

## New and optimised lithium manganese oxide cathodes for rechargeable lithium batteries

Peter G. Bruce, A. Robert Armstrong, Haitao Huang

*Centre for Advanced Materials, School of Chemistry, University of St. Andrews, St. Andrews Fife, KY16 9ST, Scotland, UK*

Accepted 18 November 1996

### Abstract

The 3 V spinel,  $\text{LiMn}_2\text{O}_{4.1}$ , has been prepared by a low temperature solution route which includes the addition of a small amount of carbon to the solution. As a result a significant enhancement of the capacity retention is obtained on cycling, reaching 50% after 300 cycles at discharge and charge rates of  $C/2$  and  $C/4$ , respectively. X-ray diffraction of the composite cathode on cycling shows that the improved capacity retention is related to a more complete conversion of the entire electrode between the cubic (charged) and tetragonal (discharged) structures. Layered and anhydrous  $\text{LiMnO}_2$  with a structure analogous to  $\text{LiCoO}_2$  is reported. The structure, refined using neutron diffraction data, as well as some preliminary results concerning the electrochemical performance are presented. A capacity of  $270 \text{ mAh g}^{-1}$  is obtained on the first charge. Capacity fade on cycling is significant for these early materials. © 1997 Elsevier Science S.A.

*Keywords:* Lithium-ion batteries; Cathodes; Manganese oxides

### 1. Introduction

The commercial success of rechargeable lithium-ion batteries, which are composed of a carbon anode, liquid electrolyte, and lithium transition metal cathode has finally laid to rest the belief in some quarters that rechargeable lithium cells, while potentially attractive, would not succeed in practice. Indeed, they are now competing successfully in the market place. In view of the realisation by manufacturers of portable electronic devices, such as mobile telephones and lap-top computers, that the development of these products depends at least as much on the electrochemistry as it does on the electronics, lithium-ion batteries are assured a bright future. However, the cost per cell must be reduced if lithium-ion technology is to penetrate the mass market [1]. This, in turn, means that the  $\text{LiCoO}_2$  cathode used in the first generation cells must be replaced by a cheaper alternative.  $\text{LiNiO}_2$  offers some improvement, however, it may be argued that lithium manganese oxide intercalation compounds offer the most attractive solution [1–3]. The arguments in favour of lithium manganese oxide cathodes have been well rehearsed, in summary they are the much lower cost of manganese compared with nickel or cobalt, lower toxicity, non-strategic nature of the materials, and familiarity within the battery industry. If rechargeable lithium batteries are to impact in a major way on the electric vehicle market, where cost per mile and tox-

icity are crucial factors, then lithium manganese oxide cathodes are an imperative. For such applications there is considerable interest in both 3 V and 4 V lithium manganese oxides, the former to be combined with a lithium metal anode. The advantage of lithium metal is its high gravimetric energy density compared with carbon, provided cycle life can be improved. Furthermore, safety concerns with high capacity carbons forces reconsideration of lithium anodes and hence 3 V cathodes. Cathodes based on lithium manganese oxide spinels are of course already at an advanced stage [1,4–11].

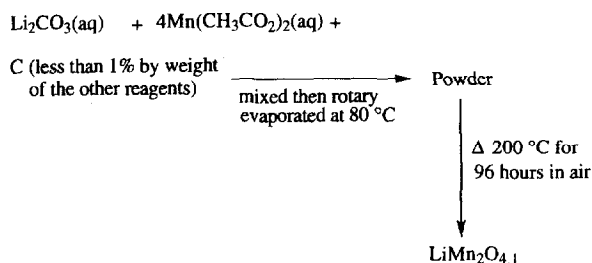
In this paper results are presented concerning two lithium manganese oxide cathodes. We have described previously an attractive, low temperature solution-based synthesis of a lithium manganese oxide spinel operating at 3 V, in which the addition of a small amount of carbon to the solution results in a cathode with a capacity retention on cycling some 50% better than the comparable material prepared without carbon [4,6,12]. The origin of this remarkable enhancement in performance, obtained at a nominal cost, is described for the first time. There is a great deal of interest in developing new Li–Mn–O phases which have the potential to combine low cost and low toxicity with high performance as a cathode in a rechargeable lithium battery. In this regard the synthesis of layered  $\text{LiMnO}_2$  has been a long-standing goal. Several groups have prepared layered lithium manganese oxides; these interesting materials are, however, in general hydrated,

contain protons or are non-stoichiometric [8,13,14]. In a recent review, Thackeray et al. [8] states that a manganese analogue of  $\text{LiCoO}_2$  has not been prepared. Here we report the synthesis of anhydrous and stoichiometric  $\text{LiMnO}_2$  with the  $\text{LiCoO}_2$  structure.

## 2. Experimental

### 2.1. 3 V spinel

This material is synthesised by the following solution-based route [4,6,12].



X-ray powder diffraction (XRD) was carried out using a Philips PW 1050 diffractometer operating in Bragg–Brentano geometry with  $\text{Cu K}\alpha$  radiation and an analysing monochromator to reduce fluorescence. Electrochemical studies were carried out using three-electrode cells composed of lithium metal counter and reference electrodes along with a composite working electrode all of which were immersed in 1 M  $\text{LiAsF}_6$  (Lithco, battery grade) in rigorously distilled propylene carbonate (Aldrich, 99+%) . The composite electrode consisted of a mixture of spinel:carbon black:polytetrafluoroethylene (PTFE) (80:13:7) by weight. The electrochemical experiments were controlled by a Biologic Macpile multichannel instrument. All electrochemical studies were carried out in an M Braun high integrity argon-filled glove-box.

