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ALUMINUM CHLORINE BATTERY

By Jose' Giner and Brian Burrows

First Quarterly Report

October 1968

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Prepared under Contract No. NAS 12-688 by

TYCO LABORATORIES, INC.

Waltham, Massachusetts 02154

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ALUMINUM CHLORINE BATTERY

By Jose' Giner and Brian Burrows

Tyco Laboratories, Inc.

Waltham, Massachusetts 02154

SUMMARY

A molten salt system based on Al and Cl_2 carbon electrodes with an $AlCl_3$-alkali chloride eutectic as electrolyte offers promise as a rechargable, high energy density battery, which can operate at a relatively low temperature and may withstand sterilization.

With the aim of developing such a system, work has been carried out during the present period to obtain pure NaCl-KCl-$AlCl_3$ electrolytes and to do preliminary studies of both Al and Cl_2 electrodes. Different commercial aluminum chloride materials have been investigated. Using cyclic voltammograms it has been found that the major impurity in all these materials is Fe^{3+}.

A treatment with highly dispersed Al powder has been partially successful in purifying this electrolyte. Investigation of the Al anode shows the feasibility of steady state current densities up to 50 ma/cm^2, both in cathodic and anodic directions. At higher current densities, transients are observed which can be interpreted as being due to passivation by formation of a layer of solid salt.

Preliminary experiments on the Cl_2 electrode using porous graphite as substrate show that graphite is severely attacked by the melt. The attack caused considerable swelling, suggestive of interplanar attack. Presumably, $AlCl_3$ is responsible since graphite is stable in alkali-halide melts. More amorphous graphites and carbons will be investigated.

INTRODUCTION

A great deal of effort over the past seven years has been directed toward the development of batteries with energy densities of the order of 200 watt-hrs/lb. The negatives in these high energy density systems are characteristically selected from the most electronegative of the metals. The use of electronegative metals such as Li or Na necessitates the use of electrolytes which are aprotic. Organic and molten salt media have both been used; however, since aprotic organic electrolytes can be used at ambient temperatures, these have received by far the greater amount of attention.

Major disadvantages of cells based on aprotic organic electrolytes are instability of positive plates (resulting in short shelf life) and low conductivity. The chief disadvantage of molten electrolyte batteries being presently investigated is the necessity for high temperature operation, which introduces many problems relating to materials of construction, safety, etc. Furthermore the insulation needed to keep these high temperature batteries in an operating condition leads to a degradation of the energy density of the battery.

It seems possible to overcome the problems associated with the high working temperatures of the present molten salt systems, while still retaining the advantages of high energy density and relatively efficient electrode processes, by using a cell composed of an Al negative and a Cl_2 positive in a low temperature electrolyte of molten $AlCl_3$-NaCl-KCl. The operating temperature of this system would be in the range 120 to 150°C, with a theoretical energy density of 650 watt-hr/lb. Furthermore it should be possible to obtain a cell operable at even lower temperatures by using as electrolyte a melt of $AlCl_3$ with one or more of the other alkali chlorides (LiCl, RbCl, CsCl), all

of which are lower melting than NaCl or KCl.

The theoretical energy density of 650 watt-hr/lb for the Al-Cl_2 system compares favorably with that of 754 watt-hrs/lb for the Li-CuF_2 (propylene carbonate) system and of 990 watt-hr/lb for the Li-Cl_2 (molten salt) system. Another advantage of the Al-Cl_2 system would be that solid Al is easier to handle and much less hazardous than molten Li or Na. The hazards of the Cl_2 electrode common to both the Li-Cl_2 and the proposed new system will be reduced to some extent by the lower working temperatures; the same methods suggested for this electrode in the high temperature cell (adsorption and occlusion on porous carbon or graphite) can be used here.

To devise a practical, workable cell more knowledge is required of the reactions that take place at the anode and cathode of the particular system, as well as a knowledge of the electrolyte properties and of the interaction of the complete system.

The work carried out during this present report period has been concerned with (a) a literature search for data on $AlCl_3$-alkali halide eutectics, (b) preparation and purification of the low melting $AlCl_3$-KCl-NaCl eutectic electrolyte, and (c) preliminary studies of the polarization behavior of Al and Cl_2 electrodes in this eutectic electrolyte.

LITERATURE SURVEY ON $AlCl_3$ EUTECTICS

The available data on $AlCl_3$-alkali halide eutectic is listed in Table I. It can be readily seen that much work has been done on the $AlCl_3$-NaCl, $AlCl_3$-KCl and the $AlCl_3$-NaCl-KCl mixtures. The other alkali halides, however, have received but scant attention.

It is interesting to note that LiCl, RbCl, and CsCl all have lower melting points than NaCl and KCl. This, however, is not the most important feature for the formation of eutectics with low melting points. As can be seen from Figs. 1 and 2, the lowest

TABLE I

$AlCl_3$-ALKALI HALIDE EUTECTIC MELTS

System	Composition mole %	Eutectic mp °C	Reference no.
$AlCl_3$-LiCl	60	114	10, 16
$AlCl_3$ - NaCl	62	112	1, 2, 3, 4, 6, 7, 9, 10
	60	115	12, 14, 15, 16
	59	123	
	50	150	
	66	93	
$AlCl_3$ - NaCl	61	108	2, 4, 16
$AlCl_3$ - KCl	67	128	2, 3, 4, 5, 6, 9, 10 13, 17
$AlCl_3$ - KCl	71-65.5	114-149	16
$AlCl_3$ - KCl-NaCl	60-14-26	93	2, 3, 8, 9, 16
	63.5-16.5-20	88-9	
	62.13-12.7-25.17	94	
	66-14-20	70	
$AlCl_3$ - RbCl			
$AlCl_3$ - CsCi	74.6	148	11

