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HYDRODYNAMIC INSTABILITIES IN ELECTROLYTIC GAS EVOLUTION[*]

B. MAZZA, P. PEDEFERRI and G. RE
Istituto di Chimica-Fisica, Elettrochimica e Metallurgia del Politecnico di Milano,
Centro di Studio del C.N.R. sui Processi Elettrodici, Milano, Italy

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Abstract—Both the direct evidence from cine pictures and the analysis of systematic electrochemical investigations support a general explanation of the anode (or cathode) effect, which is based on the conditions of hydrodynamic instability described by Helmholtz and Taylor. Further confirmation of this hydrodynamic interpretation is provided by recent critical current density studies carried out to ultimately establish a method for *in situ* determination of the alumina content in cryolite–alumina melts.

NOMENCLATURE

I	current density
E	electrode potential
ϕ	specific heat flow
ΔT	wall temperature, relative to liquid
R_c	critical rate of gas evolution
I_c	critical current density
ρ_L	density of liquid
ρ_G	density of gas
γ	surface tension
g	acceleration
r	radius of wire
Δr	thickness of gaseous envelope enclosing the wire
z	electrode reaction valence
F	Faraday's constant
M_G	molecular weight of gas
N	equivalent concentration of electrolytic solution
Δc	supersaturation degree of dissolved gas in electrolytic solution
p	pressure
λ	wavelength
$C_{Al_2O_3}$	alumina concentration

INTRODUCTION

Research into non-consumable anodes to replace the carbon anodes in industrial aluminium electrolysis is progressing[1–8]. Innovations in the anode and cell design and in the operating conditions can therefore be expected. This, in particular the different nature of the anode process (evolution of oxygen instead of carbon dioxide) and the different interactions between fluorine and anode material, will influence the conditions for the onset of the anode effect. In addition, the explanation of this anomalous effect is still one of the most controversial topics in electrochemistry (the main theories are reviewed below).

The authors of this paper consider it worth while to present an abridged discussion of their results concerning the electrochemical and morphological aspects of electrolytic gas evolution and associated anomalous effects, in both molten salts and aqueous solutions[9–19]. This work has been carried out for some 15 years, initially together with the late Prof. Piontelli. Later development of this research is then described[20].

MECHANISM OF THE ANODE EFFECT (REVIEW)

The different theories suggested to explain the anode effect in the aluminium electrolysis are based on the following hypotheses[21, 22].

(i) Change in sign of the electric charge of the anode gas bubbles[23–26]. In the presence of sufficient oxides, this charge would be positive. At low oxide contents, it would be negative, and the gas bubbles would then be attracted electrostatically by the anode to cause an increase in resistance.

(ii) Variations of the interfacial tension at the three-phase boundary anode–bath–gas, and consequently of the wettability of the anode. With decreasing oxide content, the anode would be wetted by the bath to a lesser extent, until a continuous gaseous layer finally would envelope the anode[27–29].

According to other authors, however, wettability would be affected primarily by the composition of the anode gas[30–32]. Wetting of the anode by the bath would occur when oxygen was formed by the anode reaction ('normal' electrolysis) and would stop when oxygen would be replaced by fluorine at low alumina contents in the bath.

(iii) Alteration in the surface state of the anode due to various possible processes[†] involving the formation of solid layers or surface films with highly insulating properties, preventing a 'normal' electrolysis[33–45]. Current could only flow by penetrating this layer or film. The formation of layers or films on the anode surface would alter the wetting conditions; the poorer wettability would be a result and not a cause of the anode effect.

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[†] For example, mechanical breaking up of the anode caused by the release of fluorine; reaction between the gaseous electrolysis products, *eg* CF_4, COF_2 *etc*, and the carbon of the anode; anodic discharge of ions resulting from the cryolite dissociation; separation of bath components, *etc*.

(iv) Reaching of limit current conditions for the discharge of oxygen containing ions[46–49], with the consequent discharge of fluorine containing ions and adsorption of one or a few monolayers of discharged products. As a result, the surface electrical resistance would be increased or the wettability lowered.

(v) Formation of a gaseous film on the anode from the bath, the bath having become supersaturated with gas desorbed from the anode surface[50].

(vi) Evaporation of the bath close to the anode. Such an interpretation is suggested by the existence of an anode (or cathode) effect in the electrolytic gas evolution from aqueous solutions occurring at sufficiently high *cd*s to raise the temperature at the electrode to above boiling point of the solution[51, 52]. In the case of cryolite baths where the relative content of the aluminium fluoride tends to increase in the anode region during electrolysis, evaporation of the aluminium fluoride might be expected to result in a gaseous layer around the anode.

(vii) Hydrodynamic instability in the electrolytic gas evolution[17–19]. This hypothesis is treated in more detail in the following paragraph.

(viii) Change in the structure of the electrolyte (oxygen would be bound to two Al-atoms instead of one Al at the onset of the anode effect): this would be the primary reason for the observed macroscopical changes[53].

