JOURNAL OF APPLIED ELECTROCHEMISTRY 11 (1981) 325–333

The breakdown of passive films on active metal anodes by halide ions in oxidizing molten salts

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Received 22 July 1980

The various effects of halide ions on calcium, zinc and magnesium anodes in oxidizing molten salts can be related to a corrosion model involving a nonstoichiometric passive film containing an excess of metal ions. Competitive adsorption between passivating and aggressive anions attracted to the positively charged surface determines the stability of the film. The addition of chloride ions in molten $LiNO_3$ leads to pitting corrosion of the calcium anode and improvement of the open-circuit potential by as much as 1.3 V. In molten $NaNO_3$ and KNO_3, the formation of passivating peroxide and superoxide anions greatly diminishes the effects of added chloride ions on the calcium anode. In molten $LiClO_4$ and $NaClO_3$, breakdown of the passive film occurs spontaneously due to the direct reaction of calcium with the molten oxyhalide salt to produce sufficient chloride ions to activate the anode. The best performance of the calcium anode is obtained in the oxyhalide molten salts.

1. Introduction

The use of active metal anodes in oxidizing electrolytes requires the presence of a passivating film that restricts the direct reaction of the anode with the solution, yet readily permits the passage of ions across the film during electrochemical discharge. In lithium/thionyl chloride cells, the protective film is reported to be lithium chloride [1–3], while in lithium/water systems the passivating film consists of lithium oxide and lithium hydroxide [4, 5]. In calcium/molten nitrate systems, cell performance is determined largely by a protective calcium oxide film [6]. The addition of certain halide salts that promote pitting corrosion can greatly improve both the electrode kinetics and the open-circuit potential of the calcium anode in molten nitrate electroltyes [7]. This study reports the investigation of halide effects on the passivating film formed on calcium and other active metal anodes in molten nitrates, nitrites, chlorates and perchlorates.

The major motive for this work was to improve the performance of active metal anodes used in thermal batteries in which the molten salt serves both as the electrolyte and as the oxidizer [6, 8]. Another important motive was to obtain a better understanding of the corrosion process involved in the breakdown of passivating films. Specific anion effects on corrosion are well documented in the literature [9–11], yet there is a general lack of agreement on the manner in which the anions operate [11, 12]. Proposed mechanisms for corrosion often do not give proper consideration to effects due to the composition of the electrolyte [10]. An even larger problem is the fact that there is no general recognition, as yet, of a specific theory that explains the passivity of metals [13–14].

2. Experimental

Measurements were generally made at a constant temperature of 350° C in a shallow platinum lid similar to that described previously [15]. A fibreglass filter (Gelman, type A, 0.3 mm thickness) was used as a separator between the electrodes and the platinum lid. The lid was placed on a ceramic hot-plate and the working and counter electrodes were mechanically lowered, side-by-side, until they were in contact with the fibreglass filter. After positioning the L-shaped reference electrode (0.1 m Ag^+/Ag) and thermocouple probe, the system was heated to above 100° C before the electrolyte

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salt (~0.6 g) was added. Upon melting, most of the electrolyte was contained by the thin fibreglass filter, thus minimizing temperature gradients and convection effects. All salts used were reagent grade and were dried in a vacuum oven overnight or longer at 130° C prior to use. Several tests were conducted in a dry box (Vacuum/Atmospheres) containing argon to eliminate any effects due to the possible presence of water.

The working electrode generally consisted of a calcium disc (ROC/RIC, 99%), 1.25 mm thick and 6.35 mm in diameter (0.32 cm^2), spot-welded to a Ca/Fe bimetallic disc of the same diameter but only 0.3 mm in thickness. The aluminium lead wire was then spot-welded to the Fe side of bimetal, and the back and edges of the disc were masked off by a thin layer of Sauereisen cement (No. 1). A nickel disc with a nickel lead wire was used as the counter electrode. Studies of magnesium, zinc and aluminium were made in a similar manner except that no bimetal was used in preparing the electrodes.

