INTERFACIAL BOUNDARY BETWEEN CARBON ANODES AND MOLTEN SALT ELECTROLYTE

Wojciech Gebarowski[1], Camilla Sommerseth[1], Arne Petter Ratvik, Espen Sandnes[1], Lorentz Petter Lossius[2], Hogne Linga[2], Ann Mari Svensson[1]

[1]Dept. of Materials Science and Engineering, Norwegian University of Science and Technology, NO-7491 Trondheim, Norway
[2]Hydro Aluminium, Årdalstangen, Norway
[3]SINTEF Materials and Chemistry, NO-7465 Trondheim, Norway

Abstract

The properties of calcined petroleum cokes (CPC), used in the anodes in the Hall-Héroult process, are important for the electrochemical behaviour of the anodes. CPCs from different sources vary not only in impurity level but also in microstructure. The trend of available CPCs for anode production indicates an increase in impurities as well as introduction of more isotropic structure. Hence, a better understanding of the behaviour of these materials during electrolysis is essential for optimizing performance. In previous studies, different anode cokes were characterized with respect to anode overpotential and the gas evolution during polarization. Present work focuses on investigation of the interfacial contact between the anode and the molten salt electrolyte. The interfacial contact is important for the electrochemically active area of the porous electrodes, which is different from the geometric area. The focus is on the assessment of electroactive area by measurements of the double layer capacitance, which may be performed during electrolysis. This is a great advantage as the active surface area is known to depend on the polarization. Double layer capacitance is compared for anodes made from very different carbons, and correlated to the overpotential.

Introduction

Prebaked carbon anodes used in electrolysis of aluminium have a significant influence on the economy of the process. Despite relatively high current efficiency of industrial electrolysis reaching more than 90 % [1], the process is very energy-consuming due to high cell voltage – about 4 V. The total contribution in cell voltage related to the anode is 1.93 V [2]. This value consists of anode electrochemical overpotential (~1.12 V), resistance due to gas bubbles evolution (~0.48 V) and electronic resistance of anode material (~0.33 V) [2]. Therefore reaching the lowest possible voltage drop influences the overall process economy positively. Other factors which impact the costs of process are an excessive consumption of anodes by dusting and CO_2/air- burn as well as unexpected failures. The problem of producing optimal quality anode becomes more complex due to use of multiplicity of input source materials (CPC and pitch) with different physical and chemical properties.

As the operational overpotential related to anodes during electrolysis is a very important factor it has been the subject of several studies in the past *i.a.* [3–10]. Due to differences in experimental setups, the general difficulty in proper estimation of iR drop in a cell and differences in reference electrodes the absolute values obtained in various papers are not consistent.

However one general observation recurs – electrodes made of graphite always exhibit higher overpotential than carbon materials. It is still not clear how the total overpotential of various anode materials is affected by the actual differences in electrochemical reactivity, and differences in electrochemically active surface area, and how both of these relate to surface chemistry and impurities. Since in all studies the geometrical surface area of the working electrode is applied for the calculation of the current density (CD), differences in the real current density may occur due to differences in the electroactive surface area. Considering the strong dependence of the anode potential on the current density (especially in the range of higher CD), the influence of apparent to real surface area ratio on the potential values can be substantial.

