

THE HIGH RATE DISCHARGE CHARACTERISTICS OF SILVER CHROMATE, SILVER MOLYBDATE, AND SILVER TUNGSTATE CATHODES IN MOLTEN NITRATE ELECTROLYTES

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Summary

Silver chromate, silver molybdate, and silver tungstate are promising solid cathode materials for molten nitrate electrolyte thermal battery cells. All three compounds show open circuit potentials more positive than the reversible Ag^+/Ag couple. The dominant reduction process for all three cathodes at high rates is clearly the reaction to form metallic silver. Potentiostatic discharges at -0.200 V *versus* the 0.1 m Ag^+/Ag reference indicates that all three cathode materials are capable of sustaining high current densities. Galvanostatic studies show that all three cathodes are capable of sustaining current densities over 500 mA cm^{-2} without excessive polarization. Cell discharges using lithium anodes demonstrate that the Ag_2CrO_4 , Ag_2MoO_4 and Ag_2WO_4 cathodes can provide a practical alternative to the AgNO_3 cathode for high rate, molten nitrate electrolyte thermal batteries.

Zusammenfassung

Silberchromat, Silbermolybdat und Silberwolframat sind erfolgversprechende Materialien für geschmolzene Nitratelektrolyte in Thermobatteriezellen. Alle drei Verbindungen zeigen höhere positive Potentiale im offenen Stromkreis als das Paar Ag^+/Ag . Der dominierende Reduktionsprozess für alle drei Kathoden bei höherer Entladungsgeschwindigkeit ist offensichtlich die Reaktion zu metallischem Silber. Die potentiostatische Entladungen von -0.200 Volt zu einer 0.1 m Ag^+/Ag Referenz zeigt, dass alle drei Kathodenmaterialien fähig sind, hohe Stromdichten aufrechtzuerhalten. Galvanostatische Messungen haben gezeigt, dass die drei Kathoden eine Stromdichte von mehr als 500 mA cm^{-2} aufrechterhalten, und zwar ohne übermäßige Polarisierung. Die Entladung der Zellen, versehen mit Lithumanoden beweist, dass die Ag_2CrO_4 , Ag_2MoO_4 und Ag_2WO_4 Kathoden praktische Alternativen für die AgNO_3 Kathode in Thermobatterien mit geschmolzenen Nitratelektrolyten und höherer Entladungsgeschwindigkeit sein können.

Introduction

Nitrate melts are of interest as electrolytes for a new generation of advanced thermal batteries with low operating temperatures, high rate discharge capability, high cell voltages, and high energy and power densities [1, 2]. Another potentially important use of nitrate melts is as heat transfer fluids for solar energy converters [3]. Both applications demand a better understanding of the chemical and electrochemical processes that occur in nitrate melts. This paper will focus on the processes most relevant to the thermal battery community. However, the implications of the chemistry of the transition metal oxyanions in nitrate melts to applications other than high rate battery cathodes should be apparent.

Several papers have outlined the characteristics of lithium and calcium anodes in molten nitrates [4 - 6]. To date, all studies of high rate cathode materials for molten nitrate electrolyte thermal batteries have focused on the soluble nitrates of lead, cadmium or silver [7 - 9]. A recent study has shown that thermal battery cells using soluble cathode materials with lithium anodes may show serious performance degradation at high temperatures or at open circuit [5]. Lithium metal that is present in the anode tends to reduce chemically any cathode materials that diffuse into the anolyte. This reaction gradually forms a layer of the reduced cathode material that decreases the effectiveness of the anode. Difficulties like these with the soluble cathode materials (AgNO_3 , $\text{Pb}(\text{NO}_3)_2$, $\text{Cd}(\text{NO}_3)_2$) have directed our attention to alternative cathode materials that would demonstrate the high rate capability and the favorable reduction potentials characteristic of the soluble cathode materials.

This paper reports the characteristics of cathodes based on the silver salts of the oxyanions of the (VI) valence state of chromium, molybdenum, and tungsten.

Experimental

All the salts used in these studies were reagent grade purity. The NaNO_3 and KNO_3 were dried under vacuum at 120°C overnight before use, while the LiNO_3 was dried at $150 - 170^\circ\text{C}$ for several days under vacuum. Nitrate eutectic compositions were made by melting measured quantities of the nitrate salts together in a quartz vessel followed by cooling, grinding, and further drying. The AgNO_3 , Na_2WO_4 , K_2MoO_4 and K_2CrO_4 were used "as received" for the metathesis reactions.

The Ag_2MoO_4 , Ag_2WO_4 and Ag_2CrO_4 were synthesized by the metathesis reactions of silver nitrate and the corresponding sodium or potassium salt in aqueous solution using Milli-Q water [10, 11]. The silver salts were dried at 40°C , overnight, under vacuum before use. The possibility of residual water in the silver salts may contribute to the total cathodic currents reported; however, extended periods under vacuum at 40°C did not produce

significant additional weight loss in the samples. Thus, the total water content of the silver salts is likely to be quite small. After drying, the Ag_2CrO_4 was blood red, the Ag_2MoO_4 was a very pale yellow-white, and the Ag_2WO_4 was a cream-colored material.

