

POLAROGRAPHY IN MOLTEN SALTS

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In view of the several comprehensive reviews that have appeared on polarography in molten salt solvents in recent years¹⁻⁴, it seems appropriate to consider this subject in relation to techniques in aqueous and non-aqueous solvents, and in relation to other electroanalytical techniques in molten salts. No attempt will be made at comprehensive coverage.

TYPES OF MELTS

From the practical viewpoint, melts may be classified according to melting points which may limit the available techniques. The lowest melting, with working temperatures up to 250°, are typified by the LiNO₃-NaNO₃-KNO₃ eutectic, NaNO₃-KNO₃ eutectic, LiClO₄, and ammonium formate. With these solvents it is possible to use the dropping mercury electrode, or hanging mercury drop electrode, or various solid microelectrodes such as are commonly used in aqueous or non-aqueous solvents at room temperature.

At temperatures above 250°, the vapour pressure of mercury becomes large enough to prohibit the convenient use of mercury electrodes. A relatively large range of working temperatures is accessible to solid microelectrodes insulated by glass or quartz.

For temperatures up to 550° we have used platinum sealed in a special glass having the thermal properties of lead glass but lacking the reducible lead ion⁵. Using fine gauge platinum wire sealed in Jena Supremax glass, Stromatt⁶ was able to work in NaCl-KCl melts at 716°. Tungsten or molybdenum wires sealed into quartz permit work up to about 1000°. A limitation to the use of these metals, however, is imposed by their being attacked by moderately strong oxidizing species, such as UO₂²⁺.

A special situation is encountered when an insulation of glass or quartz is prohibited by the corrosive nature of the melt, as with carbonates, hydroxides, or fluorides. Manning⁷ has used boron nitride as an insulator, but it is difficult to avoid creepage of melt between electrode and insulator. Saito, Suzuki and Goto⁸ have used a graphite sheath around the "dipping" type of molybdenum electrode, supporting the graphite out of electrical contact with the electrode. Other electroanalytical techniques, notably potentiometry, coulometry and chronopotentiometry, have been carried out without using an insulating seal by bringing the electrode directly through the solution-gas interface⁹. Such techniques should also be valuable in extending the useful temperature range of electroanalytical measurements in less corrosive melts.

Chemically, a more fundamental classification of melts can be based upon the acid-base characteristics of the melt, using the Lewis definitions of acids

as electron-pair acceptors and bases as electron-pair donors. On this basis, alkali metal nitrates, perchlorates and sulphates would be very weakly acidic and basic, possessing neither donor nor acceptor properties to an appreciable degree. Alkali metal hydroxides, carbonates, and halides possess predominantly basic properties, whereas bisulphates, pyrosulphates and metaphosphates are predominantly acidic in character. Likewise, melts containing covalent halides, such as AlCl_3 , are predominantly acidic.

As polarographic solvents, alkali metal halides are especially interesting because they act as weakly basic solvents, forming anionic halide complexes with heavy metal cations, and serving as a supporting electrolyte of high conductivity and large decomposition potential. Lithium chloride-potassium chloride eutectic is especially attractive because of its low melting point (352°C). The anodic polarization limit is imposed by chlorine evolution at a graphite anode, and by metal dissolution, in general, at metallic anodes. At relatively low temperatures (up to 450°C) the cathodic limit is imposed by deposition of lithium metal. At high temperatures, owing to the vapour pressure of potassium, the deposition of potassium is favoured, while at intermediate temperatures, an alloy is formed. Platinum has a pronounced tendency for alloying with lithium, and for this reason the use of platinum cathodes is limited to potentials below -2.0 V vs the platinum(II)/Pt reference. Tungsten, on the other hand, is not attacked by liquid lithium and can be safely used to the ultimate cathodic limit of lithium-containing melts, if care is taken to avoid contact between silica or silicates and molten lithium, which attacks these materials. Molten sodium is stable to silica, and therefore sodium chloride-potassium chloride (equimolar mixture, m.p. ca. 670°C) is somewhat less limiting, although its high melting point prohibits the use of borosilicate glass.

