NEW BATTERY MATERIALS

Progress Report
For period, April 1 - September 30, 1977

MASTER

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March, 1978

Prepared for:

U. S. Department of Energy under Contract
Number EC-77-S-02-4506

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ABSTRACT

Lithium ion conductivities of solid solutions formed between Li_4SiO_4 and Li_5AlO_4 have been measured. The conductivity of $\text{Li}_{4.5}\text{Al}_{.5}\text{Si}_{.5}\text{O}_4$ is comparable to the best previously known lithium ion conductors. The structural type is that of Li_4SiO_4 , and x-ray lattice parameters were determined across the range of solid solution. No solid solutions were found which had the Li_5AlO_4 (antifluorite structure).

Thermodynamic calculations based on available and estimated data suggest that lithium silicate is unstable with respect to attack by molten lithium at 700 K, and that Li_5AlO_4 may also be marginally unstable. Experimentally, the materials appear to have quite good stability at lower temperatures (300°C), but both Li_5AlO_4 and $\text{Li}_{4.4}\text{Al}_{.4}\text{Si}_{.6}\text{O}_4$ were attacked at 720K within a period of a few hours.

The intermetallic systems Li-Sb and Li-Bi, and the oxide systems Li- $\text{Li}_2\text{Ti}_3\text{O}_7$ have been studied as possible positive electrode systems for lithium batteries. Large lithium chemical diffusion coefficients were found in all 3 systems. Associated kinetic data (particle diffusion coefficients, partial conductivities, etc.), were calculated and thermodynamic data (emf versus composition) were obtained.

Beta LiAl was studied in considerable detail by coulometric titration and potentiostatic and galvanostatic transient techniques. Its range of existence was found to extend from 47 atom % to 55 atom % of lithium, between the voltages 300 to 70 mV with respect to pure lithium. Chemical diffusion coefficients in this phase are very large, lying between $2 \times 10^{-6} \text{ cm}^2/\text{sec}$ at the lithium rich end and $10^{-4} \text{ cm}^2/\text{sec}$ at the lithium deficit end of its range of existence.

SECTION A.

Introduction

The work performed under this contract is aimed at the study and development of materials of possible utility in advanced battery systems, in particular, in high temperature cells using lithium as the anode (negative electrode) material. During the present reporting period, the work performed falls into two main categories.

First, the assessment of the utility of solids which have structures related to those of lithium orthosilicate or lithium oxide (antifluorite structure), as solid electrolytes or separators in advanced lithium batteries, and the further study and development of such materials.

Second, the study of mixed ionic-electronic conducting materials as possible electrodes in such cells, and the development of techniques for the evaluation of their thermodynamic and kinetic properties.

SECTION B.

Lithium Solid Electrolytes

1) Lithium Orthosilicate based materials

Prior to the commencement of this contract, it had already been shown that by doping lithium orthosilicate, Li_4SiO_4 , with lithium phosphate, Li_3PO_4 , a great enhancement of the lithium ion conductivity could be obtained [1,2]. The conductivity of these materials at temperatures of interest (350 to 450°C) was high enough to encourage further investigation of silicate systems as possible solid electrolytes in advanced lithium batteries.

In order to explore further the influence of doping on Li_4SiO_4 , an investigation of the Li_5AlO_4 - Li_4SiO_4 system was undertaken. In this case lithium is introduced into the silicate structure in excess, rather than in deficiency, as is true of the phosphate doping. It was also considered likely that by doping with the aluminate the thermodynamic stability of the material with respect to attack by molten lithium would be improved. The results of this study have been submitted for publication [3] and will be only briefly summarized here. An extended solubility of Li_5AlO_4 in Li_4SiO_4 was found, extending from the pure silicate up to 50 mole % aluminate. Throughout this region the solid solution has the lithium orthosilicate structure, and lattice parameters have been determined throughout this range. Maximum lithium ionic conductivity was found at the aluminate rich end of the solid solution. Conductivities were comparable to those found in the phosphate system; again electronic conductivities were negligibly small. These results indicate that the silicate structure can exhibit high lithium ion conductivity when doped in quite different ways. Further doping studies will be undertaken in the future, especially

in those systems which appear most likely to be stable with respect to the electrode material with which they will be in contact. Conductivity data are plotted for a number of compositions in Figure 1.

