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Room temperature discharge characteristics of Li/NH_4NO_3–$LiNO_3$–amide cells using silver salts as active cathode materials

G. E. McMANIS, A. N. FLETCHER, D. E. BLISS, M. H. MILES

Chemistry Division, Research Department, Naval Weapons Center, China Lake, California 93555-6001, USA

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The discharge characteristics of cells using lithium anodes in conjunction with nitrate–amide melt electrolytes and silver salt cathodes are presented. The use of insoluble or sparingly soluble silver salts as active cathode materials for ambient temperature galvanic cell cathodes can allow higher rate discharges than otherwise possible using melt reduction as the cathode reaction. The cathode materials studied were: Ag_2CrO_4, Ag_2MoO_4, Ag_2WO_4, Ag_3PO_4, Ag_2SO_4, $AgIO_3$, $AgIO_4$, AgF, AgCl, AgBr, AgI, Ag_4RbI_5 and Ag_2O. The reduction characteristics of silver ions added to nitrate–amide melts are also presented.

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1. Introduction

The electrochemistry of the lithium anode in non-aqueous media is an area of great technological importance and has been the subject of a great deal of recent research [1–3]. The high-cell voltages and inherently high-energy density of cells using lithium anodes make them attractive for both ambient temperature and thermal battery applications where gravimetric and volumetric energy density can be deciding factors in determining the feasibility of a system.

Unfortunately, the half-cell studies of the lithium anode provide less than half of the information necessary to construct a practical battery cell. A significant amount of research has also been directed toward the exploration of the potential utility of insoluble silver salts as cathode materials both for ambient temperature batteries [4–9] and for thermal battery [10, 11] applications. This study is one part of a series describing the development of an 'ambient temperature thermal battery'. This novel battery concept combines many of the inherent advantages of a thermal battery with the convenience of an ambient temperature battery. The thermal batteries in use today offer extremely high reliability and long shelf life. Although long shelf life reserve batteries using lithium anodes are known [12], the usual methods of activation are frequently quite complex and often result in a lower reliability than that obtainable from thermal batteries.

The ambient temperature thermal battery, like conventional thermal batteries, has an electrolyte that is solid and non-ionically conductive until the battery is activated by a heat source. Unlike the conventional thermal battery, the electrolyte consists of two distinct solid phases that melt together on activation to form a single, homogeneous liquid phase that does not solidify (either through freezing or through vitrification) until the ambient temperature falls below normal environmental minimums. After activation by a heat pulse, an ambient temperature thermal battery could cool to room temperature and still deliver useful electrical energy for prolonged periods. Another important advantage of this concept is that the electrolyte is solid and not electrically or ionically conductive until the activating heat source is applied. Hence, the ambient temperature thermal battery should retain the long shelf life and high reliability that is characteristic of the conventional thermal battery.

Typical military storage specifications require

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that a battery system be capable of storage at temperatures between −40 and 71° C. Thus, the mixtures chosen for the ambient temperature thermal battery task must have a melting point above 71° C and must either have a low vapour pressure at that temperature or have a meltable physical barrier that prevents diffusion of the amides and the possibility of premature activation. Those components must then mix rapidly on activation to form a eutectic composition that does not solidify above −40° C and that has a relatively high ionic conductivity at more reasonable discharge temperatures. These criteria are quite demanding and require careful study of the phase diagrams of the individual components as well as a detailed study of the electrochemistry of the liquid phase. Our preliminary survey of candidate electrolyte materials has identified the nitrate–amide metals as a promising mixture. Fortunately, many studies by Soviet agricultural scientists in search of a liquid fertilizer detail the phase diagrams of several nitrate–amide mixtures of particular interest for the ambient temperature thermal battery application [13].

