

## SPINEL ELECTRODES FOR LITHIUM BATTERIES — A REVIEW\*

M. M. THACKERAY\*\*, L. A. DE PICCIOTTO, A. DE KOCK, P. J. JOHNSON,  
V. A. NICHOLAS and K. T. ADENDORFF

National Institute for Materials Research, CSIR, P.O. Box 395, Pretoria 0001  
(South Africa)

(Received November 1, 1986)

### Summary

This paper briefly reviews recent electrochemical data of several transition-metal oxide and sulphide spinel compounds of general formula  $A[B_2]X_4$  that have been employed as cathode materials in both room-temperature and high-temperature (400 °C) lithium cells. Particular attention is given to the performance of the oxide spinels  $M_3O_4$  ( $M = Fe, Co, Mn$ ) that have like A- and B-type cations, the lithium spinels  $Li[M_2]O_4$  ( $M = Ti, V, Mn$ ) and  $LiFe_5O_8$ , and the thiospinels  $CuCo_2S_4$  and  $CuTi_2S_4$ . Reaction processes and the structural characteristics of the reaction products are highlighted.

### Introduction

Spinel compounds having the general formula  $A[B_2]X_4$  are currently receiving attention as possible solid-solution electrodes for room-temperature lithium batteries; their electrochemical performance in high-temperature cells has also been investigated. Research conducted thus far has revealed that, of the oxide spinels, the systems  $Li_xM_3O_4$  ( $M = Fe, Co, Mn$ ) and the lithium spinels  $Li_{1+x}[M_2]O_4$  ( $M = Ti, V, Mn$ ) can accommodate at least one lithium ion per formula unit at room temperature most readily; limited data on the family of thiospinels have been published.

In a cubic spinel with prototypic symmetry  $Fd\bar{3}m$ , the anions, X, form a cubic-close-packed array; the A-cations occupy one-eighth of the available tetrahedral sites (8a) and the B cations one-half of the octahedral sites (16d). The remaining tetrahedra (8b, 48f) and octahedra (16c) form the interstitial space of the structure. In general, room temperature insertion of lithium into the interstitial octahedral sites (16c) of an oxo-spinel causes a displacement of the A-cations into the remaining empty octahedral sites, which results in

\*Based on a paper presented at the 3rd International Meeting on Lithium Batteries, Kyoto, Japan, May 27 - 30, 1986.

\*\*Author to whom correspondence should be addressed.

a partially-ordered rocksalt phase  $(\text{Li}_x\text{A})_{16c}[\text{B}_2]_{16d}\text{O}_4$  at  $x = 1$ ; the  $[\text{B}_2]\text{X}_4$  spinel framework is unperturbed by the lithiation reaction. An important structural feature is that the interstitial space of this  $[\text{B}_2]\text{X}_4$  spinel framework contains a 'diamond' network of face-shared tetrahedra (8a) and octahedra (16c) that offers three-dimensional conduction pathways for the  $\text{Li}^+$  ions. An additional attractive feature of spinels is that a wide range of transition-metal cations may be stabilized on the B-sites of the framework, which offers the possibility of tailoring the redox potentials of the spinel electrode; this invites a detailed exploration of this family of compounds, particularly the thiospinels, as previous studies of framework structures have indicated that  $\text{Li}^+$  ions should be most mobile in close-packed arrays of large polarizable anions.

## Discussion

Initial studies of the electrochemical performance and structural characteristics of oxo-spinel electrodes in room-temperature and high temperature lithium cells were carried out on magnetite,  $\text{Fe}_3\text{O}_4$  [1, 2]. At room temperature the inserted  $\text{Li}^+$  ions enter the interstitial octahedral sites of the spinel and displace the tetrahedral A-site cations, domino-fashion, into neighbouring octahedral sites to yield a defect rocksalt phase  $(\text{Li}_x\text{Fe})_{16c}[\text{Fe}]_{16d}\text{O}_4$  for the range  $0 < x < 1$ . The open-circuit voltage of an  $\text{Li}/\text{Li}_x\text{Fe}_3\text{O}_4$  cell drops continuously from 3.1 V at  $x = 0$  to 1.2 V at  $x = 1.0$ , indicative of a single-phase reaction during which lithium is inserted into the vacant octahedral sites of the defect rock-salt structure (Fig. 1). Both the open-circuit voltage *versus* composition curve and lithium analyses of chem-

