JOURNAL OF SOLID STATE CHEMISTRY 22, 297–308 (1977)

Electrochemical Investigation of the Chemical Diffusion, Partial Ionic Conductivities, and Other Kinetic Parameters in Li_3Sb and Li_3Bi

W. WEPPNER AND R. A. HUGGINS

Department of Materials Science and Engineering, Stanford University, Stanford, California 94305

Received March 5, 1977; in revised form April 29, 1977

The galvanostatic intermittent titration technique (GITT) has been used to electrochemically determine the chemical and component diffusion coefficients, the electrical and general lithium mobilities, the partial lithium ionic conductivity, the parabolic tarnishing rate constant, and the thermodynamic enhancement factor in "Li_3Sb" and "Li_3Bi" as a function of stoichiometry in the temperature range from 360 to 600°C. LiCl, KCl eutectic mixtures were used as molten salt electrolytes and Al, "LiAl" two-phase mixtures as solid reference and counterelectrodes. The stoichiometric range of the antimony compound is rather small, 7×10^{-3} at 360°C, whereas the bismuth compound has a range of 0.22 (380°C), mostly on the lithium deficit side of the ideal composition. The thermodynamic enhancement factor in "Li_3Sb" depends strongly on the stoichiometry, and has a peak value of nearly 70 000; for "Li_3Bi" it rises more smoothly to a maximum of 360. The chemical diffusion coefficient for "Li_3Sb" is 2×10^{-5} cm^2 sec^{-1} at negative deviations from the ideal stoichiometry and increases by about an order of magnitude in the presence of excess lithium at 360°C. The corresponding value for "Li_3Bi" is 10^{-4} cm^2 sec^{-1} with high lithium deficit, and increases markedly when approaching ideal stoichiometry. The activation energies are small, 0.1–0.3 eV, depending on the stoichiometry, in both phases. The mobility of lithium in "Li_3Bi" is about 500 times greater than in "Li_3Sb" with a lithium deficit. The ionic conductivity in "Li_3Sb" increases from about 10^{-4} Ω^{-1} cm^{-1} in the vacancy transport region to about 2×10^{-3} where transport is probably by interstial motion at 360°C. For "Li_3Bi" a practically constant value of nearly 10^{-1} Ω^{-1} cm^{-1} is found at 380°C. The parabolic tarnishing rate constant shows a sharp increase at higher lithium activities in "Li_3Sb" whereas in "Li_3Bi" it has a roughly linear dependence upon the logarithm of the lithium activity. The tarnishing process is about 2 orders of magnitude slower for "Li_3Sb" than for "Li_3Bi." Because of the fast ionic transport in these mixed conducting materials, "Li_3Sb" and "Li_3Bi" may be called "fast electrodes."

I. Introduction

Kinetic quantities, notably the diffusion coefficients and the partial conductivities, are importantly related to a number of materials properties and phenomena. Some important examples are tarnishing processes, solid state reactions, reduction of ores, sintering processes, and the incorporation of electroactive species in battery electrodes. Knowledge of such parameters is also of theoretical interest for the study of the disorder and transport mechanisms in solids.

New types of high energy and power density batteries present a special need for electrode materials with high chemical diffusion coefficients, as well as the (usually more recognized) large changes of Gibbs free energy and composition with regard to the electroactive ions. In the past, quantitative data have often not been available to estimate the kinetic behavior of electrodes, and approaches to improvements in electrodes have generally been empirical. One method that has been used to compensate at least partially for low diffusion coefficients in otherwise interesting

ISSN 0022–4596

materials is to increase the surface area. However, this may have deleterious effects, such as an increase in volume and weight, e.g., by requiring extra supporting material.

Because of its low atomic weight and the high Gibbs formation energy of many of its compounds, lithium is of special interest at present as the electroactive ion in high energy and power density batteries. It is known that it reacts up to a 3 : 1 atomic ratio with group Va elements, which can, therefore, act as high capacity sinks or sources for lithium. Experiments undertaken to investigate the kinetic parameters of "Li_3Sb" and "Li_3Bi" as model cathode materials of this type are reported in this paper. The techniques employed on these materials can, of course, be applied to the investigation of a wide variety of other proposed electrode materials.

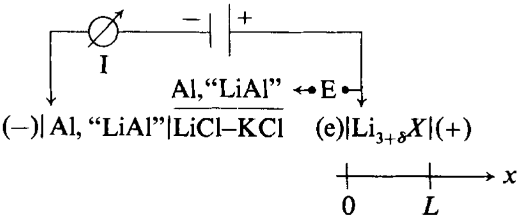
The compounds between lithium and antimony or bismuth are often described as being between ionic and metallic compounds. There has long been controversy over their degree of ionic or metallic character, and experimental evidence in favor of each postulate has been reported (*1–6*). "Li_3Sb" and "Li_3Bi" have been shown to be electronic semiconductors (*7–11*). NMR measurements also indicate rather rapid movement of the lithium ions in Li_3Sb (*12*). "Li_3Bi" and β-"Li_3Sb," which exists below 650°C, are reported to have the same cubic (DO_3) structure, which is isotypic with BiF_3 (*3*, *13–15*). The cubic array of body centered sites in the simple cubic lithium ion framework are alternately occupied by lithium and bismuth or antimony, respectively. This structure can also be described as an fcc arrangement of Sb or Bi, with both all the tetrahedral and all the octahedral interstices filled by Li. At higher temperatures, "Li_3Sb" has an ordered hexagonal structure isotypic with Na_3As or Cu_3P (*14*, *16*).

Besides the trilithium compounds, other phases with lower lithium contents also exist, which form first when lithium is electrochemically titrated into antimony or bismuth. However, experiments indicate that their diffusion kinetics are apparently quite slow; as a result, with only modest currents the trilithium phases form on top of the electrodes almost immediately. The cell voltage is not appreciably reduced by this fact, since the Gibbs formation energies (per lithium) of the several phases are not very different (*17*). The trilithium phases predominantly determine the kinetics of Sb and Bi electrodes and are investigated here. Though they have chemical and structural similarities, these two systems show considerable differences. This work demonstrates that electrochemical techniques also may be useful for metallurgical work, e.g., the study of alloys.

