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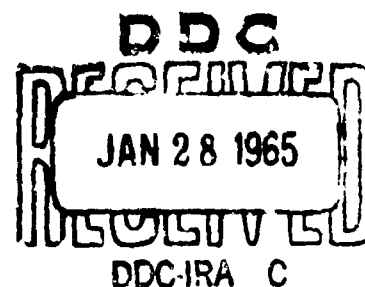The Valency of Aluminum Ions and the
Anodic Disintegration of the Metal

by

M.E. Straumanis and K. Poush

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Department of Metallurgical Engineering
of the
University of Missouri at Rolla
Rolla, Missouri
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The Valency of Aluminum Ions and the Anodic

Disintegration of the Metal

M.E. Straumanis and K. Poush
Department of Metallurgical Engineering and Materials Research
Center of the University of Missouri at Rolla
Rolla, Missouri

Abstract

It follows from coulometric measurements that Al from
Al-amalgam goes into solution in basic electrolytes as a tri-
valent ion. In all probability the same also happens in
acidic solutions. Therefore, the deviation from Faraday's
law cannot be explained by the formation of lower valency
ions as a first step in anodic dissolution of Al. Experi-
ments made in aqueous solutions of $NaOH$, HNO_3, KNO_3 and
$K_2Cr_2O_7$ showed that at anodic current densities between 20
and 300 ma/cm^2 dark, nearly black films, which constantly
broke down, are formed on the Al electrode. Microscopic
examinations revealed the presence of a multitude of metallic
particles entangled in the hydrated Al-oxide flakes, causing
the dark color of the latter. Depending upon the conditions,
the diameter of the metallic particles varied from almost
10^{-5} to 10^{-2} mm. Such a disintegration of Al was also ob-
served when the partially amalgamated metal came simply in
contact with distilled H_2O: dark flakes of hydroxide, con-
taining a multitude of smallest Al particles, were formed.

There are indications that the disintegration of Al is caused by the forcible breakdown (e.g. by the current or Hg) of the oxide layers firmly sticking to the surface of the metal. Upon breaking down of the film smallest Al particles are torn from the metal, which remain on the film. This behavior explains the deviation from Faraday's law and the negative difference effect. No lower valency Al-ions are necessary for this explanation.

Problem and Literature Review

The discoverer of metallic Al, Wöhler, and Buff found in 1857 (1) that upon anodic dissolution of Al more metal dissolved than calculated from Faraday's law, that is, from the number of coulombs which passed the anode. Since that time the search for the reasons of this deviation did not stop. Wöhler himself rejected the idea tha Al could initally go into solution as an ion of lower valency, e.g. in form of Al^+:

$$Al \longrightarrow Al^+ + e \qquad /1/$$

because he could not syntheisze Al - lower valency compounds. However assuming that Al^+ is very unstable and immediately reacts outside the anode with H_2O or H^+ according to the simplified equation:

$$Al^+ + 2H^+ \longrightarrow Al^{3+} + H_2, \qquad /2/$$
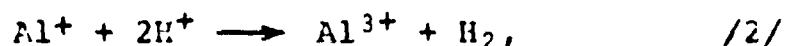
the deviation from Faraday's law can well be understood. Therefore, no Al^+ ions are expected to be present in the

solution after the electrolysis. However, it has to be assumed that only one part of the Al atoms go into solution according to /1/, but the largest part of them release 3 electrons at once or successively upon dissolution:

$$Al \longrightarrow Al^{3+} + 3e \qquad /3/$$
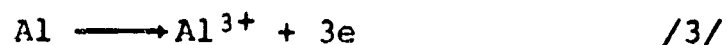
because the departure from Faraday's law is not as severe as would follow from Eq. /1/. Nevertheless the idea of initial lower valency of ions of metals going anodically into solution found some appreciation (2). The conditions became more complicated and the idea of lower valency ions less probable, when it was found that the dark anodic product which covers the anode during electrolysis in aqueous solutions, especially in the presence of oxidizers, contains metallic Al (3,4). Already long time ago it was assumed that this Al was formed by a disproportionation reaction:

