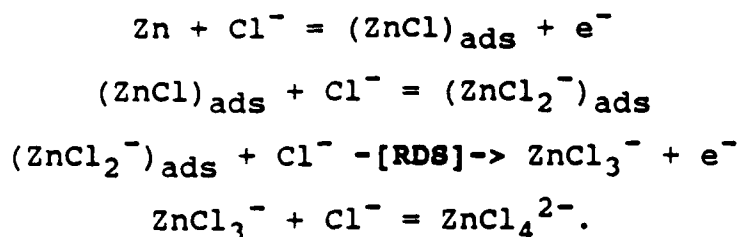


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(activation) process were surface redox reactions which did not interact with solution entities. A mechanism consistent with these data (i.e., one with nine or more individual steps) is essentially unattainable for these melts.

A detailed kinetics analysis of the dissolution of zinc in basic binary and ternary (i.e., added ZnCl_2) MEIC- AlCl_3 was carried out. The reaction order of chloride was 3 while the reaction orders of AlCl_4^- and ZnCl_4^{2-} were zero. These data were consistent with the following atomistic steps:



Since the zinc electrode was not reversible in these melts, a full kinetics analysis was not possible.

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FINAL REPORT

**Metal/Metallion
System In Low
Temperature
Molten Salts**

Grant No. AFOSR-88-0079

Francis M. Donahue

Leif Simonsen
Russell Moy
Sarah Mancini

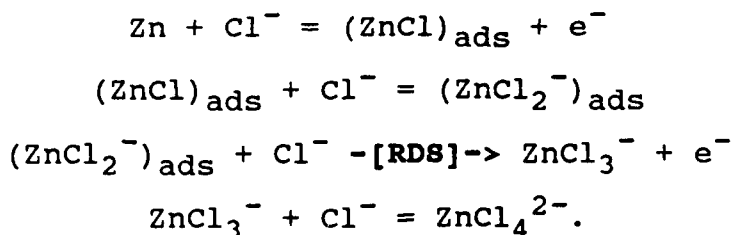
Chemical Engineering Department
The University of Michigan
Ann Arbor, MI 48109-2136

April 1989

ABSTRACT

Potential arrests on open circuit following passivation of aluminum electrodes and cathodic stripping immediately following passivation were studied in acidic low temperature molten salt solutions (1-methyl-3-ethylimidazolium chloride, MEIC, and aluminum chloride binaries). A model of 'classes' of charge transfer processes which could be responsible for the processes occurring during open circuit decay and cathodic stripping were proposed. Comparison of the arrest potentials (which correlated reasonably with the potentials associated with maximum current densities during stripping) with melt composition indicated that the electrochemical processes responsible for the passivation and depassivation (activation) process were surface redox reactions which did not interact with solution entities. A mechanism consistent with these data (i.e., one with nine or more individual steps) is essentially unattainable for these melts.

A detailed kinetics analysis of the dissolution of zinc in basic binary and ternary (i.e., added ZnCl_2) MEIC- AlCl_3 was carried out. The reaction order of chloride was 3 while the reaction orders of AlCl_4^- and ZnCl_4^{2-} were zero. These data were consistent with the following atomistic steps:



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INTRODUCTION

This report has been divided into two sections, representing the completion of the studies initiated under Grant No. AFOSR-85-0027. Specifically they involve kinetics analyses of aluminum passivation in binary acidic low temperature molten salts and the dissolution kinetics of zinc in basic binaries and ternaries.

1. MECHANISM OF ALUMINUM PASSIVATION.^a

The potential of anodically passivated aluminum rotating cylinder electrodes decayed on open circuit through two repeatable potential arrests. It is likely that these well defined potentials are established by three redox reactions. Aluminum ions usually have a valence of three and elementary steps of an electrochemical mechanism rarely involve the transfer of more than one electron, so it is conceivable that each of these potentials represents one of the electron transfers. An electrochemical mechanism to describe aluminum electrochemistry in chloroaluminate electrolytes must therefore include subvalent aluminum intermediates. However, in the absence of analytical data for dissolved sub(tri)valent aluminum in these melts, it must be assumed that the intermediate species are adsorbed on the surface.