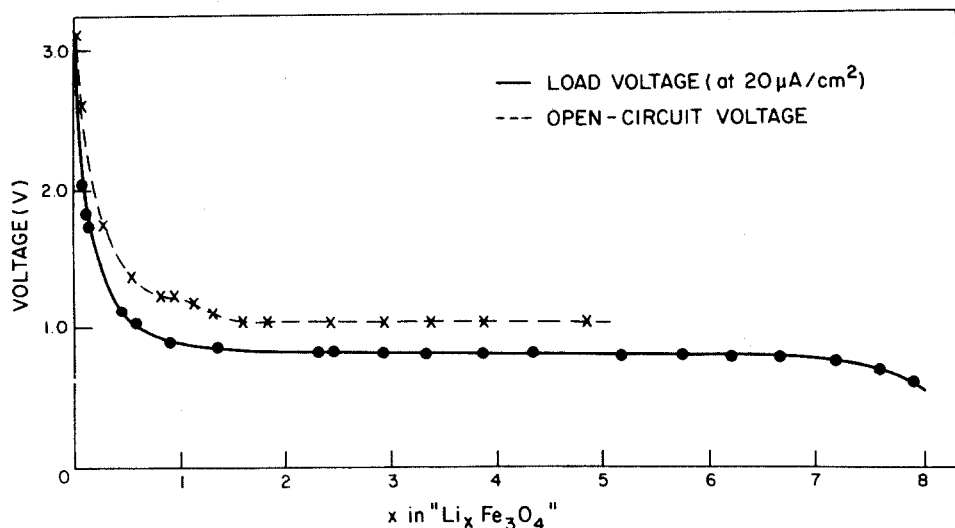


Fig. 1. Discharge behaviour of an  $\text{Li}/1 \text{ M LiClO}_4$  in propylene carbonate/" $\text{Li}_x\text{Fe}_3\text{O}_4$ " cell. " $\text{Li}_x\text{Fe}_3\text{O}_4$ " refers to the overall composition of the electrode, not necessarily to a single phase compound.

ically lithiated  $\text{Fe}_3\text{O}_4$  samples indicate that further lithium may be incorporated into the structure, up to a composition  $\text{Li}_{\sim 1.5}\text{Fe}_3\text{O}_4$  [2]. For  $x > 0.5$  the open-circuit voltage plateau in Fig. 1 indicates a multiphase reaction process; the discharge products generated on this plateau have not been identified as they are poorly crystalline; it is believed that for  $1.5 < x < 8.0$  the lithiated spinel disproportionates into  $\text{Li}_2\text{O}$  and  $\text{Fe}$ .

In  $\text{Li}_x\text{Fe}_3\text{O}_4$  samples, the lithium in excess of  $x = 1$  must necessarily occupy tetrahedral sites (8a) that share faces with the octahedral 16c sites. This result is surprising as the tetrahedral (8a)–octahedral (16c) distance in  $\text{Li}_{1.5}\text{Fe}_3\text{O}_4$  is very short, *viz.*, 1.83 Å. Samples of  $\text{Li}_x\text{Fe}_3\text{O}_4$  with  $x > 1$  are unstable in air, igniting spontaneously, which suggests that some of the lithium in excess of  $x = 1$  diffuses to the particle surface and is readily oxidised. An alternative explanation that has been given for the pyrophoric nature of extensively lithiated  $\text{Fe}_3\text{O}_4$  samples is that insertion of lithium beyond  $x = 1$  is accompanied by the extrusion of finely divided metallic iron which burns when the sample is exposed to air [3]; this explanation, however, could not be verified by Mössbauer spectroscopy [4], no room-temperature extrusion of iron could be detected for  $x \rightarrow 2.0$ , but on exposure to air, samples with  $x > 0.5$  are oxidised by delithiation to yield a two-phase product of  $\text{Fe}_3\text{O}_4$  and a lithium-inserted  $\text{Li}_x\text{Fe}_3\text{O}_4$  phase.