The half-cell experimental technique is a modification of a method that has been reported in a previous communication [12]. Half-cell studies of the cathodes used an open-pan method where 20 - 30 mg of cathode material was pressed into a platinum mesh (60-mesh, 1/4 in. dia.). The electrolyte was held in an inverted platinum crucible cover with a 37-mm disk of Gelman (Type A) glass-fiber filter paper as a binder. For the half-cell studies, the counter electrode was a large platinum disk isolated by approximately 2 cm from the cathode on the platinum pan. The cathode studies had simple nitrate oxidation as the anode reaction. Because of the relatively large distance separating the anode and the cathode, the presence of NO_2 from nitrate oxidation was not a significant factor influencing the cathodic process. For the cathode half-cell the reference electrode was 0.1 m AgNO_3/Ag in equimolar $\text{NaNO}_3\text{-KNO}_3$.

Full scale thermal battery cell testing used an inert atmosphere, large diameter, cell testing device described in a recent communication [5]. The anode material used in the battery cells was a lithium-iron composite prepared by methods described previously [4]. Cell discharges were carried out under an atmosphere of flowing, pre-purified argon. All cell discharges were performed at constant temperature and constant current.

High-rate cell discharges and potentiostatic half-cell studies used a high current potentiostat/galvanostat (PAR, Model 371). Lower rate galvanostatic discharges used a constant current source (Keithley, Model 221).

Data collection devices included a Hewlett-Packard data logger (Model 5051A) with four digital multimeters (Hewlett-Packard Model 3438A); a Houston (Omnigraphic, Model 2000) X-Y recorder; a Hewlett-Packard X-Y-T recorder (Model 7047A); and a Houston Instruments (Omniscribe) Y-T recorder.

Results

The Ag_2CrO_4 cathode in nitrate melts

Figure 1 shows the potentiostatic discharge of a thin Ag_2CrO_4 cathode on a platinum mesh current collector. The cathode was potentiostatted at -0.200 V vs. the Ag^+/Ag reference. The high discharge rate capability appears to be a characteristic of the cathode material and the melt. These experiments were conducted at 320°C in a non-deaerated melt. An examination of the platinum mesh current collector after the experiment shows a large silver deposit with a wide-bladed dendritic structure.

Figure 2 shows the galvanostatic discharge of two similar Ag_2CrO_4 cathodes at 320°C . The first cathode (A) was discharged at a current density of 250 mA cm^{-2} while the second (B) was discharged at a current density

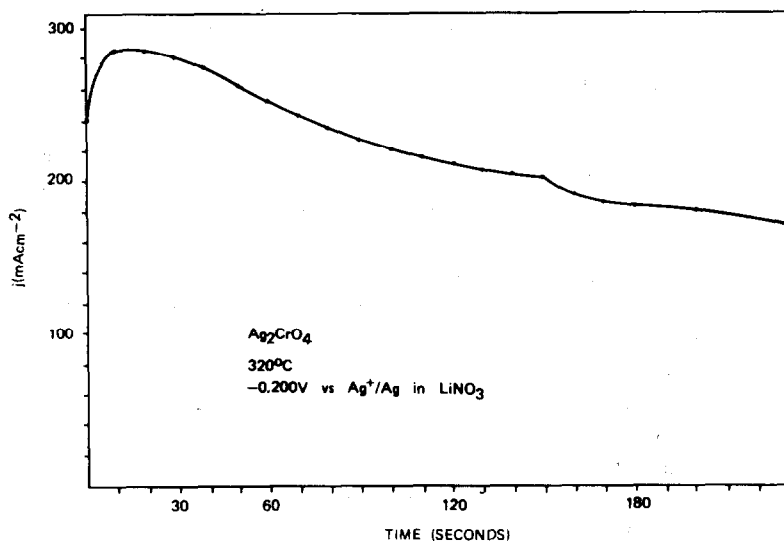


Fig. 1. Potentiostatic discharge of an Ag_2CrO_4 cathode on a platinum mesh current collector. The cathode was potentiostatted at -0.200 V vs. the Ag^+/Ag reference. The electrolyte was LiNO_3 at $320 \pm 10^\circ\text{C}$. Anode area was 0.32 cm^2 .

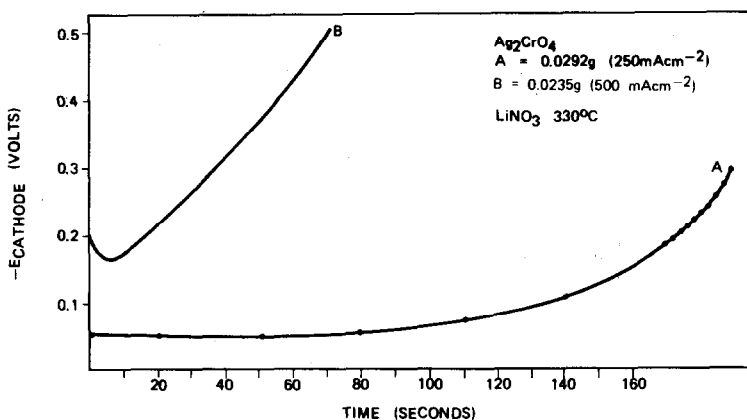


Fig. 2. Galvanostatic discharge of the Ag_2CrO_4 cathode on a platinum mesh substrate at 250 mA cm^{-2} (curve A, 29.2 $\text{mg Ag}_2\text{CrO}_4$) and 500 mA cm^{-2} (curve B, 23.5 $\text{mg Ag}_2\text{CrO}_4$). The discharges were in molten LiNO_3 at $330 \pm 10^\circ\text{C}$.

of 500 mA cm^{-2} . Of particular interest is the relatively sharp change in potential when the cathode material is exhausted. This corresponds to the reduction of approximately 79% of the silver present in the cathode, assuming 1 electron per silver atom.

