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MADISON, WISCONSIN

Low Valent Aluminum as a Product of Anodic Oxidation in Aqueous Solution

BY ESKO RAIJOLA AND ARTHUR W. DAVIDSON[1]

In the electrolysis, between an aluminum anode and a platinum cathode, of various aqueous solutions, aluminum dissolves anodically with an initial mean valence number significantly lower than 3, and hydrogen is evolved at the anode. In solutions of oxidizing agents the valence number is lower than in halide solutions, and the amount of hydrogen given off is smaller. The lowest valence number observed, 1.67, was attained in the electrolysis of an aluminum chloride–aluminum nitrate mixture. Experiments with various oxidants in a divided cell revealed the presence in the anolyte of reduction products other than hydrogen. By means of a flowing electrolyte it was shown that in some instances the primary reducing agent can be transferred from one vessel to another. All of these facts may be interpreted in terms of primary anodic oxidation of aluminum partly to the unipositive state.

The anomalous behavior of an active aluminum anode was first observed almost a century ago by Wöhler and Buff,[2] who noted, during the electrolysis of an aqueous sodium chloride solution between aluminum electrodes of rather low purity, not only that hydrogen was evolved at the anode, but also that the dissolution of aluminum corresponded, on the assumption of oxidation to the tripositive ion, to a current efficiency of 130%. These authors specifically rejected the obvious explanation of a valence state of aluminum lower than 3. Turrentine,[3] in order to account for the evolution of hydrogen at an aluminum anode—termed by him an example of "reversed electrolysis"—postulated the existence of unipositive or dipositive aluminum, or both; he, however, made no direct determination of current efficiency. There appears to have been no systematic investigation of this apparent anomaly until Mazzitelli[4] repeated the experiments of Wöhler and Buff with an anode of pure aluminum, and obtained in one electrolysis an apparent valence number of 1.95. Meanwhile, other workers demonstrated the occurrence of parallel phenomena in acetone,[5] in liquid ammonia,[6,7] in anhydrous acetic acid[8,9] and in ethanol.[9] Indeed, the pattern of divergent behavior is so consistent that it is surprising to encounter the statement[10] that an aluminum anode in 15% aqueous sulfuric acid is so uniformly oxidized to a valence state of 3 that such a system may be used for coulometric measurements.

The present paper, which reports the results of a study of the electrochemical oxidation of an active aluminum anode in a number of different aqueous solutions under various conditions, definitely establishes, it is believed, the existence of an aluminum ion of low valence number. The fact that the

mean valence numbers obtained are in many cases lower than 2, together with the electron structure of aluminum, make it almost certain that this ion is Al^+.

Experimental

The general method used in this investigation has been thoroughly described in a previous paper.[3] For most of the experiments, current was supplied through a simple undivided cell from a full-wave rectifier capable of furnishing up to 24 volts. The cathode consisted of a platinum foil. The aluminum rod used as anode, of 99.996% purity, was obtained from the Aluminum Company of America.[11] The electrolytes were of reagent quality, and were further purified by recrystallization when necessary. Except where otherwise noted, an inert atmosphere was maintained by the passage of nitrogen through the cell. The quantity of electricity passing through the circuit was determined by means of a silver coulometer.

In at least one electrolysis with each electrolyte, a second weighed piece of aluminum was immersed in the cell near the anode. In no case was there any appreciable decrease in weight of this test piece during the electrolysis. Hence there is no evidence of non-electrolytic corrosion of the aluminum.

In conformity with previous practice, the initial mean valence number V_i, of the aluminum ions resulting from anodic oxidation was determined by means of the equation

$$V_i = \frac{\text{wt. of Ag deposited in coulometer} \times 26.98}{107.88 \times \text{wt. of Al lost from anode}}$$

Results

Electrolysis in Halide Solutions.—A series of typical initial mean valence numbers obtained in an undivided cell with several halide electrolytes at varying concentrations and current densities is shown in Table I. In most instances, for a given set of conditions at least two (sometimes three)

(1) University of Kansas, Lawrence, Kansas. Fulbright Lecturer, Turku, Finland, 1954–1955.

(2) F. Wöhler and H. Buff, *Ann.*, **103**, 218 (1857).

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

(4) A. Mazzitelli, Master's Thesis, University of Kansas, 1949.

(5) U. Sborgi and P. Marchetti, *Nuovo Cimento*, **22**, 151 (1921).

(6) M. C. del Boca, *Helv. Chim. Acta*, **16**, 565 (1933).

