ELECTRODE REACTIONS IN MOLTEN SALTS

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While studies of thermodynamic properties of molten salts, such as equilibrium potentials, molar volumes and phase diagrams, and transport properties, such as conductivity and viscosity, are quite well advanced, the study of the electrode reactions in these media, which is the essence of electrochemistry, is at a very early stage of development. The neglect of electrode reaction studies in molten salts probably arises from two factors common to high temperature heterogeneous reactions. 1) The reaction rate is so high that usual methods of investigation expose only diffusion control and 2) the effects of small impurities may be overwhelming and cause serious irreproducibility of measurements. The latter is particularly serious when one considers the corrosiveness of many molten salts, difficulties with containers, atmospheres, etc. As a result, with a few exceptions, most studies of electrode reactions in molten salts are still semiquantitative, and concerned with identifying the rate-controlling step and the path(s) of reaction, or if diffusion controlled, the intermediates and products of the overall reaction, and diffusion coefficients of the reacting species. Very little has been accomplished in quantitatively determining kinetic parameters of molten salt reactions, such as exchange currents, reaction rate constants, or transmission coefficients. The most important methods by which these are accomplished in aqueous systems at ordinary temperatures are (1):

1) Current-voltage curves in which each point is obtained under a steady state condition of electrolysis. The analysis of the Tafel slopes (i. e. , the slope of the plot of overvoltage, η , vs. log i, the current density) provides the kinetic data and insight into mechanisms.

2) Transient D. C. techniques or voltammetry, including polarography with slow or rapid scanning procedures and potentiostatic and galvanostatic methods. In all cases equations relating current, voltage and time may be derived, a criterion for diffusion control set up, and departures from diffusion control interpreted in terms of kinetic parameters and mechanisms. The use of these methods in conjunction with the rotating disc electrode has proved to be extremely effective in many cases.

3) A. C. impedance measurements in which the frequency dependence of the impedance is measured to obtain a polarization resistance and pseudocapacity identified with the electrode reaction and from which a rate constant may be calculated and mechanisms deduced. Before this can be done, however, the double layer capacity and resistance of the solution must be determined in the absence of the electrode reaction.

Current Voltage Curves and the Oxygen Electrode

For the first method (steady state current voltage curves) to show any kinetic properties a rather slow reaction is required; and in molten salts only a few gas electrode reactions are slow enough to have been successfully studied by this method. An example of this is the work of Janz et al (2) on the anodic evolution of oxygen from carbonate melts on platinum and gold electrodes in the temperature range of 600° to 900°C. The overall reaction for this system is:

$$CO_3^= \rightarrow CO_2 + 1/2\ O_2 + 2e \qquad [1]$$
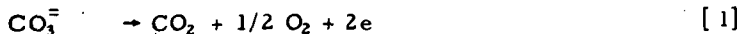
The first question raised by Janz et al was whether the reaction proceeded by direction oxidation of $CO_3^=$ ion as in [1] or by a prior dissociation,

$$CO_3^= \rightleftharpoons CO_2 + O^= \qquad [2a],$$

followed by electrochemical oxidation of the oxide ion,

$$O^= \rightarrow 1/2 O_2 + 2e \qquad [2b]$$

From the temperature coefficient of the overvoltage and the effect of gas composition (CO_2/O_2 ratio) on the overpotential, it was concluded that prior dissociation was involved. The next question considered was the detailed mechanism of the oxidation of oxide ion shown in [2b]. The processes considered were:

$$O^= + M \rightarrow M-O + 2e \qquad [3]$$

followed by either:

$$M-O + O^= \rightarrow M + O_2 + 2e \quad [4a], \quad \text{or } MO + MO \rightarrow 2M + O_2 \quad [4b], \text{ where M}$$

is the metal of the electrode. If [3] were rate controlling, the Tafel slope would be RT/F[*]. If [4a] were rate controlling the Tafel slope would be RT/F at high current density and $RT/3F$ at low current density. If [4b] controlled the rate the Tafel slope would be $RT/4F$. The observed Tafel slopes derived from the polarization curves at 600°C corresponded closely to the values calculated for step [4a] both at high and low current density. Thus the mechanism for oxygen evolution at this temperature from molten carbonate was identified as dissociation [Reaction 2a], followed successively by surface oxide formation [Reaction 3], and electrochemical oxygen gas formation [Reaction 4a], the last being rate controlling. At higher temperatures (near 800°C), the Tafel slopes are not linear and the gas evolution mechanism is not easily ascertained. A change in rate controlling step to oxide formation [Reaction 3] is not ruled out.