It is generally agreed that the double layer capacitance correlates with the electroactive surface area. It is typically measured by electrochemical impedance spectroscopy, which allows for assessment of the active surface area during electrolysis. The latter makes it a very powerful tool, as surface wetting properties are known to depend on the polarization, and the active area might also change during the experiments. The capacitance of the double layer of carbon electrodes in cryolitic melts in laboratory scale measurements has been investigated in many previous studies. In case of graphite, values of C_{dl} ranging from 14-40 $\mu F \cdot cm^{-2}$ at 0.03 $A \cdot cm^{-2}$ [11] to 47-97 $\mu F \cdot cm^{-2}$ at 0.05 $A \cdot cm^{-2}$ [12] were obtained For baked carbon anodes reported values of C_{dl} are in average 104 $\mu F \cdot cm^{-2}$ at 0.05 $A \cdot cm^{-2}$ [12], 110-130 $\mu F \cdot cm^{-2}$ at 1.2 V [13], an average of 140 $\mu F \cdot cm^{-2}$ at 1.2 V [14], an average of 350 $\mu F \cdot cm^{-2}$ in the range 0-0.15 $A \cdot cm^{-2}$ [15]. Thus, there is a large scatter of measured values of double layer capacitances in the literature. The main reason is an inhomogeneity of the microstructure of measured materials – even similar materials can differ due to the type of carbon and pretreatment of the electrode surface. This effect is clearly visible in aqueous electrolytes [16]. Also, little is currently known on how impurities and surface chemistry would influence the electrochemical reactivity and electrolyte wetting. Second reason lies in the different frequencies used for the calculation of the double layer capacitance. Still, even though the absolute values of C_{dl} are different in the various works their relative values should be correct.

The aim of this work is to improve the methodology of double layer capacitance measurements by electrochemical impedance spectroscopy. Measurements of the double layer capacitances were obtained for anodes made from very different carbon materials (graphite and cokes), and changes over short periods of time were monitored. The double layer capacitance was also

obtained different polarization conditions and correlated to measured overpotential for each sample.

Materials and Methods

The electrochemical experiments were performed in a closed furnace with an inert atmosphere maintained by passing argon with 100 ml·min^{-1} flow rate, as described previously [10]. As electrolyte, a cryolite melt with CR = 2.3 composed of synthetic Na$_3$AlF$_6$ ($\geq$97 %, Sigma-Aldrich), 9.8 wt% excess of AlF$_3$ (industrial grade, in-house sublimed) and 9.4 wt% of γ-Al$_2$O$_3$ ($\geq$99.5 %, Merck) was used. The temperature of the electrolyte during experiments was maintained at 980 °C. Tested samples were made from 4 different single source calcined petrol coke (CPC) with a grain size limited to 0-2 mm (the fractions were 2-1, 1-0 and mill product) and correspond to samples used in previous works [9,10], with the same labels: anode 1 and anode 4. These anodes showed the differences in terms of overpotential and have completely different microstructure – anode 1, 2 – anisotropic, anode 3, 4 – isotropic. Furthermore, the cokes differ in terms of the microstructure, with a higher fraction of edge planes at the surface of anode 4 (80 % vs. 60 %), and also a higher content of acidic oxygen surface groups in the coke of anode 4. For comparison purposes also ultrapure graphite was tested or measured. The graphite has a lower fraction of edge planes in the surface (40 %) and a corresponding higher fraction of basal planes. The working electrodes with different geometrical area (Figure 1) were shielded by boron nitride (BN) parts to expose only the vertical surface in order to minimize effect of gas bubbles evolution accompanying the anodic reactions. The design of this type of electrode and its damping effect on voltage noise during polarization was presented previously [10]. In present work only two different dimensions of the anodes were used – 0.5 and 0.75 cm of height. As a reference electrode an Al pseudo-reference electrode was used. It consisted of a closed bottom alumina tube where the ~1.6 g of pure aluminium was placed. The tube had a hole above the aluminium melt level to introduce the electrolyte. As an electrical contact to aluminium pool a tungsten wire shielded by alumina tube was used. The graphite crucible with shielded bottom by alumina disc acted as a cathode.

