TITANIUM DISULPHIDE AS A CATHODE MATERIAL IN LITHIUM BATTERIES — A REVIEW

E. J. FRAZER and S. PHANG

CSIRO, Institute of Earth Resources, Division of Mineral Chemistry, P. O. Box 124, Port Melbourne, Victoria 3207 (Australia)

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Summary

The preparation, structure, intercalation reactions, and electrochemical properties of TiS_2 are reviewed. In particular we discuss the suitability of TiS_2 as a cathode material in secondary organic electrolyte-lithium batteries. Titanium disulphide is attractive for this application because of its ability to form intercalation compounds with alkali metals such as lithium. We conclude that it adequately fulfils most of the recognized criteria for a cathode material. The success of the Li-TiS₂ system for high rate applications depends on the behaviour of TiS_2 at high current densities and under deep discharge conditions. Other factors such as the conductivity of the electrolyte and the recharge ability of the lithium electrode also need to be considered.

1. Introduction

High energy density batteries are needed for both traction and load levelling applications. The choice of alkali metals as anode materials for these batteries is logical when seeking high energy densities. The present development of high temperature cells such as Na-S and Li(Al)-FeS using alkali metals seems promising. Room temperature primary lithium batteries such as Li-SOCl₂ and Li-SO₂ have been available for some time. The production of room temperature secondary lithium batteries would be advantageous, and this has led to the search for suitable cathode materials.

The dichalcogenides of Groups IVB, VB, and VIB transition metals have drawn considerable interest because of their layered structure and high alkali metal diffusivity. The properties of many transition metal dichalcogenides have been reviewed by Whittingham [1], Murphy and Trumbore [2], and Trumbore [3]. The present review is not to duplicate that work, but to examine more closely the physico-chemical properties of TiS₂. Emphasis has been placed on its potential as a cathode material in secondary organic electrolyte-lithium batteries [4 - 10]. While room temperature systems are considered here, the use of solvate melt [11, 12] and molten salt [8, 13 - 15] electrolytes is very promising and should be noted.

The factors which make TiS_2 an attractive cathode material for lithium cells have been summarized by Gaines *et al.* [5]. They include: (i) good rate capability and a high theoretical specific energy (480 W h kg⁻¹) when coupled with a lithium anode, (ii) near insolubility in many organic electrolytes, (iii) high electrical conductivity ($2 \times 10^2 \Omega^{-1} \text{ cm}^{-1}$ at 25 °C), (iv) a charge/discharge mechanism involving the intercalation of lithium between the TiS₂ layers, and (v) a reasonably low cost. Although other systems based on TiS₂ (*e.g.*, Cu-TiS₂) are being investigated [16 - 18], only the Na-TiS₂ and Li-TiS₂ systems have been subjected to serious engineering projections for large scale applications [5, 19].

2. Preparation

There are three main methods for preparing TiS_2 : (i) by disproportionating TiS_3 at ~ 600 °C to TiS_2 and sulphur, (ii) by reacting TiCl_4 with H_2S to form TiS_2 and HCl, and (iii) by heating metallic titanium and sulphur together. The high temperature disproportionation reaction was considered difficult to control, producing TiS_2 with substantial crystalline imperfections [20]. Thorp *et al.* [21, 22] produced $\text{Ti}_x S_2$ where $1.00 \le x \le 1.02$ with a particle size of $1 - 25 \,\mu$ m, using method (ii). They claimed that the product was suitable as a cathode material in secondary batteries.

Thompson et al. [23] prepared $\text{Ti}_x S_2$ where $0.9 \le x \le 1.2$. Nonstoichiometric compounds were formed only on the metal-rich side of TiS_2 (i.e., x > 1.0), but for x < 1.0 a two phase region existed between TiS_2 and TiS_3 . It was therefore concluded that TiS_2 was the stoichiometric phase limit of the $\text{Ti}_x S_2$ series. Winn and Steele [24] were the first to report the preparation of stoichiometric TiS_2 and to define the thermodynamic stability range. An elemental synthesis at ~600 °C was used to produce powder samples [24], while single crystals of defined stoichiometry were prepared by a chemical vapour transport technique [25].

