NEW BATTERY MATERIALS

Progress Report

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ABSTRACT

Ionic conductivities of solid solutions formed between Li_4SiO_4 and Li_2SO_4 have been measured. The conductivity of $0.7 \text{ Li}_4\text{SiO}_4 \cdot 0.3 \text{ Li}_2\text{SO}_4$ is comparable to the best lithium ion conductors previously found in other lithium silicate solid solution systems. At low Li_2SO_4 concentrations the solid solutions have the Li_4SiO_4 structure; from 30 - 50 m/o Li_2SO_4 the Li_3PO_4 structure is found. Other work on Li_4SiO_4 type electrolytes includes thermodynamic measurements on Li_5AlO_4 , conductivity studies involving other dopant systems and the development of ac techniques for the study of the dependence of conductivity on microstructure.

Very high lithium conductivities have been obtained in polycrystalline samples of lithium nitride, the conductivities are comparable to those found in single crystal samples.

Work on the lithium-aluminum electrode system has been extended to include a detailed study of the kinetics of Li diffusion in the α -phase

I. INTRODUCTION

This is the second semi-annual progress report prepared under a contract aimed at the study and development of new materials of possible utility in advanced lithium battery systems. Work completed during the first 6 months of this project is described in Progress Report C00-4506-1 (March, 1978).

As in the earlier reporting period two main areas of research have been pursued. The first of these relates to lithium conducting solid electrolytes, suitable for application at elevated temperatures ($\sim 400^{\circ}\text{C}$) in batteries in which lithium is the active anodic (negative electrode) constituent. Work on the lithium silicate and lithium phosphate type of electrolytes has involved studies of the effect of several different kinds of dopant on the ionic conductivity, an assessment of the stability of the presently known electrolytes at high lithium activities, and a study of the effect of polycrystalline electrolyte density (as affected by preparative conditions) on the ionic conductivity. Since October 1, 1977, work on polycrystalline lithium nitride, possibly the best lithium ion conductor yet found, has been included in this program.

The determination of the thermodynamic and kinetic properties of Li-Al alloys, a negative electrode material currently under development for use in lithium-metal sulfide high temperature battery systems, has continued with studies of the α phase. Some results for the β phase were given in the previous report.

This report describes only work in those areas where a reasonable degree of completeness has been achieved at the time of writing. Several other topics are under active investigation. For example, in the last report,

work on the ternary system Li-Ti-O was described which demonstrated that several phases in this system could act as positive electrode materials with extremely attractive kinetic properties. Other systems, of a similar type are being investigated but results of these studies at the present time are far from complete, and discussion of them will be deferred.

II. LITHIUM CONDUCTING SOLID ELECTROLYTES

A. Ionic Conductivity in Solid Solutions with the Lithium Orthosilicate and Lithium Orthophosphate Structures.

Since it was first demonstrated [1-3] that doping with lithium phosphate, Li_3PO_4 , greatly increased the lithium ionic conductivity of lithium orthosilicate, Li_4SiO_4 , a number of other dopant systems have been studied. Sufficiently high conductivities have been obtained to make these materials of interest as possible solid electrolytes in high temperature cells which utilize lithium as the anode material. In the last six months, work has been performed in the following areas which are aimed at assessing the utility of such electrolytes and at improving their properties for battery application: 1) conductivity studies of different dopant systems; 2) structural studies and phase relationships in different dopant systems; 3) effect of density and preparative procedure on conductivity; 4) thermodynamic assessment of the stability of the electrolytes in high lithium activity environments.

Conductivity Studies

In the previous report conductivity data for the system $\text{Li}_5\text{AlO}_4\text{-Li}_4\text{SiO}_4$ were presented. In the present reporting period, conductivity studies on the system $\text{Li}_2\text{SO}_4\text{-Li}_4\text{SiO}_4$ have been completed and preliminary information obtained on the systems $\text{Mg}_2\text{SiO}_4\text{-Li}_4\text{SiO}_4$, and $\text{Li}_3\text{VO}_4\text{-Li}_4\text{SiO}_4$.

