ELECTRODE REACTIONS IN MOLTEN SALTS

D. Inman

Department of Metallurgy and Materials Science, Imperial College of Science and Technology, London SW7 2BP, U.K.

ABSTRACT

Many types of electrode reaction occur in molten salts but, relative to aqueous solutions, little is known concerning their kinetics and mechanisms.

After a general survey, detailed attention is given to the cathodic deposition of metals and non-metals from halide and oxy-anionic melts, including the dependence of the structures of the metallic deposits on the corresponding electrochemical parameters.

For liquid metal deposits the very rapid charge transfer steps dominate the behaviour of the overall reaction. This phenomenon is related to the metal-molten salt interfacial structure. For solid metal deposits produced by single step processes, the focus of interest is their nucleation and growth. If these deposits are produced by multi-step processes from transition metal ions the chemical complications often obscure the structural phenomena.

Finally, future prospects for high temperature electrode reaction studies are cited and discussed.

INTRODUCTION

It is difficult to provide a short review of such a broad and diverse topic as electrode reactions in molten salts, even if this is restricted to the high-temperature inorganic systems. This paper will therefore comprise an overview of the results and conclusions which have been and will be discussed in more detail elsewhere.

The inorganic molten salts extend from the low-melting nitrates through the ionic and partially ionic halides, to the very high-melting silicates; they can be usefully subdivided into the simple ionic melts, the oxyanionic melts, the polymeric or network melts, the molecular melts and the aqueous melts, although an increasing number of intermediate types such as AlCl3-NaCl, where Lewis acidity (and
The absence of the complicating influences of an associated liquid such as water might lead us to suppose that atomic events at molten salt/metal (particularly liquid metal) interfaces would be relatively simple. However, the complexity of many molten salt electrode processes in practice due, for example, to the effects of adsorption and coupled chemical reactions along with the difficulties of conducting experiments on these interfaces at high temperatures, have frustrated many of our efforts to gain a better understanding of these phenomena. Nevertheless, understanding of electrode processes in fused salts has increased very rapidly in recent years.

Starting with the Manhattan project in the second world war, much of the modern fundamental work has been stimulated by, and supported because of, the technological applications of molten salts. The increasing diversity of these technological applications does however have its adverse features: although a coherent body of literature is built up over the years if the industrial interest is large and continuous (e.g. in aluminium electrowinning), if it is small and ephemeral then its influence is divergent, at least in regard to our general fundamental understanding of electrode processes in molten salts. Thus the end of the molten salt reactor experiment at Oak Ridge can be seen to mark the end of a golden era of molten salt electrochemistry (and chemistry!).

Nevertheless some present or potential technological applications, viz. the electro-extraction and electro-forming of refractory metals and high temperature fuel cells and batteries for energy conversion and storage have generated a considerable body of fundamental information.

Perhaps the biggest improvements over the last thirty years or so have been with regard to electrochemical instrumentation. It is now common to apply the techniques well known to aqueous solution electrochemists to molten salts. Techniques such as chronopotentiometry and, latterly, particularly linear sweep voltammetry, have been very useful in providing us with the "electrochemical spectra" of unknown and perhaps, in the stoichiometric sense, complicated electrode processes.

These techniques however are not very helpful with regard to understanding the kinetics and mechanisms of charge transfer processes proper, and we should not attempt to extract too much information from them in this regard.

Perhaps the most surprising development of recent years is the applicability of many of the concepts of aqueous solution electrode processes to those occurring in molten salts. One can cite such phenomena as the coupling of chemical reactions to charge transfer processes, the (presumed) presence of multi-ionic layers on the...
solution side of metal-melt interfaces, the adsorption of ions, the occurrence of charge transfer and reaction overpotential, the key importance of Lux-Flood acidity-basicity to electrode reactions in oxyanionic melts, the occurrence of surface film phenomena, the formation of less common species such as \( \text{O}_2^{2-} \) and \( \text{O}_2^- \) in oxidising media and so on.

In this article, the many types of electrode reaction encountered in molten salts will be listed but in particular the cathodic metal ion/liquid metal reactions in molten halides will be compared with those involving solid metals, and in turn these reactions in halides will be compared and contrasted with processes involving both metals and non-metals, (viz. Pb, Cd and C) in oxyanionic melts. Much of this latter work is very recent and relates to other presentations at this symposium whereas in the former case (solid metals) the interest centres on the dependence of the structures and morphologies of the deposits on the electrochemical parameters of the corresponding reduction processes and on this basis to the electrical control of these processes and their products.