Whittingham [20] used method (iii) to produce fine, particulate, stoichiometric TiS_2 having a high degree of crystalline perfection. The material was claimed to be particularly suitable for use as a cathode material. His study suggested that titanium sponge with particle size -4 +40 mesh (~0.5 - 5.0 mm) should be reacted with a very slight excess of sulphur to minimize the formation of titanium-rich TiS_2 . Temperature control was exercised by differentially heating the reaction tube, thereby maintaining the titanium at a reaction temperature between 475 and 600 °C. At temperatures greater than 700 °C, it was found that titanium atoms occupied positions between the sulphur layers (see Section 3) even though the overall composition was stoichiometric [23, 26]. Holleck and Driscoll [7] have described the preparation of stoichiometric TiS_2 at somewhat higher temperatures. Titanium disulphide was produced when the reaction zone was kept at 750 - 900 °C, whereas TiS_3 was formed at lower temperatures (~550 °C).

3. Structure

The dichalcogenides of Groups IVB and VB exhibit the CdI_2 structure, whereas those in Group VIB exhibit the MoS_2 structure [27]. The structure of TiS_2 consists of laminae or "sandwiches" that are stacked upon each other. Each "sandwich" is formed by a layer of titanium atoms between two layers of sulphur atoms in a hexagonally close-packed arrangement; each titanium atom is surrounded octahedrally by the sulphur atoms. It has been found [28] that the disulphides and diselenides of the Group IVB metals adopt the octahedral form, whereas those in Group VIB possess the trigonal prismatic form. Both forms, however, appear in the Group VB dichalcogenides.

Figure 1(a) illustrates the structure of TiS_2 in which the covalently bound S-Ti-S "sandwiches" are held together by weak van der Waals forces. Should the TiS_2 be metal-rich, the excess titanium atoms occupy octahedral sites in the van der Waals gap, as shown by position A in Fig. 1(b). One effect of this is the pinning together of the structure, and this, in turn, hinders the movement of "guest" atoms or molecules into the van der Waals layers. On the other hand, excess sulphur leads to the destruction of the covalently bound "sandwich" and the formation of TiS_3 having a monoclinic structure. A layered structure is, however, still retained with S-S layers facing each other [7, 29].

The unit cell dimensions of TiS₂ were reported by Wilson and Yoffe [30] (a = b = 3.409 Å, c = 5.694 Å) and by Thompson *et al.* [23] (a = b = 3.4073 Å, c = 5.6953 Å). The latter authors also calculated the theoretical density of TiS₂, using their own lattice parameters, and obtained a value of 3.2449 g cm⁻³, which compares favourably with the experimentally determined value of 3.242 g cm⁻³. Chianelli *et al.* [31], using powder XRD, reported bond lengths in the TiS₂ crystal of Ti-S = 2.4279 Å, S-S = 3.4073 Å (unit cell translation of the *a*-axis), and S-S = 3.462 Å (interlayer S-S distance).

There is at present some controversy as to whether TiS_2 is a semiconductor with a 1 eV band gap or a metal [28]. The calculations of Myron and Freeman [32] and the optical data of Beal *et al.* [33] indicate that TiS_2 is a semiconductor, whereas X-ray [34] and transport property [35] studies support the metallic status. Indeed, the term "semimetallic" has often been used [23, 36] in discussing the properties of TiS_2 .

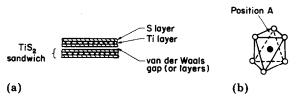


Fig. 1. (a) Stacking sequence of titanium and sulphur layers in TiS₂. (b) Octahedral site symmetry for the titanium atom in TiS₂, where \bullet represents titanium and \circ represents sulphur.

4. Intercalation reactions and diffusion

The layered structure of TiS_2 allows the inclusion of atomic and molecular species in the spaces between the basic dichalcogenide units. This phenomenon is known as intercalation. Among the atoms and molecules that have been intercalated in TiS_2 are the alkali metals [27, 37, 38], Lewis base molecules such as aliphatic and aromatic amines (*e.g.*, NH₃, pyridine, aniline, tributylphosphine, and s-collidine) [39], and organometallic complexes such as cobaltocene and chromocene [40].