II. Principles and Theory

The kinetic properties of "Li_3Sb" and "Li_3Bi" were investigated as a function of stoichiometry and temperature by the means of the galvanostatic intermittent titration technique (GITT) described in a previous paper (*18*). This electrochemical technique for the study of the kinetics of electrodes in batteries combines both transient and steady state measurements and allows an extensive determination of the kinetic and thermodynamic properties as a function of stoichiometry. The use of galvanostatic pulses also eliminates some significant experimental limitations in other techniques.

The following galvanic cell is employed:



(I)

where X represents either antimony or bismuth. L is the length of the sample. A LiCl–KCl eutectic mixture is used as a molten salt electrolyte for lithium ions at temperatures above 352°C. The two-phase mixtures of Al and "LiAl" have defined activities of their components and act as lithium electrodes. The lithium activity of this two-phase system, which does not depend on the overall composition, is about 300 mV lower than in pure Li (*17*, *19*).

After a steady state voltage of the galvanic cell (I) is established, a constant electrical current I_0 is applied in either direction. This produces a time-independent concentration gradient $\partial c_{\mathrm{Li}}/\partial x$ of the lithium ions in the mixed-conducting $Li_{3+\delta}X$ electrode immediately at the phase boundary with the electrolyte, according to the equation

$$I_0 = -Sq\tilde{D}(\partial c_{\mathrm{Li}}/\partial x)|_{x=0}. \qquad (1)$$

S, q, and $\tilde{D}$ are the contact area between the sample and the electrolyte, the elementary charge, and the chemical diffusion coefficient, which may be assumed to be constant for sufficiently small amounts of charge transport, respectively. The voltage E is observed as a function of time. From the solution of Fick's second diffusion law with the appropriate initial condition of a homogeneous lithium distribution over the sample and the two boundary conditions $\partial c_{\mathrm{Li}}/\partial x$ $(x = 0) =$ const (I_0) and $\partial c_{\mathrm{Li}}/\partial x$ $(x = L) = 0$, the theoretical time dependence for short times is

$$\begin{aligned}\frac{dE}{dt^{1/2}} &= \frac{2V_{\mathrm{M}}I_0}{SF(\tilde{D}\pi)^{1/2}}\frac{dE}{d\delta}\\ &= -\frac{2kTV_{\mathrm{M}}I_0}{SqF(3+\delta)(\tilde{D}\pi)^{1/2}}\\ &\quad\times\frac{\partial \ln a_{\mathrm{Li}}}{\partial \ln c_{\mathrm{Li}}} \qquad (t \ll L^2/\tilde{D}), \qquad (2)\end{aligned}$$

where V_M, F, a_{Li}, and δ are the molar volume of the sample, Faraday's constant, the lithium acitivity, and the stoichiometric parameter of the sample, respectively. This method has the advantage, compared to other transient techniques, that the IR drop of the cell does not interfere with the proper maintenance of the initial and boundary conditions, but is only added as a time-independent constant to the cell voltage. The term $dE/d\delta$, the change of the steady state voltage with the stoichiometry of the electrode, takes into account that Fick's second law yields the concentration of lithium at $x = 0$, whereas the voltage is a measure of the activity at that interface. $dE/d\delta$ is determined by turning off the current after the time interval τ and measuring the new steady state voltage of the galvanic cell (I) while the stoichiometry has changed by the amount

$$\Delta\delta = I_0\,\tau M_X/m_X F, \qquad (3)$$

where M_X and m_X are the atomic weight and the mass of the component X in the sample. By repeated application of this procedure over the total range of existence of the Li_3X phase, both the transient voltage change at a constant current flux and the change of the steady state voltage can be determined as a function of stoichiometry. The chemical diffusion coefficient $\tilde{D}$ may thus be determined at the different stoichiometries at which the individual titrations have been carried out.

If the time τ of the current flux is small compared to $L^2/\tilde{D}$, i.e., the solution (2) given above is valid for the entire period τ, and $dE/d\delta$ may be considered as approximately constant, Eq. (2) may be transformed into the convenient equation

$$\tilde{D} = \frac{4}{\pi\tau}\left(\frac{m_X V_M}{M_X S}\right)^2\left(\frac{\Delta E_{\mathrm{s}}}{\Delta E_{\mathrm{t}}}\right)^2 \qquad (\tau \ll L^2/\tilde{D}), \quad (4)$$

where ΔE_{s} is the change of the steady state voltage and ΔE_{t} is the total change of the voltage during the current flux without considering the IR drop. This is illustrated in Fig. 1.

Besides the chemical diffusion coefficient, other kinetic quantities may also be derived as a function of the stoichiometry from the same experiments. For a predominantly electronic conducting sample the partial ionic conductivity of the lithium, which is assumed to be the predominant mobile ionic species, is given by

$$\sigma_{\mathrm{Li}} = -\frac{4}{\pi}\frac{V_{\mathrm{M}}m_X I_0 \Delta E_{\mathrm{s}}}{M_X S^2(\Delta E_{\mathrm{t}})^2} \qquad (\tau \ll L^2/\tilde{D}). \qquad (5)$$

The chemical diffusion coefficient $\tilde{D}$, which is a measure of the transport of species in a