All of the open-circuit, constant current and potentiostatic studies were made with the use of a digital PAR Model 173 potentiostat/galvanostat. The potential of the anode with respect to the reference electrode as well as the cell voltage were continually recorded using a strip chart recorder (HP 7100B). In the more critical experiments, the potential of the anode versus time was also monitored with an *X–Y* recorder (HP 7047A). The temperature was read to 1° C using a Fluke Model 2165A digital thermometer readout, and the cell potential was displayed by a Fluke Model 8040A multimeter. The cell resistance was measured periodically with a Hewlett-Packard milliohmmeter (Model 4328A) designed to avoid measurement errors due to contact potential differences and electrolyte polarization.

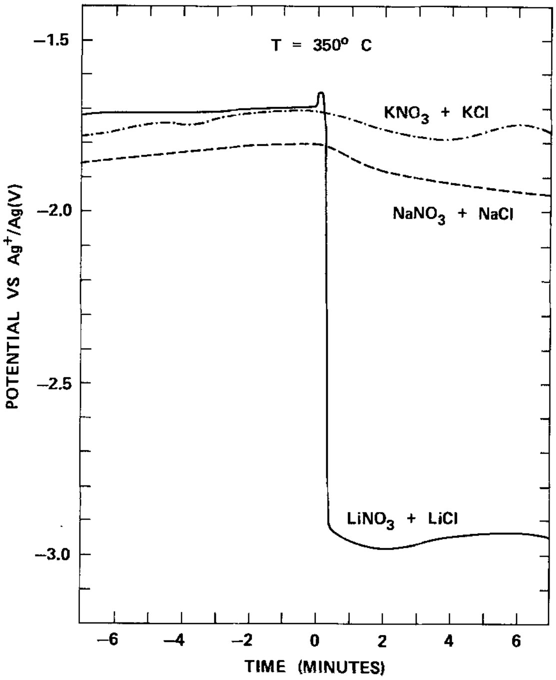

Fig. 1. Effects of additions of 10 mol% chloride salts on the open-circuit potentials of the calcium anode in molten KNO$_3$, NaNO$_3$ and LiNO$_3$ at 350° C. Chloride additions were made at time zero.

3. Results

The behaviour of the calcium anode in molten nitrates depends greatly upon the control of the passivating calcium oxide film. For example, the calcium anode in molten LiNO$_3$ at 350° C appears to establish a fairly stable open-circuit potential versus the Ag$^+$/Ag reference electrode; however, the addition of LiCl (10 mol%) produces a dramatic shift in potential to a value about 1.3 V more negative. Typical effects on the open-circuit potential of the calcium anode by additions of 10 mol% chloride salts are given in Fig. 1. The effect of chloride ions on the calcium anode potential is much greater in molten LiNO$_3$ than in either molten NaNO$_3$ or KNO$_3$. A summary of similar studies of the effects of various halide salts on the open-circuit potentials of the calcium anode at 350° C is given in Table 1. In every case, the effects of halide additions were larger in molten LiNO$_3$ than in molten NaNO$_3$ or KNO$_3$. Studies in molten nitrites also showed that chloride additions had a greater effect on the calcium anode in LiNO$_2$ than in NaNO$_2$. A slight decrease in cell resistance was often observed shortly following the chloride addition in experiments exhibiting large changes in potentials; for example, in the molten LiNO$_3$ experiment shown in Fig. 1, the cell resistance dropped from 8 to 6 Ω within a minute or two of the LiCl addition.

In molten LiClO$_4$, a sudden shift in the open-circuit potential of the calcium anode occurs spontaneously between 240–280° C without the addition of any extraneous chloride ions (Fig. 2).

Table 1. Effects of halide salt on the calcium anode open-circuit potential at 350° C.

