

The electrochemistry of nitrate–amide melts: reactions of the calcium anode in room temperature nitrate–amide melts

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The discharge characteristics of calcium anodes in room temperature nitrate–amide melts are strongly dependent on the acidity of the melt. A significant increase in the potentiostatic discharge current is noted on acidification of LiNO_3 –acetamide–urea melts with the strong acid NH_4NO_3 . Acidic species act to break down the passivating film on the anode. No significant depassivation is noted on addition of halides. Galvanostatic discharges at varying current densities and different melt compositions show the effects of a passivating film on the observed anode potential. Discharges of galvanic cells based on the calcium anode in nitrate–amide melt electrolytes have been demonstrated at current densities above 1 mA cm^{-2} using a AgCl cathode.

1. Introduction

In a separate study [1], we presented some of the physical and chemical characteristics of a novel class of ionic liquid electrolytes, the nitrate–amide melts. Several of these melts are found to show relatively high conductivities, melting points below room temperature and a characteristic, supercooled liquid phase. Melts of 0.2 mole fraction NH_4NO_3 or LiNO_3 in a solvent consisting of 0.6 mole fraction acetamide and 0.4 mole fraction urea[†] are unusually resistant to spontaneous nucleation and may be stored for long periods at -20°C without crystallization [1]. Both the LiNO_3 –amide and NH_4NO_3 –amide melts show glass transitions near -40°C .

Because of the remarkable stability of the supercooled liquid phase, the low toxicity of nitrates and amides and the relatively high room temperature conductivities that we have observed, nitrate–amide melts are attractive candidates for ambient temperature battery elec-

trolytes. To this end, we are investigating the characteristics of calcium anodes in room temperature nitrate–acetamide–urea melts.

Other workers have investigated the characteristics of several anodes in electrolytes using a molten acetamide solvent at or near 100°C [2, 3]. Some research has focused on the acid–base chemistry of amide melts, particularly as it affects the reduction characteristics of O_2 and a variety of cations [4–9].

This paper will detail the characteristic reactions of calcium anodes in two different nitrate–amide melts. Future communications will detail the characteristic reactions of several soluble and insoluble cathode materials in nitrate–amide melts as well as the performance and discharge characteristics of nitrate–amide electrolyte galvanic cells.

2. Experimental details

The acetamide and urea used were reagent grade

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† The 0.2 mole fraction nitrate (either LiNO_3 or NH_4NO_3) amide melts use a mixture of 0.6 mole fraction acetamide and 0.4 mole fraction urea as the amide component. This communication will use the term ‘ LiNO_3 –amide melt’ or ‘ NH_4NO_3 –amide melt’ to refer to 0.2 mole fraction nitrate in the acetamide–urea mixture.

chemicals (Eastman Kodak Chemical) dried over P_2O_5 under vacuum. A further purification of the acetamide was carried out only where indicated and consisted of recrystallization from spectro grade acetone and benzene. The final product from the recrystallization was dried overnight under vacuum at $40^\circ C$. All glassware contacting the melts was cleaned in chromic acid and rinsed repeatedly in Milli-Q water and spectro grade methanol or spectro grade acetone followed by thorough bake drying before use. The nitrate–amide melts were prepared in sealed pyrex vessels at $120^\circ C$ in a vacuum oven. Once prepared, the melts were cooled to room temperature, handled and stored in a glove bag with a dry atmosphere maintained at a relative humidity of less than 0.5%. Karl Fischer analysis of the melts showed water content to be below 0.05% (by weight of water).

The Pb/PbO quasi-reference electrode was constructed by isolating a lead wire in a melt-filled capillary. This quasi-reference appears to be quite stable for prolonged periods in all of the melts discussed here. Calcium anodes were prepared by spot-welding a calcium disc (6.3 mm diameter, 0.13 mm thick) to a calcium/iron bimetal disc. The calcium and bimetal discs were degreased either in cyclohexane or a cyclohexane–pentane mixture and then cleaned in a dilute solution of nitric acid in dimethyl formamide before spot-welding. Electrode lead wires were 18 or 22 gauge nickel wire spot-welded to the bimetal. Calcium samples for the corrosion studies were discs (6.33 mm diameter, 0.13 mm thick) cleaned in a nitric acid–dimethyl formamide solution.

