

Table I. Heats of activation (kcal/mole)

Metal	Cu	Hg	Ni	Pt	Co
Hydrogen evolution	10	9-24	5-16	5	3-5
Solvated electron	7.2	8.3	8.5	27	2.5

$\phi - W_e$  has any meaning at all, it is the activation energy to form solvated electrons at an infinite distance from the metal. Electrons can be solvated rather closer to the metal than this; the activation energy can be expected, therefore, to be rather smaller than that suggested by Matthews.

We believe that the closest point to the metal at which an electron may be considered to be solvated lies in the plane through the center of the first layer of water molecules which are in contact with the metal surface. In this position the electron will lie approximately in the inner Helmholtz plane and the work required to separate an electron from a metal by a distance  $a$ , the radius of a water molecule, may be estimated on the basis of a model for the work function of a metal discussed by Loeb.<sup>33</sup> The work required to remove an electron is considered in two parts. (a) at points closer to the metal than a critical distance  $x_0$ , the electron moves in a constant field  $e/4x_0^2$ . The work done in taking an electron from the metal to  $x_0$  is  $e^2/4x_0$ ; (b) at distances larger than  $x_0$  the electron moves against a mirror image force. The work required to take an electron from  $x_0$  to  $\infty$  is  $e^2/4x_0$ . The work function is the sum of these two parts and equals  $e^2/2x_0$ . For metals, with  $\phi < 5$  ev,  $x_0 > a$  and the work required to separate the electron from the metal by a distance  $a$  becomes  $ae^2/4x_0^2$ . The activation energy for the solvation of an electron in this position becomes  $ae^2/4x_0^2 - W_e$ . Metals with  $\phi > 5$  ev have  $x_0 < a$  and the activation energy is given by  $\phi - e^2/4a - W_e$ .

Experimental values of the heats of activation for the deposition of hydrogen at copper,<sup>34</sup> mercury,<sup>34</sup> nickel,<sup>34</sup> platinum,<sup>34</sup> and cobalt<sup>35</sup> surfaces in aqueous electrolytes are compared, in Table I, with values of  $\Delta H$  calculated on the basis of the model we suggest above.

The agreement between the experimental heats of activation for hydrogen evolution and the calculated heats for the formation of solvated electrons is encouraging. Experimental verification of the role played by the solvated electron in the evolution of hydrogen is only available for mercury, however the calculated values of  $\Delta H$  do suggest that it may also play a dominant role in the evolution of hydrogen at copper, nickel, and cobalt surfaces. Platinum has a large work function and the activation energy for the formation of solvated electrons at the platinum-electrolyte interface is therefore large. Consequently it appears improbable that hydrogen evolution *via* the formation of solvated electrons will be significant at a platinum surface. However, in general  $\Delta H$  for the formation of a solvated electron at the inner Helmholtz plane is not large and the formation of a solvated electron as a step in the evolution of hydrogen should not be discounted on the grounds that it will lead to negligible rates of hydrogen evolution.

### The Cathodoluminescence of Terbium-Activated Indium Orthoborate

F. J. Avella (pp. 1225-1226, Vol. 113, No. 11)

W. L. Wanmaker and A. Brill<sup>36</sup>: In the paper under discussion it was stated that in one of our papers we described the photoluminescence of  $Tb^{3+}$  in alkaline

<sup>33</sup> L. B. Loeb, "Static Electrification," Springer Verlag, Berlin (1958).

<sup>34</sup> R. Parsons, "Handbook of Electrochemical Constants," Butterworths, London (1959).

<sup>35</sup> R. Piontelli, L. P. Bicelli, M. Graziano, and A. L. Vecchia, *Atti. Accad. Nazi. Lincei. Rend. Classe, Sci. Fis. Mat. Nat.*, 32, 445 (1962); *Chem. Abstract*, 58, No. 52653g (1963).

<sup>36</sup> N. V. Philips' Gloeilampenfabrieken, Eindhoven, The Netherlands.

earth borates<sup>37</sup> but did not report on the cathodoluminescence. We should like to point out that in section 5 of the paper cited by the authors we did in fact give cathode-ray efficiencies (p. 491), namely a radiant efficiency (energy conversion efficiency) of about 2%. Moreover in another paper<sup>38</sup> we gave a radiant efficiency of 2.2% for  $2CaO \cdot Na_2O \cdot B_2O_3 \cdot 0.15 Tb$ . This means that these phosphors have an efficiency of about 25-30% of that of willemite ( $Zn_2SiO_4 \cdot Mn$ ).<sup>39</sup> They are, therefore, comparable with those described in the paper under consideration.