Our previous studies of the discharge characteristics of thermal battery cells with lithium/molten nitrate electrolyte directed us toward several silver salts that are potentially useful high-rate cathode materials. Those studies are documented in several separate communications [10, 11]. The general electrochemical characteristics of nitrate–amide melts have been discussed in several communications [14–17]. The role of melt acidity in governing the discharge characteristics of calcium [15] and lithium anodes [17] in nitrate–amide melts as a function of melt acidity has been briefly explored. Some of the physical characteristics of binary nitrate–amide melts have been explored by other researchers [18–21]. This work will attempt to integrate our previous studies of anode half-cell reactions with our knowledge of the electrochemistry of complex silver salts to produce complete galvanic cells using nitrate–amide electrolytes. The objective of this manuscript is to discuss some of the factors influencing the discharge characteristics of ambient temperature thermal battery cells after activation. In particular, we wish to present here some of the characteristics of lithium/nitrate–amide cells using insoluble and sparingly soluble silver salts as cathodes.

2. Experimental details

All the chemicals used in this study are of reagent grade or higher purity. Ammonium nitrate was dried under vacuum for several days before use; urea was used as received. Silver salts that were used as received were Ag_2O, $AgIO_3$, $AgIO_4$, AgCl, AgBr, AgI, Ag_2SO_4, Ag_4RbI_5, $AgNO_3$ and AgF. Other silver salts including Ag_3PO_4, Ag_2CrO_4 Ag_2MoO_4 and Ag_2WO_4 were synthesized by metathesis reactions using silver nitrate and solutions of the corresponding sodium or potassium salt of the anion desired in milli-Q or distilled deionized water.

All nitrate–amide melts were prepared, stored and handled under an atmosphere of flowing air that had been dried to less than 0.5% relative humidity. Each melt was prepared by fusing the components at 120° C in a sealed Pyrex vessel. The vessel was agitated occasionally to aid dissolution. Once the mixture was completely liquid, the melt was cooled to room temperature and opened under the dried air atmosphere. A Karl Fischer analysis of melts prepared in this manner has indicated a total water content below 0.05% water by weight.

All the experiments reported here used a room temperature nitrate–amide melt composed of 0.10 mole fraction of NH_4NO_4 and 0.10 mole fraction of $LiNO_3$ in an amide solvent consisting of 0.6 mole fraction of acetamide and 0.4 mole fraction of urea. For brevity, we shall refer to this composition as the '$LiNO_3$–NH_4NO_3–amide melt'.

Lithium anodes used for this work were prepared by pressing a layer of lithium foil onto a 0.32 cm^2 disc of stainless steel mesh in a helium-filled glove box. The lithium anodes were scraped with a scalpel blade immediately before immersion in the melt to help present a clean lithium surface. All cell testing using lithium anodes was performed in a nitrogen filled glove bag.

The reference electrode used in the cyclic voltammetry studies was a lead wire immersed in a melt consisting of 0.001 mole fraction

$Pb(NO_3)_2$ in the $LiNO_3$–NH_4NO_3–amide melt. The potential of this reference was approximately −0.70 V versus the saturated ferrocene–ferrocinium couple on platinum electrodes in the $LiNO_3$–NH_4NO_3–amide melt. The use of the ferrocene–ferrocinium reference redox couple as a potential reference for non-aqueous media has been advocated by Bard and Faulkner [22].

Potentiostatic experiments used a PAR potentiostat–galvanostat (model 371). Galvanostatic experiments used a Keithley constant current source (model 225). The data collection system has been described previously [23]. Cyclic voltammetry and chronopotentiometry used an electrochemical cell of conventional three-electrode design. Ancillary recording and electrochemical instrumentation has been previously described [14]. All melts used for cyclic voltammetry were handled and used in the dark as much as possible. Cyclic voltammetric measurements of silver ion-containing melts were conducted in the absence of light.

