

SOLID LITHIUM ION CONDUCTORS FOR BATTERY APPLICATIONS

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Summary

The phase equilibria and conductivities of the LiF-LiH, LiF-LiOH, LiF-Li₂O, Li₂S-Li₂O, Li₂S-LiCl and Li₂S-LiBr systems were investigated. All ternary single phases and two-phase mixtures are solid electrolytes which are thermodynamically stable in respect of reaction with elemental lithium (anode) and at practically useful, low lithium activities (cathode). The conductivity normally increases with decreasing thermodynamic stability and *vice versa*. The conductivity may be optimized in the case of solid solutions by selecting a composition with a decomposition voltage just above the value required by the cathode material employed. All materials are isotropic in structure and no dendrite formation was observed. This allows their use in rechargeable, thin film electrolyte batteries.

Introduction

Practically useful electrolytes for lithium batteries require stability against reaction with lithium (or other materials of high lithium activity) used as anode material and against reaction with cathode materials of low lithium activity. Only metastable equilibria are achieved in many presently developed cases. Notably, for rechargeable (secondary) batteries and thin film electrolytes it is desirable, however, to provide *thermodynamic* stability at any state of battery discharge. In addition, a high ionic conductivity and ionic transference number are required, and the kinetic problem of the formation of electronic short-circuiting dendrites must be avoided.

Approach

In view of the complex thermodynamic constraints, the present approach to new solid lithium electrolytes attempts to keep the number of components small in order that the chemistry of the cell for a complete discharge process shall be as simple as possible. Since most binary lithium compounds are now well characterized (without finding a thermodynamically stable *and* fast conducting solid electrolyte), the search was extended to new ternary systems. Many successful approaches for other conducting

cations (e.g., Ag_4RbI_5 or Cu_4KI_5) used the addition of another salt with the same anion but a different cation. This approach usually results in instability against reaction with elemental lithium in the case of lithium ion conductors [1]. The reason for this behaviour is the high thermodynamic stability of most lithium compounds compared with most other compounds with the same anion. Contact of such a ternary compound with lithium will result in the "replacement" of the less stable cation and the formation of the more stable, binary lithium compound.

If, by contrast, two binary lithium salts (which are both stable with lithium) are used to form a ternary with lithium as the only cation but with two different anions, the product will also be stable against lithium (except in the hypothetical case in which a more Li-rich compound will exist). The decomposition voltage of the ternary compound has a value in between the decomposition voltages of the two binary compounds. The precise value must be determined experimentally. This concept has been successfully demonstrated previously in finding new solid electrolytes in the ternary systems $\text{Li}_3\text{N-LiHal}$ (Hal = Cl, Br, I) [2, 3].

The present study has investigated the phase equilibria and conductivities of the systems LiF-LiH , LiF-LiOH , $\text{LiF-Li}_2\text{O}$, $\text{Li}_2\text{S-Li}_2\text{O}$, $\text{Li}_2\text{S-LiCl}$ and $\text{Li}_2\text{S-LiBr}$. Lithium fluoride was employed because it had the highest thermodynamic stability of the binary lithium salts (decomposition voltage: 6.1 V at room temperature). Lithia and Li_2S show the antifluorite type structure which appears to be favorable for ionic transport in solids. Both single phases and two-phase mixtures were investigated. Composite electrolytes have, in several cases, shown enhanced ionic transport compared with the pure compounds [4].

Experimental

Phase equilibria were studied by high temperature DTA up to 1500 °C using niobium ampoules sealed under argon gas, and by Guinier-Simon X-ray investigation as a function of temperature. Conductivities were measured by a.c. impedance techniques over a frequency range from 1 Hz to 170 kHz [2, 5]. Molybdenum electrodes were employed. The partial electronic conductivities of the samples were evaluated from Hebb-Wagner d.c. polarization measurements [6] using lithium as the negative and molybdenum as the positive electrode. All binary starting chemicals were 99.9% pure (CERAC/PURE, Butler, Wisc.). The samples were annealed in molybdenum boats under dry argon. The composition was varied in increments of 5 - 10 mol-%.

Results

Lithium fluoride and LiH both have the NaCl type structure with nearly the same lattice parameter. There is, nevertheless, only a small temperature

regime, from about 550 to 630 °C, of complete miscibility. The minimum temperature exists at 65 mol% LiH. The miscibility gap ranges from 50 - 60 to 90 - 100 mol% LiH at room temperature. The conductivity shows Arrhenius type behaviour within the single phase regions (Fig. 1). The partial electronic conductivity is several orders of magnitude lower at any temperature. A transition from extrinsic to intrinsic behaviour of the conductivity is observed at high LiH contents, which indicates low disorder of the material. The lowest activation enthalpy (1.15 eV) is observed at an intermediate composition of 50 mol% LiH. The pre-exponential factor is the same for all compositions within the limit of error. A deviation from the Arrhenius law is observed within the miscibility gap, which is due to the variation of the relative amounts of both compounds with temperature in this composition range. The conductivity varies monotonically with temperature at any composition within the single phase and two-phase regions.

