Anode overvoltages on the industrial carbon blocks

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Abstract 40 years ago W.Haupin stressed that anode overvoltages on the carbon materials have a scatter more than 300 mV under the same current density. This is a reason to attempt to find out the reason for greater differences because decreasing the overvoltage promises high energy saving. Experiments in lab.cells in galvanostatic conditions have been conducted to determine the overvoltages for the smelter anodes used in Sayanogorsk and Boguchany smelters (Russia) (more than 80 curves currents-overvoltages are received). Overvoltages are compared with other carbon block properties. Recommendations to use these values as a parameter of carbon block quality were made.

Keywords: carbon anode, anodic overvoltage, sodium cryolite, stationary polarization, I-interrupt, carbon reactivity

1 Introduction

The main reaction that takes place in an aluminum cell in the general case can be represented by the equation

$$Al_2O_3 + xC = 2Al + (3-x)\, CO_2 + (2x-3)\, CO \tag{1}$$

where x - symbolizes the variable number of moles of carbon involved in the reaction [1, 2].

Reaction (1) consists of half reactions that take place on the cathode and the anode of the cell. The anodic reactions can be written in a simplified form as:

$$2O^{2-} + C = CO_2 + 4e; \tag{2}$$

$$O^{2-} + C = CO + 2e \tag{3}$$

At industrial current densities, the amount of CO gas generated due to the reaction (3) is much lesser than the amount of CO_2 being a product of the reaction (2) [3-7].

When the reaction (1) and the reactions (2) - (3) proceed with a finite rate from left to right (with current supplied), the potentials of the cathode and the anode deviate from their equilibrium values φ_c^0 and φ_a^0.

The difference between the polarized anode potential φ_a^i and φ_a^0 is the anodic overvoltage

$$\eta_a = \varphi_a^i - \varphi_a^0 \tag{4}$$

The overvoltages on the electrodes lead to an increase in the cell's voltage drop and thereby to an increase in the energy consumption.

The anodic overvoltage at industrial current densities constitutes 10-15% of the cell's voltage drop [9] and, therefore, contributes significantly to the energy consumption. It makes the study of possible ways to reduce the anodic overvoltage being of particular interest.

The anodic overvoltage consists of two components: activation and concentration [8]. The activation component is due to the subsequent slow chemical reaction of the decomposition of intermediate surface chemisorbed complexes of C_yO with the

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formation of CO_2 and CO gases. Taking into account the formation of intermediate complexes, the anodic reactions can be written in the form [1, 8]:

$$2O^{2-} + 2yC = 2C_yO \rightarrow CO2 + (2y-1)\ C + 4e \quad (5)$$

$$O^{2-} + yC = C_yO \rightarrow CO + (y-1)\ C + 2e \quad (6)$$

The concentration (or diffusion) component is due to the slow transport of oxygen ions to the anode surface.

At industrial current densities and alumina concentrations not less than 1 wt.%, the concentration component, according to model estimates using the equations given in [8], does not exceed 25 mV, while the activation component reaches hundreds of millivolts, being the main part of η_a. It is known [1] that η_a obeys Tafel equation ($\eta_a = a + b \cdot lgi_a$) within a limited range of i_a. The origin of Tafel equation is carefully analyzed by Dorreen et. al [3].

Since the activation component is correlated with surface reactions, the η_a depends on the nature of the carbon anode; the technology of manufacturing, which determines the structure of surface layers; the impurities in the anode material, which can accelerate or slow down the decomposition of C_yO complexes [2].

The works of many researchers [9-25] are devoted to the anodic overvoltage measurements. For a given current density, the overvoltage values differ greatly for differently graphitized materials and for different classes of structural ordering. The values of η_a naturally increase with the transition from a less ordered structure of the material (industrial anode block) to a more ordered structure (pyrolytic graphite). The reason for this is a stronger bond between the carbon atoms in the graphite than that in the industrial anode block, which requires a large energy to break it during the decomposition of C_xO complexes in graphite compared to the same process in the industrial anode.

According to the different researchers [10, 11, 23], there is a significant difference in the magnitude of overvoltage even for one class of carbon materials; the difference in overvoltages can reach more than 300 mV when measured on samples made from different industrial anode blocks. It can be assumed that in different experiments carbon materials of different degree of graphitization, as well as with different content of impurities, were used, which, apparently, affected the structure of surface layers and their reactivity [26-32].