HYDRODYNAMIC INSTABILITIES IN THE ELECTROLYTIC GAS EVOLUTION

Anomalous phenomena such as 'anode effects' are always encountered at gas evolving electrodes when the *cd* attains sufficiently high values, independent of the nature, polarity, or geometrical configuration of the electrode, and independent of the nature and properties of the bath (molten salts, aqueous or other media). Furthermore, analogous anomalous phenomena ('burnout') occur when the gaseous evolution is the result of the boiling of liquids in contact with a hot wall.

In both cases, three regions corresponding to different morphological aspects of the gas evolution can be distinguished on the characteristic *S*-shaped curves E/I (electrode potential *vs* *cd*) or $\Delta T/\phi$ (wall temperature, relative to liquid *vs* specific heat flow) as the gas evolution rate (*ie* I or ϕ) is increased.*

At first the gas evolves in the form of separate bubbles (Fig. 1a, a'): this is the 'normal electrolysis' (corresponding to the 'nucleate boiling'). In this range bubble size increases with increasing *cd*. Then coalescence of the bubbles occurs, resulting in a 'transition period' in which the electrode surface (or the hot wall in the case of boiling) is covered by irregular gaseous blankets in violent motion. In this period (corresponding to the 'unstable film boiling') the gas evacuation becomes more and more difficult.

Under these conditions there is a drop in the *cd* (or in the specific heat flow) and an increase in the electrode potential (or in the wall temperature).

Finally the 'anode (or cathode) effect' occurs (corresponding to the 'burnout' and 'film boiling'). The electrode (or the hot wall in the case of boiling) is now enclosed with a permanent continuous gaseous envelope (Fig. 1b, b').

The strong analogy between the phenomena of 'burnout' and those of anode (or cathode) effect

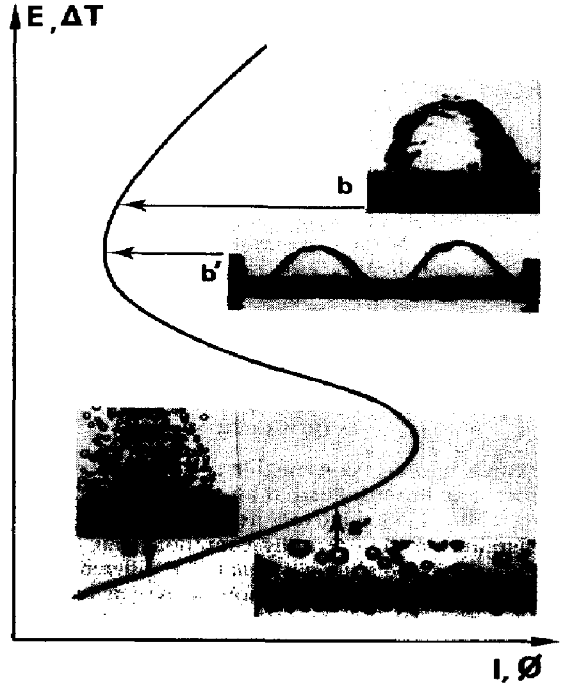

Fig. 1. Schematic illustration of the characteristic curves E/I or $\Delta T/\phi$ and morphological aspects of the gas evolution in electrolysis or boiling of liquids. (a), (a'): Evolution of separate bubbles ('normal electrolysis', or 'nucleate boiling'). (b), (b'): 'Anode (or cathode) effect', or 'film boiling'. Photographs shown here (× 2.5) refer to chlorine evolution on platinum anodes from 2 N HCl aqueous solution, at room temperature. (a), (b): Plane horizontal electrode facing upwards (circle-shaped, 0.5 cm^2 area); $I_c = 30$ A/cm^2. (a'), (b'): Horizontal wire electrode (1 mm dia); $I_c = 32$ A/cm^2. The insulating material limiting the electrode surfaces is boron nitride.

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* High speed cinematographic techniques (up to about 5000 frames per second) have been applied by us to investigate the morphological aspects of the electrolytic gas evolution from aqueous solutions, chloride and cryolite–alumina melts placed in suitable see-through cells[13–16, 18, 19]. The most significant results have been assembled in a 16 mm film: 'Hydrodynamic instabilities in electrolytic gas evolution', with the assistance of A. Berbenni, Istituto di Cinematografia Scientifica, Politecnico di Milano.

Direct observations of the phenomena in laboratory aluminium electrolysis cells have been made also by other authors[31, 32, 54–57] employing photographic or cinematographic techniques (owing to the considerable experimental difficulties, these observations, with the exception of[57], were made within a very small size wall-less cell consisting of a single drop of molten electrolyte between electrodes). A comprehensive photographic study of the gas evolution in aqueous electrolysis is also reported[51].

In the case of boiling the application of high speed cinematographic techniques dates back to the fifties[58] or shortly before, and is yet of great interest[59].

