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CATHODE WEAR IN ELECTROWINNING OF ALUMINUM INVESTIGATED BY A LABORATORY TEST CELL

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Abstract

The lifetime of an aluminum electrolysis cell is mainly determined by the cathode wear, especially for high amperage cells utilizing graphitized carbon cathodes. The cathode wear mechanisms are, however, complex and still subject to debate. Laboratory tests using inverted cell configurations have previously been used to study commercial cathode materials. Here we report on results obtained in the last 5 years for three different commercial cathode materials. The current density applied in the tests was in the range from 0 to 2 A/cm^2 and the rotation speed of the cathode was from 0 to 125 rpm, corresponding to surface velocity 0-19.6 cm/s. The wear mechanisms with respect to current density, limiting current of Al_4C_3 formation and mass transport are discussed. In addition, similarities and differences between wear observed in the laboratory and in industry cells are discussed.

Introduction

The combination of high thermal conductivity, high electrical conductivity and low sodium expansion, compared to traditional anthracitic, semi-graphitic and graphitic carbon materials, make graphitized carbon cathodes the state-of-the-art cathode material in Hall-Héroult aluminum electrolysis cells. The retrofit of old cells to graphite cathodes is also advantageous when smelters gradually raise the cell amperage, and with it the current density. Despite the excellent properties, the graphitized cathode material experiences higher local wear rate compared to the traditional carbon materials. The observed wear rate by industry is: graphitized > graphitic > anthracitic carbon [1].

Cathode wear has become one of the decisive factors which determine the lifetime of the electrolysis cell, especially for the high amperage cell utilizing graphitized carbon materials. The typical observed wear rates are in the range 2-6 cm/year, although parts of the cell see less wear. The uneven wear of the cathode usually gives a cross-section profile resembling a "W" shape or sometimes a "WW" shape [1-4]. It is usually the deepest wear that determines the cell life. To reduce the cathode wear and prolong the lifetime of the cell, it is important to understand the reasons for the uneven wear.

One of the main reasons for the carbon material loss is believed to be the formation, dissolution and transport of aluminum carbide (Al_4C_3) away from the surface [1]. In principle, Al_4C_3 could be formed through both chemical routes described by Reaction 1 and 2 and/or an electrochemical route according to Reaction 3. The chemical formation of Al_4C_3 according to Reaction) and 2 is thermodynamically favorable at the electrolysis temperature [5]. Reaction 1 is however kinetically hindered due to the passive alumina skin present on the aluminum surface as it is likely that the oxygen potential is not low enough in the cell to avoid the oxide skin. Reaction 2 relies on a significant amount of intercalated sodium, which was also argued to be unlikely since highly graphitized carbon has been observed to have highest wear rate but at the same time have minimal Na uptake [1, 6].

$$4Al(l) + 3C(s) \rightarrow Al_4C_3(s) \qquad (1)$$
$$\Delta G(960\ ^\circ C) = -147.6\ kJ/mol$$

$$4Na_3AlF_6(l) + 12Na(in\ C) \rightarrow Al_4C_3(s) + 24NaF(l) \qquad (2)$$
$$\Delta G(960\ ^\circ C) = -217.4\ kJ/mol$$

$$4Al^{3+} + 3C(s) + 12e^- = Al_4C_3(diss) \qquad (3)$$

A tremendous amount of research works have been conducted over the last decades to study the wear mechanisms as well as to establish a "standard accelerated" test method for ranking of commercial carbon cathode materials in terms of wear resistance [7-13]. Although the underlying mechanisms are still under debate, it is generally accepted that the formation of Al_4C_3 is electrochemical in nature. The chemical reactions however, cannot be completely ruled out when fluoride melt is present and/or the Na activity is high.

The Al_4C_3 formed can dissolve and be transported through the metal and bath before being oxidized by the anode gases or at the anode surface. "Fresh" bath should be available in order to continue the wear process. Though the formation of Al_4C_3 is likely to be electrochemical in nature, the wear rate is not proportional to the current density in all current range. Gudbrandsen *et* al.[14] found that the limiting current (i_L) was 0.1 A/cm^2 in their cathodic dissolution experiments at CR equal 1.8 at 960 °C. According to Reaction 3, the limiting current for Al_4C_3 formation can be expressed as Equation 4

$$i_L = 12 \times F \times c_{Al_4C_{3,sat}} \times k \qquad (4)$$

where F is Faraday constant equal to 96485 A·s/mol, $c_{Al4C3,\ sat}$ is the saturation of Al_4C_3 in bulk (mol/m^3), and k is the mass transfer constant in (m/s).