**CLASSIFICATION OF ELECTRODE REACTIONS**

Many electrode reactions in molten salts, especially metal-metal ion reactions, are subject to mass transfer rate control but it is now recognised that there are several significant exceptions and many slow, i.e. classically irreversible, reactions do occur. Under laboratory conditions mass transfer will generally take place by linear diffusion but in certain circumstances spherical diffusion and convection can augment this process and their effects are difficult to distinguish from kinetic and catalytic complications arising from chemical reactions coupled to charge transfer processes. Also it is sometimes difficult to distinguish the effects of the discharge of adsorbed ions from non-Faradaic multilayer charging, particularly at short times.

The types of cathode process encountered are:

(i) reduction of the solvent cation to a liquid metal product, e.g. Na from NaCl. The processes are complicated by the back reaction in which the metal dissolves in the melt to form electronically conducting solutions.

(ii) reduction of a solute cation to a liquid metal product, e.g. Pb from PbCl\(_2\) in NaCl. These processes frequently exhibit adsorptive effects (see below).

(iii) reduction of a solute cation in a single step to a solid metal product, e.g. Ag from AgCl in NaCl, Cr from CrCl\(_2\) in LiCl-KCl (see below). These processes frequently exhibit the post-charge transfer complications of deposit nucleation and growth.
(iv) reduction of a solute cation by a multiple step process to a solid metal product (e.g. Ta from TaF₅ in LiF). These can involve the formation of insoluble or soluble intermediate oxidation states which may or may not disproportionate and/or inhibit the thermodynamically predicted overall process. Electro-nucleation and growth processes probably play a part in these processes as well, although this may be obscured by the gross complication of the behaviour of the intermediate oxidation state.

As well as multiple charge transfer steps, the overall process may involve the coupling of the dissociation of complexed precursors to the main charge transfer process (e.g. Mo from MoCl₃ in LiCl-KCl).

(v) reduction of an oxy-anion to produce a non-metal (e.g. C from Na₂CO₃ in LiCl-KCl).

(vi) reduction of a dissolved gas (e.g. ½O₂ + 2e —► O²⁻) which, superficially, is the simplest of oxygen electrodes but in practice is complicated by the formation of such ions as O₃²⁻ and O₃.

(vii) reduction of a solute cation to a soluble product. These may involve metal ions (e.g. Cr³⁺ + e —► Cr²⁺) or non-metal ions (e.g. NO₃⁻ + 2e —► NO₂⁻ + O²⁻ or S²⁻ + 2e —► 2S²⁻). The types of anode process encountered are:

(a) oxidation of a solute cation to a soluble product (e.g. Cr²⁺ — e —► Cr³⁺).

(b) oxidation of an anion to a gaseous product, e.g. 2Cl⁻ — 2e —► Cl₂.

(c) anodic production of a solid film on the electrode surface. Post-charge transfer chemical reactions in oxygen evolution reactions such as M + ½O₂ —► MO, or direct participation of the metal electrode in the electrode reaction, M + O²⁻ —► MO + 2e, or dissolution-precipitation reactions of the type M —► M²⁺ + 2e followed by M²⁺ + O²⁻ —► MO, can lead to these solid films.

The anodic production of sulphur can be even more complicated as in this case, in addition to the interaction of the product with the substrate, there is the possibility of sulphur atom/ion catenation parallel to the electrode surface.

CHARGE TRANSFER PROCESSES INVOLVING LIQUID METALS

These processes are generally so rapid (in the steady state mass transfer controls the rate of the overall reaction) so that special relaxation techniques are needed for the measurement of their kinetics. Nagy and his collaborators have recently made several improvements to data collection in this area as in the past many of the techniques have not been applied correctly. (1) Because of this, doubts surround the quantitative significance of many of the published values of, e.g., exchange current density. Nevertheless, on the basis of the data now available, it is possible to develop a qualitative picture of the
events taking place at the metal-melt interface. This should form the basis of future quantitative investigations using these improved techniques.