Electrochemical measurements were performed using potentiostat with power booster (IM6e and PP201 by Zahner-Elektrik). The measurement procedure consisted of five steps: impedance spectroscopy at open circuit potential (OCP) every 5 min for 30 min after immersion electrode to the electrolyte, polarization at constant current density of 1 A·cm^{-2} by a period of 3.5 min followed by EIS at OCP every 5 min for 30 min, EIS at different potentials and finally EIS in psudo-galvanostatic mode (voltage perturbation with maintaining constant current density of 1 A·cm^{-2}). EIS measurements were carried out at frequency range 500-10 kHz with 20 mV$_{pp}$ AC amplitude except EIS at 1 A·cm^{-2} that, due to higher noise, were performed at frequency range 150-10 kHz with 50 mV$_{pp}$ AC amplitude. The whole measurement procedure was programmed in order to keep all steps with identical time periods for all tested samples. The double layer capacitance of electrodes was calculated from a higher frequencies range (150-50 kHz) assuming simple equivalent circuit of resistance, inductance and capacitance in series, see Figure 2. Fitting of spectra was performed by ZView software (Scribner Associates).
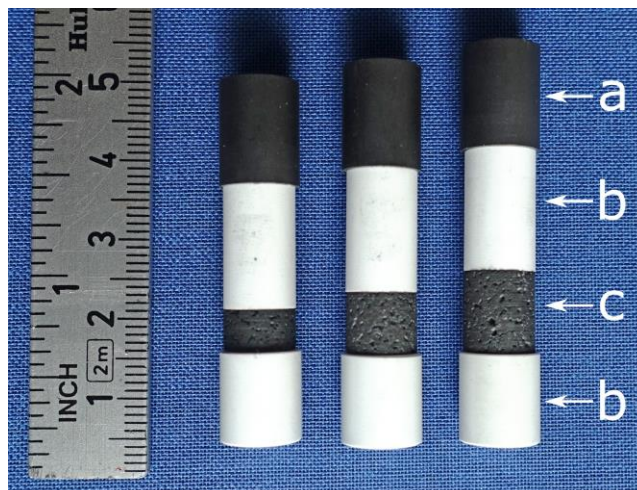

Figure 1. Electrodes used in electrochemical measurements; a – graphite connector, b – boron nitride shields, c – carbon sample
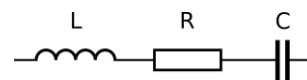

Figure 2. Equivalent electrical circuit used for fitting impedance spectra.

The inductance (L), resistance (R) and capacitance (C) represent the inductance of leads to the cell, resistance of electrolyte between working and reference electrodes (including lead to the working electrode) and capacitance of working electrode.
Presented results in first part of this work (except EIS at 1 A·cm^{-2}) were performed on one batch of samples in order to keep better consistency. One repetition on the similar batch of samples was made to check repeatability of measurements.