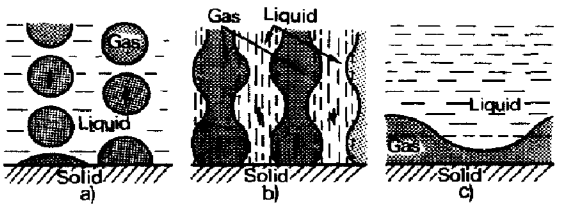

Fig. 2. Schematic illustration of the hydrodynamic instabilities which intervene in the gas evolution in electrolysis or boiling of liquids, in the case of plane, horizontal electrodes or heated surfaces facing upwards. (a): Evolution of separate bubbles. (b): 'Column-wise' evolution: its break-down corresponds to the Helmholtz instability. (c): 'Laminar' evolution: its break-down corresponds to the Taylor instability.

applies to the morphological aspects of the gas evolution even before reaching the critical condition, as well as to several phenomenological laws which regulate the onset of such a critical condition. Hence it would seem appropriate to envisage basically common causes for the two types of phenomenon. This led us to propose an explanation of the anode (or cathode) effect taking into account the well known conditions of hydrodynamic instability described by Helmholtz and Taylor, which are commonly considered to cause the boiling crisis and the 'burn-out'[60–74].

For the sake of simplicity, let us consider a plane and horizontal structure (electrode or hot wall) facing upwards. By increasing the *cd* (or the specific heat flow), the gas evolution in the form of bubbles rising separately (Fig. 2a) is transformed by the interactions in the vertical direction (*ie* perpendicular to the solid surface) into a continuous 'column-wise' evolution, with the gaseous streams flowing upwards and the liquid streams downwards (Fig. 2b). The stability of this configuration depends on the relative speed of the counterflowing streams of gas and liquid, *ie* on the rate of gas evolution. Above the critical value of the relative speed, every small disturbance at the boundary surface between two contiguous streams (Fig. 2b) grows, until the boundary surface breaks. Thus a partial gas blanketing may occur and extend over the entire solid surface (Fig. 2c) if the net of the gaseous jets was sufficiently close. Therefore the transverse interactions (*ie* parallel to the solid surface) play a very important role too. This hydrodynamic instability which causes the 'column-wise' configuration to collapse is known as the Helmholtz instability[75–81].

On the other hand, the stability of a 'laminar' configuration, with the gas (being the lighter) lying underneath the liquid under rest conditions (Fig. 2c), depends on the wavelength of the disturbances at the horizontal boundary surface between the two fluid layers. Taking into account the surface tension effects, it may be shown that, in order to maintain a stable gaseous layer underneath the liquid phase, the disturbance wavelength must be smaller than a certain critical value or else the boundary surface oscillates until it breaks.

This instability which causes the 'laminar' configuration to collapse is known as the Taylor instability[82–85]. And it is precisely the critical wavelength of the Taylor instability that determines the critical spacing of the gaseous jets in the 'column-wise' configuration below which, exceeding a critical value of the rate of gas evolution leads to complete and steady gas blanketing on the solid surface.

It may be shown that the transition from 'column-wise' configuration to 'laminar' configuration takes place when the rate of gas evolution exceeds a critical value R_c defined by the following expressions*[*eg* 74, 69]:

$$R_c = \left[\frac{\rho_L \gamma}{\rho_G(\rho_G + \rho_L)}\right]^{1/2} \cdot \left[\frac{g}{\gamma}(\rho_L - \rho_G)\right]^{1/4}$$

in the case of plane, horizontal electrodes or heated surfaces facing upwards (Fig. 2), and:

$$R_c = \left[\frac{\rho_L \gamma}{\rho_G(\rho_G + \rho_L)}\right]^{1/2} \cdot \left[\frac{g}{\gamma}(\rho_L - \rho_G) + \frac{1}{(r + \Delta r)^2}\right]^{1/4}$$

in the case of horizontal wire electrodes or heated surfaces of radius r (Fig. 3).

In agreement with the hypothesis that the anode (or cathode) effect is of hydrodynamic nature, a proportionality relationship between critical current density I_c and critical value R_c may be postulated[17].

In aqueous solutions, these theoretical predictions have been confirmed by us experimentally[15–17], with a close quantitative agreement in the case of wire electrodes, where the absence of boundary effects admitted by the theory can be considered true, at least for high enough values of the ratio: length to radius of the wire.

More especially, since the term (g/γ) $(\rho_L - \rho_G)$ in the above-mentioned R_c expression is negligible with respect to the other term $1/(r + \Delta r)^2 \simeq 1/r^2$ for the r values considered by us†, correlations of the type $I_c \div 1/r^{1/2}$ and $I_c \div \gamma^{1/2}$‡ are found to fit the experimental results really well. Thus the critical *cd* increases with increasing surface tension, while it is well known that on the basis of the 'static' theory of the contact angle a reverse dependence law would be expected. As a matter of fact, according to the 'hydrodynamic' theory the surface tension acts in the sense of damping the disturbances at the boundary surface between counterflowing streams of gas and liquid in

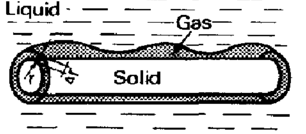

Fig. 3. Schematic illustration of the 'laminar' gas evolution in electrolysis or boiling of liquids, in the case of horizontal wire electrodes or heated surfaces of radius r: its break-down corresponds to the Taylor instability.