On silver electrodes the reaction is apparently much faster than on platinum and gold since almost no polarization was observed by Janz below a current density of 10^{-4} amp/cm^2, and Kronenberg (3) reports the reaction to be reversible on silver between 400° and 600°C since he found the potential to obey the Nernst equation with variation of the partial pressure of CO_2 and O_2. In fuel cell applications the frequent use of silver as a catalyst for the oxygen electrode in molten carbonate systems undoubtedly arises from this property.

A. C. Impedance Measurements

The third method listed above, A. C. impedance measurements, has proved to be very difficult to apply to molten salt reactions, and with a few exceptions (4), has not been used. Where it has been attempted the results have been difficult to interpret because of the inability to determine the double layer capacity of the solution in an unambiguous manner. The ambiguity of this value arises not only from difficulties with adsorption of trace impurities but from theoretical difficulties regarding the applicability of the value obtained in the absence of the reducible species (5).

Rapid-Scan Polarography in Analytical Chemistry

The second method, that involving D. C. transients, has proved to be the most valuable for the study of molten salt systems. The use of rapid-scan polarography and a few other techniques included in this group will now be illustrated in their application to analytical chemistry. The first of the analytical methods to be adapted to molten salts was polarography. This has been expertly reviewed by Laitinen and Osteryoung (4). Except for very low temperature melts, dropping mercury can not be used as an electrode. In most cases either the "dipping"

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[*]In all calculated Tafel slopes it is assumed that the symmetry factor, $\beta = 1/2$.

electrode of Lyalikov and Karmazin (4), or solid microelectrodes have been used. To make a dipping electrode, a wire is sheathed with an insulating tube and inert gas bubbled slowly through the tube. As the liquid rises and falls in the tube, alternately contacting the wire and mixing with the bulk, an action analogous to a dropping electrode is obtained and polarographic waves have been obtained which have been useful in analysis. Solid microelectrodes have been successfully used but difficulties have been encountered with changing of their area due to the dendritic deposits usually obtained from molten salts, and to instability of seals in these media.

Some interesting recent work on analysis in molten systems using rapid-scan polarography and other D. C. transient methods is that of Manning and Mamantov (6). These authors worked mostly in molten fluoride electrolytes at temperatures of 500° to 600°C, and used a pyrolytic graphite indicator electrode and a platinum wire dipped in the melt as a "quasi-reference" electrode. It is hard to say what electrode reaction the "quasi-reference" represents: it is less noble than the Pt, Pt^{++} electrode potential by at least one volt, which would represent a vanishingly small concentration of Pt^{++}, certainly insufficient to give a stable and reproducible electrode. It is, however, surprisingly stable, and may represent a redox reaction of an impurity common to the melts, possibly iron. The observed potential is not far from the Fe^{3+}/Fe^{2+} potential in fluorides, and iron is a common impurity.

Nickel in the alkali fluoride ternary eutectic was determined by rapid-scan polarography and anodic stripping techniques. At high scan rates the limiting current was proportional to concentration in the range studied (10-100 ppm Ni) and the electrode reaction was reversible. Since the reaction appeared to be diffusion controlled at high scan rates, the diffusion coefficients and the activation energy of diffusion (the current limiting process) could be calculated from the linear plots of peak current at known concentration vs. the square root of the scan rate. An activation energy of 18 kcal/mole was found which is about twice the value found by Senderofi and Mellors (7) for transition metal ions in the same solvent, and the diffusion coefficient of 4.5×10^{-6} cm²/sec at 600°C is lower by a factor of at least 2 than one would expect. These anomalous values suggest the possibility that the electrode process is not truly diffusion limited and that some kinetic process may be involved as well, or that some experimental difficulties have interfered.

