JOURNAL OF SOLID STATE CHEMISTRY 88, 411–418 (1990)

Variation of the Preexponential Factor and Activation Energy for Lithium Diffusion in Cubic Titanium Disulfide

P. G. BRUCE[1] AND M. Y. SAIDI

Department of Chemistry, Heriot-Watt University, Riccarton,
Edinburgh, Scotland EH14 4AS, United Kingdom

Received January 18, 1990

The chemical, $\tilde{D}$, and self diffusion, D, coefficients for lithium transport within the cubic polymorph of TiS_2 have been determined as a function of temperature and composition by ac impedance measurements. Both $\tilde{D}$ and D vary with the lithium content, reaching maxima at 23°C of 5.6×10^{-10} and 6.9×10^{-9} cm^2sec^{-1}, respectively. The Arrhenius plots for the self diffusion coefficient are linear; however, the preexponential factor and activation energy vary significantly with composition displaying a broad minimum centered at $x = 0.5$. This behavior is associated with interactions between the mobile ions; two possible models for ion interactions are presented, either or both of which may be important in these systems.

Introduction

The formation of a cubic polymorph of titanium disulfide, TiS_2–C, has been reported (*1*, *2*); up to one lithium per TiS_2–C formula unit may be reversibly intercalated into the host structure. The cubic polymorph can be prepared by the oxidative extraction of copper from the thiospinel $CuTi_2S_4$ at room temperature without disrupting the basic spinel framework. However, studies of stoichiometric $CuTi_2S_4$ have shown that a small quantity of copper remains after oxidation, yielding a final composition $Cu_{0.07}Ti_2S_4$ (*3*). Early reports indicated that if an excess of titanium is present in the starting material all of the copper could be removed; we have been unsuccessful in our attempts to reproduce this result. The composition of the intercalation host used throughout this paper is the titanium-rich $Cu_{0.07}Ti_{2.05}S_4$; the crystal structure of lithium intercalates based on this host, $Li_xCu_{0.07}Ti_{2.05}S_4$, has been determined (*4*). The structure may be derived from that of spinel with which it shares the $Fd3m$ space group; it consists of cubic close-packed sulfide ions within which there are two sets of octahedral sites, one set occupied completely by titanium ions, designated 16(*d*), and the other, designated 16(*c*), by lithium ions along with the excess titanium. The residual copper partially occupies one-eighth of the tetrahedral, 8(*a*), sites, these sites being fully occupied by copper in $CuTi_2S_4$ itself. Li^+ ions diffuse along pathways formed by face sharing between the octahedral 16(*c*) and tetrahedral 8(*a*) sites. Since the amount of residual copper and excess titanium is small the composition closely approaches TiS_2. We will therefore refer to the intercalation host,

---

[1] To whom correspondence should be addressed.

0022-4596/90 $3.00

$Cu_{0.07}Ti_{2.05}S_4$, as TiS_2–C. In comparison, the conventional layered polymorph of TiS_2 can reversibly accommodate up to one Li^+ ion in octahedral sites located between the van der Waals bonded sheets of sulfur atoms.

Cubic TiS_2 offers a potentially attractive alternative to the layered polymorph for application as a cathode in electrochemical cells, particularly rechargeable lithium batteries. This is largely as a result of the isotropic expansion and contraction of the lattice on inserting and removing lithium, which should preserve particle contact in the cathode, as well as the absence of solvent co-intercalation. In view of the potential technological interest in TiS_2–C as a battery cathode and because of the scientific interest in comparing diffusion in two and three dimensions within two host structures of similar composition, it is important to characterize the kinetics of Li^+ transport in cubic titanium disulphide. The structure of $Li_xCu_{0.07}Ti_2S_4$ and the lithium diffusion coefficient at room temperature have been reported (*3, 5*). Here we present the results of ac impedance measurements on Li_xTiS_2–C ($Li_xCu_{0.07}Ti_{2.05}S_4$) and extract the variation of both chemical and self diffusion coefficients for lithium as a function of composition and temperature. Such studies permit access to the fundamental parameters of lithium ion transport, namely the preexponential factor and the activation energy for self diffusion. Data are presented covering the range of compositions $0.1 < x < 0.9$, Li_xTiS_2–C.

Experimental

Where the materials being handled were of an air-sensitive nature manipulations were carried out in an argon-filled Millar–Howe glove box with an oxygen and water level of less than 1 and 7 ppm, respectively.