PURIFICATION OF MELTS

Lithium salts in particular tend to retain traces of moisture very tenaciously, and require careful dehydration because of their tendency to hydrolytic decomposition. For preparing lithium chloride-potassium chloride eutectic, we have used a vacuum-HCl treatment¹⁰ to remove the bulk of the water at low temperatures, raising the temperature gradually to avoid sintering of the moist salt, and fusing in a full atmosphere of dry HCl gas to prevent hydrolytic decomposition. It is our experience that hydroxide very rapidly attacks glass or silica and that once this attack has occurred, it can no longer be reversed by HCl-vacuum treatment. Although anhydrous silicate species do not appear to be electroactive, hydrated species yield cathodic residual currents that are particularly intractable. If Reagent grade LiCl and KCl are used to prepare a eutectic melt, using vacuum-HCl treatment to avoid hydrolytic decomposition during dehydration, it is commonly observed that black, carbonaceous particles, evidently originating from solvents used in the preparation of LiCl, are present. The particles show, upon spectroscopic analysis, traces of ten or twelve heavy metals, probably present as the metals formed by carbon reduction. The carbonaceous particles can readily be oxidized with gaseous oxygen or air, with the result that the heavy metals are put into solution. With certain sources of reagent grade LiCl, we have observed no carbonaceous particles, but instead a purplish coloration due to

an unknown material that shows reducing properties against strong oxidants such as chromate, and also is reducible since it shows excessive residual currents. It is sometimes but not reproducibly removed by oxidation with gaseous oxygen, although it resists the action of chlorine. A simple estimate of total contamination by heavy metals, noble to cadmium, is obtained by an observation of the equilibrium potential of cadmium against cadmium(II) produced by displacement⁵. Similarly, a measurement of the zinc potential is a measure of total metals noble to zinc. Typically, a total concentration of the order of 10^{-3} M may be thus observed. By displacement of heavy metals using magnesium, a convenient purification up to the deposition potential of magnesium(II) can be achieved. If the addition of a small concentration of Mg^{II} is harmful, as in the study of strongly reducing species such as hydride, or in cases where Mg^{II} is a precipitant as in the reduction of chromate(II), pre-electrolysis using a controlled potential to avoid lithium discharge and stirring to permit quantitative deposition, is effective but tedious.

In our experience chlorine treatment, theoretically effective in removing hydroxide or oxide by oxidation to oxygen, has the limitation that residual chlorine is difficult to remove quantitatively. Some hydrogenous species such as hydrated silica escape oxidation. As a result, the residual current levels are typically an order of magnitude higher than with melts purified by the vacuum-HCl method. It is significant that the retention of chlorine seems to become increasingly serious at higher temperatures, in line with the appearance of highly coloured solutions¹². Even the solubilities of inert gases generally increase with temperature¹³.

REFERENCE ELECTRODES

A general review of reference electrodes in molten salts is available¹⁴. For this reason the present discussion will be restricted in scope.

In much of the early work, ill-defined reference electrodes analogous to the mercury pool electrode in aqueous polarography have been used. Thus, electrodes such as platinum, silver, or graphite having a relatively large surface area have been used under conditions such that a definite potential-determining system is not present. Not only is the reference electrode potential poorly reproducible from experiment to experiment, but appreciable and variable polarization can occur due to the passage of a variable current during a single experiment, rendering an uncertainty in the slopes of current-voltage curves¹⁵.

For the low-melting nitrate systems, molten salt analogues of the aqueous calomel or silver-silver chloride electrodes have been used. More often, however, $AgNO_3/Ag$ is used because of its convenient preparation by anodization of silver.

In chloride melts, the chlorine electrode may be regarded as the fundamental reference electrode²¹, in analogy to the hydrogen electrode in water and other protonic solvents. Because of its inconvenience, most practical work is done with electrodes such as Pt^{II}/Pt , which is convenient and reproducible at temperatures below 500° (ref. 20), or $AgCl/Ag$, either using pure silver chloride (m.p. 455°) or a solution of silver chloride in an alkali chloride solvent. Special electrodes involving glass or porcelain as a

conductive junction are useful in applications where no appreciable quantities of current must be passed through the electrode.

