

# MEASUREMENT OF ANODIC OVERVOLTAGE BY A MODIFIED CURRENT INTERRUPTION METHOD IN CRYOLITE-ALUMINA MELTS<sup>①</sup>

Yang Jianhong, Lai Yanqing, Xiao Jin, Li Jie and Liu Yexiang

*Department of Nonferrous Metallurgy,*

*Central South University of Technology, Changsha 410083, P. R. China*

J. Thonstad

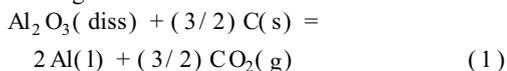
*Norwegian University of Science and Technology, Norway*

**ABSTRACT** Generally, there are reasons to believe that the experimental technique has been inadequate in some works on anodic overvoltage measurements in aluminium electrolysis, therefore, the overvoltage data are not quite correct. Several causes affecting the precision of measurements were analyzed, a cell configuration (vertical carbon anodes, insulated bottom and inner wall of graphite crucible as cathode) was used for overvoltage studies. An improved current interruption technique was used with current interrupted in less than 2 μs and a simulation was applied to the oscillating potential decay curve.

**Key words** anodic overvoltage current interruption method aluminium electrolysis

## 1 INTRODUCTION

In the electrolytic production of aluminium, the cell consists of a carbon anode and an aluminium metal cathode. The dominant potential-determining reaction is:



When current flows through the cell, the measured anode potential (polarization potential) versus the aluminium reference electrode is higher than the reversible potential for reaction (1). The difference between the anode polarization potential and the reversible potential is the anodic overvoltage:

$$\eta_a = E_i - E_{\text{rev}} \quad (2)$$

where  $E_i$  is the measured polarization potential when current flows and  $E_{\text{rev}}$  is the reversible potential for reaction (1), which is -1.164 V at 1010 °C and -1.187 V at 970 °C<sup>[1]</sup>.

Although the anodic process and the measurement of anodic overvoltage in cryolite-alumi-

na melts have been the subjects of numerous investigations<sup>[2]</sup>, such problems as the reaction mechanism and the rate-determining step of the anode reaction are still controversial and need clarification. As Grjotheim *et al*<sup>[2]</sup> have shown, the experimental information available is characterized by major divergence regarding the magnitude and the type of anodic overvoltage.

Normally there are two methods to measure anodic overvoltage in the molten salt systems: one is the current interruption<sup>[2-5]</sup>, the other is the AC impedance spectroscopy<sup>[2,6-9]</sup>. The former seems simple, but there are many factors, such as the quality and limitation of apparatus, cell design, electrode geometry, gas bubble and external circuit etc. affecting the precision of the method. For the latter, a complex calculation is required unless a simple extrapolation versus the inverse square root of frequency is found to be satisfactory besides the influential factors similar to those mentioned above. The AC impedance spectroscopy is a promising technique and can

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give more useful information. So far, both methods need to be improved to reach higher precision.

The aim of the present study was to improve the current interruption technique for the measurement of anodic overvoltage and to find the main factors which influence the measurement of anodic overvoltage of carbon materials in order to study the anode reaction mechanism and the effect of additives on the anodic overvoltage in aluminium electrolysis. The technique for measurement of anodic overvoltage can be applied not only in cryolite-alumina melts but also in other molten salt systems.

## 2 GENERAL COMMENTS

As reviewed by Grjotheim *et al*<sup>[1]</sup>, the key problems to be solved for measuring anodic overvoltage in aluminium electrolysis are two aspects. Firstly, the current and/or potential oscillations are quite pronounced on the horizontal anodes facing downwards, imitating the industrial anode, which may seriously affect the precision of measurements at high current densities (cds). Secondly, unless the reference electrode is located very close to the working electrode and the current density is low, the results must be corrected for the ohmic voltage drop.

Although the anodic process and the measurement of anodic overvoltage in cryolite-alumina melts have been the subjects of numerous investigations, the difficulties involved in performing reliable measurement of anodic overvoltage have not been completely overcome. The reported data concerning overvoltage of carbon anodes are rather scattered and partly conflicting, which is most likely caused by one or more of the following factors.