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* Where ρ = density, γ = surface tension, g = acceleration due to gravity, Δr = thickness of the gaseous layer, L (subscript) = liquid, G (subscript) = gas.

† Values ranging from 0.1 to 0.5 mm.

‡ γ was varied by addition to the solution of surface-active agents.

the 'column-wise' configuration, *ie* of hindering the onset of the Helmholz instability.

Regarding the acceleration acting on the system,* its influence on the critical *cd* is found to be negligible for wire electrodes, being overcome by the geometrical effects expressed by the term $1/r^2$; on the other hand, in the case of plane electrodes a correlation of the type $I_c \div g^{1/4}$ has been proved.

Regarding the other factors affecting the critical *cd*, an analysis has been developed in[17] by taking account of Faraday's laws and by assuming that the gas supply to the evolving bubbles takes place through a layer of electrolytic solution which is supersaturated with respect to this gas. The result is that the following correlation may be deduced.†

$$I_c \div zF \frac{\rho_G}{M_G}\left(\frac{N}{\rho_L}\frac{\Delta c}{\rho_G}\right)^n R_c.$$

Data processing yields $n = 0.25$ for anodic chlorine or oxygen evolution.

Regarding in particular the influence of the external pressure,‡ a correlation of the type $I_c \div p^{0.25}$ has been observed experimentally, which agrees with the theoretical predictions ($I_c \div \rho_G^{0.25}$, being $R_c \div \rho_G^{-0.5}$) if the only gas density is assumed to be affected. For cathodic hydrogen evolution $n = 0.29$, $I_c \div \rho_G^{0.21}$, and $I_c \div p^{0.21}$.

The 'hydrodynamic' theory also leads us to predict that the gaseous envelope which encloses the wire electrode during the anode (or cathode) effect§ is not even in thickness, but it shows a wave-like surface whose most probable wavelength may be deduced from the following expressions:

$$\lambda = \frac{\sqrt{3}\,2\pi}{[(g/\gamma)(\rho_L - \rho_G)]^{1/2}}$$

in the case of a plane horizontal electrode facing upwards (Fig. 2c), and:

$$\lambda = \frac{\sqrt{3}\,2\pi}{[(g/\gamma)(\rho_L - \rho_G) + 1/(r + \Delta r)^2]^{1/2}}$$

in the case of a horizontal wire electrode (Fig. 3)[85].

Still with reference to aqueous solutions and wire electrodes with relatively high length/radius ratio, the correlation $\lambda \div r$ (under conditions in which the term (g/γ) $(\rho_L - \rho_G)$ is still negligible with respect to $1/(r + \Delta r)^2 \simeq 1/r^2$) has been proved experimentally to agree with theoretical predictions[17]. Like for the film boiling, the agreement is closer in the case of vertical wires. As a matter of fact, owing to surface tension, coalescence phenomena occur on horizontal wires so that the observed wavelengths do not correspond exactly to the Taylor instability predictions.

In the case of relatively short wire electrodes, with radius sufficiently high to make the corresponding wavelength comparable to the length of the wire, without the latter being an exact multiple of the former, there is not longer a stabilization of the gaseous envelope.

Finally, in the case of plane electrodes, the λ values predicted by the theory are in the order of a few cm, and therefore, owing to the small size of our bench scale electrodes, the wavelength at the gas–liquid interface during anode (or cathode) effect is actually determined by the boundary conditions, and only one halfwave can form. In this connection a very essential factor appears to be the nature of the insulating material limiting the electrode working surface: *eg* no permanent anchorage of the gaseous envelope at the boundary line of the electrode is obtained if Teflon is used as insulator.

To sum up, the interpretation which we have formulated concerning the hydrodynamic origin of the anomalous phenomena encountered in the electrolytic gas evolution from aqueous solutions covers comprehensively the different morphological aspects for the different conditions ('nucleate', 'column-wise' and 'laminar' configurations, and transitions from one configuration to the other). In particular the 'hydrodynamic' interpretation also accounts for the abrupt occurrence of the anode (or cathode) effect and its dynamic characteristics (oscillations, *etc*).

On the other hand, this theory is also consistent with the results of the systematic investigations carried out by us concerning the following electrochemical aspects:

(i) shape of the curves: electrode potential *vs* current density;

(ii) influence on the critical *cd* of many factors, such as: polarity, nature, shape, size, orientation,|| and surface state of the electrode,¶ nature and shape of the insulator defining the electrode surface; composition and temperature** of bath; stirring of bath and mechanical vibration transmitted to the electrode;†† external pressure; acceleration acting on the system, *eg* under conditions of reduced gravity, *etc*.

