

DISCHARGE CHARACTERISTICS OF LITHIUM/MOLTEN NITRATE THERMAL BATTERY CELLS USING SILVER SALTS AS SOLID CATHODE MATERIALS

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Summary

Thermal battery cells using molten nitrate electrolytes and liquid lithium anodes have been evaluated using several silver salts with low solubility in molten nitrates as solid cathode materials. These cathode materials do not readily diffuse into the anolyte and, thus, do not have parasitic reactions with the lithium anode. Furthermore, the solid cathode materials have voltammetric characteristics as favorable as many soluble silver salt cathodes. This paper presents the effects of temperature, current density, and cathode material on cell discharge characteristics.

Introduction

Low melting mixtures of alkali metal nitrate salts show promise as electrolytes for intermediate temperature (150 - 400 °C) thermal battery systems [1 - 6]. The $\text{LiNO}_3\text{-KNO}_3$ eutectic composition has a melting point of 124 °C and is stable at temperatures above 400 °C. An intermediate-temperature thermal battery system using molten $\text{LiNO}_3\text{-KNO}_3$ eutectic could function efficiently at temperatures 200 °C cooler than conventional thermal batteries that use the LiCl-KCl eutectic electrolyte which melts at 352 °C. The resultant heat loading of an enclosed space by the nitrate electrolyte thermal battery would be far lower than that produced by conventional thermal batteries during comparable discharge lifetimes.

The liquid lithium anode in molten nitrates allows extremely high discharge rates at temperatures above the 180 °C melting point of lithium. A separate study has shown the dramatic effect of the temperature on the discharge of lithium anodes in molten nitrate electrolytes [3]. Below 180 °C, the lithium anode performs much like the calcium anode. The discharge current density of the solid lithium anode is limited by a passivating Li_2O film. Above 180 °C, the lithium anode is molten and the passive film forms on an unstable liquid anode surface. The physical integrity of the film is

easily breached and the passage of lithium ions across the anode-electrolyte interface proceeds essentially unimpeded. As a result, cells using the liquid lithium anode may be discharged at extremely high rates in a molten nitrate electrolyte [3 - 5]. Current densities over 1000 mA cm^{-2} have been reported for optimized cell designs using a silver nitrate cathode and the liquid lithium anode in molten lithium nitrate [5].

Unfortunately, soluble cathode materials such as silver nitrate tend to diffuse throughout the electrolyte during the cell discharge. Silver ions that reach the anolyte are chemically reduced onto the anode surface as they react with the elemental lithium. The elemental silver thus formed on the anode surface degrades cell performance. The vigorous chemical reaction of liquid lithium and silver ions in molten silver nitrate may also lead to anode deflagration [6].

This paper will focus on the discharge characteristics of thermal battery cells using four cathode materials based on silver salts with a relatively low solubility in molten nitrates. Ag_3PO_4 , Ag_2CrO_4 , Ag_2MoO_4 and Ag_2WO_4 . Our objective is to improve the characteristics of thermal battery cells using these cathodes.

Experimental

All of the chemicals used in this study were reagent grade or higher purity. Lithium nitrate and potassium nitrate were dried at $120 - 140^\circ\text{C}$ for several days under vacuum before use. The $\text{LiNO}_3\text{-KNO}_3$ eutectic was formed by prefusing the mixture in a quartz tube at 300°C and cooling in air dried to less than 0.5% relative humidity.

The thermal battery cells consisted of a lithium anode attached to an iron backing, two electrolyte-saturated glass fiber filter discs 47 mm in diameter (Gelman, type A), and a cathode consisting of the silver salt pressed onto a disc of stainless steel screen (SS304, 60 mesh) having the same diameter as the anode. Experiments using no active cathode material have shown that the reduction of the nitrate melt on the steel mesh and cathode backing rapidly passivates the steel surface at high current densities. Thus, we can safely conclude that nitrate reduction on the cathode backing does not substantially contribute to the total cathodic currents during high rate discharge.