In a third paper<sup>40</sup> we have given data on more efficient Tb-activated phosphors under cathode-ray excitation, namely on  $LnPO_4 \cdot Tb$  (where  $Ln = Y, La, Gd$ ). For  $GdPO_4 \cdot Tb$  we found an efficiency of 5%, i.e., about 65% of that of willemite.

**F. J. Avella:** The author is grateful to Dr. Wanmaker and Dr. Brill for supplying the information on the cathodoluminescence efficiency of their borate as well as their phosphate phosphors. References to the former<sup>37,38</sup> were inadvertently omitted, while the latter reference<sup>40</sup> was not available during preparation of the paper under discussion.

It should be noted, however, that their statement of comparable performance applies only to the Tb-activated borates containing the alkaline earths. The data given in Table I of the paper under discussion show that  $InBO_3 \cdot Tb$  is nearly equal to willemite in cathodoluminescence conversion efficiency and is, therefore, significantly more efficient than the alkaline earth borates as well as  $GdPO_4 \cdot Tb$ .

### The Repeatability of the Anode Effect in Cryolite-Alumina Melts

B. J. Welch and R. J. Snow (pp. 1338-1340, Vol. 113, No. 12)

R. Piontelli, B. Mazza, and P. Pedferri<sup>41</sup>: The recent systematic research work carried out in this Laboratory<sup>42</sup> has thrown much more light on both the overvoltage phenomena and the anode effect conditions at the cryolite-alumina melts.

The influence of the shape, orientation, and size of the anodes has been confirmed for both by investigating the behavior of the anodes represented in Fig. 1.

The apparent overvoltage on these, also before the intervention of the anode effect, includes a large ohmic contribution due to the presence of the gaseous phase in the anodic layer and on the anode surface. This contribution depends (besides on the alumina content of the baths) on the circumstances controlling the gas evacuation and thus on the shape of the anodes (being obviously greater on the anodes of the types: B, C, F, on which the permanence of the gases is favored). This statement is confirmed by the influence of mechanical vibrations impressed on the anode assembly which, by enhancing the gas evolution, reduces the ohmic contribution to the apparent overvoltage. The ohmic character of this contribution is also confirmed by the oscillographic recordings of the electrode voltage at the current inlet and outlet. Thus the amount and configuration of the gaseous phase in the anodic

<sup>37</sup> W. L. Wanmaker and A. Brill, *Philips Res. Repts.*, 19, 479 (1964).

<sup>38</sup> W. L. Wanmaker, A. Brill, and J. W. ter Vrugt, *This Journal*, 112, 1149 (1965).

<sup>39</sup> A. Brill and H. A. Klasens, *Philips Res. Repts.*, 7, 401 (1952); A. Brill, in Kallmann-Spruch, "Luminescence of Organic and Inorganic Materials," p. 479, John Wiley & Sons, Inc., New York (1962).

<sup>40</sup> A. Brill, W. L. Wanmaker, and R. E. Schuil, in "Riehl-Kallmann-Vogel," International Symposium on Luminescence, Verlag Karl Thieme, K. G., Munich, Germany, p. 314 (1965).

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<sup>42</sup> R. Piontelli, B. Mazza, and P. Pedferri, *R. C. Accad. Lincei.*, 36, 759 (1964); *ibid.*, 37, 3 (1964); *Metallurgia Ital.*, 57, 51 (1965); *Electrochimica Acta*, 10, 1117 (1965); *Aluminio*, 34, 623 (1965); R. Piontelli, *Electrochimica Metallorum*, 1, 191 (1966).