Figure 1 also shows data, obtained at this laboratory, of a load voltage *versus* composition curve when an  $\text{Li}/\text{Li}_x\text{Fe}_3\text{O}_4$  cell is discharged continuously at  $20 \mu\text{A cm}^{-2}$ . At this current density the cell voltage over most of the discharge is  $\sim 0.8$  V. It is evident that for a discharge voltage  $> 0.8$  V, almost 100% of the  $\text{Fe}_3\text{O}_4$  electrode capacity ( $962 \text{ mA h g}^{-1}$ ) can be achieved from this type of cell. Similar discharge curves have been obtained from cells containing  $\text{Co}_3\text{O}_4$  and  $\text{Mn}_3\text{O}_4$  cathodes [5, 6]. Cells of  $\text{Co}_3\text{O}_4$  discharge at  $\sim 1.0$  V, whereas  $\text{Mn}_3\text{O}_4$  cells discharge at a significantly lower voltage (0.3 V) which renders  $\text{Mn}_3\text{O}_4$  an unattractive cathode material for this type of cell.  $\text{Li}/\text{LiFe}_5\text{O}_8$  cells show similar electrochemical behaviour to  $\text{Li}/\text{Fe}_3\text{O}_4$  cells when discharged at room temperature [7].  $\text{LiFe}_5\text{O}_8$ , which is an inverse spinel, designated  $\text{Fe}[\text{Li}_{0.5}\text{Fe}_{1.5}]\text{O}_4$ , can accommodate one lithium ion per  $\text{Fe}[\text{Li}_{0.5}\text{Fe}_{1.5}]\text{O}_4$  unit. The rocksalt phase  $(\text{LiFe})_{16c}[\text{Li}_{0.5}\text{Fe}_{1.5}]_{16d}\text{O}_4$ , which is generated on lithiating this spinel, maintains the tetragonal symmetry of the host structure due to the retention of the long-range order of the lithium and iron ions on the B-sites (16d) of the spinel structure.

In the lithiated spinels  $\text{Li}_x\text{Fe}_3\text{O}_4$ ,  $\text{Li}_x\text{Co}_3\text{O}_4$  and  $\text{Li}_x\text{Mn}_3\text{O}_4$  the A-site cations restrict  $\text{Li}^+$ -ion diffusion through the interstitial space of the  $[\text{B}_2]\text{X}_4$  spinel framework [2, 8, 9]. Cyclic voltammetry studies have shown that the lithium insertion reactions for  $x \leq 1$  are irreversible [5]. Attention has therefore been focussed primarily on the lithium spinels  $\text{Li}[\text{M}_2]\text{O}_4$  ( $\text{M} = \text{Mn}, \text{Ti}, \text{V}$ ) in which the  $\text{Li}^+$  ions reside in the interstitial space of the  $[\text{B}_2]\text{X}_4$  framework. These materials are particularly attractive, as lithium can be not only inserted into, but also extracted from, their structures, which offers the possibility of significantly increasing their usefulness as working electrodes in lithium cells.

Of particular interest is the system  $\text{Li}_{1+x}[\text{Mn}_2]\text{O}_4$ , in which the  $[\text{Mn}_2]\text{O}_4$  framework remains intact for both lithium insertion and extraction over the range  $-1 < x < 1$  [9-12]. Complete removal of lithium by chemical oxidation of the spinel in sulphuric acid results in the novel manganese dioxide phase,  $\lambda\text{-MnO}_2$ , which has the atacamite structure [10]. However, studies have shown that electrochemical extraction of lithium from  $\text{LiMn}_2\text{O}_4$  at  $15 \mu\text{A cm}^{-2}$  proceeds easily to a composition  $\text{Li}_{0.4}\text{Mn}_2\text{O}_4$ ; thereafter, lithium extraction becomes more difficult (Fig. 2) [11]. Lithium insertion into  $\text{LiMn}_2\text{O}_4$  induces a Jahn-Teller distortion as a result of the increased  $\text{Mn}^{3+}$ -ion concentration, which reduces the crystal symmetry from cubic in  $\text{LiMn}_2\text{O}_4$  to tetragonal in  $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$  ( $0.1 \leq x < 1.0$ ) [9, 12, 13]. This distortion produces a two-phase electrode with a flat, open-circuit voltage response, at 2.9 V, over a wide compositional range (Fig. 3).