Results and Discussion

A typical Nyquist plot of EIS measurement for investigated samples is shown in Figure 3a), and the corresponding Bode plot is shown in Figure 3b). The capacitance values were determined from the equivalent circuit shown in Figure 2. Using such a simple equivalent circuit was based on the assumption that for sufficiently high frequencies no faradaic reactions occur (or occur at negligible rate), such that the only contributions to the imaginary impedance are the double layer capacitance and the inductance from the external leads. The vertical part of curve on the Nyquist plot demonstrates only small change of real part of impedance over this frequency range which indicates no faradaic charge transfer. Therefore other elements in the electrical circuit model which represent charge transfer, diffusion, adsorption etc. can be omitted. Values at the highest frequencies were used to calculate inductance which value was fixed during fitting points of spectra between frequencies from 150 to 50 kHz. Calculating value of inductance at the highest frequency was performed to minimize contribution from the capacitance on the total impedance.
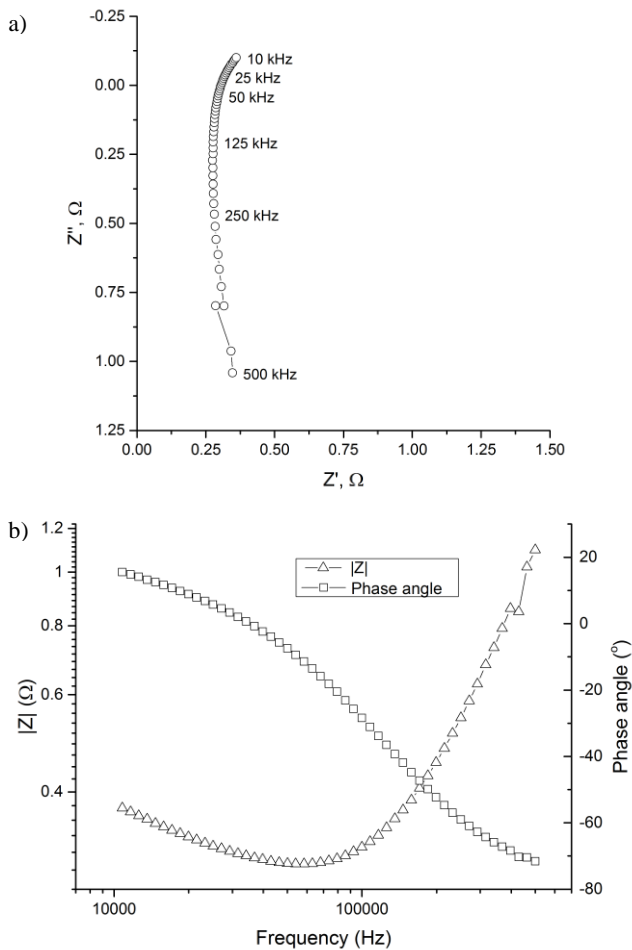
a)

b)

Figure 3. Nyquist (a) and Bode (b) plots measured at open circuit potential.

After immersion of the anodes in the electrolyte they exhibited relatively low capacitance – the highest for the graphite sample, slightly lower for the anode 1 and much lower for anode 4 (Figure 4). The values of capacitance should correspond to the wetting properties – higher value indicates a larger interfacial contact surface area. Therefore, without any current applied, the "fresh surface" of the graphite was better wetted by electrolyte than the tested anodes. The lower values of capacitance for the coke anodes could be related to the fact that these have significantly higher porosities/lower density compared to the graphite, and in particular anode 4 has a high fraction of large pores [17,18], and therefore a lower geometric surface area, provided that the electrolyte is not intruding the pores. Another difference to graphite is the fact that the coke anodes were machined to make proper size electrode. Thus machining could change their surfaces providing worse wettability, especially in case of anisotropic anode 4 which is characterized by much higher hardness. There is also visible in Figure 4 a constant increase of the capacitance for all the anodes, hence there is some conditioning of the surface upon immersion in the electrolyte causing an improved interfacial contact over time even at zero-current conditions. The low capacitance values of unpolarized samples could also be caused

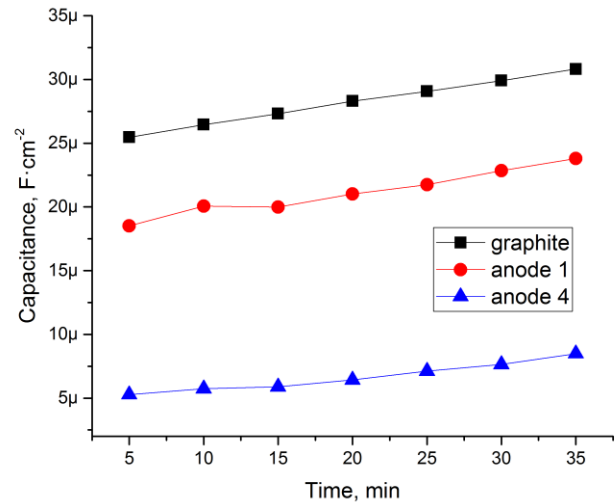by a relatively long time of soaking electrolyte after immersion [13].

Figure 4. Anodes capacitances changes during time at open circuit potential after immersion to the electrolyte.

