienced at higher CR. From basic electrochemistry, the NaF content in the diffusion layer towards the cathode is not independent of the current density. Higher current densities will lead to increased CR at the interface, resulting in higher NaF/AlF$_3$ ratio and higher Na activity. This is also in accordance with the observed increase in sodium expansion with increased current density.

All tested materials show a rapid increase in sodium expansion with increasing cathodic current density in the region 0-0.2 A/cm^2 (Figure 6). This is probably due competing reactions, e.g. the formation of aluminium carbide instead of aluminium at the cathode at low current densities [11]. Possibly, also the Na formation may be slower than the diffusion rate of Na into the electrolyte. The increase in the sodium expansion above this low current region is believed to be directly related to the increased cryolite ratio at the cathode surface due to diffusion phenomena related to the cathode reaction.

As a consequence, the cathode block will experience large differences in Na penetration and expansion during start-up. In addition to macroscopic stress over the cathode block, the block may also experience much higher microscopic stresses than previously anticipated. If this conveys to the wear rate experienced later in the service lifetime of the cathode, remains to be examined.

Apparent Diffusion Coefficients

The diffusion coefficient is not expected to vary with the current density (Figure 7). Also, the current model fitting of the expansion curves may not be representative for the true diffusion coefficients, as the model does not take into account a changing activity of Na at the interface between the electrolyte and the cathode. The low diffusion coefficients at low current densities are therefore partly related to the absence of sodium at the interface, as discussed above. The levelling out of the diffusion coefficients at higher current densities is in accordance with an almost linear relation between the activity of sodium, or more precisely, the cryolite ratio at the cathode-electrolyte interface, and the current density [12].

Also the fact that the rim of the cylindrical sample will experience equilibrium with the sodium activity at the interface before the mid of the sample may introduce errors to the model, *i.e.*, the observed expansion curves are only representative for the outer part of the sample cylinders, and as such, introduces inconsistencies to the model.

Implications for the Start-Up Strategy

Common practice today is start-up with bath only, without the presence of metal. The "only bath" strategy inherently means that the cryolite ratio becomes very high at the periphery of the cathode (Figure 8), which experiences a very high and rapid sodium penetration. Our experiments show that this may have a more detrimental effect than previously thought. Adding aluminium during start-up may counteract the fast Na penetration and rapid expansion since the formation of Na in this case predominantly takes place at the aluminium-bath interface. In theory, this should not be a problem, as carbon is not well wetted by Al. Na will then be distributed more evenly throughout the metal pad and the cathode carbon surface will experience a more balanced Na activity. Also, a slightly acidic bath may be beneficial, mainly because this gives lower concentrations of sodium, in addition to having a lower density than a neutral bath. A lower density may reduce or prevent the formation of a bath film between the aluminium pad and the carbon cathode.

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