The spinel $Cu_{0.6}Ti_{2.05}S_4$ was prepared by heating a powdered mixture of copper (Aldrich, 99.995%), titanium (Aldrich, 99.9%), and sulfur (Strem, 99.99%) in a sealed, evacuated, silica tube. Initially the mixture was heated slowly from 25 to 450°C and maintained at the latter temperature for 24 hr; this was followed by slow heating to 650°C, the mixture remaining at this temperature for 2 weeks. Excess titanium was used in an attempt to ensure removal of all the copper by subsequent oxidation; however, as mentioned in the Introduction, this proved unsuccessful.

Extraction of copper from $Cu_{0.6}Ti_{2.05}S_4$ was carried out by addition of the solid to an excess of a 5% (v/v) solution of Br_2 in dry acetonitrile. The mixture was stirred continuously for 3 days, then filtered and thoroughly washed with acetonitrile and CS_2.

The copper content of the resulting material was determined by atomic absorption analysis using a Pye Unicam SP9. The solid was dissolved in concentrated sulfuric acid and the composition for the intercalation host determined to be $Cu_{0.07}Ti_{2.05}S_4$.

The crystalline solid before and after copper removal was also analyzed by powder X-ray diffraction using a high resolution Stöe-Guinier camera.

So that electrochemical measurements would be restricted to the TiS_2–C electrode, cells containing three electrodes were employed throughout. The working electrode was prepared by pressing finely ground TiS_2–C onto a 13-mm stainless steel grid. A counter electrode was formed by cutting a 13-mm disk from 0.3-mm-thick lithium foil (Alfa, 99.99%) and a ring-shaped lithium reference electrode was similarly formed from the foil.

The electrolyte consisted of a 1.4 M solution of $LiAsF_6$ (Strem, 99.99%, electrochemical grade) in 2-methyl THF (Aldrich, 99%). The salt was used as received; however, it proved essential to carefully purify the 2-methyl THF which was achieved by the following procedure. The solvent was first refluxed over calcium hydride for 4 hr under argon then distilled at 77°C through a 1-m vigreux column also under argon. The middle fraction was retained from the distillation and passed down an alumina column which had been activated by heating to 250°C under vacuum. The electrolyte was prepared by adding $LiAsF_6$ to the purified 2-methyl THF, below 0°C. If the solvent is purified using less rigorous procedures it discolors on addition of the salt or upon contact with lithium metal. However, using the above procedures, electrolytes could be prepared which remained stable and colorless in cells for many weeks.

Cylindrical Teflon-bodied cells with stainless steel end pieces were used for all electrochemical measurements. The cells were assembled by placing the lithium counter and TiS_2 working electrodes in contact with the stainless steel end pieces. Whatman pads, grade GF/D and GF/F, were soaked with electrolyte; one low porosity GF/F pad was placed next to the working electrode and two GF/D pads were placed between this and the lithium counter electrode. The ring reference electrode was placed between the two GF/D pads. The entire cell assembly was compressed between the stainless steel end pieces until a stable voltage was obtained. The cell was placed in a stainless steel gas-tight container fitted with electrical connections and a thermocouple; this allowed removal of the cell from the glove box for the ac measurements. The container was placed in an oil bath thermostated to ±0.5°C. ac impedance measurements were carried out using a Solartron 1286 potentiostat and 1250 frequency response analyzer, both devices being under the control of a Merlin microcomputer. Data were collected over the frequency range from 10^{-3} to 5×10^4 Hz.

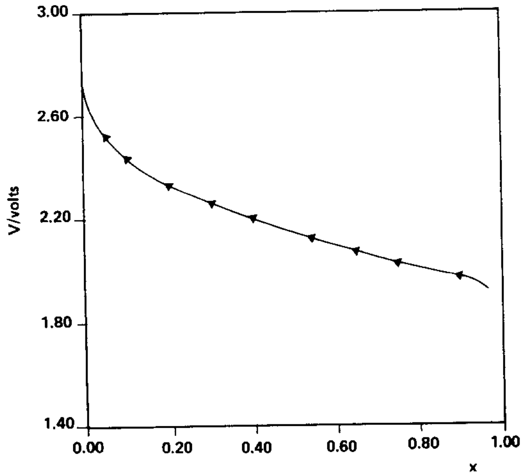

FIG. 1. Open circuit voltage, V, vs composition, x, in Li_xTiS_2–C.