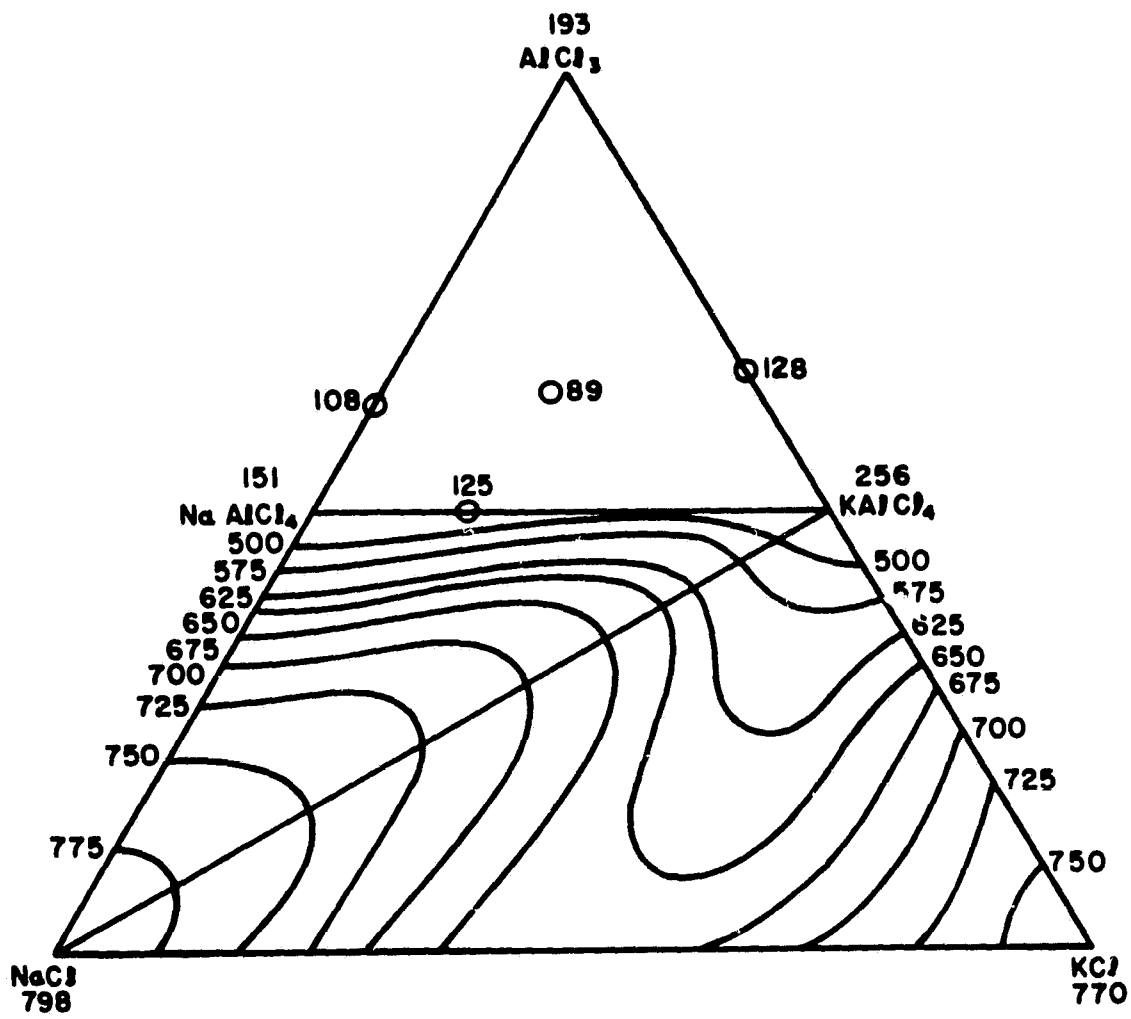

Fig. 1 Phase diagram for the system $AlCl_3$-NaCl-KCl
O . . . Eutectics
Temperature in °C
from Fisher and Simon [2]

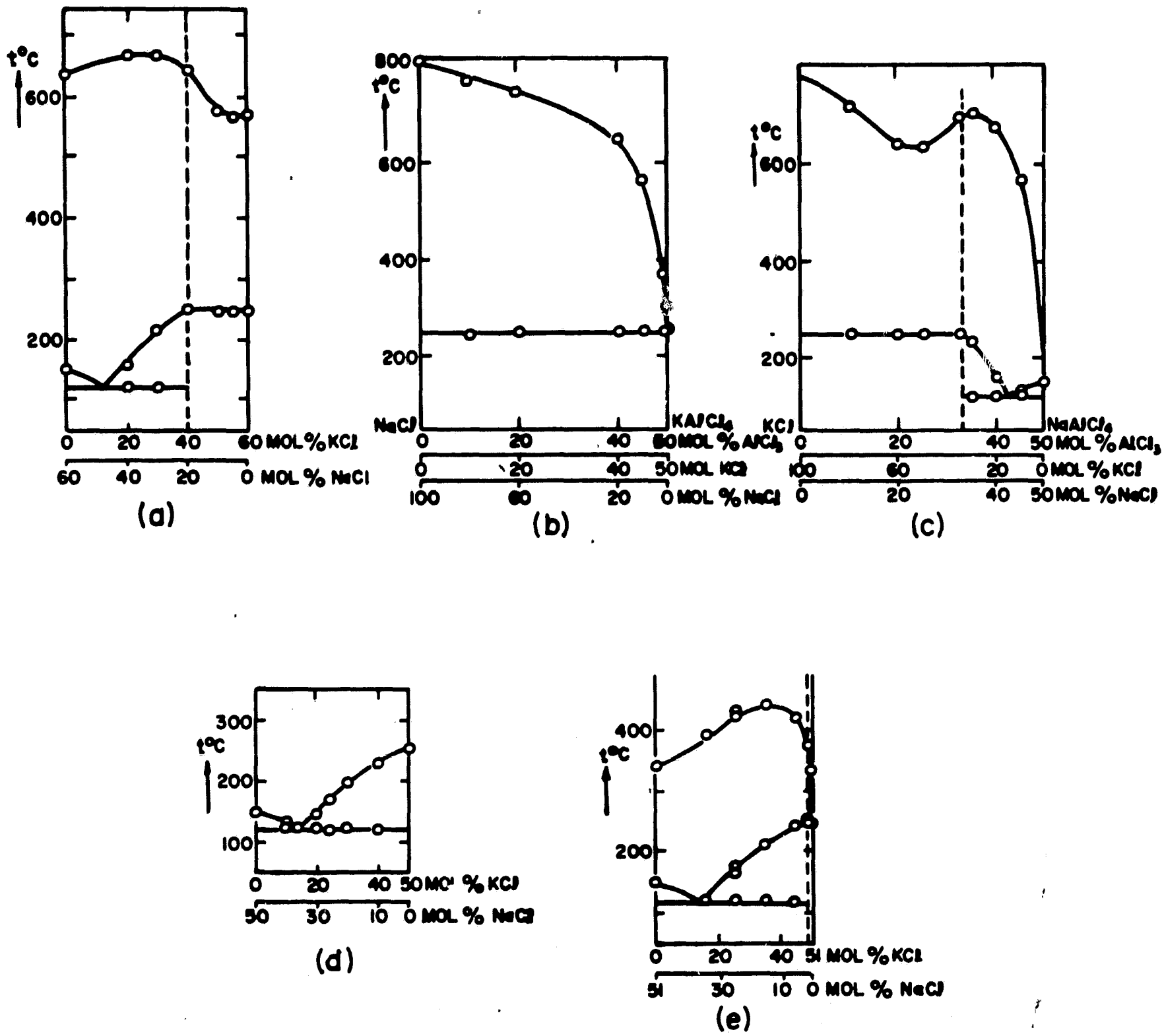

Fig. 2 Cross sections from the phase diagram for the system $AlCl_3$-NaCl-KCl (a) Section through the ternary system at 49 Mol % $AlCl_3$; (b) The pseudo-binary section: NaCl-$KAlCl_4$; (c) The section: KCl-NaCl Cl_4 ; (d) Section through the ternary system at 50 Mol % $AlCl_3$; pseudo-binary system: $NaAlCl_4$-$KAlCl_4$; (e) Section through the ternary system at 40 Mol % $AlCl_3$

