ON THE INITIATION OF ANODE EFFECT IN CHLORIDE MELTS

Ulf Erikson and Reidar Tunold
Institutt for Teknisk Elektrokjemi
Norges Tekniske Høgskole (NTH)
Universitetet i Trondheim
7034 NTH, NORWAY

ABSTRACT

The gas evolution process and the initiation of anode effect (AE) have been studied in chloride melts on different shapes of electrodes made of various materials. The critical cd (ccd) has been determined as a function of composition. The value of ccd varied from about 1 A cm$^{-2}$ in pure NaCl melts to 20-35 A cm$^{-2}$ in melts containing 20-30wt% MgCl$_2$. The formation and detachment of bubbles have been studied by visual inspection and by short film sequences.

A mechanism for the initiation of anode effect is proposed.

INTRODUCTION

The anode effect (AE) which manifests itself as a blocking of the anode surface inhibiting current transfer, is a well-known phenomenon especially occurring in molten salt systems such as in cryolite/alumina and other halide based melts. It is even found in aqueous solutions where it also occurs in connection with the cathodic hydrogen evolution, making this phenomenon a general electrode effect. The mechanism for initiation of AE may however be different in different systems. Several possible causes for AE have been proposed, which can be summarized briefly as follows:

i) Formation of an insulating solid compound on the anode surface (1-4)

ii) Deteriorating wettability between the anode and the melt due to:
a) changes in surface tension (5,6)
b) formation of surface-compounds (7-12) or gaseous anode products (13,14)

iii) Mass transfer problems due to

a) transport of gas bubbles away from the anode surface becoming rate controlling, resulting in gas blanketing of the surface (15,16)
b) spontaneous formation of a gas film from a supersaturated melt in the vicinity of the anode surface (17,18)

iv) Electrostatic attraction of negatively charged gas bubbles to the anode (19,20)

v) Thermal effects, IR-heating of the anode/electrolyte interface resulting in vapourization of the electrolyte close to the anode (21).

A main problem in proposing a comprehensive theory is the rather large differences in critical cd s observed in different melts, from about 0.1 A cm⁻² in some fluoride melts (22) to 20-35 A cm⁻² in some chloride melts and in aqueous solutions, as found in the present investigation.

In the present work we have studied AE in chloride melts. The critical cd for the onset of AE has been studied as a function of the MgCl₂-content in the binary mixture with NaCl and in quaternary mixtures with NaCl, KCl and CaCl₂ in the temperature range of 750-830°C. The gas evolution process including bubble formation and detachment, and the formation of a gas film, was studied visually and by making film sequences. A mechanism for the initiation of AE is proposed.

EXPERIMENTAL

Cell, melts and electrodes

Most of the experiments were carried out in a transparent gold film silica furnace (Trans Temp. Inc., USA).

Alkali chlorides were purified by heating in vacuum, melting and recrystallization. Magnesium chloride and calcium chloride were heated by slowly increasing the temperature to about 400°C in HCl-atmosphere. The magnesium chloride was thereafter distilled in vacuum. Calcium chloride was finally melted under HCl atmosphere and then filtrated through a silica frit. All handling of the purified salts was performed in a dry box atmosphere. The final salt mixture was contained in a transparent silica-tube (55 mm φ) with bottom.
The following types of anodes were used:

- Spectrographic graphite, Grade II (4.56 mm φ) from Johnson, Matthey Chemical Ltd., England, encapsulated in boron nitride. These electrodes were conically shaped with the active anode area facing downwards and with a typical area of 0.5 cm$^2$
- Glassy carbon rods, 3mm φ, type GC-30 from Tokai Carbon Co., Ltd., Japan
- Spectrographic graphite rods, same quality as above
- A tungsten rod, 1.8 mm φ (99.9% purity), from Tungsten Manufacturing Co. Ltd., England

As a counter electrode, a Mg/Ni alloy rod shielded by a quartz tube was employed.

Measuring procedures

The ccd was measured by using a voltage sweep method at two different sweep-rates, $v = 0.33 \text{ Vs}^{-1}$ and $v = 3.44 \text{ Vs}^{-1}$. Occasionally a "semi-potentiostatic" method was employed, where the cell voltage was kept constant allowing the cell current to stabilize before proceeding to a higher voltage.