Results and Discussion

A. *Open Circuit Voltage vs Composition*

The open circuit voltage, V, as a function of lithium composition, x, in Li_xTiS_2–C is shown in Fig. 1, and is similar to that presented in (5). The compositions were stepped galvanostatically at 10 μA cm^{-2} and equilibrium was judged to have been achieved when the voltage varied by less than 1 mV in 72 hr. The open circuit voltage is a measure of the chemical potential of lithium in TiS_2–C compared with that in lithium metal; for a simple metallic system of noninteracting Li^+ ions the variation of voltage with composition should depend only on the changes in configurational entropy which is itself given by

$$\frac{RT}{F} \ln \left(\frac{\text{No. of occupied site}}{\text{No. of empty sites}}\right). \quad (1)$$

The observed variation of voltage with composition is much greater than can be accounted for by configurational entropy alone indicating that, as in the case of layered TiS_2, repulsions between guest charges are important in these materials.

B. *ac Impedance Results*

An example of an ac impedance plot obtained for Li_xTiS_2–C is shown in Fig. 2. The

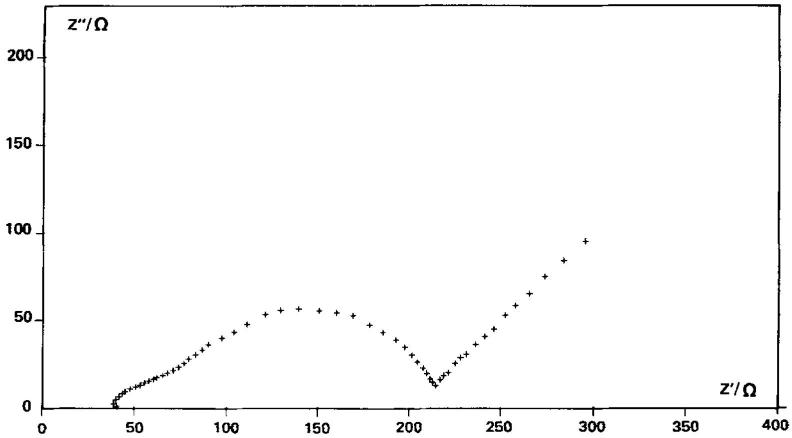

FIG. 2. Complex impedance plot for $Li_{0.1}TiS_2$–C at 39°C.

high frequency intercept on the Z'-axis corresponds to conduction within the electrolyte; two semicircles are evident at lower frequencies. Based on the capacitances obtained from these semicircles both are associated with processes occurring at or near the surface of the working electrode. At yet lower frequencies the impedance takes the form of a spike inclined at an angle near 45°; this is associated with the diffusion of lithium in TiS_2–C.

Originally we attempted to use propylene carbonate as a solvent for the electrolyte, in part because of its lower volatility compared to 2-methyl THF. However, it was noted that with propylene carbonate-based electrolytes the magnitude of the electrode impedance increased consistently with the passage of time and in some cases one of the semicircles grew to dominate the overall impedance. It is difficult, even with reasonable care, to remove certain impurities present in propylene carbonate, particularly 1,3-propylene diol, and such impurities may explain both the observed impedance response and the fact that equilibration of cells after discharge in the presence of propylene carbonate-based electrolytes is very much slower than with electrolytes based on 2-methyl THF. This suggests that the use of 2-methyl THF based electrolytes for secondary lithium batteries is advantageous because it ensures superior interfacial properties at the cathode as well as good cyclability at the lithium electrode.

C. Lithium Diffusion in TiS_2–C

For all compositions and temperatures studied only cells with low frequency, diffusional, impedances possessing angles in the range from 42 to 47° were considered further. It is important to recall that even in the absence of a supporting electrolyte diffusional impedances can arise in the electrolyte, however since Li^+ diffusion in the solid state is much slower than in 2-methyl THF we may assume that the observed low frequency impedance arises from diffusion within the electrode.

The diffusional or Warburg impedance is of the form

$$Z_w = A_w\omega^{-0.5} - jA_w\omega^{-0.5}, \qquad (2)$$

where ω is the angular frequency of the ac signal and, if all the Li^+ ions are mobile, A_w is given by

