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The Effects of Li_2SO_4 Addition, Moisture, and LiOH on the Ionic Conductivity of Li_5AlO_4*

R. M. BIEFELD AND R. T. JOHNSON, JR.

Sandia Laboratories,† Albuquerque, New Mexico 87185

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The ionic conductivity and thermal properties of $80Li_5AlO_4+20Li_2SO_4$, $75Li_2SO_4+25LiOH$, and $50Li_2SO_4+50LiOH$ composite polycrystalline samples have been determined in both wet and dry environments. A large increase in the ionic conductivity of $80Li_5AlO_4+20Li_2SO_4$ in a wet environment above ~350°C is due to the presence of LiOH. This same increase in conductivity is found for the two $LiOH+Li_2SO_4$ mixtures and is related to a eutectic reaction in the Li_2SO_4–LiOH system. The phase diagram for the Li_2SO_4–LiOH system was determined and supports this conclusion. The conductivity of $80Li_5AlO_4+20Li_2SO_4$ in a dry environment is thermally activated $[\sigma=\sigma_0 \exp(-E/kT)]$ with $E=0.66$ eV and $\sigma_0=450\ (\Omega\text{-cm})^{-1}$. The addition of Li_2SO_4 to Li_5AlO_4 increases the total conductivity but decreases the electronic conductivity. Pressed pellets of Li_5AlO_4 and $80Li_5AlO_4+20Li_2SO_4$ are stable in lithium up to at least 550 and 450°C, respectively.

Introduction

Lithium ion conducting solid electrolytes are being studied because of interest in battery applications and in obtaining knowledge about ionic transport mechanisms. The lithium ion conduction properties of several solids which have been discussed in recent papers (*1–8*) are presented in Fig. 1. One of the materials under investigation in our laboratory is Li_5AlO_4. Although Li_5AlO_4 does not have as high a conductivity as some of the other materials, it is of interest because of its stability in the presence of molten lithium and its high activation energy for conduction which is necessary for thermal battery applications (*9*). A previously reported (*8*) transition in Li_5AlO_4 to a highly conductive state above ~400°C (Fig. 2) has been shown (*6*) to be caused by the presence of LiOH which can be introduced by exposure to moisture. A recent report (*10*) indicated that the addition of Li_2SO_4 to Li_5AlO_4 decreases the temperature of the transition of Li_5AlO_4 to the high conductivity state from ~400 to 350°C and reduces the electronic contribution to the conductivity. The studies reported herein confirm the reduction in the electronic conductivity but show that the shift in the transition for the Li_5AlO_4–Li_2SO_4 materials is associated with the formation of LiOH upon exposure to moisture. Specifically, this paper reports on the effects of moisture and LiOH on the conductivity, thermal, and structural properties of a mixture of 80 mole% Li_5AlO_4 and 20 mole% Li_2SO_4. The conductivity of two LiOH and Li_2SO_4 compositions, the phase diagram of the LiOH–Li_2SO_4 system, and the effects of molten lithium on Li_5AlO_4 and Li_5AlO_4 plus Li_2SO_4 pressed pellets are also presented.

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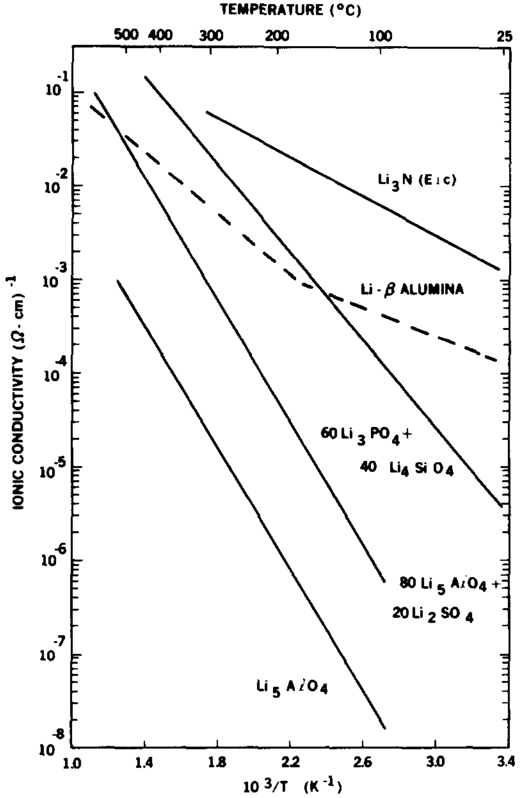

