ELECTROCHEMISTRY OF MOLTEN NITRATE ELCTROLYTES AND APPLICATIONS FOR HIGH VOLTAGE LITHIUM CELLS

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Molten nitrate electrolytes exhibit much lower melting points than halide electrolytes. For example, the $LiNO_3$-KNO_3 (42-58 mol%) eutectic melts at 124°C while the LiCl-KCl (58-42 mol%) eutectic melts at 352°C, i.e., a difference of more than 200°C. Furthermore, molten nitrate electrolytes offer high ionic conductivity, low viscosity, and chemical stability over a wide temperature range. The $LiNO_3$-$NaNO_3$ (56-44 mol%) eutectic melts at 187°C and has an ionic conductivity of 1.14 S/cm and a viscosity of 0.00298 Pa·s at 327°C. The $LiNO_3$-KNO_3 and $LiNO_3$-$NaNO_3$ melts are chemically stable towards decomposition up to 470°C, thus both eutectics provide stability over a wide liquid temperature range. Table 1 presents various nitrate eutectic as well as several nitrate-nitrite eutectics.

The electrochemistry of molten nitrates is characterized by reduction to the oxide and nitrite

$$2\,Li^+ + LiNO_3 + 2e^- \rightarrow LiNO_2 + Li_2O_{(s)} \quad [1]$$

and oxidation to NO_2 and O_2 gases (1)

$$LiNO_3 \rightarrow Li^+ + NO_{2(g)} + 1/2\,O_{2(g)} + e^- \quad [2]$$

The cation of the nitrate salt significantly influences the electrochemical kinetics of the reduction reaction as well as the fate of the oxide ion produced (1). The nitrate reduction occurs most readily in $LiNO_3$ melts, and the Li_2O formed is stable. The weaker electric field around the larger Na^+ and K^+ ions allows the formation of peroxide or superoxide ions in the nitrate melt, thus the electrochemical reduction of molten $NaNO_3$ forms peroxide and the reduction of molten KNO_3 yields superoxide (1). In the $LiNO_3$-KNO_3 and $LiNO_3$-$NaNO_3$ eutectic melts, the electrochemical reduction yields predominantly Li_2O. In fact, this insoluble Li_2O film blocks further reduction of the molten nitrate and allows the electrostability region to be extended to the reversible reduction of lithium ions, i.e., $Li^+ + e^- = Li$ (2,3). This provides an electrochemical window of 4.5 V for molten $LiNO_3$ at 300°C as well as for the $LiNO_3$-KNO_3 and $LiNO_3$-$NaNO_3$ eutectics (2). Therefore, the use of lithium anodes with 4 V cathode materials is possible in molten nitrate electrolytes that contain sufficient $LiNO_3$. The passivating Li_2O film acts as a solid electrolyte interface (SEI) that makes the use of lithium anodes possible in the oxidizing molten nitrate electrolytes. Due to the relatively low melting point of lithium (mp=180.5°C), mechanical stability must be provided by the use of a lithium-boron matrix to immobilize the lithium (4) or by the use of higher melting lithium alloys.

Metal oxide cathode materials are stable in molten nitrates but not in molten chloride melts. The chloride ions rapidly attack the oxide at these high temperatures similar to the breakdown of passivating oxide films by chloride ions in corrosion processes. Thus, new high voltage cathode materials developed for commercial lithium-ion batteries can be used in molten nitrate electrolytes but not in chloride melts. Preliminary studies at China Lake, SAFT, and Sandia have shown that $LiCoO_2$ and $LiMn_2O_4$ high-voltage cathode materials are stable in molten nitrates. Previous work at China Lake has shown that insoluble silver salts such as Ag_2CrO_4 and Ag_3PO_4 can provide over 3 volts per cell and sustain high discharge current densities (5).

Possible applications for molten nitrate electrolytes include thermal batteries for missiles as well as missile defense systems. It should be possible to double the cell voltage and energy density of present Li/LiCl-KCl/FeS_2 thermal batteries (2.0 V, 44 W·h/Kg) by the use of a 4 V cathode material. Another possible application for molten nitrate electrolytes is batteries for oil/gas and geothermal boreholes (6). Low-melting molten nitrate electrolytes could also be used in batteries for alarm systems that activate if there is a fire. Various molten nitrate electrolytes could be used as shown in Table 1. Research at China Lake, however, has identified $LiNO_3$-KNO_3 and $LiNO_3$-$NaNO_3$ as the best electrolyte systems for applications in lithium batteries.

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Table 1. Selected Eutectic Data For Molten Nitrate and Nitrate-Nitrite Systems.[a]

System	Mol%	Tm (C)
$LiNO_3$-KNO_3-$CsNO_3$	37-39-24	97
$LiNO_3$-KNO_2	40-60	108
$LiNO_3$-$NaNO_3$-KNO_3	37.5-18-44.5	120
$LiNO_3$-KNO_3	42-58	124
$LiNO_3$-$LiNO_2$	30-70	147
$LiNO_3$-$RbNO_3$	30-70	148
$LiNO_3$-$CsNO_3$	57-43	174
$LiNO_3$-$NaNO_3$	56-44	187
$NaNO_3$-KNO_3	46-54	222

[a]From "Physical Properties Data Compilations Relevant to Energy Storage. 1. Molten Salts: Eutectic Data", NSRDS-NBS 61, Part 1, U.S. Department of Commerce, Issued March 1978.)