Equation 4 demonstrates that the amount of Al_4C_3 formed by the electrochemical reaction is determined by the solubility of Al_4C_3 in bulk and the mass transfer coefficient. The solubility of carbon in aluminum is 105 ppm counted as Al_4C_3 at 960 °C. The solubility in bath can be two orders higher. Ødegård revealed that Al_4C_3 had maximum solubility around 2 wt% at CR=1.8 at 1020 °C and varied with bath composition [15]. In a typical industry bath composition the solubility is about 1 wt%. Empirical expressions for the solubility and mass transfer coefficient for a vertical rotating cylinder electrode are presented in a later section.

The wear rate results reported here are based on an "inverted cell" configuration originally designed by Rafiei *et* al. [16]. The test cell has been utilized by the authors since 2010 and several modifications has been made [11-13]. This "accelerated" test cell was initially designed to explore the possibility to rank commercial carbon cathode materials at standard operating conditions. Recently the method has been used to investigate the cathode wear dependency on several parameters, e.g. current densities, hydrodynamics and rotation speeds, in order to better understand the wear mechanisms.

Experimental

Materials

Three types of commercial carbon cathode materials were used in the wear test, namely high density graphitized (A), graphitized (B) and anthracitic (C). The physical properties of these materials, including density, porosity and electrical resistivity, have been published previously [13]. Cathode A has the highest density and lowest porosity. Cathode B has the highest porosity. The electrical resistivity of cathode A and B are comparable, while cathode C has three times higher electrical resistivity.

Laboratory Test Cell - "Inverted Cell"

A schematic drawing of the "inverted cell" with a vertical rotating cathode is shown in Figure 1. Carbon samples were cathodic polarized during the test, while the crucible was positive charged and acted as anode.

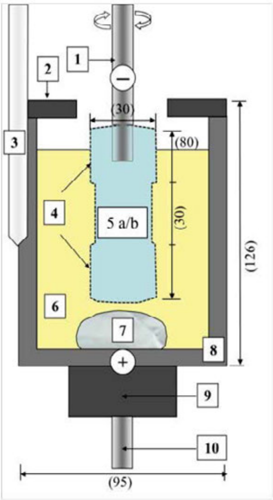

Figure 1. Schematic drawing of the experimental set-up. Dimensions in mm are in parenthesis. 1) rotating cathode connecting rod, 2) sintered alumina lid, 3) thermal couple, 4) Si_3N_4 lining covering both ends, 5 a/b) carbon sample (cathode), a/b represents sample with/without slots, 6) electrolyte, 7) aluminum metal (100 g), 8) graphite crucible (anode) , 9) graphite support, 10) anode lead.

A few high density graphitized samples had slots on the top part of the sample surface, which was used to study the influence of hydrodynamics on the cathode wear. The results have been discussed elsewhere [8]. For a slotted sample, the measurements in this report were taken from the parts without slots.

The initial electrolyte composition is shown in Table I with the cryolite ratio (CR) equal to 2.14. The vertical electrode rotation speeds used were 0, 50, 80 100 and 125 rpm at constant current density (CD = 1 A/cm^2) to study the influence of mass transfer on the cathode wear. A speed of 50 rpm corresponds to a surface velocity of 0.08 m/s, which is a typical linear speed of the bath and metal pad in industrial cells. In addition, the cathodic current density was set to 0, 0.2, 0.5, 1, 1.5 and 2 A/cm^2 at constant electrode rotation speed of 50 rpm. All the tests reported here were conducted for 24 hours at 960 °C. The numbers of samples for each test are summarized in Table II and Table III. Two tests without aluminum present initially were also performed for high density graphitized samples. The detailed test set up and test procedures were given elsewhere [11].

Table I. Electrolyte or bath composition, unit in wt%.

Cryolite/Na_3AlF_6	74.8
Excess AlF_3	12.0
Al_2O_3	8.2
CaF_2	5.0

Table II. Wear tests (number of experiments) at different rotation speeds and constant current density (CD = 1 A/cm^2).