2) Materials with the antifluorite structure

Materials with the defective antifluorite structure, such as Li_5AlO_4 , have been previously shown to have a very high lithium ion conductivity above a transition at about 400°C [4]. Later work by Johnson et al. [5] however, has shown that this transition is dependent upon the presence of small quantities of water in the material, and that by completely drying the samples and atmosphere this jump in conductivity is eliminated. Interest in materials with the antifluorite structure, however, continues because it is now known that some of them form wide ranges of solid solution with Li_4SiO_4 as discussed above and also because the possibility exists that the high conductivity shown by Li_5AlO_4 in the presence of small quantities of water may be duplicated by other dopant schemes.

Several attempts have therefore been made to dope either Li_2O or Li_5AlO_4 . A small increase in the conductivity of lithium oxide was obtained by doping with lithium fluoride (10 and 20 mole %) but attempts to dope Li_5AlO_4 with lithium phosphate and lithium orthosilicate were unsuccessful. At the present time, it appears therefore that the lithium oxide antifluorite structure is less able to support wide variations in stoichiometry than is the lithium orthosilicate structure, and thus we are less able to control and optimize the ionic conductivity in this structure.

3) Thermodynamic Stability of lithium solid electrolytes

One of the most important requirements of a solid electrolyte is that it should be stable in contact with the electrode materials with which it is to be used. In assessing the utility of the lithium orthosilicate type of electrolytes, attention so far has been focused on the question of their stability at high lithium activities. Unfortunately, few thermodynamic data are available for these compounds. Data available from the literature are:

$$\Delta G_f^{700K} (\text{Li}_4\text{SiO}_4) = - 482.8 \text{ k cal/mole [6]}$$

$$\Delta H_f^{298K} (\text{Li}_3\text{PO}_4) = - 502.6 \text{ k cal/mole [7].}$$

No data are given for Li_5AlO_4 , however, from a consideration of the phase diagram and a knowledge of the free energies of formation of lithium oxide and LiAlO_2 [8] it is possible to estimate the following range:

$$- 545.7 \text{ k cal/mole} \leq \Delta G_f^{700K} (\text{Li}_5\text{AlO}_4) \leq - 492.4 \text{ k cal/mole.}$$

No information, of course, is available for the solid solutions between lithium silicate and either lithium phosphate or lithium aluminate.

Using the above data we can calculate the free energies of the reactions of these compounds with molten lithium:

Based on the exact stoichiometries given in these equations, we find the following values:

$$\Delta G_{\text{I}} = - 4.4 \text{ k cal/mole}$$

$$5.2 \text{ k cal/mole} \leq \Delta G_{\text{II}}^{700\text{K}} \leq 58.5 \text{ k cal/mole}$$

$$\Delta G_{\text{III}}^{298\text{K}} = - 20 \text{ k cal/mole}$$

Thus, it appears that lithium orthosilicate and lithium phosphate are unstable to attack by lithium, whereas, lithium aluminate is probably marginally stable to attack by molten lithium at 700K. However, in any actual battery there will be an excess of lithium present, able to dissolve the aluminum or silicon produced by these reactions. In order to estimate the magnitude of this extra free energy of solution, calculations were performed based on available literature data for the activities of silicon [9] and aluminum [10], in molten lithium.

The additional free energy of solution depends on the relative amounts of the silicate or aluminate and the lithium, but for a 3 mole % solution of silicon in lithium (saturated) an additional 33 k cal/mole of lithium orthosilicate are obtained and for 1 mole of Li_5AlO_4 , 5.6 k cal/mole are obtained on forming a saturated 13 mole % solution of aluminum in lithium.