It seems expedient to conduct a systematic study of anode overvoltage on samples made from industrial anode blocks of different suppliers, which are obviously obtained using several different technologies, using different pitches and cokes and the proportions of their quantities. The study of a connection between the overvoltages and the properties of anode blocks is the aim of this work.

2 Experiments

To study the correlation between the anodic overvoltage and other properties of industrial carbon anodes being ordinarily measured, more than 80 samples were tested in the laboratory set-up which consists of the electrical furnace, potentiostat Autolab PGSTAT302N with Booster20A amplifier and electrolysis cell depicted in **Fig.** 1.

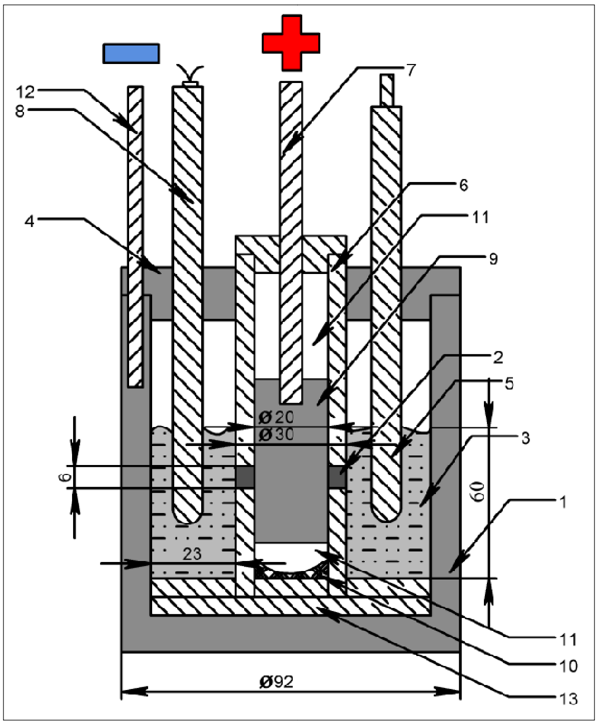

Fig. 1. Schematic representation of experimental three electrodes cell. Numbers in the picture: 1 - graphite crucible h = 110 mm, d_{int} = 76 mm, d_{ext} = 92 mm; 2 - Test sample d_{ext} = 30 mm, d_{int} = M20, h = 6 mm; 3 - bath; 4 - graphite cover; 5 - Reference electrode Al/Al^{+3} in the BN shield; 6 – BN tube; 7 - Anodic current lead made of stainless steel, protected by an alundum tube (not shown); 8 - Thermocouple; 9 - Graphite connector between the sample and the current lead; 10 - protective sealing coating based on BN; 11 - space filled with kaolin wadding; 12 - cathodic current lead made of stainless steel, protected by an alundum tube (not shown); 13 – BN insulating plate

The potentiostat is controlled via the NOVA software v.2.1.2. The thermocouple is connected to the thermostat.

2.1 Samples and bath preparation

All the samples tested in the cell were provided by «RUSAL ETC» with the properties measured with routine anode quality control methods. These properties were : baked apparent density γ_a, compressive strength σ_{comp}, carboxy reactivity residue (CRR), carboxy reactivity dust (CRD), air reactivity residue (ARR), air permeability AP, specific electrical resistivity ρ and ash (in wt.%) A. The samples were made out of anode blocks and were machined to have a cylindrical (or disc) shape with 30 mm diameter and 6 mm height. Before the measurements, each sample was dried at 150°C for 15 hours. During the measurements, the sample was fixed to the graphite connector with a threaded connection.

The active surface area was determined from four measurements of the height and the diameter of the sample as it is shown in Table 1.

Table 1. Calculation of active surface area

Parameter/number of measurement	#1	#2	#3	#4	Average
Height of the sample, cm	0.52	0.49	0.53	0.49	0.506
Diameter of the sample, cm	2.91	2.90	2.91	2.91	2.907
Active surface area, cm^2					4.624

Sodium cryolite with NaF/AlF_3 molar ratio (CR) equal to 2.25 is used as an electrolyte. Cryolite was preliminarily synthesized out of dried NaF and AlF_3 individual salts. The concentration of smelter grade alumina Al_2O_3 is 2.2 wt.%.