$$A_w = \frac{V_M(dV/dx)}{Fa(2\tilde{D})^{1/2}}, \qquad (3)$$

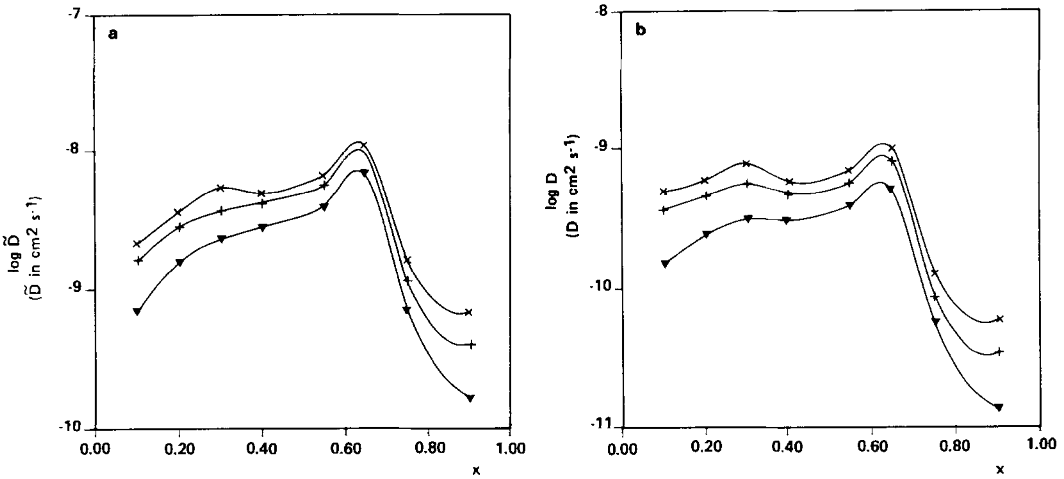

FIG. 3. (a) The logarithm of the Li^+ chemical diffusion coefficient, $\tilde{D}$, and (b) the logarithm of the Li^+ self-diffusion coefficient, D, as a function of the lithium content, x, in Li_xTiS_2–C at three temperatures: ▼, 23°C; +, 37°C; ×, 44°C.

where V_M is the molar volume of the cathode material, dV/dx is the gradient of the open circuit voltage vs composition curve, F is Faraday's constant, a is the active surface area of the cathode, and $\tilde{D}$ is the chemical diffusion coefficient for lithium. For each composition studied dV/dx was obtained from Fig. 1; the gradient is almost invariant with temperature over the range studied here. The surface area, a, was taken as the geometrical area of the electrode (0.3 cm^2), recognizing that this is an underestimate due to the rough surface of the electrode; however, it is anticipated that "a" will vary little with composition for the same electrode and not at all with temperature. By substituting values for V_M, dV/dx, a, and A_w into Eq. (3) the chemical diffusion coefficients were extracted. The composition dependence of $\tilde{D}$ at three of the temperatures studied is presented in Fig. 3a. The chemical diffusion coefficient corresponds to the coupled diffusion of both Li^+ ions and electrons arising from the requirement to maintain electroneutrality within the electrode. It may be expressed in terms of the self-diffusion coefficient of the lithium ions, D, the transport number of the electrons, t_e, and the thermodynamic enhancement factor for lithium atoms in the electrode, $(d \ln a)/(d \ln c)$ (*7*).

$$\tilde{D} = Dt_e\,(d \ln a)/(d \ln c) \tag{4}$$

Since, in the case of Li_xTiS_2–C, t_e approaches unity and $(d \ln a)/(d \ln c)$ may be obtained from the open circuit voltage–composition curve,

$$\frac{d \ln a}{d \ln c} = \frac{(dV/dx)Fx}{RT} \tag{5}$$

D may be readily obtained from $\tilde{D}$. The thermodynamic enhancement factor varies continuously at room temperature from 4.55 at $x = 0.1$ to 11.50 at $x = 0.9$. The variation of the self-diffusion coefficient with composition at three temperatures is presented in Fig. 3b. The chemical and self-diffusion coefficients exhibit a similar variation with composition which does not change markedly with temperature. Both $\tilde{D}$ and D increase with increasing lithium content until at around $x = 0.65$ they begin to

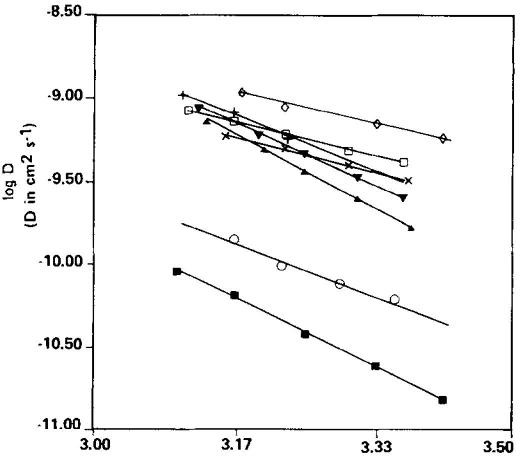

FIG. 4. Arrhenius plot of the lithium ion self diffusion coefficient, *D*, for different values of *x*: ▲, 0.1; ▼, 0.2; +, 0.3; ×, 0.4; □, 0.55; ◇, 0.65; ○, 0.75; ■, 0.9.