Cell design was adapted from that described previously [10]. The electrolyte was held in a 37 mm diameter glass fibre filter disc (Gelman, type A) resting in a platinum crucible cover. The counter electrode was a polished platinum disc.

Electrochemical instrumentation used for this study included a constant current source (Keithley, model 225), a potentiostat/galvanostat (PAR, model 371), an x – y recorder (Houston Instruments, omnigraphic model 2000) and a y – t recorder (Houston Instruments, Omniscrite). In addition, a data logger system consisting of a thermal printer (Hewlett Packard, model 5150A) and four digital multimeters

(Hewlett Packard, model 3438A) was used to monitor experiments.

3. Results and discussion

Observations in molten acetamide at $100^\circ C$ have shown the rate of reaction of the amide with calcium to be fast and to evolve gaseous products that include hydrogen [2, 3]. In a separate study [1], we showed that the electrochemical stability region in room temperature nitrate–amide melts is considerably wider than the electrochemical stability region in pure amide melts over $100^\circ C$. Because of this ‘opening’ of the ‘window’ as the temperature decreases, we find the calcium anode to be more stable in nitrate–amide melts at room temperature than in the pure amide solvent at elevated temperatures.

Conventional methods for determining the electrochemical ‘window’ of nitrate–amide melts are hindered by the relatively high background current observed. The background current has several possible components including the presence of trace amounts of water, organic solvents and the contaminants resulting from amide decomposition. Preliminary window determinations in carefully purified electrolytes indicate an electrochemical stability region approximately 2V wide at room temperature for the nitrate–amide melts discussed here. Recrystallization of the acetamide does not appear to influence the background currents significantly.

Fig. 1 shows the ambient temperature ($23^\circ C$) current versus anode potential characteristics of calcium in the $LiNO_3$ –amide and NH_4NO_3 –amide melts. The curves were determined by applying a current step and noting the steady state anode potential. Superficially, both polarization curves are remarkably similar to those reported for the calcium anode in molten nitrates in the presence of depassivating chloride ions [11, 12].

The marked differences between the current versus anode potential curve of calcium in the $LiNO_3$ –amide and NH_4NO_3 –amide melts are attributable to the distinct differences in the structure, thickness and stability of the passive film formed in the two melts. In both melts, the

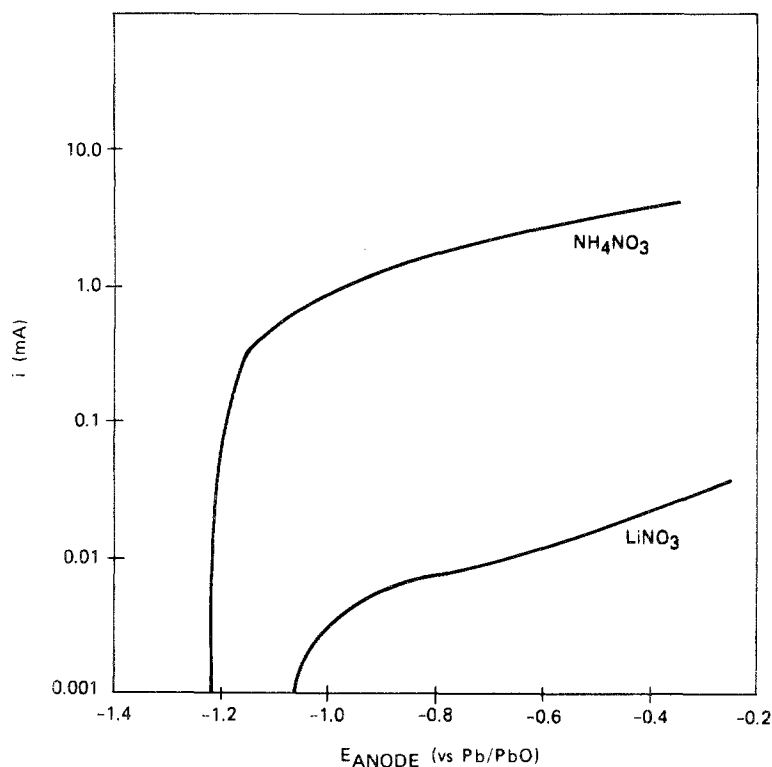
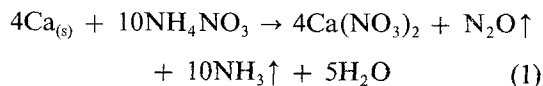