Rotation speed [rpm]		0	50	80	100	125
Graphitized	A	1	7			2
	A-S*	1	4	1	1	1
	B		5			3
	B-S*		1			1
Anthracitic	C		3			3
	C-S*					1

*) S denotes cathode samples with slots.

Table III. Wear tests (number of experiments) at different current densities with constant rotation speed 50 [rpm].

Current density [A/cm^2]		0	0.2	0.5	1	1.5	2
Graphitized	A				7		
	A-S*	2	1	1	4	2	1
	B				5		
	B-S*				1		
Anthracitic	C				3		

*) S denotes cathode samples with slots

After each test, the adhered bath at the cathode surface was carefully removed. Special care was taken to avoid loss of carbon material. The average diameters before and after each test were measured by a caliper and recorded. The wear rate was calculated as the half of this diameter change and normalized to yearly rate. The carbon consumptions were also calculated based on the volume loss and material density by Equation 5

$$c_{loss} = \pi \times h \times (r_{before}^2 - r_{after}^2) \times \rho_c \tag{5}$$

where h is the height of the sample, r_{before} and r_{after} is the average diameter before and after the wear test, respectively, and ρ_c is the density of the sample.

Theory of Limiting Current and Mass Transfer

According to Equation 4, the limiting current for producing Al_4C_3, the main source of carbon materials loss, is proportional to the solubility and mass transfer coefficient. The solubility has a maximum at CR=1.8 and varies on bath composition. An empirical equation was derived by Ødegård for CR>1.8 as expressed in Equation 6 [15]

$$\begin{aligned}\log\left(c_{Al_4C_3}\right) = 1.041 - 0.3949 \times CR - 1.274 \times 10^{-3} \\ \times (t - 1020) - 0.3028 \\ \times \left(\frac{c_{Al_2O_3}}{c_{Al_2O_3(sat)}}\right) - 2.45 \times 10^{-2} \times c_{CaF_2}\end{aligned} \tag{6}$$

where t is temperature [°C], $c_{Al2O3(sat)}$ is the saturation concentration. The concentrations in this equation are in wt%.

In the "inverted" test cell, the rotating cylinder electrode (RCE) was enclosed within a concentric cell. In this case, the critical Reynolds number (Re) for laminar flow is around 200 corresponding to rotation speeds of less than 10 rpm [17, 18]. Dimensionless group correlation has been described as Equation 7

$$\begin{gathered}Sh = 0.0791 \times Re^{0.7} \times Sc^{0.356} \\ Sh = k \times R_i / D \\ Re = R_i \times U / \nu \\ Sc = \nu / D \\ \nu = \eta / \rho\end{gathered} \tag{7}$$

where Sh denotes Sherwood number, Sc denotes Schmidt number, k is mass transfer coefficient, Ri is radii of electrode (m), D is diffusion coefficient (m^2/s], U is peripheral velocity (m/s), ν is kinetic viscosity (m^2/s), η is viscosity (Pa·s) and ρ is density (kg/m^3). Rearranging Equation 7, the mass transfer coefficient k can be described by Equation 8

$$k = 0.0791 \times U^{0.7} \times (R_i)^{-0.3} \times \nu^{-0.344} \times D^{0.644} \tag{8}$$

Equations 4 and 6-8 demonstrate that the limiting current depends on the bath composition, physical properties of bath and rotating speeds.

Results

The appearance of the tested cathode materials before and after 24 hours electrolysis at 1 A/cm current density and rotation speed of 125 rpm is shown in Figure 2. The anthracitic sample C showed more uneven wear pattern.

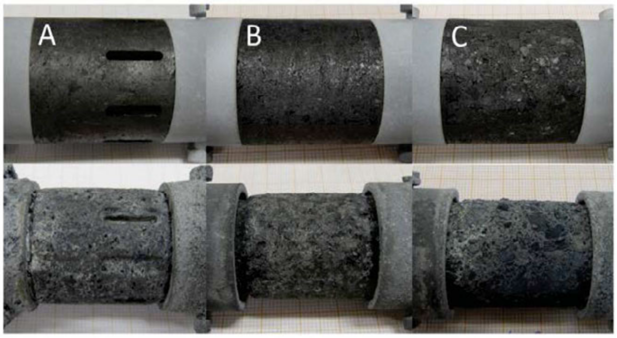

Figure 2. Appearance of tested cathode materials before (top) and after (bottom) 24 hours electrolysis at 1 A/cm current density and 125 rpm. A) high density graphitized, with slots B) graphitized and C) anthracitic.