Plots on the chart in Figure 5 depict potentials changes of the electrodes during polarization at constant current density. The values of potentials were corrected by IR drop across the electrolyte (R was read out from impedance spectra). The graphite sample is characterized by the highest overpotential what is in accord with all previous works. The coke anodes have a lower potential (about 100 mV) than graphite, but more interesting is the profile of these curves. In case of graphite and anode 1, the level of the potential is relatively stable during the polarization time. However, in the case of anode 4, the potential decreases during polarization. This indicates that the anode undergoes some kind of a slow conditioning process such that the active area of the electrode increases, causing decreasing effective current density, and hence the declining potential.
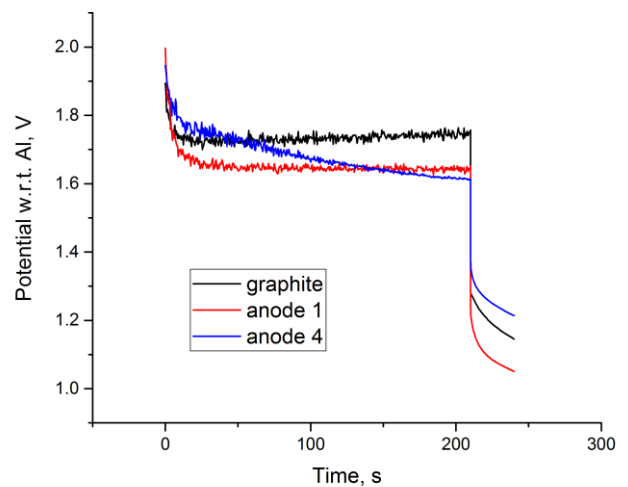

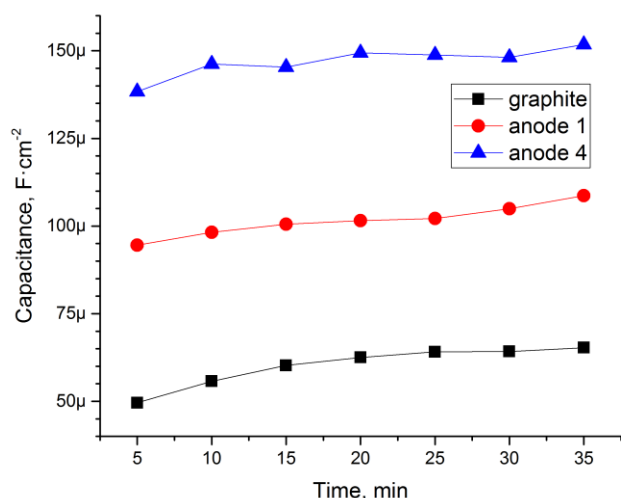Figure 5. Potential curves during polarization at constant current density of 1 A·cm^{-2}.

Figure 6. Anodes capacitances changes during time at open circuit potential after polarization by 3.5 minutes at 1 A·cm^{-2}.

Figure 7. Capacitances of anodes at different potentials.

After polarization the values of the capacitance increased significantly with respect to the values before polarization. For the graphite sample from around 31 to 50 $\mu F \cdot cm^{-2}$, for anode 1 from 24 to 94 $\mu F \cdot cm^{-2}$ and for anode 4 from 8.5 to 138 $\mu F \cdot cm^{-2}$ which gives an increase by a factor of 1.6, 3.9 and 16.2 respectively. Such large changes of the capacitance before and after polarization are likely to be caused by change of wetting properties and developing of electrode surface during oxidation. The exact reasons for the huge change of anode 4 are not known, but compared to anode 1, the coke used for anode 4 is more isotropic, a higher fraction of reactive surface sites, more impurities, and is also differing with respect to the surface oxygen groups.