The gas evolution process and the onset of AE was filmed by a 16 mm movie camera.

Melt samples were taken after each addition of MgCl$_2$ and analyzed by atomic absorption spectrometry.

RESULTS AND DISCUSSION

The critical cd

Values for the critical cd as a function of MgCl$_2$-content are shown in Fig. 1 and 2, measured by the voltage sweep method. In Fig. 1 results from the measurements in the binary system MgCl$_2$-NaCl are shown. The ccd seems to increase from values of 1-4 A cm$^{-2}$ in pure NaCl to about 30 A cm$^{-2}$ at 25 wt% MgCl$_2$, with no further increase at higher content. The same general trend is found in the quaternary system as shown in Fig. 2, but with a somewhat lower ccd. The reproducibility of the current values at different electrodes was not good and was even slightly worse at lower sweep rates. At lower sweep rates the measured ccds were somewhat reduced.

The main difference between the pure alkali chloride melts (and in
mixtures with CaCl$_2$) and melts with MgCl$_2$, is the interfacial tension which is reduced by adding MgCl$_2$ to the melts. Pure CaCl$_2$ has a surface tension of 147 dyn cm$^{-1}$ at 800°C and pure NaCl 116 dyn cm$^{-1}$ (T=850°C), whereas the surface tension of MgCl$_2$ is 62 dyn cm$^{-1}$ (23). The contact angle between a graphite surface and chlorine bubbles in molten chlorides have been determined to 120 - 175°C in pure NaCl and to 36 - 40°C in pure MgCl$_2$ (24). This means that the melt is wetting the surface better the more MgCl$_2$ is added, leading to smaller contact angles between the electrode and the gas bubbles and therefore to smaller bubbles.

**Visual observations**

Visual observations reveal large differences in the gas evolution process in NaCl melts and in melts with low MgCl$_2$ content, compared with melts with more than about 5 wt% of MgCl$_2$. The difference is shown in Fig. 3 and 4. The effect of anode geometry is also pronounced.

**Gas evolution and the initiation of AE on rod-shaped anodes**

Visual observations show that the gas evolution process in pure NaCl and in melts with a low MgCl$_2$-content (<5 wt%) is distinctly different from how it appears in melts with higher MgCl$_2$-content, as shown in Fig. 3 compared to Fig. 4. The arrows in the figures indicate bubble movements. The numbers (1) to (3) are showing stages in the gas evolution process during a continuously increasing cell voltage/current sweep.

Fig. 3 shows gas evolution in pure NaCl.

(1): The gas evolution has started and a few bubbles coalesce. The bubbles, having a large contact area with the anode, are nonsymmetrical and rather flat. This means the contact angle $\theta$ is large (see Fig. 5). No bubbles leave the anode surface directly, but move upwards in a "creeping" manner still adhering to the electrode, until they meet the boundary atmosphere/melt, where they disappear into the gas phase.

(2): The situation is similar except that the cd (and cell voltage) is higher, giving a faster growth of the bubbles. At the same time more bubbles coalesce, giving as a total effect, an increasingly larger area covered by gas bubbles.

(3): Ultimately a few large bubbles coalesce suddenly, resulting in AE. A thin continuous gas film covering the entire anode surface appears. The current immediately drops to a very small value of about 0.01 A cm$^{-2}$. The cd in such cases is 1-3 A·cm$^{-2}$.
In fig. 4, 5-10 wt% \( \text{MgCl}_2 \) has been added to the melt.

(1): The reaction has started, producing small circular bubbles having a much smaller contact area with the anode than the bubbles in fig. 3. This is probably due to the improved wetting conditions at the melt/anode-interface, resulting in a smaller contact angle \( \theta \) (Fig. 5). At this stage (i.e. at low cd) the bubbles move upwards on the surface and a few coalesce, still adhering to the electrode.

(2): When the cd is increased, more and more bubbles start to leave the electrode surface directly to the melt.

(3): After a while the gas evolution process becomes quite vigorous at very high cds. Then, suddenly, the gas evolution stops and a thin gas film is observed at the anode surface, corresponding to the onset of AE. The ccd in this case is very high, \( \approx 10^{-35} \text{ A.cm}^{-2} \).