(7) W. E. Bennett, A. W. Davidson and J. Kleinberg, THIS JOURNAL, **74**, 732 (1952).

(8) A. W. Davidson and F. Jirik, *ibid.*, **72**, 1700 (1950).

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

(10) M. Tosterud and R. C. Mason, *Trans. Electrochem. Soc.*, **90**, 221 (1946).

TABLE I

ANODIC OXIDATION OF ALUMINUM IN AQUEOUS SOLUTIONS OF HALIDES

Electrolyte	Concn., moles/l.	Current density, amp./sq. cm.	Time, hr.	V_i
NaCl	0.05	0.0026	2.5	2.57
NaCl	.05	.0086	2.5	2.51
NaCl	.05	.0143	2.5	2.52
NaCl	.05	.0400	2.5	2.51
NaCl	.50	.0026	2.5	2.58
NaBr	.10	.0026	3	2.51
KI	.10	.0080	2	2.75

values agreeing to within 0.02 unit were obtained, only the mean of which is reported here.

No significant trend of V_i value with concentration was observed, and a 15-fold increase in current density brought about only a slight decrease in V_i. Furthermore, the phenomena appear to be essentially the same regardless of the particular alkali halide used as electrolyte. During the electrolyses hydrogen was evolved not only at the cathode, but also, in smaller quantity, at the anode. A white turbidity appeared in the cell, but no gray or black coloration. At the end of the electrolysis, the electrolyte exhibited no reducing properties.

These results may best be explained in terms of the hypothesis that the primary anode reaction consists in part in the oxidation of the metal to the familiar tripositive ion, in part to a unipositive ion (about 1 Al^+ ion to every 3 Al^{+++} ions), and that the latter undergoes immediate oxidation by water approximately according to the equation

$$Al^+ + 2H_2O = Al^{+++} + H_2 + 2OH^-$$
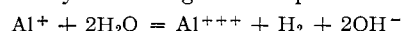
the tripositive aluminum ion being subject, of course, to hydrolysis.

Electrolysis in Solutions of Oxidizing Agents.—Since it had been observed that the V_i values attained by aluminum in liquid ammonia solutions were lower when the electrolyte contained nitrate ion,[7] it appeared to be of interest to determine whether or not the presence of this ion—or of other oxidizing ions which had not been available in liquid ammonia—would have a similar effect in aqueous solution. Results of experiments with a number of electrolytes containing oxidizing anions are shown in Table II. The value tabulated is in most cases the mean of two concordant results.

TABLE II

ANODIC OXIDATION OF ALUMINUM IN AQUEOUS SOLUTIONS OF OXIDANTS

Electrolyte	Concn., moles/l.	Current density, amp./sq. cm.	Time, hr.	V_i
NaNO$_3$	0.05	0.0029	2	2.28
NaNO$_3$	.05	.0086	2	2.39
NaNO$_3$	.05	.0143	1	2.37
KClO$_3$	.05	.0026	2	2.22
KClO$_3$	.05	.0086	2	2.24
KClO$_3$	.50	.0026	2	2.15
KBrO$_3$	.05	.0026	2	2.01
KBrO$_3$	.48^a	.0026	2	2.03
KBrO$_3$	.05	.0026	2	2.08^b
KClO$_4$	.05	.0026	2	2.63

^{a} Saturated. ^{b} In this electrolysis air, instead of nitrogen, was passed through the cell.

It is evident that in the presence of these oxidizing agents (except potassium perchlorate, which is not easily reduced in dilute aqueous solution) the V_i values are substantially lower than in halide solutions. It may be noted also that when the solution was stirred with air instead of nitrogen, other conditions remaining the same, the V_i value was increased by only 0.07 unit.

In one electrolysis with sodium chloride ($V_i = 2.49$) and one with potassium bromate ($V_i = 1.98$) as electrolyte, the hydrogen given off at the anode was collected and measured. In the first case, the

volume of hydrogen was approximately that to be expected from the reaction of the lower valent aluminum with water; in the second, only one-third of the calculated volume of hydrogen was obtained. It may be concluded, therefore, that bromate ion successfully competes with water as an oxidant for Al^+ ion.

A reasonable explanation for the fact that lower V_i values are observed in the presence of strong oxidizing agents is to be found in the hypothesis advanced in a recent paper[12]: a V_i value lower than 3 is attained only when the solution contains as solvent or solute an oxidant (electron acceptor), which oxidizes the Al^+ to Al^{+++} before the former ion can return to the anode and there give up its remaining valence electrons. To supplement this idea, we need only to make the entirely reasonable assumption that nitrate, chlorate and bromate ions are more rapid oxidants for Al^+ than is water.