Electrolyte[a]	E^{b}_{A}(before) (V)	E^{b}_{A}(after) (V)	ΔE_A(V)
$LiNO_3$, NaF	−1.66	−2.27	−0.61
$LiNO_3$, NaCl	−1.66	−2.96	−1.30
$LiNO_3$, NaBr	−1.63	−2.80	−1.17
$LiNO_3$, NaI[c]	−1.63	−2.59	−0.96
$LiNO_3$, LiCl	−1.67	−3.01	−1.34
$LiNO_3$, LiCl[d]	−1.77	−3.05	−1.28
$LiNO_3$, KCl	−1.71	−3.02	−1.31
$LiNO_2$, LiCl	−1.88	−3.01	−1.13
$NaNO_3$, NaF	−1.84	−1.94	−0.10
$NaNO_3$, NaCl	−1.77	−1.95	−0.18
$NaNO_3$, NaCl[d]	−1.72	−2.00	−0.28
$NaNO_3$, NaBr	−1.90	−2.44	−0.54
$NaNO_3$, NaI	−1.96	−2.46	−0.50
$NaNO_3$, LiCl	−1.84	−2.40	−0.56
$NaNO_2$, NaCl	−2.10	−2.16	−0.06
KNO_3, NaF	−1.78	−1.80	−0.02
KNO_3, NaCl	−1.79	−2.33	−0.54
KNO_3, NaBr	−2.02	−2.65	−0.63
KNO_3, NaI	−1.90	−2.81	−0.91
KNO_3, LiCl	−1.89	−2.20	−0.31
KNO_3, KCl	−1.71	−1.91	−0.20

[a] Amount of halide salt added was 10 mol%.
[b] Potentials were measured versus a 0.1 m Ag^+/Ag reference electrode.
[c] Violet iodine vapour evolved.
[d] Test conducted in a dry box containing argon.

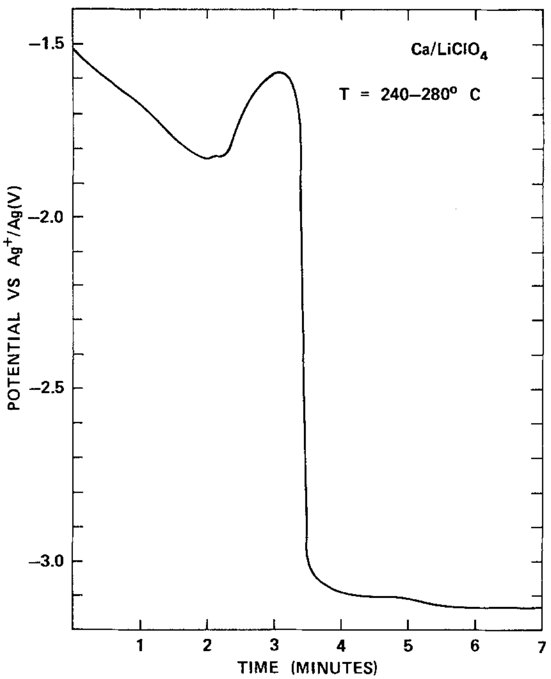

Fig. 2. Spontaneous change in the open-circuit potential of the calcium anode in molten $LiClO_4$ as the temperature increases from 240 to 280° C.

This is most likely due to a direct reaction of calcium with $LiClO_4$, such as

$$2Ca + LiClO_4 \rightarrow 2CaO + O_2 + LiCl \quad (1)$$

which produces sufficient chloride ions to activate the anode. A short period of slight gas evolution could be detected at the anode at about the time of the sudden activation. The open-circuit potential of the calcium anode in molten $LiClO_4$ at 350° C was generally slightly more negative than that observed in molten $LiNO_3$ with 10 mol% chloride ions added. Spontaneous activation of the calcium anode also occurred in molten $NaClO_3$ to give about the same potential observed in molten $LiClO_4$.

Fig. 3 presents the effect of current density on the potential of the calcium anode in molten nitrates and perchlorates at 350° C. The polarization upon discharge generally showed the same trends as found from open-circuit measurements. The effect of added chloride was again much greater in molten $LiNO_3$ than in $NaNO_3$. Kinetics for the discharge of the calcium anode were best in molten $LiClO_4$ as shown by the most electronegative potentials observed and by the small overvoltages, even at high current densities. Studies of the calcium anode discharge in molten $NaClO_3$ gave results practically identical to the results shown for molten $LiClO_4$.

Fig. 4 shows the effect of added LiCl on the open-circuit potentials of magnesium, zinc and aluminium electrodes in molten $LiClO_4$ at 350° C. Although the potential shifts are smaller than observed with calcium, definite changes were observed shortly after the addition of the LiCl. For aluminium, the only effect was that a slowly increasing potential changed to a slowly decreasing potential.

