Comparison of Electrochemical Methods to Determine Alumina Concentration in Cryolite Based Bath

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Abstract

Nowadays, there is a clear tendency to increase the potline current for higher productivity and to decrease cell voltage by squeezing the anode-cathode distance (ACD) for lower energy consumption and improved thermal balance in aluminum electrolysis cells. Both modifications require a better control of alumina concentration in the bath. Chemical analysis gives data with significant time delay and poor precision for the dissolved alumina content, depending on sampling method and analysis technique. Laboratory scale tests with well controlled environment can help understanding the impact of different factors on the dissolution kinetics. Even if many studies have been made in this field, only qualitative results are published in the open literature, which are mostly valid only for a small amount of bath. Theoretically, electrochemical techniques can reveal almost continuously the dynamics of alumina dissolution. However, the evolution of electrode surface, bubble formation, secondary reactions and grounding problems make it difficult to obtain results with satisfactory repeatability. This paper compares different electrochemical techniques used to monitor alumina concentration in cryolitic bath.

Keywords: Cryolitic bath; alumina concentration measurement; electrochemical techniques.

1. Introduction

Alumina dissolution in molten cryolite-based bath is one of the key factors that must be optimized in order to increase current efficiency in Hall-Héroult reduction cell. Quantitative understanding of this process could help choose to optimal operation parameters and thus facilitate the use of reduced ACD and increased cell current.

Experimental study of alumina dissolution kinetics has been an active field of research for the last 30 years. Analytical methods like LECO and X-rays diffraction (XRD) have been used to follow alumina content in the bath but results are inaccurate since these methods cannot distinct dissolved from non-dissolved alumina (LECO) or they measure only the crystalline phase (XRD). Furthermore, analysis is resource-consuming and results can take days to be available.

To solve these issues, electrochemical techniques have been developed. Unfortunately, most of the materials available for insertion into the bath are attacked by molten cryolite at 960 °C, consequently measurements are impacted by degradation of apparatus. Electromagnetic interference, galvanic effects, polarization and temperature control are additional factors that complicate further alumina dissolution kinetics studies. Furthermore, the only transparent

material that can resist molten cryolite for a few hours is quartz therefore tests are carried out without visualization that could help the interpretation of results.

This paper presents some common electrochemical techniques used to follow the variation of alumina content of the bath including their advantages and disadvantages.

2. Electrochemical Techniques

Electrochemical techniques presented in this paper are based on three different principles: provocation of anode-effect, determination of the real part of impedance and galvanic cell measurement. Some other techniques exist as well, but this review takes into consideration only the most known or used methods that showed promising results with cryolitic bath.

2.1. Anode-effect based technique

2.1.1. Fast sweeping voltammetry

Fast sweeping voltammetry (FSV) is an electrochemical technique derived from an alumina concentration sensor patented by Milton et al. in [1] then refined to a usable level by Tabereaux et al. [2] and Haverkamp et al. [3]. Linearly increasing DC potential is applied according to a pre-set ramp between 2 electrodes, generally made of graphite.

Current intensity responds quasi-linearly with applied potential until oxygen containing ion depletion on the anode surface. At this moment, fluorine starts to be discharged at the anode forming CF_4 and CF_6 insulating gas around the anode. This phenomenon is called the anode effect.

The critical current density where oxygen depletion takes place is closely related to the concentration of the dissolved alumina. Figure 1 shows typical FSV curves for 4 different bulk concentrations, “a” and “d” curve being respectively the lowest and highest dissolved alumina concentrations.