DROPPING ELECTRODE TECHNIQUES

The dropping mercury electrode naturally is limited to the lower melting systems, such as nitrate, perchlorate, ammonium formate, etc.^{16, 17}. It might appear reasonable to suppose that dropping electrodes of many liquid metals might be ideal for higher temperature systems. There are, however, some severe limitations. First, in principle, only relatively noble metals of moderate melting points can be considered, in order to have a reasonable range of accessible working potentials. Second, the technical difficulty of maintaining a capillary with reproducible characteristics is particularly severe in molten salt systems. The wetting characteristics of the system metal–molten salt–wall are seldom as favourable as with mercury in aqueous or non-aqueous solutions. With bismuth, its expansion upon freezing would usually break the capillary, so that it was usually necessary to prepare a new electrode for each experiment¹⁸. In practice, only very limited use of dropping electrodes of metals other than mercury has been achieved.

STEADY STATE VOLTAMMETRY

Perhaps the simplest experimental technique for current–voltage measurements is to apply by means of a polarograph a slowly changing potential to a stationary microelectrode, and record the resulting current. If the polarization rate is sufficiently slow, the steady-state current at each potential is determined by diffusion and convection at the electrode surface, independent of polarization rate. Apart from the usual difficulties with such a technique due to disturbances from vibrations and temperature gradients, molten salt work is plagued by problems such as dendritic growths of solid deposits, sensitivity to traces of impurities in the melt, creepage of melt between electrode and insulator, solubilities of metals and alloys in melts, etc.

Nevertheless, once the problems of melt purification, electrode fabrication and reference electrode preparation have been overcome, the voltammetric technique has proved to be of great use as a rapid and convenient orientation to the general electrochemical behaviour of various species in molten salts¹⁹. As an example, the behaviour of chromium(III), added as KCrCl_4 , in LiCl-KCl eutectic is illustrated in *Figure 1*. Two reduction steps are clearly revealed, and the relative heights suggest successive reductions to Cr^{II} and the metal. Formation of dendritic chromium is indicated by the gradual rise of current at the second plateau (but not the first) upon continuous polarization at constant potential. Reverse polarization shows reoxidation of chromium metal at potentials anodic to the second reduction potential, and gives an approximate measure of the reversible potential of the $\text{Cr}^{\text{II}}/\text{Cr}^0$ couple. By anodizing chromium metal using known current and time, a solution of chromium(II) can be prepared. Its current–voltage behaviour (*Figure 1*, Curve 2) shows reduction to Cr^0 and oxidation to Cr^{III} at the potentials expected from the behaviour of Cr^{III} . Thus, even though the

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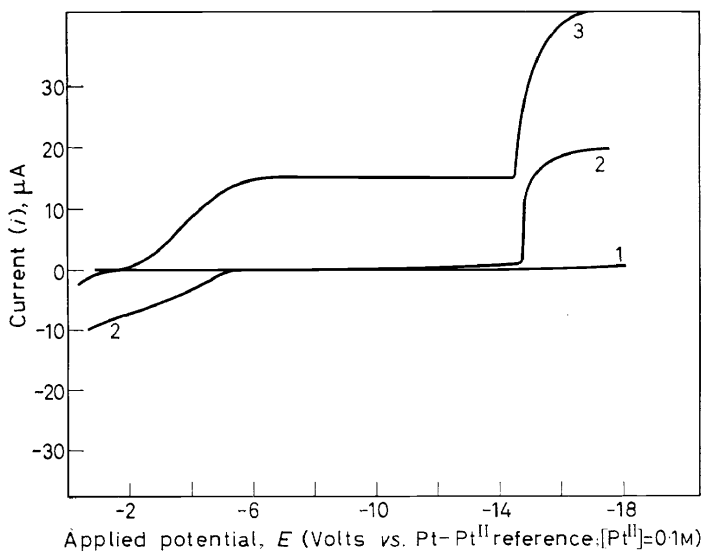


Figure 1. The behaviour of chromium (III), added as KCrCl_4 , in LiCl-KCl eutectic. Platinum microelectrode was maintained at 450°C . (1), Residual current curve. (2), Current-voltage curve of Cr^{II} . (3), Current-voltage curve of Cr^{III} .