Potentiostatic studies of the calcium and magnesium electrodes in molten $LiNO_3$ are presented in Fig. 5. Each electrode was held at a fixed potential while the current was recorded as a function of time. Addition of 10 mol% LiCl produced sharp changes in the current, suggesting breakdown of the passivating film. For the experiments shown in Fig. 5, the magnesium electrode was potentiostatted at −1.700 V (slightly anodic to its −1.74 V open-circuit potential), while the calcium elec-

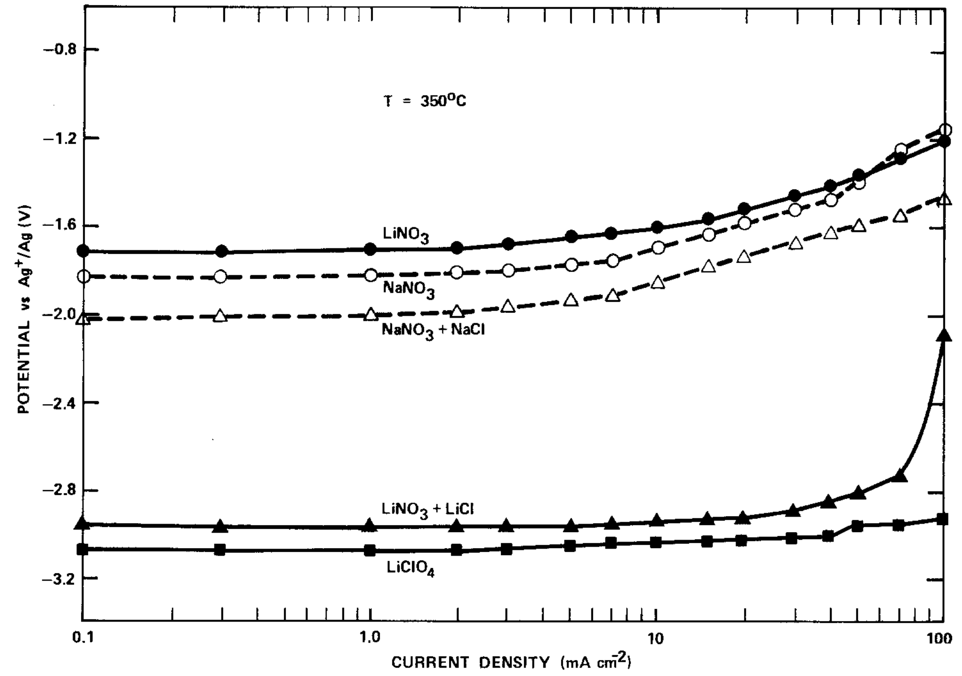

Fig. 3. Effect of current density on the potential of the calcium anode in molten $LiNO_3$, $LiNO_3$ + 10 mol% LiCl, $NaNO_3$, $NaNO_3$ + 10 mol% NaCl and $LiClO_4$ at 350° C. Geometrical electrode areas were 0.32 cm^2.

trode was left at open-circuit before potentiostatting at −2.400 V (considerably cathodic to its −1.70 V open-circuit potential). Potentiostatting the calcium electrode close to its open-circuit potential gave extremely high current surges upon addition of LiCl. Table 2 presents a summary of the potentiostatic studies of the effect of LiCl additions on calcium electrodes. Potentiostatting the calcium electrode at more electronegative potentials reduces the effect of added LiCl until practically no effect is observed at potentials more negative than about −2.5 V.

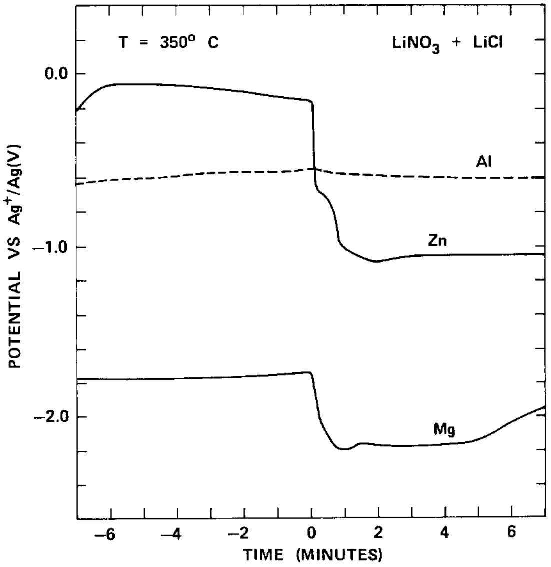

Fig. 4. Effects of additions of 10 mol% LiCl on the open-circuit potentials of aluminium, zinc and magnesium electrodes in molten $LiNO_3$ at 350° C. Chloride additions were made at time zero.