Experimental Results

An aluminum rotating cylinder electrode was passivated by the application of a 700 mV potential step for 100 seconds in an acidic chloroaluminate molten salt. The initial current response for this electrode shows the familiar current peak which verifies the passivation (Figure 1.1). The potential of the electrode was then scanned cathodically to determine the electrochemical properties of the film. The peaks in Figure 1.2 showed that the passive films on aluminum are electrochemically reduced through two processes. The peak areas were integrated to determine the total stripping charge. Figure 1.3 shows that this charge increased with subsequent experiments, and was independent of the stripping rate between 5 and 25 mV/s.

^a For details of the experimental data, see Final Report, AFOSR-85-0027, 1988, by the current authors.

The stripping peak potentials were not as repeatable as the potential arrests described previously (1), although the potentials of the peaks were consistent with the potentials for the arrests. There are other similarities between the open circuit decomposition and electrochemical reduction of the passive film. In both cases, the predominant transition occurred at the lower potential. Also, stripping charge and the open circuit decomposition times increased with sequential experiments - both of which indicate that the amount of film increases with sequential experiments. The correspondence between the data for cathodic stripping and potential arrests is strong evidence that the film is also being reduced during the open circuit decomposition.

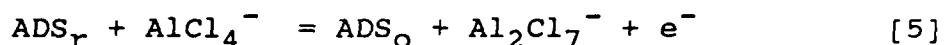
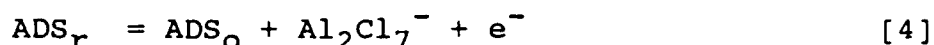
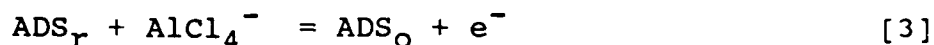
Discussion

The reversible aluminum electrode reaction in acidic melts is



On the premises that the individual steps in the reaction mechanism involve a single electron and no more than two molecular entities, the reaction given above requires at least seven steps (one for each AlCl_4^-). In addition, in the absence of evidence for soluble sub(tri)valent aluminum species, all of the intermediate steps will involve adsorbed aluminum species. The only 'permissible' solution species are AlCl_4^- and Al_2Cl_7^- .

Four 'classes' of electrochemical (i.e., charge transfer) reaction steps can be postulated for this reaction sequence. Simply stated, these steps include no dissolved species, just AlCl_4^- , just Al_2Cl_7^- , and both AlCl_4^- and Al_2Cl_7^- , i.e.,



where ADS_r and ADS_o represent the reduced and oxidized forms of the adsorbed aluminum intermediate in the redox step. On the premise that these are the only charge transfer processes which are possible in aluminum passivation, one will be able to infer the 'class' of reaction occurring at the potential arrests by observing the dependence of the arrest potential on melt composition. For example, the observed potentials for steps like [2] will be independent of melt composition while the observed potentials for steps like [4] will increase with increasing acidity of the melt. Figure 1.4 shows that the upper (associated with the II/III equilibrium) and lower (associated with the I/II equilibrium) plateau potentials were essentially independent of electrolyte composition - indicating that the respective charge transfer processes are 'class' [1] reaction types. This result indicates that the mechanism involves in excess of nine different steps - a practical impossibility to analyze with techniques and information currently available with respect to these low temperature molten salts.

