Lithium Batteries Using Molten Nitrate Electrolytes

Melvin H. Miles

Research Department (Code 474220D), Naval Air Warfare Center Weapons Division, China Lake, CA 93555-61000, milesmh@navair.navy.mil

ABSTRACT

The lithium anode is sufficiently stable in the molten LiNO$_3$-KNO$_3$ molten salt eutectic (mp = 124°C) for possible applications in thermal batteries as well as in batteries for electric vehicles. The lithium anode reaction is readily reversible in this molten nitrate electrolyte. This anode can be discharged over a temperature range of 150-350°C when the liquid lithium (mp = 181°C) is immobilized by iron powder or by a porous lithium-boron matrix. Transition metal oxide cathode materials are being investigated for possible applications in the Li/LiNO$_3$-KNO$_3$ system. The goal is a rechargeable, high energy and power density battery that can deliver 4 V per cell.

Introduction

There exists eutectic data for thousands of inorganic molten salt systems (1), yet the behavior of the lithium anode has only been explored in a few of these systems. The actual use of lithium anodes in molten salt electrolytes is confined mostly to thermal batteries for military applications. Thermal batteries originated with German scientists during World War II and used a calcium anode and calcium chromate (CaCrO$_4$) cathode with the high-melting LiCl-KCl electrolyte (mp = 352°C), i.e., Ca/LiCl-KCl/CaCrO$_4$. Thermal batteries today use lithium alloys or liquid lithium anodes (LAN) and the iron disulfide (FeS$_2$) cathode with the LiCl-KCl electrolyte or variations of this halide electrolyte such as the all-lithium LiBr-LiCl-LiF eutectic that melts at 430°C. The high ionic conductivity of molten salts also makes them very attractive for secondary battery applications that require high power densities such as in electric vehicles. The high temperature Li/LiCl-KCl/FeS$_2$ system has been extensively studied for this application. Batteries using the lithium anode with molten salt electrolytes that have different chemistries and lower melting points would be attractive for both military and commercial applications. Furthermore, the use of molten salts that are compatible with new cathode materials such as LiMn$_2$O$_4$ that yield 4 V per cell with lithium anodes could significantly increase the energy and power densities of batteries.

Molten Nitrate Systems

Five molten nitrate systems are presented in Table I that also gives the eutectic compositions and melting points along with the available ionic conductivity closest to the eutectic (2).

Table I. Eutectic data and ionic conductivities for molten nitrate systems (1, 2)

<table>
<thead>
<tr>
<th>System</th>
<th>Mol %</th>
<th>T(°C)</th>
<th>$\kappa$(S/cm) $\text{@ 570K}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNO$_3$-KNO$_3$</td>
<td>42-58</td>
<td>124</td>
<td>0.687 (50.12 mol % LiNO$_3$)</td>
</tr>
<tr>
<td>LiNO$_3$-RbNO$_3$</td>
<td>30-70</td>
<td>148</td>
<td>0.539 (50 mol % RbNO$_3$)</td>
</tr>
<tr>
<td>LiNO$_3$-RbNO$_3$</td>
<td>44-56</td>
<td>178</td>
<td>0.519 (50 mol % RbNO$_3$)</td>
</tr>
<tr>
<td>LiNO$_3$-NaNO$_3$</td>
<td>56-44</td>
<td>187</td>
<td>0.985 (49.96 mol % NaNO$_3$)</td>
</tr>
<tr>
<td>NaNO$_3$-RbNO$_3$</td>
<td>46-54</td>
<td>222</td>
<td>0.660 (50.31 mol % NaNO$_3$)</td>
</tr>
<tr>
<td>KNO$_3$-RbNO$_3$</td>
<td>30-70</td>
<td>290</td>
<td>0.394 (70 mol % RbNO$_3$)</td>
</tr>
</tbody>
</table>

For comparisons, the single salts melt at 264°C for LiNO$_3$, 307°C for NaNO$_3$, 334°C for KNO$_3$ and 310°C for RbNO$_3$. From Table I, it is important to note that LiNO$_3$-KNO$_3$ offers the lowest melting point and that LiNO$_3$-NaNO$_3$ provides the highest ionic conductivity. Another important consideration is that the stability of the lithium anode in molten nitrates is dependent upon the passivating Li$_2$O film, hence LiNO$_3$ must be a major component of the electrolyte (3). Therefore, only LiNO$_3$-KNO$_3$, LiNO$_3$-RbNO$_3$, and LiNO$_3$-NaNO$_3$ can be considered for use with the lithium anode.
Table II presents a comparison of physical properties of LiNO₃-KNO₃ at 570 K (297°C) with the same properties for LiCl-KCl at a much higher temperature (770 K).