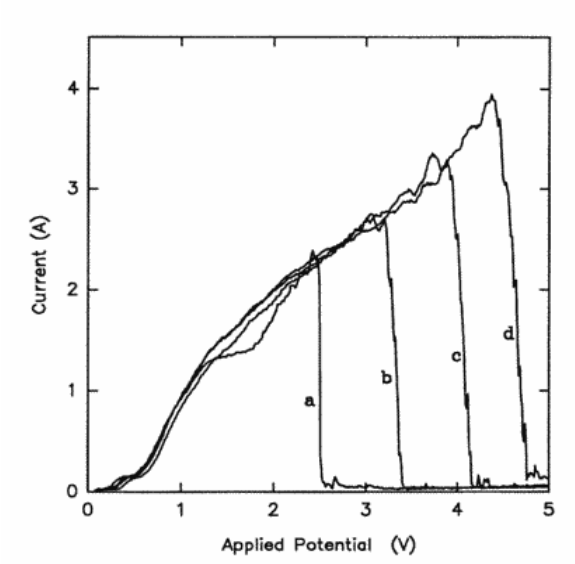

Figure 1. FSV curves obtained from different alumina concentration [3].

For each curve, 4 different parameters can be chosen in order to determine alumina concentration: voltammogram area VA, anodic effect potential PAE (measured when current drops below 60% of maximum value), highest (peak) current PC and the potential when PC is

reached (called PPC). All those parameters except PC give good results according to Haverkamp et al. [3]. Increase of reproducibility can be achieved using rotating disk electrode [4]. Fast Fourier transforms can also be used to filter high noise inherent to the technique [5].

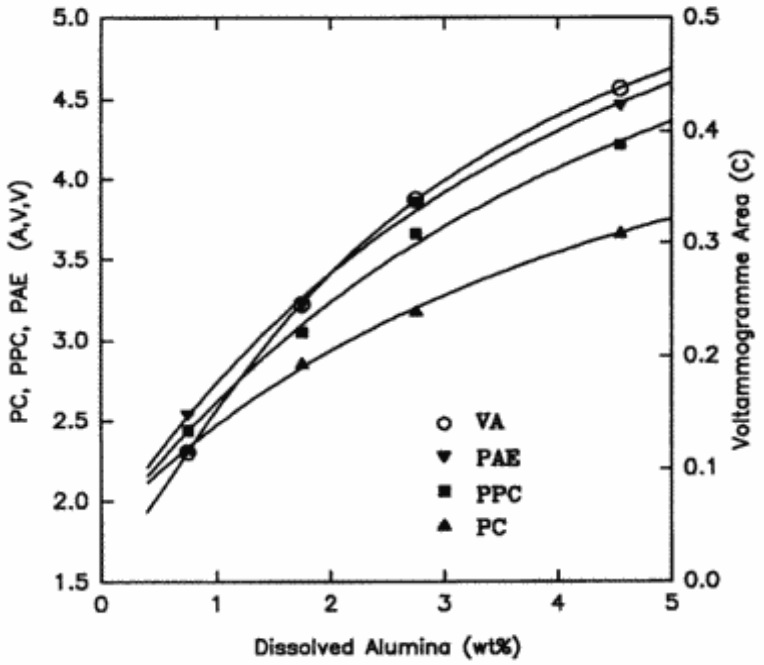

Figure 2. Example of variation of evaluation parameters with dissolved alumina content [3].

2.1.2.Chronopotentiometry

Chronopotentiometry (CP) is an important current-step technique used for the determination of the alumina concentration and was initially used for alumina content measurement by J. Thonstad in 1969 [6]. This method consists of measuring the potential to an imposed step-wise changing current between two electrodes immersed into the studied electrolyte (Figure 3). In most cases, graphite or platinum rods or the graphite crucible itself are used as electrodes [6] [7].

When a current starts to flow through the cell, the reactants next to the electrodes are consumed and a concentration gradient is formed. That phenomenon should decrease the rate of electrochemical reaction and the current itself if the potential were constant as the charge carriers are consumed. However, if the current is forced, the over-potential, necessary to maintain the same reaction rate, will gradually increase. If the current density is high enough to completely deplete the reactants at the electrode surface, the reaction controlled regime becomes diffusion controlled [6]. This change provokes a change of slope of the potential versus time curve (breakpoint). The instant when this happens, **τ**, depends on the initial bulk concentration of the reactant and can be estimated by the well-known Sand equation.

$$i\tau^{1/2} = \frac{1}{2} nF\pi^{1/2} D^{1/2} c \qquad (1)$$

where **τ** is the time constant, **i** is the imposed current density, **D** diffusion coefficient, and **c** the bulk concentration.