$$3Al^{+} = 2Al^{c} + Al^{3+} \qquad /4/$$
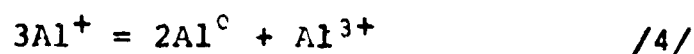
Similarly as it was in the case of Be (5,6), reaction /4/ appears to be quite impossible: it assumes growth of Al particles in an aqueous solution from nuclei. As nobody could deposit Al from such solutions because of the high reactivity of Al atoms or of its finest particles with H_2O, the latter could not be formed according to Eq. /4/. Nevertheless, Al was found later in anodic deposits by Plumb (7). Although he rejected the formation of Al according to reaction /4/, he

did not mention anodic disintegration which well might have been an explanation. Al in anodic deposits and films was also found by McCune (8) and Dmitriev et al. (9). Formation of Al blocks by dropout from an Al piece dissolving in HCl was observed by Roald and Streicher (10).

The reducing power of the anolyte, which was thought to be due to the presence of Al^+, was investigated by many authors (3, 11-17). However, the possibility that the Al particles themselves could act as reducers, was not considered until recently (2).

The intention of the present article is to show that Al goes anodically into solution as Al^{3+} (not as a lower valency ion) and that during the electrolysis a partial disintegration of the anodic metal occurs. Disintegration of Al also takes place while reacting with H_2O in presence of Hg.

Trivalency of Al Ions from Coulometric Measurements

For valency determinations of Al ions going anodically into solution a similar coulometer technique was used as with Ga (18). A piece of Al was dissolved in Hg, the amalgam was connected through a milliammeter with a plastinized Pt electrode which was in the same vessel, and the electrolyte was added. After passage of a certain amount of coulombs, the cell circuit was broken, the electrolyte quantitatively transferred into a beaker and prepared for Al determination with EDTA (19). From the amount of Al moles found and the

number $\underline{a}$ of coulombs passed, the apparent valency V of Al ions could be calculated:

$$V = a/Al(moles) \times 96400 \qquad /5/$$

However, there were two difficulties: 1. Al is only slightly soluble in Hg (0.026% at room temperature) and 2. the Al-amalgam displayed a considerable self dissolution rate especially in acidic electrolytes. The first difficulty was overcome by using several pieces (about 5 mm² each) of Al sheet. By dipping them into a $HgCl_2$ solution they were amalgamated, then rinsed in distilled water and dropped into the Hg (in a small beaker). After complete amalgamation of the Al, the beaker was flushed with distilled water, the electrolyte was introduced and the circuit was closed. H_2 developed on the Pt-cathode, in small amounts on the amalgam (selfdissolution). To cope with the second difficulty only alkaline solutions (1.0 or 0.1 N NaOH or KOH) were used, as the self-dissolution rate was much lower there. The anodic dissolution follows the reaction (3), and the produced Al^{3+} reacts immediately with OH^-:

$$Al^{3+} + 4OH^- = AlO_2^- + 2H_2O \qquad /6/$$

Aluminates (soluble) are formed at the anode and H_2 is developed at the Pt cathode. The results are given in Table 1.

Table 1

Valency of Al-ions anodically dissolving
from Al-amalgam in basic solutions

Electrolyte	Coulombs	Moles Al	V (apparent)
KOH, 1N	27,680	0.1025	2.80
" "	34,310	0.1241	2.86
" "	41,855	0.1511	2.87
" "	30,200	0.1094	2.86
NaOH 0.1N	9,992	0.0343	3.02
" "	9,992	0.0352	2.94
" :	9,705	0.0411	2.45
" "	24,611	0.0940	2.71
" "	11,553	0.0450	2.66

The apparent valency fluctuates from measurement to measurement and occasionally approaches 3. Since there is no reason why a valency should depart from the normal one (under ordinary conditions) other factors might have caused the deviation. The first is, as already mentioned, the selfdissolution rate which lowers the apparent valency and the second might still be the disintegration of Al, since the metal floats on the Hg surface (but under the electrolyte) and becomes locally quite "dry" of Hg. At such points where the current density is high, disintegration of Al may occur (see below). Experiments with thin Al foils which nearly dissolved in Hg gave apparent valencies of 2.93, indicating that there might have been a minimum of disintegration. Thus, measurements in solution bases show that Al goes anodically into solution as Al^{3+}. Such ions are also produced, without an intermediate step, in acid solutions, although a direct proof could not be provided.