REFERENCES

1. F. M. Donahue, L. Simonsen, R. Moy, and S. E. Borns. Final Report, Grant No. AFOSR-85-0027, 1988.

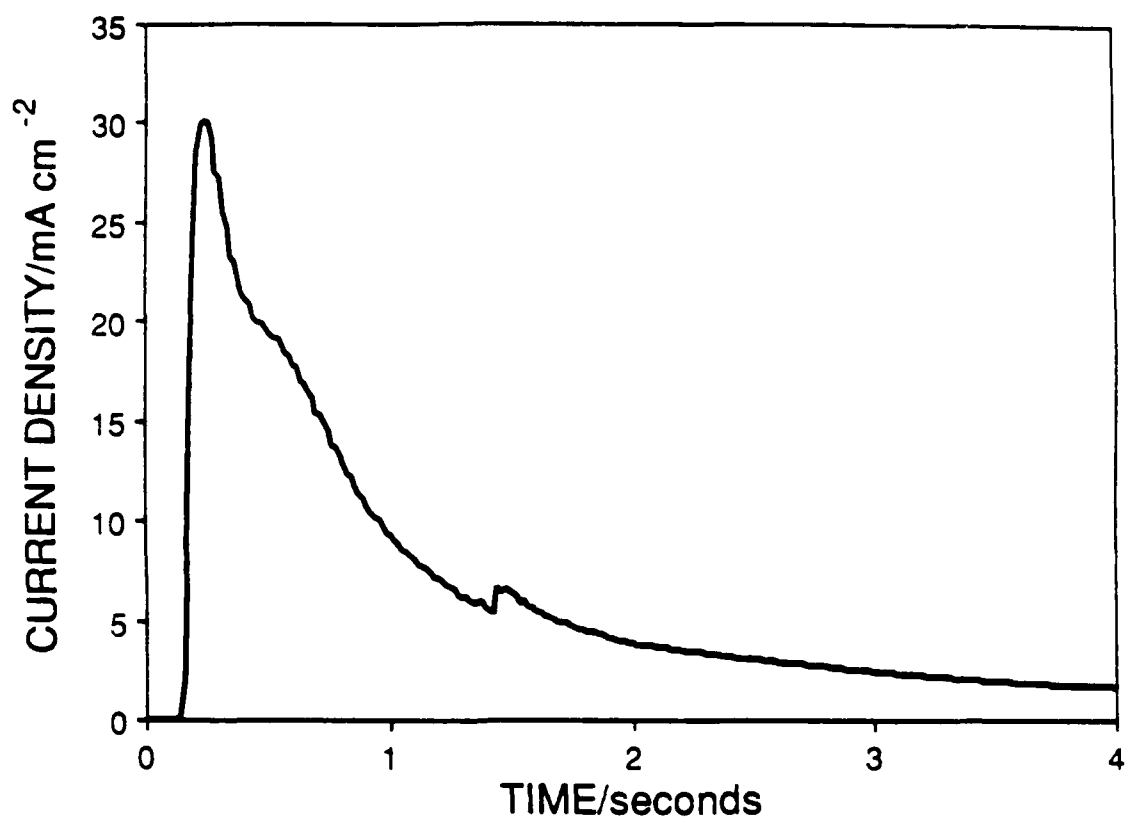


Figure 1.1. Current - Time Transient for Aluminum Passivation at 700 mV (vs. X = 0.505 reference electrode). Melt composition is X = 0.635 and the cylinder rotation rate = 1000 rpm.