An important requirement for cathode materials such as TiS₂ is a high diffusivity of alkali metal ions in their structure. Using n.m.r. studies of lithium intercalates of various layered disulphides, the self-diffusion coefficient for lithium in LiTiS₂ was estimated to be 10^{-9} cm² s⁻¹ at room temperature [41, 42]. However, the chemical diffusion coefficient of lithium in single crystal LiTiS₂ has been quoted by Whittingham [42, 43] to be $\sim 10^{-8}$ cm² s⁻¹. The latter value agrees with that measured by Winn *et al.* [25] for a crystal of composition $Li_{0.55}Ti_{1.01}S_2$, for which a value of 2×10^{-8} cm² s⁻¹ was obtained. It should be noted here that when the experimental arrangements involve mass transport along a concentration gradient, the derived diffusion coefficient is often termed a chemical diffusion coefficient in contrast to the self-diffusion coefficient, which is measured in the absence of a concentration gradient [44]. The above diffusion coefficients are amongst the highest known for lithium at room temperature. Sodium diffusion in $Na_x Ti_{1.02}S_2$ was also studied by Winn *et al.* [25]; the chemical diffusion coefficient varied between 10^{-9} and 10^{-10} cm² s^{-1} , the value decreasing with increasing x. In both cases excess titanium had a deleterious effect on diffusion rates.

The lithiation of TiS₂ is a topochemical reaction that is characterized by retention of crystallinity and lack of phase separation. Intercalation does, however, cause lattice expansion, and Whittingham [29] has reported a continuous increase in the c lattice parameter during the lithiation of TiS₂; the c-axis increased from 5.690 to 6.222 Å while the a-axis increased from 3.405 to 3.423 Å [45]. Thus, TiS₂ may be regarded as possessing a "host" lattice into which the "guest", lithium, is inserted while maintaining the basic structural features of the host. The c-axis dilation and ⁷¹Li n.m.r. shifts suggest nearly complete lithium 2s electron donation to the host layers [28]. Furthermore, among the alkali metals that have been intercalated into TiS₂, only lithium resulted in a single phase product with the general formula Li_xTiS₂ in the range 0 < x < 1 [1]. A general criterion for electrode stability is the lack of phase transformation during the charge/discharge process [27].

Lithium titanium disulphide can be obtained during the discharge of a $\text{Li}-\text{TiS}_2$ cell or by the reaction of TiS_2 with a solution of n-butyllithium in n-hexane at room temperature [37]. Rao and Francis [46] reported the lithiation of TiS_2 using a solution of lithium in hexamethylphosphoric triamide. The mechanism for intercalation, especially in the case of n-butyllithium, is not clear although the overall reaction may be given by

$$TiS_2 + CH_3(CH_2)_3 \cdot Li \rightarrow LiTiS_2 + 0.5CH_3(CH_2)_6CH_3.$$
(1)

To ascertain the exact amount of n-butyllithium used, a slight excess of HCl was added to the unreacted n-butyllithium and then back-titrated with NaOH solution [37]. Since intercalation normally involves the transfer of electrons, the enthalpy of intercalation can be used to compare the degree of electron transfer. The enthalpy of intercalation for lithium into TiS₂ is -210 kJ mol^{-1} , but it is much smaller for Lewis base molecules where there is no obvious electron transfer (e.g., NH₃ into TaS₂, -42 kJ mol^{-1}) [28, 47].

Lithiation of TiS₂ using n-butyllithium is relatively rapid, as shown in Fig. 2, being almost complete after two hours [42, 48]. It is, however, more difficult to lithiate TiS₂ containing interlayer titanium [23], and due attention must be given to the method of preparation to avoid this problem [20]. Chianelli *et al.* [49 - 51] have followed the lithiation of TiS₂, using both optical and X-ray techniques, in an attempt to gain more detailed mechanistic information. They observed cracking and rifting of the larger TiS₂ crystallites, and they suggest that cathodes should be made of particles of less than 10 μ m to avoid physical degradation [51].