Corrosion studies of calcium metal at 350° C showed that a dark film forms on the calcium surface within a few minutes of immersion in molten $LiNO_3$. When LiCl is added to the molten $LiNO_3$, the film on the calcium gradually fades and the calcium surface even becomes bright in places. Bright areas on calcium were also observed in molten $LiClO_4$, suggesting similar effects due to the chloride ions produced by Reaction 1. The bright and dark areas on the calcium surface suggest the presence of anodic and cathodic regions for the corrosion reaction [16]. Examinations using a microscope showed that many pits of various sizes and depths formed on calcium immersed for 30 minutes in molten $LiNO_3$ containing LiCl, while a fairly uniform film with only a few pits formed on calcium in pure $LiNO_3$. These results provide further evidence that the

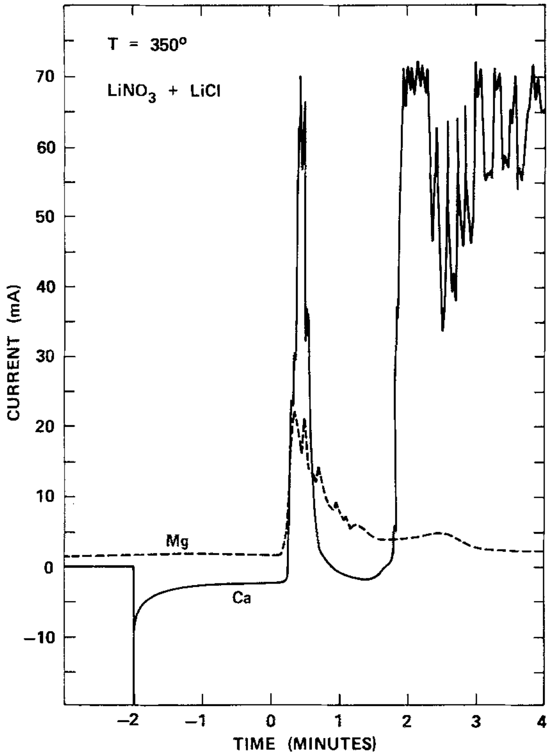

Fig. 5. Potentiostatic studies of the effects of additions of 10 mol% LiCl on calcium and magnesium electrodes in molten $LiNO_3$ at 350° C. The magnesium electrode was potentiostatted at −1.700 V while the calcium electrode was switched from open-circuit to −2.400 V at time = −2 minutes. Chloride additions were made at time zero. Geometrical electrode areas were 0.32 cm^2.

passivating anodic film is greatly modified by corrosion reactions induced by chloride ions. Studies in molten salts offer the advantage of relatively rapid corrosion processes, hence the variables affecting corrosion are more readily investigated than for the slower corrosion processes occurring at normal temperatures.

Table 2. Potentiostatic studies of the activation of the calcium anode in molten lithium nitrate at 350° C by the addition of 10 mol% lithium chloride

Anode potential (V)	*Peak current density* (mA cm^{-2})	*Activation time* (s)
−1.65	750	< 30
−2.20	650	< 30
−2.30	220	< 30
−2.40	90	< 30
−2.50	20	~ 200
−2.80	–	No effect

4. Discussion

A schematic model, presented in Fig. 6, can be used to explain the various anion effects observed for the calcium anode in oxidizing molten salts and seems to have general application to other metal–electrolyte systems involving passivating films. The proposed model involves two different interfaces due to the presence of the protective film represented by M_xA_y. At the metal–M_xA_y interface, the double layer formed consists of surplus electrons in the metal and an excess of metal ions M^{z+} within the nonstoichiometric film. The excess of positive metal ions within the M_xA_y film, in turn, electrostatically attracts an excess of anions from the surrounding electrolyte to the M_xA_y–solution interface where their adsorption on the protective film can occur in a manner similar to specific anion adsorption on a positively charged elecrode surface. Due to the charge reversal produced by this positively charged film, anions rather than cations are attracted from the solution. Competitive adsorption between passivating anions and aggressive anions determines the stability of the film.