3. Results

Table 1 lists several of the pertinent characteristics of the silver salts characterized in this work. We present the experimental and theoretical open circuit voltages wherever possible. In all cases, the open circuit voltages were defined as the stable potential reached after immersion, thus reflecting the fact that these measurements are biased by the role of the passivating film on the anode and the current drawn by the voltmeter on the cell voltage. Note that the energy density reported is calculated from the theoretical cell reactions. Energy density figures are often useful in eliminating specific systems from consideration for a particular application. However, the usual caveat must apply; these calculations represent the energy obtainable under ideal conditions if the cathode reaction were simply the reduction of Ag^+ to Ag and if no parasitic anode reactions were to occur. The cell reactions proposed should not be considered the only possible reactions, rather they should be considered only an initial approximation to the chemistry of that cell. In several instances, the published thermodynamic data were insufficient and experimental open circuit voltages were used to calculate a semi-empirical energy density. These cases are clearly labelled in Table 1. All calculated cell potentials assumed unit activity of all components.

Fig. 1 illustrates a Tafel plot for the simple reduction of an argon-saturated $LiNO_3$–NH_4NO_3–amide melt on a platinum electrode (0.479 cm^2). As with all Tafel measurements, the solution was vigorously stirred. The potentials were measured relative to a 0.001 mole fraction Pb^{2+}/Pb reference electrode.

Fig. 2 illustrates the cyclic voltammetric responses of a 0.001 mole fraction solution of $AgNO_3$ in the $LiNO_3$–NH_4NO_3–amide electrolyte. The curve shown in Fig. 2 was determined at 23° C on a platinum wire working electrode (0.385 cm^2). We have observed that prolonged electrolysis at moderate current densities in this

Table 1. Characteristics of cells tested

Cathode	*Number tested*	E_{OCV}	*Proposed cell reaction*	E^0, V	*Theoretical energy density ($Wh\,kg^{-1}$)*
Ag_2CrO_4	3	3.35 ± 0.01	$2Li_{(cr)} + Ag_2CrO_{4\,(cr)} \rightarrow 2Ag_{(cr)} + Li_2CrO_{4\,(ai)}$	3.48	540
Ag_2MoO_4	3	3.44 ± 0.01	$2Li_{(cr)} + Ag_2MoO_{4\,(cr)} \rightarrow 2Ag_{(cr)} + Li_2MoO_{4\,(cr)}$	3.43	472
Ag_2WO_4	4	3.36 ± 0.02	$2Li + Ag_2WO_4 \rightarrow 2Ag + Li_2WO_4$	—[a]	377[b]
Ag_2SO_4	4	3.42 ± 0.04	$2Li_{(cr)} + Ag_2SO_{4\,(cr)} \rightarrow Ag_{(cr)} + Li_2SO_{4\,(cr)}$	3.64	599
$AgIO_4$	6	3.50 ± 0.07	$Li + AgIO_4 \rightarrow LiIO_4 + Ag$	—[a]	307[b]
$AgIO_3$	3	3.21 ± 0.01	$Li_{(cr)} + AgIO_{3\,(cr)} \rightarrow LiIO_{3\,(ai)} + Ag_{(cr)}$	3.39	314
Ag_3PO_4	4	3.39 ± 0.05	$3Li + Ag_3PO_4 \rightarrow Li_3PO_4 + 3Ag$	—[a]	620[b]
Ag_2O	3	3.42 ± 0.03	—[c]	—[a]	—[b]

[a] Insufficient thermodynamic data.
[b] Evaluated using experimental open circuit voltage.
[c] Complex reaction.