FIG. 1. Ionic conductivity temperature dependence for several lithium ion conducting solid electrolytes: Li_3N, single crystal, electric field perpendicular to *c*-axis (*1*); Li-β-alumina, single crystal, perpendicular to *c*-axis (*2*); $60Li_3PO_4+40Li_4SiO_4$, hot-pressed polycrystalline (*3–5*); $80Li_5AlO_4+20Li_2SO_4$, hot-pressed polycrystalline (this work); Li_5AlO_4, hot-pressed polycrystalline (*6, 7*).

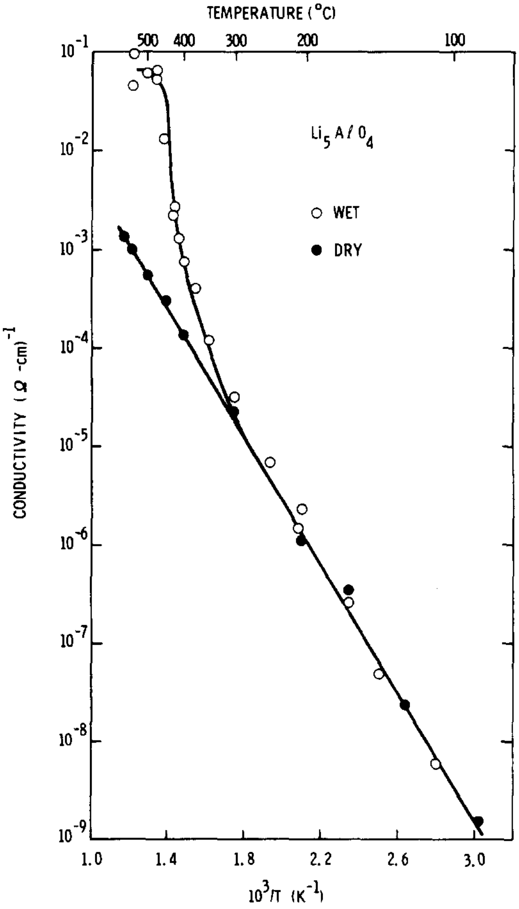

FIG. 2. Ionic conductivity temperature dependence for Li_5AlO_4 in flowing wet and dry O_2 environments. Results show transition to a high conductivity state in a wet environment at ~400°C which is associated with the formation of LiOH (*5*).

Experimental Methods

Reagent-grade LiOH and Li_2SO_4 were used as starting materials. The Li_5AlO_4 samples were prepared as described elsewhere (*6*). All materials were stored in an argon-filled glove box to prevent hydration. X-Ray powder diffraction using Cu*Kα* Ni-filtered radiation was used to determine the phase(s) present in the electrical and thermal analysis samples. Powdered specimens were used for differential thermal analysis (DTA). Samples for DTA of the Li_2SO_4–LiOH system were prepared at composition intervals of 5 mole%. Both heating and cooling curves were taken to determine the thermal events by using a Tem-Press Model TA-700 thermal analyzer, Pt sample holders, and Pt versus Pt 10% Rh thermocouples.

For conductivity and lithium compatibility experiments, disk-shaped samples (1–2 cm in diameter and ~2 mm thick) were prepared by hot-pressing as previously described (*6*). The temperatures used depended on the sample as follows: ~500°C for Li_5AlO_4; ~400–450°C for Li_5AlO_4–Li_2SO_4 mixtures;

and ~325°C for $LiOH$–Li_2SO_4 mixtures. The density of the hot-pressed disks varied from 80 to 95% of the theoretical density. The more dense samples usually contained >10 wt% LiOH [i.e., as previously reported (*6*), LiOH helps in densification of the samples].