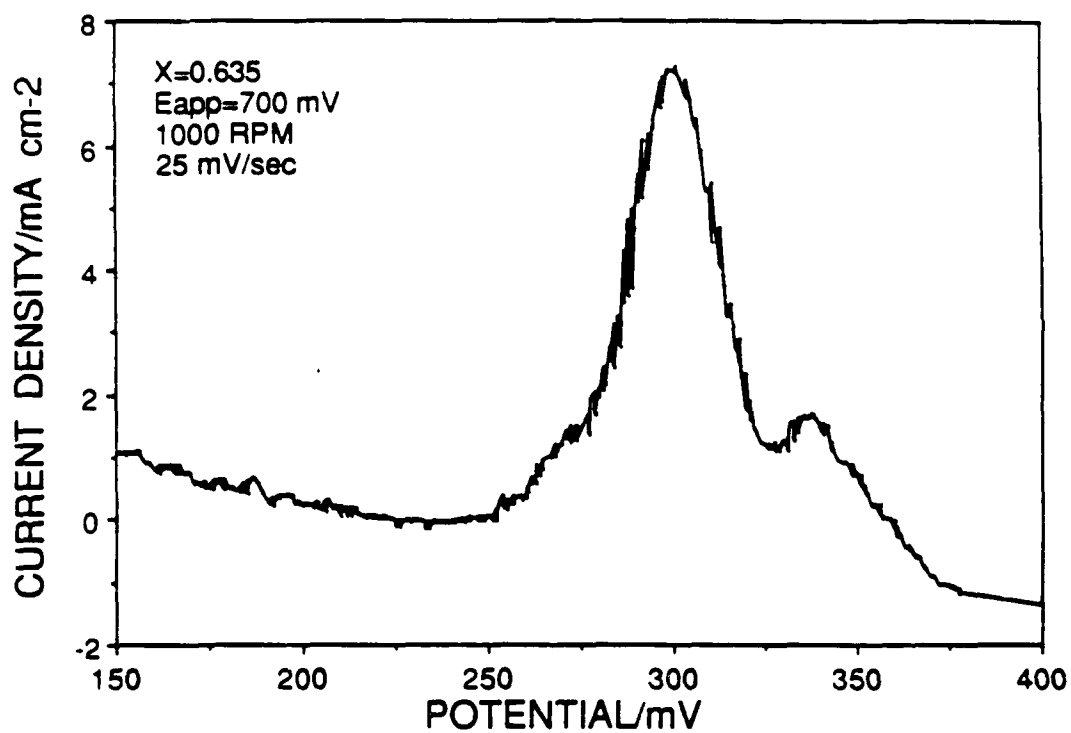


Figure 1.2. Cathodic Stripping of Passive Film.

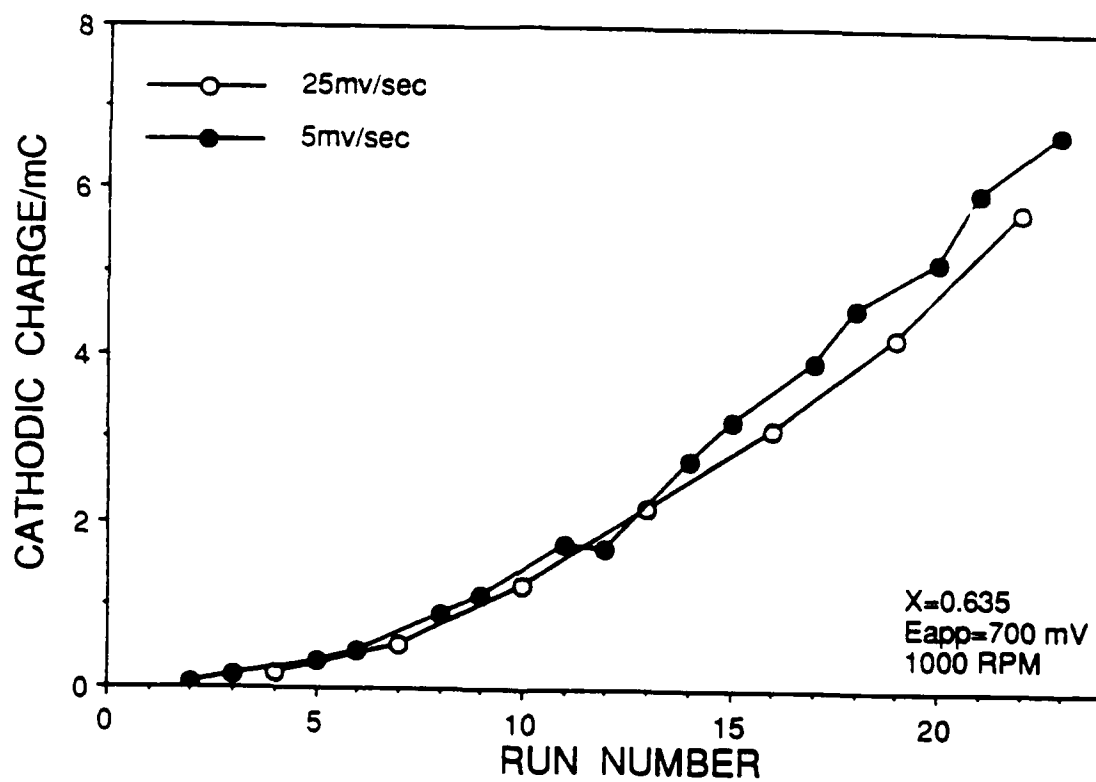


Figure 1.3. Charge Required to Strip the Passive Film as a Function of Run Number.