Iron in the same solvent (LiF-NaF-KF) and in the $LiF-BeF_2$ eutectic was determined by rapid-scan polarography (~ 1V/min) and by chronopotentiometry. Again at high scan rates the reactions appeared to be diffusion controlled and reversible. The diffusion coefficient of Fe^{2+} obtained by chronopotentiometry was larger than that from polarography and the difference has been ascribed to experimental difficulties with the chronopotentiometry. However, as noted above, the diffusion coefficient obtained by polarography may be too small. The same techniques have been applied to uranium and zirconium in LiF-NaF-KF solvent though in the latter case the relationship between wave height and concentration was erratic. This may have been due to attack on zirconium by the solvent.

Chronopotentiometry and Electroplating

Finally, an illustration of the application of galvanostatic transient techniques (commonly called chronopotentiometry) to the study of the mechanisms of the electrode reactions in electroplating of metals from molten fluorides will be presented.
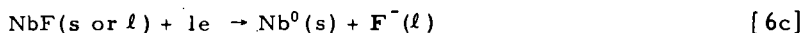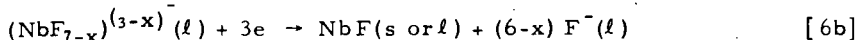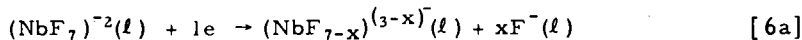
When electrodepositing metals in the solid state from molten salt electrolytes, powders and dendrites are usually obtained. However, it was shown by

Mellors and Senderoff (7) that the electrolysis of pure fluoride melts under certain conditions produces dense, thick, coherent deposits of chromium, molybdenum, tungsten, vanadium, niobium, tantalum, zirconium, and hafnium. In an effort to determine the unique properties of this system a study of the cathode reactions by chronopotentiometry was undertaken. By this method, a pulse of constant current is applied to a cell for a time long compared to the charging time of the double layer, but not long enough for convection to become significant at the electrode. In the molten fluoride at 600° to 800°C this time range was found to be a few tenths of a second to about 1 sec. During the passage of this pulse the potential-time curve is displayed on an oscilloscope and recorded photographically, the potential being taken with respect to a stable reversible reference electrode. The reference electrode used in this work was the Ni/NiF$_2$, alkali fluoride //half-cell which was reproducible under these conditions to about ±25mv. Contact between the reference electrode and electrolyte under study was made with a porous alumina bridge impregnated with the solvent which was the KF-NaF-LiF eutectic in most cases. All work was done in an argon atmosphere in a special cell in which all components were suspended from a plastic insulating cover at the top of the cell and allowed to hang in the hot zone without touching each other or the cell envelope. The cell has been thoroughly described elsewhere (7). The indicator electrode was a 1 cm^2 disc of platinum or of the refractory metal under study suspended in the electrolyte by a fine wire without the use of any insulator. The counter electrode was in almost all cases the metal under study. Cathodic chronopotentiograms at various levels of current, temperature, and concentration were run on a solution of K$_2$TaF$_7$ in KF-LiF-NaF eutectic similar to that from which tantalum is plated. They showed that tantalum is reduced to metal in two steps according to the scheme:

$$(TaF_7)^{-2}(\ell) + 3e \rightarrow TaF_2(s) + 5F^-(\ell) \qquad [5a]$$

$$TaF_2(s) + 2e \rightarrow Ta^0(s) + 2F^-(\ell) \qquad [5b]$$
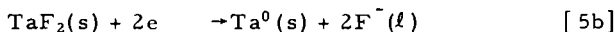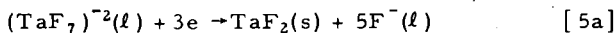
The first step is reversible and diffusion controlled. The second step by which the metal is produced, is irreversible and not diffusion controlled. Cathodic-anodic chronopotentiometry, in which a cathodic pulse of a few tenths of a second is followed immediately by an anodic pulse, serves to identify the intermediate, TaF$_2$, as a material very slightly soluble in the electrolyte. Its existence as a solid film on the electrode is believed to be the source of the irreversibility of the second step. Since the first step is diffusion controlled, the diffusion coefficient of the reacting species and activation energy for diffusion could be calculated from the data and they were shown to be of magnitude expected for an ion such as $(TaF_7)^{-2}$ which had been shown by IR spectroscopy to be the only significant tantalum-containing species present in solution.