A neutron-diffraction study has revealed an unusual structural feature in the lithiated spinel  $\text{Li}_2[\text{Mn}_2]\text{O}_4$  in which the lithium ions are distributed over both the tetrahedral A site and interstitial octahedral sites of the spinel, despite an unusually short  $\text{Li}^+-\text{Li}^+$  distance of only 1.85 Å [14]. This observation reflects almost equal tetrahedral-site and octahedral-site energies, which is one of the prerequisites for fast cation conduction in solids having a cubic-close-packed anion array. Cyclic voltammetry studies have shown that lithium insertion and extraction reactions with  $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$  are reversible over the range  $-1 \leq x \leq 1$  [15]. Further lithiation of  $\text{Li}_2[\text{Mn}_2]\text{O}_4$  to  $\text{Li}_4\text{Mn}_2\text{O}_4$  is possible, but the open-circuit voltage associated with this reaction is considerably lower ( $\sim 1.2$  V). During this process the  $[\text{B}_2]\text{X}_4$  spinel framework is destroyed; the close-packed oxide array of the spinel transforms from cubic to hexagonal packing to stabilize a layered  $\text{Li}_4\text{Mn}_2\text{O}_4$

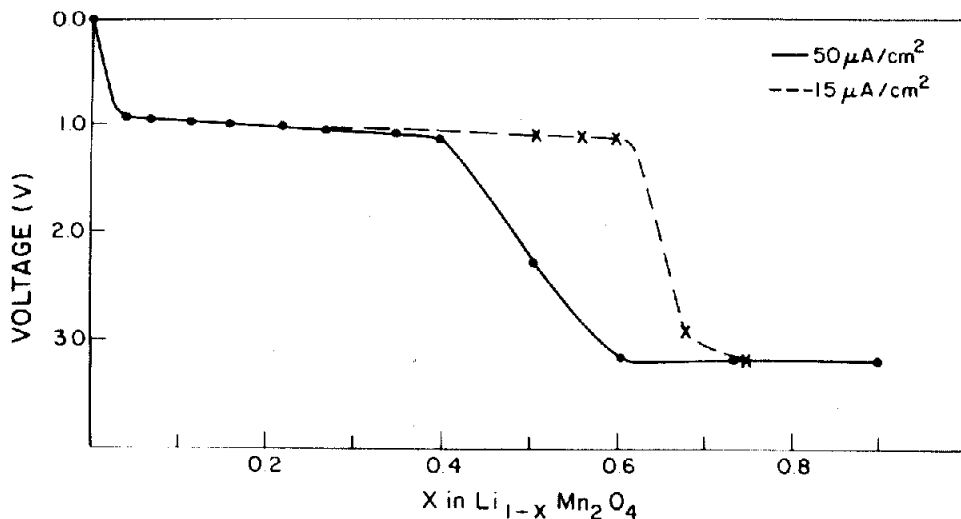


Fig. 2. Discharge behaviour of an  $\text{Li}_{1+x}\text{Mn}_2\text{O}_4/1 \text{ M LiBF}_4$  in propylene carbonate/ $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$  cell showing the open-circuit voltage vs. composition of  $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$  [11]. (Reprinted with permission from *Mater. Res. Bull.*)