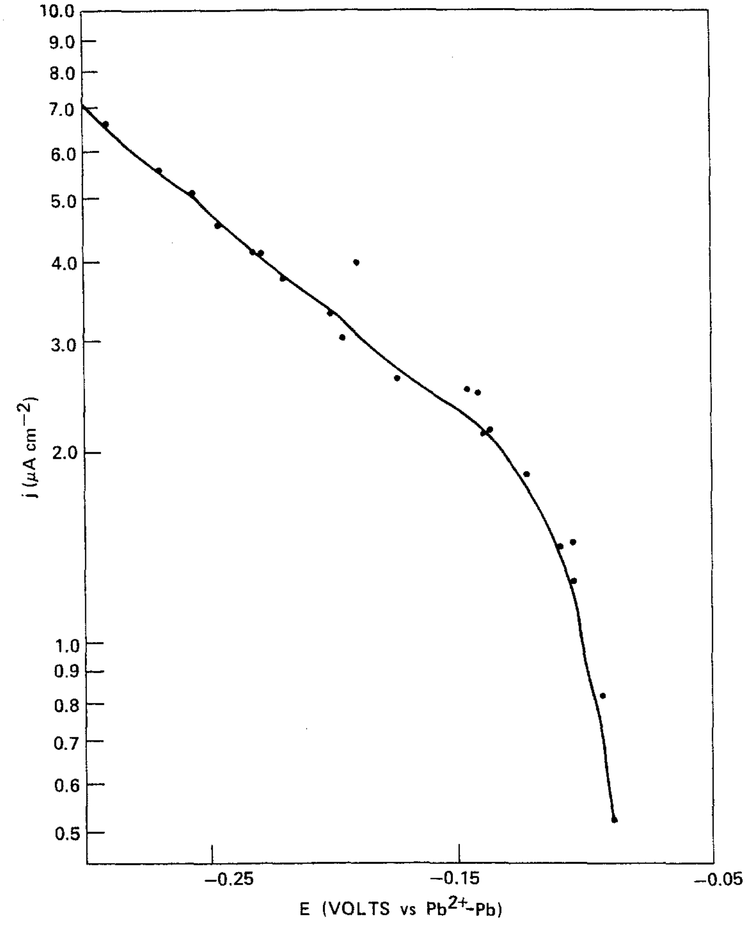

Fig. 1. Tafel plot of the reduction of the $LiNO_3$–NH_4NO_3–amide melt at 23° C on a platinum wire electrode (area = 0.48 cm^2) in an argon-saturated melt. Potentials are reported versus the Pb^{2+}/Pb reference electrode.

melt results in the deposition of dendritic silver metal.

The high-rate discharge capability of several of these lithium/silver salt cathodes in the nitrate–amide melts is illustrated in Fig. 3. The current density was held at a constant 10 mA cm^{-2}. One of the four salts (Ag_2O) is clearly chemically reactive with the acidic NH_4^+ species in the melt. It would seem that the two compounds with the highest solubility product (K_{sp}) are also those with the highest rate capability.

The discharge of three cells which demonstrate the effect of changing the cathode counter ion from chromate to molybdate to tungstate is shown in Fig. 4. The current density for the discharges shown is low (0.5 mA cm^{-2}); however, the discharge of the cells is reasonably flat over the 20-min monitoring period.

Fig. 5 shows the discharge characteristics at low rates of similar cells using cathodes of Ag_3PO_4 and $AgIO_3$. For comparison purposes, Fig. 6 demonstrates the high rate capability of nitrate–amide electrolyte cells using lithium anodes in conjunction with Ag_2O and FeS_2 cathodes. Both cells used 0.32 cm^2 lithium anodes and were discharged at 23° C and 10 mA cm^{-2}.

4. Discussion

It is quite evident from Fig. 1 that the simple reduction of the melt cannot sustain significant current densities without severe polarization. From Fig. 1 we can derive the coefficients for the cathodic processes in the linear (Tafel) region of the E versus $\log j$ plot, where j is current density ($\mu A\ cm^{-2}$). A least squares linear regression was performed on the data between −0.095 and −0.229 V to generate the line $E = a - b \log j$. The derived coefficients were found to be -8.79×10^{-2} for a and 0.215 V for b. A standard deviation of 0.0198 was calculated between the observed and the calculated data.

