NITRITE MOLTEN SALT FOR USE IN INTERMEDIATE TEMPERATURE LITHIUM CELLS

J. Poris, I. D. Raistrick and R. A. Huggins

Department of Materials Science and Engineering
Stanford University
Stanford, CA. 94305

ABSTRACT

The LiNO$_2$-KNO$_2$ (40-50 m/o) molten salt, which melts at 120°C, has been employed as an electrolyte in intermediate temperature lithium cells. The behavior of solid lithium in this electrolyte is analogous to the behavior of lithium in the similar intermediate temperature alkali nitrate electrolyte. Lithium reacts with the melt to form a thin, lithium ion conducting, protective layer which is believed to be Li$_2$O. The electrolyte is electrochemically reduced below 1.9 volts versus Li$^+$/Li, and is oxidized to lithium metal and NO$_2$ gas above 3.5 volts versus Li$^+$/Li. This electrolyte can be used in secondary cells with lithium or high lithium activity negative electrodes, and lower lithium activity positive electrodes which react reversibly with lithium.

The resistance of the protective layer on lithium increases with time as the thickness increases. Its resistance is of the order of 1-10 ohms after 10 hours at 150°C.

INTRODUCTION

Most lithium batteries presently under development operate either at the high temperatures associated with the LiCl-KCl molten salt (350-450°C), or at ambient temperatures utilizing organic solvent-based electrolytes. Intermediate temperature lithium batteries would be an attractive alternative if the problems associated with high temperature corrosion could be avoided, without sacrificing reasonable kinetic properties. Recently, the lithium chlorate and alkali metal nitrate systems have been proposed as electrolytes in intermediate temperature lithium cells (1,2).

Several battery systems are able to utilize lithium or high lithium activity negative electrodes whose potentials lie below the reduction limit of the electrolyte. This is a result of the formation of a protective layer which acts as a second electrolyte in series with the original electrolyte. A schematic drawing of this arrangement is shown.
in Figure 1. This layer must have an adequate lithium ion conductivity, a relatively small electronic conductivity, and be mechanically and chemically compatible with the original electrolyte. This appears to be the situation with lithium in some organic solvent-based cells and in the sulfur dioxide and thionyl chloride systems.

When solid lithium is exposed to the LiNO$_2$-KNO$_2$ (40-60 m/o) molten salt, which melts at 120°C, it is immediately covered by a thin layer of lithium oxide, as shown in Figure 2. This prevents a massive direct chemical reaction of the solid lithium with the molten nitrite, whilst allowing the ready transport of lithium ions across this newly formed intervening layer. This protective layer allows the use of this electrolyte in primary and secondary lithium cells with promising kinetic and energy storage properties.

**THERMODYNAMICS OF THE NITRITE ELECTROLYTE**

Solid lithium metal reduces the nitrite electrolyte at 150°C to form a thin lithium oxide layer. The identity of the other reaction product is not known at this time. It is possibly a hyponitrite species or even nitrogen gas.

The stability limits of an electrolyte define the potential range within which the electrolyte is stable to electrochemical reduction or oxidation by a chemically inert electrode. The reduction and oxidation potentials of this nitrite electrolyte were determined by cyclic voltammogram experiments. The voltage of an inert platinum electrode was swept at a constant rate between two voltage limits while the current and voltage with respect to a lithium reference electrode were recorded. Figure 3 shows that a reduction reaction occurs at 1.9 volts versus Li$^+$/Li at 150°C. A maximum in the reduction current was observed when the potential was swept below this value. This occurs because lithium oxide, a relatively insoluble product of the reduction reaction, forms on the inert platinum electrode and prevents the further reduction of the electrolyte by blocking the transport of electronic species. If the lithium oxide is not removed, only a small current will pass until a potential is reached at which lithium (or a lithium-platinum alloy) is formed. If the lithium oxide is removed by oxidation, dissolution or any other process, a substantial reduction current will once again be observed upon lowering the potential below 1.9 volts versus Li$^+$/Li. Because the other product of the reduction reaction is not known, no theoretical calculation of the reduction potential can be made at this time.