Classical methods for characterising the electrical double ("multi") layer at any metal/electrolyte solution interface involve making measurements of the interfacial tension(2) &/or the interfacial capacitance as functions of applied potential(3). Many studies of this type have been made, particularly by Russian schools, with the following overall conclusions.

The minimum interfacial capacitances for metal/molten salt systems are of the same order of magnitude as those for, e.g., Hg/H₂O(KCl) at 25°C. The interfacial capacitance - applied potential curves are roughly parabolic in shape (at potentials close to the zero charge potential, E₀) with the minimum capacitance at a potential which coincides within experimental error with the potential of the electrocapillary maximum. While the characteristics of the electrical double ("multi") layers, as exemplified by these curves, appear to be largely independent of the nature of the metal phase, the observed capacitances do depend, both in magnitude and in potential response, on the composition of the molten salt phase; the cationic composition of these phases seems to exert the greatest influence.

The general features of the interfacial capacitance/potential plots are as follows:

(a) the profiles are parabolic with minima at E₀ (the zero charge potential);

(b) the zero charge potential for halides is the same for bromides, iodides and chlorides (same cation composition) but changes for the corresponding fluoride melt. Cₘₐₙₐₐ increases as Cl⁻ < Br⁻ < I⁻;

(c) a marked dependence of the zero charge potential on the cation composition is found (e.g. for the melts LiCl, KCl and CsCl);

(d) Cₘₐₐₓ increases with temperature and the interfacial capacitance/potential profile is very different in the low (~673K) and high (1073K) regions.

These comments apply to the alkali metal halides.

This behaviour may be interpreted in terms of an electrical multilayer with the excess charge on the melt side of a liquid metal-molten salt interface distributed across several ionic layers. Various attempts have been made to describe this layer in theoretical terms(4). However, the remarkable changes which occur in the shapes of the capacitance-potential curves as the temperature is raised, and the accompanying rapid increase of capacitance with potential has not been
adequately accounted for by these theories. Many years ago, Graves and I tried to separate the charging process from the Faradaic electrode process instrumentally by making pulse measurements at very short times (equivalent to measuring the interfacial impedance at very high frequency)\(^5\). In principle, charge rearrangement at the interface has a much shorter time constant than charge transfer across the interface. A plot of the multilayer capacitance vs potential plot for liquid lead in LiCl-KCl at low temperature (450°C) is shown in figure 1. Two regions are clearly delineated. At potentials well cathodic to the Nernst potential for Pb/Pb\(^{2+}\), the capacitance-potential plot is a very shallow parabola and in this region, which corresponds to the limiting current region in voltammetry, the concentration of lead ions at the lead metal surface equals zero and the electrode is quasi-ideally polarisable (\(i \rightarrow 0\)). Near to the Nernst potential, the capacitance rises very sharply with electrode potential and the electrode is quasi-ideally reversible (\(i \rightarrow \infty\)). Some quantitative support for this is shown in figure 2. In this region common data are obtained through varying the electrode potential externally and through poising the electrode potential by the addition of lead chloride. Whether or not there are lead ions present in the bulk melt, their concentration at the electrode surface will be zero in the quasi-ideally polarisable region. The atomic-level model on which this plot is based is that the enhanced capacitances in the quasi-ideally reversible region are adsorption pseudo-capacitances; that is, the discharge and formation of adsorbed metal ions are very rapid processes (high exchange current density) which cannot be distinguished with presently available techniques from the processes of ion rearrangement (normal charging).

Unhappily, there has not been much research activity in this area in recent years (but see \(^6\)). However, the liquid metal/molten salt interface is extremely important vis-à-vis the electrowinning of metals such as magnesium and aluminium, so that hopefully there will soon be a resurgence of interest. There is much scope for measurement of this sort over the temperature ranges spanning the melting points of these metals and of course for fast response time measurements allowing the time resolution of these fast interfacial processes.

**CHARGE TRANSFER PROCESSES INVOLVING SOLID METALS: SINGLE STEP REDUCTION.**

As will be evinced below, gross complications arise when solid metals are deposited via multi-step charge transfer processes. When however, the element concerned only exhibits one oxidation state in solution e.g. Ag\(^+\), or the element is present in solution in its lowest oxidation state e.g. Cr\(^{3+}\), then in the absence of these gross complications the phenomena of electro-nucleation and -growth play dominant roles subsequent to the primary charge transfer process. This may or may not involve the discharge of adsorbed ions, as discussed above, for liquid metals where these subsequent complications...
are absent.