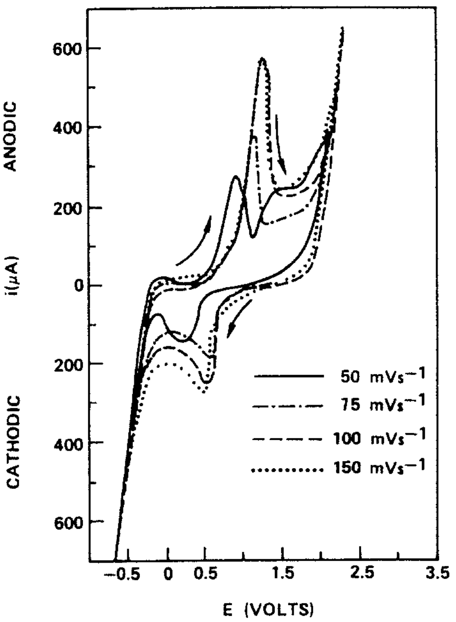

Fig. 2. Cyclic voltammetric responses of a 0.001 mole fraction $AgNO_3$ solution in the $LiNO_3$–NH_4NO_3–amide melt on a platinum wire electrode (area = 0.38 cm^2) at 23° C.

The cyclic voltammetric traces shown in Fig. 2 for 0.001 mole fraction silver nitrate melts show quite clearly the dramatic increase in the total cathodic current on the addition of even a small amount of silver ions when compared to those for blank melts [14]. The silver ion reduction wave is diffusion-limited as shown by the linear dependence of peak current on the square root of the scan rate. The data shown in Fig. 2 indicate that the species being reduced during the major cathodic process has a diffusion coefficient of approximately 1×10^{-7} cm^2 s^{-1}, where the silver species is reduced in a one-electron step. This low diffusion coefficient is undoubtedly due to the relatively viscous melt (195 ± 6 mPa s^{-1} at 25° C).

The rounded reduction wave and the sharp oxidation wave are characteristic of metal deposition and stripping. The presence of only one significant cathodic process before solvent reduction contraindicates the existence of significant quantities of a silver–acetamide adduct as might be expected from work by other

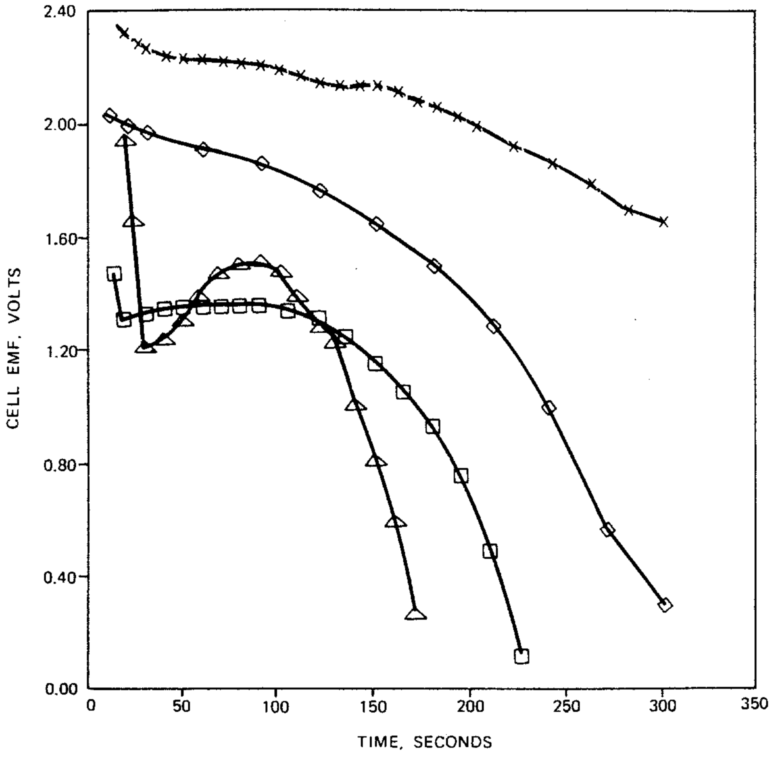

Fig. 3. Constant current discharge (at 10 mA cm^{-2}) of representative Li/Ag_2O, Li/Ag_2SO_4, Li/Ag_2CrO_4, and $Li/AgIO_4$ cells at 23° C in the $LiNO_3$–NH_4NO_3–amide electrolyte. □, Ag_2CrO_4; △, Ag_2SO_4; ◇, $AgIO_4$; ×, Ag_2O.