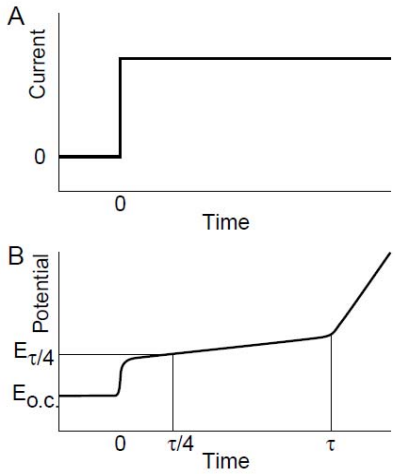

Figure 3. Imposed current and potential response curves [8].

τ should be kept at very short transition time in order to minimize gas formation at the anode causing perturbations of the linearity in the diffusion layer [7]. High current densities are needed to get measurable transition time which causes an aggressive anode oxidation [9].

2.2. Impedance-based techniques

2.2.1. Bath conductivity with impedancemetry

Impedancemetry has been mainly used to study the electrical conductivity of molten electrolyte as function of the chemical composition and temperature since higher conductivity reduces heat dissipation caused by ohmic resistance. This technique can also be useful to determine Al_2O_3 concentration since it has an impact on electrolyte conductivity.

Works done by Hives et al. [10] and Uher et al. [11] consist of measuring impedance of melts while forcing high frequency (6 - 60 kHz) AC current through molten electrolyte. High frequency must be used in order to minimize double layer capacitance, charge transfer resistance and diffusion. Very high frequency (more than 100 kHz) should however be avoided to reduce the influence of wire inductance. The real part of the measured impedance is composed of the ohmic resistance of the bath and the wiring as well as the polarization term. Quantitative correlation between alumina concentration and conductivity of the melt can then be found.

In the experiments described in Hives et al. [10], the liquid was contained in a tube-type cell, composed of a cylindrical graphite crucible insulated inside by pyrolytic boron nitride tube. The bottom of the crucible as well as a tungsten rod inserted at the middle into the liquid served as electrodes.

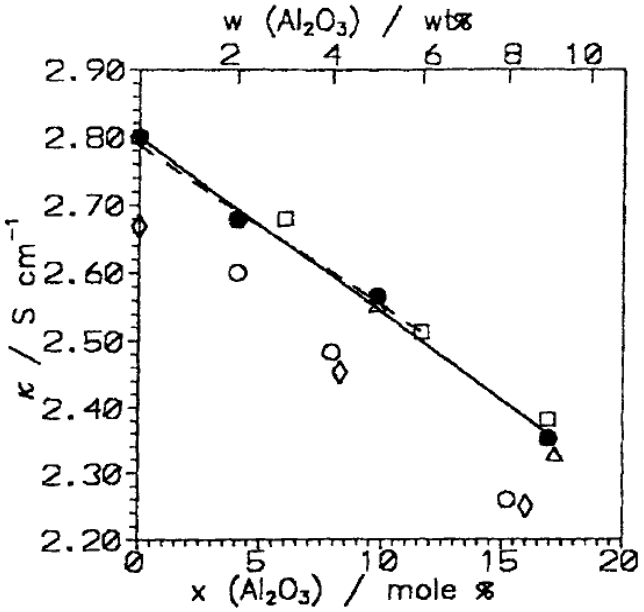

Figure 4. Variation of conductivity with alumina content, obtained by Hives et al. [10].

2.2.2. Continuously varying cell constant (CVCC) technique

The Continuously Varying Cell Constant (CVCC) approach is based on the previous method except that one of the electrodes is moveable, thus the distance between the electrodes can be changed continuously. Wang et al. [12] used a platinum disk electrode sliding inside of a pyrolytic boron nitride tube covered graphite crucible [12] [13].