Solid solutions of $\text{Li}_2\text{SO}_4\text{-Li}_4\text{SiO}_4$ could be prepared up to about 50 m/o Li_2SO_4 content. Beyond this pure Li_2SO_4 was present as a second phase and could be identified by its characteristic 570° phase transition using differential thermal analysis. From 0 - 20 mole/o Li_2SO_4 the solid solutions had the Li_4SiO_4 structure; from 30 - 50 m/o the lithium phosphate structure was found.. Lattice parameters are shown in Fig. 1 (referred to the Li_4SiO_4 unit cell over the whole composition range).

Fig. 1: Crystallographic data for Li_2SO_4 - Li_4SiO_4 Solid Solutions.

For conductivity measurements, 3/8" diameter discs were produced by hot pressing at temperatures between 770°C (50 m/o Li_2SO_4) and 920°C (4.8 m/o) in graphite discs. Blocking electrodes were sputtered onto the samples and ionic conductivity data were obtained by analysis of the frequency dependence of the overall sample impedance. Conductivity data are given for solid solutions of different composition in Fig. 2. As may be seen, the maximum conductivity is obtained at 30 m/o of Li_2SO_4 . The conductivity of this sample is very close to the highest values found in the Li_3PO_4 - Li_4SiO_4 and Li_5AlO_4 - Li_4SiO_4 systems. Conductivities at 100°C, activation enthalpies and pre-exponential factors are compared for the three systems in Fig. 3, 4, and 5. The electronic conductivity of a 40 m/o sample of Li_2SO_4 - Li_4SiO_4 was measured at 200° and 300°C and found to be about 5 orders of magnitude less than the ionic conductivity.

Preliminary conductivity measurements on the system Li_3VO_4 - Li_4SiO_4 indicate conductivities very close to values previously obtained for the phosphate doping. Li_3VO_4 has the lithium phosphate structure and is therefore expected to behave similarly to Li_3PO_4 when doped into the silicate.

Mg_2SiO_4 however, appears to have a completely different effect on the conductivity. Solid solutions between Li_4SiO_4 and Mg_2SiO_4 are known to exist up to about 25 m/o of Mg_2SiO_4 [4]. Conductivities have been measured over this range between room temperature and 450°C. At the upper limit of temperature conductivities are comparable to the phosphate, aluminate or sulphate doped materials, but much higher activation enthalpies are observed. At low temperatures conductivities are about the same as Li_4SiO_4 .

Solid solutions of Li_4SiO_4 with the alkaline earth silicates are being investigated because it is expected that they will show greater thermodynamic stability than the systems investigated earlier.

Fig. 2: Ionic Conductivity of $\text{Li}_4\text{SiO}_4 - \text{Li}_2\text{SO}_4$ Solid Solutions.

LOG ($\sigma_{100^\circ\text{C}}$) VS. COMPOSITIONS
OF Li_4SiO_4 SOLID SOLUTIONS

Fig. 3: Conductivities at 100°C of the Solid Solutions.

Fig. 4: Activation Enthalpies for Conductivity.

LOG A VS. COMPOSITIONS OF
 Li_4SiO_4 SOLID SOLUTIONS

(A IN $\text{OHM}^{-1}\text{CM}^{-1}\text{K}$)

$$\sigma T = A \exp(-\Delta H / RT)$$

Fig. 5: Pre-exponential Factors

Dependence of Conductivity on Microstructure and Density

The conductivity results discussed above were obtained on dense polycrystalline samples (93 to 98 % theoretical density) produced by hot pressing. Sintering without hot pressing produces poor quality materials with lower density and lower conductivity. ac methods, developed in this laboratory can now be used to clearly distinguish between the true bulk conductivity and impedances due to grain boundaries, etc. This technique has two important applications: 1) the true ionic conductivity can often be extracted from a low quality ceramic material; 2) ac conductivity experiments can be used to effectively monitor the effect of the preparative procedure on the overall electrical properties.