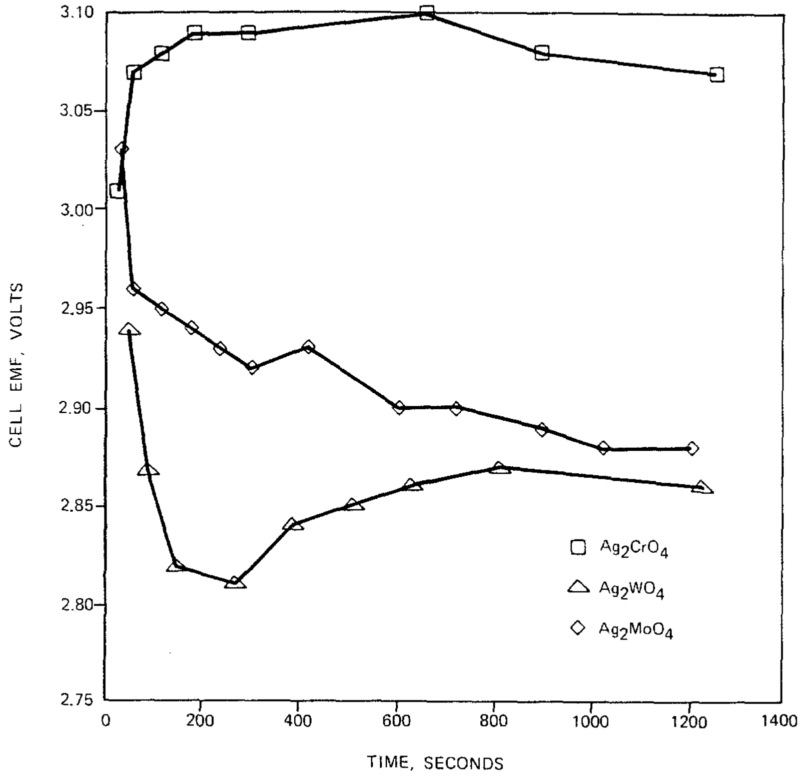

Fig. 4. Galvanostatic discharge of a Li/Ag_2CrO_4, a Li/Ag_2MoO_4 and a Li/Ag_2WO_4 cell. Each cell was discharged at 0.5 mA cm^{-2} and 23° C in the $LiNO_3$-NH_4NO_3-amide melt.

