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.

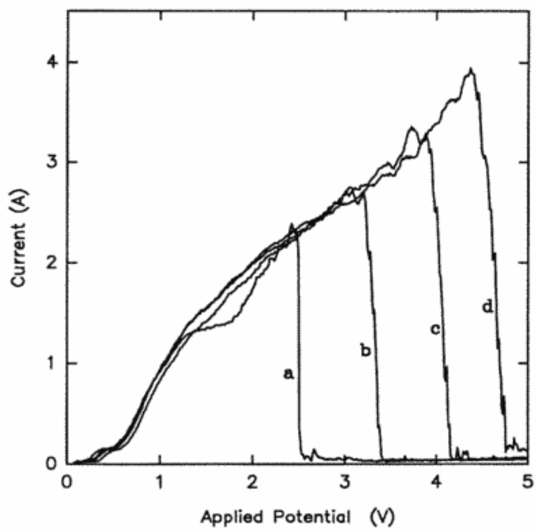

Figure 1. FSV curves obtained from different alumina concentration [3].

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

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