PHYSICAL CHEMISTRY IN MOLTEN SALT
ELECTROLYSIS OF ALUMINIUM

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ABSTRACT

This paper deals with studies on the wettability of carbon anode and carbon cathode by molten salts, the reason of initiation of anode effect and the metal fog formation in molten electrolyte. Some new investigations of lithium salt–containing anode in relation to critical current density (CCD) are also reported.

WETTABILITY OF CARBON ANODE AND CARBON CATHODE BY MOLTEN ELECTROLYTE

The wettability of carbon electrodes by molten salts is quite different when the electrodes are polarized than when they are not, because of the variation of the surface state of the electrodes, as well as the ionic concentration of the liquid layer adjacent to the electrodes during the electrolysis process of cryolite–alumina melts. The laboratory microelectrolysis cell is shown in Fig.1.

When the carbon plate was given a cathodic polarization, the molten drop gradually spread out on the carbon plate after several minutes of electrolysis, and tended to separate from the anode. This caused an interruption in electrolysis. However, the spread molten drops often collected together automatically and touched the anode again, then electrolysis resumed.

As the carbon plate was anodically polarized, good wettability of the carbon rod (now it was cathode) by the molten drop was observed. The wettability of the carbon anode by the melt was good at the beginning of electrolysis, but it became poor later, and the electrolyte even coalesced into a globe. At this moment, the current decreased suddenly and the voltage increased and an anode effect occurred (Fig.2). Sometimes, most of the melt adhered to the cathode (carbon rod) and separated from the carbon plate anode. These phenomena were consistent with those mentioned above.

When the polarities of the electrodes were changed, the back EMF of the electrolysis cell changed significantly. Hence it is possible to decrease the overvoltage during the normal electrolysis process by periodically reversing the polarities of electrodes.

When a platinum wire loop was used instead of carbon as an anode or a cathode, similar phenomena were observed. The wettability of platinum by the molten cryolite–alumina electrolyte was originally very good, but when it was used as anode and a carbon plate as cathode, after a D. C. was applied, the molten electrolyte would be repulsed by the anode and separated from it.
a while the electrolyte would touch the anode again. Thus appeared a cyclic process of electrolysis—repulsion—electrolysis. When the platinum wire loop was used as cathode and the carbon plate as anode, the electrolyte would be attracted by the cathode, and an anode effect was observed on the anode carbon plate. The Pt loop would be vibrated vigorously.

So both carbon and platinum electrodes showed the same behaviour of repulsing the electrolyte when anodically polarized, this phenomenon is called "Anodic Repulsion", and of attracting the electrolyte when cathodically polarized—this phenomenon is called "Cathodic Attraction".

ANODE EFFECT

Some characteristics of the anode effect in aluminium electrolysis may be described briefly as follows:

(1) When an anode effect occurs in one cell, the cell voltage is with high frequency (about 10000 to 20000 Hz, Fig.3). This corresponds to the appearance of electric sparking on the carbon anode. The carbon anode and aluminium bus-bar vibrate.

Fig.1 Schematic diagram of the microelectrolysis cell; 1—Ni–Cr wire conductor, 2—stainless steel tube (45 mm dia., L.600 mm), 3—carbon rod (8 mm dia.), 4—molten electrolyte, 5—carbon plate (y = 5 mm), 6—steel support.
Fig. 2 Aluminium electrolysis in cryolite–alumina melts. (a) when the carbon electrode was served as anode and the carbon plate as cathode, (b) when the carbon electrode was served as cathode and the carbon plate as anode, (c) and (d) when anode effect occurred.

Fig. 3 Cell voltage with high frequency during the anode effect in industrial aluminium electrolysis cell.

(2) During the anode effect, on the part of anode surface submerged in molten salt there appears electric sparking. The electric sparks are twinkling, and they appear first at some places, then at other places.

(3) The anode gas composition changes suddenly when an anode effect occurs. During normal electrolysis the anode gas usually consists of 75%
C0₂ and 25% CO. When an anode effect occurs, the gas composition may be changed to CO₂ 25%, CO 50%, CF₄ 22.5 and C₂F₆ 2.5%. This fact implies that there happens a change in anodic reaction from the discharge of oxygen ions to codischarge of oxygen and fluorine ions.

(4) During the anode effect, there is a jet action from the anode bottom surface when the cell voltage is over 20 V. From jet actions it was observed that there are minute gas bubbles injecting from the carbon anode into the molten bath, causing a violent stirring in the interpolar space. The jet action from the carbon anode was found in molten PbCl₂ as well as in molten cryolite–alumina salts. The reason for the jet action may be due to an expansion of anode gases at high temperature during anode effect. However, this jet action is harmful to current efficiency because the stirring action of these gas bubbles would cause much metal on the cathode to be reoxidized (see Fig.4).