Fig. 1. Current (i) versus anode potential (E_{ANODE}) curves for calcium in the LiNO_3 -amide and NH_4NO_3 -amide melts at 23°C . The anode area was 0.32 cm^2 .

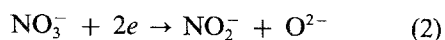
H^+ ions regulate film thickness much like Cl^- regulates the anode film thickness in molten nitrate electrolytes [11]. Much of the differences in anode polarization curves in the LiNO_3 -amide and the NH_4NO_3 -amide melts is thus directly attributable to differences in free acidic H^+ species concentration.

In the NH_4NO_3 -rich melts, the corrosion reaction at the anode is

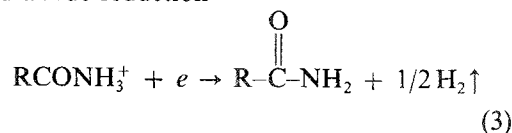


Thermodynamic calculations for this reaction yield an approximate E° of -3.08 V that is slightly higher than the observed open circuit potentials. This value does not account for the heats of solution of NH_4NO_3 or $\text{Ca}(\text{NO}_3)_2$ in the solvent. However, it does account for the presence of N_2O , H_2O and NH_3 in the gaseous products (as identified by gas chromatography and FT-IR).

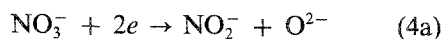
In the LiNO_3 -amide melts, the reduction of the melt by the anode is slightly more complicated and involves both nitrate reduction



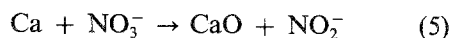
and amide reduction



We have found that high-rate electrolysis of the LiNO_3 amide melts leads to significant quantities of nitrite [1]. Furthermore, high current electrolysis produces a passive film on both platinum and gold cathodes. The passive film is soluble in water and is basic to litmus. This film may be produced by the reaction



When calcium metal is placed in the room-temperature LiNO_3 -amide melt, a grey-black passive film forms that dulls the shiny calcium surface. This film is composed of CaO produced according to the reaction



The CaO thus formed may then be attacked by the protic media to form a film of the hydroxide or a mixed oxide-hydroxide. We observe no

darkening that might be indicative of a thick passivating film on calcium anodes placed in room-temperature NH_4NO_3 -amide melts.

Calcium metal corrodes rapidly when immersed in the NH_4NO_3 -amide melt with evolution of several gaseous products including NH_3 , N_2O and H_2O . At room temperature, the reaction continues until the sample is completely consumed. The metal surface remains bright and there is no visual evidence for a passivating film. However, the initial, open circuit anode voltage (over 3 V) rapidly decays. This is indicative of passivating film formation. Interestingly, anode open-circuit potentials show a relatively large experimental scatter, while anode potentials on applied current are quite reproducible.

The passivating layer rapidly formed on calcium metal samples placed in the LiNO_3 -amide melt, causes gas evolution to slow as the metal passivates. Calcium samples stored in the room temperature LiNO_3 -amide melt show no significant weight loss over a 44-h period. At 75°C , one set of samples showed an average 30% weight loss over a 26-h period. A similar set of calcium samples placed in the NH_4NO_3 -amide melt at 75°C reacted completely and vigorously in less than 1 h. Because the products of the corrosion reaction in the LiNO_3 -amide melt are insoluble, care must be taken when using weight-loss data for a study of corrosion rates. This study does not attempt to present relative corrosion rates. Rather, we wish only to present the marked differences in anode corrosion reactions in the two melts.