Figure 3 shows the current vs. cathode potential characteristics of typical Ag_2CrO_4 cathodes on a platinum mesh substrate at 330°C . The curves were determined by applying a potential step to the cathode and noting the steady state current at the applied potential. The curve indicates

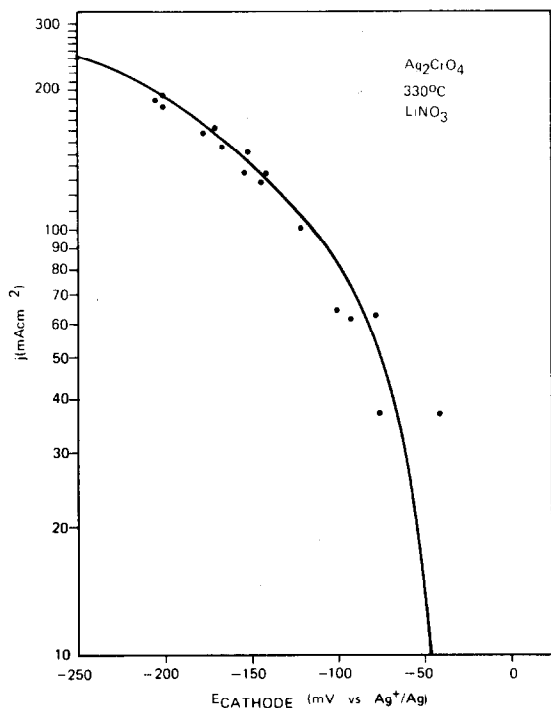


Fig. 3. Current vs. potential curve for Ag_2CrO_4 cathodes. The Ag_2CrO_4 was reduced onto a platinum mesh current collector. The curves were determined by applying a constant potential and noting the steady state current. An Ag^+/Ag reference electrode was used in the LiNO_3 electrolyte at $330 \pm 10^\circ\text{C}$.

that relatively small cathodic overpotentials are possible, even at high discharge rates. At higher rates or higher cathodic overpotentials, the reaction rapidly shifts to the next most difficult reduction process. However, reproducible measurements of the secondary cathodic processes are difficult. Measurements at very negative potentials (and, consequently, very high current densities) are difficult because the small amount of cathode material available is consumed before a stable current can be determined.

A transition to a second cathodic process is observed, but no color change that might be indicative of a lower oxidation state of chromium is noted. The potential of the secondary cathodic process during the galvanostatic experiments (*ca.* -0.8 to -1.1 V vs. Ag^+/Ag) suggests that the secondary reaction is primarily nitrate reduction. These observations do not necessarily indicate that lower oxidation states of chromium are not produced in the cathodic processes, but rather that any of the lower oxidation state chromium species produced may be reactive chemically, electrochemically inert, colorless, or present in small amounts.

Figure 4 illustrates the discharge of a typical thermal battery cell (area = 1.26 cm², $T = 370^\circ\text{C}$, current density = 500 mA/cm²). From Fig. 4 we note immediately that long, stable discharges at high rates, high cell voltages,

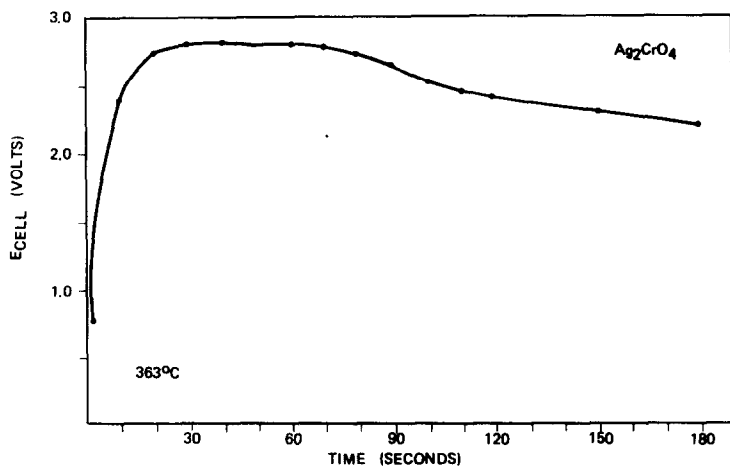


Fig. 4. A representative discharge of a 0.5 in. dia. cell using the Ag_2CrO_4 cathode in LiNO_3 - KNO_3 eutectic electrolyte with an $\text{Li}(\text{Fe})$ composite anode. The cell was discharged at 500 mA cm^{-2} at 363°C .

and moderate temperatures are possible using an Ag_2CrO_4 cathode. Similar cells using an AgNO_3 cell seldom show discharges over 90 s due to the diffusion of the soluble AgNO_3 to the anolyte where it is reduced to the metal on the anode surface.