The lithium anodes were a lithium-iron composite material consisting of approximately 9 wt.% lithium. The preparation of this material has been described in earlier communications [5, 6]. During discharge, the iron in the composite is inert and the anode is essentially a liquid lithium anode on an iron matrix. The anodes were prepared and attached to a 47 mm iron backing in a helium filled glove box (O_2 and H_2O content below 10 ppm). The anodes were transported in a pentane filled flask to an inert atmosphere cell testing device.

The inert atmosphere cell testing device has been described in detail in a separate communication [6]. Briefly, the device consists of two heated platens in a furnace with a flowing argon atmosphere. The anode is brought to thermal equilibrium at the upper platen, the cathode and electrolyte are brought to temperature on the lower platen and the two halves of the cell are brought together in the center of the furnace. The cell is then subjected to a constant current discharge using a PAR (model 371) potentiostat/galvanostat. The discharge is monitored using several Hewlett-Packard multi-meters (model 3438A) and a Hewlett-Packard thermal printer (model 5051A).

The silver salts used for the cathode materials were synthesized following classical procedures using Milli-Q water as the solvent. Silver chromate was produced from potassium chromate and silver nitrate as described in the literature [7]. Silver molybdate [8] and silver tungstate [9] were prepared in a like manner by the simple metathesis reaction of aqueous silver nitrate and aqueous solutions of the appropriate sodium salts. Silver orthophosphate was prepared from Na_3PO_4 or Na_2HPO_4 in Milli-Q water following a classical procedure [10]. All of the silver salts were washed repeatedly with Milli-Q water and dried in the dark under vacuum. The Ag_2CrO_4 was blood red, Ag_2MoO_4 was white or very faintly yellow, Ag_2WO_4 was a cream-colored material, and the Ag_3PO_4 was yellow. It should be noted that all four salts are photosensitive.

Results

The discharge characteristics of representative 0.5 in dia. thermal battery cells based on the systems $\text{Li}/\text{LiNO}_3\text{-KNO}_3/\text{Ag}_3\text{PO}_4$ and $\text{Li}/\text{LiNO}_3\text{-KNO}_3/\text{Ag}_2\text{CrO}_4$ are shown in Figs 1 and 2 as a function of temperature and current density. All discharges were performed at constant current and constant temperature.

Cells using silver orthophosphate cathodes show some performance degradation after 30 - 60 s at open circuit at 400 °C. The cells discharged for Figs 1 and 2 were activated into the load and discharged to 0 V. After discharge and several seconds at open circuit, the cell voltage would rise above 2 V. Further discharge at 100 - 250 mA cm^{-2} could then be performed to anode depletion. Forced overdischarge of these cells at high rates would simply plate lithium onto the cathode. This lithium deposit could then be discharged by changing the galvanostat polarity. In a like manner, elemental lithium may be plated onto the battery anode when the cell is charged at high rates. During charging and forced overdischarges, large quantities of NO_2 were evolved from the nitrate oxidation reaction. Furthermore, the fiberglass (SiO_2) binder is severely degraded in the vicinity of the electrode where the lithium is plated. The reaction of elemental lithium with SiO_2 has been discussed elsewhere [5].