(1) The anodic overvoltage differs among the variety of carbon materials, such as graphite, pyrolytic graphite, vitreous carbon and baked carbon anodes etc., due to their different structure, composition, density, porosity and reactivity, etc.

(2) Variables such as the carbon anode composition (quality of coke and pitch in baked carbon), baking temperature and impurities in

the anode may affect the anodic process and thus the overvoltage. Even the variations and inhomogeneity in porosity, density, composition and structure of the anode materials, resulting from minor differences in the preparation process of anodes of the same composition, could cause discrepancies in anodic overvoltage due to the changes in active surface area during electrolysis.

(3) The measurements of anodic overvoltage can be influenced by difficulties in determining the ohmic voltage drop between the reference electrode and the working electrode. Several methods have been used for this purpose, such as current pulse or interruption techniques and electrochemical impedance spectroscopy with a superimposed alternating current. Generally, the accuracy of such measurements depends on the procedure and the quality of the equipment used.

(4) Due to the fact that the anode is being consumed, the surface of the anode changes during the measurement, and also the shape of the anode may change somewhat. Hence, the current distribution may be affected, and the determination of the active electrode area may be difficult.

(5) The presence of bubbles from the anode gas evolution may interfere in the determination of the steady state potential and the ohmic voltage drop.

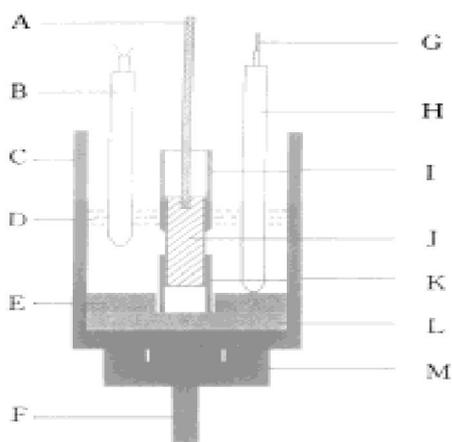
(6) The shape of the anode and the geometry of the cell can influence the current distribution and impede the escape of gas bubbles from the anode surface in laboratory cells and thus give rise to experimental errors. Concentration gradients with respect to alumina may also occur.

## 3 DESCRIPTION OF MODIFIED METHOD

There are four points in this study to improve the measurement of anodic overvoltage by means of the current interruption method in cryolite-alumina melts.

(1) Vertical anodes whose upper sheath was cut into a conic shape as shown in Fig.1 were used to facilitate bubble detachment and thus decrease the potential oscillations at constant currents. The inner wall of the graphite

crucible served as counter electrode (cathode) and the bottom of the graphite crucible was insulated with sintered alumina disks. The potential oscillations are less than 15 mV at a constant current. On horizontal anodes facing downwards the potential oscillations are quite pronounced, as mentioned above, the amplitude of oscillations is often more than 100 mV.



**Fig. 1** The experimental cell

- A—Steel rod; B—Pt-Pt10%Rh thermocouple;  
 C—Graphite crucible; D—Molten salt;  
 E—Sintered alumina plate with a hole;  
 F—Steel lead for cathode; G—Tungsten wire;  
 H—Aluminium reference electrode;  
 I, K—Sintered alumina sheaths;  
 J—Carbon anode; L—Sintered alumina plate;  
 M—Graphite support

(2) A high frequency digital oscilloscope (LS140, 200 M) was used, whose sampling time was only 5 ns per point. The oscilloscope makes it possible to trace the whole potential decay curves just a few microsecond after the current is interrupted. Customary recording equipments for this purpose, such as X-Y recorder, start responding the potential change at least 50  $\mu$ s or even 1 ms after the current is interrupted. Decay curves and extrapolated ohmic drops obtained in this way will not exactly be determined by the discharge of the double layer capacitance of the anode.