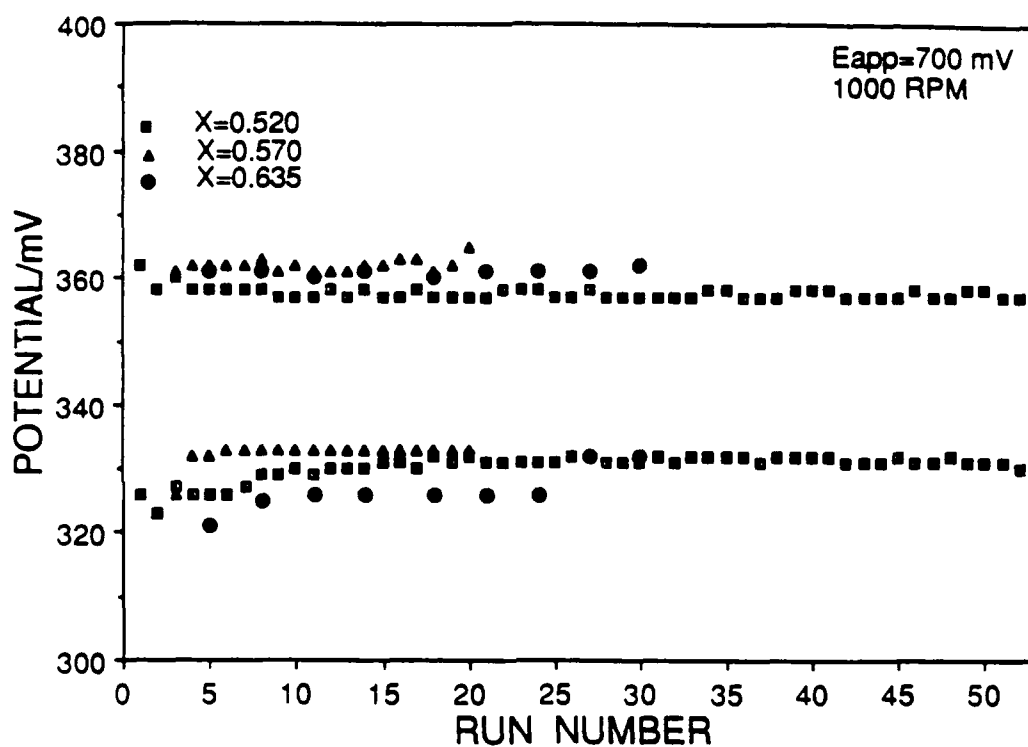


Figure 1.4. Arrest Potentials as Functions of Melt Composition and Run Number.

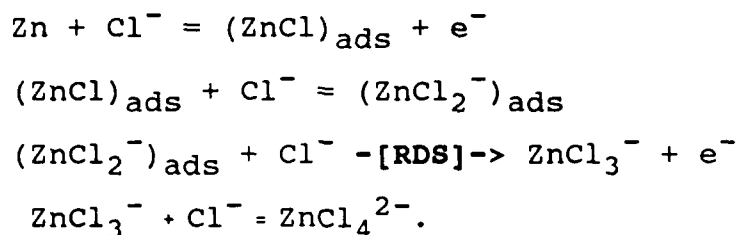
2. ZINC ELECTRODEKINETICS IN LOW TEMPERATURE MOLTEN SALTS.

Polarization curves from 0 to +200 mV overpotential were determined for each of the compositions studied (see Table 2.1) by sweeping the potential at the rate of 0.2 mV/s while the cylindrical electrode was rotated at 2000 rpm and the electrolyte temperature was 25°C (for other experimental details, see Reference 1). From these plots, Tafel slopes (base 10) and exchange current densities were determined using a 'Tafel Line Curve-fitting Program' developed in this laboratory (2). A sample polarization curve is shown in Figure 2.1. The narrow region of Tafel behavior is consistent with that found for zinc in aqueous solutions (3). Values of the Tafel slopes and exchange current densities for all compositions studied are included in Table 2.1. The anodic Tafel slope was found to be 40 mV, independent of melt composition. The estimated exchange current densities had an average value of 0.14 mA/cm^2 - independent of melt composition.