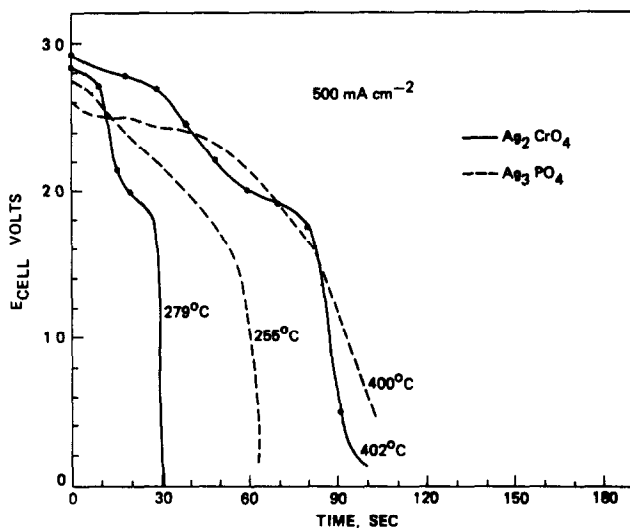


Fig 1 The effect of temperature on the discharge of $\text{Li}/\text{LiNO}_3\text{-KNO}_3/\text{Ag}_3\text{PO}_4$ and $\text{Li}/\text{LiNO}_3\text{-KNO}_3/\text{Ag}_2\text{CrO}_4$ thermal battery cells 0.5 in in diameter (1.26 cm^2) at 500 mA cm^{-2}

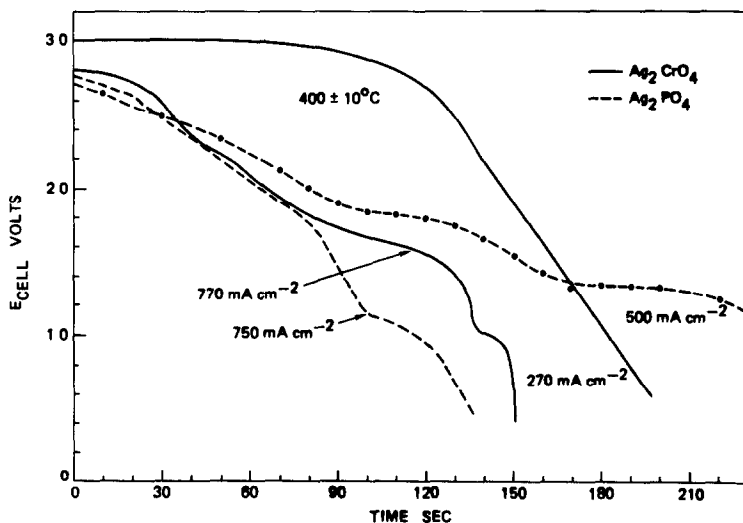


Fig 2 The effect of current density on the discharge profile of 0.5 in dia $\text{Li}/\text{LiNO}_3\text{-KNO}_3/\text{Ag}_3\text{PO}_4$ and $\text{Li}/\text{LiNO}_3\text{-KNO}_3/\text{Ag}_2\text{CrO}_4$ thermal battery cells at $400 \pm 10^\circ\text{C}$

Also shown in Figs. 1 and 2 are comparable discharges of cells using the $\text{Li}/\text{LiNO}_3\text{-KNO}_3/\text{Ag}_2\text{CrO}_4$ system. These discharges were performed at constant current and constant temperature. The silver chromate cathode cells show similar performance to cells using silver orthophosphate cathodes under conditions of forced overdischarge and charging.

Figure 3 illustrates the extremely high discharge rate capability of lithium/molten nitrate thermal battery cells. The discharges shown are representative of the 0.5 in. dia. cells using the $\text{Li}/\text{LiNO}_3\text{-KNO}_3/\text{Ag}_2\text{CrO}_4$ and the $\text{Li}/\text{LiNO}_3\text{-KNO}_3/\text{Ag}_3\text{PO}_4$ systems. Comparable rate capability has been demonstrated in cells over 1 in. in diameter.

Figures 4 and 5 show the effect of temperature and current density on the discharge characteristics of representative 0.5 in. dia thermal battery