The Ag_2MoO_4 cathode in nitrate melts

Figure 5 shows the potentiostatic discharge of a thin Ag_2MoO_4 cathode on a platinum mesh current collector. The cathode was potentiostatted at -0.200 V vs. the Ag/Ag^+ reference. The discharge curve obtained is similar to that observed for Ag_2CrO_4 under the same conditions. A small amount of NO_2 evolution is noted when the Ag_2MoO_4 cathode is first immersed in the melt. As might be expected, some cathode performance degradation is noted if the electrode is allowed to remain at open circuit

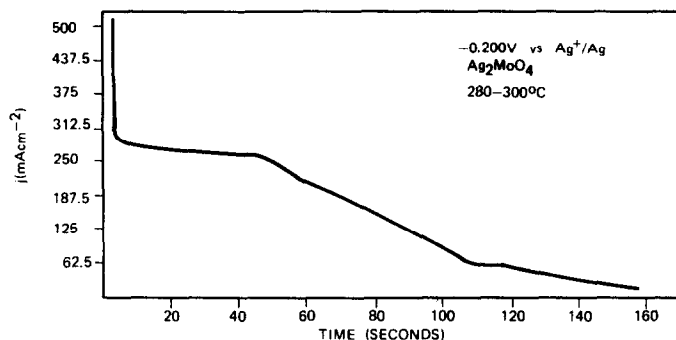


Fig. 5. Potentiostatic discharge of an Ag_2MoO_4 cathode on a platinum mesh current collector. The cathode was potentiostatted at -0.200 V vs. the Ag^+/Ag reference. The electrolyte was LiNO_3 at $290 \pm 10^\circ\text{C}$. Cathode area was 0.32 cm^2 .

for prolonged periods before the current is applied. Cells that activate into open circuit for periods up to 1 min at 370 °C show no noticeable high rate performance degradation.

An examination of the platinum mesh current collector after the experiment again shows a large silver deposit with dendrites quite reminiscent of those produced by the silver chromate cathodes.

Figure 6 shows the galvanostatic discharge of two similar Ag_2MoO_4 cathodes at 320 °C. The first cathode was discharged at a current density of 250 mA cm^{-2} while the second was discharged at a current density

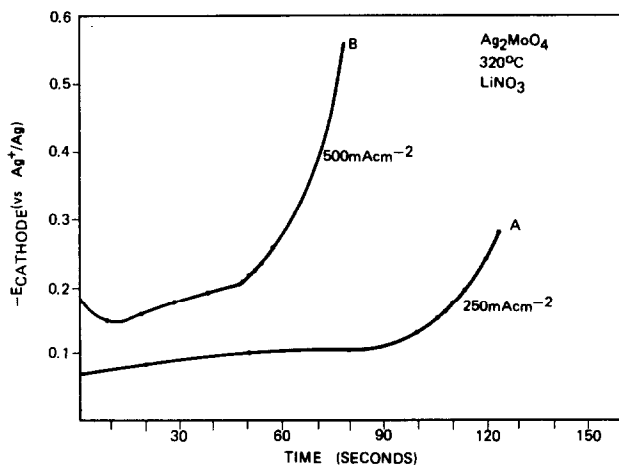


Fig. 6. Galvanostatic discharge of the Ag_2MoO_4 cathode on a platinum mesh substrate at 250 mA cm^{-2} (curve A, 26.8 mg Ag_2MoO_4) and 500 mA cm^{-2} (curve B, 25.2 mg Ag_2MoO_4). The discharges were in molten LiNO_3 at 320 ± 10 °C.

of 500 mA cm^{-2} . Again, of particular interest is the relatively sharp potential change when the readily available cathode material is exhausted. This point corresponds to the reduction of approximately 72.5% of the silver present in the cathode assuming 1 electron per silver atom.

Figure 7 shows the current *vs.* potential characteristics of typical Ag_2MoO_4 cathodes on platinum mesh substrates at 330 °C. As was the case with Ag_2CrO_4 , the measurement of steady state currents at the high overpotentials is difficult because of the rapid onset of the potential inflection due to the depletion of the small amount (20 - 30 mg) of active cathode material used in this experimental design.

Figure 8 illustrates the discharge of a typical thermal battery cell (area = 1.26 cm^2 , $T = 370$ °C, current density = 500 mA/cm^2) using an Ag_2MoO_4 cathode and a Li(Fe) anode. From Fig. 8 we call attention to the fact that long, stable discharges at high rate, with high cell voltages, are possible using an Ag_2MoO_4 cathode with a lithium anode in molten nitrate electrolytes at moderate temperatures. The two distinct potential plateaus are much more evident in cells using the molybdate cathode than in those using a chromate cathode.

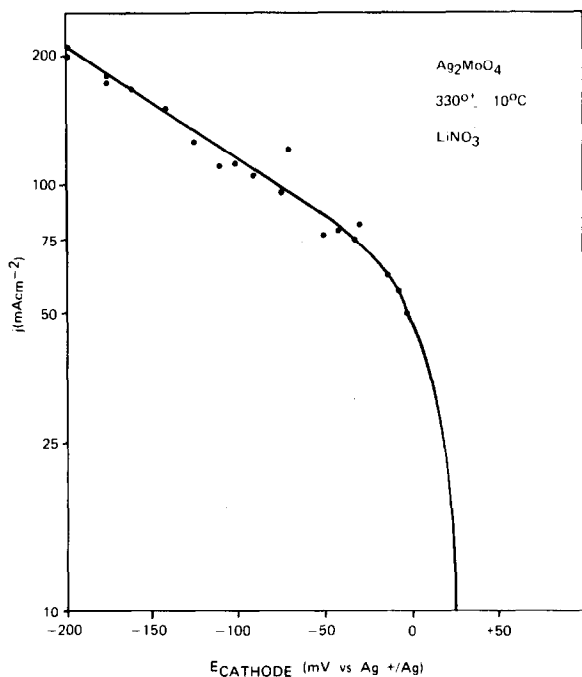


Fig. 7. Current vs. potential curve for Ag_2MoO_4 cathodes. The Ag_2MoO_4 was reduced onto a platinum mesh current collector. The curves were determined by applying a constant potential and noting the steady state cathode current. An Ag^+/Ag reference electrode was used in the LiNO_3 electrolyte at 330°C .