The interfacial potential seems to stabilize the gas film. When the potential sweep is reversed to a value somewhat lower than the voltage at the moment of initiation, the gas film disappears and normal gas evolution starts. The film vanishes from the lower end of the electrode and upwards, during a period of one to two seconds.

Conically shaped anodes, encapsulated in boron nitride

Figure 6 shows a corresponding sequence from (1) to (3) as in Fig. 3 observed in melts with a low \( \text{MgCl}_2 \) content.

In this case, however, the interface boron nitride/graphite seems to hinder the upward motion of the bubbles. Ultimately a few large bubbles coalesce, forming one large bubble covering the entire anode surface. This bubble remains at the electrode in the same way as the gas film observed on rod shaped electrodes, until the voltage is reduced to a value below the critical cell voltage necessary for initiating AE. Then the gas evolution will start as prior to AE.

At higher \( \text{MgCl}_2 \)-content (\( \geq 5 \) wt\%) gas bubbles will leave also this electrode directly to the melt. The critical cd is very high (10-35 A cm\(^{-2}\)) and the gas evolution becomes vigorous. The detachment of bubbles, however, seems not to be hindered by the edge between the graphite and the encapsulation. The AE occurs in the same manner as with the rod shaped electrodes. A thin gas film is formed spontaneously with a corresponding abrupt fall in the cd.
Changes of electrode materials and electrolyte

Tungsten anode

When using a tungsten rod as an anode in the chloride melt, the same development of AE was observed as with graphite rod electrodes. Gas evolution took place at the same time as tungsten dissolved anodically. The total cd was about 15 A cm\(^{-2}\) in a NaCl-MgCl\(_2\) melt containing 10 wt% MgCl\(_2\). In this value the anodic dissolution current is also included. This means that the mechanism of the AE is probably independent of the electrode material.

Aqueous solutions

The anode (electrode) effect was also studied in an alkaline aqueous solution where oxygen was evolved on a conically shaped graphite electrode encapsulated in boron nitride and a Pt wire electrode. The critical cd was very high, 30-40 A cm\(^{-2}\), on both types of electrodes. Very small bubbles were detached from the electrode surface in the same manner as shown in Fig. 4. The gas evolution became very vigorous with increasing cd. No large bubbles could be observed on the surface before the anode effect took place. The anode effect was initiated very suddenly also in this case. In case of the encapsulated graphite electrode one large bubble covering the whole surface was formed. On the Pt wire AE resulted in a thin gas film, as on the graphite rod electrode in the melt.

That this film really was a hydrogen film and not water vapour could be seen by the fact that the film was stable while the potential was kept constant or increased. With the reduced heating any water vapour should then condense. When reducing the potential, the film disappeared in the same way as in the molten salt systems.

GENERAL DISCUSSION

If only physical properties of the electrode/electrolyte interface are determining the initiation of AE, one should anticipate rather reproducible ccds. It seems, however, that the cd is rather irreproducible and that geometrical factors are participating. This indicates that the gas evolution process and the detachment of bubbles are the main determining factors.

We have earlier shown that AE can occur during very high current pulses before any bubble formation (17). In that case a thin gas film is probably formed from the supersaturated melt in the vicinity of the interface. Calculations have shown that in such a transient, concentration of chlorine might become thousand to ten thousand times the equilibrium saturation value in a film of thickness 10^{-4} cm. A gas film from such a layer would have a volume that is
about ten times the corresponding melt volume (17).

In melts with good wetting properties, i.e. in melts with a high content of MgCl₂, there seem to be no large effects of geometry. Bubbles detach readily from the surface. The active surface becomes smaller with increasing cd due to the increasing amount of bubbles on the surface. At the onset of AE a gas film is suddenly formed at the active surface area, covering the whole electrode. In this case the ccd is very high.

In melts with inferior wetting properties the bubbles stick to the electrode and coalesce to large bubbles with irregular shapes and which move along the electrode surface, adhering to it. The movements of the bubbles will depend on geometrical factors. The active area becomes very small with increasing current and AE occurs either by the coalescence of all existing bubbles or also here, by the sudden formation of a gas film from the supersaturated melt between the bubbles. This effect will bring about total coalescence of all bubbles.

If the active electrode surface continues into the atmosphere, the bubbles disappear into the gas phase and only a thin gas film is retained at the electrode. If an edge or another obstacle hinders the bubble movement, the electrode seems to be covered by a gas blanket. This probably also depends on the size of the electrode.