melting eutectic in the $AlCl_3$-NaCl-KCl system is formed between the intermediate compounds $KAlCl_4$, $NaAlCl_4$ and $AlCl_3$. In forecasting the type of system to be expected with the other alkali chlorides, it is therefore critical to evaluate the possibility of similar compounds being formed with LiCl, RbCl and CsCl, and their respective stabilities, which will have an important bearing on the melting points to be expected.

Considering the structure of $NaAlCl_4$[18], it is seen that the size of the interstice in which the alkali ion is located is extremely large. Even the largest alkali ion will not fill it. Thus the existence of a similar compound in all other systems is to be expected. Furthermore, since none of these ions fits the interstice perfectly, the compound will be unstable in every system; consequently a low melting point is assured. In such a case it is, however, very difficult to argue about increased or decreased stability as the ions get larger or smaller; therefore it becomes difficult to forecast which of the three remaining alkali-metal-aluminochlorides will have the lowest melting point. Thus investigation of all three systems (LiCl, RbCl, CsCl) with $AlCl_3$ is intended. Then, from all five melting points, the pair with the lowest two melting points can be selected. This, to the best forecasting ability in such diagrams, will form the lowest melting ternary eutectic, which is likely to be lower than the ~90°C found for the $AlCl_3$-$KAlCl_4$-$NaAlCl_4$ system.

Another reason for investigating other systems, apart from the search for a lower melting eutectic, is to determine the limitations of the $AlCl_3$-NaCl-KCl eutectic when considered for a cell operable below 120°C. These limitations arise from the fact that although it has a low melting eutectic (89°C), all three liquidus surfaces rise rather steeply from this point. As a result small changes in composition could result in formation of a solid phase, with resulting deterioration in performance (see behavior of Al electrode, below).

Reference to Fig. 1 also reveals that little is known about the $AlCl_3$-rich region, i.e. the low temperature region of the phase diagram. We intend to investigate this region as far as is feasible. One difficulty which we can probably anticipate is a rather high vapor pressure of $AlCl_3$, since in this region not all of the $AlCl_3$ will be present as the complex $AlCl_4^-$ ion. It has, however, been proposed[23] that in an $AlCl_3$-rich melt the following solvation process takes place

$$AlCl_3 + AlCl_4^- \rightleftharpoons Al_2Cl_7^-$$

A DTA apparatus, highly suited for phase diagram determinations, is now being set up. This apparatus is the Model 16A of T & T Controls. We expect to begin experiments on the $AlCl_3$-LiCl, $AlCl_3$-RbCl, and $AlCl_3$-CsCl systems, and on the $AlCl_3$-rich end of the ternary $AlCl_3$-NaCl-KCl system in the next quarter.

EXPERIMENTAL

The cell was a small (100 cc capacity) four-neck flask. The size was chosen in order to use small amounts of highly purified eutectic. The cell was operated in a hot-air oven, and temperature control was $\pm$ 1°C at 120°C. The oven was modified to allow for electrical connections to the various electrodes and to provide for Ar and Cl_2 gas inlets and outlets; see Fig. 3 for a photograph of the cell arrangement.

Cyclic scans were recorded in the usual manner. A triangular waveform from a function generator (Exact Electronics, Inc., type 255) was fed into the input of a Wenking potentiostat (type 61RS). The potentiostatic i-v curves were recorded on an X-Y recorder (Houston Omnigraphic, model HR-98T).

Galvanostatic polarization curves were obtained by

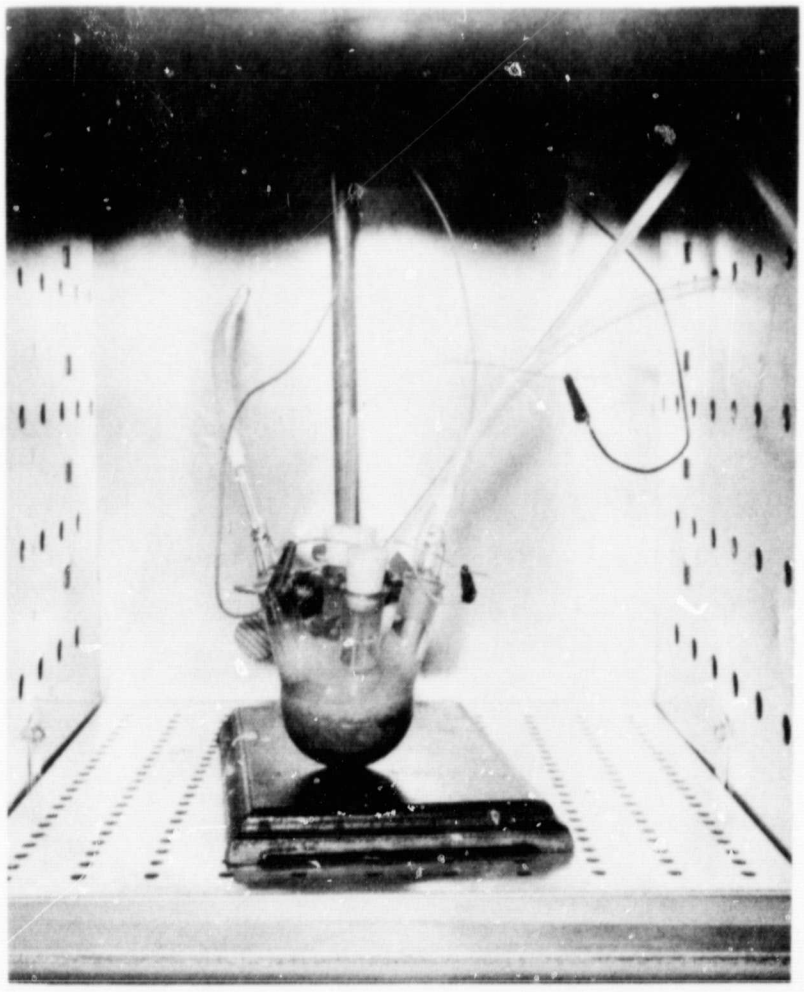

Fig. 3 Photograph showing experimental cell in oven.

supplying a constant current from a power supply and recording the overpotential on either an oscilloscope or on the X-Y recorder.