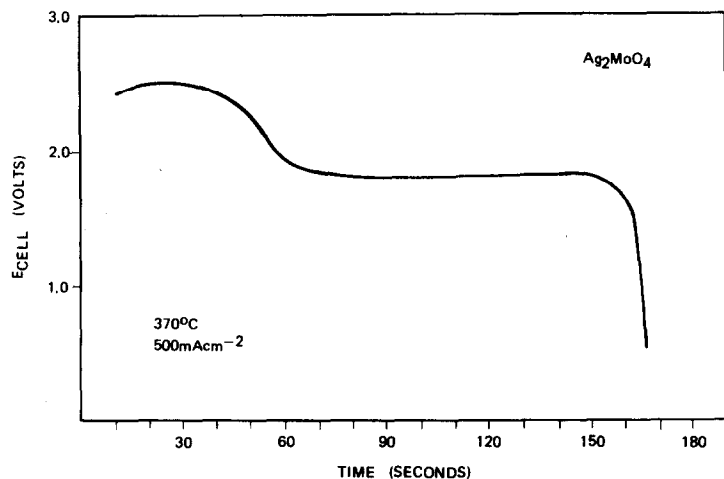


Fig. 8. A representative discharge of a 0.5 in. dia. cell using the Ag_2MoO_4 cathode in $\text{LiNO}_3\text{-KNO}_3$ eutectic electrolyte near 370°C . The cell was discharged at 500 mA cm^{-2} . The anode was an Li(Fe) composite.

The Ag_2WO_4 cathode in nitrate melts

Figure 9 shows a potentiostatic discharge of a thin layer of Ag_2WO_4 pressed on a platinum mesh current collector. The cathode was potentiostatted at -0.200 V vs. the Ag^+/Ag reference. The discharge curve obtained appears similar to that observed for Ag_2MoO_4 under the same conditions. As with the Ag_2MoO_4 cathode, a small amount of NO_2 evolution is noted when the Ag_2WO_4 cathode is immersed in the melt. The quantity of NO_2 evolved is somewhat larger with the Ag_2WO_4 than with the Ag_2MoO_4 cathode.

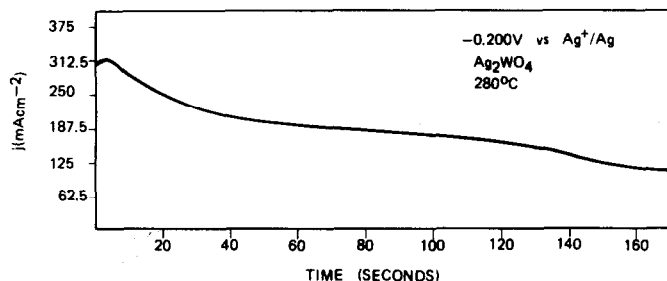


Fig. 9. A potentiostatic discharge of an Ag_2WO_4 cathode on a platinum mesh current collector. The cathode was potentiostatted at -0.200 V vs. an Ag^+/Ag reference. The electrolyte was LiNO_3 at 280°C . The cathode area was 0.32 cm^2 .

An examination of the platinum mesh current collector after the experiment shows a large silver deposit with dendritic structures similar to those observed to form from Ag_2MoO_4 cathodes.

Figure 10 shows the galvanostatic discharge of two similar Ag_2WO_4 cathodes at 330°C . The first cathode was discharged at a current density of 250 mA cm^{-2} , while the second was discharged at a current density of 500 mA cm^{-2} . The relatively rapid change in potential at cathode exhaustion that we have found to be characteristic of the silver oxyanions is again evident. In the case of the Ag_2WO_4 cathode, this point corresponds to the reduction of approximately 71% of the silver present in the cathode assuming 1 electron per silver atom.

Figure 11 shows the current vs. potential characteristics of typical Ag_2WO_4 cathodes on platinum mesh substrates at 330°C . As was the case with Ag_2CrO_4 , the measurement of steady state currents at the high overpotentials is difficult because of the rapid onset of the potential change due to the depletion of the small amount (20 - 30 mg) of cathode active material used in this experimental design.

Figure 12 illustrates the discharge of a typical thermal battery cell (area = 1.26 cm^2 , $T = 370^\circ\text{C}$, current density = 500 mA/cm^2) using an Ag_2WO_4 cathode and an $\text{Li}(\text{Fe})$ anode. From Fig. 12 we note that long, stable discharges at high rates, high cell voltages, and moderate temperatures are possible using an Ag_2WO_4 cathode.