2.2 Electrochemical measurements

The samples were tested using the stationary galvanostatic polarization method at 960 °C. Several series of 5 – 8 successive measurements were performed. The electrolyte was changed between the series. Before each series, a steel cathode had been placed in the cell to carry out purification electrolysis at a potential difference of 1.5 V for 30 minutes (to remove more electropositive metals), after which the steel cathode was removed from the cell (during the measurements the graphite crucible served as a cathode). An Al/Al^{+3} reference electrode connected to the potentiostat was immersed in the cell. The samples were polarized in a range from 0.1 to 1.0 A/cm^2 with a step basically being equal to 0.1 A/cm^2.

To determine the ohmic voltage drop the i-interrupt technique was implemented as it is shown in **Fig 2.**

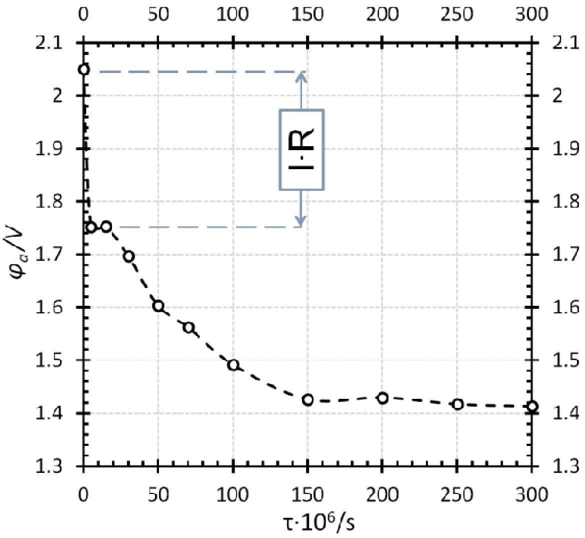

Fig. 2. Example of current-interrupt technique at i_a=0.5 A/cm^2. At $\tau = 0$ current was interrupted after 30 seconds of galvanostatic polarization. The φ_a value has been decreasing during several seconds till the stationary open circuit potential (OCP) was reached.

Each measurement was made twice to calculate the average value of φ_a and the standard deviation. If the difference between the two measurements was more than 10 mV, a control measurement was performed.

3 Results and discussion

More than 80 polarization curves for samples made of industrial carbon blocks were obtained using the same method described above to ensure, that scatter of values measured is not associated with an experimental error. The typical curve is presented in **Fig. 3**.

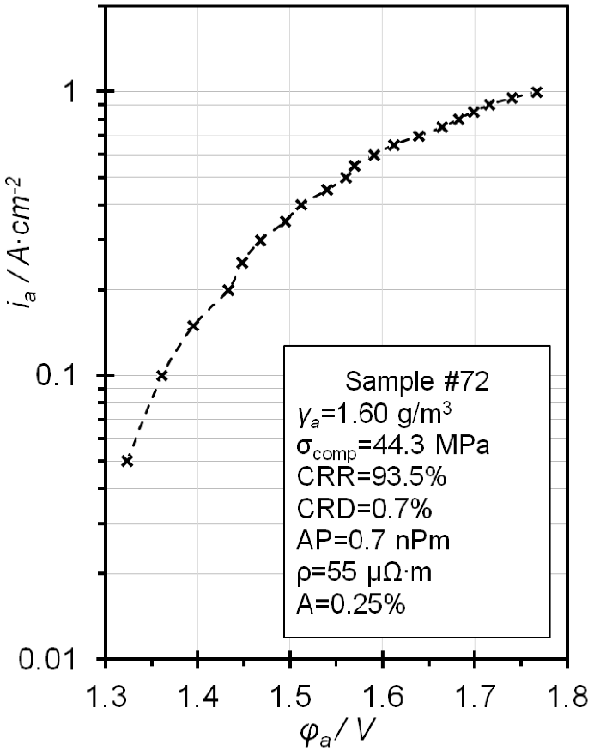

Fig. 3. Example of polarization curve for sample #72 (properties are presented in the note). The symbols have been described in section 2.1.