The above-mentioned arguments can be considered also in the case of carbon anodes (or generally insoluble anodes) in chloride melts. This case is quite

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* Reduced gravity conditions were obtained by dropping the electrolytic cell from a height of 15 m with different balance weights.

† Where z = electrode reaction valence, F = Faraday's constant, M = molecular weight, N = equivalent concentration, Δc = supersaturation degree of dissolved gas, and n is an exponent, to be determined.

‡ Pressure values ranged from 0.2 to 2 atm.

§ Or likewise the hot wire under 'burnout' conditions.

|| For example, in the case of plane, horizontal electrodes facing downwards (a geometrical condition which is encountered in the industrial aluminium electrolysis), the gas evacuation is more difficult and the coalescence of bubbles begins at lower *cd*s than in the case of the upwards-facing electrodes described before. Also the anode (or cathode) effect occurs at a much lower critical current density.

¶ Since the anomalous condition of anode (or cathode) effect is obtained from the coalescence of the bubbles evolved at the electrode, we can reasonably suppose that factors such as nature and surface state of the electrode act on the amplitude of the transition period, thus quantitatively affecting the onset of the anomalous condition itself.

** Temperature increases lower the critical *cd* because the quantity of evolved gas is increased.

†† Bath stirring and electrode shaking on the one hand displace the onset of the anode (or cathode) effect towards a higher range of *cd* (especially for those electrode shapes and orientations which favour the permanence of the gases), and on the other make the disappearance of the anomalous conditions easier.

simple indeed from a theoretical point of view, if only one kind of anion is present in the melt and therefore the anode process is always the same in the whole range of working conditions.

ANODE EFFECT IN CRYOLITE–ALUMINA MELTS

The case of the anode effect in cryolite–alumina melts is rather complicated: oxygen and fluorine containing species are present and changes in chemical configuration of the bath in the anodic region must be taken into account. As it is well known the relative content of aluminium fluoride tends to increase near the anode as a result of the electrode reaction and the transport processes.* In particular, a depletion in alumina can induce a change of the electrode reaction, and in consequence also of the surface conditions.

Thus the occurrence of the anodic anomalous phenomena could be attributed to causes quite different from the hydrodynamic instability, *eg* to anode passivation and/or change in wetting conditions. As a matter of fact, the hydrodynamic interpretation cannot be considered valid in the case of melts with low alumina contents (including the 'pure' cryolite melts), if the following is taken into account:

(i) the very low values of the critical *cd*† (*ie* of the rate of gas evolution in the critical condition), consistent with interpretations following 'static' rather than 'dynamic' lines;

(ii) the fairly slow variations in time‡ of the cell current and anode potential at the onset of the anode effect;

(iii) the reaching of limit current conditions for discharge of the oxygen containing ions prior to the onset of the anode effect§;

(iv) the much lower influence of electrode shape, size and orientation on the critical current density;

(v) the much lower influence of bath stirring and mechanical vibration transmitted to the electrode on the onset and disappearance of the anode effect;

(vi) the greater importance and persistence of the hysteresis phenomena after anode effect, in particular corresponding to: a 'residual' anode potential‖ under open circuit conditions, and a higher anodic overpotential under working conditions at the same current density. Moreover this modification which intervenes in the electrode system: graphite–bath–gas after anode effect is not influenced by the shape and orientation of the electrode and by the mechanical vibration transmitted to it¶.

On the basis of both the direct evidence given by the cinematographic recording and the results of the electrochemical investigations, we have proposed[18] the following scheme for the interpretation of the anode effect in cryolite–alumina melts.

In the range of high alumina contents, *ie* of high values of critical *cd* the anode effect still corresponds to the intervention of hydrodynamic instability in the gas evolution; whereas for melts poor in alumina, *ie* for low values of critical *cd*, the anode effect corresponds to an anode passivation, due to fluorine surface compounds, which occurs as a result of the achievement of limit current conditions for discharge of the oxygen containing ions. The worse wetting properties in the latter case appear as a result of the anode passivation.

Finally in the intermediate range of alumina contents, the critical *cd* at which the anode effect occurs as a result of hydrodynamic instability in the gas evolution, can be determined by the variations of chemical–physical properties due to changes in chemical configuration of the anodic bath layer.