That electro-nucleation and -growth complications are playing a part is most straightforwardly indicated by initial potential "over­shoot" on chronopotentiograms(7). This can be eliminated by pre­depositing the metal concerned on the foreign substrate used for the working electrode. The (excess) nucleation overpotential which is ne­cessary to effect nucleation is of course analogous to the excess con­centration of a supersaturated solution. The phenomena can be studied in a more detailed way by chronoamperometry (that is by studying the current-time relationships obtained at constant applied overpotential) (8). Typical plots of this type are shown in figure 3. After initial charging, the current falls during an induction period and then rises during the subsequent continuous nucleation and growth stage before falling according to the classical diffusion-controlled model when the surface layer is completely formed. That nucleation and growth phenomena are occurring simultaneously during this process is evinced by the plots of I vs t 3/2 as functions of applied overpoten­tial shown in figure 4. However, the most important result to come out of this work is that the saturated nucleus densities (N) on the substrate increase with increasing applied overpotential. A plot of N vs η (overpotential) is shown in figure 5 along with the corre­sponding i (current density) vs overpotential plot(9). It is noteworthy that for high N values (high overpotential), the current density (i) is in its limiting region and dendritic growth is very likely to occur.

On the other hand, it can be seen that when the overpotential is low, i is a small fraction of its limiting value, dendritic formation will be very unlikely but the saturation nucleus density will be very low (i.e. the coverage of the substrate by the deposit will be poor). A consideration of these plots led to the idea of a pulsing method to optimise the electroplating of chromium in molten salts. Maximum surface coverage is obtained by applying an initial high overpotential "spike" and this is followed by much lower overpotential growth electro­lysis. The success of this process is described elsewhere(10).

CHARGE TRANSFER PROCESSES INVOLVING SOLID METALS:
MULTIPLE-STEP REDUCTION/REACTION CONTROL

Several reviews on this topic have appeared in recent years so the present position will only be summarised here(11).There are major dif­ferences between the results (mainly for the transition group refrac­tory metals) which have been obtained for fluoride melts and those for chlorides. In the former it is generally possible to reach the metal­lic state whereas in the latter the formation of insoluble, inhibiting lower oxidation state compounds often constitutes the final reduction stage observed within the available electrochemical window of the solvent. In both types of melt however, reduction to metal etc. from the highest oxidation state ions takes place by several steps.
Electroanalytical techniques such as linear sweep voltammetry and chronopotentiometry are often used to establish the stoichiometries of overall electrochemical reactions and it is this sort of technique which establishes that reduction/oxidation takes place in stages. Furthermore, by suitable analysis of the LSV or chronopotentiometric waves, the "irreversibility" of these waves may be established. At high temperatures this probably arises from factors other than slow charge transfer. As initially observed by Mellors and Senderoff, (12) the last step in the sequence of steps leading from a high oxidation state in a fluoride melt to the metal is generally slow (i.e. irreversible and rate-determining). This slow step seems to play an important part in ensuring a dendrite-free deposit by a continuous (i.e. non-pulsed) electrolysis.

Mellors and Senderoff related this slow step to the formation of a sparingly-soluble intermediate oxidation-state compound on the electrode surface. However, in some cases the stoichiometries of the compounds that they proposed are not in accord with those generally accepted. In any event, this matter needs to be looked at again in the light of current knowledge and with the improved techniques (e.g. linear sweep voltammetry) which are now available.

Although evidence has been published to support the premise that the transition (refractory) metal ions form strong complexes in fluoride melts, this does not seem to play a major role in determining the kinetics of the overall electrochemical reaction. Certainly the original electroanalytical evidence pointed to diffusion-controlled "first step" reductions. Another contrary indication was that although foreign anions such as chloride in the fluoride melt had a major effect on the form of the metal deposits (and thus presumably on the kinetics of the overall reaction and/or metal deposition step), this was unlikely to be because they displaced fluoride ions from any transition metal fluoride complexes present in the bulk melts. (Complex stability order for transition metal ions: F >> Cl > Br > I (Group A).)