(3) Current interrupters with fast switching times were used. Two models of current in-

terrupters (Model 800 with max. current 10 A and Model 805 with max. current 50 A, IR Measurement System, Scribner Associates INC., Virginia, USA) were used. For the former, the switching time is less than 1  $\mu$ s and for the latter 1 ~ 3  $\mu$ s. The duration of current interruption is quite short (10 ~ 40  $\mu$ s), and hence the state of the anode polarization will not be changed much because of the current interruption. In comparison, mechanical commutators and even ordinary galvanostats matched with functioner used by many authors can not attain such a resolution and the switching times tend to be larger than 20  $\mu$ s or even more, as tested in this study. Furthermore, mechanical commutators and ordinary galvanostats have much longer periods when the current is off.

(4) The last difficulty is the determination of the starting point (the potential at time zero without ohmic drop) of potential decay curves, or the determination of the ohmic drop. In most cases, a graphical extrapolation to time zero was used. This procedure was used in previous stage of our studies<sup>[5]</sup>. The question is what is the precision of this procedure, especially in the presence of ringing (damping oscillations) due to inductance in the circuit at fast current interruption. A mathematical simulation was put forward to solve this problem. The AC impedance spectroscopy is another way to determine the ohmic drop<sup>[6,7]</sup>, which will not be discussed here.

#### 4 EXPERIMENTAL

The experimental cell and the design of the anodes used for overvoltage studies are shown in Fig. 1. The cell was placed in a gas tight furnace under argon atmosphere. The anode geometrical surface area exposed to the melt was 3.14 cm<sup>2</sup>. In order to decrease the influence of the non-uniform porosity of the carbon anode, the surface area was increased to 9.42 cm<sup>2</sup> (the diameter from 1 cm to 1.5 cm, the height from 1 cm to 2 cm) in the present study. The upper and lower parts of the vertical anode were sheathed by close-fitting sintered alumina tubes. The upper sheath should be cut into a conical shape. The

anode was placed in a concentric position in the crucible, through a sintered alumina disk with a central hole, to achieve a uniform current distribution.

The carbon anode materials used in the present study were prepared in Zhengzhou Light Metals Institute, P. R. China. Industrial grade petroleum coke was crushed and mixed to a specified recipe (4.2% medium fraction (1 ~ 2 mm), 25.6% fine fraction (< 1 mm), 70.2% mill dust). The green paste was fabricated from the coke by mixing it with coal tar pitch (27.4%) and it was baked at either 970 °C or 1 200 °C. Cylindrical anodes of these carbon materials used for overvoltage studies were machined from drilled cores to a diameter of 15 mm.

The experiments were conducted in the Na<sub>3</sub>AlF<sub>6</sub>-Al<sub>2</sub>O<sub>3</sub> (sat.) and Na<sub>3</sub>AlF<sub>6</sub>-Al<sub>2</sub>O<sub>3</sub> (sat.)-10.9% AlF<sub>3</sub>-5% CaF<sub>2</sub> melts at 1 010 °C and 970 °C, respectively. The wall of the graphite crucible served as the cathode. Constant current was delivered by a potentiostat connected with a 0.05 Ω standard resistance to supply with constant currents. The ohmic voltage drop between the anode and the reference electrode was determined by means of the current interruption technique with a current interrupter switch (Model 800 with max. current 10 A and Model 805 with max. current 50 A, IR Measurement System, Scribner Associates INC., Virginia, USA) and a digital storage oscilloscope (LeCroy LS-140 Scopestation). The switching time and the duration of current interrupter switch were < 1 μs and 10 μs for the former and 1 ~ 3 μs and 40 μs for the latter, respectively.

The measurement was started 30 ~ 40 minutes after the anode was immersed into the melt, and two or three anodes were tested one by one for every experimental run. The cell current was decreased in steps from 12.0 A (1.28 A/cm<sup>2</sup>) to 0.6 A (0.064 A/cm<sup>2</sup>) under galvanostatic conditions. A steady state potential was normally attained in 120 ~ 180 s at 12.0 A, and the duration of the rest of the steps was only 30 s. Due to the use of a vertical anode, the gas-induced potential oscillations at a constant current were less than 15 mV when the potential had reached steady state after a certain time (30 to 180 s). After the

measurements, the diameter of the carbon anodes had decreased from 15 mm to approximately 14.6 mm, and the geometrical surface area exposed to the melt was thus lowered by about 3%.