Both Whittingham and Gamble [52] and Murphy *et al.* [45] used nbutyllithium for the lithiation of MX_2 , where M = Ti, Zr, Hf, V, Nb, Ta and X = S, Se, Te. All compounds reached a limiting composition of LiMX₂ except VSe₂, which also formed Li₂VSe₂ [45]. The corresponding crystallographic, magnetic susceptibility, pressed pellet d.c. conductivity, and superconductivity data for the above chalcogenides have also been reported [45, 52]. The Group VIB dichalcogenides, however, do not form lithium intercalation compounds with the exception of metastable LiMoS₂ [52] and LiCrS₂ [1]. Lithium intercalated compounds can also undergo hydration, and Whittingham [53] has reported a hydrated lithium titanium disulphide of formula Li_{0.4}(H₂O)₂TiS₂.

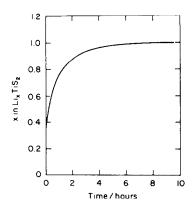


Fig. 2. n-Butyllithiation of TiS_2 (after Whittingham [42]).

5. Electrochemical properties and battery studies

The suitability of TiS_2 as a cathode material in a secondary battery depends to a large extent on the reversibility of the charge/discharge reaction. Cathodes have been constructed by hot-pressing or sintering TiS_2 and Teflon powder mixtures [7], and cells of the following type have been studied:

(2)

where MX (the solute) may be such salts as LiPF_6 , LiClO_4 , LiAlCl_4 , LiBF_4 , etc., and SOL may be such solvents as propylene carbonate, methyl acetate, methyl chloroformate, and dioxolane [5, 8, 50]. A recent report by Newman *et al.* [54] has demonstrated the explosion hazards associated with the $\text{LiClO}_4/\text{dioxolane}$ electrolyte, which is now considered unsafe for use in lithium secondary cells.

The concentration of the electrolyte solutions has usually been 1M or saturated in order to maintain high electrolyte conductivity. This is necessary since the internal resistance of cells is a determining factor in power density. The problem becomes apparent when one considers that at 25 °C the molar conductances of a 1M LiClO₄ solution in propylene carbonate [55] and a 1M aqueous solution [56] are 5.6 and 70.8 Ω^{-1} cm² mol⁻¹, respectively. An excellent review of the physico-chemical properties of some aprotic solvents that can be used in batteries has been presented by Butler [57].

When cell e.m.f.'s were studied, the cell was normally charged or discharged at very low constant current densities (~50 μ A cm⁻²), then disconnected at intermittent periods and allowed to equilibrate for 16 - 48 h [58]. Equilibrium was regarded as having been attained when there was a change of less than 10 mV in 8 h. The amount of lithium intercalated at each stage was calculated from the total charge passed [58]. Figure 3 shows the way in which the e.m.f. of TiS_2 cells decreased as the percentage of lithium intercalated into the TiS_2 increased [29]. The e.m.f. was found to be independent of the composition of the lithium electrolyte [29]. A similar pattern of behaviour was observed by Thompson [59], who measured cell e.m.f.'s under quasi-open-circuit conditions and presented evidence for the structural ordering of lithium in $Li_{x}TiS_{2}$ [59]. The continuous decrease in e.m.f. with increasing x seen in Fig. 3 is to be expected for the existence of a single phase throughout the composition range. The relationship between e.m.f. and composition for Lix TiS2 has recently been explained in terms of a regular solution [15] and a Fermi-Dirac model [60]. Basu and Worrell [61] and Nagelberg and Worrell [62] observed fairly linear relationships of e.m.f. with x for all lithium and sodium intercalates of TiS_2 and TaS_2 except Na_xTiS₂, and they proposed a model depending on random occupation of vacant sites in the interlayer gap.

The open circuit voltage (OCV) for cells of type (2) during the lithium intercalation reaction (discharge)

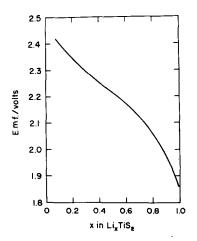


Fig. 3. E.m.f. of the cell Li/LiPF₆, propylene carbonate/TiS₂ vs. x in Li_xTiS₂ (after Whittingham [29]).

$$Li^{+} + MX_{2} + e \rightarrow LiMX_{2}$$
(3)

ranged from 2.5 to 1.5 V [1, 63]. In the case of TiS_2 , values of ~2.5 and ~1.8 V indicate the non-lithiated (fully charged) and the completely lithiated (discharged) state, respectively. Based on an average voltage of 2.15 V, the theoretical energy density of the Li–TiS₂ cell was calculated to be approximately 480 W h kg⁻¹ [5, 29]. E.m.f. measurements of cells of type (2) were used by Nagelberg and Worrell [62] to show that the free energies of intercalation for sodium-intercalated TaS₂ and TiS₂ were less negative than those reported for the corresponding lithium-intercalated compounds.