In the **Fig. 3** the anodic potential at 0.8 A/cm^2 is equal to 1.68 V with a standard deviation less than 1 mV (for two consistent measurements) which corresponds to anodic overvoltage being equal to 444 mV, which is lower than previously reported by other researchers [11, 12]. It means that the electrochemical reactivity is high, which contradicts other properties like CRR or AP. It is known that CRR indicates the energy requirements to break the bonds between carbon atoms in the anode and the active surface area for the reaction with CO_2, which is considered as a function of air permeability. The amount of ash after burnout is a measure of mineral impurities in anode blocks which can act as catalysts. The values of the named properties allow us to expect high overvoltage.

To compare 4 samples (from the same anode plant) with different air permeability the results of overvoltage measurements are represented in the Tafel plot in **Fig. 4.**

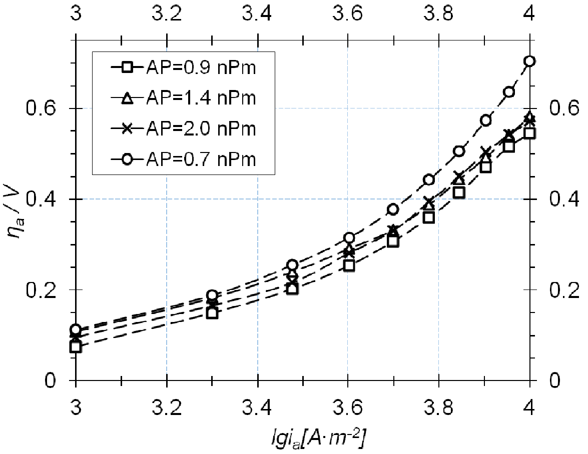

Fig. 4. Tafel plot with η_a-lgi_a dependence of 4 different samples. Air permeability is shown as one of the possible factors affecting the overvoltage.

The sample with the lowest air permeability shows the highest overvoltage in the entire range of current densities, that fully meets the expectations. The difference of more than 100 mV (**Fig. 4**, i_a=0.8 A/cm^2**)** can be explained by the low open porosity of the material, low active surface area and therefore high true current density. Another sample with slightly higher porosity shows much lower overvoltage which is probably due to the combination of several different factors.

An anodic process is basically known to be characterized by a straight line in a Tafel plot $\eta_a - lgi_a$. There are two possible explanations for the deviation observed in the curves of all samples. The first is connected with hyperpolarization that is known [13] to have a substantial value up to 60 mV at low current densities (below 0.2 A/cm^2). This kind of polarization is due to the screening effect of the bubbles reducing the active surface area. To avoid hyperpolarization high speed rotating electrode should be used. The second makes the concentration component of the overvoltage responsible for the deviation from a straight line.

After studying the entire set of samples we can make a preliminary conclusion that overvoltage usually does not directly correlate with other properties. For instance, several samples with extremely high overvoltage have very high carboxy and air reactivity, despite the fact that electrochemical and chemical reactivity are known to be affected by the same factors such as structural order of material, amount of impurities and porosity. Further investigation of the correlation between anodic overvoltage and structural, and chemical and physical properties, are required.

To compare the entire set of samples from two plants, an overvoltage of 0.8 A/cm^2, being similar to industrial current densities, was chosen. **Fig. 5** depicts the scatter in the anodic overvoltage measured in the same laboratory cell under identical conditions and in some cases even in a single series of measurements (without electrolyte being changed).