It is tempting to suggest that foreign anions such as chloride adsorb on the electrode (the interface behaves like a soft metal) where they are in a position to inhibit the formation of the vital intermediate lower oxidation state compound. A further point concerns whether the experimental work is correct or whether at least one of the chronopotentiometric steps is due to the reduction of an impurity in the melt. Some of the original work has been reproduced by other authors but of course their results may have been subject to the same artefacts, if they exist(13).

It is probably impossible to arrive at a general explanation of these results and also those obtained in chlorides, and it will be necessary to have recourse to the rather specific chemistry of these elements and their compounds.
Finally, seemingly clear cut evidence for the coupling of a rate-determining chemical reaction to a charge transfer process has been obtained for MoCl, in molten NaCl - 80 mol % KCl at 1033K(13). Schematically a complex ion which is normally electroinactive itself (at least within the available solvent electrochemical window) dissociates to form an electroactive species 0,

\[ Z \rightleftharpoons 0 \]

and this is followed by the reaction

\[ 0 + ne \rightarrow R \]

where \( Z \) represents the complex ion, \( 0 \) the oxidised species and \( R \) the reduced species (metal). Experimentally a single chronopotentiometric wave is observed for MoCl, concentrations < 2.10^{-2}M. Although the transition times themselves obeyed Sond's equation, the shifts of \( e_{\pi/4} \) (the quarter-wave potential; i.e. that at a quarter of the transition time) with applied current and the slopes of the so-called log plots (\( e \) vs log \( f(t) \)) suggest an irreversibility having chemical rather than electrochemical origin. Using Vetter's treatment for a homogeneous rate-controlling prior chemical step as a very rough approximation, and identifying the reaction overpotential \( \eta_r \) in this treatment with \( e_{\pi/4} \), the following overall reaction pathway was postulated:

\[
\begin{align*}
M_{0.2}^{6+} & \overset{\text{slow}}{\rightarrow} 2Mo^{3+} \quad \text{(rds)} \\
Mo^{3+} + 3e & \rightarrow Mo \quad \text{(fast)}
\end{align*}
\]

At high Mo(III) concentrations, two chronopotentiometric reduction waves are observed (Figure 6): The more cathodic one, which is absent at low concentrations, is shorter than the first. The parameters of this second wave were not consistent with its being due to the reduction of another oxidation state of molybdenum. A higher oxidation state would have produced a new wave at more anodic potentials, while a lower oxidation state would have produced a wave having a larger transition than the initial one and would have been apparent at all concentrations. However, this second wave is certainly due to molybdenum since addition of more MoCl, causes the transition time of the second wave to increase. Thus this second wave probably corresponds to the direct reduction of a multi (probably di-) nuclear complex to metallic molybdenum. This study provides additional quasi-quantitative support for the earlier observations of Mellors and Senderoff who employed the eutectic melt LiCl-KCl as solvent(14).

CATHODIC CHARGE-TRANSFER PROCESSES IN OXY-ANIONIC MELTS

Some of the difficulties involved in depositing metals from halide melts have been mentioned above. Although the form of the de-
posit is always a problem (from the point of view of electroplating), the metals themselves are at least inert in these halide solvents although insoluble lower-oxidation-state compounds often inhibit their cathodic electrodeposition.

This is not so in oxyanionic melts where the cathodic activity of the oxyanion often masks the deposition of the metal. Alternatively, the oxidising power of the oxyanion may be sufficient to form an oxide on the metal surface after electrodeposition.

The oxyanion itself of course contains a reducible component (viz. C in CO$_3^{2-}$, N in NO$_3^-$, etc.) and it may be possible to electrodeposit the corresponding element by a direct cathodic process.