It should be noted here that corrosion reaction rates (and observed current densities or anode potentials) in the nitrate-amide melts are particularly sensitive to moisture. The LiNO_3 -amide melt is hygroscopic and much more negative anode potentials are noted when the melt is exposed to ambient atmosphere (10–15% relative humidity) for periods as short as 15 min. The NH_4NO_3 -amide melt is far less hygroscopic.

Figs 2 and 3 show representative galvanostatic discharges of calcium anodes in the LiNO_3 -amide and NH_4NO_3 -amide melts at room temperature ($\sim 23^\circ\text{C}$). The relatively high rate capability of the calcium anode in the NH_4NO_3 -amide melt (Fig. 2) reflects the lack

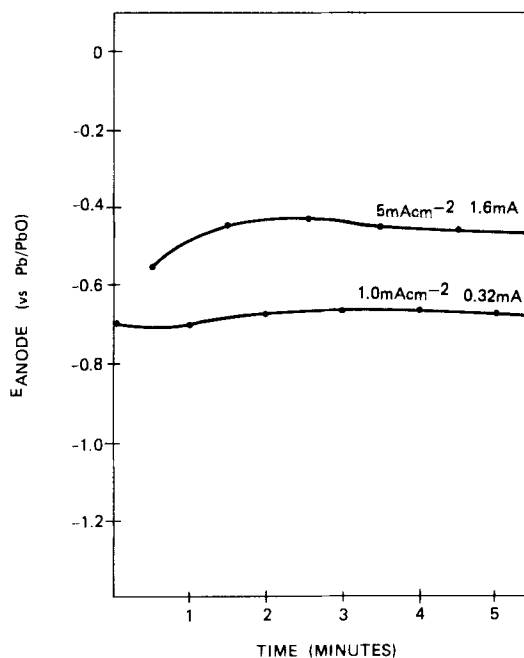


Fig. 2. Galvanostatic discharge curves for calcium anodes in the NH_4NO_3 -amide melt at 1 mA cm^{-2} and at 5 mA cm^{-2} . The temperature was 23°C and the anode area was 0.32 cm^2 .

of a stable passivating film on the anode in that melt. With increasing temperature, anode rate capability rises as does the calcium corrosion rate.

In the LiNO_3 -amide melt (Fig. 3), the significantly lower discharge rates shown are a reflection of the magnitude of the effect of the passivating film structure on the anode discharge characteristics. In the NH_4NO_3 -amide melt (Fig. 2), the film is thin or unstable and quite high current densities may be applied without severe polarization. In the LiNO_3 -amide melts, the film is quite thick. The migration of Ca^{2+} ions through the film into the solution is hindered, and relatively high anode overpotentials are noted at moderate or low current densities. These results are similar to those reported for the calcium anode in molten nitrates [11, 12].

Fig. 4 provides further illustration of the dramatic effect of the cation predominant in the melt (NH_4^+ versus Li^+) on the anode discharge characteristics. In Fig. 4, a calcium anode was held at constant potential of -0.500 V versus the Pb/PbO reference. The current obtained from the calcium anode in the LiNO_3 -amide