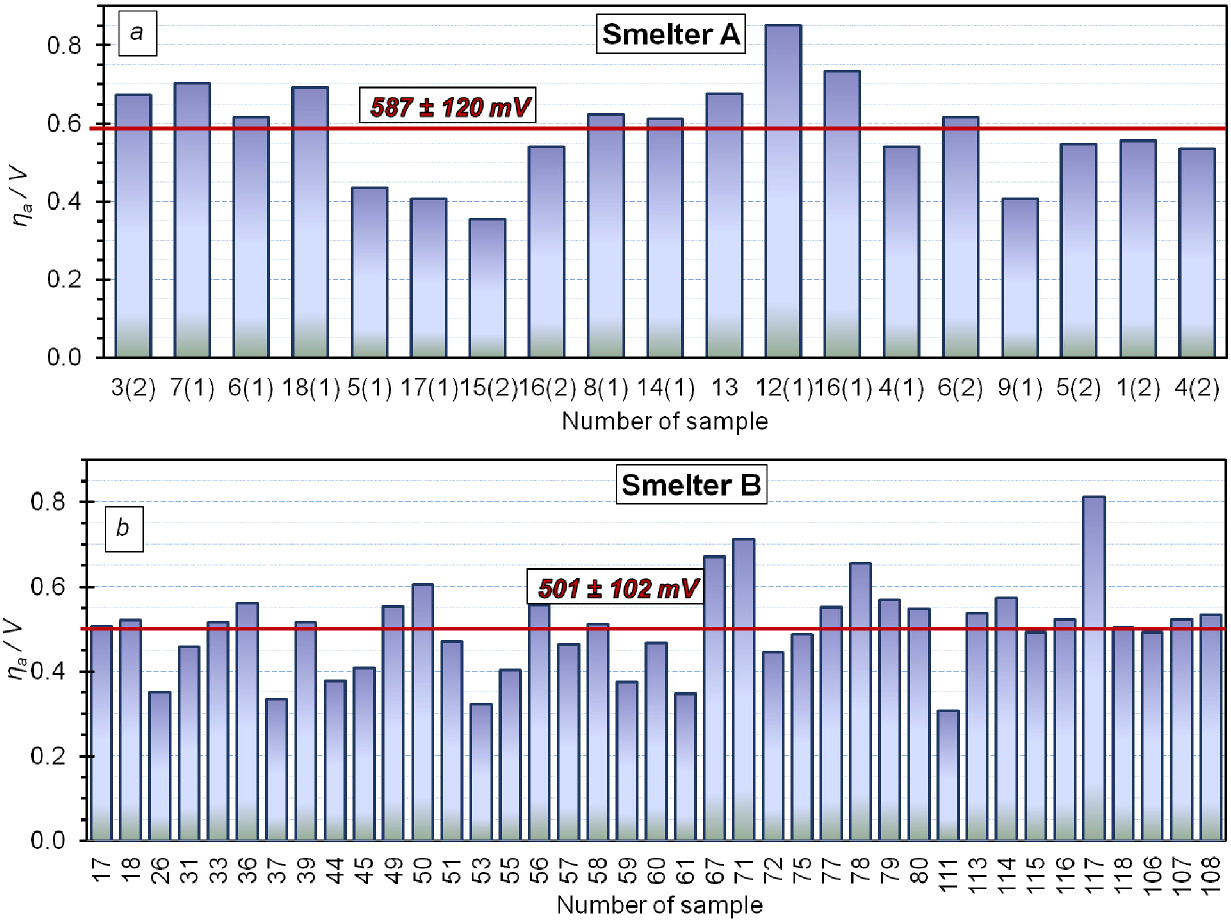

Fig. 5. The set of η_a values at i_a=0.8 A/cm^2 for anodes from a) Sayanogorsk smelter and b) Boguchany smelter with average values and standard deviations marked in the diagram.

Plant A has been considered to have low-quality anodes when compared with plant B. Nevertheless, it has higher overvoltage which is considered to be connected with low porosity, high purity and high structural order due to higher baking temperature or even heat up rate. The standard deviation of 120 mV for smelter A is another indicator, showing more variability in quality and manufacturing processes. The average values for both smelters are in a good agreement with data from previous studies. The absence of a direct correlation between overvoltage and anode quality indices suggests further studies directed at the characterization of the formation of structure during coke-pitch interaction [27] at high temperatures, graphitization processes and impurities behavior would be valuable.

4 Conclusions

The anodic overvoltage is an important aluminium smelter performance indicator which can be used to characterize the homogeneity and electrochemical reactivity industrial anode materials. Along with CRR, AP, apparent density and other quality control parameters, overvoltage indicates the structural order, chemical composition and quality of the anode as a dissipative system. It is noteworthy that overvoltage does not always correlate with other properties, which means that the stationary polarization method (or an alternative method to determine overvoltage) could be an additional descriptor of anode performance. The range of more than 300 mV has been confirmed using the same laboratory cell and even during one series of measurements. This makes further investigation into potential methods of controlling and reducing anodic overvoltage an attractive idea.

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