As an example the true bulk resistivity R_b and the grain boundary resistivity R_g are tabulated below for three different densities of the material $\text{Li}_{4.3}\text{Si}_{1.7}\text{Al}_{1.3}\text{O}_4$ at 25°C. As can be seen, a good value for R_b can be obtained from a low density sample even when the grain boundary impedance is one order of magnitude greater than the true resistance.

Density ($\text{g}\cdot\text{cm}^{-3}$)	R_b ($\Omega\text{ cm}$)	R_g ($\Omega\text{ cm}$)
2.4	1.5×10^6	negligible
1.83	1.4×10^6	1.5×10^6
1.69	1.3×10^6	1.4×10^7

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 ortho-silicate type of electrolytes, attention so far has been focused on the question of their stability at high lithium activities. The free energy of formation of Li_4SiO_4 is known:

$$\Delta G_f^{700\text{K}}(\text{Li}_4\text{SiO}_4) = -482.8 \text{ k cal/mole} \quad [5]$$

and from this it is possible to calculate the free energy change for the reaction:

Thus, it appears that lithium orthosilicate-at 700K is-unstable with respect to attack by pure molten lithium. The reduction in lithium activity necessary to ensure stability, however, is not large: a decrease in the Li activity of about a factor of 2 causes ΔG_I to become positive. In particular the corresponding value for ΔG_I calculated at a lithium activity corresponding to the two phase Al, LiAl alloy electrode is + 23.3 k cal/mole at the same temperature. The lithium silicate family of electrolytes should therefore be quite stable at all but the highest lithium activities, assuming the absence of interfering reactions.

The free energy of formation Li_5AlO_4 is not available in the literature. However, from a consideration of the phase diagram and a knowledge of the free energies of formation of lithium oxide and LiAlO_2 [6] it is possible to estimate the following range:

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

This leads to a free energy change for the reaction:

of

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

Taking into account the solubility of Al in molten Li, an additional -5.6 k cal/mole are obtained. Thus, overall:

$$- 0.4 \text{ k cal/mole} \leq \Delta G_{\text{II}}^{700\text{K}} \leq 53.9 \text{ k cal/mole}$$

As ΔG_{II} is close to zero it was decided to attempt to measure $\Delta G_f^{700\text{K}}$ (Li_5AlO_4), using the galvanic cell

Preliminary emf measurements give a free energy of formation value for Li_5AlO_4 of ~ -497 k cal/mole, i.e., very close to the unstable edge of the range calculated above. No information, of course, is available for the solid solutions between lithium silicate and either lithium phosphate or lithium aluminate. 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 solutions with respect to attack by molten lithium,

At low temperatures (320°C) tubes fabricated by isostatically cold pressing a 50 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 Li_4SiO_5 - Li_5AlO_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 pure molten lithium at the upper limit of operating temperature for a lithium-metal sulfide 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.

B. Recent Work on Lithium Nitride

Introduction

Fast ionic conductivity in both single crystal and polycrystalline Li_3N has been reported [7-10]. The conductivity data for the polycrystalline material were obtained from ac conductivity measurements, using ionically blocking electrodes. In these samples an appreciable grain boundary resistance, which was strongly dependent on the microstructure [9], was found to influence the overall ionic conductivity at moderate temperatures. In order to assess the influence of this on the actual transport of lithium through the electrolyte, dc measurements were carried out, which are reported here. The results show a large discrepancy between the ac and dc conductivities for polycrystalline Li_3N samples, which is in contrast to results from single crystal measurements [10].

Sample Preparation and Conductivity Measurements

The preparation of pure Li_3N and of disc shaped polycrystalline samples has been reported previously [7,9]. Cold pressed samples were sintered in a purified nitrogen atmosphere at 750°C for $1/2 - 1$ hour. Both faces of a sample were polished flat, using emery paper. Lithium electrodes, protected on one side by molybdenum discs, were pressed onto each side of the sample.

The assembly was then placed between two spring loaded electrodes in a conductivity cell. To ensure good contact at the electrode-electrolyte interface a current was passed back and forth through the sample, which was maintained at 170°C , until no noticeable change in the resistivity was found. Then the dc conductivity was measured as a function of temperature between 20 and 170°C . To check for ohmic behavior, the conductivity was measured at various constant current levels (Typ. .05 to 10 mA.).