It has been established[19, 20] that an Al electrode is a stable reference in this ternary eutectic and all potentials are referred to this electrode. A coil of pure Al wire, contained in a fritted compartment to prevent concentration changes taking place in the vicinity of the electrode, formed the reference. A similar coil of Al wire served as the counter electrode. A Pt needle microelectrode was used for recording background i-v curves. This electrode was made in the usual way be sealing Pt into glass.

Preparation and Purification of $AlCl_3$-NaCl-KCl Eutectic Melt

All experimental work has been carried out with the ternary $AlCl_3$-NaCl-KCl eutectic mixture with a composition of 66 mole % $AlCl_3$, 14 mole % KCl and 20 mole % NaCl. The melting point of this eutectic is 70°C; the experiments were carried out at 120°C. "Baker Analyzed" NaCl and KCl was used to make up the eutectic, but $AlCl_3$ from a number of suppliers was tried. The salts were weighed out in the correct proportions, well-mixed and fused in a purge-type dry box. The molten eutectic was poured into the electrochemical cell and allowed to solidify before being removed from the dry box.

Initially, "Baker Analyzed" anhydrous $AlCl_3$ was used. This was certified ad being 99% pure. When the salt was mixed and heated on a hot plate in a dry box, a greyish-brown melt was readily formed. Other investigators[21] have also observed this coloration and attribute it to carbonaceous material and the presence of $FeCl_3$ impurity in the $AlCl_3$. Filtration of the molten eutectic through a fine (25 micron) glass frit did not appear to change the color at all but did remove some particulate matter.

Cyclic scans at a Pt wire microelectrode were run in order to observe the background current and obtain an indication of the

melt purity. A typical scan is shown in Fig. 4. It can be seen that the anodic decomposition limit was + 2.0 v vs. Al. This limit presumably corresponds to Cl_2 evolution. The reduction wave observed at + 1.0 v vs. Al was suspected to be reduction of ferric ions (see below). It was thought that the addition of powdered Al metal might effect the reduction of ferric ions via the reaction;

$$Al + Fe^{3+} \rightarrow Fe + Al^{3+} .$$

A marked reduction in the background current was indeed observed after addition of Al powder (see Fig. 4), although the color of the melt did not change. Bubbling Cl_2 through the melt had the effect of darkening the color and little improvement in background current resulted.

A batch of high purity $AlCl_3$ (99.999%) was obtained from Koch-Light Laboratories (Great Britain) in the expectation that problems with $FeCl_3$ impurity would be avoided. We experienced considerable difficulty, however, in getting a salt mixture made up with this material to melt. A number of procedures were tried–including heating under reduced pressure, heating in a sealed tube, heating with an excess of $AlCl_3$, and ball-milling the salts–but without success. The problem was due to the fact that $AlCl_3$ was not anhydrous inspite of the supplier's specifications.

Subsequently, experiments were carried out with $AlCl_3$ from Fluka Chemicals (Switzerland) which is supposedly anhydrous as well as iron-free. A ternary mixture made up with this material melts readily on a hot plate and forms a clear melt except for a darkish yellow coloration. A cyclic scan obtained in this melt is shown in Fig. 5. It appears that $FeCl_3$ is still present as an impurity. The deliberate addition of a small amount of $FeCl_3$ resulted in the i-v curve shown in Fig. 6.

The curves of both Figs. 5 and 6 were obtained on Pt electrodes starting at a potential of 1.1 v (vs. Al). From this

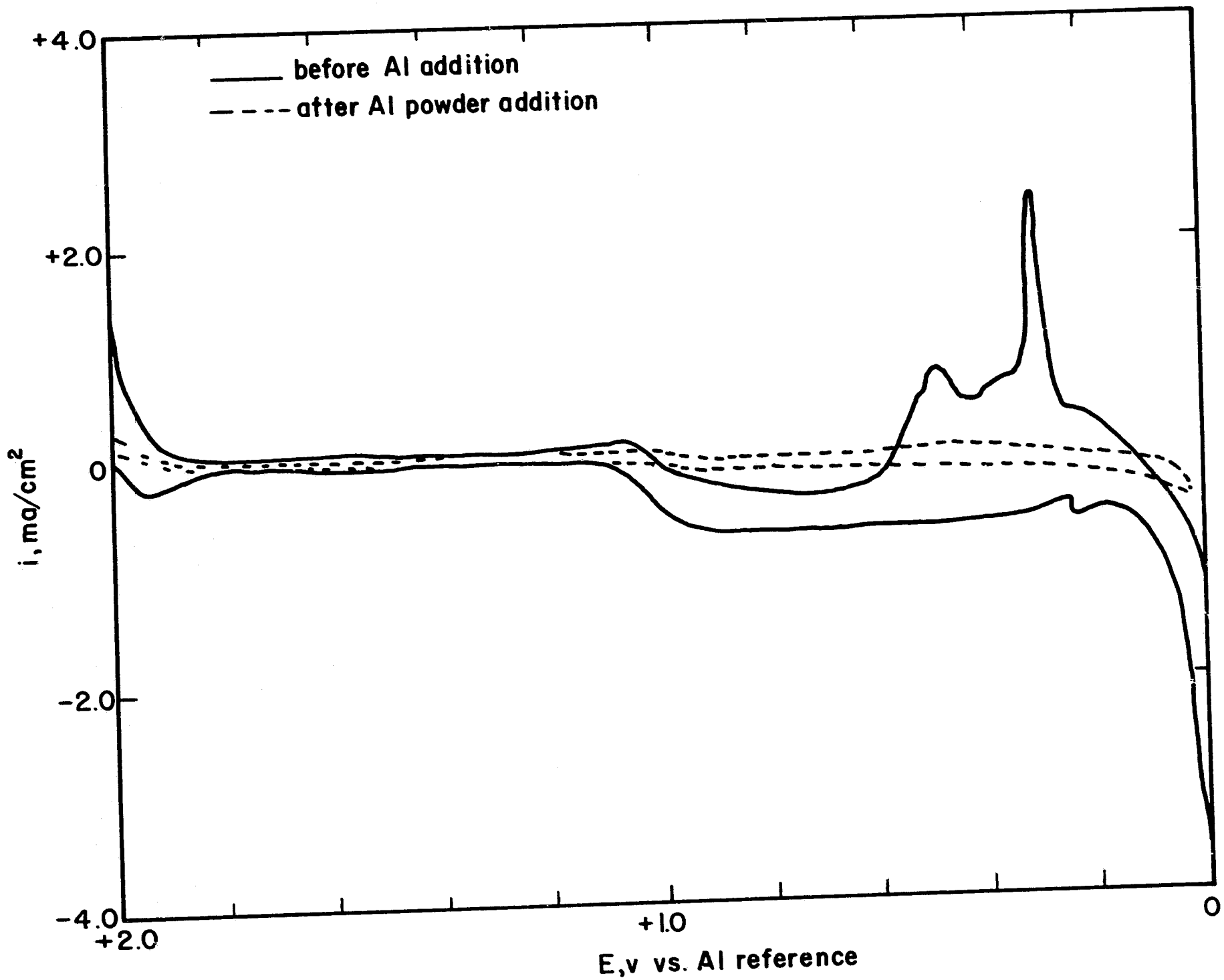

Fig. 4 Background i-v scan at Pt in eutectic melt made up with "Baker Analyzed" $AlCl_3$ (anhydrous 99%). ——— Before Al powder addition; ------ after Al powder addition. Scan rate 40 mv/sec.