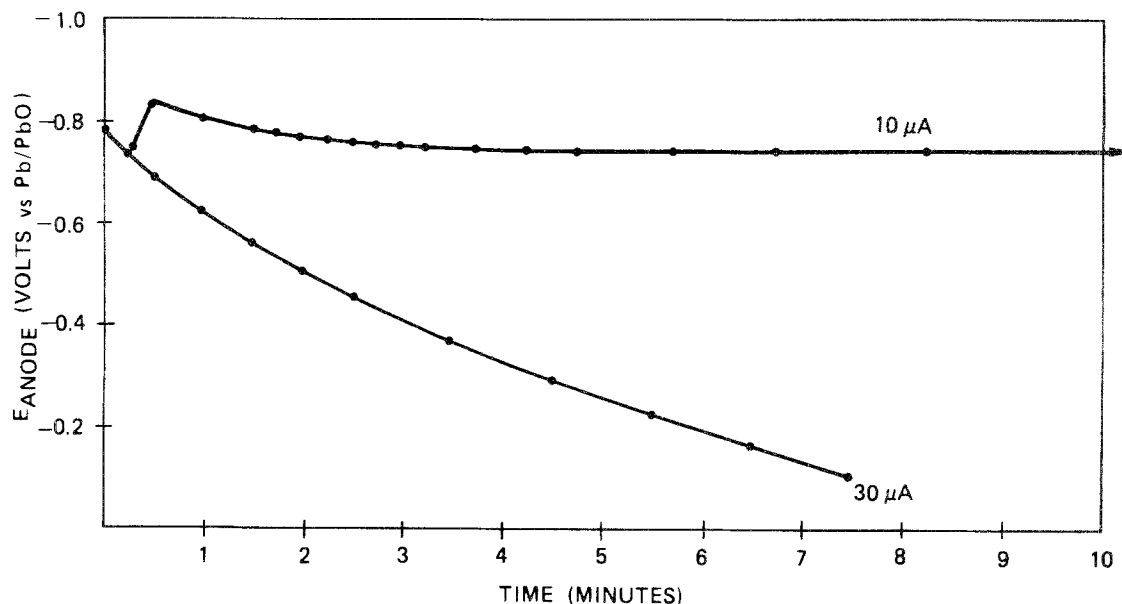


Fig. 3. Galvanostatic discharge curves for calcium anodes at 0.01 and 0.1 mA cm^{-2} in the LiNO_3 -amide melt at 23°C . The anode area was 0.32 cm^2 .

melt is significantly lower than in the NH_4NO_3 -amide melt.

In Fig. 5, as in Fig. 4, a calcium anode was held at -0.500 V versus the Pb/PbO quasi-reference electrode in the LiNO_3 -amide melt. At time 0, sufficient of the NH_4NO_3 -amide melt was added to bring the melt to 11 wt % NH_4NO_3 . The relatively slow increase in the anodic current is apparently a reflection of the

slowness of mixing in the quiescent electrolyte rather than any significant barrier to film breakdown. A similar effect is noted on addition of water or other Brønsted-Lowry acid to the melt. The relatively low solubility of most halides in the nitrate-amide melts prohibits their effective use as depassivating agents.

Fig. 6 demonstrates the discharge of a galvanic cell at 0.1 mA cm^{-2} and 23°C . The elec-

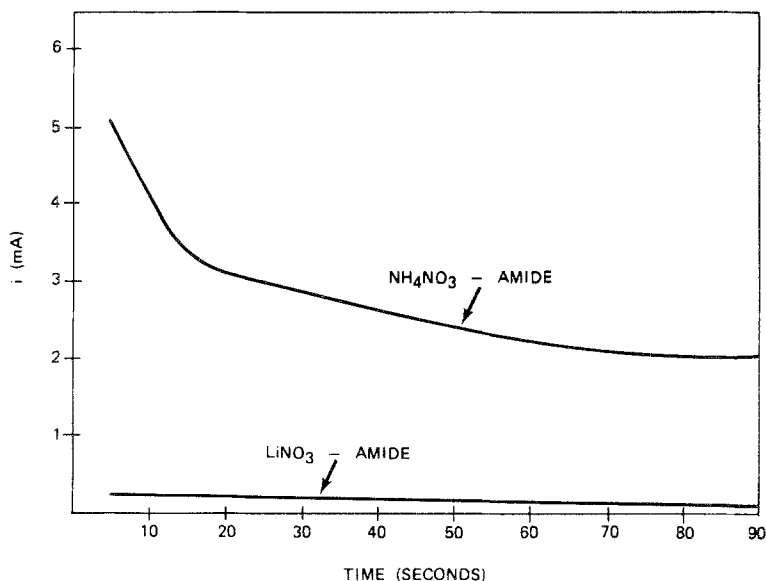


Fig. 4. Potentiostatic discharges of calcium anodes in the NH_4NO_3 -amide melts and LiNO_3 -amide melts. The anode potential was -0.500 V versus Pb/PbO . The temperature was 23°C and the anode area was 0.32 cm^2 .