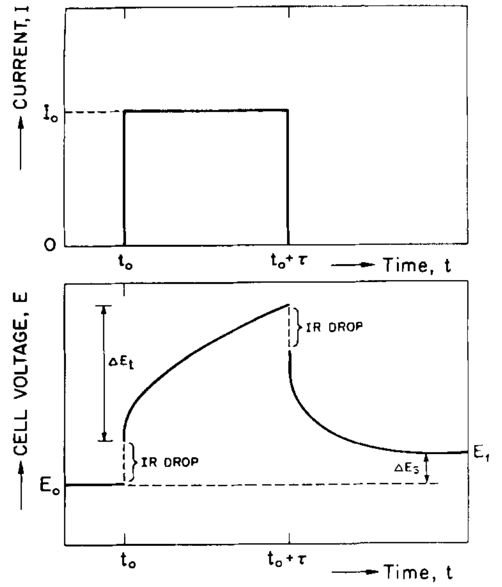


FIG. 1. Principle of the galvanostatic intermittent titration technique (GITT). Starting at time t_0 with the galvanic cell (I) in equilibrium, a constant current I_0 is applied while the transient voltage E_t is measured as a function of time. The change of the steady state voltage, ΔE_s, following the current pulse $I_0\tau$ determines the dependence of the cell voltage on the concentration of the electroactive species. The IR drop is constant and therefore has no influence in this method.

concentration gradient, is related to the component diffusion coefficient for Li by

$$\tilde{D} = D_{K_{\mathrm{Li}}}\, \partial \ln a_{\mathrm{Li}} / \partial \ln c_{\mathrm{Li}} \qquad (6)$$

in a material which is a predominantly electronic conductor, as is the case here. The component diffusion coefficient is related to the rate of random motion in the absence of a concentration gradient. The term $\partial \ln a_{\mathrm{Li}}/\partial \ln c_{\mathrm{Li}}$, called the thermodynamic enhancement factor, which can be quite large in some cases (e.g., "Li_3Sb"), is due to the interaction of electronic and ionic fluxes in a concentration gradient. The greater electronic mobility results in an internal electric field, which acts to enhance the diffusional driving force acting on the ions. This matter is discussed in more detail elsewhere (*18*).

The component diffusion coefficient is determined by

$$D_{K_{\mathrm{Li}}} = -\frac{4kTm_X V_{\mathrm{M}} I_0 \Delta E_{\mathrm{s}}}{\pi c_{\mathrm{Li}} q^2 M_X S^2 (\Delta E_{\mathrm{t}})^2} \qquad (\tau \ll L^2/\tilde{D}), \quad (7)$$

where k is Boltzmann's constant and T is the absolute temperature. $D_{K_{\mathrm{Li}}}$ is related to the general mobility b_{Li} and the electrical mobility u_{Li} by the Nernst–Einstein equation

$$D_{K_{\mathrm{Li}}} = kTu_{\mathrm{Li}}/q = b_{\mathrm{Li}}kT. \qquad (8)$$

If one can assume a value for the correlation factor f, it is also then possible to compare the electrochemical measurements with determinations of the tracer diffusion coefficient using the relationship

$$D_{T_{\mathrm{Li}}} = fD_{K_{\mathrm{Li}}}. \qquad (9)$$

From the dependence of the chemical diffusion coefficient upon the stoichiometry it is also possible to calculate Tammann's parabolic rate constant k_{t} for the tarnishing of the neighboring phases by the growth of a Li_3X layer

$$k_{\mathrm{t}} = \left| \int \tilde{D}/(3+\delta)\, d\delta \right|. \qquad (10)$$

The integration extends from the stoichiometry where the neighbor-phase starts to be formed up to the stoichiometry at which k_{t} is determined.

III. Experimental Considerations

The LiCl–KCl eutectic used as a molten salt electrolyte was purchased (spectrographically pure) from Anderson Physics Laboratories, Urbana, Illinois. Alumina crucibles have been proved to have sufficient compatibility to be used as the container, even at high lithium activities.

The reference and counter electrodes were prepared by electrochemically titrating lithium into a spiral of pure aluminum wire up to about 35 mole% lithium, using a molten lithium metal anode and the same electrolyte as described above. Al, "LiAl" electrodes have the advantage of being solid at the experimental temperatures and of having a lower lithium activity than pure lithium. Because of the last fact, the electronic leakage current of the electrolyte is reduced (*20*), thermodynamic stability is achieved (*21*), and corrosion is reduced.

The trilithium compounds were prepared from the pure Va metals by an electrochemical titration process similar to the preparation of the counter and reference electrodes, but using Al, "LiAl" as the anode. In this way the composition of the sample is better defined because of the much lower electronic leakage rate through the molten salt than when a pure lithium anode is used. The antimony samples were in the form of dense polycrystalline pellets with thicknesses of 0.1–0.2 cm and initial areas of 1–2 cm^2. Since the incorporation of the Li into the Sb to form the Li_3Sb phase occurs by an insertion reaction, the volume change was accommodated primarily by a thickness increase. Thus the area of the electrolyte/Li–Sb alloy interface was observed to not change appreciably during the experiments. The initial dimensions (pure Sb) were used for the calculations. More precise measurements were not warranted by the precision of the kinetic data. In the bismuth case a molybdenum bucket was used, because the bismuth is liquid at the experimental temperature. The surface area of the Li–Bi alloy was thereby maintained at about 0.6 cm^2.

Molybdenum wire was used as the electronic lead, as it is not chemically attacked and exhibits a negligible solubility for lithium in this activity range (*22*). The experiments were carried out in a helium-filled dry box. A PAR potentiostat was used as the constant current source.

The current densities used for the kinetic study of "Li_3Sb" were about 0.1–1 mA/cm^2. Those for "Li_3Bi" were usually larger by a factor of 10–100, due to the greater chemical diffusion coefficient in that case. The constant current pulse times were typically 10–100 sec. Periods of 10–20 min were usually sufficient to reach the new equilibrium voltage in both cases.

IV. Results

The steady state cell voltages observed after each galvanostatic titration step are shown in Figs. 2 and 3 for the single phases $Li_{3+\delta}Sb$ and $Li_{3+\delta}Bi$, respectively, as a function of the stoichiometry of the sample. The composition values for the "Li_3Sb" phase were shifted by a factor of about 10^{-4} in order to make the inflection point occur at the ideal 3 : 1 stoichiometric composition, since that is what is expected from theoretical considerations (*23*).