Electrolysis in Chloride–Nitrate Mixtures.—In the anodic oxidation of aluminum in liquid ammonia, it was observed that lower V_i values were obtained with halide–nitrate mixtures as electrolytes than with either halide or nitrate alone. In order to determine whether or not this would occur also in aqueous solutions, a series of electrolyses was carried out in mixed sodium chloride–sodium nitrate solutions. The total concentration was kept constant at 0.10 M, and the current density at 0.0035 amp./sq. cm. The valence numbers found are listed in Table III and plotted in Fig. 1.

TABLE III

ANODIC OXIDATION OF ALUMINUM IN NaCl–NaNO$_3$ MIXTURES

Mole % NaCl in solute	V (mean of 2 meas.)	Mole % NaCl in solute	V (mean of 2 meas.)
0	2.32	60	2.28
10	2.17	70	2.37
20	1.91	80	2.46
30	1.93	90	2.51
40	2.08	100	2.57
50	2.16		

These results are analogous to those observed for liquid ammonia solutions, the minimum V_i value being found in a solution containing 4 moles of nitrate to 1 of chloride.

A similar series of expts. was carried out with mixed aluminum chloride–aluminum nitrate solutions, at a total concentration of 0.1 M and a current density of 0.0143 amp./sq. cm. Careful checks showed no appreciable non-electrolytic corrosion of the aluminum even in these electrolytes. The results, similar to those obtained in the previous series, need not be reported in detail; for the nitrate and the chloride alone the V_i values were 2.40 and 2.54, respectively, whereas a minimum value of 1.73 was found for the solute containing 30 mole % of chloride. A plausible explanation for the lower V_i values occurring in chloride–nitrate mixtures lies in the probable catalysis by chloride ion of the reduction of nitrate by Al^+ ion.

In the 30% AlCl$_3$–70% Al(NO$_3$)$_3$ solution only, a gray deposit was observed in the electrolyte after

(12) M. D. Rausch, W. E. McEwen and J. Kleinberg, THIS JOURNAL, **77**, 2093 (1955).
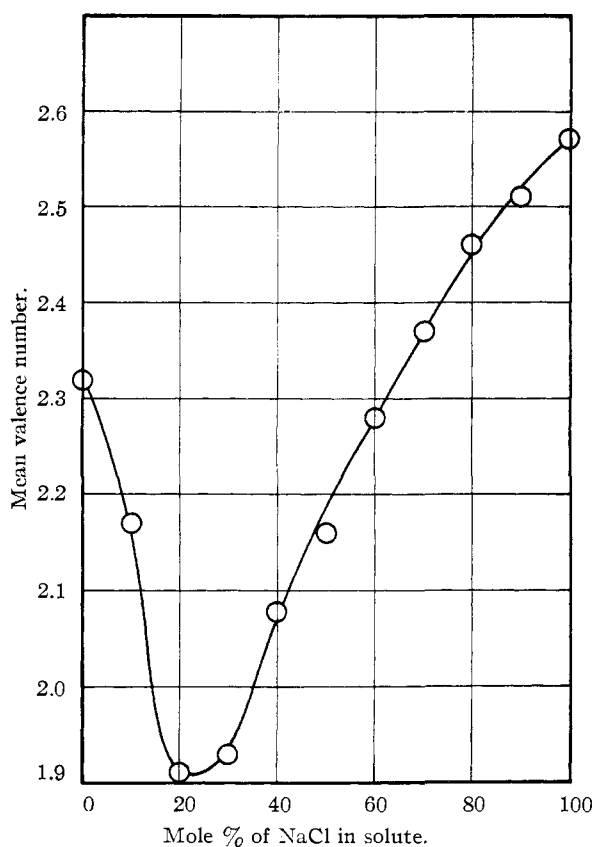
Fig. 1.—Variation of V_i with composition of electrolyte.

electrolysis had proceeded for a few minutes. This expt. was repeated in the divided cell to be described presently; the electrolysis was continued for 2.5 hours, by which time a considerable amount of dark gray substance had appeared, but in the anolyte only. Incidentally, the valence number found in this case, the lowest so far observed in aqueous solution, was 1.67, corresponding to 2 unipositive ions to 1 tripositive. After filtration, washing and drying, the solid was found to be readily soluble both in warm dilute acid and in alkali solution. Its gray color is believed to be due to the presence of metallic aluminum, formed by disproportionation of Al^+ ion according to the equation

$$3Al^+ = Al^{+++} + 2Al$$
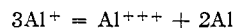
Analogous disproportionation has been observed in the case of indium, both in acetic acid[8] and in ammonia solutions,[13] as well as for beryllium in aqueous solutions.[14] No explanation is as yet available for its occurrence, in the case of aluminum, exclusively in these particular mixed solutions.