CONCLUSIONS

The critical cd for the initiation of anode effect depends on the wetting properties of the melt/electrode interface, being large in melts with good wetting properties and rather small in melts with high interfacial tensions.

The wetting properties as well as geometrical factors, decide the size of gas bubbles and the coalescence, detachment and transport of bubbles away from the surface. The AE is probably created by the sudden formation of a gas film from the supersaturated melt. The magnitude of the ccd then depends on the active, bubble free interface.
REFERENCES

(1) K. Arndt and H. Probst, Z. Electrochem. 29, 323 (1923)
(2) L.N. Antipin and N.B. Tyurin, Zhur. Fiz. Khim. 31, 1103 (1957)
(3) E. Pruvot, Allumina 22, 709 (1953)
(4) Y. Kanaya and N. Watanabe, Denki Kagaku 40, (6) 417 (1972)
(5) K. Grjotheim and C. Krohn, Freiberger Forschungshefte B82, 63 (1964)
(6) E.A. Zhemchuzhina, Izv. Akad. Nauk. SSSR Met. (3) (1965)
(7) W. Rudorff, G. Rudorff, J. Endell and G. Ruess, Z. Anorg. Chem. 256, 126 (1948)
(8) C. Krohn, Lic. Thesis, Inst. Uorg. Kjemi NTH (1963)
(9) Yu.I. Aleksandrov and V. P. Mashovets, J. Appl. Chem. USSR 39, (11) 2346 (1966)
(10) V.P. Mashovets and Yu.I. Aleksandrov, J. Appl. Chem. USSR 43, (3) 814 (1970)
(11) P. Mergault, C.R. Acad. Sc. Paris 240, 765 (1955)
(12) N. Watanabe and T. ASAue, J. Electrochem. Soc. Japan 39, 107 (1971)
(13) M. Fréjaques, Bull. Soc. Franca. Electr. 9, 684 (1949)
(14) A. Vajna, Met. Ital. 44, 585 (1952)
(15) R. Piontelli, A. Berbenni, B. Mazza and P. Pedeferrri Electrochim. Met. 4, (3) (1966)
(16) B. Mazza, P. Pedeferrri and G. Re, Electrochim. Acta. 22, 87 (1978)
(17) R. Tunold and T. Berge, Electrochim. Acta 12, 849 (1974)
(18) H. Vogt, Electrochim. Acta 29, (2) 167 (1984)
(19) H. Wartenberg, Z. Elektrochem. Met. 32, 330 (1926)
(20) P. Drossbach and P. Krahl,
Z. Elektrochem. 62, 178 (1958)

(21) H.H. Kellogg
J. Electrochem. Soc. 97, (4) 133 (1950)

(22) J. Thonstad, F. Nordmo and J.K. Rødseth,
Electrochim. Acta 19, 761 (1974)

(23) K. Grjotheim, J.L. Holm, B. Lillebuen and H.A. Øye,
Acta Chem. Scand. 26, 2050 (1972)

(24) K. Grjotheim, A.H. Schultz and H.A. Øye,
Met. 26, 236 (1972)
Figure 1. Critical Current Density (CCD) vs MgCl₂ Content, Binary System NaCl-MgCl₂, Voltage Sweep Measurements, \( v = 3.44 \, \text{V s}^{-1} \), \( T = 830 \pm 5^\circ\text{C} \).

Figure 2. CCD vs MgCl₂ Content, Quaternary System NaCl-KCl-CaCl₂-MgCl₂, Voltage Sweep Measurements, \( v = 3.44 \, \text{V s}^{-1} \), \( T = 750^\circ\text{C} \).

Figure 3. Gas Evolution on a Rod Shaped Anode in Pure NaCl, Low CCD.

Figure 4. Gas Evolution in MgCl₂-NaCl Melt, High CCD.
Figure 5. Gas Bubble and Contact Angle, Melt/Solid/Gas in Melts with a) Good Wetting Properties, b) Inferior Wetting Properties.

Figure 6. Gas Evolution on Conically Shaped Anodes Encapsulated in Boron Nitride, in Melts without MgCl$_2$ or with a Low MgCl$_2$-Content.