All handling of the sintered samples was carried out in a helium glove

box.

Results and Discussion

The temperature dependence of the dc conductivity, which shows an Arrhenius type behavior, is shown for two samples in Fig. 6. For comparison, the ionic conductivity as found from ac measurements, using ionically blocking electrodes [9] is shown in this figure. The activation enthalpy for the dc conductivity 28.7 kJ/mole, is somewhat higher than that from the ac measurements, 24.1 kJ/mole, but the dc conductivity is much larger than the ionic conductivity found from the ac experiments, and also does not show the influence of the grain boundary resistance [9].

It is difficult to rule out the possibility of a large electronic contribution to the dc conductivity, however, after removal of the lithium electrodes, the dc conductivity, measured between two molybdenum disc electrodes was smaller than $10^{-6} \text{ ohm}^{-1} \cdot \text{cm}^{-1}$. Remeasuring the dc conductivity with lithium electrodes gave reproducible results.

Replacing the Li-electrodes by sputtered Mo-(blocking) electrodes, showed essentially the same ac response as reported previously [9], with no indication of a significant electronic conductivity.

The conduction mechanism is still unclear. So far the results indicate a possible dependence on the lithium activity, and thus on the stoichiometry of the material. More research is indicated.

Fig. 6: DC conductivity of polycrystalline Li_3N using lithium electrodes. For comparison the ionic conductivity, as found from ac measurements, using ionically blocking electrodes, is shown (dashed line) [3].

II. THERMODYNAMIC AND TRANSPORT PROPERTIES OF THE LITHIUM-ALUMINUM NEGATIVE ELECTRODE

The use of pure lithium in high temperature solid state and molten salt batteries imposes severe problems and design limitations, due to the high reactivity of molten lithium. Therefore, there is considerable interest in the use of the two phase system Al, β -LiAl as a possible anode system that has a lower (by 0.3 volts) lithium activity. By decreasing the lithium activity, i.e., by sacrificing 0.3 volts with respect to an all lithium anode, many more electrolytes can be used which are marginally stable or unstable with respect to lithium. The same is also true for materials used in the battery enclosure. During use, the composition of the lithium-aluminum electrode traverses a two phase region consisting of a saturated solid solution of Li in Al (the α -phase) and the intermetallic compound LiAl (the β phase). The emf versus composition curve, determined over the α , β and γ phases is shown in Fig. 7. Detailed thermodynamic and kinetic data for the β phase were given in the last Progress Report. During the present reporting period this work was extended to include the α phase.

The galvanic cell used in this study was

The chemical diffusion coefficient, $\tilde{D}_{Li}$, of lithium in α -aluminum was measured at various temperatures, using both galvanostatic and potentiostatic methods. In the potentiostatic measurements a constant electrode potential was maintained at 1 mV positive of the "Al, LiAl"

Fig. 7: The coulometric titration curve for the system Li-Al at 423°C, as a function of at% of incorporated lithium.

two phase reference electrode, and the transported charge, Q , was measured as a function of time. From this the diffusion coefficient was calculated.

In the galvanostatic method, a constant current was applied to the cell and the electrode potential was monitored as a function of time. The chemical diffusion coefficient was calculated using the Sand equation [11]

The values of $\tilde{D}$ obtained by both methods were in excellent agreement with each other, as is shown in Fig. 8. The chemical diffusion coefficient, which shows an Arrhenius type behavior, is plotted as a function of the inverse temperature:

$$\tilde{D}_{Li} = .155 \exp (-119.4 \times 10^3 / RT) \text{ cm}^2/\text{sec}$$

where the activation enthalpy, H , = 119.4 kJ/mole. At 400°C these results are in good agreement with previously reported values [12,13]. They are slightly lower at higher temperatures, see Fig. 8.

Fig. 8: Temperature dependence of the chemical diffusion coefficient of lithium in α phase LiAl. Previously reported results [12,13] are shown for comparison.

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