The average wear rate as a function of rotation speeds for the three commercial cathode materials is shown in Figure 3. The tests were carried out with CR=1 A/cm^2 for 24 hours and the dimensional changes were recalculated to cm/year.

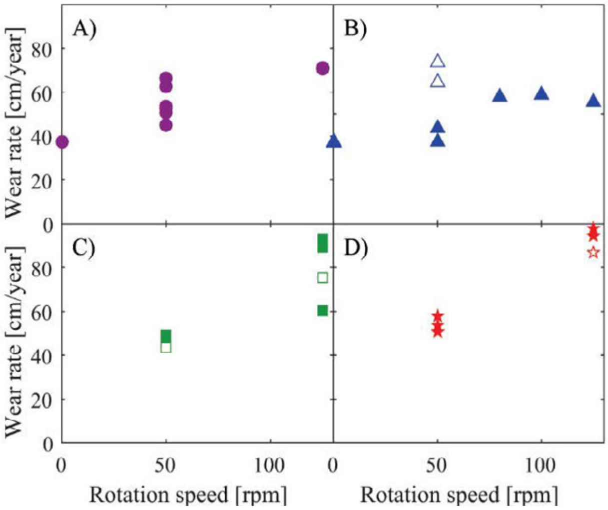

Figure 2. Average wear rates v.s. rotation speeds recalculated to cm/year for three types of cathode materials. A) high density graphitized, B) high density graphitized with slots, open triangle markers represent tests without initial aluminum present in the cell, C) graphitized. Open square and star markers represent the cylinder samples with slots.

The wear rate at stationary bath (no rotation) is significant. This indicates that the natural convection is sufficient to circulate the bath for the formed Al_4C_3 to be dissolved and transported away from the cathode surface and the saturated bath is replaced by "fresh" bath to retain the wear process. With increasing rotation speeds, the forced convection enhances the mass transfer, so that the wear rate increases correspondingly. This could be observed in most of the tests. The rough sample surface after tests made it, however, challenging to obtain accurate measurements and reproducibility is to some degree dependent on subjective interpretation by the person doing the measurements. Consequently, some scatter may be anticipated in spite of equal experimental conditions. The uncertainties due to the measurements have been evaluated. The standard deviations were between 2-6 cm/year after normalization. To avoid confusions in figures, error bars are only shown in Figure 4. The values are representative.

The relationship between wear rate and total cathodic current density for the high density graphitized cathode at constant rotating speed of 50 rpm is shown in Figure 4.

The results clearly demonstrate that there was no wear without polarization, which proves that the cathode wear or the formation of Al_4C_3 is electrochemical in nature. The wear rate is, however, not proportional to the current density. There seems to be a plateau for current densities between 0.2 A/cm^2 (the lowest current applied in the tests) and up to about 1 A/cm^2. The constant wear rate region has the characteristic features of a limiting current, which is in agreement with Gudbrandsen *et* al. [14]. In this case, the limiting current is below 0.2 A/cm^2. The wear rate increased again in the high current density region, which implied another wear mechanism may need to be taken into consideration.

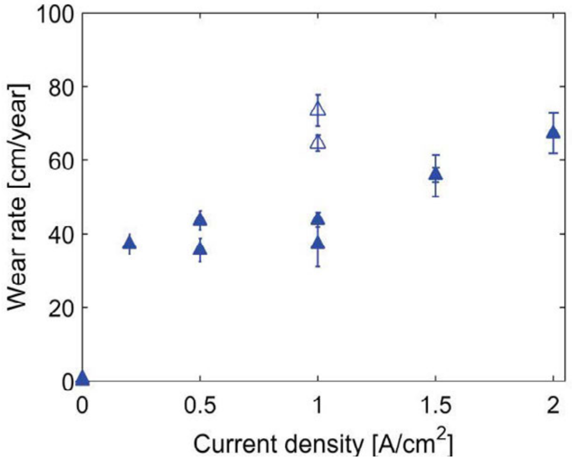

Figure 3. Wear rate as a function of current density for high graphitized carbon material at constant rotation speed of 50 rpm. Open triangle markers represent the tests without adding initial aluminum metal.