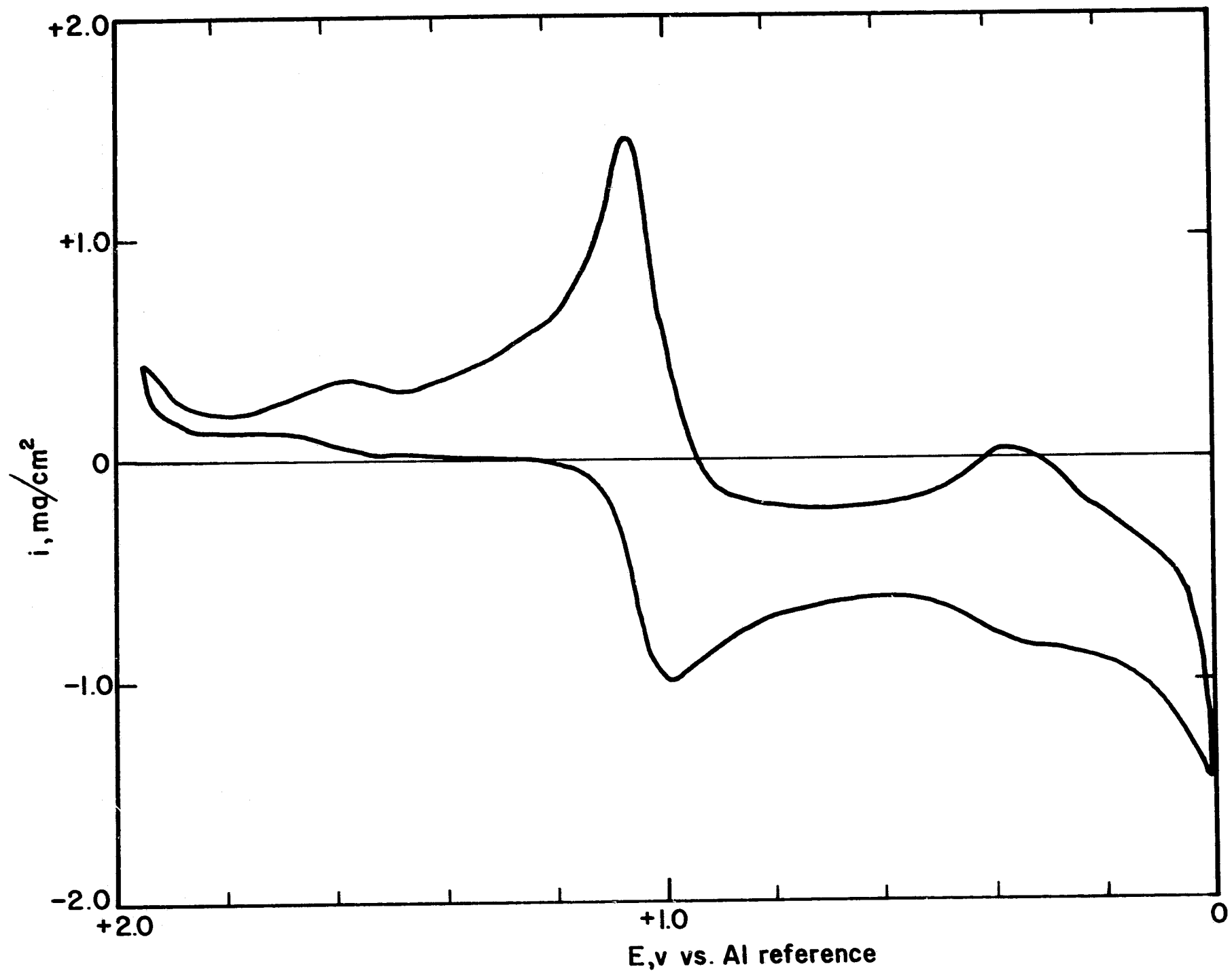

Fig. 5 Background i-v scan at Pt in eutectic melt made up with Fluka $AlCl_3$ (anhydrous and iron "free"). Scan rate 160 mv/sec.