From Fig. 2 it is seen that the stoichiometric range for the antimony compound is rather small, about 7×10^{-3}, and it extends only slightly to the lithium deficit side. At a deviation of -1×10^{-3} from the ideal stoichiometry a second phase, Li_2Sb (*17*, *24*), begins to form, as indicated by the observation of a constant voltage representative of a two-phase region. Most of the existence range lies

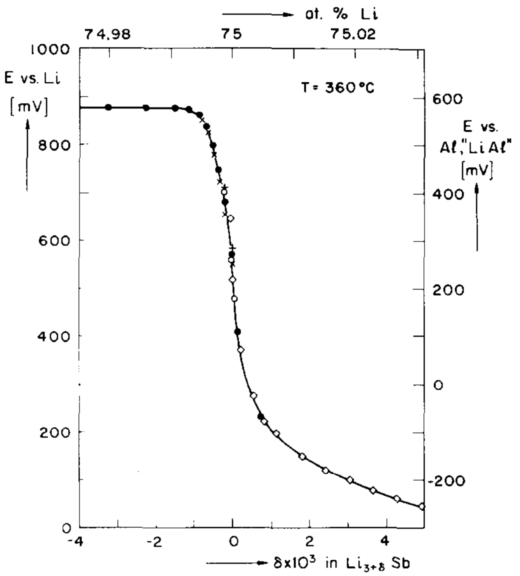


FIG. 2. The steady state voltage of "Li_3Sb" as the sample-electrode in cell (I) as a function of the amount of lithium electrochemically titrated into the sample (coulometric titration curve) at 360°C. The horizontal part indicates the coexistence of the trilithium compound with Li_2Sb. Five different symbols indicate data points taken from different experimental sequences, i.e., Li pumped in or out. Their consistency indicates the extremely high resolution of this technique.

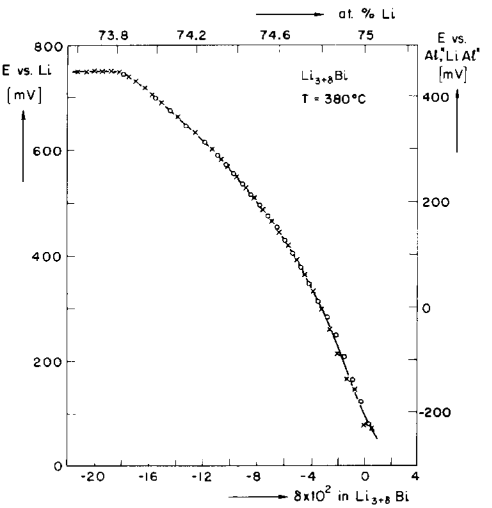


FIG. 3. The coulometric titration curve for "Li_3Bi" in cell (I) at 380°C. The horizontal part is due to the coexistence of the "Li_3Bi" (with the minimum lithium concentration) and LiBi.

on the lithium excess side of $Li_{3+\delta}Sb$. To the contrary, Fig. 3 shows that the bismuth compound has a wider range of stoichiometry, about 2.2×10^{-1}, and by far the larger part extends over the lithium deficit region. Up to about 7% of the lithium ions may be missing. No adjustment of the stoichiometry was found necessary in this case, because the experimental error was much smaller than the stoichiometric range. The second-phase LiBi is formed when more lithium is removed from the sample. On the other hand, pure lithium coexists with $Li_{3+\delta}Bi$ containing a small excess of lithium.

The reported cell voltages are equilibrium values which were observed to be constant within ±1 mV over periods of several hours. Only at high lithium activities, corresponding to voltages E less than about 150 mV versus Li was a small drift in E observed with time. At lower Li activities the electronic conductivity of the salt (lithium solubility) was negligible, as evidenced by the fact that titrations forward and backward gave very reproducible results, as seen by the superposition of data taken upon both adding and subtracting Li in Fig. 2.

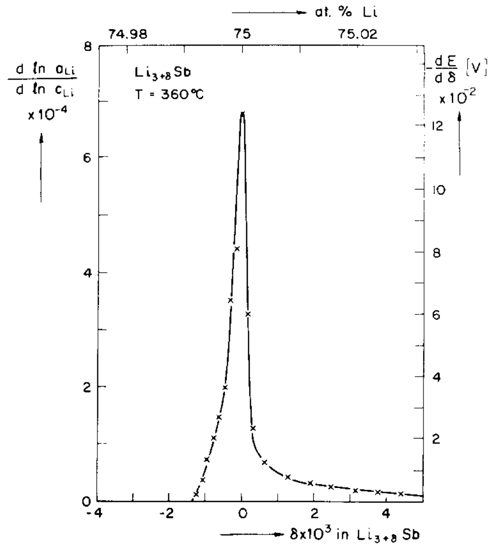


FIG. 4. The thermodynamic enhancement factor versus the deviation from the ideal stoichiometry, as derived from the slope $dE/d\delta$ (shown on right-hand ordinate) of the coulometric titration curve of "Li_3Sb" (Fig. 2), at 360°C.

Correspondingly, the slope $dE/d\delta$, or $\partial \ln a_{Li}/\partial \ln c_{Li}$, the thermodynamic enhancement factor, is large and strongly dependent on the stoichiometry in the case of $Li_{3+\delta}Sb$. This quantity is more than 100 times smaller for $Li_{3+\delta}Bi$ where it changes smoothly with the stoichiometry. This behavior is graphically shown in Figs. 4 and 5. Equation (2) has been used for the relation between the slope $dE/d\delta$ of the coulometric titration curve and the thermodynamic factor, which causes the chemical diffusion coefficient to be greater than the component diffusion coefficient.