Anodic Disintegration of Al

Disintegration experiments were made in the solutions of NaOH, HNO$_3$, KNO$_3$ and K$_2$Cr$_2$O$_7$ as electrolytes.

NaOH. In 1 N NaOH the Al electrode dissolved slowly evolving H$_2$ according to the reaction

$$Al + OH^- + H_2O = AlO_2^- + 1.5H_2 \qquad /7/$$
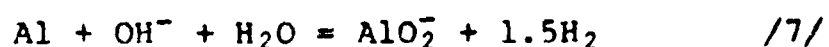
As soon as the switch connecting the Al with the Pt electrode through the battery and resistance was closed, the selfdissolution rate of the Al anode dropped (positive difference effect) and H$_2$ was evolved on the Pt (20). At anodic current densities between 20 and 300 ma/cm the Al surface became black and black flakes fell onto the bottom of the beaker. The flakes were rinsed in distilled water, then treated with acetone and collected on a slide for microscopic examination. Only at high magnifications, of about 1500x, using oil immersion objectives and reflected light, bright shiny metallic particles of various sizes could be seen in a milky looking layer of Al oxide or hydroxide. The shape of the particles was irregular (Fig. 1). In transmitted light the same particles were opaque, thus establishing the metallic nature of the particles. The black color of the anodic flakes was caused by the presence of the finely divided metal in the oxide layer. The color of such a metal is, according to Ketelaar (21), in agreement with the theoretical expectations. X-ray diffraction patterns of the black particles were made

and it was found that they consist of aluminum oxide beta trihidrate. Because of the background darkening produced by this compound and the low concentrations of Al in the flakes, the lines of this metal could not be detected on the films. HNO_3. Al does not dissolve in this acid because of formation of a tight oxide layer on the surface of the metal. However, an anodic current of about 300 ma/cm^2 produced in 0.25 N HNO_3 similar results as in NaOH. The anode surface became dark and gray clouds of particles and flakes fell to the bottom of the beaker. There was only little gas evolution on either electrode and no attack of the Al by the acid with open circuit. Nevertheless the finest particles dissolved slowly in the HNO_3. Microscopic examination of the washed and dried flakes revealed groups of fine particles and of objects with plane surfaces having a bright metallic luster, embedded in a milky background (Fig. 2). The large plane surfaces exhibited tiny dark spots. X-ray diffraction patterns revealed again that the flakes consisted mainly of aluminum oxide.

Ultrasonic vibration of the electrolyte at 50 ma/cm^2 accelerated the production of particles which fell from the anode and collected in dark, nearly black patches on the cell bottom.