The half cell electrochemical reaction associated with the oxidation of the nitrite electrolyte is believed to be:

$$\text{NO}_2^- = \text{NO}_2(g) + e^-$$  \hspace{1cm} (1)
This can be combined with the lithium reduction half cell reaction:

\[ \text{Li}^+ + e^- = \text{Li}(s) \]  
(2)

The chemical oxidation reaction for the nitrite electrolyte is therefore:

\[ \text{LiNO}_2 = \text{Li(s)} + \text{NO}_2(g) \]  
(3)

This was observed to occur experimentally at 3.5 volts versus Li⁺/Li at 150°C in a cyclic voltammogram experiment, as shown in Figure 4. Using the free energies of formation of LiNO₂ (3) and NO₂(g) (4) at 150°C, a theoretical potential of 3.4 volts versus Li⁺/Li can be estimated for this reaction, which is in quite good agreement with the experimental results. The stable potential range of this system is therefore 1.9 to 3.5 volts versus Li⁺/Li, similar to some organic solvent-based lithium electrolytes.

SECONDARY CELL APPLICATIONS

Suitable positive electrode materials must be found in order to construct a nitrite secondary lithium cell. The combination of negative and positive electrode materials must provide an adequate specific energy. This requires a maximization of the capacity for lithium and the cell potential and a minimization of the molecular weights of both the negative and positive electrode materials.

Several positive electrode materials which have been used in other lithium cells were tried in the nitrite electrolyte. V₂O₅, Na₀.₄WO₃, Na₀.₅WO₃, MoO₃, TiS₂, FeS and FeS₂ all reacted chemically with the nitrite melt and released a gaseous product. The composition of these gases and the final products of these reactions are not known at this time.

An alternative approach to positive electrode materials in the nitrite electrolyte is the use of lithium-containing binary or ternary alloys. These typically have higher lithium activities than oxides or sulfides, hence lower cell potentials. A capacity of 1/2 of a lithium per metal ion in an oxide is common, while some binary alloys react with up to 3 lithiums per metal ion. Therefore a secondary cell with an alloy positive electrode material may well have a smaller cell potential but a larger capacity than a cell with a typical oxide electrode. The specific energy of a secondary cell with an alloy positive electrode should be similar to that of a cell with an oxide reactant if the molecular weights are comparable. One possible disadvantage of using alloy positive electrodes is that they may be corroded by the nitrite melt because of their high lithium activity. If their potentials are below the reduction limit potential of the electrolyte, they will be oxidized by the nitrite ions. This phenomenon also occurs on the negative electrode, as will be discussed in a later section of this paper.
The lithium-bismuth system has been studied in the LiCl-KCl electrolyte at elevated temperatures (5). The high temperature results indicated that this would be a good system to study in the nitrite electrolyte. Electrodes were prepared by two different methods. Elemental bismuth was mechanically pressed onto a steel screen and was used directly. Another method of electrode preparation was to melt the bismuth in a molybdenum bucket at approximately 300°C in a helium-filled dry box. Lithium was then added a little at a time while the temperature was raised to keep the mixture in a molten state. The maximum temperature was a function of the composition of the mixture, as determined by the lithium-bismuth phase diagram. A steel screen was then dipped into the molten alloy and removed. The amount of the alloy which froze onto the screen was then weighed and used as an electrode of that specific composition. The bismuth-containing electrode was then placed in the nitrite electrolyte along with a lithium electrode at 150°C. Electrochemical experiments were performed in order to determine the equilibrium potential versus composition (coulometric titration) curve for this system. Current was passed through the cell with a galvanostat while the amount of charge was monitored with a coulometer. This allowed the calculation of the amount of lithium added to or subtracted from the electrode. The voltage of the electrode was monitored on a chart recorder. When equilibrium was attained, the voltage and composition of the electrode were recorded. This was repeated over the compositional range of interest for this electrode system. The solid line in Figure 5 shows the equilibrium coulometric titration curve for the lithium-bismuth system in the nitrite melt at 150°C. A two-phase mixture of Bi and LiBi exists from x=0 to x=1 at a potential of 0.833 volts versus Li⁺/Li. This is similar to the results obtained in the LiCl-KCl melt at elevated temperatures, except for the fact that bismuth is molten above 271°C and dissolves an appreciable amount of lithium. The titration curve in the LiCl-KCl melt at 380°C is shown as a dashed line in Figure 5 (5). There is virtually no solubility of lithium in solid bismuth at 150°C. A second two-phase plateau consisting of LiBi and Li₃Bi exists from x=1 to x=2.8. Once again, this is similar to the high temperature data (5). The potential of this plateau was measured as a function of temperature in the LiCl-KCl melt (5). If these data are extrapolated, a value can be predicted at 150°C, as shown in Figure 7. The potential experimentally measured in the nitrite melt, 0.797 volts, agrees well with the extrapolated value of 0.803 volts. The Li₃Bi phase has a width of approximately 0.2 lithiums per bismuth in both the nitrite and chloride melts, as shown in Figure 5. The maximum theoretical specific energy can be calculated from the equilibrium coulometric titration curve obtained using the nitrite electrolyte. A value of 233 watt-hours/kg is thereby assigned to the lithium-bismuth system at 150°C.