The reaction orders of the species involved in the anodic partial process were determined by appropriate substitution of perturbed current density as a function of the concentration of the species of interest at a fixed electrode potential. The reaction order of chloride ion was found to be 3 [experimentally, 2.9] while the orders for the aluminum and zinc chloroanions were found to be 0 [experi-

mentally, 0.09 and -0.08, respectively]. A plot of the data used in the determination of the chloride ion reaction order is shown in Figure 2.2. Further, the absence of composition dependence on the exchange current density suggests that the electrochemical reaction orders of these species is zero.

These data are consistent with the following proposed anodic reaction mechanism



This mechanism is analogous to that found for zinc dissolution in aqueous solution (substituting hydroxide ions for the chloride ions, of course) (3) and is consistent with data obtained previously for the transport controlled dissolution of zinc (1,4). Since the zinc electrode was not found to be reversible in these melts, it is not possible to fully verify the proposed mechanism.

Table 2.1. Kinetics Parameters for Zinc Dissolution in Binary and Ternary Low Temperature Molten Salts

Binary Mole Fraction AlCl_3	Third Component (mM ZnCl_2)	Tafel Slope/mV	Exchange Current Density/ mA/cm^2
0.350	0	40	0.09
0.350	0	40	0.06
0.350	0	40	0.07
0.375	0	41	0.14
0.375	0	38	0.11
0.400	0	41	0.17
0.400	0	41	0.18
0.400	0	40	0.18
0.400	0	36	0.08
0.400	0	39	0.08
0.400	50	41	0.10
0.400	100	41	0.10
0.400	100	40	0.15
0.400	200	41	0.12
0.400	200	41	0.16
0.400	300	42	0.14
0.400	300	43	0.15
0.425	0	39	0.19
0.425	0	39	0.20
0.450	0	42	0.18
0.450	0	42	0.20

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1. F. M. Donahue, L. Simonsen, R. Moy, and S. E. Borns. Final Report, Grant No. AFOSR-85-0027, 1988.
2. D. M. Donahue and F. M. Donahue. Unpublished results.
3. J. O'M. Bockris, Z. Nagy, and A. Damjanovic. J. **Electrochem. Soc.**, 119, 285 (1972).
4. L. R. Simonsen and F. M. Donahue. Accepted for Publication, **Electrochimica Acta**.