3% aqueous KNO_3. Anodic dissolution of Al in this electrolyte produced very similar results, only the white oxidic material was more abundant (Fig. 3). To study the shape of the particles, electron microscopic pictures were made. The
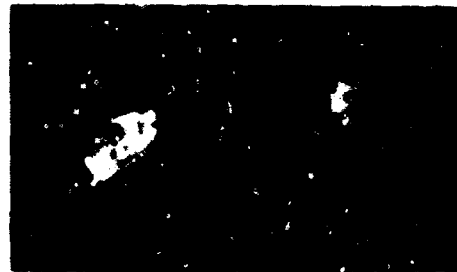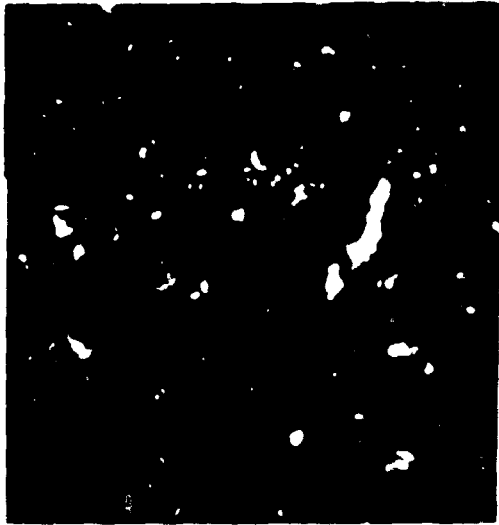
collected flakes were suspended in ethyl alcohol with an ultrasonic vibrator and then drops of the suspension were allowed to dry on a small piece of a 200 mesh Cu screen. The magnification was determined from the size of latex spheres which had a diameter of 0.557 micron. As can be seen from Fig. 4, the particles look like leaflets torn off the Al surface.

3% $K_2Cr_2O_7$ aqueous solution. In this solution the initial current dropped very quickly from 150 ma to 2 ma, but upon adding a few ml of 1 N NaOH to the bichromate solution a current of 3 ma could be maintained for some time, which then dropped to nearly zero. However, after one hour under current, finely divided black particles accumulated beneath the anode, which were collected, washed and dried. In the reflecting light of the microscope aggregates of shiny particles appeared held together by a thin network of Al oxide or hydroxide (Fig. 5). This time the x-ray diffraction patterns revealed the presence of faint 200 and 111 lines of metallic Al in addition to the usual oxide pattern.

Disintegration of Al in H_2O in presence of Hg

It was observed that on Al pieces (wire or foil) floating on Al-amalgam under distilled H_2O, some dark gray substance was formed around and on the unamalgamated portions in about 0.5 hours. The H_2 (no current was applied) developing according to the reaction /8/.

$$Al + 3H_2O = Al(OH)_3 + 1.5H_2 \qquad /8/$$

partially carried the dark grey particles to the water sur-
face. However, particles of gray color did not form after
complete amalgamation of the pieces. Large quantities of
fluffy, white hydrated Al-oxide beta trihydrate (bayerite),
as revealed by x-ray diffraction pictures, were also obtained
as a consequence of reaction /8/. The nearly black material
was carefully removed with a suction tube, to avoid mixing
with the white oxide, and transferred to a glass slide.
After drying some of the black materials was examined with an
optical microscope. Bright spots with metallic luster of
the magnitude of about 10^{-5}mm in diameter embedded in the
oxide flakes, appeared in relfected light. The spots became
opaque in transmitted light (Fig. 6). Furthermore, as the
particles appeared flat and faded with time they could only
be of metallic Al. These results show that Al can also dis-
integrate in presence of Hg and possibly even with a faster
rate if an anodic current were applied. The same process
may occur with other metals, e.g. Sn (22).

Discussion and Conclusions

Although the coulometric measurements (Table 1) show
that Al goes into solution as an Al^{3+} ion only in some mea-
surements and in basic solutions, the trivalency of Al-ions
can, nevertheless, be postulated as occurring throughout
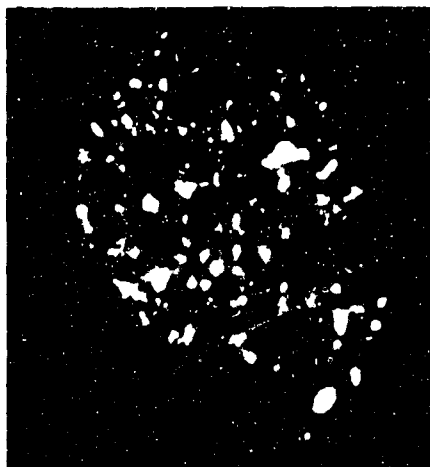because the departure from the valence 3 is well understood:

Fig. 5. Al hydroxide flakes containing metallic Al particles
formed during anodic dissolution of Al in 3% $K_2Cr_2O_7$.