## 5 RESULTS AND DISCUSSION

### 5.1 The source of the ringing on the potential decay curves

When the current was interrupted, a large ringing (potential oscillation) was found to increase with increasing current as shown in Fig. 2. The question is where did the ringing come.

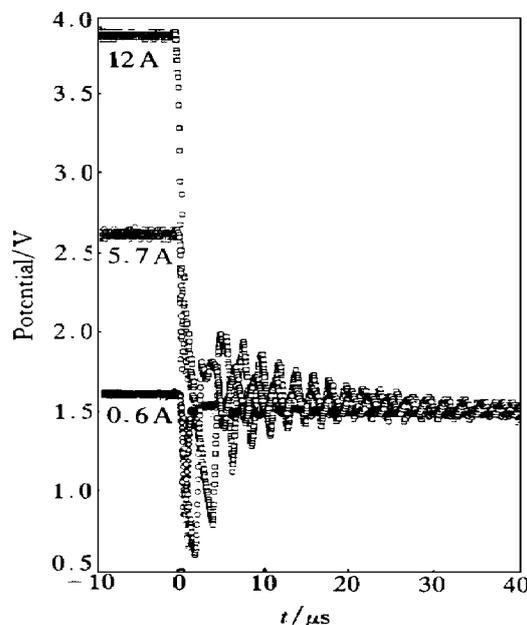
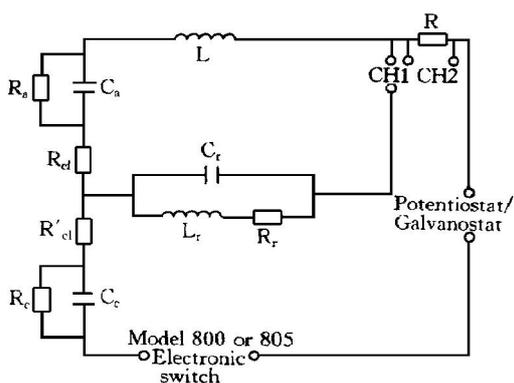


Fig. 2 Typical potential decay curves after current interruption (I = 12, 5.7, 0.6 A, t = 1 ~ 2 min, respectively)

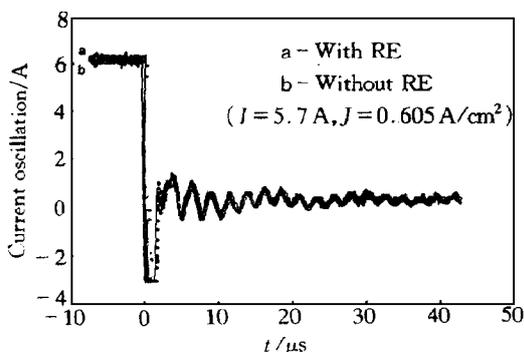
In order to answer this question, the tests were made. The voltage oscillation (actual current oscillation in the circuit) between both ends of the 0.05 Ω standard resistance in the external circuit, shown in the equivalent circuit and set-up connection presented in Fig. 3, was measured by means of channel 2 (CH2) on the oscilloscope, at the same time the potential ringing between the reference electrode and the anode was measured by means of channel 1 (CH1). As

shown in Fig. 4, after the current was interrupted the current oscillations (current ringing) in the microsecond time domain were observed and it was the same regardless of the presence or absence of the reference electrode. And the current ringing has the same tendency to increase with increasing current as potential ringing, see Fig. 5. Simulation tests with electronic components instead of the real cell system in the equivalent circuit also gave similar results regardless of the