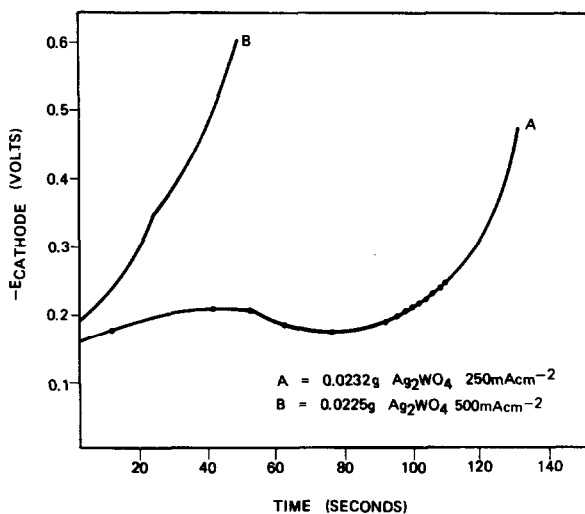


Fig. 10. Galvanostatic discharge of the Ag_2WO_4 cathode on a platinum mesh substrate at 250 mA cm⁻² (curve A, 23.2 mg Ag_2WO_4) and 500 mA cm⁻² (curve B, 22.5 mg Ag_2WO_4). The discharges were in molten LiNO_3 at $330 \pm 10^\circ\text{C}$.

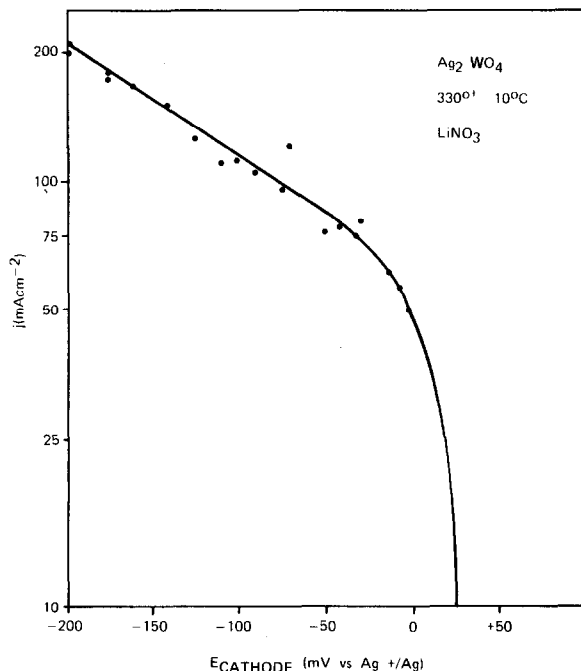


Fig. 11. Current vs. potential curve for Ag_2WO_4 cathodes. The Ag_2WO_4 was reduced onto a platinum mesh current collector. The curves were determined by applying a constant potential and noting the steady state cathode current. An Ag^+/Ag reference electrode was used in the LiNO_3 electrolyte at $330 \pm 10^\circ\text{C}$.

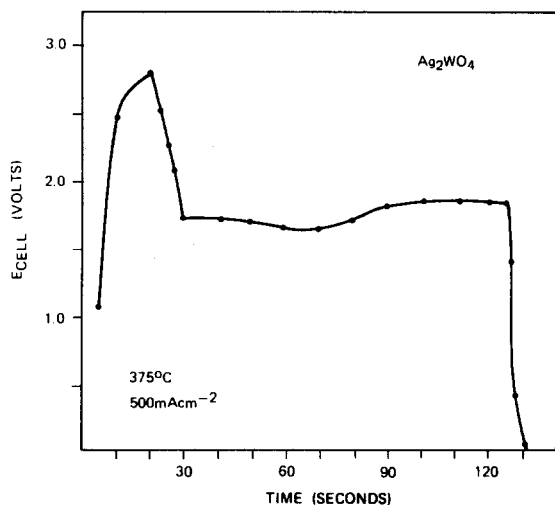
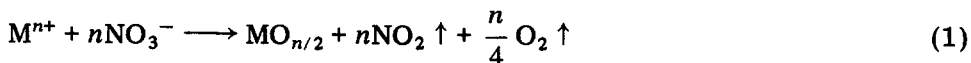


Fig. 12. A representative discharge of a 0.5 in. dia. cell using the Ag_2WO_4 cathode in $\text{LiNO}_3\text{-KNO}_3$ eutectic electrolyte with an Li(Fe) composite anode. The cell was discharged at 500 mA cm^{-2} at 375°C .

In the cell discharges of the solid cathode materials, the second potential plateau becomes more apparent in the order $\text{Ag}_2\text{CrO}_4 \ll \text{Ag}_2\text{MoO}_4 < \text{Ag}_2\text{WO}_4$. In each case, the first plateau corresponds to a reduction of the solid cathode material. The nature of the second plateau is still under investigation.

Discussion

We have observed that cationic species with large charge-to-size ratios (e.g., Fe^{3+} , Ni^{2+} , Co^{3+} , and Cu^{2+}) act as Lux-Flood acids [13] since they decompose molten nitrates with precipitation of the insoluble transition metal oxide and evolution of NO_2 .



This decomposition reaction has been noted in several other studies of molten nitrates [14 - 17]. Table 1 lists the characteristics of several metal ions considered as possible cathode materials. Also listed in Table 1 are the charge to size ratio (Z_e/r) of several cations of interest, and the change in the free energy of activation for the nitrate reduction reaction due to the electric field of a cation at one ionic radius.