Discussion

The general assumption in the calculations provided here is that the wear rate was determined only by the formation, dissolution and transportation of Al_4C_3. Formation of Al_4C_3 was assumed to be the only source for carbon material loss. In this case, according to Equations 4 and 6-8, the limiting current density was proportional to the solubility of Al_4C_3 in the bath and the mass transfer coefficient. To derive the limiting current analytically, the bath composition, solubility and physical properties of the bath are required. Several useful empirical relations are available through previous research [19]. The bath used in the present tests, specified in Table 1, has a viscosity of 2.86×10^{-3} Pa·s and a density of 2056 kg/m^3, which give a kinematic viscosity of 1.39×10^{-6} m/s^2. The solubility limit of Al_2O_3 in this melt was 8.17 wt% and the corresponding solubility of Al_4C_3 derived by Equation 6 was 0.70 wt%. If the cylinder electrode rotated at a speed of 50 rpm, the mass transfer coefficient estimated from Equation 8 would be 5.88×10^{-6} m/s, which results in a limiting current density of 0.068 A/cm^2. The diffusion coefficient in this calculation was chosen to be 9.0×10^{-10} m^2/s. The calculated theoretical limiting current density was much lower than the current densities applied in the reported wear tests.

The amount of electrochemical formed Al_4C_3 could be calculated by Faraday's law according Reaction 9

$$m_{Al_4C_3} = (\frac{Q}{F}) \times (\frac{M_{Al_4C_3}}{z}) \tag{9}$$
$$Q = i \times A \times t$$

where Q is the total charge, M_{Al4C3} is the molar mass, i is the current density, A is the area, t is the time of electrolysis and z=12 according to Reaction 4.

Figure 5 shows the carbon consumption as a function of current density for high density graphitized carbon material at constant rotation speed of 50 rpm after 24 hours electrolysis. Open triangle markers represent the tests without adding initial aluminum metal. Dashed lines are the calculated carbon consumption at limiting current i_L = 0.068 A/cm^2 as derived above.

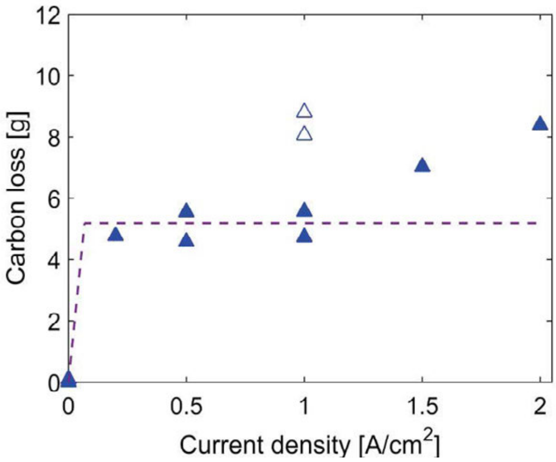

Figure 4. Carbon loss as a function of current density for high density graphitized carbon material at constant rotation speed of 50 rpm. Open triangle markers represent the tests without adding initial aluminum metal. Dashed lines are the calculated carbon consumption at i_L = 0.068 A/cm^2.

There is no doubt that the carbon loss is associated with the current, since no current resulted in no wear. The theoretical carbon consumption is only proportional to the current density until the limiting current is reached and then remained constant with further increased total cathodic current. The calculated carbon consumption fits well the experimental data until the cathodic current density exceeded 1 A/cm^2. The current used to produce Al_4C_3 is limited by the solubility of Al_4C_3 and mass transfer and does not rely on the applied total cathodic current. The limiting current density for this particular bath and rotating speed was close to the estimated value of 0.068 A/cm^2. That is also in agreement with industrial observations: When the local current density was reduced by half, the wear rate did not decrease correspondingly. However, for the areas that the current were cut completely, the wear stopped.