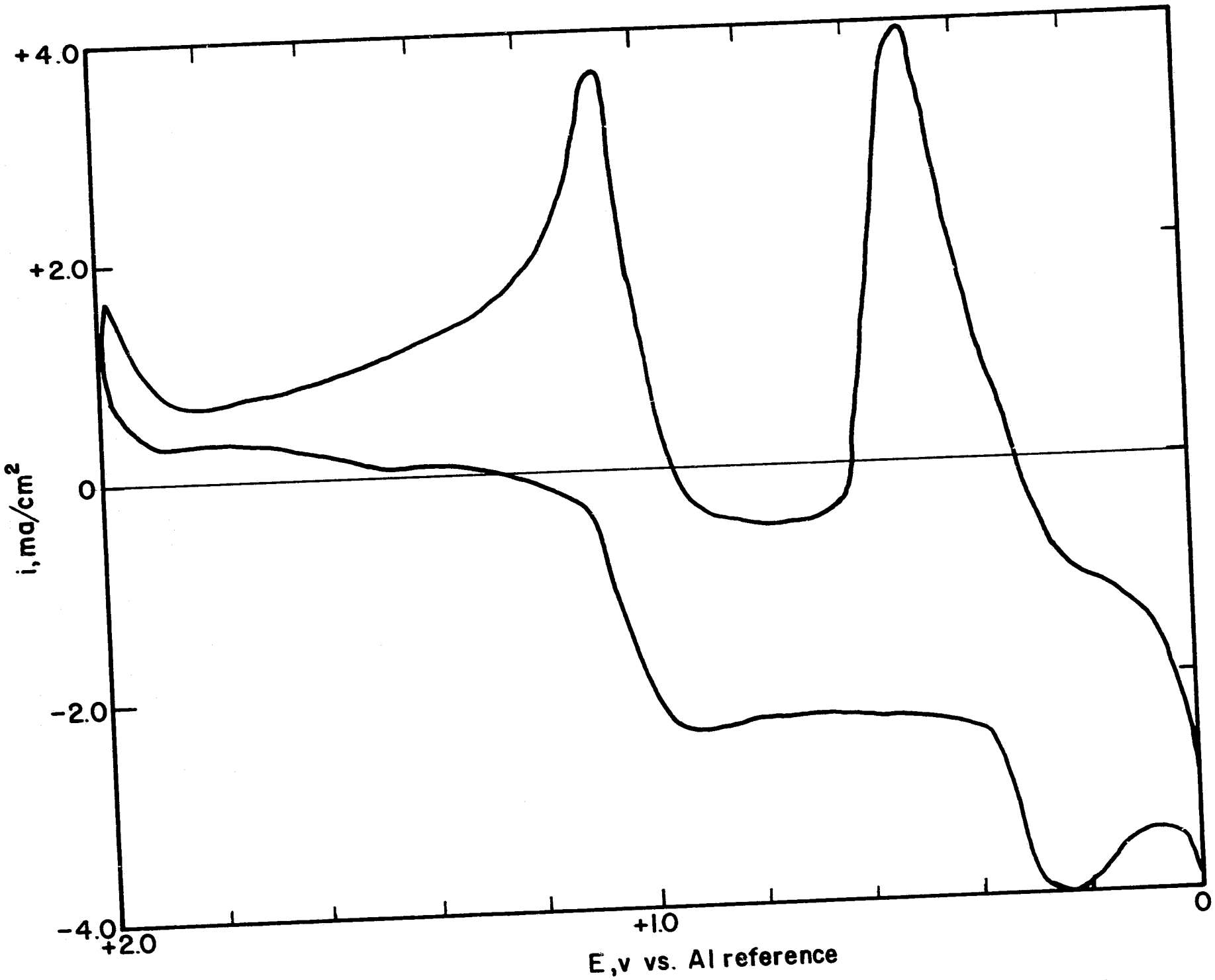

Fig. 6 Effect of a small addition of $FeCl_3$ to the eutectic melt made up with Fluka $AlCl_3$. Scan rate 160 mv / sec.

starting point the potential was linearly decreased to zero, then increased linearly to 2 v, and then decreased again without a waiting time to 1.1 v. The qualitative shape of the curve is the same in both cases. The following characteristics were noted:

(a) A more or less pronounced cathodic current peak was observed at about 1 v, probably due to reduction of Fe^{3+} incorporated in some layer close to the electrode. (This layer can be an adsorption layer or a still undeveloped diffusion layer.)

(b) Cathodic limiting current at more negative potential appears to correspond to the steady state reduction of Fe^{3+} to Fe^{2+}.

(c) A cathodic peak at about 200 mv seems to correspond to the reduction of Fe^{3+} (and Fe^{2+}) to Fe.

(d) An anodic peak at about 500 mv apparently corresponds to oxidation of Fe to Fe^{2+}. The current drop after the peak can be attributed to depletion of Fe or, more probably, to some passivation.

(e) After this passivation a relative cathodic current is observed that can be attributed to reduction of Fe^{3+}.

(f) Finally, the anodic peak at 1.1 v can be interpreted as being due to oxidation of the passive film (Fe^{2+} - salt ?) formed at 500 mv and of the underlying Fe. Any dissolved Fe^{2+} is oxidized to Fe^{3+} at potentials higher than 1.2 v.

From the comparison of Figs. 5 and 6 it seems reasonable to identify the major impurity present in $AlCl_3$ as Fe.

The presence of the $FeCl_3$ should not affect the behavior of the Cl_2 electrode in any way; thus, we can investigate this electrode in the impure melt. However, the reduction of the Fe (III) species will probably have a deleterious effect on the performance of the Al electrode. Before meaningful data on the Al electrode can be obtained, it will be necessary to purify the $AlCl_3$ by sublimation so as to remove the $FeCl_3$ impurity, unless treatment of the melt with Al powder is sufficient.

Although the cell was operated in the atmosphere (closed and under an Ar blanket), some moisture was undoubtedly admitted during transfers and during replacement of electrodes. To determine qualitatively how serious the effect of moisture could be, humidified argon was bubbled through the melt for a short period. It was observed that clouds of HCl gas were formed and a thin white deposit was left on the upper parts of the cell. No precipitate could be observed to form in the electrolyte. According to Letisse and Tremillon[25] the reaction between H_2O and the equimolar $NaCl$-$AlCl_3$ melt is as follows

$$2\,AlCl_4^- + H_2O \rightarrow 2\,HCl + Al_2OCl_5^- + Cl^-$$

It is presumed that a similar, if not identical, reaction occurs in the ternary eutectic.

Al Electrode

A preliminary investigation of the polarization behavior of an Al electrode (40 mil diam., 99.999%) in the ternary $AlCl_3$-NaCl-KCl eutectic has been carried out. A polarization curve is shown in Fig. 7. It can be seen that in the current density range of + 400 ma cm^{-2} to - 200 ma cm^{-2} a linear polarization curve was obtained.

The overpotential values were determined galvanostatically and represent the instantaneous overvoltage (at times shorter than microseconds). Thus, the plotted polarization is the ohmic polarization; (the high value of this polarization does reflect in part the large separation between working and reference electrodes). The galvanostatically determined overvoltage remained constant for several milliseconds, indicating no activation polarization. After a certain transition time which according to the used current density varied from minutes to milliseconds, a fast rise of polarization was observed. Such polarization increases at long waiting

