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Aluminum Electrochemistry in Liquid Ammonia

L. Maya

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ALUMINUM ELECTROCHEMISTRY IN LIQUID AMMONIA

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ALUMINUM ELECTROCHEMISTRY IN LIQUID AMMONIA

L. Maya

ABSTRACT

The electrochemistry of aluminum in liquid ammonia was investigated using potassium amide as supporting electrolyte. Anodic dissolution of the metal in this medium is feasible using a glassy carbon cathode and becomes significant at approximately +2.2 V from the solvated electron couple. The dissolution efficiency is limited by the interference of solvated electrons which discharge at the anode. The generation of solvated electrons is one of the cathodic processes and their migration could not be completely prevented in a divided cell. In addition to this, electrodeposition of potassium at the glassy carbon cathode also takes place leading to its eventual catastrophic disintegration. This apparently takes place through the disruption of the glassy carbon structure. The presence of electroactive aluminum species produced in situ by anodic dissolution or added as $LiAl(NH_2)_4$ was detected by means of cyclic voltammetry which revealed the appearance of a cathodic response at about +100 mV from the solvent decomposition limit.

1. INTRODUCTION

The electrochemistry of aluminum in liquid ammonia was the subject of some attention in the past.[1-8] Central to that effort was the search for aluminum species with an oxidation number lower than three. This search was prompted, in part, by observations[3] in the potentiometric titrations of solutions of aluminum salts of inflections, suggestive of intermediate oxidation states, with potassium metal solutions.

In a series of coulometric studies aluminum was found, with the exception of nitrate-containing media, to require three electrons for both the reduction of Al(III) species and the anodic dissolution of the metal. In the presence of nitrate, a transient lower valent species was

detected. Apparently this species, generated in the course of anodic dissolution of the metal, was oxidized by nitrate, thus decreasing the coulometric requirements by an average of up to 1.5 electrons for obtaining the final Al(III) product.

The early work of Taft and Barham[1] considered the possibility of electrodepositing aluminum metal from liquid ammonia solutions as an alternative to the molten salt processes. That work failed to obtain positive results and only later it was found possible to reduce aluminum to the amalgam.[8]

The present reinvestigation of the system was undertaken in order to evaluate the anodic dissolution of aluminum as a synthetic route leading to alkali tetra-amido aluminate salts. Thus electrolysis was envisioned as an alternative to other synthetic approaches such as those based on the action of alkali metal solutions on aluminum metal,[9] on its amalgam,[10] or the action of ammonia on $LiAlH_4$.[11] The latter approach is limited to the preparation of the lithium salt because the other alkali tetrahydro aluminates are not readily available.

The electrochemical approach to the preparation of a given alkali tetra-amido aluminate requires the use of the corresponding alkali metal amide as supporting electrolyte. Use of a basic medium represents a marked departure from the electrochemical studies cited above which were conducted in acidic media, that is, containing ammonium ions. These ammonium ions were either added as supporting electrolyte or formed as a consequence of ammonolytic reactions of the starting aluminum salts. Therefore it was also of interest to determine the electrochemical

characteristics of a basic medium, which is an unexplored field, and its effect on the electrochemistry of aluminum.

2. EXPERIMENTAL

Electronic grade ammonia was condensed over sodium, left in contact overnight at -78°C and transferred into the electrochemical cells. High purity aluminum wire (6N from Alfa Products), 1.5 mm diameter was used to make electrodes. Other materials used as auxiliary electrodes were Pt, Au, Cu and glassy carbon (3 mm rod from Tokai Electrode Manufacturing Co., Tokyo, Japan). Silver wire was used as quasi-reference electrode. Vacuum tight seals were made after constriction of Pyrex tubing around the wire leads and sealing with epoxy glue. The tubes containing the electrodes entered the cells through standard ground glass joints or Ace-Thred adaptors (Ace Glass Co., Vineland, NJ). Potassium amide was prepared from high purity potassium metal (99.95% from Alfa Products). Lithium tetra-amido aluminate was prepared[11] from $LiAlH_4$ (Aldrich). All manipulations were conducted in the absence of air using a vacuum line and a dry argon glove box.