The next graph (Figure 7) shows the capacitance calculated at different potentials with respect to Al pseudo reference electrode. Because of current limitations of the main potentiostat measurements were performed up to 1.5 V vs. Al which corresponded to 139, 128 and 49 mA·cm^{-2} DC for anode 1, anode 4 and graphite respectively. As is visible from Figure 6, there is decrease of capacitance with increasing potential of the electrode reaching minimum at about potential 1.4 V and slight increase going to higher potentials. Similar trend can be observed in work of Kisza *et al.* [11] for pyrolytic graphite considering the same current densities. This pattern is distinct for anode 4, less for anode 1, and not visible for graphite anode, most likely due to much smaller current densities at these potentials

In figure 7 the double layer capacitance obtained at different potentials is plotted together with the corresponding current density. It is evident that in the region of potentials where the capacitance is decreasing, the current density is very small. At small current densities the reaction of carbon oxidizing to CO is favoured [19]. Prior to the evolution of CO, adsorption of CO on the surface is frequently assumed. Therefore a reduced active surface area can be an effect of adsorbed CO on the surface of the electrode. Another explanation of this phenomenon can be coverage of the electrode surface by adsorbed oxyanions. When the potential is higher, the rate of electrochemical reactions at the interface accelerates as is indicated by the rapid increase of current (Figure 8).
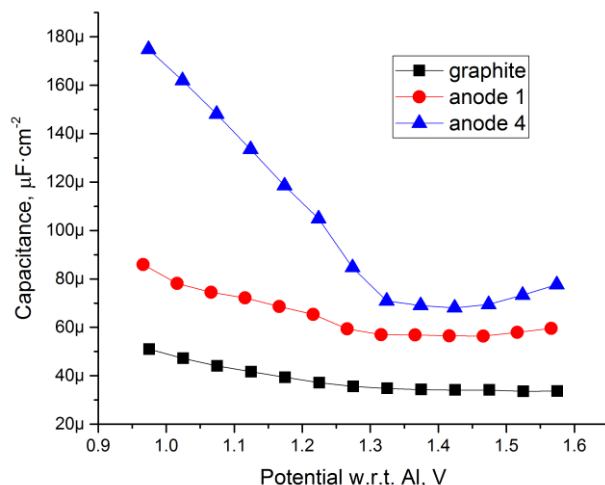
In this region double layer capacitance stabilizes. Faster generation of CO_2 establishes certain coverage of the anode by adsorbed species. The small increase of capacitance can be caused by higher consumption rates of the anode at these conditions which makes the surface rougher and more developed.
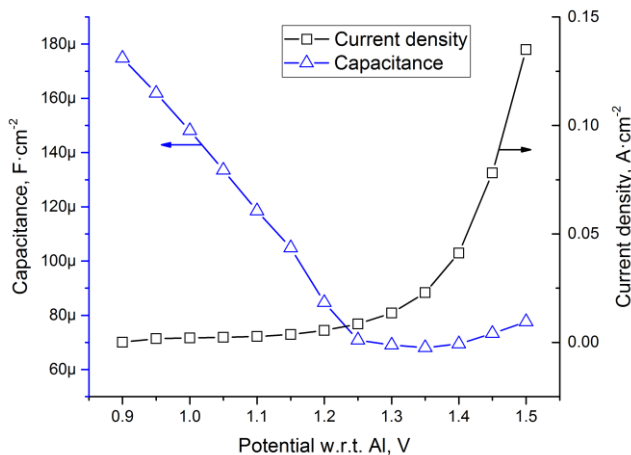

Figure 8. Anode capacitance at different potentials with corresponding current densities at these potentials.

In order to perform EIS measurements at 1 A·cm^{-2} DC current density range of measurement a power booster in pseudo galvanostatic mode was used.