A number of electrolyses, with various electrolytes, were repeated with an intermittent direct current produced by a half-wave rectifier, so that the anode was exposed to non-electrolytic action for half the duration of the electrolysis. The V_i values obtained under these conditions were in good agreement with those already reported; these

(13) A. D. McElroy, J. Kleinberg and A. W. Davidson, THIS JOURNAL, 74, 736 (1952).

(14) B. D. Laughlin, J. Kleinberg and A. W. Davidson, ibid., 77, 559 (1955).

results, also, indicate that non-electrolytic corrosion of the aluminum is negligible.

Electrolyses in a Divided Cell.—In order that reductions occurring in the neighborhood of the anode might be more closely observed, several electrolyses were carried out in the divided cell shown in Fig. 2.
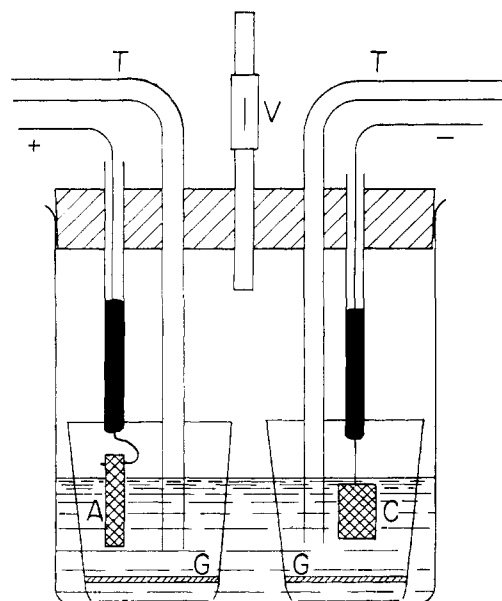

Fig. 2.—Divided cell.

This consisted simply of a beaker in which were set two Gooch type glass crucibles with sintered glass disks GG; one of the electrodes, A and C, was placed inside each of the crucibles. Nitrogen entered the cell through the tubes TT and escaped through the Bunsen valve V. A sample of anolyte or of catholyte for analysis could be obtained simply by removal of the appropriate crucible. Results obtained with this cell are summarized in Table IV.

TABLE IV

REDUCTION NEAR AN ALUMINUM ANODE

Electrolyte	Added oxidizing agent	Reduction products found after electrolysis		Probable reaction in anolyte
		In catholyte	In anolyte	
$NaNO_3$	...	NO_2^-	NO_2^-	$Al^+ + NO_3^- + 2H^+ =$ $Al^{+++} + NO_2^- + H_2O$
$NaCl$	$FeCl_3$	None	Fe^{++}	$Al^+ + 2Fe^{+++} = Al^{+++}$ $+ 2Fe^{++}$
$KClO_4$	...	None	Cl^-	$3Al^+ + ClO_3^- + 6H^+ =$ $3Al^{+++} + Cl^- + 3H_2O$

Reduction in Solutions Not in Contact with the Anode.—Some experiments analogous to those previously described for a magnesium anode[15] were undertaken in order to determine whether or not the unipositive aluminum ion is sufficiently long-lived to bring about reductions at an appreciable distance from the anode at which it originates. For this purpose, several electrolyses were carried out in a cell in which sodium chloride or sodium nitrate solution was allowed to flow from an elevated reservoir, past an aluminum rod serving as anode, into

(15) R. L. Petty, A. W. Davidson and J. Kleinberg, ibid., 76, 363 (1954).

a solution of an oxidant contained in a separate vessel. In control experiments in which the only

Electrolyte	Oxidizing agent	Observation
NaNO₃	Ammoniacal AgNO₃ soln.	Black finely divided substance: metallic Ag
NaCl	K₃Fe(CN)₆ and FeCl₃	Dark blue ppt.: Prussian blue
NaCl	KMnO₄	Dark brown ppt.: MnO₂

variation from these conditions consisted in the use of a platinum instead of an aluminum anode, there was no evidence of reduction. With the aluminum anode, although the quantities of reduction product obtained were small, they were nevertheless adequate for identification. The results are summarized in Table V.