Preliminary electrolysis experiments were conducted in a single-compartment cell provided with a connection to the vacuum line and ports for the working, reference and auxiliary electrodes. An additional port was available for the introduction of solid samples. Additional experiments were conducted in a two-compartment "U" shaped cell having a fine porous glass frit between the two segments of the cell. The cells had a working capacity of about 15 mL. The instrumentation used consisted of a Model 173 Potentiostat, Model 179 Coulometer, Model 175 Signal

Generator and a Model 174A Polarographic Analyzer all from Princeton Applied Research. A Neslab instrument cryostat was used to maintain a low temperature bath at -50°C in which the cells were immersed. Unless otherwise stated the experiments were conducted at a 0.1 M concentration of potassium amide.

3. RESULTS AND DISCUSSION

Preliminary experiments were conducted to establish the electrochemistry of the supporting electrolyte. Voltammograms run on a Pt bead electrode showed a working range of +.5 to -1.3 V between the anodic and cathodic currents limits using the silver wire as quasi reference electrode. The cathodic limit was found, by visual inspection, to correspond to the generation of solvated electrons which formed blue streamers of this species as they diffused away from the electrode. After reaching the cathodic limit, the anodic scan portion of the voltammogram, showed a distinct response due to the oxidation of the solvated electrons. This behavior is quite similar to that observed in a neutral medium containing KI as supporting electrolyte[12] although in the latter case the working range extends from +.6 to -2.6 V from the $Ag/AgNO_3$ reference electrode. Observation of the generation of solvated electrons allowed for assigning a value to the potential of the silver quasi-reference electrode in 0.1 M KNH_2 of +.75 V from the solvated electron generation-discharge couple. The +.75 V value was found to be reproducible within ±25 mV in a number of different runs. This value validates Jolly's estimate for the $Ag/Ag(NH_2)_2^-$ couple of +.95 from the

e^-(solv) couple which was reported as accurate to only several tenths of a volt.[13]

The anodic limit in the amide-containing medium on a platinum electrode seems to be controlled by oxidation of the electrode to some surface amide species. Alternatively, the limit could be controlled by oxidation of the electrolyte itself to generate species such as hydrazine, azide or nitrogen, although the latter seems unlikely since no generation of gas was observed. Anodic processes based on the oxidation of the electrolyte, unless catalyzed by Pt, might not be operational since on an aluminum electrode the anodic limit is .5 V more positive than on Pt and corresponds to the dissolution of aluminum.

3.1 ANODIC DISSOLUTION OF ALUMINUM

The aluminum anodes used were first subjected to an activation process with the expectation that this would serve to eliminate surface oxide species. This consisted in poising the electrode at a voltage cathodic enough to generate solvated electrons and passing approximately 0.1 coulomb. This was found to be enough current to generate a distinctly blue solution.

In preliminary experiments, conducted with a single-compartment cell, no dissolution of the aluminum electrode occurred unless the auxiliary electrode was glassy carbon. With other electrode materials a copious amount of solvated electrons was generated at the cathode and these were then discharged at the aluminum electrode. In the case of gold as auxiliary electrode, partial dissolution of this material took place. This was detected by the observation of auride ions[14] by cyclic

voltammetry on an additional Pt-bead test electrode while gold deposition occurred at the anode. In the case of glassy carbon the electrolyses could be conducted in quiescent solutions at current densities of about 0.5 mA/cm^2 without the visible formation of solvated electrons at the cathode. Under these conditions, current efficiencies for the dissolution of aluminum were about 70% as found by analyses of the residue after evaporation of the ammonia. Current efficiencies were lower in stirred solutions. In a typical experiment, lasting a few hours, about five coulombs were passed. No pressure due to gaseous products was observed after freezing the cell in liquid nitrogen. Apparently failure to obtain 100% efficiencies was due to the discharge of electrons at the anode. It seems that the cathode processes with glassy carbon were the generation of electrons and the electrodeposition of potassium. The energetics of these two processes are quite close, the potential difference being only 10 mV.[13] Examination of the glassy carbon under a microscope showed pitting. The presence of potassium was observed in the EDX spectrum upon examination of the electrode on a scanning electron microscope. This observation was not completely conclusive because of the presence of potassium in the electrolyte which could leave a residue of electrolyte in the pores in spite of soaking and washing cycles. Definite proof that potassium electrodeposition did indeed take place was obtained by the fact that the electrode, upon continued use, degraded to the point where it was pulverized. This powder was collected, washed in acid to remove any residue of electrolyte, and then it was subjected to complete dissolution in a HNO_3-$HClO_4$ mixture. The powder contained 0.67% K, equivalent to a total of a few milligrams

of potassium, thus accounting in part for the current passed on the electrode.