The carbon consumption increases again at the current density region above 1 A/cm^2. The reason for this behavior is not fully understood. The trend of the data in Figure 6 is, however, similar to the Na expansion as a function current density [6]. Na expansion is known to be related to the Na activity in the bath. This similarity implies that the increased Na activity at high current densities may cause increased carbon consumption. The chemical formation Al_4C_3 according Reaction 2 depends on the Na activity. At low current density region, the Na activity is low and the amount of Al_4C_3 formed by this reaction may be limited. In the high current density region, however, when Na activity is high, the amount of Al_4C_3 formed by this reaction may become significant, observed as increased carbon consumption.

The limiting current density depends on the mass transfer in the melt. For a static bath with no stirring or at low rotating speed, the circulation of the bath is dominated by natural convection. The natural convection in the bath is induced by the density difference between the bath in the vicinity of cathode surface and in bulk, as well as the temperature gradient in the bath. With polarization, the bath in the cathodic diffusion layer becomes more basic compared to the bulk due to increased NaF activities [20]. The corresponding density is also higher for the bath in the diffusion layer. Natural convection is likely with respect to the particular test cell set up, so that the carbon loss even in the static bath is quite significant. Increasing rotating speed over a certain level will eventually change the convection from natural convection control to forced convection control. The forced convection enhances the mass transfer and the corresponding limiting current for Al_4C_3 formation, which leads to increased material loss.

Figure 6 shows the carbon consumption as a function of rotation speed for different types of carbon materials. The current density was kept at 1 A/cm^2 for all tests. The calculated carbon consumptions are also displayed in the Figure. Region 1 and 2 in the Figure represents the natural convection region and the forced convection region, respectively. The calculations imply that the transformation from natural to forced convection control occurs at a rotating speed slightly below 50 rpm. These theoretical calculations do not consider the different properties of carbon materials and therefore should be the same for all materials.

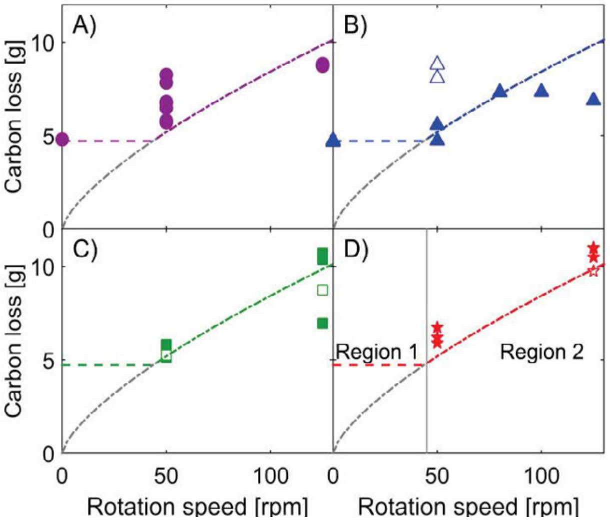

Figure 6. Carbon consumption as a function of rotation speed for A) high density graphitized, B) high density graphitized with slots, open triangle makers represent test without adding initial aluminum, C) graphitized, D) anthracitic. Open square and star markers represent the cylinder samples with slots. For a slotted sample, the measurements were taken from the parts without slot. Dashed and dash-dotted lines are calculated carbon consumptions. Region 1 and 2 represents natural convection region and forced convection region respectively.

The actual wear rates were expected to be higher than the theoretical calculations due to the formation of anode gas bubbles, which may give additional agitation to the bath and therefore faster mass transfer. The test results, despite some scattering, follow the trend of the theoretical calculations, which implies that the wear process is mass transfer controlled. This test method is, however, quite demanding in its practical execution. Especially at high rotating speeds, where the alignment of the vertical electrode is difficult and may cause vibrations that introduces additional uncertainties.

Dependence of Limiting Current on Bath Composition

The solubility of Al_2O_3, as well as the viscosity and density of the bath varies with bath composition, which leads to different Al_4C_3 solubility and mass transfer coefficient. The limiting current density and the amount of carbon loss due to Al_4C_3 formation will then change correspondingly. Figure 7 illustrates these changes as a function of the CR ratio in the range 1.8 and 4, i.e. from acidic bath to basic bath.