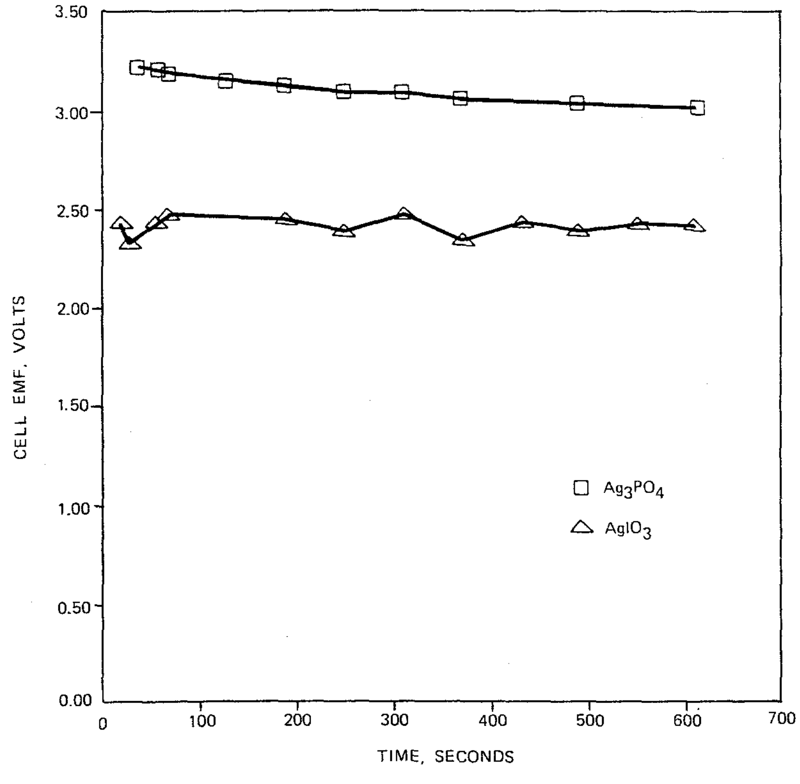

Fig. 5. Galvanostatic discharge of representative cells using Ag_3PO_4 and $AgIO_3$ cathodes in the $LiNO_3$-NH_4NO_3-amide melt electrolyte with lithium anodes at 0.5 mA cm^2.

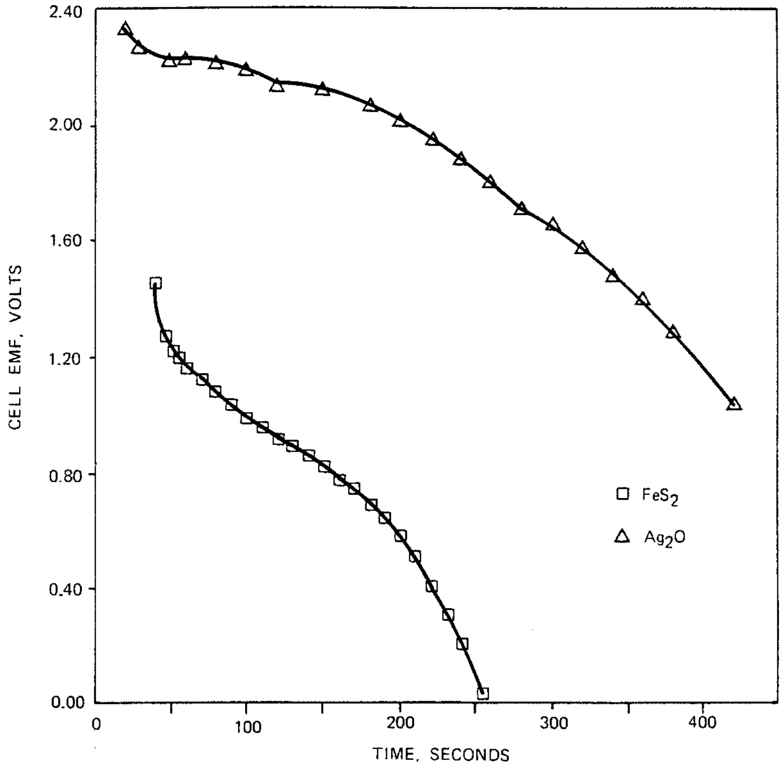

Fig. 6. High-rate discharge ($10\,mA\,cm^{-2}$) of lithium anode cells using FeS_2 and Ag_2O cathodes in the $LiNO_3$–NH_4NO_3–amide melt at 23° C.

researchers [24–26]. This can be directly attributed to the relatively high melt acidity of the NH_4NO_3–$LiNO_3$–amide melt. Some evidence for such an adduct is present as a small shoulder on the cathodic and anodic traces. The effect of melt acidity on the stability of the silver–amide adduct is the subject of ongoing research.