For the calcium anode in molten nitrates, the protective film consists of insoluble calcium oxide containing an excess of calcium ions that produce a positive shift from the true equilibrium potential [7]. Nitrate ions attracted to the calcium oxide–solution interface act as passivating agents by repairing the oxide film when breaks occur. The displacement of NO_3^- ions from the calcium oxide surface by the added Cl^- ion hinders this repair process and leads to thinning of the oxide film and pitting corrosion. As the excess calcium ions pass into the solution, the true equilibrium potential is approached. The addition of NaF has a much smaller effect than NaCl on the calcium anode in molten $LiNO_3$ (Table 1). Fluoride ions, known for their lack of specific electrode adsorption [17, 18], cannot readily displace the nitrate ions from the calcium oxide surface. A similar anion effect with calcium is found in aqueous electrolytes where passivation occurs at high concentrations of NaOH and breakdown of this passivation is produced by the addition of NaCl [19]. The OH^- ions probably act as the passivating agent in this system, and the displacement of OH^- by Cl^- at the film–solution interface leads to the breakdown of passivity.

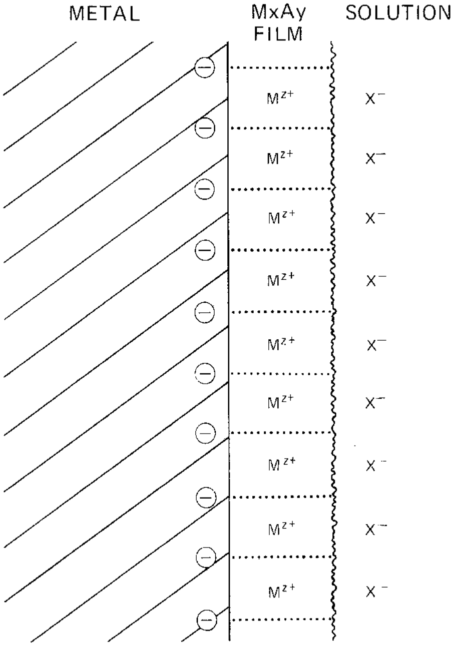

Fig. 6. Schematic model for relating anion effects on corrosion. The nonstoichiometric film is represented by M_xA_y, M^{z+} represents the excess metal ions within the film, and X^- represents the anions electrostatically attracted to the film–solution interface. Actual films will not necessarily be uniform and may vary considerably in thickness.

The major challenge for the model presented in Fig. 6, or for any other model or theory proposed, is to explain the striking difference between the effects on the calcium anode of added chloride ions in molten $LiNO_3$ and molten $NaNO_3$ or KNO_3. Why does the addition of chloride ions produce much smaller effects on the calcium anode in molten $NaNO_3$ and KNO_3 than in molten $LiNO_3$ (Figs. 1 and 3 and Table 1)? The key to this difference can be found by consideration of the direct reaction of molten nitrates with calcium

$$14Ca + 6NO_3^- \rightarrow 14CaO\downarrow + 2N_2\uparrow + N_2O\uparrow + 3O^{2-} \qquad (2)$$

to produce excess oxide ions [7, 20]. Previous work has shown that oxide ions are relatively stable in molten $LiNO_3$ and simply precipitate as insoluble Li_2O [21]. In the presence of large metal cations, however, oxides are more reactive and preferentially form the more soluble peroxides in molten $NaNO_3$ and superoxides in molten KNO_3 [21–25]. Therefore, in molten $LiNO_3$, the added Cl^- ions need only to compete with passivating NO_3^- ions for adsorption at the CaO–solution interface and readily cause extensive breakdown of the passivating oxide film. In molten $NaNO_3$ and KNO_3, the formation of the passivating O_2^{2-} and O_2^- anions blocks the aggressive action of the added Cl^- ions, hence smaller potential shifts for the calcium anode are observed (Figs. 1 and 3 and Table 1). The larger and more polarizable O_2^{2-} and O_2^- anions offer difficult competition to the Cl^- ions for specific adsorption at the film–solution interface. In molten $NaNO_3$ and KNO_3, the larger Br^- and I^- ions tend to compete more effectively with O_2^{2-} and O_2^- than the smaller halide ions for adsorption at the positively charged passivating film (Table 1).