Ionic conductivity measurements were made by using a two-terminal technique over the frequency range from 5 to 5×10^5 Hz (*6, 7, 11*). Ionically blocking silver foil electrodes were pressed onto the sample in a BN holder. The electronic conductivity was determined from dc polarization experiments at voltages of ~0.1 V. Dry samples (i.e., samples free of LiOH) for Li_5AlO_4–Li_2SO_4 mixtures were obtained by annealing in a dry environment at temperatures above the decomposition temperature for LiOH ($T \geq 450$°C) for 16–24 hr. The relative humidity of the dry flowing gas was always less than 4% as determined by an EG&G Model 660 dew point hygrometer. Before making the electrical measurements in wet environments, the samples were exposed to wet flowing air with a room temperature relative humidity greater than 70% at sample temperatures of 100, 400, or 500°C for 16–24 hr.

Compatibility tests of Li_5AlO_4 and Li_5AlO_4–Li_2SO_4 mixtures with molten lithium were carried out by immersing pressed pellets of these materials into a bath of molten lithium at ~200°C contained in a stainless-steel crucible in an argon-filled glove box. The lithium bath was heated from ~200°C to a maximum temperature of 550°C. The samples were held for 1–2 hr at temperature intervals of ~50°C and then removed for visual examination and X-ray diffraction analysis.

Structural and Thermal Results

The phase diagram of the Li_2SO_4–LiOH system is shown in Fig. 3. The solid circles represent the thermal discontinuities obtained from differential thermal analysis. The phases present in the various regions of the phase diagram were determined from X-ray powder diffraction. A new compound $3LiOH \cdot Li_2SO_4$ was found in this system. The thermodynamic features present in the Li_2SO_4–LiOH system are summarized as follows:

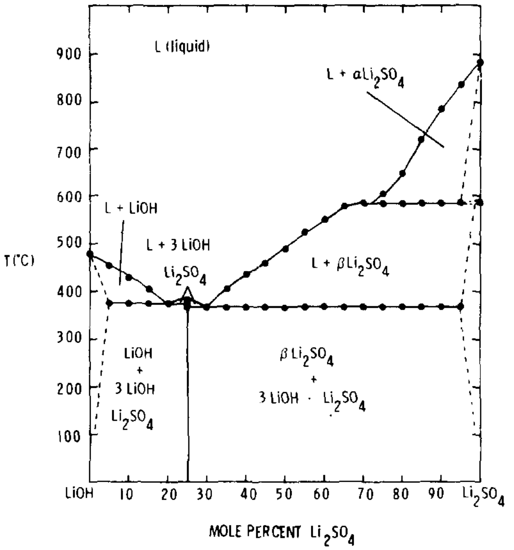

FIG. 3. The phase diagram for the Li_2SO_4–LiOH system. The solid circles represent the thermal discontinuities as determined by differential thermal analysis. The reported phases were confirmed by X-ray diffraction. The broken-line curves indicate the uncertainty of the solid solution ranges for the end members.

(A) The solid state phase transformation for Li_2SO_4 at 580°C, α-Li_2SO_4 = β-Li_2SO_4.

(B) The melting points for LiOH and Li_2SO_4 at 470 and 875°C, respectively.

(C) A metatectic reaction at ~95 mole% Li_2SO_4 and 575°C, α-Li_2SO_4 = β-Li_2SO_4 + liquid.

(D) A eutectic reaction at ~30 mole% Li_2SO_4 and 360°C, liquid = β-Li_2SO_4 + $3LiOH \cdot Li_2SO_4$.

(E) The congruent melting of the compound $3LiOH \cdot Li_2SO_4$ at 375°C.

(F) A second eutectic reaction at ~20 mole% Li_2SO_4 and 365°C, liquid = LiOH + $3LiOH \cdot Li_2SO_4$.