The question of the electrodeposition of oxidisable metals such as lead and cadmium from molten nitrates has been the subject of controversy since 1983. Until then it had been assumed that although these metals could be directly electrodeposited on, e.g., platinum substrates, they were rapidly oxidised to the corresponding oxides. In 1983 Miles, McManis and Fletcher gave an alternative interpretation to the effect that the oxides were formed directly by the electro-reduction of the corresponding nitrato-complexes in molten KNO$_3$, molten LiNO$_3$, and KNO$_3$- LiNO$_3$, eutectic (viz. Pb(NO$_3$)$_2$ + 2e $\rightarrow$ PbO + NO$_2^-$). This conclusion was based on the absence of anodic waves in linear sweep voltammetry for metal dissolution after the cathodic deposition even at very high scan rates (i.e. to 1000V/s)(15). However, in recent studies on Cd$^{2+}$ and Pb$^{2+}$ in the equimolar NaN$_3$ - KN$_3$ melt at 260°C, we have found evidence (using Hg substrates) of the direct electrodeposition of the corresponding metals using linear sweep voltammetry and chronopotentiometry(16). The important factors in obtaining these results are:

(i) the use of mercury to lower the thermodynamic activity of the primary metallic product;
(ii) the use of high sweep rates; and
(iii) the use of low concentrations of solute.

Certainly on platinum indicator electrodes our experimental results were in accord with those of Miles et alia. Some examples of the results obtained for lead ions with mercury electrodes are shown in figures 7 and 8. Even at this low lead concentration the anodic dissolution wave corresponding to lead deposition disappears at the lowest sweep rate (0.02V s$^{-1}$). For the longer deposition time in this case the concentration of lead at the electrode surface is sufficient for oxidation to intervene.

As figure 9 shows, the Randles-Sevcik equation is obeyed by the reduction wave and this leads to a $D_{Pb^{2+}}$ value of 2.13.10$^{-6}$ cm$^2$ s$^{-1}$. Furthermore the plot of anodic peak current vs lead nitrate concentration shown in figure 10 (drawn for a sweep rate of 2.0V s$^{-1}$ and concentrations lower than 10.75.10$^{-3}$m, to avoid lead oxidation problems)
is a straight line as would be expected if the anodic current is due
to the dissolution of lead. Similar results were obtained for cad-
mium. This work will be published in detail elsewhere but at this
stage it appears that it is not necessary to invoke the "reduction
of complex" model of Miles et alia to explain the differing results
with substrates, sweep rates and concentrations, although it should
be emphasised that the results presented here apply strictly to NaN03-
KNO3 melts at 260°C, and the temptation to generalise should be resis-
ted.

As mentioned above, the oxyanion in these melts contains a re-
ducible component and many authors have concerned themselves with stud-
dies of the electroreduction of these anions (17) (18) (19).
We have recently been studying the electrodeposition of carbon from
the carbonate ion dissolved in LiCl-KCl-NaCl at 450°C(20). Earlier work
has involved the electrodeposition of carbon from carbonates them-
'selves (21,22) and from carbonate dissolved in NaCl-KCl (23).
Tungsten, stainless steel and platinum substrates and cyclic voltam-
metry and chronopotentiometry were employed in this study. A typical
linear sweep voltammogram for the stainless steel substrate is shown
in figure 10. The single reduction wave generally observed occurs at
e = -1.745V (Pt) -1.90V (stainless steel) and -2.05V (W) with regard
to the 0.4M Ag/Ag(I) reference electrode. This corresponds to the
process:

\[ \text{CO}_3^{2-} + 4e \rightarrow C + 3\text{O}_2^- \]

but the wave is irreversible as upon reversal of the sweep scan only a
small oxidation peak at about -0.95V was observed. As indicated in
figure 12 the cathodic peak current increases linearly with the square
root of sweep rate although the plot did not pass through the origin.
The details of this investigation will be published elsewhere, but on
the basis of the electrochemical results it was possible to devise a
method of carbon "plating" by pulse potentiostatic electrolysis.

THE FUTURE

Electrode reactions in molten salts are certainly not as straight-
forward as was once thought, nor are they easy to investigate experi-
mentally. Nevertheless, the absence of spectacular advances in recent
years is perhaps surprising; part of the reason for this is the ra-
ther small number of researchers interested in this field, scattered
throughout the world and having diverse technological aims. There is
not too much scope these days for non-mission-orientated research.

The central questions concerning the kinetics and mechanisms of
electrode processes are:
(i) what is the nature of the pre-charge transfer state at the elec-
trode surface? (Are we concerned with "bare" ions, complexed ions or
adsorbed ions? How does the energy level of this state differ from
that of the ion in the bulk state? What is the "geometry" of this
(ii) what are the individual steps of the charge transfer process proper, what is the reaction pathway within this process and ipso facto, what is the rate-determining step? At the moment we have to admit that we know very little about these central questions in spite of the improvements in the techniques applied, both electrochemical and otherwise, over recent years.