IN SITU DETERMINATION OF THE ALUMINA CONTENT OF CRYOLITE–ALUMINA MELTS

It is well known that in the industrial eletrolytic production of aluminium a method for the *in situ* analysis of the alumina concentration in the baths would be desirable. Traditionally, feeding of the alumina into the electrolysis cells is discontinuous and the anode effect is used as a sign of low alumina concentration. As far as we know, attempts involving

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* Studies in cells having a soluble anode of metallic aluminium have shown instructively that this phenomenon occurs magnified under such conditions, and the possible effects of the accumulation of aluminium fluoride in the anodic region were demonstrated. When increasing the *cd*, anomalous increments of the anode potential were obtained which corresponded to a passivity condition due to separation of aluminium fluoride as a solid phase[86]. Like the case of the anode effect with carbon anodes, addition of alumina and temperature increase displace the onset of the anomalous anode condition towards a higher range of current density. (It is remarkable that, in chloride melts, the temperature influence on the critical *cd* at which the anode effect occurs is exactly opposite, but also in this case the addition of oxides or carbonates attenuates the lowering of critical *cd* with increasing temperature.)

† In the order of the tens of A/dm^2, instead of the values in the order of the several hundreds of A/dm^2 which are found in the case of melts with high alumina contents, as well as in the cases of chloride melts and aqueous solutions.

‡ In the order of the several tens of seconds, instead of the abrupt changes in the order of 10^{-3} s which are met in the case of melts with high alumina contents, as well as in the cases of chloride melts and aqueous solutions.

§ On the other hand, the presence of steps in the anode potential *vs* time galvanostatic curves is followed by the onset of the anode effect only in the case of baths very poor in alumina, while no evidence of these steps is found in adequately rich baths. A general connection between limit current conditions and anode effect, therefore, is untenable.

‖ *Vs* a carbon reference electrode.

¶ In the case of melts poor in alumina the persistence of this modification may last quite a few tens of minutes and is annulled in advance only if the anode is removed from the bath for a few minutes. In the case of melts with high alumina contents the persistence of the described hysteresis effects (which are immediately annulled by shaking the anode) amounts to a few hundreds of seconds for those anodes where the permanence of the gases is favoured, whilst for those anodes where the gas evacuation is easy hysteresis effects may only be observed in the oscillograph patterns.

the static measurement of voltages, *eg* of oxygen electrodes (see[87] for an extensive survey of the literature), electrodes based on insoluble oxides, like Cr_2O_3 or SnO_2[5, 87], or of electrodes of type: Al(liq.)/Na_3AlF_6 with a boron nitride envelope [86, 88–90] have not led to any practical results.

A different approach can be based on the easy-to-perform measurement of the critical *cd* producing the anode effect in the bath. In fact, as is well known, the critical *cd* is an increasing function of the alumina content in the bath (the other conditions being equal), according to $I_c = K + C_{Al_2O_3}^{1/2}$[11, 12, 14]*. However, the wide scattering of experimental results so far has hampered the utilization of such a relationship for the aforementioned purposes[91]. Recently, an improved alumina concentration meter of this type has been presented[92].

A systematic research into the variance in critical *cd* has been carried out by us in both aqueous solutions and molten salts, including the cryolite–alumina melts[20]; the purpose mainly was to specify the most suitable conditions so as to minimize the scattering of experimental results. It was found that the scattering of critical *cd* values† is less for wire and spherical electrodes than for plane or otherwise shaped electrodes. This appears to be further confirmation of the hydrodynamic interpretation of the anode effect and in general of the anomalous phenomena which are always encountered at gas evolving electrodes when the *cd* attains high enough values. In fact, for wire and spherical electrodes, owing to the absence of disturbing boundary effects, the onset of the anode (or cathode) effect is relatively definite and reproducible, and transition periods under these conditions are virtually absent. On the contrary, for plane or otherwise shaped electrodes it may be reasonably supposed that the boundary effects (together with the nature and surface conditions of the electrode, *etc*) act on the amplitude of the transition period, thus determining a wider scattering of critical current density.

This research can lead to the development of a practical measuring electrode as soon as electrically conducting materials resistant to the anodic attack in cryolite–alumina melts at 1000° and which may be easily obtained in the desired geometric form become available.