The DTA curves obtained by heating Li_5AlO_4, $80Li_5AlO_4+20Li_2SO_4$, and $75Li_2SO_4+25LiOH$ are shown in Fig. 4. For dry Li_5AlO_4 and $80Li_5AlO_4+20Li_2SO_4$ no thermal events are present up to 580°C. For Li_5AlO_4 and $80Li_5AlO_4+20Li_2SO_4$ in a flowing wet gas, thermal events are observed at ~450 and 360°C, respectively. The thermal event for Li_5AlO_4 at 450°C has been shown to be associated with the formation of a eutectic between LiOH and Li_5AlO_4 (*6*). Also, shown in Fig. 4 is the thermal event at 360°C for $75Li_2SO_4+25LiOH$ which corresponds to one of the eutectic temperatures for the Li_2SO_4–LiOH system. The event at 360°C for $80Li_5AlO_4+20Li_2SO_4$ in a wet environment is probably due to the formation and melting of a eutectic mixture between LiOH and Li_2SO_4.

X-Ray diffraction analyses for as-prepared $80Li_5AlO_4+20Li_2SO_4$ samples show no indication of the presence of LiOH or $3LiOH{\cdot}Li_2SO_4$. However, as previously reported, up to 10 wt% of LiOH can be present in a sample before X-ray diffraction will indicate its presence (*6*). Also, no evidence for solid solution formation between Li_5AlO_4 and Li_2SO_4 was found by X-ray powder diffraction.

The compatibility studies of Li_5AlO_4 and $Li_5AlO_4+Li_2SO_4$ mixtures indicated that both materials were physically and structurally compatible with molten lithium up to 450°C. At 500 and 550°C the $Li_5AlO_4+Li_2SO_4$ mixtures began to crumble; however, X-ray diffraction analysis still indicated the presence of both Li_5AlO_4 and Li_2SO_4 in the residues. The Li_5AlO_4 pellet remained inert to lithium up to 550°C. The pellets were always coated by lithium after removal from the bath. Penetration of lithium into the pellets increased with increasing tempera-

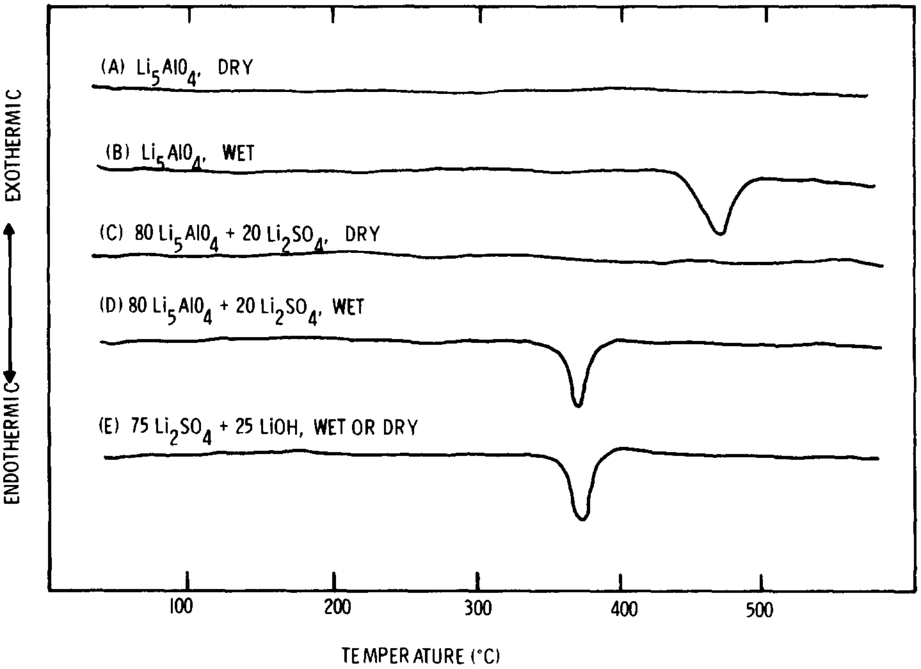

FIG. 4. Heating differential thermal analysis curves for the indicated materials and conditions. The wet and dry environments were introduced by flowing O_2 or argon gas over the samples. Results indicate that the transitions for wet Li_5AlO_4 (450°C) and wet $80Li_5AlO_4+20Li_2SO_4$ (360°C) are due to the presence of LiOH.

ture until at 500°C the $Li_5AlO_4 + Li_2SO_4$ pellet began to disintegrate. Complete penetration of lithium into the Li_5AlO_4 pellet did not occur at 550°C during exposure times of 1–2 hr.