steady state currents were relatively poorly reproducible from one experiment to another, the method was of enormous value in orienting further and more exact experimentation. The reversible potential of $\text{Cr}^{\text{II}}/\text{Cr}^0$ was determined more exactly by coulometric generation of various concentrations of Cr^{II} , interrupted by potential measurements against a stable

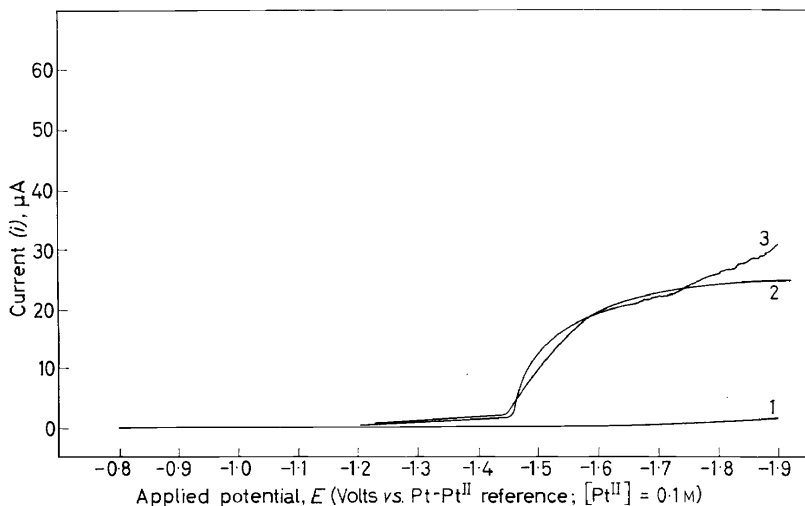


Figure 2. Distortions of polarograms due to dendritic growths of solid deposits in the case of zinc. Platinum microelectrodes, 0.121 mm^2 . (1), Residual current curve, 450°C . (2), $[\text{Zn}^{\text{II}}] = 0.066 \text{ M}$, 450°C . (3) $[\text{Zn}^{\text{II}}] = 0.066 \text{ M}$, 390°C .

reference electrode. The reversible potential of Cr^{III} , Cr^{II} could likewise be determined more accurately by coulometric generation of Cr^{III} from Cr^{II} using an inert anode. In this way, we have assembled an extensive e.m.f. series in LiCl-KCl^{20-22} using voltammetry as a guide. Diffusion coefficients in general can be more accurately determined by chronopotentiometry than from steady-state currents, once more using voltammetry as a guide.

The problem of distortions of polarograms due to dendritic growths of solid deposits is illustrated by the behaviour of zinc, as shown in *Figure 2*. A smooth curve was obtained at 450° (above the melting point) whereas distortions due to dendrite formation are seen on the curve recorded at 390° (below the melting point).

LINEAR SWEEP VOLTAMMETRY

Based upon experience in aqueous solutions, it would seem that linear sweep voltammetry and cyclic voltammetry would have so many inherent advantages as to supplant steady state voltammetry. Merely by increasing the polarization rate from 1 mV/sec or less to 100 mV/sec or more, the time scale of polarization can be shortened so much that convection no longer plays an appreciable role in mass transport. Thus, for reactions without kinetic complications, purely diffusion controlled currents can be readily observed. Thus, in principle, it should be possible to achieve greater reproducibility and to observe curves which contain more information, e.g., about diffusion coefficients, electron transfer kinetics, and the presence of kinetic complications in the electrode reaction mechanism.

While some noteworthy experiments have indeed been described²³, this method has not, up to now at least, lived up to expectations. It is perhaps worthwhile to speculate on the contrast between molten salt research and aqueous solution research in this respect. Of course, in any solvent, an important theoretical limitation in linear sweep voltammetry is that the diffusion-controlled peak currents are proportional to the square root of polarization rate whereas the current due to charging the electrical double layer is proportional to the first power of polarization rate. In molten salts, double layer capacitances are, in general, higher than in conventional solutions. This factor can be especially troublesome when a solid deposit is formed at the electrode with a large change of electrode area. On the other hand, when a liquid metal is deposited upon a solid, the surface area may be decreased, but what is more important, especially with platinum indicator electrodes, an attack of the surface may occur with the formation of a liquid alloy of platinum. Reverse polarization to remove the deposited metal (e.g. lead or cadmium) leaves a roughened platinum surface.