Several simple cells have been tested using silver salts as cathode materials. These cathode materials offer the possibility of reduction potentials nearly as favourable as that of the silver ion reduction, yet, being insoluble they cannot migrate to the anode and cause parasitic reactions there. The role of parasitic reactions between soluble cathode materials on lithium anodes has been discussed in other works in relation to their use in molten nitrates [27]. Fig. 3 clearly shows the benefits of these cathodes over more commonly used cathode materials such as FeS_2. FeS_2 cathodes in conventional thermal batteries sustain high current densities with minimal polarization but suffer from low cell voltages and a ubiquitous voltage spike. Cells using silver salts as cathodes generally do not suffer these problems.

The use of transition metal oxyanions (e.g. tungstates, molybdates, chromates or their iso or heteropolyanions) has proved a useful approach to the problem of preparing relatively sparingly soluble cathode materials for use in molten nitrate electrolyte thermal batteries. The effect of changing the transition metal centre of the counter ion in one group of oxyanions is shown in Fig. 4. It is clear that the heavier counter ions degrade cell performance not only in terms of their energy density capability (Table 1) but in terms of their overall rate capability. As in molten nitrates, the tungstate and molybdate salts perform poorly in comparison to the chromate [10, 11]. Since the stoichiometries and structures of the vanadates have been 'a confused and disputed area' [28a], we chose not to include any silver vanadate salts in this study.

We have not reported many details of the discharge characteristics of cells using the silver halides as cathodes because we have found that cells using those cathodes tend to have a large variability between experiments. In general, the rate capability of cathodes based on silver halides does not encourage further effort.

The silver oxide and silver orthophosphate cathodes appear quite attractive for use in an ambient temperature thermal battery system. The photosensitivity of the phosphate salt indicates that some care in preparation and handling will be required in assembly. While the silver oxide cathode is quite unstable in the more acidic melts and thus may be unsuitable for the high acidity of high-rate cells using high NH_4^+ concentrations, it may be well suited for use in cells using more neutral melts like the $LiNO_3$– NH_4NO_3–amide used in this study.

One possible problem with these cathodes that remains under investigation is the question of the possible formation of a $Ag(NH_3)^{2+}$ silver complex quite analogous to that formed in Tollen's reagent. The melt ammonia concentration increases during discharge as some of the NH_4^+ species in the melt are reduced. Thus, after activation the melt gradually becomes saturated with the cathode material (including silver ions) and with ammonia. Those cathode materials that are attacked (Ag_2O) by the melt should be considered particularly prone to this reaction. At this time, we cannot eliminate the possibility of explosive 'fulminating' silver species formation [28b], particularly in cells that have been activated and partially discharged.

6. Conclusions

Several silver salts have been demonstrated as cathode materials for ambient temperature cells using nitrate–amide melts as the electrolyte. These silver salts provide a range of rate capabilities, open circuit voltages and energy densities. In every case, the apparent reduction mechanism is to the metal. We have observed no unambiguous evidence for any intercalation phenomena in the chromates, molybdates or tungstates as might be expected from earlier work. The reduction of the silver ions in solution in the slightly acidic melts shows no clear evidence of a silver amide complex. For most envisaged applications, cells based on the lithium anode in conjunction with a silver chromate, silver oxide, or silver orthophosphate cathode and a slightly acidic electrolyte provide quite attractive cell voltage, current density and discharge duration characteristics.

Obviously, the best solution for the problem of the choice of an optimum cathode for an ambient temperature thermal battery is one which sustains the required current density with minimal polarization. However, using the most effective high-rate cathodes (e.g. Ag_2O or Ag_2CrO_4) for long-term discharges is contraindicated by the solubility of these materials in the more acidic melts. The use of a silver salt as an active cathode material will thus have to depend on the rate and voltage requirements of the individual application and on as yet unresolved questions of the safety of silver salt cathodes in ammonia-containing melts. In all likelihood the total amount of those hazardous species will be small and the anode should act to chemically reduce any soluble $Ag(NH_3)_2^+$ species in solution.

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