Some typical transient results are presented in Fig. 6. The cell voltages E are plotted as a function of $t^{1/2}$ for a $Li_{3+\delta}Bi$ sample for short times, all starting at the same deviation from the ideal stoichiometry, $\delta = -0.08$. In agreement with theoretical considerations, straight lines are observed whose slopes are a measure of the chemical diffusion coefficient and the known thermodynamic factor. An important indication that the data are being correctly interpreted is the dependence of the slope upon the current density. According to

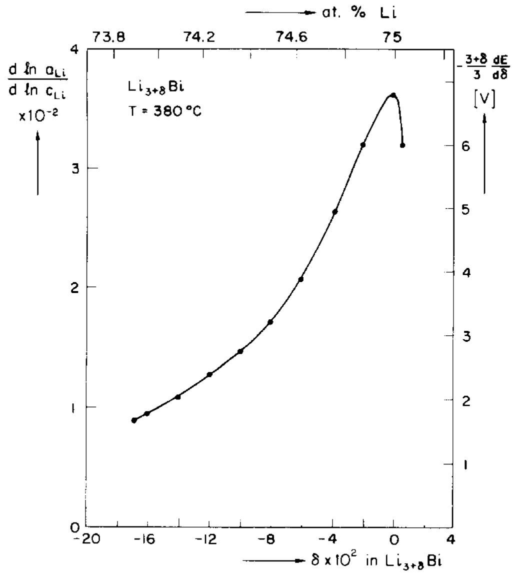


FIG. 5. The thermodynamic enhancement factor for "Li_3Bi" as a function of the deviation from the ideal stoichiometry at $T = 380°C$. The change of the steady state voltage with the stoichiometry is plotted at the right-hand side.

Eq. (2) a linear relationship should be obtained. This is indeed observed with excellent precision, for nine different values of current density.

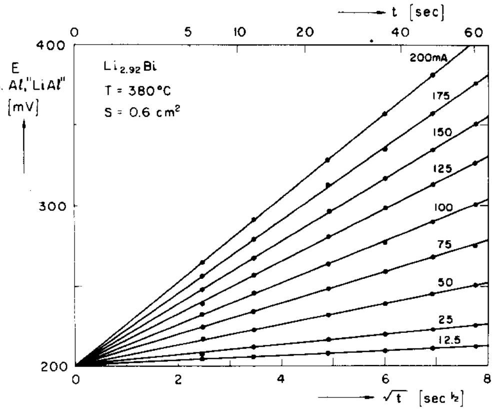


FIG. 6. The voltage response as a function of the square root of time for several different galvanostatic currents applied to cell (I) with a "Li_3Bi" working electrode at 380°C. In all cases the same starting voltage of 200 mV with reference to an Al, "LiAl" electrode, corresponding to a deviation of -0.08 from the ideal stoichiometry, has been used. The slope of the straight lines is proportional to the current density.

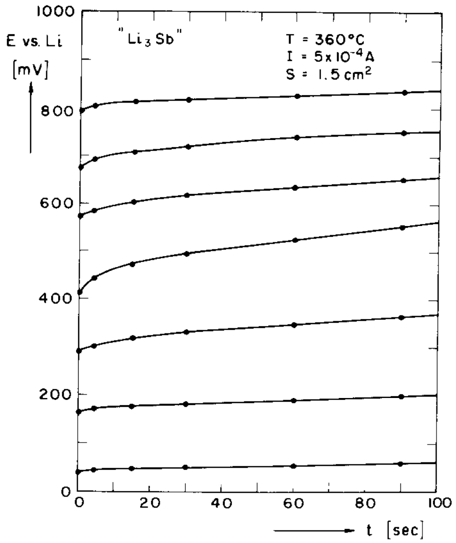


FIG. 7. The transient voltage of cell (I) with a "Li_3Sb" electrode as a function of time for several different initial voltages, corresponding to different sample compositions at 360°C. For intermediate compositions greater polarization is observed.

Typical results of measurements of the dependence of the transient voltage upon the stoichiometry are shown in Fig. 7 for $Li_{3+\delta}Sb$, which has the narrow existence range and rapidly changing thermodynamic factor. The voltage is shown as a function of time for seven different stoichiometries. The same current density (3.3×10^{-4} A/cm²) was used for all experiments. In spite of that ΔE_t varies markedly. This is partly due to a changing chemical diffusion coefficient, but

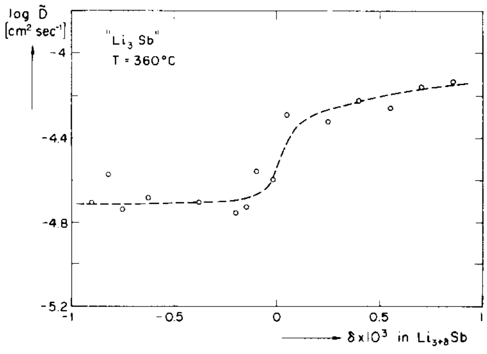


FIG. 8. The chemical diffusion coefficient of "Li_3Sb" as a function of the deviation from the ideal stoichiometry at 360°C.

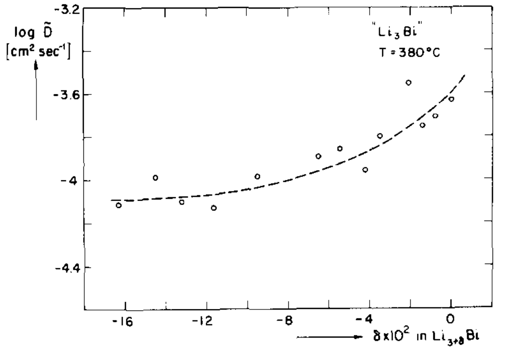


FIG. 9. The chemical diffusion coefficient of "Li_3Bi" as a function of the deviation from the ideal stoichiometry at 380°C.

mostly due to the strong change of the thermodynamic factor, as will be seen later.