The positive electric field around the metal cation greatly affects the chemistry of alkali metal compounds. For example, the alkali metals burn in air to yield lithium monoxide, sodium peroxide and potassium superoxide [26]. The strong electric field around the small lithium ion restricts the spread of negative charge from the oxygen anion towards another oxygen atom, making the formation of higher oxides difficult. Similar effects apparently operate in molten nitrates, since higher oxides form only in molten $NaNO_3$ and KNO_3. Previous studies showed that Li_2O is stable in both molten $LiNO_3$ and KNO_3, while Na_2O reacts in the KNO_3 melt [21]. Cyclic voltammetric studies in molten nitrates also show decreasing stability of the oxide with increasing radius of the alkali metal cation [21]. The metal cation also exerts striking effects on the electrode reduction of molten nitrates [15, 21]. The observation that molten $LiNO_3$ is more readily reduced than molten $NaNO_3$ or KNO_3 is reflected by the oxidation of added I^- ions to I_2 vapour in molten $LiNO_3$, whereas no apparent reaction occurs in molten $NaNO_3$ or KNO_3 (Table 1). This obviously diminishes the effectiveness of added iodide ions in molten $LiNO_3$.

Although experimental care was exercized to minimize water contamination, $LiNO_3$ is extremely hygroscopic and can retain water even at 350°C [21]. Therefore, several experiments were conducted in a dry box filled with argon to determine if water retention by $LiNO_3$ is a factor in the different behaviour observed for the calcium anode in this salt. Tests of the calcium anode in molten $LiNO_3$ and $NaNO_3$ in the dry box gave chloride ion effects quite similar to those observed in the open atmosphere (see Table 1). The lack of any large effects due to water was not unexpected since previous cell studies using $LiNO_3$ in closed and open systems showed that the presence of air or moisture had little effect on test results [6]. The only significant difference in the dry box studies was the very stable calcium anode potential in molten $LiNO_3$ following the addition of LiCl. In the open atmosphere, it is likely that film-repairing processes involving oxygen or water may occur that cause changes in the potential. The calcium anode potential in molten $NaNO_3$ responded slowly to the addition of NaCl and showed fluctuations similar to tests in the open atmosphere. Competing effects involving film breakdown and repair due to Cl^- and O_2^{2-} ions could explain this behaviour.

Another challenge for any model or theory is to explain the excellent results for the calcium anode in both molten $LiClO_4$ and $NaClO_3$, whereas results in molten $LiNO_3$ differ considerably from those in molten $NaNO_3$. The direct reaction of calcium with molten $LiClO_4$ or $NaClO_3$ forms chloride ions and oxygen gas rather than the excess oxide ions formed in molten nitrates, hence no peroxide or superoxide ions result. According to the model presented in Fig. 6, therefore, the Cl^- ions produced in the molten oxyhalide salts need only to compete with ClO_4^- or ClO_3^- anions for adsorption at the film–solution interface. These oxyhalide anions apparently offer even less competition for adsorption than nitrate ions, thus Cl^--induced breakdown of the passivating film occurs readily. In support of these arguments, the thermal decomposition of $LiClO_4$ and $NaClO_3$ also yields mostly chlorides and oxygen as final products rather than oxide and chlorine formation [27].

These studies of calcium in molten $LiClO_4$ and $NaClO_3$ illustrate how the normally passivating ClO_4^- and ClO_3^- anions can produce the effects of aggressive anions by undergoing reactions that form chloride ions. The breakdown of the passivity of aluminium in aqueous ClO_4^- solutions also suggests reaction with the metal to produce chloride ions [11, 28].

The thinning of the passivating calcium oxide film observed in the presence of chloride ions may result from reactions such as

$$CaO + Cl^- \rightarrow CaO \ldots Cl^- \rightarrow Ca + OCl^- \quad (3)$$

whereupon the OCl^- formed probably decomposes to oxygen and Cl^-. By such formation and breaking of O–Cl bonds, chloride ions would act as a catalyst for the decomposition of calcium oxide in addition to hindering the repair of breaks in the film by passivating anions.