Fig. 6. Al particles embedded in a bayerite flake; particles
formed due to disintegration of Al in presence of Hg
during reaction /2/. A-in reflected and B-in trans-
mitted light. 1430x.

this happens due to the selfdissolution of the Al amalgam (H_2-evolution on its surface) and due to partial disintegration of those parts of Al which became not completely amalgamated (Fig. 6). Thus, no lower valency Al ions are formed from the amalgam and there is no reason to believe that such ions are produced by a pure Al anode.

Al disintegrates anodically in a manner that is clearly film controlled: depending on the adherability and other properties of the protective layers formed in various electrolytes, the process of disintegration may be different as well as the shape and size of the particles separating from the bulk metal. The particles are embedded in a film consisting of a hydrated Al oxide (Fig. 3, 5, 6), mainly beta bayerite (23). In NaOH as an electrolyte, this reagent may dissolve these oxides, and the particles may appear free (Fig. 1).
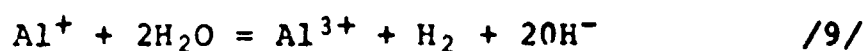
There is a question why disintegration of the anode occurs and why the separated particles are embedded in the oxide layer? If an active metal such as Al is anodically polarized in aqueous solutions, the oxide film present can thicken. The composition and, therefore, the properties of these films depend largely on the electrolyte and the applied voltage (24). For one or another reason these films do not cover the metal anodes uniformly and the anodic current will follow the path of least resistance. At places where the film is thin or not formed at all (e.g. on inclusions), the

current density will be high and anodic dissolution will occur around such high resistance spots, undermining them. After some time the respective spot, still containing some metal adhering to the protective layer, may drop out. If the protective film is not dissolved by the electrolyte, the metallic particles will appear embedded in the film. Of course, the ions going anodically into solution exhibit some pressure on the oxide layer and aid the separation. The shape of the metallic particles must, therefore, be irregular and of various sizes as determined by the places of least resistance of the adhering film. This conclusion is confirmed by the Fig. 3, 4, and 5. A new oxide film is formed on places where the metal dropped out and the dropout can occur again after some time. It is clear that with such a mechanism of disintegration its rate, and the particle size and shape will depend on the composition of the electrolyte, the temperature (4) and the current density (25). In electrolytes which do not further formation of strongly adhering protective films, there may be, with other reasons also excluded, no anodic disintegration at all.

The disintegration of Al, partially amalgamated, proceeds in H_2O in a similar manner: Hg atoms spreading between the oxide film and the metallic surface forcibly loosen the former. The film upon breakdown takes with it tiny Al parts cracking of the bulk material, as they stick firmly to the film (Fig. 6). These particles cause the nearly black color

of the flakes (21) separating from Al or other metals (5, 6
22, 25, 26). If the particles are well protected by a film
from the action of H_2O, as in case of Al, embedded in bayer-
ite, the residue keeps its dark color even in water for a
comparatively long time (several days) but where the pro-
tection is weak, as with Mg, the dark flakes become white in
the presence of moisture much faster (26).

The reducing ability of the anolyte, or of parts of the
electrolyte being in close vicinity to the anode, is ex-
plained simply by the action of the fine metallic dispersion
of the active metal coming in contact with an oxidizer, which
may be added to the electrolyte, or which may be the solvent
itself, e.g. H_2O. According to the lower valency theory, the
action of Al^+ with H_2O is as follows:

$$Al = Al^+ + e \qquad\qquad /1/$$
$$e + H^+ = 0.5H_2 \qquad \text{at the cathode}$$
$$Al^+ + 2H_2O = Al^{3+} + H_2 + 2OH^- \qquad /9/$$