**Table II. Physical properties (ionic conductivity, viscosity, density, surface tension) of LiNO₃-KNO₃ (40 mol % LiNO₃) at 570 K compared with LiCl-KCl (58.8 mol % LiCl) at 770 K.**

<table>
<thead>
<tr>
<th>System</th>
<th>( \kappa ) (S/cm)</th>
<th>( \eta ) (Pa·s)</th>
<th>( d ) (g/cm³)</th>
<th>( \gamma ) (J/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNO₃-KNO₃ (570 K)</td>
<td>0.64</td>
<td>0.00327</td>
<td>1.82</td>
<td>0.112</td>
</tr>
<tr>
<td>LiCl-KCl (770 K)</td>
<td>1.85</td>
<td>0.00213</td>
<td>1.62</td>
<td>0.126</td>
</tr>
</tbody>
</table>

For comparisons, the ionic conductivity of aqueous 1 M KCl at 25°C is 0.112 S/cm, thus both molten salts offer excellent ionic conductivities.

The IR voltage loss is an important factor for batteries operating at high currents. For a typical battery cell thickness (L) of 2 mm, the equation \( R = \frac{W}{4L} \) yields IR = 0.1 V for LiCl-KCl and IR = 0.3 V for LiNO₃-KNO₃ at a discharge rate of 1 A/cm². Although the calculated IR loss is somewhat higher for the LiNO₃-KNO₃ cell, this system is operating at a much lower temperature (297°C vs. 497°C). The activation energy for the ionic conductivity is 13.8 kJ/mol in LiNO₃-KNO₃ (50.12 mol % LiNO₃) and 16.3 kJ/mol in LiCl-KCl (58.8 mol % LiCl). The activation energy for the viscosity of LiNO₃-KNO₃ is very similar to that of water (15.6 kJ/mol).

**Lithium Anode in Molten Nitrates**

Every electrochemical system has an electrostability region over which the electrolyte can be neither oxidized nor reduced. This electrochemical window is shown in Fig. 1 for molten LiNO₃ at 300°C.

The electrochemical oxidation of the molten LiNO₃ (Eq. 1)

\[
\text{LiNO}_3 \rightarrow \text{Li}^+ + \text{NO}_3^- + \frac{1}{2} \text{O}_2 + e^-
\]

begins at about 1.1 V vs. Ag⁺/Ag or 4.5 V vs. Li⁺/Li. The electrochemical reduction of LiNO₃ (Eq. 2)

\[
\text{LiNO}_3 + 2e^- \rightarrow \text{Li}_2\text{O} + \text{O}_2
\]

occurs at about -0.9 V vs. Ag⁺/Ag, thus these two reactions define an experimental 2.0 V electrostability region for molten LiNO₃ at 300°C.

The use of the lithium anode in molten nitrates is possible because of a blocking or passivating film that forms on the electrode surface by the reaction of lithium ions from the melt with the oxide ions produced by Eq. 2, i.e., \( 2\text{Li}^+ + \text{O}_2^- \rightarrow \text{Li}_2\text{O} \). This insoluble Li₂O film blocks further reduction of LiNO₃ and allows the electrostability region to be extended to the reversible reduction of lithium ions, i.e.,

\[
\text{Li}^+ + e^- \rightarrow \text{Li}
\]

This provides an electrochemical window of 4.5 V for molten LiNO₃ at 300°C, thus the use of lithium anodes with 4 V cathode materials is possible in this electrolyte. The passivating Li₂O film acts as a solid electrolyte interface (SEI) that is an excellent conductor of lithium ions. Passivating films make possible the use of lithium anodes in other oxidizing solvents such as thionyl chloride (SOCl₂), bromine trifluoride (BrF₃) and molten perchlorates (3).

The molten nitrate must contain sufficient lithium ions in the melt for the rapid formation of the insoluble Li₂O film. Oxide ions are much more soluble in NaNO₃ and KNO₃ melts. Furthermore, oxide ions are readily converted to aggressive peroxide (O₂⁻) and superoxide (O₂⁻) ions in NaNO₃ and KNO₃ melts (4). Therefore, the use of the lithium anode in molten nitrate batteries is restricted to eutectic melts that contain appreciable amounts of LiNO₃. Increased mechanical stability for the liquid lithium anode can be provided by the use of iron powder or a porous lithium-boron matrix to immobilize the lithium.