Resistance values were measured as function of distance between the electrodes in order to separate the ohmic resistance of the bath from all the other terms influencing the impedance. In fact, the slope of the resistance vs distance curves, obtained with fixed surface electrodes, depends only on the resistivity, Equation (2):

$$\frac{dR}{dL} = \frac{\rho}{A} \tag{2}$$

Although the technique was mainly used for bath conductivity with various additives, some alumina concentration tests were realized as well. Figure 5 shows an example of the variation of conductivity with alumina concentration at different temperatures, obtained with the CVCC method by Yang et al. [13].

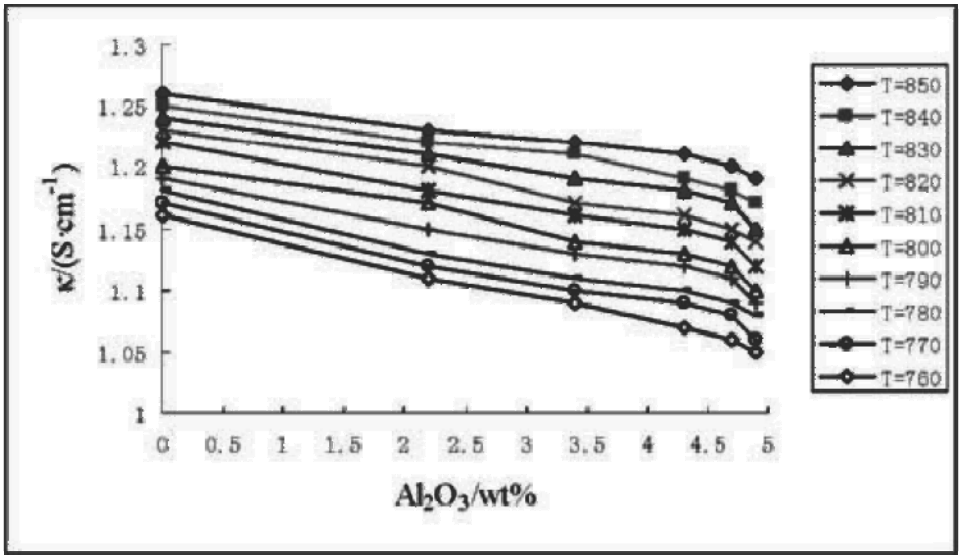

Figure 5. Conductivity of Kf-NaF-AlF3 melt CR = 1.41 at different temperatures.

2.2.3. Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) is another impedancemetric technique. It consists of imposing a given DC potential between 2 electrodes and superposing a low amplitude AC potential with varying frequency on it while measuring the current response of the system. Frequency sweeping in a wide range (around 1Hz – 100 kHz) is used in order to obtain a Nyquist diagram of complex impedance (imaginary vs real parts of the impedance at different frequencies).

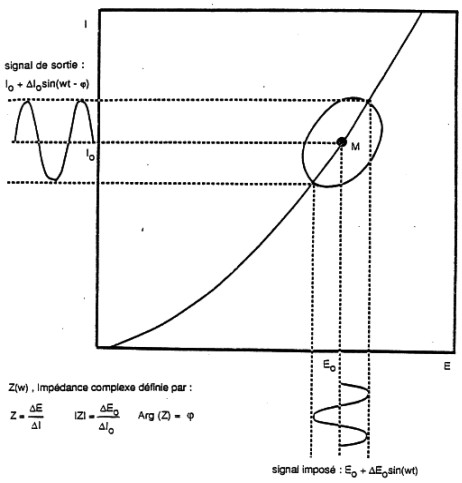

Figure 6. Conductivity of Kf-NaF-AlF3 melt CR = 1.41 at different temperatures [14]**.**

E. Prat [14] and Picard et al. [15] reported that the Nyquist curve obtained during aluminum electrolysis intersects the real (horizontal) axis at points A and B (Figure 7). Z_O(A) obtained at high frequency (10 - 100 kHz) at point A corresponds to the pure ohmic resistance of the bath while Z_{O+ct}(B) acquired at point B at low frequency (15 - 25 Hz) is the sum of ohmic and charge transfer resistances. The difference Z_{O+ct}(B) - Z_O(A) gives the charge transfer resistance which is inversely proportional to the alumina concentration. The advantage of this method is that the dependency of charge transfer on alumina concentration is stronger than that of the ohmic resistance at low alumina content.