The use of a liquid pool of low-melting metal as an indicator electrode is limited by the tendency for creepage of melt between the liquid metal and its container, forming a large-capacitance interface connected to the bulk of the solution by a film of appreciable resistance. The RC charging time constant of the electrode becomes large, and the current-voltage curves become meaningless.

As has been emphasized above, a practical problem in molten salt work is the difficulty of removing traces of reducible impurities. As a result, it

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often occurs in practice that the residual current levels may be acceptable using indicator electrodes of very small area (of the order of 10^{-3} – 10^{-2} cm²) and slow polarization rates. On the other hand, in linear sweep voltammetry, the area of the indicator electrode must be relatively large (usually 0.1 cm² or more) to observe linear, rather than hemispherical, diffusion. In most practical molten salt work the residual currents become unmanageably large with the relatively rapid polarization rate used in linear sweep voltammetry. Perhaps more attention should be paid to the use of very small indicator electrodes with the appropriate equations for hemispherical diffusion. Under these conditions, the main limitation would be the complications due to dendrite formation.

DIPPING INDICATOR ELECTRODES

Lyalikov and Karmazin²⁴, in 1948, introduced a "dipping" electrode in which an inert gas is bubbled around the end of a metal electrode dipping into the surface of the melt, so as to expose a variable area of electrode to the melt in an intermittent fashion. In this way, at least one of the features of a dropping electrode could be achieved, namely, a periodic reproducible fluctuation of electrode area with time. Lyalikov and coworkers described the polarograms in analogy with classical polarography, and found that the wave height was proportional to the square root of the rate of bubble formation. A similar relationship was found by Flengas²⁵, who evaluated the solubility products of AgCl and AgBr in molten KNO₃–NaNO₃ at 250°C.

The dipping electrode technique was modified by Hills, Inman and Oxley²⁶ who used a flat electrode in place of the needle-shaped electrode originally used by Lyalikov and Karmazin. Goto, Suzuki and Saito⁸ re-examined the question of the geometry of the electrode by studying the polarography of various ions in aqueous solutions, and designed an electrode which had the advantage of not requiring a metal–glass seal directly exposed to the melt. As has been pointed out above, this is a significant factor, particularly in corrosive melts.

Saito, Suzuki and Goto⁸ used their improved dipping electrode in the form of a molybdenum wire surrounded by a quartz gas jacket for LiCl–KCl eutectic melts, and by a graphite jacket for NaF–KF–LiF ternary eutectic melts.

OTHER INDICATOR ELECTRODES

Black and deVries²⁷ and Chovnyk^{28, 29} and Okada and coworkers³⁰ in their early work used a rotated as well as a stationary platinum micro-electrode and noted a marked increase in sensitivity as expected. It should be pointed out, however, that the sensitivity limit is generally imposed by residual impurities in the melt. In a more fundamental study, involving the use of the rotated disc electrode, Delimarskii, Panchenko and Shilina³¹ were able to calculate diffusion coefficients of metal ions in LiCl–KCl eutectic using the Levich equation³².

THE EQUATIONS OF POLAROGRAPHIC WAVES

Some contradictory observations have appeared on the shapes of current-voltage curves in molten salts. For reversible reactions involving soluble products there is general agreement that just as in aqueous solution or conventional non-aqueous solvents, the Heyrovsky-Ilkovic equation (Eq. 1) is valid

$$E = E_{1/2} + \frac{RT}{nF} \ln \frac{i_d - i}{i} \quad (1)$$

In Eq. (1), the surface concentration of oxidant is proportional to $(i_d - i)$, while the surface concentration of reductant is proportional to i .

The contradiction has centred around reduction of metal ions directly to the metal, where conventional theory would lead to Eq. (2)

$$E = \text{const} + \frac{RT}{nF} \ln (i_d - i) \quad (2)$$

since the concentration (activity) of reduction product would be expected to be constant.