Every species that we have observed to be a strong Lux-Flood acid also has a large, positive charge-to-size ratio. In an earlier communication, we reported that only those metal ions having a larger charge-to-size ratio than the melt cation cause new reduction waves when added to nitrate

TABLE 1

Characteristics of cations of interest as cathode active materials in molten nitrates

Cation	r ($\times 10^{10}$ m)	Ze/r ($\times 10^9$ C/m)	$-\Delta G_{\text{solv}}$ (kJ/mol)	$-\Delta \Delta G^{0\#}$ ^a (kJ/mol)
Ag ⁺	1.26	1.27	5.31×10^2	40.7
Pb ²⁺	1.20	2.67	22.3×10^2	85.6
Cd ²⁺	0.97	3.30	27.6×10^2	105.6
Ni ²⁺	0.72	4.45	37.2×10^2	142.6
Ca ²⁺	0.72	4.45	37.2×10^2	142.6
Fe ³⁺	0.64	7.51	94.1×10^2	240.7

^aCalculated using $\epsilon = 27$.

melts [7, 9]. Cations with large charge-to-size ratios deform the bidentate [18 - 21] nitrate ligand and weaken the N-O bond that is broken in the slow electrochemical step.

The potential field of many transition metal cations is sufficiently strong to allow facile scission of the N-O bond. The chemical decomposition of the nitrate ligand with precipitation of the metal oxide occurs whenever cations with Ze/r ratios large enough to cause breakage of the N-O bond are added to the melt. The electrochemical reduction of the nitrate anion is catalyzed by cations that have Ze/r ratios larger than that of the cation of the melt but too small to cause decomposition of the ligand.

The free energy of activation for the reduction of nitrate ions can be represented by

$$\Delta G^{0\#} = \Delta G_0^{0\#} - \frac{zFe}{4\pi\epsilon_0\epsilon r} \quad (2)$$

Where $\Delta G_0^{0\#}$ is the free energy of activation for nitrates in the absence of the electric field of a cation [12]. As the electric field of the ion (Ze/r) becomes large and positive, the free energy of activation for the reduction of the nitrate anion becomes small. Thus, the Lux-Flood acidity of a cation in nitrate melts can be related to the change in the free energy of activation for the reduction of the nitrate anion produced by the cation.

We find that addition of lead ions as PbCl₂ to molten lithium nitrate at 375 °C produces a small but visible amount of nitrogen dioxide. Subsequent cyclic voltammetric scans show a new reduction wave [7, 9]. By contrast, the same experiment performed with the high Ze/r cation Ni²⁺ (added as NiCl₂) produces relatively large amounts of nitrogen dioxide in a vigorous and rapid reaction. Subsequent cyclic voltammetry shows no new reduction waves that might correspond to either reduction of the solvated cation or to catalyzed nitrate reduction. As shown in Table 1, the ions that react most strongly are those with large solvation energies and large Ze/r ratios.

The decomposition reactions that the nitrate melts undergo in the presence of the transition metal cations effectively prohibit the use of common cathode materials such as TiS_2 and FeS_2 . A practical cathode material should be nonreactive and insoluble. In molten nitrates, only salts having cations chosen from the IA or IIA groups, Ag, Tl, Pb or Cd, form salts that are consistently nonreactive. Of these, only silver appears to form a metallic deposit [7 - 9]. Examination of eqns. (1) and (2) leads to the prediction that transition metal cations surrounded by oxide ligands should show a far lower Lux-Flood acidity than the simple nitrate solvated metal cation, because the total charge of the complex becomes less positive as the strongly bonding, and doubly negative charged, oxide ligands are added. The negatively charged oxide ligands lower the effective Z_e for the complex. Furthermore, the added ligands increase the radius (r) of the complex.

The Lux-Flood acid reactions of several transition metal oxides and oxoanions have been studied in molten nitrates [22 - 25]. For example MoO_3 decomposes the melt to form the stable MoO_4^{2-} anions [24, 25]. This suggests that the stable oxyanions of certain transition metals (*e.g.*, CrO_4^{2-} , MoO_4^{2-} , WO_4^{2-} , VO_4^{2-}) are potential cathode materials when complexed with silver to form insoluble, readily reducible, materials with inherently low Lux-Flood acidity.

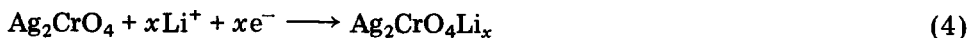
The characteristics of the silver chromate, silver molybdate, and silver tungstate cathodes in propylene carbonate and other organic solvents have been discussed in several recent papers [10, 26 - 29]. There appear to be no studies of these cathode materials in molten nitrates.

The major reduction process at all three cathodes appears to be

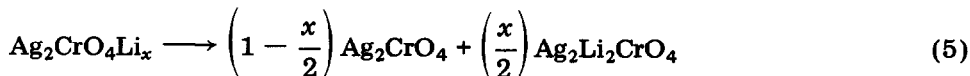


where M = Cr, Mo or W. This is analogous to results reported at low rates in a variety of organic solvents [10, 26 - 29].