Additional experiments were conducted in a divided cell with the hope of attaining higher dissolution efficiencies; however this was not possible because of infiltration of solvated electrons into the anode compartment. These species were present at a relatively low concentration, to the point of not being visible, but detectable by electrochemical means. The presence of solvated electrons was detected by a displacement of the flat portion of the voltammogram, run on the aluminum electrode, into the anodic response. This is illustrated in Figure 1(A) and reflects a continuous oxidation process up to the cathodic limit. Discharge of the infiltrated electrons took place by continued electrolysis at a relatively low current density.

Attempts were also made to improve the rate of the aluminum dissolution by passing larger currents on larger area aluminum electrodes. This approach failed because of excessive generation of solvated electrons. Apparently the area of the glassy carbon electrode limited the current that could be passed through the cell.

The anodic dissolution of aluminum in basic media differs from that in acid media in several respects. The anodic process in acid media, with AlI_3 as electrolyte, leads to the formation of $Al(NH_2)_2I \cdot 2NH_3$.[2] In the presence of nitrate and NaBr or NH_4Br as electrolyte, the product is a complex mixture containing aluminum, bromide, amide, nitrate and traces of nitrite to which no simple formula could be assigned.[4] In contrast with these observations, the dissolution in basic media leads to a product assumed to be tetra-amide aluminate on the basis of the