In the early fused salt literature Eq. (1) was given by Panchenko³³ and by Delimarskii and coworkers³⁴ while Eq. (2) was reported valid by Black and deVries²⁷ and by Laitinen, Liu and Ferguson¹⁹ and by Maricle and Hume¹². Gaur and Behl³⁵ found that Eq. (1) best described Sn^{II} reduction while Eq. (2) worked better for Pb^{II} and Cd^{II} waves in $\text{MgCl}_2\text{-KCl-NaCl}$.

Skobets³⁶, in considering this problem, expressed the view that several extraneous factors could cause an appreciable portion of the current-voltage curve to become linear. Among these factors are anode polarization; inclusion of iR drop, time lag in recording, presence of reducible impurities, etc. Analysis of such a linearized curve, he said, will show an acceptably linear plot of E against $\ln (i_d - i)/i$ but not against $\ln (i_d - i)$.

It should be noted that in many cases of linear $\ln (i_d - i)/i$ plots the slopes did not conform to the theoretical value of $2.3 RT/nF$. Delimarskii and Kalabalina³⁷ observed such behaviour for the polarography of several metal oxides in molten boric oxide and suggested that Eq. (3) for an irreversible process is valid:

$$E = E_{1/2} + \frac{RT}{n_a aF} \ln \frac{i_d - i}{i} \quad (3)$$

Eq. (3) can be rigorously derived for a totally irreversible charge transfer reaction at steady state, *regardless of the nature of the reduction product*. Along the same lines, in recent work, Saito, Suzuki and Goto⁸ proposed that Eq. (3) is valid for several metal deposition reactions in LiCl-KCl eutectic and in LiF-NaF-KF eutectic. Here the explanation is implausible because of the requirement that the charge transfer reaction is totally irreversible, when the weight of the evidence, especially for LiCl-KCl , is that the electrode reactions of many metals are rapid and reversible⁵.

Delimarskii and Gorodyskii³⁸ considered a more detailed kinetic scheme which will allow Eq. (1), (2) or (3) to be obeyed depending upon the kinetic

parameters that are involved. Their scheme involved a series of three consecutive reactions involving respectively mass transport of reactant, charge transfer and removal of product. Their final expression is

$$i = \frac{(i_d/\kappa') - (K''/K') [a_m'' - (i_m'' - i)/\kappa''] \exp(nFE/RT)}{(1/K') \exp(an_aFE/RT) + (1/\kappa')} \quad (4)$$

where a_m'' is the maximum activity of product at electrode surface,
 $i_m'' = \kappa'' a_m'' =$ maximum rate of removal of product corresponding to its maximum activity,

and $i_d = \kappa' a_0' =$ maximum rate of mass transport of reactant from activity a_0' in bulk of solution,

K' and $K'' =$ equilibrium constants for charge transfer and product mass transport reactions.

Eq. (4) reduces to Eq. (1) when $1/K' \ll (1/\kappa')$ and $i_d \leq i_m''$ or when the discharge rate is high and the rate of mass transport of product is greater than that of reactant.

On the other hand, when $1/K' \ll (1/\kappa')$ and $i'' = i_m''$, when the mass transport of product is at a maximum, Eq. (4) reduces to Eq. (2).

Finally, when $K'' \ll K'$, and the back reaction of charge transfer can be neglected, or for a totally irreversible process in which the rate of removal of product can be neglected, Eq. (4) reduces to Eq. (3).

There remains to be discussed the question of the mechanisms by which the reaction product can be removed from the electrode surface. In classical polarography, the removal of product into the mercury drop is by diffusion, at a rate comparable to diffusion rates in aqueous solution. Eq. (1) then typically holds for reversible reactions. On the other hand, if the electrode is solid, mass transport into the electrode is negligible and Eq. (2) would be expected to hold.

The reported failure of Eq. (2) for reversible reactions in molten salts could be caused by (i) diffusion of metal into the electrode, (ii) solubility of metal in the melt, or (iii) removal of metal by an extraneous reaction. These causes will be examined in turn.