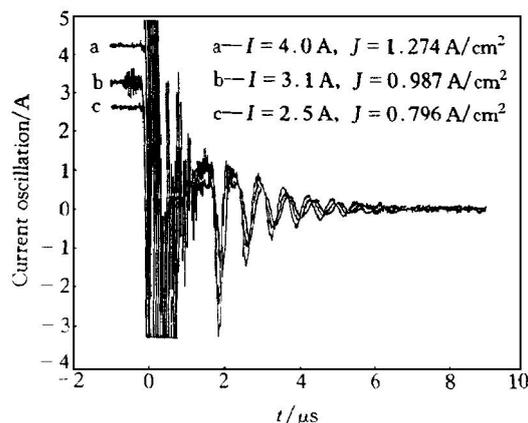


**Fig.3** Equivalent circuit of the measuring set-up

$R_a, C_a$  — Anodic charge transfer resistance and capacitance;  $R_c, C_c$  — Cathodic charge transfer resistance and capacitance;  $R_{cl}, R'_{cl}$  — Electrolyte resistances;  $R_r, C_r$  and  $L_r$  — Charge transfer resistance, capacitance and pseudo-inductance at the reference electrode;  $R$  — Standard resistance ( $0.05 \Omega$ ); CH1, CH2 — Measurement channels of oscilloscope



**Fig.4** Typical current oscillation between both ends of standard resistance ( $0.05 \Omega$ )



**Fig.5** Typical current oscillation at different currents ( $I = 4, 3.1, 2.5 \text{ A}$ , respectively)

presence or absence of an equivalent of a reference electrode. Hence, it seems that the potential ringing in the microsecond time domain after the current is interrupted is mainly originated from the entire circuit including the electronic switch itself. Actually, the electronic switch can be regarded as a high input resistance when the current is interrupted and it functions in the oscillation in the RIC (Resistance-Inductance-Capacitance) circuit.

### 5.2 Anodic overvoltage measurement and calculation

A typical potential decay after current interruption is presented in Fig.2. It is seen that the discharge of the polarized anode results in an oscillating decay. Customarily a graphical extrapolation to time zero is used in the current interruption measurements, but due to the disturbing oscillations, the precision of this procedure is in doubt. To clarify this problem and to make the treatment of experimental data more efficient, an analytical simulation was tested as well. The primary goal of both methods is to determine the overpotential at zero time  $\eta(0)$ , free from the ohmic voltage drop.

Although the reference electrode does not cause the oscillation, the whole loop shown in Fig.2 can still be regarded as a resistance-inductance-capacitance (RIC) damped oscillation cir-

cuit. Hence, the time dependence of the potential oscillations can still be expressed by the equation:

$$\eta_{po}(t) = \exp(-at) (C_1 \sin \omega_a t + C_2 \cos \omega_a t) \quad (3)$$

where the angular frequency  $\omega_a$  is related to the resonance frequency of the inductive subcircuit and the frequency  $a$  to the resistance in the circuit, and  $C_1, C_2$  are constants and  $t$  is the time.

In addition to the oscillations in the overvoltage coming from ringing of the circuit, the exponential overvoltage decay due to the discharge of the large capacitance of the carbon anode is recorded:

$$\eta_{an}(t) = \eta(0) \exp(-t/(R_a C_a)) \quad (4)$$

where  $R_a$  and  $C_a$  are the charge transfer resistance at the carbon anode and the related capacitance.

The total overvoltage decay will thus be described by the equation

$$\eta(t) = \eta(0) \exp(-t/(R_a C_a)) + \exp(-at) (C_1 \sin \omega_a t + C_2 \cos \omega_a t) \quad (5)$$

which for the fitting procedure is turned into the form

$$\eta(t) = A \exp(-Bt) + \exp(-Ct) \times (D \sin Et + F \cos Et) \quad (6)$$

in which  $A, B, C, D, E$  and  $F$  are constants to be evaluated by the fitting procedure.

An example of the representation of the experimental overvoltage decay by Eq.(6) is presented in Fig.6.

In Fig.6, the dots are experimental data recorded, the solid line is the overvoltage decay curve, the dash curve is the simulation curve of the potential oscillation. The overvoltage decay curve according to Eq.(4) or the first term in Eq.(6) is obviously very close to a straight line, which indicates the graphical method for the extrapolation of overvoltage decay to zero time (extrapolation by hand on the potential oscillation curves) was theoretically reasonable.