In Fig. 8 the chemical diffusion coefficient $\tilde{D}$ is shown as a function of composition for a $Li_{3+\delta}Sb$ sample at 360°C, making use of Eq. (4). At negative deviations from the ideal stoichiometry the chemical diffusion coefficient is found to be smaller by about an order of magnitude than in the presence of excess lithium. This may be attributed to a higher mobility for lithium interstitials, which are assumed to be the dominant defects at positive values of δ, compared to lithium vacancies, which presumably prevail when there is a lithium deficit.

Similar behavior is found over the large range of negative deviations from the ideal stoichiometry in the case of $Li_{3+\delta}Bi$, as shown in Fig. 9. For a large lithium deficit, the chemical diffusion coefficient is only weakly dependent on the stoichiometry, but it increases markedly when approaching $\delta = 0$, because of an increasing contribution by lithium interstitials to the chemical diffusion process.

Figures 10 and 11 illustrate the temperature dependence of the chemical diffusion coefficient for $Li_{3+\delta}Sb$ and $Li_{3+\delta}Bi$, in each case for two different stoichiometries. For $Li_{3+\delta}Sb$ the activation energy in the region of excess lithium is about 0.2 eV, whereas it is nearly 0.3 eV in the lithium deficit case. Even smaller values are observed for $Li_{3+\delta}Bi$. The activation energy at large negative deviations from the ideal stoichiometry is 0.13 eV, and somewhat less than 0.1 eV for $\delta = 0$.

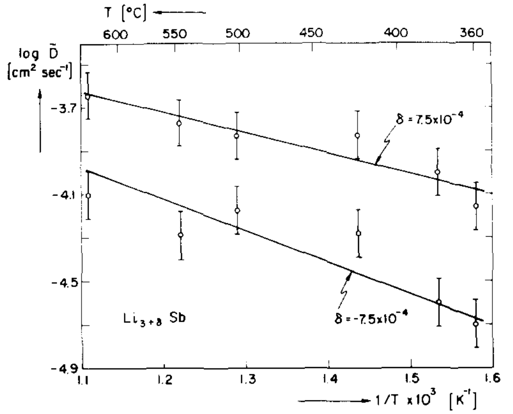


FIG. 10. The chemical diffusion coefficient of "Li_3Sb" as a function of the inverse absolute temperature for the deviations $+7.5 \times 10^{-4}$ and -7.5×10^{-4} from the ideal stoichiometry. The slopes of the straight lines correspond to activation energies of about 0.2 and 0.3 eV, respectively.

The partial ionic lithium conductivities, calculated by using Eq. (5), are plotted in Figs. 12 and 13 as a function of the stoichiometry. In the case of the Sb compound the ionic conductivity increases by more than an order of magnitude from vacancy to interstitial type conduction. "Li_3Bi" has an ionic conductivity approximately independent of the deviation

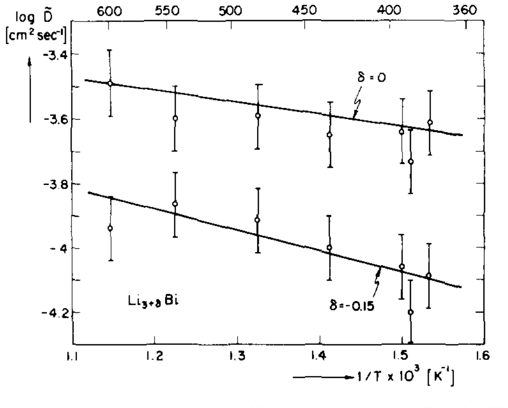


FIG. 11. The chemical diffusion coefficient of "Li_3Bi" plotted versus the inverse absolute temperature for a stoichiometric deviation of −0.15 and ideal stoichiometry.

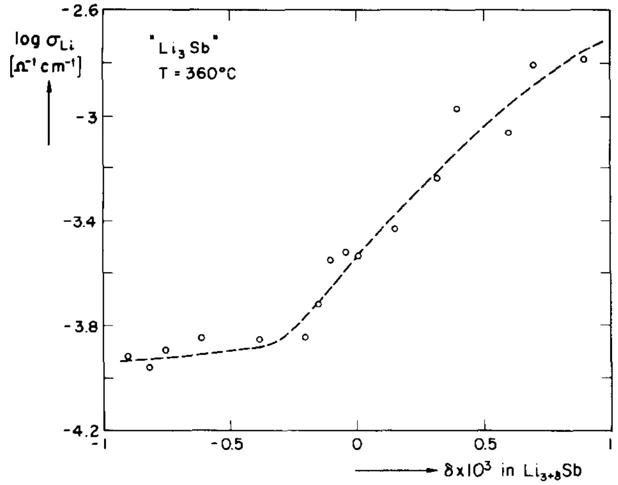


FIG. 12. The partial ionic conductivity of lithium in "Li_3Sb" as a function of the deviation from the ideal stoichiometry at 360°C.

from ideal stoichiometry, possibly due to extensive disorder in the lithium sublattice. Especially worth mentioning are the high values of the partial ionic conductivities in both these materials. They are comparable to those of good solid electrolytes.

The composition dependences of the component diffusion coefficient and the electrical and general mobilities of the lithium ions are similar to those of the partial conductivities. These data are plotted in Figs. 14 and 15 for $Li_{3+\delta}Sb$ and $Li_{3+\delta}Bi$, respectively.

The parabolic tarnishing rate constants k_t have been determined from the integral of the chemical diffusion coefficient as a function of the stoichiometry, using Eq. (10). With the help of the coulometric titration curve the relation between δ and the cell voltage, or the lithium activity, according to Nernst's equation, is known, and k_t can be plotted as a function of the lithium activity. This is done in Figs. 16 and 17 for the whole range of existence of the trilithium compounds. For "Li_3Sb" a sharp increase in the rate constant is observed with the increasing contribution of faster species to the transport in the sample. In the case of "Li_3Bi" a more linear dependence of the parabolic rate constant upon the logarithm of the lithium activity is found, due to a rather constant chemical diffusion coefficient and an approximately linear dependence between the cell voltage E and the deviation from the ideal stoichiometry δ in the coulometric titration plot. Figures 16 and 17 are especially suitable for determining optimal conditions for operating a battery in which such phase changes are involved.