The testing and cycling of battery type Li-MX₂ cells was usually performed using constant currents with switching at preset cell voltages. The cell voltage was followed until the preset values were reached, whereupon the current was reversed [7, 63, 64]. Holleck *et al.* [6, 7] tested TiS₂ electrodes in propylene carbonate and methyl acetate electrolytes. Using the constant current technique (~0.3 mA cm⁻²), capacities of 0.4 - 0.8 moles of lithium per mole of TiS_2 were obtained over 300 cycles at 100% discharge depth. Limiting composition and reaction rates were determined using potentiostatic discharge/charge cycles. In propylene carbonate electrolytes, 50% of the theoretical capacity was obtained at current densities exceeding 4.5 mA cm^{-2} , while in methyl acetate electrolytes 93% was obtained at current densities greater than 6 mA cm^{-2} . It was also reported that the charge process occurred at a higher rate than the discharge process in both electrolytes under these conditions [7]. Vaccaro et al. [65] used long-term chronoamperometry to show that the discharge rates attainable were controlled by the rate of lithium ion diffusion within the TiS_2 . In a more recent report, Holleck et al. [66] described the operation of 0.5 - 5 A h Li–TiS₂ cells for 100 - 200 cycles at the 4 - 6 h rate using a LiAsF₆/

2-methyltetrahydrofuran electrolyte. The same system is also being investigated by Shen *et al.* [67] with a view to spacecraft applications.

Whittingham [8] reported the shallow galvanostatic cycling of Li- TiS_2 cells in $LiClO_4$ /tetrahydrofuran + dimethoxyethane electrolytes. Using only 4% of the cell's theoretical capacity, 1100 cycles at 1 mA cm⁻² were obtained. The effect of TiS₂ stoichiometry and surface area on the discharge capacity and rate have also been reported [20]. It was shown that, for a given polarization, cells containing stoichiometric TiS₂ of small crystal size could be discharged at far higher rates than cells containing large crystals. In situ optical and XRD techniques have also been used to study the mechanism of the cell discharge reaction [50, 51]. Gaines et al. [5] achieved 150 - 250 cycles at greater than 60% material efficiency in $LiClO_4/dioxolane$ with charge/discharge rates of 2.5 and 10 mA cm⁻², respectively. A pulse discharge regime (105 s at 2.5 mA cm^{-2} , 15 s at 10.0 mA cm⁻²) was also used in an attempt to be more representative of the urban driving environment. It was found that active material utilization in the pulse discharge experiments was comparable with that observed at constant current discharge with a base rate of 2.5 mA cm^{-2} . Because of the safety problem with LiClO₄/dioxolane referred to above, alternative electrolytes are now being investigated. Rao et al. [68] have reported limited cycling of Li-TiS₂ cells with a LiSCN/1.3-dioxolane + 1.2-dimethoxyethane electrolyte. While 80 - 90% of the theoretical charge was obtainable on the first discharge, the overall cell performance and life were very sensitive to charge/discharge rate, electrode loading, and impurities [68, 69]. Other electrolytes such as lithium closoboranes [70] and $LiB(C_6H_5)_4$ [71] are also being evaluated.

Using low currents (0.2 mA), Murphy and Carides [63] observed two potential plateaux while studying Li–TiS₂ cells containing LiClO₄/propylene carbonate electrolytes, and they attributed these to the formation of LiTiS₂ (~2.0 V) and Li₂TiS₂ (~0.5 V). The electro-intercalation of up to three moles of lithium per mole of TiS₂ was reported by Dahn and Haering [72], Basu and Worrell [73], and Johnson and Worrell [74]. The latter authors used the sodium-intercalated compound Na_{0.18}TiS₂ and found that the OCV decreased from 2.6 to 1.8 V during lithium intercalation. In general, the cell cycling characteristics were unsatisfactory when Li₂TiS₂ and Li₃TiS₂ were formed, apparently because of the phase changes involved [63, 72]. Capacity decrease and cell failure on cycling have often been attributed to problems associated with the lithium electrode [2, 6, 7, 64, 75]. More recent studies have indicated that the performance of lithium-aluminium alloys may be superior to pure lithium [64, 76, 77].