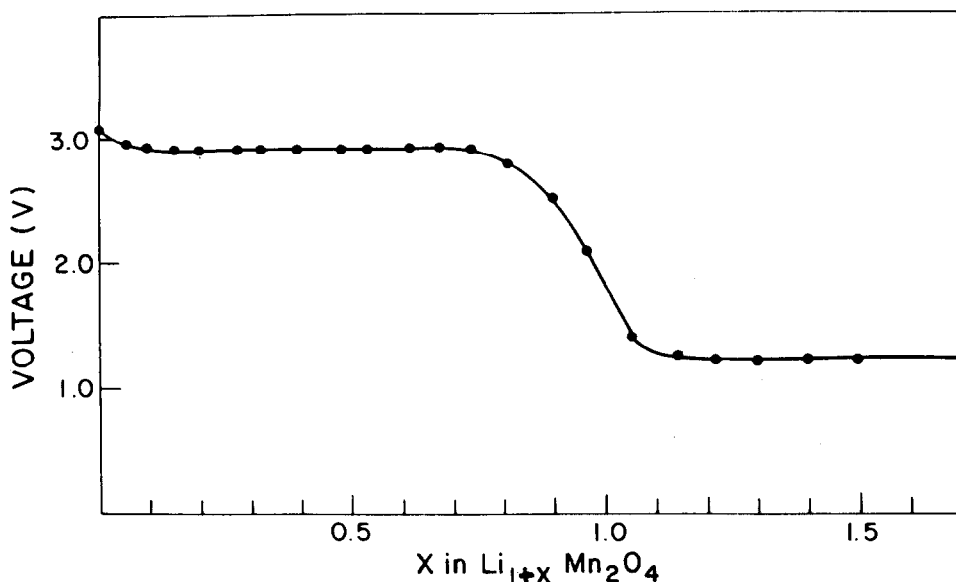


Fig. 3. Open-circuit voltage vs. composition of  $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$  in the cell  $\text{Li}/1 \text{ M LiBF}_4$  in propylene carbonate/ $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$  [9]. (Reprinted with permission from *Mater. Res. Bull.*)

phase with  $\text{Mn}^{2+}$  ions in alternate octahedral-site basal planes, and with  $\text{Li}^+$  ions occupying the tetrahedral sites of the other basal planes [16].

Lithium insertion/extraction reactions with  $\text{LiV}_2\text{O}_4$  and  $\text{LiTi}_2\text{O}_4$  have also been studied both chemically and electrochemically [17 - 19]. Lithium insertion results in the two ordered rocksalt phases  $(\text{Li}_2)_{16c}[\text{V}_2]_{16d}\text{O}_4$  and  $(\text{Li}_2)_{16c}[\text{Ti}_2]_{16d}\text{O}_4$ . Lithium extraction from  $\text{LiV}_2\text{O}_4$  to a composition  $\text{Li}_{0.27}\text{V}_2\text{O}_4$  is accompanied by migration of some vanadium ions from the B-sites to the interstitial octahedral sites of the spinel structure. This process reduces the crystal symmetry from cubic to trigonal symmetry. In  $\text{Li}_{0.27}\text{V}_2\text{O}_4$  the structure resembles that of  $\text{Li}_{0.22}\text{VO}_2$ , obtained by delithiation of the layered  $\text{LiVO}_2$  structure [20]. In  $\text{Li}_{0.22}\text{VO}_2$  the vanadium cations are distributed in a 2:1 ratio between alternate cubic-close-packed oxygen layers; in the  $\text{LiV}_2\text{O}_4$  spinel this ratio is 3:1. Further delithiation of the spinel results in a defect rocksalt structure in which the vanadium ions are almost randomly distributed over the octahedral sites of the structure [5]. Preliminary X-ray diffraction data and cyclic voltammetric data show that a similar process occurs during delithiation of  $\text{LiTi}_2\text{O}_4$  [5, 18]; the spinel structure is not regenerated on insertion of lithium into extensively delithiated samples at room temperature. Attempts to stabilize the  $[\text{V}_2]\text{O}_4$  spinel framework during delithiation by doping the tetrahedral sites of  $\text{LiV}_2\text{O}_4$  with a small concentration of zinc met with partial success [21].

The relative discharge behaviour of lithium cells with  $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ ,  $\text{Li}_{1+x}\text{Ti}_2\text{O}_4$  and  $\text{Li}_{1+x}\text{V}_2\text{O}_4$  cathodes when discharged continuously to  $x = 1.2$  at  $20 \mu\text{A cm}^{-2}$  is shown in Fig. 4. The relatively high polarization