REFERENCES

1. B. Marincek (Swiss Aluminium Ltd.), Fr. 1,533,262, 19 Jul. 1968; Swiss Appl. 17 May 1966–28 April 1967.
2. V. V. Stender and V. V. Trofimenko, *Khim. Teckhnol.* **12**, 41 (1969).
3. H. J. Klein (Swiss Aluminium Ltd.), Ger. Offen. 2,059,866, 09 Jun. 1971; Swiss Appl. 05 Dec. 1969.
4. Swiss Aluminium Ltd., Patent Specification 1,295,117, The Patent Office, London (1972).
5. M. Rolin, *Rev. Int. hautes Temp. Refract.* **9**, 333 (1972).
6. H. Alder (Swiss Aluminium Ltd.), Ger. Offen. 2,425,136, 12 Dec. 1974; Swiss Appl. 25 May 1973.
7. H. Alder (Swiss Aluminium A.G.), Ger. Offen. 2,438,891, 20 Feb. 1975; Swiss Appl. 13 Aug. 1973.
8. H. Alder (Swiss Aluminium Ltd.), Ger. Offen. 2,446,668, 24 Apr. 1975; Swiss Appl. 16 Oct. 1973.
9. R. Piontelli, B. Mazza and P. Pedeferri, *R.C. Accad. Lincei* **36**, 759 (1964).
10. R. Piontelli, B. Mazza and P. Pedeferri, *R.C. Accad. Lincei* **37**, 3 (1964).
11. R. Piontelli, B. Mazza and P. Pedeferri, *Metallurgia ital.* **57**, 51 (1965).
12. R. Piontelli, B. Mazza and P. Pedeferri, *Electrochim. Acta* **10**, 1117 (1965).
13. R. Piontelli, A. Berbenni, B. Mazza and P. Pedeferri, *Electrochim. Metall.* **1**, 279 (1966).
14. R. Piontelli, B. Mazza and P. Pedeferri, *J. electrochem. Soc.* **114**, 652 (1967).
15. R. Piontelli, B. Mazza, P. Pedeferri and A. Tognoni, *Electrochim. Metall.* **2**, 257 (1967).
16. A. Tognoni, B. Mazza, P. Pedeferri and R. Piontelli, *Electrochim. Metall.* **2**, 377 (1967).
17. B. Mazza, P. Pedeferri, R. Piontelli and A. Tognoni, *Electrochim. Metall.* **2**, 385 (1967).
18. B. Mazza, P. Pedeferri and A. Tognoni, *Chim. Ind. (Milan)* **52**, 123 (1971).
19. B. Mazza, P. Pedeferri and A. Tognoni, *Proceedings European Conference on the Development of Molten Salts Applications*, p. 77. Battelle, Geneva (1973).
20. B. Mazza, P. Pedeferri and G. Re, *Metallurgia ital.* **68**, 582 (1976).
21. L. Ferrand, *Histoire de la Science et de Techniques de l'Aluminium et ses Développements Industriels*, Vol. 1 and 2. Humbert, Largentière, France (1960).
22. A. Fontana and R. Winand, *Electrochim. Acta* **16**, 279 (1971).
23. H. Wartenberg, *Z. Elektrochem.* **32**, 330 (1926).
24. H. Wartenberg, *Z. Elektrochem.* **33**, 526 (1927).
25. P. Drossbach, *Z. Elektrochem.* **55**, 38 (1951).
26. P. Drossbach, T. Hashino, P. Krahl and W. Pfeiffer, *Chemie-Ingr-Tech.* **33**, 84 (1961).
27. V. P. Mashovets, *L'Électrométallurgie de l'Aluminium.* ONTI, Moscou (1938).
28. A. I. Belyaev, M. B. Rapoport and L. A. Firsanova, *Metallurgie des Aluminiums.* VEB Verlag Technik, Berlin (1956).
29. A. I. Belyaev, E. A. Zhemchuzhina and L. A. Firsanova, *Physical Chemistry of Fused Salts.* Metallurgy Press, Moscow (1957).
30. A. Vajna, *Alluminio* **20**, 29 (1951).
31. A. Vajna, *Metallurgia ital.* **44**, 585 (1952).
32. A. Vajna, *Bull. Soc. Fr. Electns* 7^e Série, **II**, No. 14, 85 (1952).
33. K. Arndt and H. Probst, *Z. Elektrochem.* **29**, 323 (1923).
34. K. Arndt, *Z. Elektrochem.* **33**, 236 (1927).
35. V. Schischkin, *Z. Elektrochem.* **33**, 83 (1927).
36. Finkelstein, *Legkié Metally*, p. 24. July–August (1937).
37. W. Rüdorff, U. Hofmann, G. Rüdorff, J. Endell and G. Ruess, *Z. anorg. Chem.* **256**, 126 (1948).
38. E. Pruvot, *Alluminio* **22**, 709 (1953).
39. P. Mergault, *C.r. hebd. Séanc. Acad. Sci., Paris* **240**, 765 (1955).
40. L. N. Antipin and N. G. Turin, *J. phys. Chem. USSR* **31**, 1103 (1957).
41. P. Mergault and A. Ahmadi, *C.r. hebd. Séanc. Acad. Sci., Paris* **250**, 849 (1960).
42. Y. I. Aleksandrov and V. P. Mashovets, *J. appl. Chem. USSR* **39**, 2346 (1966).

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[*] Where $C_{Al_2O_3}$ = alumina concentration (w/o referred to cryolite), and K is a constant.

[†] At least 10 determinations of the critical *cd* were carried out during an experiment, and each experiment was repeated at least three times under the same operating conditions as regards the factors which were possible to control. The dispersion of results was represented in terms of the root–mean–square deviation.