3. Conclusions

Titanium disulphide fulfils many of the requirements of a useful cathode material. The lithium intercalation reaction takes place with a large free energy of reaction (-206 kJ mol^{-1}), and this is of importance in determining energy density. Intercalation involves only one phase over the composition range $0 \le x \le 1$, and this should be beneficial for electrode stability. However, although the lattice expansion on intercalation is only 10%, cracking and rifting of larger TiS₂ crystallites may still cause mechanical degradation of practical electrodes. Alkali metal diffusivity is a limiting factor in current density and hence power density, and therefore stoichiometric TiS₂ must be produced without titanium in the van der Waals layers. The solubility of TiS₂ in many organic solvents is apparently negligible, and this should reduce loss of active material and increase shelf life. Since TiS₂ has semimetallic properties, its conductivity should not be a major factor determining the internal resistance of Li-TiS₂ cells. The thermodynamic reversibility of the electro-intercalation reaction has been generally confirmed. However, large active material utilization at high current densities (e.g., 60% at ~ 7.5 mA cm⁻²), especially after extended galvanostatic cycling, has been reported by only one research group. Further work to confirm this observation is desirable. Finally, whether TiS_2 and, in particular, the Li-TiS₂ system are successful contenders for high rate secondary applications depends on various additional factors such as the overall economics of production, the conductivity/stability of the organic electrolyte, and the rechargeability of the lithium electrode.

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References

- 1 M. S. Whittingham, Prog. Solid State Chem., 12 (1978) 41.
- 2 D. W. Murphy and F. A. Trumbore, J. Cryst. Growth, 39 (1977) 185.
- 3 F. A. Trumbore, Pure Appl. Chem., 52 (1979) 119.
- 4 M. S. Whittingham, Science, 192 (1976) 1126.
- 5 L. H. Gaines, R. W. Francis, G. H. Newman and B. M. L. Rao, Proc. 11th Intersoc. Energy Conv. Eng. Conf., Lake Tahoe, Nevada, 1976, p. 418.
- 6 G. L. Holleck, J. R. Driscoll and F. S. Shuker, Proc. 27th Power Sources Symp., Atlantic City, N. J., 1976, p. 80.
- 7 G. L. Holleck and J. R. Driscoll, Electrochim. Acta, 22 (1977) 647.
- 8 M. S. Whittingham, U.S. Patent 4,009,052 (1977).
- 9 M. S. Whittingham, Chemtech., 9 (1979) 766.
- 10 M. S. Whittingham, J. Solid State Chem., 29 (1979) 303.
- 11 B. M. L. Rao and L. P. Klemann, J. Electrochem. Soc., 127 (1980) 761.
- 12 G. H. Newman and L. P. Klemann, *Ext. Abstr.*, Vol. 80-2, Electrochemical Society, Princeton, 1980, p. 136.
- 13 Y. M. F. Marikar and D. Inman, Ext. Abstr., Vol. 79-2, Electrochemical Society, Princeton, 1979, p. 397.