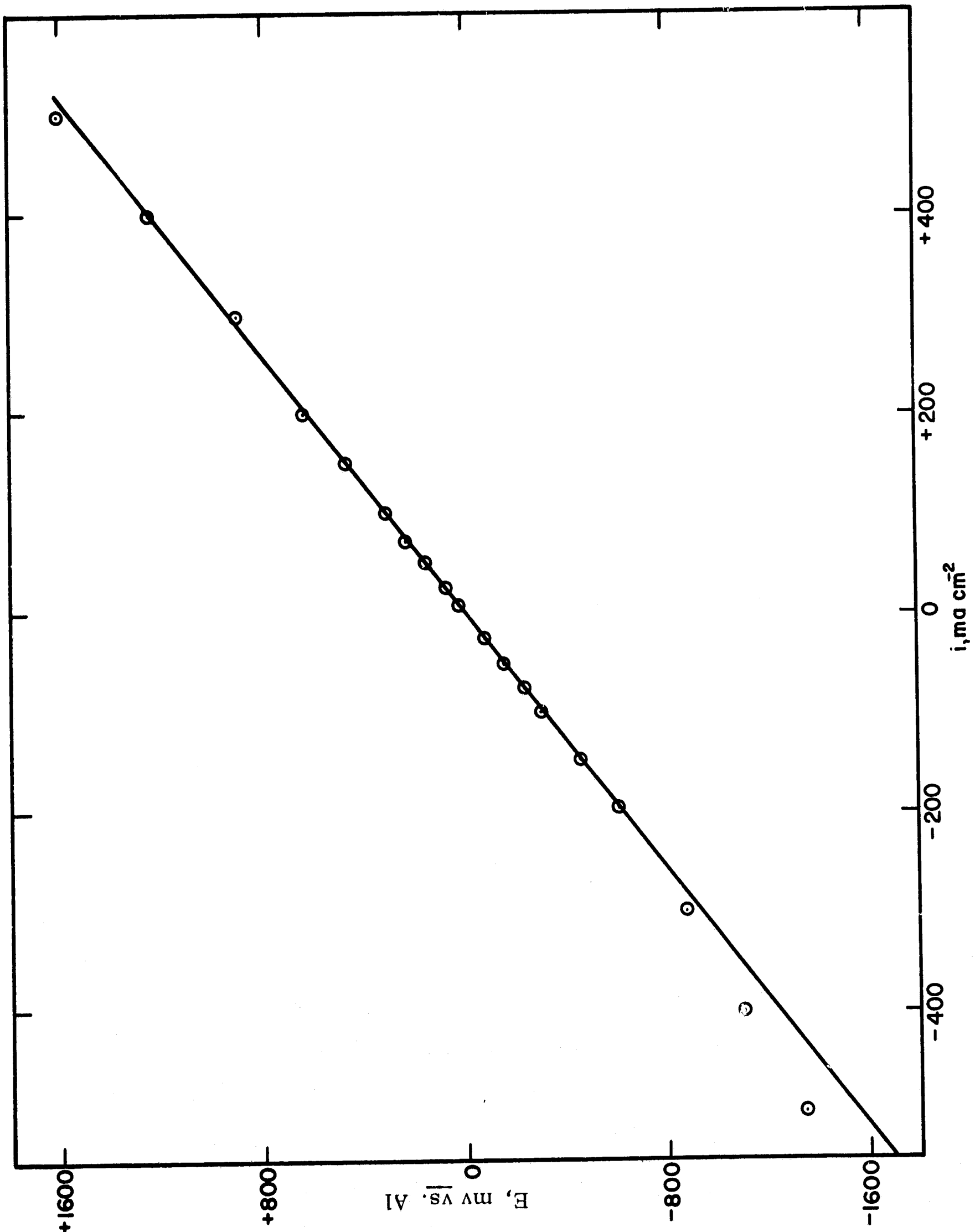

Fig. 7 Galvanostatic polarization curve for an Al electrode in the ternary eutectic melt.

times were also observed by Piontellii and co-workers[22].

These polarization increases are reflected as passivation peaks in potential-current curves. Thus a slow voltammetric scan (100 mv min^{-1}) at an Al electrode revealed apparent passivation peaks when the electrode was polarized from the open circuit potential in either the anodic or the cathodic direction; (see Fig. 8 which is a composite of two scans). The anodic peak was barely observable on a freshly immersed Al electrode, but it became larger with increasing time of immersion. Pre-cathodization accelerated this increase of anodic peak height. The behavior suggests that the size of the anodic peak is related to the extent to which the surface is covered with some removable surface film. presumably an oxide film present on the surface before immersion.

The magnitude of the peaks depends, as mentioned, on the electrode pretreatment, but current densities higher than 50 ma/cm^2 for reasonable times are observed both for the charge and discharge of the Al-electrode. This indicates that the Al-electrode may be suitable for charge and discharge at high rates.

The most likely explanation for the occurrence of the anodic peak would appear to be a saturation effect. As the Al electrode is anodized, Al^{3+} ions are discharged. These ions rapidly complex to form $AlCl_4^-$ anions[23]. The local concentration of these species would, in a quiescent solution build up to such an extent that a saturated condition could result in the vicinity of the electrode surface. Phase diagram considerations would then force the precipitation of $NaAlCl_4$ or $KAlCl_4$ on or near the electrode surface, resulting in an effective passivation of the electrode. An alternative explanation in terms of oxide formation associated with impurities in the melt does not appear likely in view of the observation already mentioned, that the anodic peak increases with time of immersion.