Reaction /9/ is according to Davidso. (17). However, if all
3 reactions are summed up, one obtains:

$$Al + H^+ + H_2O = Al^{3+} + 1.5H_2 + 2OH^- \qquad /10/$$
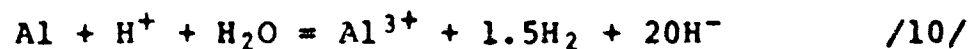
which is nothing more than the direct reaction of Al (here
in form of finest particles) with H^+ and H_2O. Reduction of
other substances dissolved in the electrolyte proceeds simi-
larly. Uncommon ions like Al^+, the presence of which cannot

be proved in the anolyte, are, therefore, unnecessary for the explanation of the reducing power of the anolyte. Fine metallic particles dispersed in the electrolyte do the same. In fact metallic dust (e.g. of Al, Zn, Fe, etc.) is well known as a reducer of organic substances. Whether this reduction proceeds indirectly through the atomic H formed (27) or directly by transfer of the valence electrons from the metal is of lesser importance. The question how this transfer occurs, whether all 3 electrons pass over to the reducer molecules simultaneously or in succession is also insignificant because at present there is no possibility to check the guess anyway.

Acknowledgement

REFERENCES

1. F. Wohler and H. Buff, Liebigs Ann., 103, 218 (1957).

2. Literature see in M.E. Straumanis, J. Electrochem. Soc. 108, 1087 (1961).

3. J.W. Turrentine, J. Phys. Chem. 12, 448 (1908).

4. E. Raijola and A.W. Davidson, J. Am. Chem. Soc. 78, 556 (1956).

5. M.E. Straumanis and D.L. Mahtis J. Less-Comm. Met. 4 213 (1962).

6. M.E. Straumanis and D.L. Mathis J. Electrochem. Soc. 109, 434 (1962).

7. R.C. Plumb, ibid 105, 498 (1956).

8. H.W. McCune, ibid, 106, 63 (1959).

9. V.A. Dmitriev, O.I. Avdeeva and Y.I. Sozin, Dokl. Ak. Nauk. Ser. Khim 6, 176 (1961).

10. B. Roald and M.A. Streicher, J. Electrochem. Soc. 97. 283 (1950).

11. M.D. Raush, W.E. McEwen and J. Kleinberg, J. Am. Chem. Soc. 77, 2093 (1955).

12. A.W. Davidson, J. Kleinberg, W.E. Bennett and A.D. McElroy ibid. 71, 377 (1949).

13. M. Sborgi and P. Marchetti, N. Cimento 22, 151 (1921).

14. P. Brouillet, I. Epelboin and M. Froment, Compt. rend. 239, 1795 (1954).

15. I. Epelboin and M. Froment, ibid. 238, 2416 (1954).

16. I. Epelboin, Z. Electrochem. 59, 691 (1955).

17. A.W. Davidson in C.A. Hampel's "Encycl. of Electrochemistry", Reinhold Publ. Corp., New York 1964, p. 48.

18. M.E. Straumanis and K.A. Poush, J. Electrochem. Soc. 111, 795 (1964).

19. H.A. Flaschka, "EDTA Titrations", Pergamon Press, New York, 1959, p. 84.

20. M.E. Straumanis and Y.N. Wang, J. Electrochem. Soc. 102 304 (1955).

21. J.A. Ketellar, "Chemical Constitution", Elsevier Publ. Co., New York, 1953, p. 292.

22. M.I. Rumpel, A.W. Davidson, and J. Kleinberg, Inorg. Chem. 3, 935 (1964).

23. R.K. Hast, Tr. Farad. Soc. 53, 1020 (1957).

24. L. Young, "Anodic Oxide Films", Academic Press, New York, 1961.

25. W.J. James, M.E. Straumanis and J. L. Reed "Anodic Dissolution of Zn in KNO_3" Tech. Rep. No. 10 to ONR, 1964.

26. M.E. Straumanis and B.K. Bhatia, J. Electrochem. Soc. 110, 357 (1963).

27. H.H. Uhlig and R. Krutenat, ibid. 111, 1303 (1964).