- 14 G. Vassort, M. Gauthier, A. Belanger and W. A. Adams, Ext. Abstr., Vol. 80-2, Electrochemical Society, Princeton, 1980, p. 303.
- 15 Z. Tomczuk, K. E. Anderson, D. R. Vissers and M. F. Roche, J. Electrochem. Soc., 127 (1980) 1881.
- 16 A. Bottini, M. Lazzari, G. Razzini, B. Rivolta, G. De Felici, M. A. Vaso and B. Scrosati, J. Electroanal. Chem., 96 (1979) 165.
- 17 B. Scrosati, M. A. Vaso and M. Lazzari, J. Electrochem. Soc., 126 (1979) 699.
- 18 M. Lazzari and B. Scrosati, J. Electrochem. Soc., 127 (1980) 773.
- 19 B. M. L. Rao, in S. Gross (ed.), Proc. Symp. Battery Design and Optimization, Vol. 79-1, Electrochemical Society, Princeton, 1979, p. 457.
- 20 M. S. Whittingham, U.S. Patent 4,084,046 (1978).
- 21 A. J. Thorp, F. Clamp, R. Feld, J. E. Page-Gibson and K. Archer, U.S. Patent 4,137,297 (1979).
- 22 A. J. Thorp, F. Clamp, R. Feld, J. E. Page-Gibson and K. Archer, U.S. Patent 4,203,861 (1980).
- 23 A. H. Thompson, F. R. Gamble and C. R. Symon, Mater. Res. Bull., 10 (1975) 915.
- 24 D. A. Winn and B. C. H. Steele, Mater. Res. Bull., 11 (1976) 551.
- 25 D. A. Winn, J. M. Shemilt and B. C. H. Steele, Mater. Res. Bull., 11 (1976) 559.
- 26 S. Takenchi and H. Katsuda, J. Jpn. Inst. Met., 34 (1970) 758.
- 27 B. A. Marmaduke and L. F. Donaghey, Proc. 11th Intersoc. Energy Conv. Eng. Conf., Lake Tahoe, Nevada, 1976, p. 467.
- 28 B. G. Silbernagel, Mater. Sci. Eng., 31 (1977) 281.
- 29 M. S. Whittingham, J. Electrochem. Soc., 123 (1976) 315.
- 30 J. A. Wilson and A. D. Yoffe, Adv. Phys., 18 (1969) 193.
- 31 R. R. Chianelli, J. C. Scanlon and A. H. Thompson, *Mater. Res. Bull.*, 10 (1975) 1379.
- 32 H. W. Myron and A. J. Freeman, Phys. Rev. B,9 (1974) 481.
- 33 A. R. Beal, J. C. Knight and W. Y. Liang, J. Phys. C,5 (1972) 3531.
- 34 D. W. Fischer, Phys. Rev. B,8 (1973) 3576.
- 35 A. H. Thompson, K. R. Pisharody and R. F. Koehler, Jr., Phys. Rev. Lett., 29 (1972) 163.
- 36 F. R. Gamble and T. H. Geballe, in N. B. Hannay (ed.), Treatise on Solid State Chemistry, Vol. 3, Plenum Press, New York, 1976, p. 89.
- 37 M. B. Dines, Mater. Res. Bull., 10 (1975) 287.
- 38 J. Bichon, M. Danot and J. Rouxel, C. R. Acad. Sci., Ser. C, 276 (1973) 1283.
- 39 F. R. Gamble, J. H. Osiecki, M. Cais, R. Pisharody, F. J. DiSalvo and T. H. Geballe, Science, 174 (1971) 493.
- 40 M. Danot, J. Bichon and J. Rouxel, Bull. Soc. Chim. Fr., 8 (1972) 3063.
- 41 B. G. Silbernagel, Solid State Commun., 17 (1975) 361.
- 42 M. S. Whittingham, in J. D. E. McIntyre, S. Srinivasan and F. G. Will (eds.), Proc. Symp. Electrode Materials and Processes for Energy Conversion and Storage, Vol. 77-6, Electrochemical Society, Princeton, 1977, p. 784.
- 43 M. S. Whittingham, in P. Hagenmuller and W. van Gool (eds.), Solid Electrolytes, Academic Press, London, 1978, p. 367.
- 44 B. C. H. Steele, in G. R. Belton and W. L. Worrell (eds.), *Heterogeneous Kinetics at Elevated Temperatures*, Plenum Press, New York, 1970, p. 135.
- 45 D. W. Murphy, F. J. DiSalvo, G. W. Hull, Jr. and J. V. Waszczak, *Inorg. Chem.*, 15 (1976) 17.
- 46 B. M. L. Rao and R. W. Francis, J. Phys. Chem. Solids, 37 (1976) 345.
- 47 F. R. Gamble and B. G. Silbernagel, J. Chem. Phys., 63 (1975) 2544.
- 48 M. S. Whittingham and M. B. Dines, J. Electrochem. Soc., 124 (1977) 1387.
- 49 R. R. Chianelli, J. Cryst. Growth, 34 (1976) 239.
- 50 R. R. Chianelli, J. C. Scanlon and B. M. L. Rao, J. Electrochem. Soc., 125 (1978) 1563.
- 51 R. R. Chianelli, J. C. Scanlon and B. M. L. Rao, J. Solid State Chem., 29 (1979) 323.