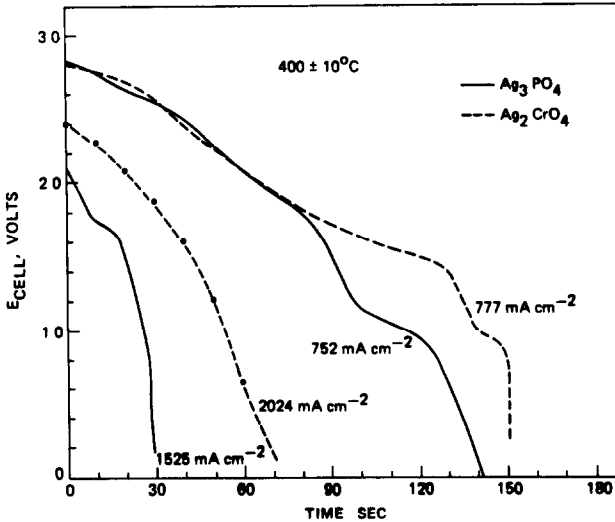


Fig 3 The high rate discharge of $\text{Li}/\text{LiNO}_3\text{-KNO}_3/\text{Ag}_3\text{PO}_4$ and $\text{Li}/\text{LiNO}_3\text{-KNO}_3/\text{Ag}_2\text{CrO}_4$ cells 0.5 in. in diameter at 400°C

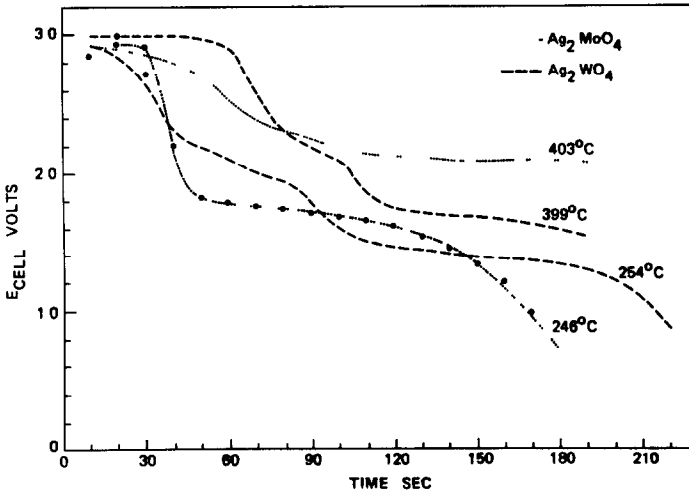


Fig 4 The effect of temperature on the discharge of $\text{Li}/\text{LiNO}_3\text{-KNO}_3/\text{Ag}_2\text{MoO}_4$ and $\text{Li}/\text{LiNO}_3\text{-KNO}_3/\text{Ag}_2\text{WO}_4$ thermal battery cells 0.5 in. in diameter (1.26 cm^2) at $250 \pm 10 \text{ mA cm}^{-2}$

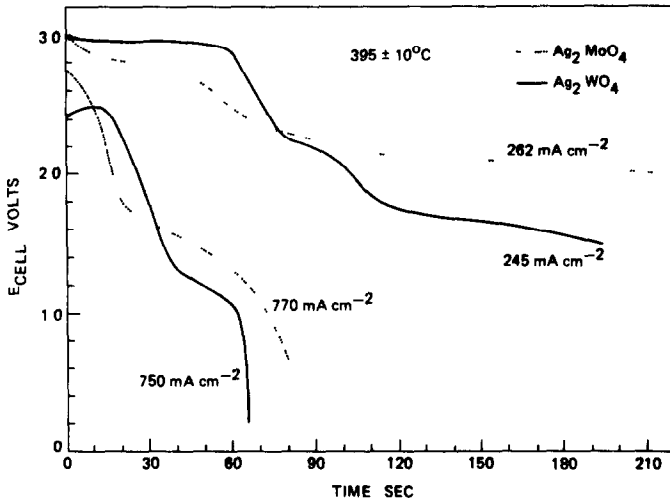


Fig 5 The effect of current density on the discharge profile of 0.5 in dia $\text{Li}/\text{LiNO}_3\text{-KNO}_3/\text{Ag}_2\text{MoO}_4$ and $\text{Li}/\text{LiNO}_3\text{-KNO}_3/\text{Ag}_2\text{WO}_4$ thermal battery cells at $395 \pm 10^\circ\text{C}$

cells based on the systems $\text{Li}/\text{LiNO}_3\text{-KNO}_3/\text{Ag}_2\text{MoO}_4$ and $\text{Li}/\text{LiNO}_3\text{-KNO}_3/\text{Ag}_2\text{WO}_4$. The most significant feature of cell discharges using either of these two cathode materials is the presence of several distinct and well-defined potential plateaux. Previous studies have shown that $\text{Li}(\text{Fe})$ composite anodes (like those used in this study) have a single anode potential plateau during galvanostatic discharge [5].