Conductivity Results

The frequency dispersion of the conductivity for these materials is similar to that previously reported for Li_5AlO_4 (*6, 7*). Because of the similarity of the value for the bulk resistance obtained from complex plane analysis or by using the real component of the impedance at its closest approach to the real axis, the latter impedance values were used as previously discussed (*7*). Because a detailed analysis of the frequency dispersion was not attempted, the data presented here could include grain boundary resistances and should be taken only as being representative of polycrystalline material.

The conductivity results for Li_5AlO_4 and $80Li_5AlO_4 + 20Li_2SO_4$ in both wet and dry environments (flowing air) are shown in Fig. 5. As previously described, the conductivity increase for Li_5AlO_4 in a wet environment above ~400°C is due to the presence of LiOH and the formation of a liquid phase (*6, 7*). For $80Li_5AlO_4 + 20Li_2SO_4$ in a wet environment a large increase in the conductivity above ~350°C is observed. Below 350°C the conductivity appears to be thermally activated ($\sigma = \sigma_0 e^{-E/kT}$) with $E = 0.66\,eV$ and $\sigma_0 = 450$ $(\Omega\text{-cm})^{-1}$. The conductivity for $80Li_5AlO_4 + 20Li_2SO_4$ in a dry environment shows a thermally activated behavior over the temperature range examined. Changes in the density of the samples from 80 to 95% of theoretical density had no effect on the conductivity characteristics.

The conductivity results for two mixtures of LiOH and Li_2SO_4 are shown in Fig. 6. Both of these mixtures have essentially identical conductivity characteristics with a large increase in conductivity at ~350°C. Both Li_2SO_4 (*12*) and LiOH (*6*) are known to exhibit sharp increases in conductivity but at temperatures of ~575 and ~400°C, respectively. The conductivity increase observed here for Li_2SO_4–LiOH mixtures at ~350°C appears to be associated with formation of the $Li_2SO_4 + LiOH$ eutectic. Furthermore, the transition temperature for these mixtures does not appear to be significantly dependent upon composition, at least over the composition range examined.

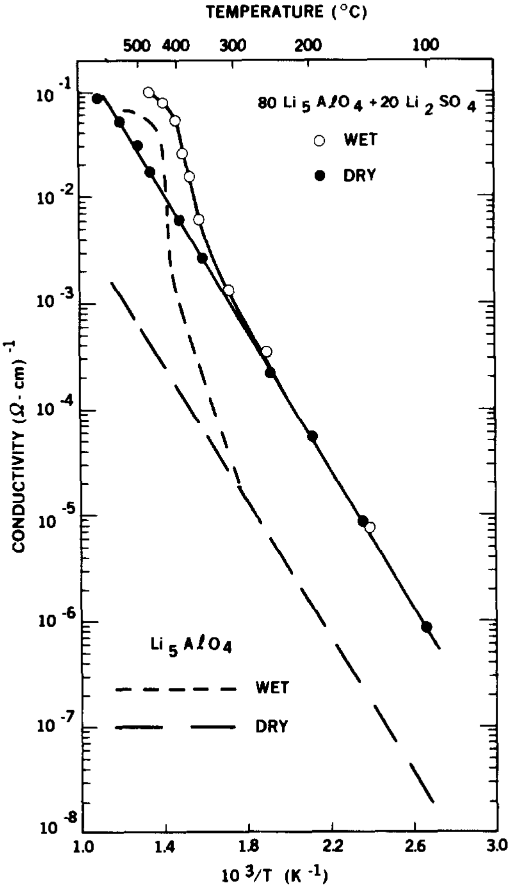

FIG. 5. Ionic conductivity temperature dependence of $80Li_5AlO_4 + 20Li_2SO_4$ upon exposure to wet and dry air environments. Also given by broken lines are similar data for Li_5AlO_4 (see Fig. 2). Results show that the addition of Li_2SO_4 to Li_5AlO_4 increases the magnitude of the conductivity and shifts the transition to the high conductivity state from ~400°C (300–450°C) to ~350 (330–420°C).