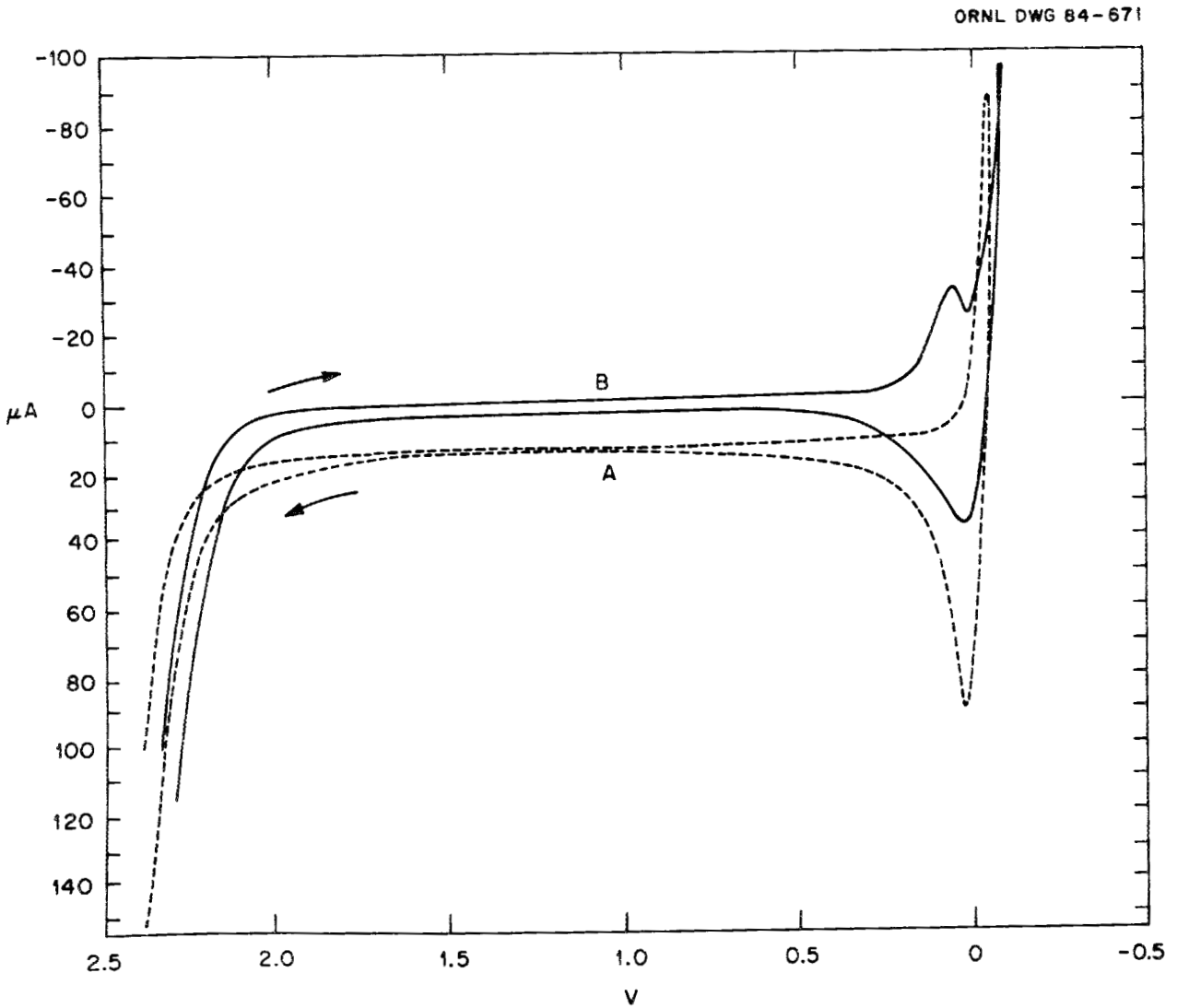

Fig. 1. Cyclic voltammograms on aluminum electrodes 0.6 cm^2 geometric area: (A) in the presence of solvated electrons; (B) in the presence of electroactive aluminum species. Run at -50°C and 50 mV/sec. Potential scale refers to the solvated electron couple.

known chemistry of aluminum in liquid ammonia. However, this product was not isolated because of the relatively small degree of dissolution achieved. The cathodic processes differ in that, in acid media, hydrogen is evolved from the reduction of NH_4^+; this prevents the interference caused by the discharge of solvated electrons at the anode that was observed in the basic medium.

Electrodeposition of potassium as one of the cathode processes in basic media is an interesting phenomenon. The capacity of the glassy carbon to accommodate the potassium is limited due to its disordered structure. Upon reaching a given limit of potassium loading the catastrophic disintegration of the glassy carbon takes place. It is conceivable that graphite, which is known to intercalate potassium, might be a longer lasting cathode.

3.2 ELECTROACTIVE SPECIES OF ALUMINUM

Cyclic voltammetry on platinum electrodes failed to detect electroactive aluminum species either formed in situ by anodic dissolution of aluminum metal or introduced as lithium tetra-amido aluminate. This failure might reflect surface characteristics of the platinum rather than the absence of aluminum species. That this might indeed be the case is supported by difficulties experienced with Pt electrodes in ethylenediamine[15] or with benzophenone in liquid ammonia.[16] The latter observation was actually confirmed in the course of the present work. In this case, the typical voltammogram of benzophenone, as observed on gold, could not be obtained on a Pt-bead electrode.

Additional attempts using the aluminum electrode as test electrode to run cyclic voltammograms showed a reduction wave just prior to the cathodic limit, that was reproducible for both electrogenerated aluminum or $LiAl(NH_2)_4$ and were not related to the material of the auxiliary electrode which could supply the species being reduced, Fig. 1(B). This response was observed with Pt, Cu and glassy carbon as counter electrodes. However, the observation was limited to aluminum electrodes that had been activated after passage of a few coulombs and resulted in aluminum dissolution. Apparently active sites, clean of surface species are required for the reduction of aluminum species in solution. The appearance of the reduction wave just prior to the solvent decomposition limit is reminiscent of the prewaves caused by adsorption phenomena.[17] However it seems that this phenomenon might not be operational here since the anodic portion of the prewave is absent. Another argument against this possibility is the fact that adsorption prewaves are not observed on voltammograms of organic moieties in liquid ammonia[16,18] which would be expected to be more prone to such behavior. An additional experiment using differential pulse polarography was conducted to confirm the presence of aluminum species. The idea behind this experiment was that the different time regime (one order of magnitude slower scan rate) would eliminate artifacts caused by phenomena unrelated to the reduction of aluminum species. In this case the wave prior to the cathodic limit was observed as a shoulder using an activated aluminum electrode.

Finally, attempts were made to electrodeposit aluminum from solutions containing $LiAl(NH_2)_4$ at a concentration level of .01 M on a

number of different substrates. All these attempts failed since at any significant level of current density the production of solvated electrons was favored. No significant amounts of aluminum were deposited in one case even after passage of 30 coulombs with the concurrent formation of solvated electrons.

4. CONCLUSIONS

Potassium amide in liquid ammonia provides a potentially useful medium for electrochemical studies of metallic or organic moieties. The anodic dissolution of aluminum metal in liquid ammonia with potassium amide as supporting electrolyte is feasible but its efficiency is limited by the interference of cathodic processes. The dissolution of aluminum proceeds at a potential about +2.2 volts from the solvated electron couple while the reduction of aluminum electroactive species occurs, as observed by cyclic voltammetry on activated aluminum electrodes, at about +70 mV from the same reference.

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