Like the cells using Ag_3PO_4 cathodes, cells using Ag_2MoO_4 or Ag_2WO_4 cathodes show a significant loss in cell voltage and high rate discharge capability after 30 - 60 s at 400°C in the $\text{LiNO}_3\text{-KNO}_3$ eutectic at open circuit.

Discussion

The fundamental similarity in the primary cathode reactions of electrochemical cells using any of the four solid cathode materials discussed here is best illustrated by the fact that cells using the liquid lithium anode and any one of the cathode materials show open circuit cell voltages of 3.4 - 3.5 V at 300°C in molten $\text{LiNO}_3\text{-KNO}_3$ eutectic electrolytes. These cell potentials are well within experimental error of the values calculated for the cell $\text{Li}/\text{LiNO}_3\text{-KNO}_3/\text{AgNO}_3$ at 300°C (3.475 V) assuming unit activity of silver nitrate [3].

The silver orthophosphate cathode appears to function primarily through the reduction of the silver salt to silver metal (evidenced by silver deposits) and free orthophosphate anions.



Some cell discharge performance degradation is noted on prolonged periods at open circuit (30 - 45 s at open circuit at 400 °C). This degradation is probably due to the dissolution of small amounts of Ag_3PO_4 with the concomitant migration of silver ions to the anode where they are reduced chemically by the anode as described previously [6]

Molten nitrate electrolyte thermal battery cells using silver chromate cathodes often show more than one potential plateau during galvanostatic discharge (Figs 1 and 2) However, at the extremely high current densities used in this study, those plateaux tend to be somewhat ill-defined

The reduction of silver chromate proceeds with the formation of dendritic silver and CrO_4^{2-} ions.



The CrO_4^{2-} ions impart the brilliant yellow color to the melt that is characteristic of chromate solutions. The high solubility of lithium chromate in molten nitrates prevents the products of the silver chromate reduction reaction from blocking the cathode surface during discharge [11]

Traces of a green discoloration are frequently observed in the electrolyte wafers after cell discharge The green discoloration is quite intense and is found most frequently in the vicinity of the anode as determined during post-discharge analysis The green color apparently is produced by the direct chemical reduction of Cr(VI) to Cr(III) by the elemental lithium present in the anode.

In a separate study [11], we described the reactions that occur in half cell discharges of Ag_2CrO_4 , Ag_2MoO_4 , and Ag_2WO_4 cathodes in molten nitrates Other researchers have investigated these materials in various organic-solvent-based electrolytes [12 - 17]. One distinctive discharge characteristic of cells using the silver chromate, molybdate, or tungstate cathodes in organic based electrolytes is the presence of multiple discharge plateaux These have been attributed to the two (or more) step reduction of the cathode material via an intercalation reaction [14 - 17] In all three cases, the evidence supports the reduction of the silver salt to silver metal Although the Ag_2CrO_4 cathode has been the subject of several investigations [14 - 16], the Ag_2MoO_4 and Ag_2WO_4 cathodes have not been as thoroughly studied [17]

Molten nitrate electrolyte thermal battery cells using either the silver molybdate or silver tungstate cathode show two more distinct discharge plateaux. These plateaux are reminiscent of those observed 200 - 400 °C cooler in organic solvents at current densities two or more orders of magnitude lower than in our experiments. Just as is observed in the organic-solvent-based cells, the first plateau in the molten nitrate electrolyte thermal battery cells is most likely associated with the simple reduction of the silver salt to silver metal and the lithium (or potassium or lithium-potassium) salt of the anion (molybdate or tungstate). This is substantiated by the silver dendrites that are formed during the first potential plateau