There is prime need now for:
(a) more electrochemical measurements using the full range of modern techniques in a complementary manner in well defined and purified systems. In particular the techniques need to become more diagnostic viz. thin-layer electroanalytical techniques in order to avoid mass transfer complications in studying electrode processes, particularly those involving coupled chemical reactions and ring-disc electrode voltammetry, particularly for studying electrode processes involving soluble intermediates.
(b) more coupling of structural techniques (both in situ and ex situ) with the electrochemical techniques mentioned above(24). For example, in principle soluble intermediates could be studied "spectro-electrochemically" at the rings of ring-disc electrodes using fibre-optics. Insoluble intermediates (and products) are best studied ex situ after potentiostatic preparation. Studies of electrocrystallisation phenomena are developing and these are important both from the pure and the applied points of view. An important question concerns the special effects (if any) of using molten salt solvents for this purpose. Another question concerns the effects of adsorbed ions on the initial electro-nucleation step. The correlation of the fundamental electrochemical parameters of a metal deposition process and the properties of the subsequent deposits is of course extremely important in devising new electroplating processes.
(c) finally, the study of other interfaces such as the solid electrolyte-molten salt interface is worthy of attention as well as the related topic of semi-conductor electrodeposition (25) and the semi-conductor-molten salt interface.

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Fig. 1. Capacitance-potential curve of lead in LiCl-KCl eutectic at 450°C

Fig. 2. Log (capacitance increase)-potential curve of lead in LiCl-KCl eutectic at 450°C (Symbols as in Fig. 1).

Fig. 3. Potentiostatic current transients for the electrodeposition of chromium on Nb stabilised 20/25 stainless steel: 0.30 cm², c = 0.039 mol dm⁻³ (overpotentials indicated in mV).

Fig. 4. I-t⁻¹/² plots for potentiostatic current transients obtained on tungsten: 0.0452 cm², c = 0.042 mol dm⁻³ (overpotentials indicated in mV).
Fig. 5. Example of characteristic curves in the electrocrystallisation of chromium under potentiostatic conditions: tungsten, $c = 0.346$ mol. dm$^{-3}$. (a) Sampled current voltammogram (sampling time: 0.1 s), (b) Saturation nucleus density vs overpotential.

Fig. 6. Molybdenum (III) in NaCl-KCl (20:80 mole %). Double-step chronopotentiogram. Stoichiometric concentration of MoCl, $7.10^{10}$ mol$_1$ dm$^{-3}$, y-axis 0.5V cm$^{-1}$, x-axis 0.15 s cm$^{-2}$. 

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Fig. 7
Concentration of Pb(NO$_3$)$_2$ = 1.07.10$^{-3}$m. T = 260°C.
NaNO$_3$/KNO$_3$ = 1 mole/1 mole
Mercury electrode 6mm$^2$ Reference potential Ag/Ag$^+$ 0.1m

sweep rate 2.0 Vs$^{-1}$

sweep rate 1.0 Vs$^{-1}$

Fig. 8
Concentration of Pb(NO$_3$)$_2$ = 1.07.10$^{-3}$m. T = 260°C.
NaNO$_3$/KNO$_3$ = 1 mole/1 mole
Mercury electrode 6mm$^2$ Reference potential Ag/Ag$^+$ 0.1m

sweep rate 0.1 Vs$^{-1}$

sweep rate 0.02 Vs$^{-1}$
Fig. 9. Randles-Sevcik plot. $I_p$ vs $(sweep\ rate)^{1/2}$

Fig. 10. Anodic dissolution of lead in mercury
Sweep rate = 2 V/S
Fig. 11 Typical voltammograms obtained at a stainless steel electrode for the reduction of Na$_2$CO$_3$, $T = 450^\circ$C, electrode area $1.57 \times 10^{-1}$ cm$^2$. $[\text{Na}_2\text{CO}_3] = 7.87 \times 10^{-2}$ mol/kg.

Fig. 12 Relationship between peak current and $(\text{sweep rate})^{1/2}$ for the reduction of Na$_2$CO$_3$ at a stainless steel electrode.