Thus, under these conditions the silicate seems certain to dissolve in molten lithium at 700 K, and the aluminate case is finally balanced but attack by the lithium is a possibility. A more accurate value for the free energy of formation of Li_5AlO_4 is required before an accurate prediction can be made. With regard to the solid solutions, all that can be said is that dissolving the aluminate in the silicate will probably tend to increase the stability of the silicate, whereas dissolving phosphate in the silicate will probably tend to decrease its stability. Determinations of the free energies of solid solution would be necessary before quantitative predictions can be made.

By way of contrast sodium beta alumina is stable in the presence of molten sodium by virtue of 1) the much greater free energy of formation of sodium beta alumina (~ 1995 k cal/mole) and 2) the complete insolubility of aluminum in sodium.

Several experiments have been performed in an attempt to assess the stability of Li_4SiO_4 and its solid solution with respect to attack by molten lithium salt.

At low temperatures (320°C) tubes fabricated by isostatically cold pressing a 40 mole % Li_5AlO_4 in Li_4SiO_4 solid solution and sintering showed good corrosion resistance. Lithium was electrochemically pumped backwards and forwards through the electrolyte tubes at high current densities (up to 100 milliamps/cm²) for extended periods of time (up to 120 hrs.). At higher temperatures however (450°C) both Li_5AlO_4 and $\text{Li}_4\text{SiO}_4\text{-Li}_5\text{AlO}_4$ solid solutions showed evidence of attack by molten lithium. The surface of the electrolyte becomes black, and microprobe analysis indicates that silicon is removed preferentially from the solid solution.

X-ray diffraction showed no evidence of any other phases besides the original one, but optical microscopy indicated that lithium attacked preferentially along grain boundaries. At the present time the overall conclusion would be that the materials under investigation show less than satisfactory resistance to molten lithium at the upper limit of operating temperature for a lithium-metal sulphide battery. In the future attempts will be made to characterize the corrosion products more fully, and to obtain precise thermodynamic data about some of the electrolyte materials of interest.

In addition, the influence of other dopants selected to produce increased thermodynamic stability, will be investigated.

SECTION C.

Electrode Materials

During the present reporting period, work was performed on several materials of possible interest as electrodes in high temperature lithium batteries. These systems were:

- 1) Lithium-Bismuth
- 2) Lithium-Antimony
- 3) Lithium-Lithium Titanate
- 4) Lithium-Aluminum.

Study of the first three materials systems was only partially funded by the Department of Energy as the projects were instigated with funding from alternative sources. Results of these studies have been published in detail elsewhere, and will be only briefly summarized here. [11 - 15]. The lithium aluminum study was funded entirely by the Department of Energy.

1) Lithium-Antimony and Lithium-Bismuth Intermetallic Systems

Using galvanic cells of the type:

The thermodynamic properties of the intermetallic systems lithium-antimony and lithium-bismuth were determined. The lithium-X ratio was changed systematically by coulometric titration. The thermodynamic quantities, such as the standard free energies, enthalpies and entropies of formation were obtained as a function of composition for the Li_3X phases. LiBi and Li_2Sb were found to be the only other phases in these systems.

In addition, chemical diffusion coefficients were determined as a function of composition for the phases Li_3Sb and Li_3Bi , by an intermittent galvanostatic technique, developed in this laboratory. Chemical diffusion coefficients in these systems were very high: 1×10^{-5} to $6 \times 10^{-5} \text{ cm}^2/\text{sec}$ in Li_3Sb , and 8×10^{-5} to $2 \times 10^{-4} \text{ cm}^2/\text{sec}$ in Li_3Bi . These high values of diffusion coefficient imply high specific powers for cells utilizing such fast electrodes. In addition the thermodynamic data allow the maximum specific energies to be calculated for lithium cells with antimony or bismuth cathodes. These are 500 and 290 watt hr. per kilogram, respectively, at 370°C .