### 5.3 On Tafel curve Bending down

In Fig.7, the solid dots are the overvoltage calculated from the experimental data. A Bending-down phenomenon is observed at a high cur-

rent density, which is obviously unreasonable. To search for the cause of these Bending-down phenomena, it was assumed that the Tafel curve should be a straight line in the experimental

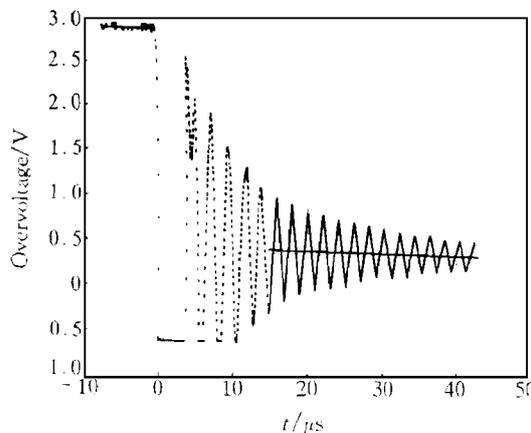


Fig.6 The fit of potential decay curve of carbon anode polarized at 12 A for 2 min (Anode area : 9.42 cm<sup>2</sup>)

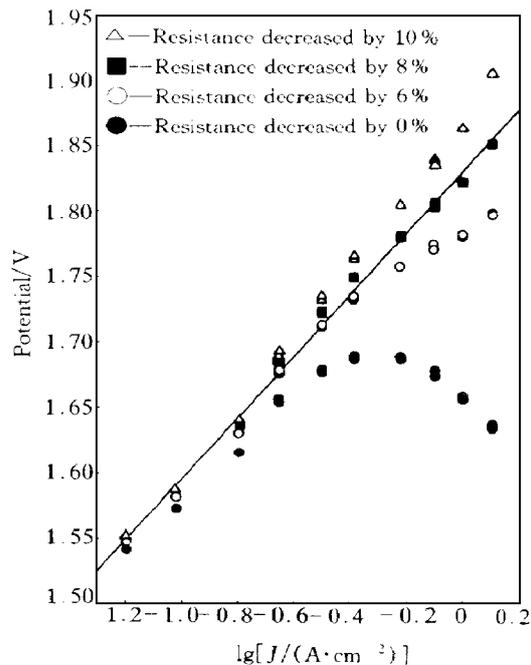


Fig.7 A typical Bending-down of Tafel curve at a high current resulted from determination of higher ohmic drop due to lag of experimental set-up

current density range. Resistance ( $R$ ) was obtained from the measured ohmic drop ( $IR$ ) and reduced identically by a few percent at the corresponding current. Then, the Tafel curves were recalculated using the reduced resistance. The open dots, solid squares and triangles in Fig. 7 show the Tafel curves when the resistances were reduced identically by 6%, 8% and 10%, respectively. The squares give a straight line, the open dots still bend down, the triangles bend up, which means that when the ohmic drop is reduced too high, the Tafel curve would bend down, and when it is reduced too low it would bend up. It was also noticed that the Tafel curve was not affected too much under the low current density range with the determination of ohmic drop.

Obviously, the ohmic drop was determined higher than its real value in the measurement, due to the delay of electronic switch and disturbing of double layer discharge. This resulted in lower Tafel coefficients.

#### 5.4 Effect of carbon powder on anodic overvoltage

Three or four identical anodes were measured in succession in one experiment, i. e., in the same melt, on the same day. The anodic overvoltage was found to increase slightly with sequence. One possible reason for that might be the accumulation of carbon dust in the melt during the experiment. To check this hypothesis, the effect of carbon powder added into the electrolyte was studied on carbon anodes. The results showed that the anodic overvoltage increased markedly with increasing of carbon content in the electrolyte. Obviously, the effect of carbon dust should be considered when experiments to determine the overvoltage of carbon anodes run for long time. So it is possible that when Haarberg et al.<sup>[8]</sup> found that the anode potential increased with time, it might be due to the effect of carbon dust.

## 6 CONCLUSIONS

A current interruption method with four main points of improvement was used to measure the overvoltage of carbon anodes in cryolite-alumina melts. The source of potential ringing in the domain of microsecond time after the current was interrupted was analyzed. It comes mainly from the entire circuit, not only from double layer inductance of reference electrode. Carbon powder or carbon dust present in the melt has an effect on anodic overvoltage during long time of measurement. The improved current interruption method can also be used for other molten salt systems.

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