It was found in a see-through cell that during normal electrolysis in cryolite–alumina melts the anode gas bubbles could leave the carbon anode freely, but when the electric current density was raised to the critical value, the gas bubbles on the anode would be tightly pulled up and stuck on the whole anode surface to form a thin continuous film, at that time an anode effect occurred. The anode gases were already ionized and attracted electrostatically by the carbon anode. When the current was cut off, the gas film contracted all at once to form a single bubble which stayed on the undersurface of the anode.

From the above facts we can infer that the direct reason of anode effect may be related to the electrostatic attraction of ionized gas bubbles by the anode. This is due to the newly formed gases, such as CF₄, C₂F₆ and CO, being

![Fig.4 Jet action from carbon anode during the anode effect in cryolite–alumina melts.](image-url)
more easily polarized, they can be attracted electrostatically by the anode at high potential. This gas film sticks firmly to the anode surface and penetrates into the pores and fissures of the carbon anode.

The above viewpoint may be confirmed by the appearance of electric sparks on the anode during the anode effect. On industrial cell, the carbon anode is very big. It may be 12 m² in one piece. During the anode effect, the gas film is not actually continuous, which may be in shape of a network. At the boundaries of gas bubbles there are some electrolyte. The electric sparks first appear at some localities, then they move to other places. So the electric sparks are twinkling. The occurrence of electric sparks means ionization of gas bubbles. When the electric charges of gas bubbles are neutralized in some places, there the electric sparks will disappear.

In industrial aluminium electrolysis cells, for quenching the anode effect we usually make the anode and cathode short-circuited for a short time, i.e., by splashing the negatively charged liquid aluminium in the cell to the anode, so that the electric charges on the gas bubbles can be neutralized. This is a support for the electrostatic attraction theory.

Therefore, the primary reason for the initiation of anode effect may be the anodic repulsion by gases exerted to the molten electrolyte, and the direct reason may be due to an electrostatic attraction of gases by the anode at high anodic potential.

**INFLUENCE OF LITHIUM SALT ADDITION TO CARBON ANODE ON ANODE EFFECT**

The result of lithium salt addition to carbon anode on anode effect was investigated by critical current density measurements.

In the experiments spectroscopic graphite electrode of ø 6 mm was used as anode. The electrode was impregnated in molten LiF at 900°C for 2 hours. The results of CCD—Al₂O₃ concentration measurements are plotted in Fig.5.

It was seen that the CCD values increased with Al₂O₃—content in the melts. It was very interesting to say that the lithium salt—containing anodes are usually with higher CCD values than those without. The reason is that the lithium salt—containing carbon anode may be much better wetted by the molten bath, and the gas bubbles on the anode may be expelled more easily by the molten electrolyte. So this kind of carbon anode is very useful in preventing the frequent occurrence of anode effect in aluminium electrolysis cells, and it can decrease the cell voltage by decreasing the ohmic overvoltage of gas film on the carbon anode.

For preparing the lithium salt—containing carbon anode there are two methods: (1) by impregnation in molten LiF, (2) by adding Li₂Co₃ to the carbon paste and forming the anode. The second method has been used in Söderberg cells for over 3 years with good operational results.
Visual observations of several molten salt electrolysis processes were made in a two-compartment see-through quartz cell. The electrolysis of aluminium, magnesium, lead, zinc, sodium and potassium were studied. The colour of the melt in the anode compartment was pale yellow for fluoride-chloride melts and red for chloride melts, caused by the presence of dispersed anode gases during electrolysis. In the cathode compartment, streamer of metal fog were formed. The colours of the metal fog were purple for aluminium, grey for magnesium, lead and zinc, blue for sodium and green for potassium (Table 1).

The metal fog tended to sink to the bottom of the cell, which indicated that it had a higher density than that of the melt (Fig.6). The metal fog also penetrated into the anode compartment, probably due to convection and diffusion in the melt. The most probable explanation of the nature of the metal fog...
| Metal | Molten salt composition | Bath temperature (°C) | Colours Before electrolysis | After electrolysis |
|-------|-------------------------|------------------------|----------------------------|-------------------|
|       |                         |                        | both compartments         | Anode compartment | Cathode compartment |
| Al    | NaF–AlF₃–Al₂O₃–NaCl     | 800                    | White transparent         | Pale yellow       | Purple             |
| Mg    | NaCl–KCl–MgCl₂          | 800                    | White transparent         | Red               | Grey               |
| Pb    | NaCl–KCl–PbCl₂          | 800                    | White transparent         | Red               | Grey               |
| Zn    | NaCl–KCl–ZnCl₂          | 800                    | White transparent         | Red               | Grey               |
| Na    | NaCl                    | 800                    | White transparent         | Red               | Blue               |
| K     | KCl                     | 800                    | White transparent         | Red               | Green              |
is that it consisted of dispersed metal particles. This chemically unstable phase dissolved easily in the melt and was oxidized quickly by the anode gases.

Key words: wettability, anode effect, Li-salt containing carbon electrode.

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