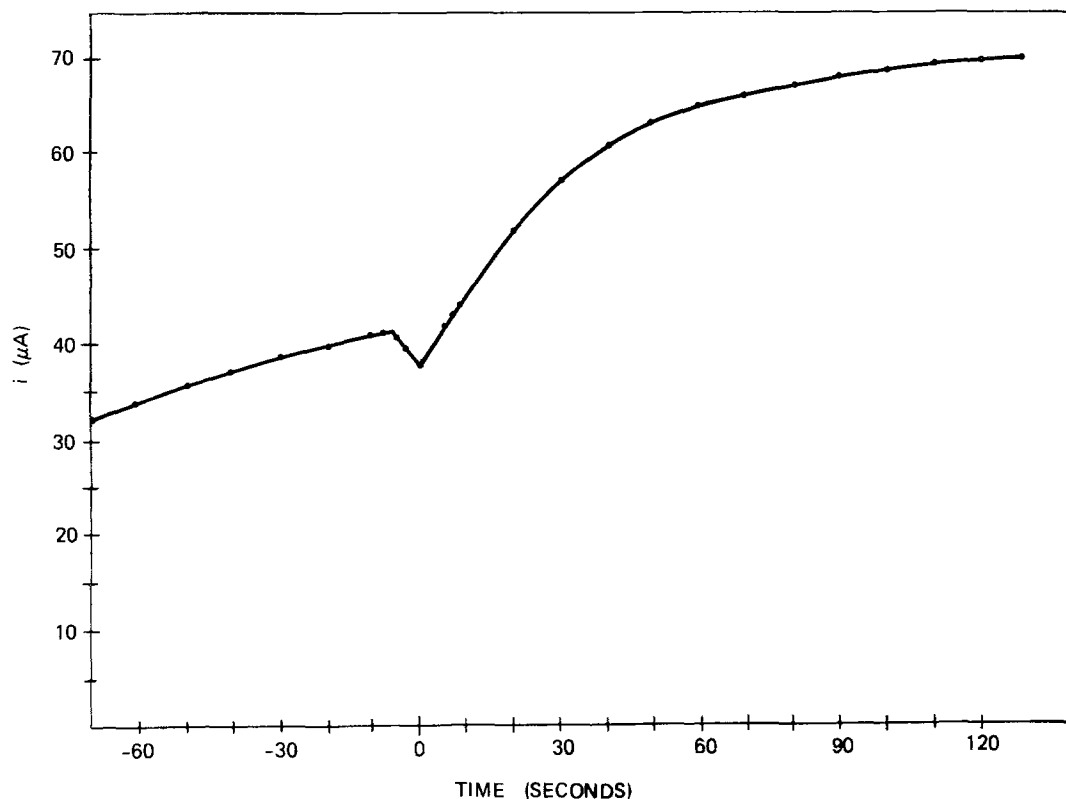


Fig. 5. Effect of the addition of the Brønsted-Lowry acid, NH_4NO_3 , on the discharge of calcium anodes at a constant potential of -0.500 V (versus Pb/PbO) in the LiNO_3 -amide melt. The NH_4NO_3 -amide melt was added at time 0 to bring the NH_4NO_3 content to 11 wt %. The total nitrate (NO_3^-), acetamide and urea mole fractions remained constant. The anode area was 0.32 cm^2 and the discharge temperature was 23°C .

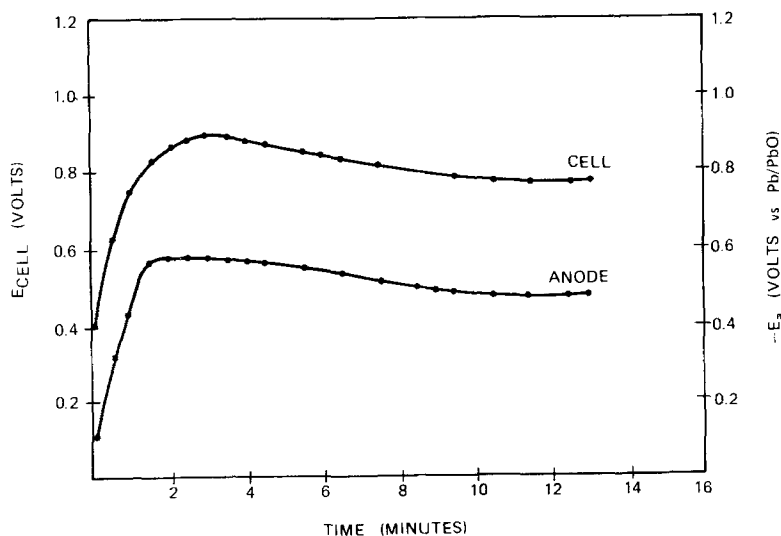


Fig. 6. Galvanostatic discharge of a representative Ca/AgCl cell using the LiNO_3 -amide electrolyte melt at 23°C . The cell area was 0.32 cm^2 and the current density 0.1 mA cm^{-2} .