decrease rapidly with further increases in *x*. To investigate the temperature dependence of the Li^+ ion self-diffusion Arrhenius plots were prepared for all compositions; these are presented in Fig. 4. The anticipated linear relationship between log *D* and reciprocal temperature is observed. Such thermally activated processes are determined by the activation energy, *E*, and the preexponential factor, *A*; therefore the values of these parameters have been extracted from the data by a least-squares fitting method. The compositional dependence of *E* and log *A* are similar and shown in Fig. 5; in each case the variation is extreme with a broad minimum in both log *A* and *E* occurring in the region of $x = 0.5$. Such trends pose questions concerning the nature of Li^+ ion transport in Li_xTiS_2–C. Variation of log *A* and *E* with composition has been observed for Li^+ in layered TiS_2 by NMR (*8*).

The Li^+ ions in Li_xTiS_2–C are located in octahedral sites which share common edges; the ions do not diffuse between these sites directly through a shared edge but pass through vacant 8(*a*) tetrahedral sites which bridge pairs of octahedral sites. If ion transport occurred by Li^+ ions hopping from an octahedral site through the intervening tetrahedral site to a neighboring octahedral site, in isolation from each other then *E* and *A* should vary little with composition. In general, the activation energy for ion transport is expected to vary with com-

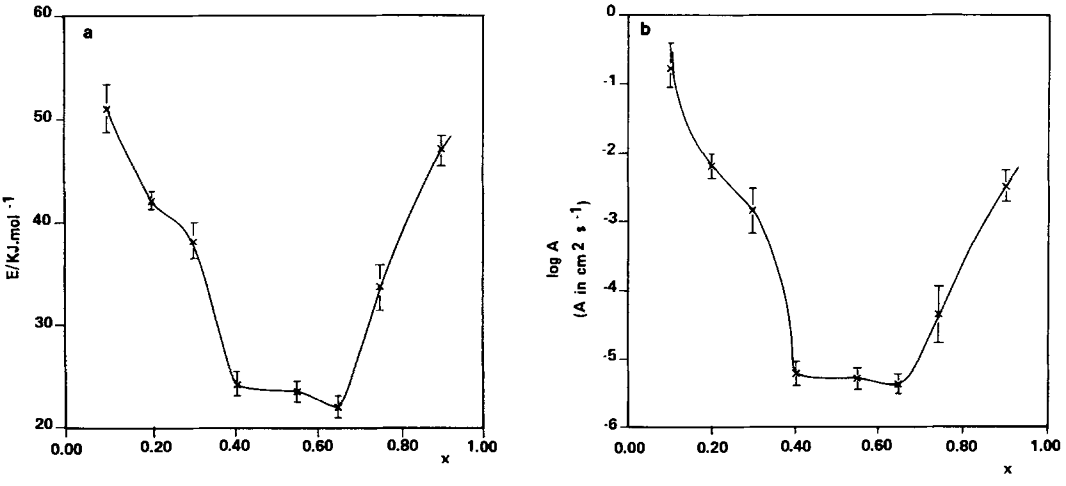

FIG. 5. Composition dependence of (a) the activation energy, *E*, and (b) the logarithm of the preexponential factor, *A*, obtained from Arrhenius plots in Fig. 4.

position due to changes in the size of the bottlenecks through which ions have to pass between sites in intercalation electrodes; however, based on the crystallographic data for Li_xTiS_2–C (*4*) the bottlenecks vary little over the composition range studied for this compound. Li^+ ions are not isolated from each other. Even at $x = 0.1$ the concentration of Li^+ ions is high and mutual repulsions between the Li^+ ions in their edge sharing sites are to be expected. The presence of ion interactions is indicated by the following results.