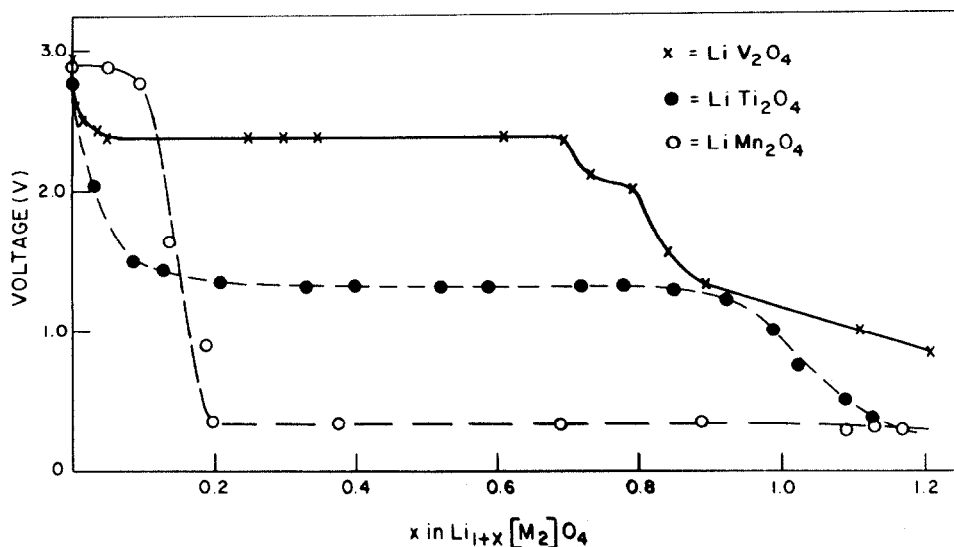


Fig. 4. Electrochemical behaviour of  $\text{Li}/1 \text{ M LiClO}_4$  in propylene carbonate/ $\text{Li}_{1+x}[\text{M}_2]\text{O}_4$  cells ( $\text{M} = \text{V}, \text{Ti}, \text{Mn}$ ) when discharged at  $20 \mu\text{A cm}^{-2}$ . The data were recorded at this laboratory.

observed in  $\text{Li}/\text{Li}_{1+x}\text{Mn}_2\text{O}_4$  cells is attributed to a low  $\text{Li}^+$ -ion mobility in the manganese spinel.

Lithium insertion reactions with spinel ferrites have also been demonstrated, but limited electrochemical data are available for these systems [22].

The family of thiospinels has not yet been extensively characterized. Thus far, electrochemical studies on  $\text{CuCo}_2\text{S}_4$ ,  $\text{CuNi}_2\text{S}_4$ ,  $\text{CuFe}_2\text{S}_4$  and  $\text{Co}_3\text{S}_4$  have shown  $\text{CuCo}_2\text{S}_4$  to be the most promising cathode material [23 - 25]. Reactions of lithium with  $\text{CuCo}_2\text{S}_4$  are topochemical and are reversible up to three  $\text{Li}^+$  ions per mole; this corresponds to an electrode capacity of  $262 \text{ mA h g}^{-1}$  compared with  $240 \text{ mA h g}^{-1}$  for layered  $\text{TiS}_2$  which can incorporate one  $\text{Li}^+$  ion, reversibly, per formula unit. Like  $\text{TiS}_2$ ,  $\text{CuCo}_2\text{S}_4$  is capable of extended cycling, but it operates at a lower cell voltage.

Of particular interest is the thiospinel  $\text{CuTi}_2\text{S}_4$ . It has been reported recently that copper can be extracted from the A-sites of the spinel structure to yield the novel cubic titanium disulphide phase,  $c\text{-TiS}_2$ , with the atacamite structure [26]. This material behaves almost identically to layered  $\text{TiS}_2$  in a lithium cell [27].

Finally, the performance of a few selected spinels have been investigated in high-temperature cells of the type

$\text{Li-Al}/\text{LiCl}, \text{KCl}/\text{Spinel}$  cathode

The anode consists of a solid lithium-aluminium alloy and the electrolyte is a molten eutectic mixture of  $\text{LiCl}$  and  $\text{KCl}$ . The cells operate at  $400^\circ\text{C}$  [1, 7, 28, 29].

Particularly good electrochemical behaviour has been reported for the oxide spinels  $\text{Fe}_3\text{O}_4$  and  $\text{LiFe}_5\text{O}_8$  [1, 29]. Electrode capacities in excess of  $600 \text{ mA h g}^{-1}$  have been obtained from these materials. The reaction sequence that occurs during the electrochemical reduction of iron oxide cathodes has been well characterized [3]. For example, when an  $\text{Fe}_3\text{O}_4$  cathode is used, lithium is inserted into, and iron extruded from, the oxide lattice to yield the intermediate phases  $\text{LiFe}_5\text{O}_8$  (spinel),  $\alpha\text{-LiFeO}_2$  (rocksalt) and  $\text{Li}_5\text{FeO}_4$  ("antifluorite-like") with increasing lithium concentration and decreasing iron concentration; the final discharge products are  $\text{Li}_2\text{O}$  (antifluorite) and  $\alpha\text{-Fe}$ . All the oxide products of the discharge reaction have a cubic-close-packed anion lattice. The cells operate reversibly. During a charge cycle oxidized iron is incorporated back into the oxide lattice; lithium ions leave the lattice and are reduced to metallic lithium on the Li-Al anode. Unfortunately, these cells tend to lose capacity with continuous cycling, particularly if discharged too deeply, because of the slow dispersion of  $\text{Li}_2\text{O}$  into the electrolyte.