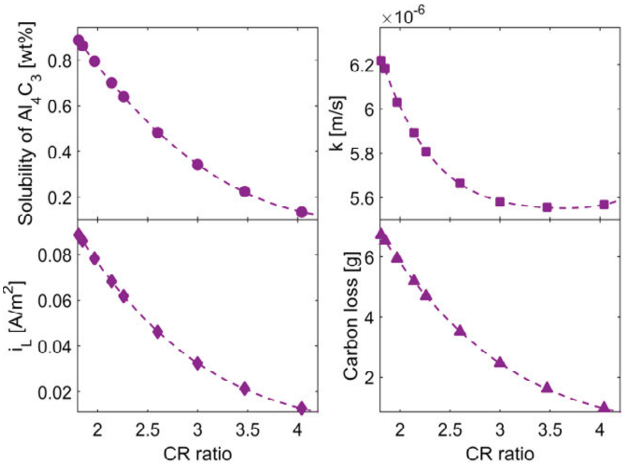

Figure 7. Solubility of Al_4C_3, mass transfer coefficient, *k*, limiting current density (i_L), and carbon loss as a function of bath CR ratio. Caron loss is calculated based on 24 hours electrolysis in the present "inverted cell". Markers represent the calculated points and the dashed lines are polynomial fitting curves.

The calculations demonstrate that increasing the acidity of the bath will increase both Al_4C_3 solubility and mass transfer coefficient (for mass transfer coefficient valid from CR less than around 3.5), and therefore increase the limiting current density and carbon loss. The carbon loss dependency on CR is significant. For example, increasing the excess AlF_3 from 5 wt% to 10 wt% will increase the carbon loss by 14 %. This calculation is based on the wear test set up, where the carbon cathode is exposed directly to the bath and without any aluminum protection layer.

In fact, when the smelters increase the cell amperage gradually, many other improvements are also introduced to the cell to optimize the operation. For example, the amount of excess AlF_3 is increased for improving current efficiency. Despite some advantages, increased bath acidity will increase the solubility of Al_4C_3, which may contribute to increased carbon loss as discussed previously.

Cathode Wear in Laboratory Test Cell and in Industrial Cells

The cathode wear process in the laboratory and the industry cells is similar, which is mainly due to the formation, dissolution and transport of Al_4C_3. The measured wear in the test cell is, however, more than 10 times higher than in the industry with respect to the graphitized carbon cathode, even in a stationary bath. The main difference between the two cells is that in the test cell, the cathode is exposed to fresh bath, whereas in the industrial cell, the cathode is to a much larger degree protected by the aluminum pad. The Al_4C_3 solubility is round 0.70 wt% and 0.01 wt% in the bath in the test cell and liquid aluminum, respectively. According to the observed wear rates in the industrial cells, the aluminum pad is, however, not likely the main source for dissolving and transporting the formed Al_3C_4 in the wear process. Sludge, rich in bath and alumina, has been reported present on the carbon cathode surface, most likely moving with metal pad. The bath in sludge has been found to be less acidic than the bulk, and more or less neutral. It has been also suggested that the cathode is covered by a thin film of bath with similar composition as the sludge. If neutral sludge were the main source for dissolution and transport of Al_4C_3, the carbon loss would be around 45 % lower than that in the test cell environment.

Both the test results and theoretical calculations have demonstrated that the cathode wear is strongly dependent on the local bath chemistry and mass transfer condition. The uneven wear along the cathode surface in industrial cells is actually expected due to the dynamic local environment. The local current density is also important in terms of magneto-hydrodynamic driven (MHD) flow which is related to mass transfer; and Na activity which is related to chemical formation of Al_4C_3 by Reaction 2.

Conclusion

One of the main reasons for the cathode material loss is the formation, dissolution and transport of Al_4C_3. The formation of Al_4C_3 is electrochemical in nature. The wear process is mass transfer controlled. The material loss is proportional to the supplied total cathodic current density only up to a limiting current determined by Al_4C_3 solubility and mass transfer. The mass transfer coefficient for the test cell running at 1 A/cm^2 and a rotating speed of 50 rpm is close to 5.88×10^{-6} m/s, and the limiting current in this case is around 0.068 A/cm^2, which is less than 10 % of the total supplied current. It is the limiting current that determines the amount of material loss. The rotating speed and bath chemistry have a great impact on this. At high current densities, when the Na activity is high, the chemical formation of Al_4C_3 by Reaction 2 cannot be neglected, which might be a plausible reason for the increasing amount of carbon loss at current densities above 1 A/cm^2.

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