The lithium-antimony system has also been studied at elevated temperatures in the LiCl-KCl melt (5). It should exhibit a greater theoretical specific energy than the lithium-bismuth system because of the smaller molecular weights and higher potentials of the antimony alloys.
Lithium-antimony electrodes were prepared in a similar manner to the lithium-bismuth electrodes. Lithium and antimony were reacted in a helium-filled dry box. The mixture was equilibrated, ground into a fine powder and pressed into small pellets. A pellet was then placed in a molybdenum noose and used as an electrode. The method of dipping a steel screen into the molten mixture could not be used because iron reacts with antimony at the temperatures required to keep the mixture in a molten state. The equilibrium coulometric titration curve was obtained for this system using the nitrite electrolyte and is displayed as the solid line in Figure 6. The corresponding curve in the LiCl-KCl melt is shown as a dashed line in the same figure (5). Both curves show a two-phase plateau from $x=0$ to $x=2$, and a two-phase plateau from $x=2$ to $x=3$. The temperature dependence of the plateau potentials measured in the chloride melt is shown in Figure 7 (5). If these are extrapolated, they can be compared to the values obtained in the nitrite melt at 150°C. The experimentally obtained potential of the Sb-Li$_2$Sb plateau in the nitrite melt, 0.958 volts, is slightly higher than the extrapolated value from the chloride melt data, 0.947 volts. Similarly, the Li$_2$Sb-Li$_3$Sb plateau potential found in the nitrite, 0.930 volts, is higher than the value obtained from the chloride melt experiments, 0.914 volts. The maximum theoretical specific energy calculated from the titration curve utilizing the nitrite melt is 535 watt-hours/kg.

NITRITE CORROSION REACTION

A spontaneous chemical corrosion reaction occurs in all cells which employ an electrode which forms a protective layer. This is a consequence of the electrode potential being below the reduction limit potential of the electrolyte. The electrode is oxidized by the electrolyte while the electrolyte is reduced by the electrode.

Several properties of the protective layer, the dissolution rate, mechanical stability, thickness, ionic and electrical conductivity will control the rate of this corrosion reaction. This is an important property to quantify, since the corrosion reaction decreases the capacity of the electrode.

An experiment was devised to estimate the magnitude of this corrosion current. A constant lithium activity of 0.01 volts versus Li$^+$/Li was maintained on an inert nickel electrode in a nitrite melt saturated with lithium oxide. This was done to simulate the high lithium activity present at a lithium electrode, while minimizing the dissolution of the lithium oxide layer. If the potential were below 0.0 volts versus Li$^+$/Li, lithium plating would occur. The inert electrode should differ from a lithium electrode only by the morphology of the metal-protective layer interface. The current which passes through this electrode is due to the reduction of nitrite ions, the only species capable of being reduced at this potential. The electrons in the nickel electrode can reduce a nitrite ion only if there is a discontinuity in the protective layer, or an operable electronic
transport mechanism. This may be the result of a break in the layer, as shown in Figure 8. Another possible mechanism could be the local dissolution of the layer resulting in a thinner region, which increases the probability of electron tunnelling.