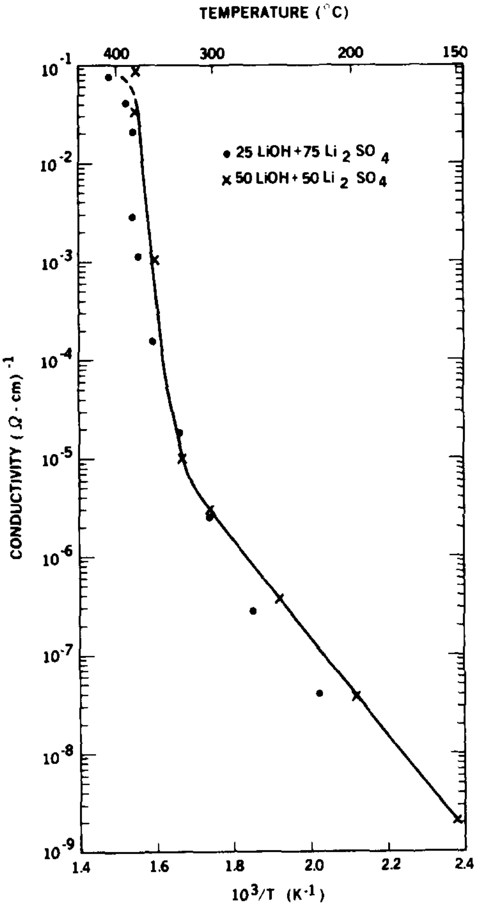

FIG. 6. Ionic conductivity temperature dependence of $LiOH+Li_2SO_4$ materials. A solid line is drawn only through the data for $50LiOH+50Li_2SO_4$ for clarity. Results show a transition to a high conductivity state at ~350°C (330–390°C).

These results in conjunction with the thermal and structural data suggest that LiOH is responsible for the increase in conductivity observed for $80Li_5AlO_4+20Li_2SO_4$ in a wet environment at high temperatures. The mechanism for conduction in these samples is not known; however, several possible explanations including grain boundary and surface conduction have been previously discussed (*6, 7*).

The conductivity for $80Li_5AlO_4+20Li_2SO_4$ in a dry environment is thermally activated $[E=0.66\text{ eV},\ \sigma_0=450\ \Omega\text{-cm})^{-1}]$ over the temperature range examined with $\sigma \sim 0.1\ (\Omega\text{-cm})^{-1}$ at 600°C. This represents a large increase over the conductivity for Li_5AlO_4 which under the same conditions is thermally activated with $E=0.67$ eV and $\sigma_0=5\ (\Omega\text{-cm})^{-1}$. The large increase in conductivity upon addition of Li_2SO_4 is similar to the results found for the Li_3PO_4–Li_4SiO_4 system (*4, 5*) where the conductivity characteristics have been associated with the existence of a solid solution. Although solid solutions between Li_5AlO_4 and Li_2SO_4 were not observed the similarity in the conductivity characteristics of the two systems suggests that Li_2SO_4 may form a limited solid solution with Li_5AlO_4. However, there is not enough information at present to determine whether the increase in conductivity is due to changes in the lithium ion distribution, such as the introduction of lithium ion vacancies, or to effects of the sulfate ion. The dependence of conductivity on the amount of Li_2SO_4 present in the sample is being investigated.

Measurements of the electronic contribution to the conductivity were made at only a few temperatures. The observed electronic conductivities were of the order of 1% of the total conductivity for the $80Li_5AlO_4+20Li_2SO_4$ samples. This can be compared to 3–20% electronic conduction for Li_5AlO_4 (*6*). Thus the addition of Li_2SO_4 to Li_5AlO_4 decreases the electronic contribution to the total conductivity.

The increased lithium ion conduction and decreased electronic conduction of $Li_5AlO_4+Li_2SO_4$ mixtures and their stability in molten lithium makes these materials of possible interest for use as solid electrolytes in thermal battery systems.

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