A similar study with a solution of K$_2$NbF$_7$ in the same solvent showed a three step reduction:

$$(NbF_7)^{-2}(\ell) + 1e \rightarrow (NbF_{7-x})^{(3-x)-}(\ell) + xF^-(\ell) \qquad [6a]$$

$$(NbF_{7-x})^{(3-x)-}(\ell) + 3e \rightarrow NbF(s \text{ or } \ell) + (6-x)F^-(\ell) \qquad [6b]$$

$$NbF(s \text{ or } \ell) + 1e \rightarrow Nb^0(s) + F^-(\ell) \qquad [6c]$$

The first two steps are diffusion controlled and reversible, the last step is not diffusion controlled and irreversible. Cathodic-anodic chronopotentiometry showed that the intermediate produced in step 2, NbF, is only slightly soluble in a solution in which the mean valence of niobium is close to 4, but is rapidly attacked and dissolves in a solution in which the mean valence of niobium is 5. It is significant that in order to plate niobium, the mean valence of the solution must be less than 4.2, while in the case of tantalum coherent plates can be obtained from a pentavalent solution. In the latter case the intermediate is not attacked or dissolved by the pentavalent solution. As in the case of tantalum, the irreversibility of the metal producing step [6c] is believed to arise from a solid film of NbF on the electrode.

The study of zirconium deposition by chronopotentiometry was made difficult by interference of an alkali metal reduction wave with that of zirconium, but it was shown that the plating occurs as a single 4-electron irreversible reduction. The irreversibility is believed to arise from a corrosion reaction in which potassium metal is produced by attack of the zirconium by the electrolyte: i. e., $Zr + 4KF \rightarrow ZrF_4 + 4K(g)$.

Chronopotentiometric studies of the reduction of molybdenum and tungsten solutions to metal were made difficult by the instability of the very dilute solutions required for chronopotentiometric work. While the plating solutions are stable, the 10- to 50-fold dilutions required for chronopotentiometry are not. However, it was shown that in both cases the metal is produced in single step irreversible reductions. The irreversibility is believed to arise from the slow dissociation of a polynuclear to mononuclear anion preceding the reduction step.

The chronopotentiogram of $Cr^{3+} \rightarrow Cr^0$ showed a reversible step, $Cr^{3+} \rightarrow Cr^{2+}$ followed by the irreversible step $Cr^{2+} \rightarrow Cr^0$. The origin of the irreversibility has not been ascertained. That for $Fe^{3+} \rightarrow Fe^0$ showed two diffusion-controlled reversible steps $Fe^{3+} \rightarrow Fe^{2+} \rightarrow Fe^0$. It is significant that in the cases of iron and of nickel, coherent deposits cannot be obtained. Only dendrites can be formed over a thin diffusion layer of metal. The nickel reduction is also probably reversible, or very nearly so (6).

These results suggest that the necessary, though not sufficient condition for the electrodeposition of dense, coherent, thick deposits of metals from molten salts is that there be some irreversibility in the metal producing step of the electrode process. It is probable that the solid films, corrosion of the electrode, or slow chemical steps which cause the irreversibility inhibit the continued growth of dendrites and foster nucleation of new crystals.

BIBLIOGRAPHY

1. P. Delahay, New Instrumented Methods in Electrochemistry, Chap. 8, Interscience, New York (1954).

2. G. J. Janz, F. Colom and F. Saegusa, J. Electrochem. Soc., 107, 581 (1960). G. J. Janz and F. Saegusa, ibid., 108, 663 (1961).

3. M. L. Kronenberg, ibid., 109, 753 (1962).

4. H. A. Laitinen and R. A. Osteryoung in "Fused Salts," Ed. B. R. Sundheim, McGraw Hill, N. Y. pp. 265-272 (1964).

5. A. D. Graves, G. J. Hills and D. Inman, "Advances in Electrochemistry and Electrochemical Engineering, Vol. 4, Ed. Paul Delahay, Interscience, N. Y., pp. 162-166 (1966).

6. D. L. Manning, J. Electroanalyt. Chem., 6, 227 (1963); ibid., 7, 302 (1964); D. L. Manning and G. Mamantov, ibid., 7, 102 (1964).

7. S. Senderoff and G. W. Mellors, Science 153, 1475 (1966); J. Electrochem. Soc., 112, 840 (1965); Ibid., 113, 66 (1966).

   G. W. Mellors and S. Senderoff, ibid., 112, 266 (1965); 113, 60 (1966); Can. Pat. 688,546 (1964).