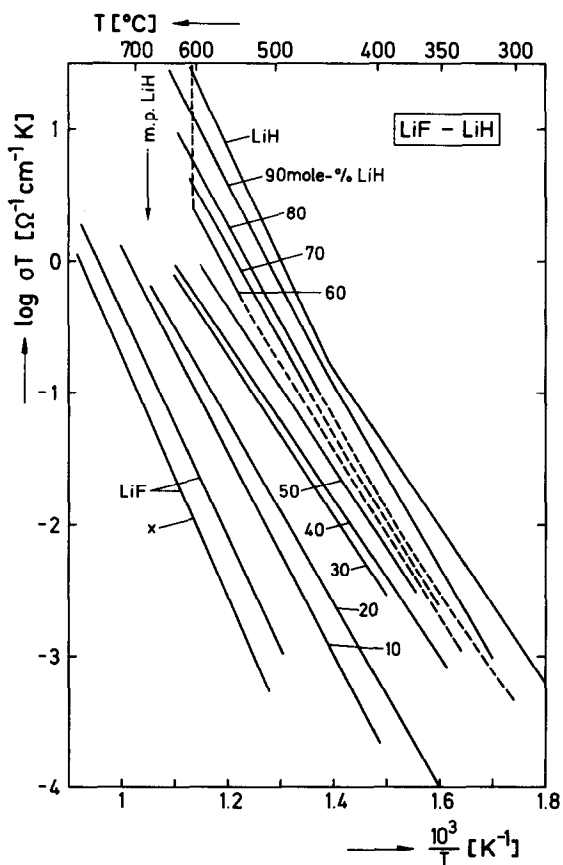


Fig. 1. Conductivities of LiF-LiH solid solutions as a function of temperature. The broken lines indicate the conductivities of the two-phase mixtures within the miscibility gap and the typical increase at the melting point at 60 mol-% LiH. For pure LiF both the results of single crystal (x) and polycrystalline material are shown.

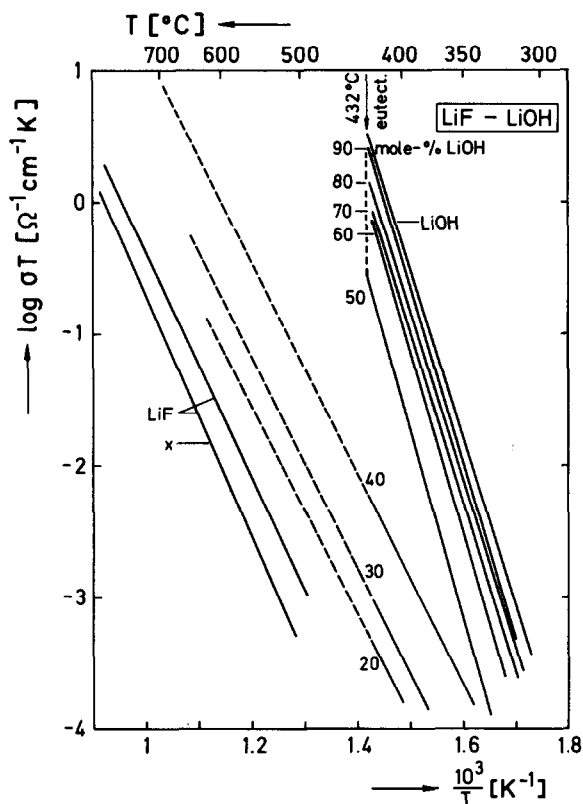


Fig. 2. Conductivities of two-phase mixtures of LiF and LiOH as a function of temperature. The broken lines indicate the conductivity after the sample becomes partially molten. Continuous paths of melt are observed above 50 mol% LiOH.

All other systems melt eutectically at 432 (LiF-LiOH), 800 (LiF-Li₂O), 955 (Li₂S-Li₂O), 580 (Li₂S-LiCl) and 530 °C (Li₂S-LiBr). The solid solubilities are small. The ternary samples investigated were two-phase mixtures of the binary lithium salts in all cases. The ionic conductivities are shown in Fig. 2 as a function of temperature for the system LiF-LiOH as an example. The activation enthalpy is nearly the same as for pure LiF up to 40 - 50 mol% LiOH. Lithium hydroxide forms isolated, high conducting grains. The conductivity is controlled by continuous paths of LiOH above 50 mol%. Lithium fluoride acts as an inert, second phase which is a geometrical restriction for the current density. This behaviour is also reflected by the conductivity above the partial melting at the eutectic temperature. For any given temperature, the conductivity increases with the amount of the thermodynamically less-stable material. The two-phase mixtures which have been investigated in the present study do not show any enhancement over the superior conducting binary lithium salt.

Conclusion

The experiments indicate, as a rule, the existence of a balance between the ionic conductivity and the thermodynamic stability of the solid electrolytes. If the conductivity is high, the decomposition voltage is low and *vice versa*. A high ion binding energy prevents an easy change of sites in the lattice.

The continuous variation of the thermodynamic stability within the solid solution phases allows, by the application of the specific cathode material, the conductivity of such an electrolyte to be optimized by changing the composition until the decomposition voltage is just above the value required.

All investigated materials have isotropic structures. This is related to the observation that no dendrites are formed during discharge and charge. It seems attractive therefore to employ thin, solid films of these solid electrolytes in order to decrease the internal cell resistance in the case of high power density applications.

References

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