Figures 4 and 5 show the effect of temperature and current density on the discharge characteristics of representative $\text{Li}/\text{LiNO}_3\text{-KNO}_3/\text{Ag}_2\text{MoO}_4$ and $\text{Li}/\text{LiNO}_3\text{-KNO}_3/\text{Ag}_2\text{WO}_4$ thermal battery cells. All of the cells shown in Figs. 4 and 5 were 0.5 in. in diameter and were discharged at constant temperature and constant current.

The second plateau during discharge has several possible explanations. However, we note that the discharges are quite similar to those observed for cells using intercalation cathodes. An intercalation reaction of the sort



(M = Mo or W)

is conceivable, particularly given the relative insolubility of Li_2MoO_4 and Li_2WO_4 . The differences in solubility of Li_2CrO_4 as opposed to Li_2MoO_4 or Li_2WO_4 alone may explain the relatively small secondary potential plateaux that we observe during discharge of chromate cells as compared with the molybdate or tungstate cells. It is reasonable to expect that an intercalation reaction would be difficult for any substance that goes into solution as readily as the alkali metal chromate salts dissolve in molten nitrates.

A comparison of Figs. 1, 2, and 3 with Figs. 4 and 5 clearly shows that most important performance characteristics of $\text{Li}/\text{LiNO}_3\text{-KNO}_3/\text{Ag}_2\text{MoO}_4$ and $\text{Li}/\text{LiNO}_3\text{-KNO}_3/\text{Ag}_2\text{WO}_4$ thermal battery cells are clearly inferior to the comparable Ag_2CrO_4 and Ag_3PO_4 cells. For example, the cell voltages observed during high rate discharges of cells using Ag_2MoO_4 or Ag_2WO_4 are much lower than those observed for Ag_3PO_4 and Ag_2CrO_4 cathode thermal battery cells. Furthermore, the discharge lifetime over 2 V is obviously far shorter for cells using either silver molybdate or silver tungstate cathodes than for cells using silver phosphate or silver chromate cathodes at comparable temperatures and current densities.

Conclusions

The Ag_2CrO_4 and Ag_3PO_4 show promise for intermediate temperature, high-rate thermal batteries using molten nitrate electrolytes. Cells based on either the Ag_2CrO_4 or the Ag_3PO_4 cathode can sustain current densities over 750 mA cm^{-2} when used in $\text{LiNO}_3\text{-KNO}_3$ eutectic electrolyte with liquid lithium anodes.

Cells using Ag_2CrO_4 cathodes show no significant performance degradation even after 60 s at open circuit at 400°C . Comparable cells using the soluble silver nitrate cathode often have anode deflagrations after periods shorter than 10 s at open circuit. Some loss in cell voltage is noted for the $\text{Li}/\text{LiNO}_3\text{-KNO}_3/\text{Ag}_3\text{PO}_4$ cells after 30 - 45 s at open circuit at 400°C . In addition, cells using either silver orthophosphate or silver chromate cathode may be subjected to charging or forced overdischarge without apparent adverse consequences.

Cells using liquid lithium anodes and silver molybdate or silver tungstate cathodes degrade significantly after brief periods (30 - 45 s) at open circuit at 400 °C. Both cells have many discharge characteristics that are inferior to comparable cells using either Ag_2CrO_4 or Ag_3PO_4 cathodes. Cells using either Ag_2MoO_4 or Ag_2WO_4 cathodes show two distinct potential plateaux reminiscent of those observed in organic-solvent-based electrolytes at low rates at room temperature. Neither Ag_2MoO_4 nor Ag_2WO_4 cathodes can sustain the extremely high current densities possible with Ag_3PO_4 and Ag_2CrO_4 cathodes.

Acknowledgment

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