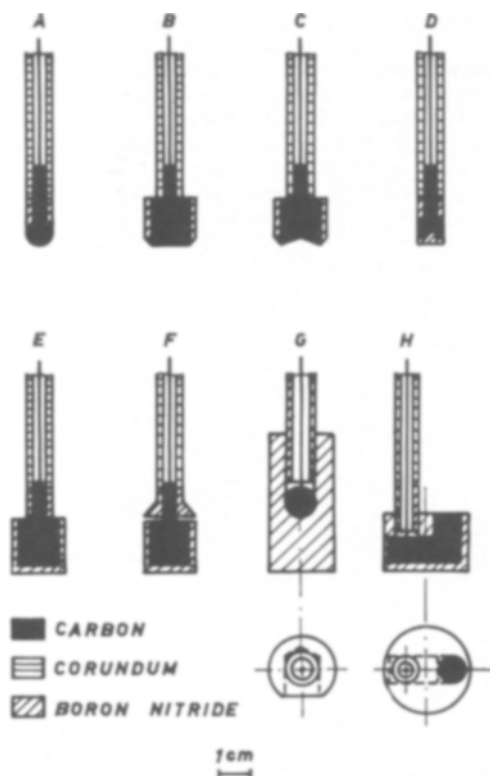


Fig. 1. Types of anodes investigated (sectional views)

region appear to be decisive also for the appearance of the anode effect occurring when the gaseous phase prevents any efficient wetting of the electrode surface.

Since this condition is obtained by the coalescence of the bubbles evolved at the electrode surface, a close analogy subsists with the phenomena encountered in the boiling of liquids in contact with a heated solid surface.

Films (up to 5000 frames/sec) on the anode effect phenomena, on carbon anodes in chloride melts, give direct evidence of this point.<sup>43</sup> By increasing the current density one can distinguish three typical regimes in the gas development. In the lowest current density range the gas development takes place in a nucleate form (Fig. 2a). Then coalescence of bubbles occurs (Fig. 2b) and after a transition period, in which the anode surface is covered by irregular gas blankets in violent motion (Fig. 2c), a condition is reached in which the anode is practically insulated from the bath by a permanent continuous gaseous film (Fig. 2d).

As far as the carbon-cryolite alumina melts are concerned, the quoted experiments (see footnote 42) prove that it is more appropriate to define a critical current intensity of appearance of the anode effect ( $G_c$ ) rather than a critical current density, in so far as the size factor influence does not follow any simple proportionality law. The relationships established (in the laboratory experiments) may be summarized by the formula

$$G_c \approx \psi \cdot (a + bT) \cdot A^n \cdot \{c + [\text{Al}_2\text{O}_3]^m\} \quad [1]$$

where  $T$  is the bath temperature,  $A$  the apparent anode area,  $[\text{Al}_2\text{O}_3]$  the alumina content of the bath,  $\psi$  a factor which depends only on the shape of the anode, and  $a$ ,  $b$ ,  $c$ ,  $n$ ,  $m$  are constants ( $n < 1$ ;  $m \approx 0.5$ ).

For  $T$  in  $^{\circ}\text{C}$ ,  $A$  in  $\text{cm}^2$ ,  $[\text{Al}_2\text{O}_3]$  in w/o (referred to cryolite), and  $G_c$  in amperes, the following expression is obtained in the  $[\text{Al}_2\text{O}_3]$  range 1-10 w/o and in the temperature range  $1000^{\circ}$ - $1150^{\circ}\text{C}$

$$G_c = \psi x \{5.5 + 1.8 \cdot 10^{-2} (T - 1050)\} \times A^{0.9} x \{-0.4 + [\text{Al}_2\text{O}_3]^{0.5}\} \quad [2]$$

<sup>43</sup> R. Piontelli, A. Berbenni, B. Mazza, and P. Pedferri, *Elettrochimica Metallorum*, 1, 279 (1966).