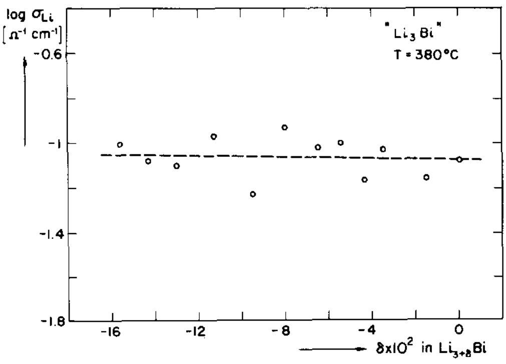


FIG. 13. The partial ionic conductivity of lithium in "Li_3Bi" as a function of the deviation from the ideal stoichiometry at 380°C.

V. Discussion

The galvanostatic intermittent titration technique has proved to be a powerful tool for the investigation of a large variety of important

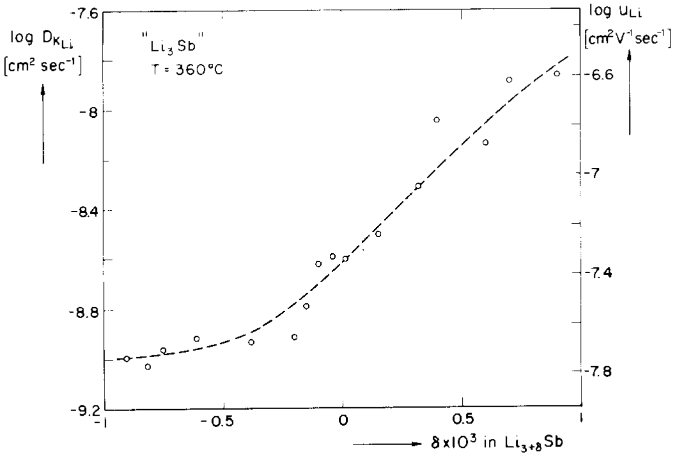


FIG. 14. The component diffusion coefficient D_K and the electrical mobility u of lithium in "Li$_3$Sb" as a function of the stoichiometry at 360°C. The general mobility (velocity per unit general acting force) is obtained by dividing the electrical mobility by the elementary charge.

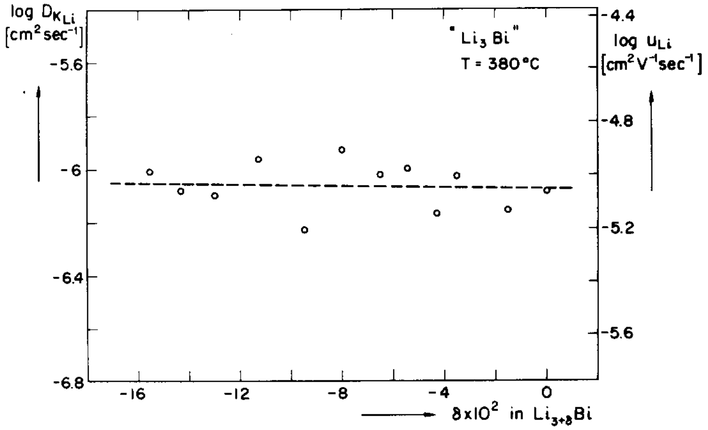


FIG. 15. The component diffusion coefficient D_K and the electrical mobility u of lithium in "Li$_3$Bi" as a function of the stoichiometry at 380°C. The general mobility is given by dividing the electrical mobility by the elementary charge.

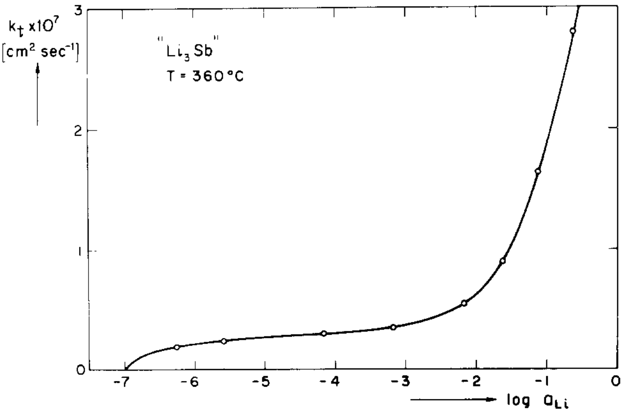


FIG. 16. The parabolic tarnishing rate constant for the growth of "Li$_3$Sb" on a Li$_2$Sb substrate as a function of the lithium activity at 360°C. The values suddenly increase due to the presence of a more mobile lithium species.

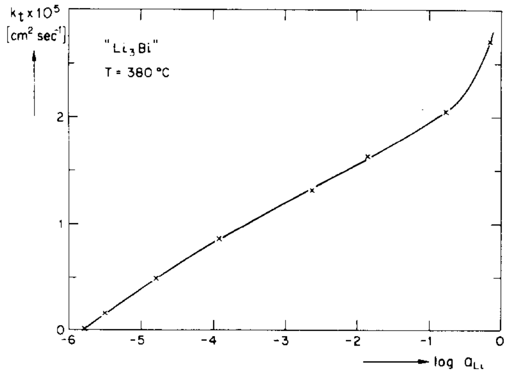


FIG. 17. The parabolic tarnishing rate constant for the growth of "Li_3Bi" on a LiBi substrate as a function of the lithium activity at 380°C.

kinetic properties of trilithium antimony and bismuth phases. An important advantage is that the transport quantities can be deduced from only relatively simple observations of electrical currents and the time dependence of voltages. Compared to other techniques, the experimental set up and measurements are easy to achieve. In the case of investigations of the suitability of materials for electrodes in batteries it is even possible, and perhaps desirable, to carry out the experiments *in situ*. Ordinarily, different experimental arrangements have to be used for the determination of the various kinetic parameters. In this case, all this information can be derived from a single type of experiment. The stoichiometry may be changed systematically in a well-defined way without having to prepare or analyze a series of samples. This makes data as a function of composition easily available. The parabolic rate constant k_t is likewise usually only determinable as a function of the activity of one of the components by use of a large number of separate experiments. Thus, it is usually only reported for a single activity value.