ZINC DISSOLUTION

X=0.375 mol% 2000 RPM 25C

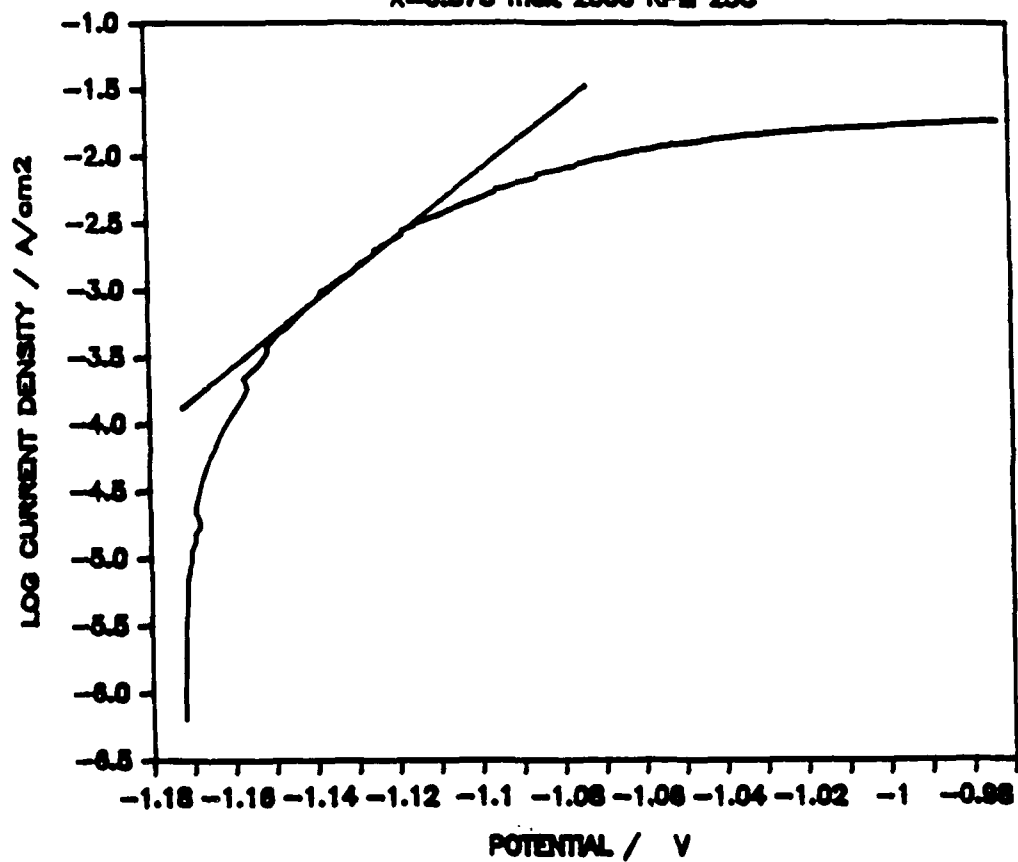


Figure 2.1. Sample Anodic Polarization Curve for Zinc Dissolution in Low Temperature Molten Salts.

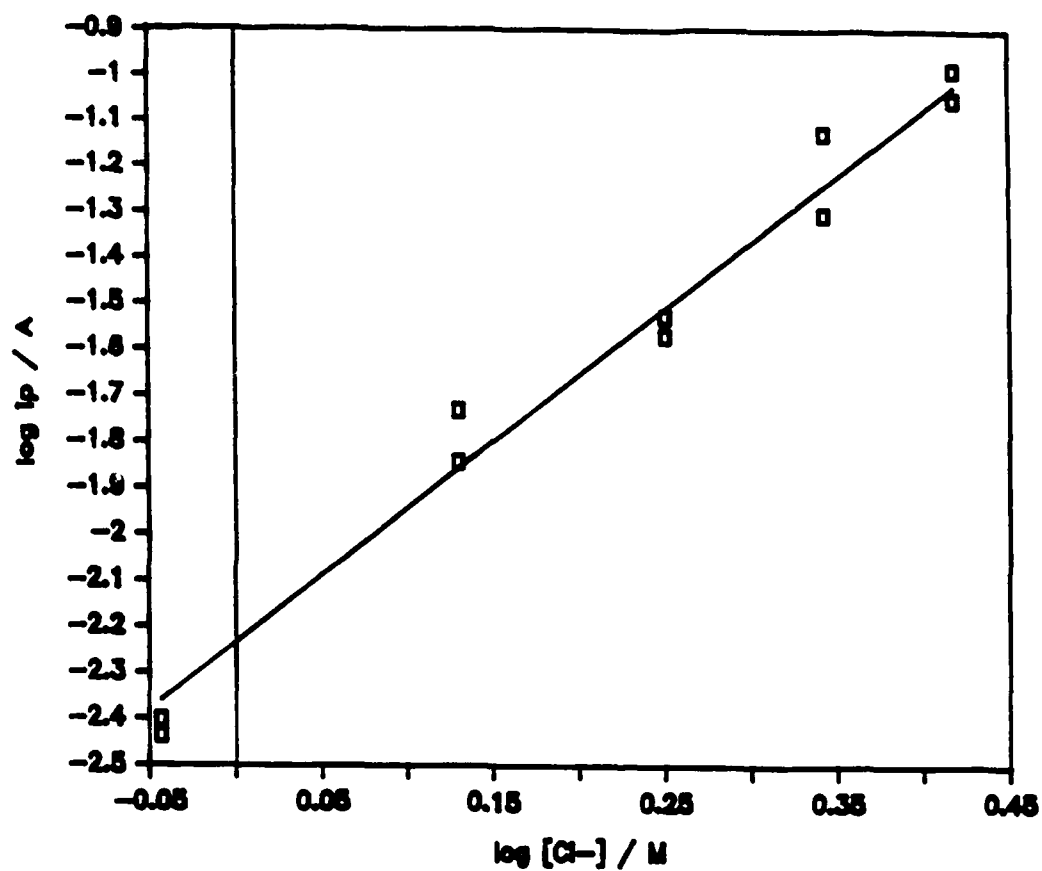


Figure 2.2. Plot Used to Determine the Anodic Reaction Order for Chloride Ion in the Electrodisolution of Zinc in Low Temperature Molten Salts.