2) The Lithium-Lithium Titanium Oxide System [15]

Recent work on cathode materials for lithium batteries has been focused primarily on the di-chalcogenides of group 4, 5, and 6 transition metals, for example TiS_2 . In such materials the lithium ions are inserted into the van der Waals layers between neighboring S-Ti-S blocks. The possibility also exists that framework structures with tunnels form a suitable geometric arrangement for fast diffusion of inserted alkali metal ions. In order to examine this kind of material the lithium-titanate, $\text{Li}_2\text{Ti}_3\text{O}_7$, which has the ramsdellite structure was selected.

The experimental arrangement was identical to that described in the previous section. As lithium was added to $\text{Li}_2\text{Ti}_3\text{O}_7$ ($\text{Li}_{2.3+\delta}\text{Ti}_{3.4-\delta}\text{O}_8$) an irreversible phase transition to a spinel structure took place at about $\delta = .3$ (at 700K). From $\delta = 1$ to $\delta = 2$ a two phase region consisting of the spinel structure and a sodium chloride structure was found. Chemical diffusion coefficients in the ramsdellite and sodium chloride phases were extremely rapid (greater than or equal to $10^{-5} \text{ cm}^2/\text{sec}$ at 700 K) and

voltages versus lithium (average approximately 1.6 V) were sufficiently high to warrant further investigation of similar systems.

3) The Lithium-Aluminum System

Although lithium aluminum alloy is a promising candidate for use as the negative electrode material in lithium-iron sulphide high temperature molten salt batteries, presently available information on both the kinetic and the thermodynamic properties of this intermetallic system is inadequate.

During the charge-discharge cycle, the composition of the lithium-aluminum electrode traverses a 2 phase region consisting of a saturated solid solution of lithium in aluminum (α) and the beta phase "LiAl".

Emf measurements by Yao et al [16] showed a constant voltage of 300 mV versus pure lithium for this two phase region; more recent measurements of Salman [10] have been concentrated in the lithium rich side of the phase diagram. Several measurements of the chemical diffusion coefficient of lithium in beta LiAl have been made [17-19]. There is however very poor agreement, the reported values diverging by several orders of magnitude.

In the present reporting period therefore a study of beta LiAl was undertaken to determine a) the chemical potential of lithium as a function of composition across this phase, b) the chemical diffusion coefficient and associated kinetic parameters again as a function of composition. The galvanic cell:

was used for the measurements. Lithium was added to, or removed from, the beta lithium aluminum working electrode and the emf versus composition curve shown in Figure 2 was obtained.

The chemical diffusion coefficient was determined both by the galvanostatic intermittent titration technique developed in this laboratory [11,13,14] and also by a potentiostatic method. The variation of chemical diffusion coefficient is shown in Figure 3. As may be seen, on the lithium excess side of $\text{Li}_{1.0}\text{Al}$, the chemical diffusion coefficient is virtually constant, but increases quite rapidly at lower concentration of lithium. In the future this work will be extended to include the α phase of LiAl .

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Figure 1.

Figure 2.

Figure 3.

FIGURE CAPTIONS

Figure 1: Ionic conductivity of lithium orthosilicate - lithium aluminate solid solutions. Composition given as mole fraction of aluminate.

Figure 2: Coulometric titration curve of $\beta\text{-Li}_{1+\delta}\text{Al}$ at 415°C .

Figure 3: Compositional dependence of chemical diffusion coefficient of Li in $\beta\text{-Li}_{1+\delta}\text{Al}$.

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1. Lithium Ion Conducting Solid Electrolytes in the System Li_4SiO_4 - Li_5AlO_4 . Y-W. Hu, C. Ho, I. D. Raistrick and R. A. Huggins, Submitted to J. Phys. Chem. Solids.
2. Ionic Conductivity of Li_4SiO_4 and its Solid Solutions, Y-W. Hu, I. D. Raistrick and R. A. Huggins. Extended Abstract submitted to the Electrochemical Society. To be presented at the Electrochemical Society Meeting in Seattle, May, 1978.
3. Thermodynamic and Transport Properties of β - LiAl , C. J. Wen, B. A. Boukamp and R. A. Huggins. Extended Abstract submitted to the Electrochemical Society. To be presented at the Electrochemical Society Meeting in Seattle, May, 1978.