(i) Although alloying of several low melting metals with platinum occurs at relatively low temperatures, the alloys are typically liquids rich in low melting metal. The activity of deposited metal does not deviate markedly from that of the pure metal. Such alloying is much less pronounced for electrodes such as tungsten and molybdenum. Diffusion rates into solid metals are so slow that, except for very short transient currents or rapidly changing potentials, a constant activity of deposited metal must be observed.

(ii) Metal solubility in molten salts is typical only of metals in their own salts. For metals in salts of other metals, either no reaction, or a displacement reaction is the common situation. For example, cadmium has an appreciable solubility in cadmium chloride, but negligible solubility in LiCl-KCl.

(iii) Metal removal by extraneous reaction is by far the most probable of these three causes. If the only extraneous reactions were the oxidation of metal by the ions of a more noble metal, and all reactions were reversible,

then the presence of the noble metal ions should be evident through the appearance of a residual current, and a subtraction of the residual current should make an adequate correction. On the other hand, a species such as water or hydroxyl or hydrated silicates might be more reactive with freshly deposited metal than in direct reaction with the electrode. Under these conditions, a catalyzed hydrogen discharge would occur at potentials corresponding to the foot of the polarographic wave, and S-shaped curves typical of Eq. (1) would be observed.

A special type of extraneous reaction might involve the dissolution of metal in an abnormal oxidation state that would be exceptionally reactive towards hydrogen-containing species. An examination of the polarogram of cadmium(II) in LiCl-KCl as reported by Laitinen, Liu and Ferguson¹⁹, and reproduced in *Figure 3* reveals that the relative extent of curvature at the foot of the wave *increases* with increasing concentration of cadmium(II),

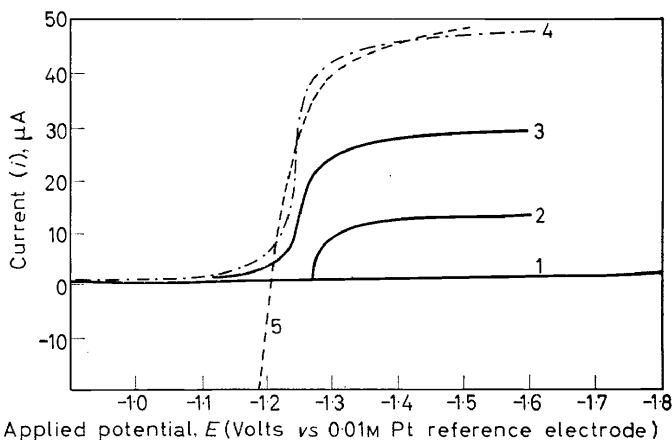


Figure 3. Polarograms of cadmium(II) chloride. Effect of increase of cadmium(II) concentration on relative extent of curvature at the foot of the wave. (1), Residual current. (2), (3), (4) 2.4 mg, 5.8 mg and 9.7 mg of CdCl_2 added to approximately 4 ml of melt. (5), Reverse polarogram of curve (4).

just the reverse of what would be expected on the basis of a fixed concentration of residual impurity reacting with deposited metal. On the other hand, the degree of interaction of deposited Cd metal with Cd(II) to form Cd_2^{2+} , a well-established species in molten CdCl_2 , would increase with increasing Cd(II) concentration. Thus a catalytic cycle would be set up involving reduction of hydrogen-containing species by Cd(I), where the latter is formed by electro-reduction of Cd(II). It is significant that the half-wave potential of the wave shifts in the anodic direction with increasing Cd(II) concentration, as expected from Eq. (2), rather than remaining constant, as would be expected from Eqs. (1) or (3). Also, the reverse polarization curve follows Eq. (2).

From these considerations, Eq. (2) could be expected to hold only for melts that have been rigorously freed of extraneous reactants. Another

possibility that should not be overlooked is that reversible electrode processes may be rendered irreversible by the presence of extraneous impurities. Thus oxide or hydroxyl could form stable complexes with metal ions, and cause irreversible behaviour with metal deposition either by introducing a kinetic complication into the deposition reaction or by causing a codeposition of oxide or hydroxide with the metal. The importance of careful preparation of melts, therefore, should once more be emphasized.

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