On figure 9 the calculated values of capacitance were plotted versus potentials of these materials during constant current polarization at 1 A·cm^{-2}, as evaluated in the previous work [10]. There is a certain correlation between the active surface area and the values obtained for the overpotentials. The higher capacitance and hence higher active surface area the lower potential were observed during constant current polarization. However, the differences in the potentials of anode 2 and 3 are not so significant while differences in C_{dl} are high. It means that various materials

perform differently not only due to active surface area differences, but also from other surface properties as well as the concentration of sulfur and metallic impurities which can decrease overpotential [8,19].
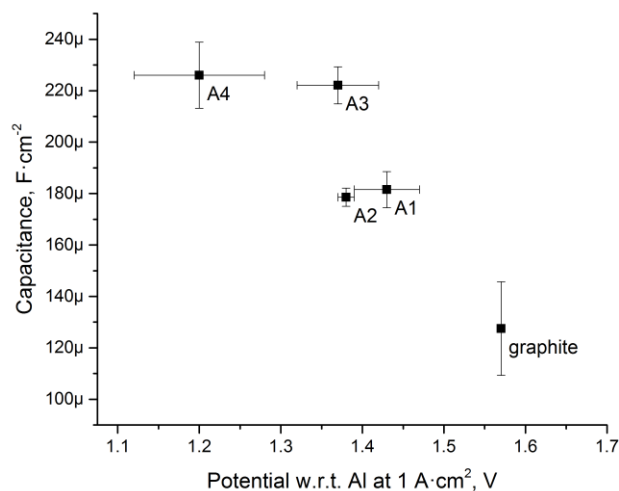

Figure 9. Anodes capacitances measured at current density 1 A·cm^{-2} and their potentials at this current density taken from previous work [10]. A1 – anode 1; A2 – anode 2; A3 – anode 3; A4 – anode 4.

It was found that the measured C_{dl} correlates well with the permeability of the tested materials (Figure 10). This is reasonable considering that permeability to some extent is a measure of the macroporosity of the materials.

Because current density usually has been related to the geometrical area of the electrode, which can be very different from the active surface area for various materials, the local rates of the electrochemical reactions may be very different, and thus the measured overpotentials will differ.
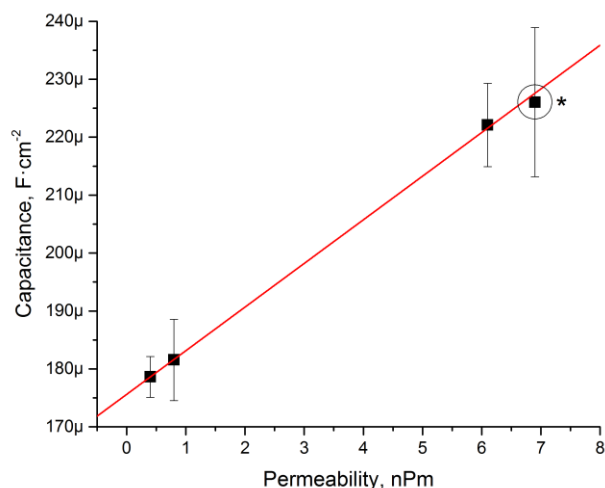

Figure 10. Permeability of anode materials and measured anodes capacitances measured at current density 1 A·cm^{-2}. (* value of permeability 6.9 nPm may be even higher due to limitation of measuring apparatus)

Jarek and Thonstad [13] made a correction of current densities using active surface area from the double layer capacitance. After this correction, the curves on Tafel plots for different carbon materials moved closer to each other. It is thus very important when one try compare different anode materials in terms of their electrochemical properties to identify also the differences in the wetting properties. The cause of differences in wetting properties is still not well known, and this area certainly deserves further investigations.

Conclusions

Performed measurements showed substantial increase of double layer capacitance after polarization of anode. Different values of capacitances for tested anode materials were found which correlated, to a certain extent, with observed polarization potentials. Therefore the differences in overpotential can be partly explained by different active surface areas of the anodes, which influences the real current density during polarization. A strong dependence between the double layer capacitance and permeability of anode materials was observed.