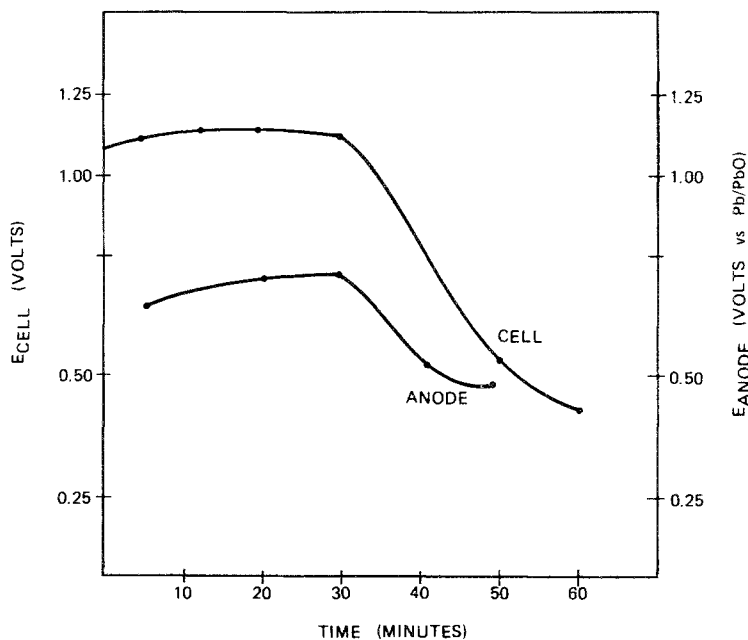


Fig. 7. Galvanostatic discharge of a representative Ca/AgCl cell using the NH_4NO_3 -amide electrolyte melt at 23°C . The cell area was 0.32 cm^2 and the current density 1.0 mA cm^{-2} .

trolyte was the LiNO_3 -amide melt. The anode was a calcium disc of 0.32 cm^2 area. The cathode was silver chloride pressed onto a nickel mesh. The separator was one sheet of the glass fibre filter paper saturated with the electrolyte. Fig. 7 shows a similar discharge at 23°C and 1.0 mA cm^{-2} for an identically constructed cell using the NH_4NO_3 -amide melt. The higher current-carrying capability of cells using the NH_4NO_3 -amide melt over those using the LiNO_3 -amide melt reflects differences in passivating film structure, melt conductivities and melt viscosities.

4. Summary

Calcium anodes discharged in LiNO_3 -amide melts show much higher anode polarizations than similar anodes discharged in NH_4NO_3 -amide electrolytes. This difference is attributed to the effect of melt acidity on passive film structure. Addition of the Brønsted-Lowry acid NH_4NO_3 to calcium anodes held at constant potential in the LiNO_3 -amide melt significantly increases the anodic current by breaking down the passivating film. The relatively low solubility of halides prevents significant depassivation by halide ions.

Corrosion rates, anode potential, and anode

current versus potential characteristics in the LiNO_3 -amide melt are a function of the water content of the melt. Exposure of the hygroscopic LiNO_3 -amide melts to the ambient atmosphere for more than a few minutes may invalidate experimental results. The NH_4NO_3 -amide melts are far less hygroscopic. Both melts show some promise as novel electrolytes for ambient temperature battery systems.

Galvanic cells based on calcium anodes, AgCl cathodes, and nitrate-amide electrolytes have been demonstrated at room temperature and useful current densities. Cells using the NH_4NO_3 -amide melt electrolyte show higher calcium corrosion rates but also show higher discharge rate capability than cells using the LiNO_3 -amide melt electrolyte.

Acknowledgements

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