- 52 M. S. Whittingham and F. R. Gamble, Mater. Res. Bull., 10 (1975) 363.
- 53 M. S. Whittingham, Mater. Res. Bull., 9 (1974) 1681.
- 54 G. H. Newman, R. W. Francis, L. H. Gaines and B. M. L. Rao, J. Electrochem. Soc., 127 (1980) 2025.
- 55 R. Jasinski, in P. Delahay and C. W. Tobias (eds.), Advances in Electrochemistry and Electrochemical Engineering, Vol. 8, Interscience, New York, 1971, p. 253.
- 56 R. Haase and K. H. Ducker, Z. Phys. Chem. (NF), 46 (1965) 140.
- 57 J. N. Butler, in P. Delahay and C. W. Tobias (eds.), Advances in Electrochemistry and Electrochemical Engineering, Vol. 7, Interscience, New York, 1970, p. 77.
- 58 J. N. Carides and D. W. Murphy, J. Electrochem. Soc., 124 (1977) 1309.
- 59 A. H. Thompson, J. Electrochem. Soc., 126 (1979) 608.
- 60 M. Armand, Thèse d'Etat, Ecole d'Electrochimie, Grenoble, 1977.
- 61 S. Basu and W. L. Worrell, in J. D. E. McIntyre, S. Srinivasan and F. G. Will (eds.), Proc. Symp. Electrode Materials and Processes for Energy Conversion and Storage, Vol. 77-6, Electrochemical Society, Princeton, 1977, p. 861.
- 62 A. S. Nagelberg and W. L. Worrell, J. Solid State Chem., 29 (1979) 345.
- 63 D. W. Murphy and J. N. Carides, J. Electrochem. Soc., 126 (1979) 349.
- 64 B. M. L. Rao, R. W. Francis and H. A. Christopher, J. Electrochem. Soc., 124 (1977) 1490.
- 65 A. J. Vaccaro, T. Palanisamy, R. L. Kerr and J. T. Maloy, *Ext. Abstr., Vol. 80-2*, Electrochemical Society, Princeton, 1980, p. 188.
- 66 G. L. Holleck, K. M. Abraham and S. B. Brummer, in B. B. Owens and N. Margalit (eds.), Proc. Symp. Power Sources for Biomedical Implantable Applications and Ambient Temperature Lithium Batteries, Vol. 80-4, Electrochemical Society, Princeton, 1980, p. 384.
- 67 D. Shen, S. P. S. Yen, S. K. Khanna and R. B. Somoano, *Ext. Abstr., Vol. 80-2*, Electrochemical Society, Princeton, 1980, p. 139.
- 68 B. M. L. Rao, D. J. Eustace and J. A. Shropshire, J. Appl. Electrochem., 10 (1980) 757.
- 69 B. M. L. Rao and J. A. Shropshire, *Ext. Abstr.*, Vol. 80-2, Electrochemical Society, Princeton, 1980, p. 191.
- 70 J. W. Johnson and M. S. Whittingham, J. Electrochem. Soc., 127 (1980) 1653.
- 71 G. H. Newman and L. P. Klemann, *Ext. Abstr.*, Vol. 80-2, Electrochemical Society, Princeton, 1980, p. 182.
- 72 J. Dahn and R. R. Haering, Mater. Res. Bull., 14 (1979) 1259.
- 73 S. Basu and W. L. Worrell, *Ext. Abstr.*, Vol. 79-2, Electrochemical Society, Princeton, 1979, p. 72.
- 74 W. B. Johnson and W. L. Worrell, Ext. Abstr., Vol. 79-2, Electrochemical Society, Princeton, 1979, p. 74.
- 75 J. Broadhead and F. A. Trumbore, in D. H. Collins (ed.), *Power Sources*, 5, Academic Press, London, 1975, p. 661.
- 76 J. O. Besenhard, J. Electroanal. Chem., 94 (1978) 77.
- 77 E. J. Frazer, J. Electroanal. Chem., in press.