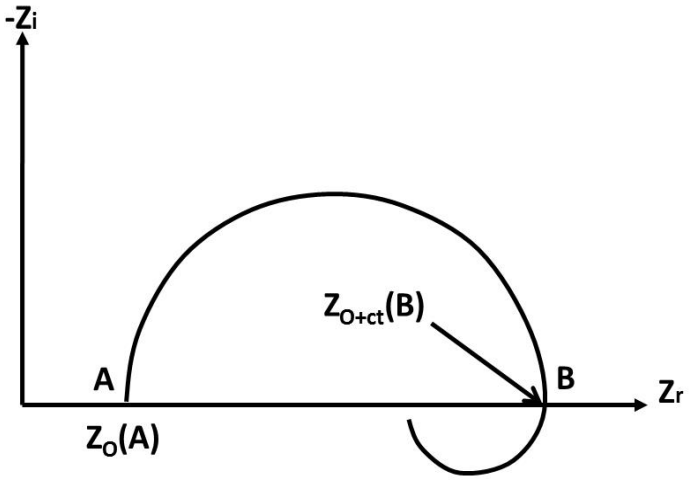

Figure 7. Complex impedance Nyquist plot from EIS scan.

2.3. Galvanic cell effect

2.3.1. Electromotive force

Electromotive force (EMF) measurements can be used to estimate alumina concentration. There are only a few papers using that technique for alumina dissolution kinetics and mainly limited to works of Vasyunina et al. [16] and Rolseth et al. [17].

The Nernst equation can be used to determine the activity of oxide containing ions (and thus alumina concentration) in molten cryolite from the open circuit electromotive force of a galvanic cell, Equation (3):

$$\Delta E = \frac{RT}{6F} \ln a_{Al_2O_3} \tag{3}$$

Rolseth et al. [17] used Cr/Cr_2O_3 with stabilized zirconia-Al/Mo electrode pair, common in steel industry to measure EMF. Such a system gives acceptable results only for Al_2O_3 content higher than 3wt%. Electrodes are very reactive to cryolite lasting only about 20 seconds before a pronounced shift in readings.

Another technique consists of putting a cryolite bath saturated in alumina into a crucible and comparing it with another crucible containing the studied liquid with unknown concentration of alumina. The experimental setup assures electrical contact without mixing between the two electrolytes [16]. The cell is kept at uniform temperature. Inert platinum electrodes are inserted in both cells. The evolution of EMF in time between the two electrodes is recorded. The EMF value becomes constant when alumina is fully dissolved (Figure 8). Noise in the measured EMF values can be probably caused by unsolved solid particles.

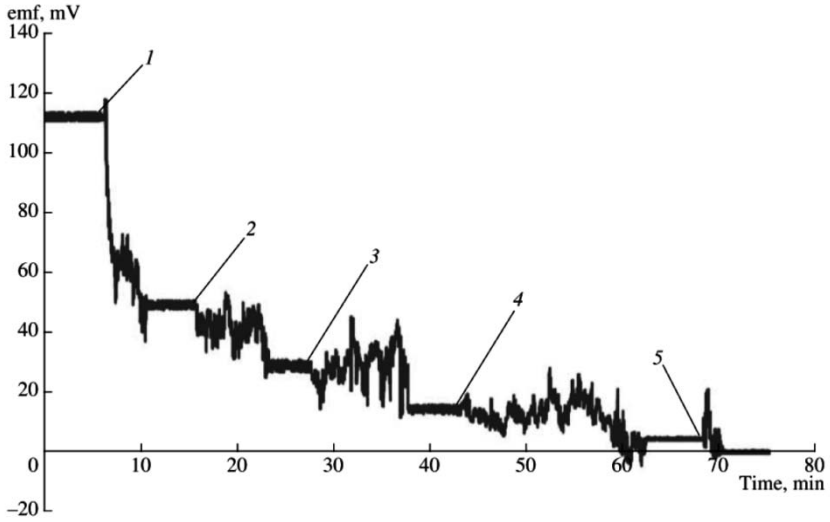

Figure 8. Temporal evolution of EMF due to 5 consecutive alumina additions [16].