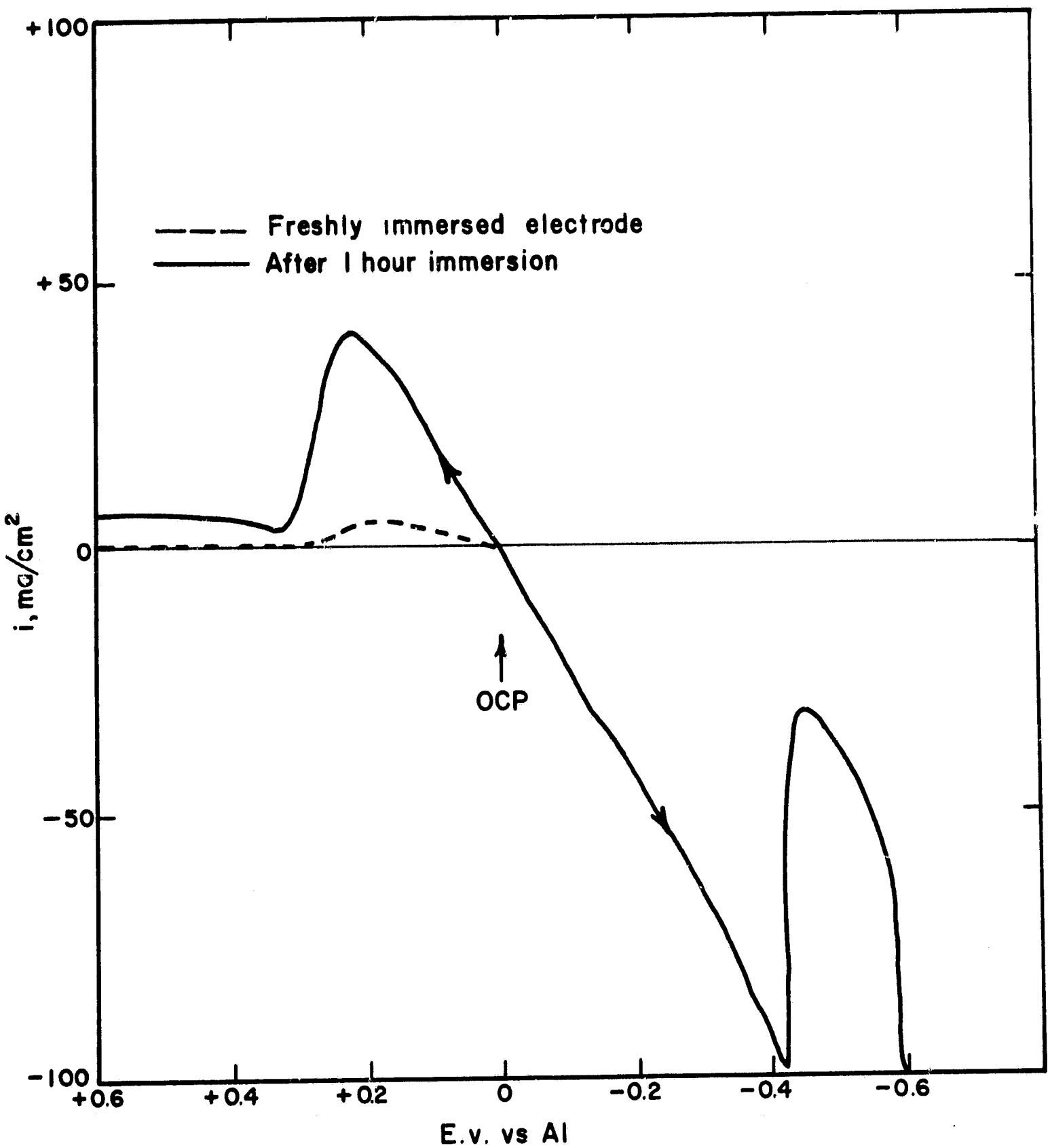

Fig. 8 Slow voltammetric scan (100 mv/min) at Al electrode in the ternary eutectic melt. The curve is composite being made up from separate positive -going and negative -going scans.

The explanation for the cathodic peak is not apparent at this time, unless it is related to the presence of $FeCl_3$ impurity. Both the anodic and cathodic polarization phenomena will be investigated in more detail in the next quarter. A rotating electrode assembly is being designed that will allow investigation of the Al electrode behavior under controlled diffusion conditions and consequently enable an analysis of the polarization behavior with some certainity. Furthermore, as already mentioned, special effort will be made to purify the $AlCl_3$ before investigating the Al electrode in detail.

Cl_2 Electrode

Graphite used as a substrate for the Cl_2 electrode was obtained from Speer Carbon Products (grade 37-G electrographite). Electrodes 3/8" in diameter by 5" in length with an internal gas entry were machined from a block of this material. Experiment revealed, however, that the electrolyte wet the porous graphite quite readily and in a short period of time considerable swelling of the electrode in contact with the melt was noticed. (see Fig. 9). Upon removing the electrode from the melt it was apparent that the graphite had lost its structural integrity. This behavior is in contrast to that observed by Swinkels[24] where the same graphite electrode was not wet by molten LiCl at 650°C. As a result of this absorption of electrolyte into the electrode, it was not possible to obtain reliable data.

Disintegration of the graphite is presumably a consequence of interplanar reactions with the formation of intercalation compounds. This problem can probably be avoided by the use of carbon or moulded graphite-carbon electrodes, which have a more amorphous structure. The graphite used to date has a total porosity of 0.273 cc/gm and a density of 1.35 gm/cc (Speer Carbon Products data). In the next quarter we plan to investigate

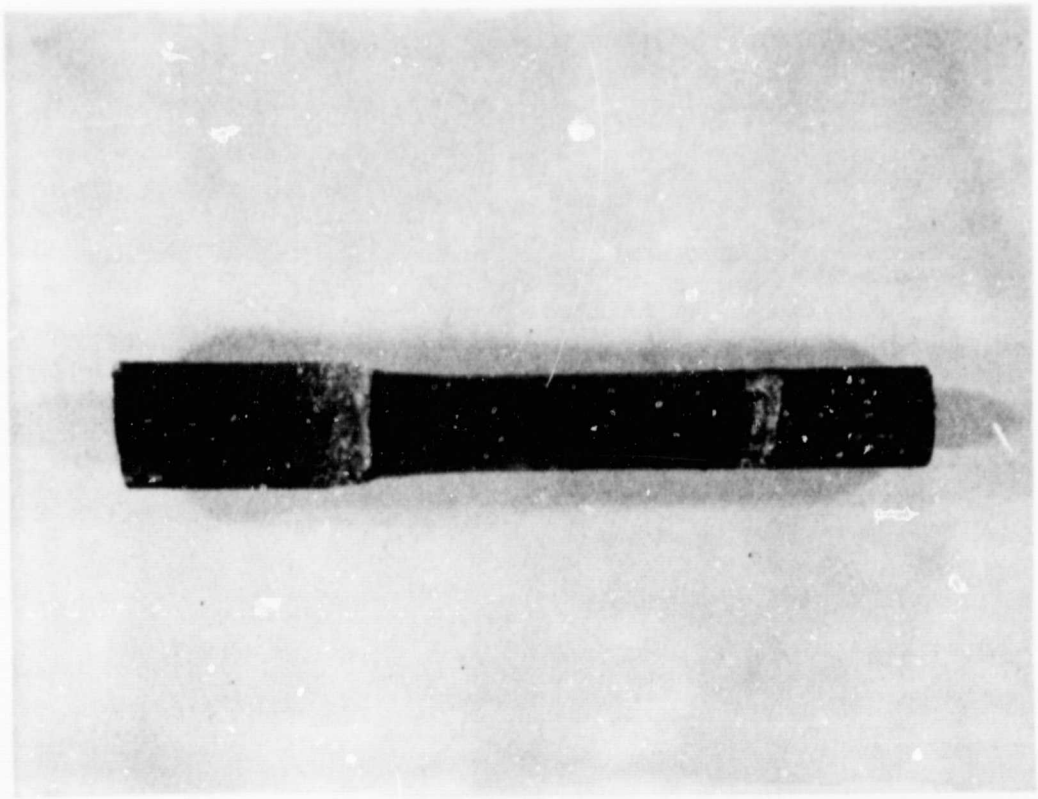

Fig. 9 Photograph of graphite electrode after immersion in the melt for 2 hours. Graphite was Grade 37-G (Speer Carbon Products), density 1.35 gm/cc, total porosity 0.273 cc/gm.

carbon and carbon-graphite of lower average pore size but with both higher and lower porosities in the expectation that a reduced amount of wetting and subsequent absorption of electrolyte will result. We also expect that a lower and more uniform pore size will make it easier to control the position of the three-phase boundary by adjustment of the Cl_2 gas back pressure.

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