The lithium ion conductivity has been found to be very high in "Li_3Sb," and especially in "Li_3Bi," comparable to that of fast solid ionic conductors. Therefore, these materials may be called "fast electrodes." The large amount of lithium that can be incorporated into antimony and bismuth, in spite of their relatively high weight and low voltage (with reference to lithium), produce rather favorable energy densities (*25*, *26*) and in combination with their high chemical diffusion coefficients, make them favorable candidates for use in high power density batteries. The theoretical (maximum) energy densities for lithium cells with Sb and Bi electrodes are 500 and 290 Wh per kilogram of reactants at about 370°C, respectively. The bismuth phase has more favorable kinetic properties, however.

As seen from Figs. 2 and 3, the experiments with "Li_3Sb" and "Li_3Bi" were not extended until total equilibrium with pure lithium was reached, because of slow voltage drift in this region. This may probably be attributed to the instability of the LiCl–KCl melt in contact with pure lithium (*21*). There is also an increasing electronic conductivity in the molten salt electrolyte with increasing lithium activity (*20*).

The possible influence of the molybdenum bucket and wires, as well as a change of the lithium solubility in the melt with lithium activity, on the experimental results was checked by carrying out blind experiments without the sample but with an otherwise identical experimental situation. It was found that the interaction of lithium with the auxiliary equipment is negligible compared to the amount of lithium diffusing into the sample. Also, the change in the electrical double layer charge between the electrolyte and the electrode does not have a marked influence on the observed results, assuming values reported in the literature for the double layer capacitance.

A further interesting result of this investigation is that the lithium compounds with antimony and bismuth show large differences with regard to their ranges of stoichiometry and prevailing defect types, although β-"Li_3Sb" and "Li_3Bi" have the same structure, and antimony and bismuth have practically identical ionic radii (*14*) and are chemically very similar. This fact should be the object of further investigation.

Acknowledgment

This work was funded by a grant from the Institute for Energy Studies at Stanford University, which has supported one of the authors (W.W.) on a Standard Oil of California visiting professorship. The earlier grant of a NATO Scholarship through the German Academic Exchange Service (DAAD) is also gratefully acknowledged.

References

1. E. Mooser and W. B. Pearson, *Phys. Rev.* **101**, 1608 (1956).
2. W. Klemm, *in* "Trabajos reunión intern. reactividad sólidos, Madrid, 1956," Vol. 1, p. 447.
3. O. G. Folberth, *Z. Naturforsch. A* **15**, 739 (1960).
4. C. E. Messer, *in* "The Alkali Metals, Int. Symp. Nottingham 19–20 July 1966," p. 183, Spec. Publ. No. 22, The Chemical Society, London (1967).
5. B. W. Mott, *in* "The Alkali Metals, Int. Symp. Nottingham 19–20 July 1966," p. 92, Spec. Publ. No. 22, The Chemical Society, London (1967).
6. G. F. Voronin, *Zh. Fiz. Khim.* **44**, 1538 (1970).
7. G. Grube, H. Vosskühler, and H. Schlecht, *Z. Elektrochem.* **40**, 270 (1934).
8. E. Mooser and W. B. Pearson, *Phys. Rev.* **101**, 492 (1956).
9. Ya. A. Ugai, *Vop. met. Fiz. Poluprov., Akad. Nauk SSSR Tr. 4-go, Soveshch. Moscow*, 107 (1961).
10. R. Gobrecht, *Phys. Status Solidi* **13**, 429 (1966).
11. G. Steinleitner, W. Freyland, and F. Hensel, *Ber. Bunsenges. Phys. Chem.* **79**, 1189 (1975).
12. G. W. Ossmann and J. W. McGrath, *J. Chem. Phys.* **49**, 783 (1968).
13. E. Zintl and G. Brauer, *Z. Elektrochem.* **41**, 297 (1935).
14. G. Brauer and E. Zintl, *Z. Physik. Chem. B* **37**, 323 (1937).
15. R. Hultgren, R. L. Orr, P. D. Anderson, and K. K. Kelly, "Selected Values of Thermodynamic Properties of Metals and Alloys," pp. 533, 534, 842, Wiley, New York (1963).
16. M. Masmann, *Z. Krist.* **122**, 399 (1966).
17. W. Weppner and R. A. Huggins, to appear.
18. W. Weppner and R. A. Huggins, to appear.
19. N. P. Yao, L. A. Herédy and R. C. Saunders, *J. Electrochem. Soc.* **118**, 1039 (1971).
20. R. J. Heus and J. J. Egan, *J. Phys. Chem.* **77**, 1989 (1973).
21. R. N. Seefurth and R. A. Sharma, *J. Electrochem. Soc.* **122**, 1049 (1975).
22. F. A. Shunk, "Constitution of Binary Alloys," 2nd suppl. p. 479, McGraw-Hill, New York (1969).
23. C. Wagner, *in* "Progress in Solid State Chemistry" (H. Reiss and J. O. McCaldin, Eds.), Vol. 6, p. 1, Pergamon, Oxford (1971).
24. R. Gérardin and J. Aubry, *C. R. Acad. Sci. Ser. C* **278**, 1097 (1974).
25. Rheinisch-Westfälisches Elektrizitätswerk AG, Fr. Demande 2,206,593, 7 June 1974, Ger. Appl. P. 2254870.5, 9 November 1972.
26. J. O. Besenhard and H. P. Fritz, *Electrochim. Acta* **20**, 513 (1975).