3. Comparison of the Different Techniques

Techniques based on anode-effect		
	Advantages	**Disadvantages**
FSV	▪ Good sensitivity for low alumina concentration ▪ Fast data recording frequency ▪ Limited perturbation of the bath	▪ Electrode conditioning required ▪ Poor repeatability (sensitivity to electrode geometry and degradation, impurities and gas bubble formation) ▪ Poor sensitivity at high alumina concentration
Chronopo-tentiometry	▪ Transition time is independent of electrode geometry [8] ▪ Very fast data recording frequency	▪ High current density tend to promote oxidative attack of electrode surface [9] ▪ Caution must be taken to choose anodic current density ▪ Gas bubble formation can stir the bath ▪ Poor repeatability ▪ Recording of very fast answer to step current requires special equipment
Techniques based on impedance measurement		
	Advantages	**Disadvantages**
Ohmic bath conductivity	▪ Almost linear variation with alumina concentration ▪ Simple set-up ▪ Not perturbing method (no net reaction takes place) ▪ Kinetics of alumina dissolution can be followed continuously ▪ Not sensitive to the	▪ Change of ohmic resistance with alumina concentration is very small (in the magnitude of the order of noise) ▪ Convenient to follow evolution of dissolved alumina content but ohmic resistance of the bath cannot be completely separated from other components (charge transfer resistance, polarization, contact resistance in the electronic conductors etc.) ▪ Can be perturbed by change of temperature, bath stirring and solid particles

	impurities in the electrodes	▪ Very high sensitivity to the electrical grounding of the studied cell
CVCC	▪ Permit to separate ohmic resistance of the bath from the other components of the signal and thus conductivity of the bath is independent of the test frequency ▪ Almost linear variation with alumina concentration ▪ Not sensible to the impurities in the electrodes	▪ Method used for cryolite conductivity and not to follow the kinetics of dissolution of alumina ▪ Need expensive equipment (potentiostat, actuator, position encoder) ▪ Bath stirring by the moving electrode can affect alumina dissolution ▪ Change of ohmic resistance with alumina concentration is very small (in the magnitude of the order of noise) ▪ Can be perturbed by change of temperature, bath stirring and solid particles ▪ Very high sensitivity to the grounding of the studied cell
EIS	▪ Good sensitivity for low alumina concentration ▪ More sensible for the change in alumina concentration than ohmic resistance measurement	▪ Long sweeping time ▪ Complicate, time consuming evaluation of the results ▪ Poor sensitivity at high alumina concentration ▪ Perturbing method (electrochemical reaction, gas bubble formation at low frequency) ▪ Sensitive to the impurities
Galvanic cell measurements		
	Advantages	**Disadvantages**
EMF	▪ Simple theory ▪ No expensive equipment ▪ Kinetics of alumina dissolution can be followed continuously	▪ Measured voltage perturbed by gas bubble formation, solid particles etc., noise ▪ More precise at higher alumina concentration [17] ▪ Very short sensor life ▪ Results can be affected by temperature and impurities

4. Conclusions

Different electrochemical techniques have been compared in this paper. In spite of extensive efforts carried out on this field during the past 40 years, no practically available methods have been found up to now to follow kinetics of alumina dissolution in cryolite-based bath even in a well-controlled laboratory environment. In-situ measurements are even more problematic due to the extremely strong magnetic field and line-current perturbing the already sensitive techniques and the life expectancy of sensors is also very short.

While traditional analytical methods are slow and often inaccurate, electrochemical techniques are also subject to various phenomena, resulting in poor accuracy and repeatability, caused by electrode degradation, magnetic fields, electrode polarization, gas bubbles, etc. The determination of alumina concentration using electrochemical methods still needs further refinement in order to give accurate and repeatable results.

5. Acknowledgements

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