1. Considerable experimental evidence exists supporting the presence of lithium ion ordering in the conventional polymorph of titanium disulfide (*9*), and although screening of the ion repulsions by the electrons may be more efficient in the three-dimensional TiS_2–C structure than in the two-dimensional layered TiS_2, it is unlikely to be complete in the former.
2. If ion interactions leading to ordering are important in Li_xTiS_2–C then it is to be anticipated that the influence of ordering will be a maximum at specific compositions, most notably $x = 0.5$, which corresponds to occupancy of one-half of the octahedral sites by Li^+ ions. The deep minimum observed in Fig. 5 and centered on $x = 0.5$ would therefore seem to support the importance of Li^+ ion repulsions. The inflection observed at lower x values in Fig. 5 may arise from a similar cause.
3. The fact that the variation in configurational entropy is not sufficient to explain the change in open circuit voltage with composition is direct evidence for interactions between the mobile charges.

At present there are no precise theories which describe the influence of ion repulsions on the transport of guest ions in intercalation compounds, therefore only a qualitative discussion is appropriate here. However, cooperative interactions between mobile ions have received considerable attention in recent years; two models may be identified which appear capable of explaining departures from simple hopping behavior, considering each model in turn.

The conductivity, σ, of an ionic conductor when measured at high frequencies is generally observed to follow a power law dependence on the angular frequency, ω, of the applied electric field, i.e., $\sigma \alpha \omega^n$, where $0 < n < 1$ (*10*). It may be shown that such a dependence can arise from the reorganization of the ions around a given ion when that ion hops to a neighboring vacant site. As a result, a relaxation of the mobile ions occurs after each hop and this introduces a drag on the hopping ion which should depend on the concentration of the mobile ions. This model has been developed in recent years, by, among others, Funke (*11*) and is generally applicable to hopping ion motion in concentrated systems; it should therefore be applicable to Li_xTiS_2–C. Whether such ionic relaxation effects could lead to the observed dependence of the activation energy and the preexponential factor on composition is unclear at present.

A second explanation for the observed trends in logs A and E is possible which also depends on ion interactions. Repulsions between mobile ions leading to ordering, even if only extending over a short range, could result in the immobilization of a proportion of the intercalated ions in an electrode; only the remaining disordered ions would be capable of diffusion. Generally the analysis of the ac data to obtain the diffusion coefficients involves the use of Eq. (3) which contains the term dV/dx. Fundamentally x should refer to the content of "mobile" ions in the electrode and not the "overall" guest ion content. In our analysis of ac data for Li_xTiS_2–C presented above it was assumed that all the guest ions are mobile; if this is not so then based on Eq. 3 an "apparent" diffusion cofficient is obtained which contains within it the true diffusion coefficient and a term which depends on the proportion of guest ions that are mobile. The activation energy and preexponential factor associated with the apparent diffusion coefficient may thus contain terms in addition to those relating to the true diffusion coefficient. Since the tendency to form ordered structures varies markedly with composition, logs A and E relating to the apparent diffusion coefficient may also vary markedly. Ordering is expected to be particularly prominent in the region of $x = 0.5$ which is not inconsistent with the trends observed in Fig. 5.

Presently, we are determining the self-diffusion coefficient as a function of temperature and composition in other systems so that the generality of the trends observed here may be determined and the nature of the mechanism underlying the observations further elucidated.

Acknowledgments

P.G.B. wishes to thank the S.E.R.C. and the Royal Society of Edinburgh for financial support.

References

1. R. Schöllhorn and A. Payer, *Angew. Chem. Int. Ed. Eng.* **24,** 67 (1985).
2. S. Sinha and D. W. Murphy, *Solid State Ionics* **20,** 81 (1986).
3. A. C. W. P. James, J. B. Goodenough, and N. J. Clayden, *J. Solid State Chem.* **77,** 356 (1988).
4. I. Abrahams, M. Y. Saidi, and P. G. Bruce, *Mater. Res. Bull.,* in press.
5. A. C. W. P. James and J. B. Goodenough, *Solid State Ionics* **27,** 37 (1988).
6. C. Ho, I. D. Raistrick and R. A. Huggins, *J. Electrochem. Soc.* **127,** 434 (1980).
7. W. Weppner and R. A. Huggins, *J. Electrochem. Soc.* **124,** 1568 (1977).
8. K. Matsumato, R. Nagai, T. Asai, and S. Kawai, *Solid State Ionics* **25,** 233 (1987).
9. A. H. Thompson and F. J. Di Salvo, *in* "Intercalation Chemistry" (M. S. Whittingam and A. J. Jacobson, Eds.), Chap. 18, Academic Press, San Diego (1982).
10. A. K. Jonscher, *Nature* (*London*) **267,** 673 (1977).
11. K. Funke, 7th Int. Conference on Solid State Ionics, Japan (1989).