Acknowledgements

References

[1]   H. Kvande, W. Haupin, Cell voltage in aluminum electrolysis: A practical approach, Jom. 52 (2000) 31–37.

[2]   K. Grjotheim, B. Welch, Aluminium Smelter Technology, Aluminium-Verlag. (1988).

[3]   J. Thonstad, E. Hove, On the anodic overvoltage in aluminum electrolysis, Can. J. Chem. 42 (1964) 1542–1550.

[4]   E.W. Dewing, Anodic Phenomena in Cryolite-Alumina Melts, J. Electrochem. Soc. 122 (1975) 358–363.

[5]   S. Jarek, J. Thonstad, Wetted surface area and polarization potential of carbon anodes in cryolite - alumina melts, Light Met. (1987) 399–407.

[6]   G.M. Haarberg, L.N. Solli, A. Sterten, Electrochemical studies of the anode reaction on carbon in NaF-AlF3-Al2O3 melts, Light Met. (1994) 227–231.

[7]   Y.-X. Liu, J. Thostad, J.-H. Yang, On the electrocatalysis of doped carbon anodes in aluminium electrolysis, Aluminium. 72 (1996) 836–840.

[8]   J.-H. Yang, J. Thonstad, Q.-X. Zhang, A. Kisza, Y.-X. Liu, On electrocatalysis of doped carbon anodes in aluminium electrolysis, Part II: The effect of additives on

overvoltage of carbon anodes, Aluminium. 74 (1998) 427–432.

[9]   R.J. Thorne, C. Sommerseth, E. Sandnes, O. Kjos, T.A. Aarhaug, L.P. Lossius, et al., Electrochemical characterization of carbon anode performance, Light Met. 24 (2013) 1207–1211.

[10]   R.J. Thorne, C. Sommerseth, A.M. Svensson, E. Sandnes, L.P. Lossius, H. Linga, et al., Understanding anode overpotential, Light Met. (2014) 1213–1217.

[11]   A. Kisza, An Impedance Study of the Kinetics and Mechanism of the Anodic Reaction on Graphite Anodes in Saturated Cryolite-Alumina Melts, J. Electrochem. Soc. 143 (1996) 1840.

[12]   S. Jarek, Z. Orman, The faradaic impedance of the carbon anode in cryolite-alumina melt, Electrochim. Acta. (1984) 341–345.

[13]   S. Jarek, J. Thonstad, Double-layer capacitance and polarization potential of baked carbon anodes in cryolite-alumina melts, J. Appl. Electrochem. 17 (1987) 1203–1212.

[14]   J. Thonstad, Double layer capacity of graphite in cryolite-alumina melts and surface area changes by electrolyte consumption of graphite and baked carbon, J. Appl. Electrochem. 3 (1973) 315–319.

[15]   J. Thonstad, The electrode reaction on the C, CO2 electrode in cryolite-alumina melts—II. Impedance measurements, Electrochim. Acta. 15 (1970) 1581–1595.

[16]   G.M. Swain, 5 - Solid Electrode Materials: Pretreatment and Activation, in: C.G. Zoski (Ed.), Handb. Electrochem., Elsevier, Amsterdam, 2007: pp. 111 – V.

[17]   R.J. Thorne, C. Sommerseth, a. P. Ratvik, S. Rorvik, E. Sandnes, L.P. Lossius, et al., Bubble Evolution and Anode Surface Properties in Aluminium Electrolysis, J. Electrochem. Soc. 162 (2015) E104–E114.

[18]   C. Sommerseth, R.J. Thorne, S. Rorvik, E. Sandnes, A.P. Ratvik, L.P. Lossius, et al., Spatial methods for characterising carbon anodes for aluminium production, Light Met. (2015) 1141–1146.

[19]   P. Fellner, G.M. Haarberg, J. Hives, H. Kvande, A. Sterten, J. Thonstad, eds., Aluminium Electrolysis: Fundamentals of the Hall-Héroult Process, 3rd ed., 2001.