Other studies [10, 26 - 28] have proposed the existence of a lithium intercalation compound resulting from the discharge of Ag_2CrO_4 cathodes at moderate current densities in organic solvent-based electrolytes. The intercalation reaction



has been reported by Messina *et al.* [26 - 28] to produce a Cr(V) compound that then decomposes in a complicated reaction involving an internal electron transfer step

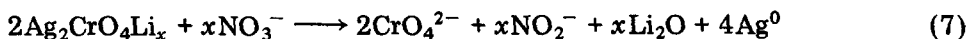


where $\text{Ag}_2\text{Li}_2\text{CrO}_4$ then reacts to form silver metal and Li_2CrO_4



The reduction to Li_3CrO_4 has also been suggested [26 - 28]. Our studies do not directly suggest the existence of this intercalation compound in molten

nitrate after high rate reductions. However, there are several significant factors that would affect the stability of such an intercalation compound in molten nitrates. First, Li_2CrO_4 is soluble in molten nitrates. Thus, we do not believe that the reaction proposed by Messina [26 - 28], the "dissolution-precipitation" that involves silver chromate going into solution followed by the precipitation of lithium chromate, can occur in molten nitrates. Second, molten nitrate electrolytes are highly oxidizing media. The reaction of the melt



to oxidize any Cr(V) species must be considered. Third, the high current densities used for these studies might act to mask the existence of any species that is either a transient or present in small concentrations. The end result of all of these factors appears to be that the step to form silver metal (whether or not it is formed *via* an intercalation compound intermediate) is accelerated in molten nitrates.

The reduction reactions at the silver molybdate and silver tungstate cathodes are more difficult to interpret. Both candidates show at least two, distinct, well-defined potential plateaus during galvanostatic cell discharge. The discharges observed in molten nitrates are quite reminiscent of those seen in organic electrolyte cells at current densities two orders of magnitude lower [29]. One discussion of these cathodes in organic electrolytes clearly demonstrated that the primary reduction reaction during the first plateau was the reduction of silver to silver metal [29]. The same paper stated that the mechanism of the second plateau was less clear and that an intercalation mechanism was one possible explanation. The nature of the second plateau in molten nitrates is still under investigation.

When cells using lithium anodes are used with chromate cathodes, a green discoloration is observed. The discoloration appears to be centered about the anode and is most likely a result of the reduction of the Cr(VI) to the Cr(III) species by elemental lithium in the anode. Activating the cell into open circuit shows no anode degradation that might be indicative of further reduction to chromium metal with the concomitant loss in anode capability. The green Cr(III) species appears to be soluble and is observed both in cells that were dissected while still molten and in cells that were quench-cooled after discharge. The predominant color of the electrolyte is bright yellow (from the CrO_4^{2-} species).

After discharge, quench-cooled molybdate and tungstate cathode thermal battery cells show some discoloration of the electrolyte wafers, primarily about the anode. It seems likely that this discoloration is analogous to the green discoloration observed in the chromate cathode cells. The brown color of the molybdate product and the grey color of the tungstate product is suggestive of a reaction between the elemental lithium of the anode and the anions in solution to form a relatively insoluble polynuclear compound.



Both the molybdate and the tungstate cathode cells show some performance degradation on activation into open circuit for prolonged periods. This slow degradation in cell voltage and current carrying capability supports the hypothesis that some insoluble, resistive material is forming at the anode surface. Table 2 compares several important characteristics of silver chromate, molybdate and tungstate cathodes.

TABLE 2

A summary of the characteristics of Ag_2CrO_4 , Ag_2MoO_4 , Ag_2WO_4 cathodes

Cathode	Molecular weight	Theoretical $\text{A h g}^{-1}:\text{Ag}^+ \rightarrow \text{Ag}$	Experimental* A h g^{-1}	Percent. of* theoretical
Ag_2CrO_4	331.7	0.162	0.128 ± 0.012	79
Ag_2MoO_4	375.7	0.142	0.103 ± 0.016	72.5
Ag_2WO_4	463.6	0.116	0.082 ± 0.006	70.7

*250 mA cm^{-2} in molten LiNO_3 at $320 \pm 10^\circ\text{C}$.

Conclusions

The Lux-Flood character of the cathode materials is a strong function of the free energy of solvation for the cation in the nitrate melts. The large charge-to-size ratio of transition metal cations deforms the N-O bonds in the bidentate nitrate ligand making bond breakage and formation of the stable oxide more favored. Several silver salts of the transition metal polyacids are observed to be stable and insoluble or only slightly soluble in molten nitrates. Because of the multiple oxide bonds on the transition metal, the tendency of the central metal cation to act as a Lux-Flood acid and acquire another oxide is small. For this reason, the silver, lead, and cadmium salts of transition metal iso- and heteropolyacids offer a promising approach to insoluble, nonreactive cathode materials for high rate, molten nitrate electrolyte thermal batteries.

Silver chromate appears to be a very promising solid cathode material for molten nitrate electrolyte thermal batteries. Although the chromate products of the cathode reaction are soluble, the CrO_4^{2-} product is simply reduced to a Cr(III) species that is also soluble. As a result, there is no anode degradation after prolonged periods at open circuit. Cathode overpotentials are small, even at extremely high current densities, and the cathode efficiency at 250 mA cm^{-2} approaches 80%.

Cathodes based on Ag_2MoO_4 and Ag_2WO_4 both show some Lux-Flood acid character. Nonetheless, both are promising cathode materials, being capable of sustaining 500 mA cm^{-2} at a low overpotential. Both materials are relatively insoluble, easily prepared, and both offer readily reproducible discharge characteristics.

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