## References

- 1 M. M. Thackeray and J. Coetzer, *Mater. Res. Bull.*, 16 (1981) 591.
- 2 M. M. Thackeray, W. I. F. David and J. B. Goodenough, *Mater. Res. Bull.*, 17 (1982) 785.
- 3 M. M. Thackeray, W. I. F. David and J. B. Goodenough, *J. Solid State Chem.*, 55 (1984) 55.
- 4 J. Fontanberta, J. Rodriguez, M. Pernet, G. Longworth and J. B. Goodenough, *J. Appl. Phys.*, 59 (1986) 1918.
- 5 L. A. de Picciotto, V. A. Nicholas and M. M. Thackeray, unpublished results.
- 6 A. N. Dey and R. W. Holmes, *U.S. Patent 3,945,848*.
- 7 L. A. de Picciotto and M. M. Thackeray, *Mater. Res. Bull.*, 21 (1986) 583.
- 8 M. M. Thackeray, S. D. Baker, K. T. Adendorff and J. B. Goodenough, *Solid State Ionics*, 17 (1985) 175.
- 9 M. M. Thackeray, W. I. F. David, P. G. Bruce and J. B. Goodenough, *Mater. Res. Bull.*, 18 (1983) 461.
- 10 J. C. Hunter, *J. Solid State Chem.*, 39 (1981) 142.
- 11 M. M. Thackeray, P. J. Johnson, L. A. de Picciotto, P. G. Bruce and J. B. Goodenough, *Mater. Res. Bull.*, 19 (1984) 179.
- 12 A. Mosbah, A. Verbaere and M. Tournoux, *Mater. Res. Bull.*, 18 (1983) 1375.
- 13 J. B. Goodenough, M. M. Thackeray, W. I. F. David and P. G. Bruce, *Rev. Chim. Minér.*, 21 (1984) 435.
- 14 W. I. F. David, M. M. Thackeray, L. A. de Picciotto and J. B. Goodenough, *J. Solid State Chem.*, (1986). In press.
- 15 J. C. Hunter and F. B. Tudran, *Proc. Electrochem. Soc.*, 85-4 (1985) 444.
- 16 W. I. F. David, J. B. Goodenough, M. M. Thackeray and M. G. S. R. Thomas, *Rev. Chim. Minér.*, 20 (1983) 636.
- 17 L. A. de Picciotto and M. M. Thackeray, *Mater. Res. Bull.*, 20 (1985) 1409.
- 18 D. W. Murphy, R. J. Cava, S. M. Zahurak and A. Santoro, *Solid State Ionics*, 9 & 10 (1983) 413.
- 19 R. J. Cava, D. W. Murphy, S. M. Zahurak, A. Santoro and R. S. Roth, *J. Solid State Chem.*, 53 (1984) 64.
- 20 L. A. de Picciotto, M. M. Thackeray, W. I. F. David, P. G. Bruce and J. B. Goodenough, *Mater. Res. Bull.*, 19 (1984) 1497.

- 21 L. A. de Picciotto and M. M. Thackeray, *Ext. Abstr. 3rd Eur. Conf. on Solid State Chemistry, Regensburg, F.R.G., May 29 - 31, 1986* Vol. 1, p. 67.
- 22 C. J. Chen, M. Greenblatt and J. V. Waszczak, *Solid State Ionics*, 18 & 19 (1986) 838.
- 23 M. Eisenberg, *Proc. 28th Power Sources Symp., Atlantic City, NJ, June, 1978*, p. 155.
- 24 M. Eisenberg, *J. Electrochem. Soc.*, 127 (1980) 2382.
- 25 M. Eisenberg, *Electrochim. Acta*, 26 (1981) 955.
- 26 R. Schöllhorn and A. Payer, *Angew. Chem., Int. Ed. Engl.*, 24 (1985) 67.
- 27 S. Sinha and D. W. Murphy, *Solid State Ionics*, 20 (1986) 81.
- 28 M. M. Thackeray, S. D. Baker and J. Coetzer, *Mater. Res. Bull.*, 17 (1982) 405.
- 29 N. A. Godshall, I. D. Raistrick and R. A. Huggins, *J. Electrochem. Soc.*, 131 (1984) 543.