The model presented in Fig. 6 also provides an explanation for the rather large displacement of the open-circuit potential from the true equilibrium potential of the calcium anode. The build-up of excess calcium ions within the passivating film shifts the observed open-circuit potential in the positive direction. This effect can be demonstrated mathematically by the simple reactions

$$Ca \underset{k_c^0}{\overset{k_a^0}{\rightleftharpoons}} (Ca^{2+})_{p1} + 2e \quad (4)$$

$$(Ca^{2+})_{p1} + \text{solvent} \rightleftharpoons Ca^{2+} \ldots \text{solvent} \quad (5)$$

where the parentheses denote a substance within the passivating layer. For the electron transfer step, the current density would be given by

$$i = nFk_a^0 \exp(\alpha nFE/RT) - nFk_c^0 (a_{Ca^{2+}})_{p1} \times \exp[-(1-\alpha)nFE/RT] \quad (6)$$

where k_a^0 and k_c^0 are the formal anodic and cathodic rate constants at zero potential and n is the number of electrons involved in the reaction [29]. The observed open-circuit potential (OCP) where $i = 0$ would then be

$$E_{OCP} = \frac{RT}{nF} \ln \frac{k_c^0}{k_a^0} + \frac{RT}{nF} \ln (a_{Ca^{2+}})_{p1}. \quad (7)$$

Due to the slow transport of calcium ions across the passivating film (Equation 5), true equilibrium is not readily obtained, hence E_{OCP} becomes more anodic as excess calcium ions form within the passivating layer. The breakdown of the passivating film by chloride ions allows the excess calcium ions to pass from the film into the solution, and as Equation 5 approaches equilibrium, E_{OCP} approaches

$$E_{eq} = \frac{RT}{nF} \ln \frac{k_c^0}{k_a^0} - \frac{RT}{nF} \ln K_{eq} + \frac{RT}{nF} \ln a_{Ca^{2+} \ldots \text{solvent}} \quad (8)$$

where K_{eq} is the equilibrium constant for Equation 5. Equation 8 is simply the Nernst equation for the calcium electrode reaction. Indirect evidence suggests that the mechanism for this electrode reaction may involve monovalent calcium ions [7].

The potentiostatic results given in Fig. 5 and Table 2 support the concept that excess metal ions are contained within the passivating film. According to Equation 7, forcing the potential to more negative values decreases the amount of calcium ions within the film, hence anion attraction to the film–solution interface would also decrease. For potentials more negative than about −2.5 V, the excess of calcium ions within the film diminishes to the extent that anions are no longer attracted to the film, hence the addition of chloride ions has little or no effect (Table 2). Chronopotentiometric studies of lithium in aqueous electrolytes also indicate the existence of a concentration gradient of metal ions across the oxide layer at open circuit [30].

In general, the normal atmospheric corrosion behaviour of any metal covered by a passive film, that is reasonably stable with respect to its environment, should show similar anion effects. Oxide films on metals such as aluminium, chromium and zirconium will generally be stable, as will the oxide film on iron when the environmental pH is sufficiently high. Any breaks in the protective film are readily repaired by some active agent in the environment such as oxygen, water or certain oxygen-containing anions. Chloride and other halide anions that adsorb strongly at the positively charged oxide surface, however, can displace the passivating agent from the surface, thereby preventing film repair when a break occurs. This will lead to thinning of the oxide film and pitting corrosion. Halide-induced pitting corrosion is well known for various metals protected by stable oxide films [9, 11, 12, 31].

5. Conclusions

The experimental results for active metal anodes in oxidizing molten salts, and the corrosion model presented, lend strong support to the competitive adsorption theory of the breakdown of passive films by halide ions. Other theories [11, 12] such as film penetration by halide ions, film defects, film doping or soluble complex formation cannot explain the differing chloride ion effects observed in molten $LiNO_3$ and molten $NaNO_3$ or KNO_3. Neither do these other theories account for the excellent performance of the calcium anode in both molten $LiClO_4$ and $NaClO_3$.

Acknowledgements

The author would like to thank Dr A. N. Fletcher and Dr S. W. Benson for helpful discussions relating to the interpretation of these results.

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