The measured current density was a constant 20 microamps/cm² of nickel, similar to the corrosion current density measured in the LiNO₃-KNO₃ electrolyte, which also exhibits a lithium oxide protective layer on lithium (6). This experiment was repeated with a Li₃Bi electrode replacing the inert nickel electrode in the nitrite melt. Once again, about 20 microamps/cm² was measured for the corrosion current density. These corrosion current densities are a measure of the rate of loss of the electrode due to corrosion.

PROTECTIVE LAYER RESISTANCE

The impedance of the protective layer on lithium or lithium alloys in the nitrite melt is important because the layer is in series with the molten salt electrolyte and contributes to the total cell impedance. This determines the IR losses, a critical battery parameter.

AC techniques were used to measure the impedance of the protective layer on lithium in the nitrite melt. A small amplitude sine wave was applied between two new lithium electrodes and the response was analyzed at several frequencies. A frequency low enough to obtain a response similar to a DC resistance was chosen, 1000 Hz. The DC resistance was then measured as a function of time at different temperatures. Figure 9 shows a plot of the resistance of two reaction product layers plus the electrolyte versus time at two different temperatures. As one would expect, the resistance is greater at lower temperatures. The resistance increases with time, but it does not obey simple parabolic oxidation kinetics. This is probably a result of complicating phenomena such as electron tunneling, breaking of the protective layer and possibly local dissolution of the protective layer.

ACKNOWLEDGMENT

This work was supported by the U. S. Department of Energy under subcontracts LBL 4503110 and LBL 4519410.

REFERENCES

(1) S. S. Wang and D. N. Bennion, J. Electrochem. Soc., 130, 741 (1983).

(2) I. D. Raistrick, J. Poris and R. A. Huggins, Proceedings of the Lithium Battery Symposium, Hollywood, Fla., The Electrochemical Society, A1-4, 477 (1981).
(3) L. E. Gastwirt and E. F. Johnson, USAEC Matt-98, U. S. Government Printing Office, (1961).

(4) I. Darin and O. Knacke, *Thermochemical Properties of Inorganic Substances*, Springer Verlag, Berlin/Heidelberg, (1973).

(5) W. Weppner and R. A. Huggins, J. Electrochem. Soc., 125, 7 (1978).

(6) I. D. Raistrick, J. Poris and R. A. Huggins, Proceedings of the 16TH IECEC, 1, 774 (1981).

\[ \text{Li} \quad | \quad \text{Li}_2\text{O} \quad | \quad (\text{Li,K})\text{NO}_2 \quad | \quad (+) \]

\( T=150^\circ \)

**Figure 1**
Schematic drawing of an electrode-electrolyte system with a protective layer

**Figure 2**
Configuration of the lithium electrode in the nitrite melt at 150°C.
Figure 3
Cyclic voltammogram of the nitrite reduction reaction on a platinum electrode at 10 mV/sec and 150°C

Figure 4
Cyclic voltammogram of the nitrite oxidation reaction on a platinum electrode at 10 mV/sec and 150°C

Figure 5
Equilibrium coulometric titration curves for the Li$_x$Bi system in the nitrite and chloride melts
Figure 6
Equilibrium coulometric titration curves for the \( \text{Li}_x\text{Sb} \) system in the nitrite and chloride melts.

Figure 7
Temperature dependence of the two phase plateau potentials in the \( \text{Li}_x\text{Bi} \) and \( \text{Li}_x\text{Sb} \) systems.

Figure 8
Simulation of the lithium corrosion process in the nitrite electrolyte.

Figure 9
Resistance of two protective layers plus electrolyte versus time in the nitrite melt.