As in the case of magnesium, the formation of these reduction products provides further proof of the transitory existence of an anodic product with marked reducing properties.

TURKU, FINLAND

Unipositive Beryllium as a Product of Anodic Oxidation

BY BARBARA D. LAUGHLIN, JACOB KLEINBERG AND ARTHUR W. DAVIDSON

The electrolysis of an aqueous sodium chloride solution between beryllium electrodes in a divided cell results in the anodic conversion of the metal to both the uni- and dipositive oxidation states. The dissolution process is accompanied by anodic evolution of hydrogen; in electrolyses of short duration the quantity of hydrogen liberated corresponds to oxidation by the solvent of the unipositive beryllium formed, to the common dipositive state. During the course of longer runs metallic beryllium is deposited uniformly throughout the anolyte. The production of the metal can be accounted for only in terms of the disproportionation of unipositive beryllium: $2Be^+ = Be^{2+} + Be$. The product of the anodic oxidation of beryllium is capable of reducing permanganate ion to manganese dioxide, and silver ion to elementary silver, under conditions which do not permit the oxidizing agent to come directly in contact with the anode. These reductions offer further proof of the formation of +1 beryllium.

Strong evidence recently has been obtained to show that on the anodic oxidation of magnesium[1] and aluminum[2] in aqueous electrolytic solutions these metals are converted to oxidation states (e.g., Mg^+ and Al^+) lower than those corresponding to complete removal of their valence electrons. The fact that no substance containing either magnesium or aluminum in a lower valence state could be isolated after electrolysis is not surprising; the chemistry of magnesium and aluminum is characterized by a notable scarcity of solid compounds in which the elements exhibit any oxidation state other than that corresponding to their number of valence electrons. The present communication is concerned primarily with the anodic behavior of beryllium in aqueous sodium chloride solution. Although no compound of lower valent beryllium has been isolated, data have been found which appear to show incontrovertibly that the metal is oxidized anodically to a mixture of uni- and dipositive states. In addition, some interesting information has been collected on the anodic oxidation of the metal in the presence of other inorganic electrolytes.

Experimental

The 0.25-in. beryllium rod, from which all the electrodes used were cut, was purchased from the Brush Beryllium Company and was described as "of highest purity." The other chemicals employed were of C.P. or reagent grade. The source of direct current was a full-wave mercury tube rectifier capable of supplying up to 1000 v. The quantity of electricity passing through the cell was determined by means of a silver coulometer. Electrolyses were performed between beryllium electrodes in a divided cell similar to that described in a previous communication,[1] with compartments

of a capacity of about 100 ml. each. In experiments where the hydrogen evolved at the electrodes during electrolysis was collected, an atmosphere of oxygen-free nitrogen was maintained over both anolyte and catholyte. In other electrolyses both compartments were left open to the air. After electrolysis, the anode was washed with water and dried in an oven at 120° before weighing.

When the amount of hydrogen liberated at the anode or at both electrodes was to be determined, the effluent gas, measured after having been shaken for 30 min. with chromium(II) sulfate solution, was brought into contact, in a combustion chamber, with a platinum coil heated to dull redness. A measured excess of oxygen was then introduced into the chamber. After combustion, the gas was again shaken with chromium(II) sulfate solution. The hydrogen content could then be calculated by two semi-independent methods: either as two-thirds of the decrease in volume on combustion, or as the difference in oxygen-free gas before and after combustion. It should be emphasized that in the experiments with sodium chloride as electrolyte the initial contact of the effluent gas with chromium(II) sulfate solution gave no decrease in volume, a fact which demonstrates that neither oxygen nor chlorine is formed in the electrolytic process.

For electrolyses with a flowing electrolyte, a cell like that previously described[1] was employed.

Results and Discussion

Anodic Oxidation of Beryllium in Aqueous Sodium Chloride.—The initial mean valence number, V_i, with which beryllium entered solution when anodically oxidized was calculated by means of the equation

$$V_i = \frac{\text{wt. of Ag deposited in coulometer} \times 9.02}{107.88 \times \text{wt. of Be lost from anode}}$$

A series of typical initial mean valence numbers obtained with sodium chloride as electrolyte is listed in Table I. These values have true electrochemical significance, since control experiments showed that direct non-electrolytic reaction between beryllium and electrolyte is negligible. The beryllium cath-

(1) R. A. Petty, A. W. Davidson and J. Kleinberg, THIS JOURNAL, 76, 363 (1954).

(2) E. Raijola and A. W. Davidson, ibid., 78, 556 (1956).