43. R. Jacoud, *Métaux, Corrosion, Industrie* **505**, 299 (1967).
44. R. Jacoud, *Métaux, Corrosion, Industrie* **506**, 375 (1967).
45. N. Watanabe and T. Asaue, *J. electrochem. Soc. Japan* **39**, 107 (1971).
46. J. Thonstad, *Electrochim. Acta* **12**, 1219 (1967).
47. J. Thonstad, *Electrochim. Acta* **14**, 127 (1969).
48. J. Thonstad, F. Nordmo and K. Vee, *Electrochim. Acta* **18**, 27 (1973).
49. J. Thonstad, F. Nordmo and J. K. Rødseth, *Electrochim. Acta* **19**, 761 (1974).
50. R. Tunold and T. Berge, *Electrochim. Acta* **19**, 849 (1974).
51. H. H. Kellogg, *J. electrochem. Soc.* **97**, 133 (1950).
52. G. Kortüm, *Treatise on Electrochemistry*, p. 538. Elsevier, Amsterdam (1965).
53. S. K. Ratkje, *Electrochim. Acta* **21**, 515 (1976).
54. E. A. Zhemchuzhina and A. I. Belyaev, *Tsvetnaya Metallurgiya*, No. 5, 123 (1961).
55. A. Vajna, *Electrochim. Metall.* **3**, 376 (1968).
56. G. Derge and J. R. Schegog, *Light Metals*, Vol. 1, p. 135. TMS-AIME (1973).
57. W. E. Haupin and W. C. McGrew, *Light Metals*, Vol. 1, p. 37. TMS-AIME (1974).
58. J. W. Westwater and J. G. Santangelo, *Ind. Engng Chem.* **47**, 1605 (1955).
59. S. J. D. van Stralen, *Growth Rates of Vapor Bubbles in Boiling Pure Liquids and Binary Systems.* Paper No. 53, presented at the 27th Meeting of ISE, Zurich, September 1976.
60. N. Zuber, *Trans. ASME* **80**, 711 (1958).
61. N. Zuber and M. Tribus, University of California UCLA 58-5 (1958).
62. N. Zuber, Ph.D. Thesis. University of California (1959).
63. N. Zuber, AECU 4439 (1959).
64. Yan-Po Chang, *J. Heat Transfer, Trans. ASME* **81**, C, 1 (1959).
65. P. J. Berenson, *J. Heat Transfer, Trans. ASME* **83** C, 351 (1961).
66. R. Moissis and P. J. Berenson, *J. Heat Transfer, Trans. ASME* **85** C, 221 (1963).
67. Yan-Po Chang, *J. Heat Transfer, Trans. ASME* **85** C, 89 (1963).
68. J. D. Seader, W. S. Miller and L. A. Kalvinskas, NASA CR-243 (1965).
69. R. Siegel and E. G. Keshock, NASA TR R-216 (1965).
70. N. Zuber, M. Tribus and J. W. Westwater, in *International Development in Heat Transfer*, Part II, p. 230. ASME (1961).
71. S. S. Kutateladze, *Fundamentals of Heat Transfer*, Chap. 18. Arnold, London (1963).
72. W. M. Rohsenow, in *Modern Developments in Heat Transfer*. Academic Press, New York (1963).
73. G. Leppert and C. C. Pitts, in *Advances in Heat Transfer*, Vol. 1. Academic Press, New York (1964).
74. L. S. Tong, *Boiling Heat Transfer and Two-Phase Flow.* Wiley, New York (1965).
75. H. Helmholtz, *Berl. Monatsber.* April (1868).
76. H. Helmholtz, *Phil. Mag.* November (1868).
77. W. Thomson, *Phil. Mag.* **42**, 374 (1871).
78. W. Thomson, *Nature* **5**, 1 (1871).
79. Rayleigh, *Proc. Lond. math. Soc.* **10**, 4 (1879).
80. H. Lamb, *Hydrodynamics.* Dover, New York (1945).
81. L. M. Milne-Thomson, *Theoretical Hydrodynamics.* MacMillan, New York (1950).
82. G. Taylor, *Proc. R. Soc. Lond.* **201 A**, 192 (1950).
83. R. Bellman and R. H. Pennington, *Q. appl. Mathematics* **12**, 151 (1954).
84. Shao-Lin Lee, *J. appl. Mech.* **30**; *Trans. ASME* **85** E, 443 (1963).
85. J. H. Lienhard and P. T. Y. Wong, *J. Heat Transfer, Trans. ASME* **86** C, 220 (1964).
86. R. Piontelli, B. Mazza and P. Pedeferri, *Electrochim. Metall.* **1**, 217 (1966).
87. M. Rolin and J. J. Gallay, *Electrochim. Acta* **7**, 153 (1962).
88. R. Piontelli, B. Mazza and P. Pedeferri, *Alluminio* **34**, 623 (1965).
89. R. Winand, *Electrochim. Acta* **17**, 251 (1972).
90. R. Winand, *Electrochim. Acta* **21**, 451 (1976).
91. B. J. Welch and R. J. Snow, *J. electrochem. Soc.* **113**, 1338 (1966).
92. T. J. Johnston and N. E. Richards, Paper given at the 103rd AIME Annual Meeting, 1974 (text not included in Proceedings).