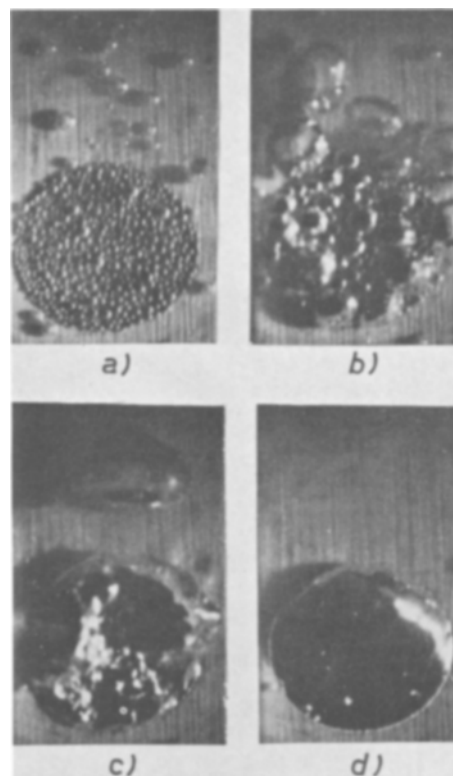


Fig. 2. Chlorine development on carbon anodes from chloride melts. Type G anode,  $A = 0.5 \text{ cm}^2$ . Bath composition: NaCl + KCl (50 w/o).  $T = 850^{\circ}\text{C}$ .  $G_c = 4.5 \text{ amps}$ . (a) nucleate bubbles ( $G = 0.6 \text{ amps}$ ); (b) coalescence of bubbles ( $G = 1.85 \text{ amps}$ ); (c) transition period; (d) anode effect. Maximum framing rate: 4800 frames/sec.

$\psi$  being equal to: 1 for type B, 1.4 for type A, about 1.3 for type D, G, E, H, and about 0.5 for type C anodes.

Mechanical vibrations impressed on the anode assembly increase the critical current intensity to a greater extent for type B and C anodes.

Always with reference to the cryolite-alumina melts, the importance in view of the appearance of the anode effect of the change in chemical configuration of the bath in the anodic region, due to current circulation, must be recalled.

As a consequence of the transference processes and of the electrode reaction, the relative content of the aluminum fluoride, as a component of the anodic bath layer, tends to increase.

This phenomenon occurs, magnified, in cells having a soluble anode of metallic aluminum.

In spite of the obvious differences in respect to the usual condition considered above, the study with the soluble anode cells is easier and instructive in showing (magnified again) the possible effects of the accumulation of aluminum fluoride in the anodic region.<sup>44</sup>

With soluble anode one may encounter anomalous voltage increments corresponding to a passivity condition which appears to be chargeable to a separation of aluminum fluoride as a solid phase. Also in this case, as in the one of the anode effect with insoluble anodes, the addition of alumina or also temperature increments<sup>45</sup> displaces the onset of the anomalous anode conditions toward a higher range of current intensity.

The increment of the aluminum fluoride relative content involves strong change in the chemical physical properties of the bath, by lowering conductivity and increasing vapor pressure.

<sup>44</sup> R. Piontelli, B. Mazza, and P. Pedferri, *Elettrochimica Metallorum*, 1, 217 (1966).

<sup>45</sup> It is remarkable that, in chloride melts, the temperature influence is exactly opposite.

In the case of the insoluble anode electrolysis<sup>46</sup>, this last effect aggravates the consequences (especially the increase of power dissipation) of the presence of the gaseous products of the electrolysis.

**B. J. Welch and R. J. Snow:** In the work presented in our paper, we were not concerned with the phenomena associated with the anode effect, but our work was directed toward elucidation of the most reproducible parameter for applications such as *in situ* alumina analysis. We fully acknowledge the great contribution made by Professor Piontelli and his co-workers in shedding light on the phenomena causing the anode effect.

<sup>49</sup> In which also overvoltage phenomena before the onset of the anode effect appear to be influenced by inhibition phenomena at the electrode surface chargeable to fluorine or to some fluorine surface compounds.

It is interesting to note that they have substantiated<sup>47</sup> our observed lack of reproducibility of the critical current density (or intensity). In an extension of our work<sup>48</sup> we have also confirmed the temperature dependence presented above and elsewhere.<sup>49, 50</sup>

In our more detailed study we observed that the point of anode effect, as defined by either cell voltage or critical current density (or intensity), is also dependent on the carbon type used as the anode. Marked differences are observed for carbons that only have small differences in graphitic structure.

<sup>47</sup> R. Piontelli, B. Mazza, and P. Pedefferri, *Metallurgia Ital.*, 57, 51 (1965).

<sup>48</sup> R. J. Snow and B. J. Welch, *Proc. Aus. I.M.&M.*, No. 221, 43 (1967).

<sup>49</sup> R. Piontelli, B. Mazza, and P. Pedefferri, *Electrochimica Acta*, 10, 1117 (1965).

<sup>50</sup> R. Piontelli, *Electrochimica Metallorum*, 1, 191 (1966).