The potentiostatic discharge behavior of the Li-B anode at 290°C in molten LiNO₃ is shown in Fig. 2.
The typical flat discharge curve shown in Fig. 2 for this anode corresponds to a sustained current density of 780 mA/cm².

The constant current discharge of the Li-B anode at 100 mA/cm² shows very flat discharge curves (E = -3.2 V vs. Ag+/Ag) in both molten LiNO₃-KNO₃ and LiNO₃-NaNO₃ at 260°C (5). The coulombic efficiencies for the lithium utilization were 92% in LiNO₃-KNO₃ and 77% in LiNO₃-NaNO₃. A markedly different behavior was observed in molten NaNO₃-KNO₃. Since there were no lithium ions in the melt, the Li-B anode showed a rapid loss of voltage due to the deterioration of lithium in this melt (5). This illustrates the necessity of LiNO₃ as a major component of the melt.

**Cathode Materials in Molten Nitrates**

Silver salts can be used with lithium anodes in molten nitrates to yield open-circuit cell current densities exceeding 3 V as illustrated in Fig. 1. Silver ions are unique in molten nitrates because they are readily reduced to the metal in reversible electrode reactions. Most other metal ions form nitrate complexes that are irreversibly reduced to the metal oxide (6). Insoluble silver salts are preferred in order to minimize the unwanted diffusion of silver ions to the anode. Previous studies have determined that the insoluble Ag₂CrO₄ and Ag₂PO₄ cathode materials can sustain current densities over 750 mA/cm² when used in the LiNO₃-KNO₃ melt with lithium anodes (7).

The use of nitrate melts totally changes the chemistry in molten salt batteries and opens the door to the use of new high voltage cathode materials. Metal oxide cathodes are especially attractive for use in the Li/LiNO₃-KNO₃ battery system. Many new types of transition metal oxides are under intensive investigation for use as rechargeable lithium ion batteries (8). Cell voltages exceeding 4 V are possible using transition metal oxides such as LiMn₂O₄ or LiCoO₂. Studies are being conducted at China Lake to determine the best high voltage cathode material to be used with the Li/LiNO₃-KNO₃ battery system. A highly reversible cathode material would provide a rechargeable molten nitrate based battery for possible application in electric vehicles. The operating temperature range of 150-350°C for the LiNO₃-KNO₃ battery would offer significant advantages over the Li/LiCl-KCl/FeS₂ molten salt battery that operates at a much higher temperature range (400-600°C).

**Discussion**

Safety is a major issue with any new high energy and power density battery system. Our studies have not revealed any significant hazards with the Li/LiNO₃-KNO₃ system at temperatures below 400°C. Lithium stability, of course, requires the presence of LiNO₃ as a major component of the melt. We have purposely tried to create rapid exothermic reactions by the electrochemical plating of lithium out of the melt at high current densities and various temperatures. Our interest in molten nitrates was kindled by their use at China Lake for the heat treatment of metals. Most organic materials, however, are not compatible with the oxidizing properties of molten nitrates and should be avoided.

Nitrate salts can thermally decompose to produce O₂, NO₂, and N₂ gases. The temperatures required, however, are well above the proposed operating temperature range for the Li/LiNO₃-KNO₃ battery (150-350°C). Standard thermal decomposition temperatures are 474°C for LiNO₃, 527°C for NaNO₃, 533°C for KNO₃, and 548°C for RbNO₃ (9).

The electrochemical oxidation of molten nitrates can produce NO₂ and O₂ gases as shown in Fig. 1. However, this reaction will not occur in the battery as long as lithium is available for oxidation. In a reversible system that uses a 4 V cathode material, charging the battery at a high current density may possibly push the cell potential into the region of the oxidation of molten nitrates (Fig. 1).

Finally, the most important issue is the energy and power density that could be expected from the new Li/LiNO₃-KNO₃ battery system using a 4 V cathode material. The theoretical energy densities are as high as 1100 Wh/kg, hence actual energy densities of 200 Wh/kg could be achievable. Single cell tests have produced 570
Wh/kg (5). Assuming a high rate discharge at 750 mA/cm² for 1 minute at a cell voltage of 3.2 V, power densities exceeding 5000 W/kg may be possible using the LiNO₃-KNO₃ melt.

Conclusions

The new Li/LiNO₃-KNO₃ battery system combined with a 4 V transition metal oxide cathode material can significantly increase the energy and power densities of thermal batteries while lowering the operating temperature of the battery by more than 200°C. Furthermore, this system is reversible and can also be used in rechargeable batteries for electric vehicles.

Acknowledgment

The author thanks In-house Laboratory Independent Research (ILIR) and the China Lake BMDO office for their support.

References