### 2.2. Layered $\text{LiMnO}_2$

$\text{NaMnO}_2$  was synthesised by high temperature solid-state reaction between  $\text{Na}_2\text{CO}_3$  and  $\text{Mn}_2\text{O}_3$  at  $700^\circ\text{C}$  under flowing argon. The resulting solid was then refluxed in a solution of  $\text{LiBr}$  in *n*-hexanol (10-fold lithium excess) in order to effect the exchange of sodium by lithium. XRD and electrochemical studies were carried out as described above for the spinel except that in the case of the layered compound 1 M  $\text{LiClO}_4$  (Aldrich, 99.9%) in propylene carbonate (PC) was employed. The composite electrode was constructed in a similar manner to the spinel. Neutron diffraction was carried out using a time of flight instrument, POLARIS, at the Rutherford–Appleton Laboratory, Oxford.

## 3. Results and discussion

### 3.1. Enhanced capacity retention of 3 V lithium manganese oxide spinels

The performance of rechargeable lithium battery cathodes based on lithium manganese oxide spinels depends critically on the composition, defect structure, morphology, and particle size of the spinel which in turn is sensitive to the conditions used in its preparation. In particular, the temperature and oxygen partial pressure used in firing such spinels during the latter stages of synthesis influences the oxygen content. High temperatures and/or low oxygen partial pressures can lead to a  $\delta < 0$  in  $\text{LiMn}_2\text{O}_{4+\delta}$ , whereas low temperature firing and/or high oxygen partial pressures can yield more highly oxidised spinels with  $\delta > 0$ .

Our solution-based synthesis described in the experimental section has the advantage that it can be carried out in air. Furthermore, the particularly low firing temperature of  $200^\circ\text{C}$  yields a single-phase product with a high surface area while retaining the spinel structure but with the composition  $\text{LiMn}_2\text{O}_{4.1}$  as we have shown previously [4,6,12]. As a result, the average Mn oxidation state is 3.6 yielding a theoretical capacity for lithium intercalation of  $178 \text{ mAh g}^{-1}$  (compared with  $148 \text{ mAh g}^{-1}$  for the stoichiometric  $\text{LiMn}_2\text{O}_4$  spinel) based on the complete reduction of all  $\text{Mn}^{4+}$ , which occurs at a potential of 3 V versus the  $\text{Li}^+/\text{Li}$  couple. This corresponds to a capacity 20% greater than the stoichiometric spinel. Writing the formula for this compound in terms of a cation deficient spinel structure,  $\text{Li}_{0.98}[\text{Mn}_{1.95}\square_{0.05}]_{\text{oct}}\text{O}_4$  or  $\text{Li}_{0.93}[\text{Mn}_{1.95}\text{Li}_{0.05}]_{\text{oct}}\text{O}_4$ , indicates that, in order to reach the rock-salt stoichiometry, these defect spinels can support an increased capacity of only 7%. Low current discharge of three-electrode cells indicates that we can obtain a capacity very close to the theoretical value of  $178 \text{ mAh g}^{-1}$  based on the manganese valency. This suggests that lithium ions can be accommodated simultaneously in the face sharing 16c and 8a sites of the  $Fd\bar{3}m$  spinel space group.

The variation of specific capacity with cycle number for composite cathodes fabricated from  $\text{LiMn}_2\text{O}_{4.1}$  is shown in Fig. 1. Results are presented for two cathodes differing only in that in one case carbon (<1% by weight of the reagents used in the solution step) was added to the solution. The remarkable enhancement in capacity (50% higher after 300 cycles) due to the addition of carbon is evident. The specific capacity of  $90 \text{ mAh g}^{-1}$  at 300 cycles exhibited by the material prepared with carbon represents excellent capacity for such a 3 V lithium manganese oxide spinel.

The question arises as to the origin of the enhanced capacity retention with carbon. Our previous studies have established that the composition of the spinel is not altered by the addition of carbon, furthermore the powder XRD patterns of the spinels prepared with and without carbon are identical indicating that neither structure nor particle size are modified. Scanning electron micrographs (SEM) confirm the identical particle size distribution and morphology. Dissolution of the spinel

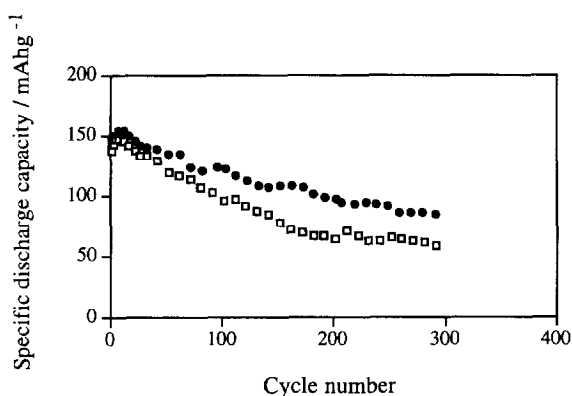


Fig. 1. Variation of the specific discharge capacity (based on mass of active material) with the number of cycles for the 3 V lithium manganese oxide cathode. Cycling was carried out galvanostatically at discharge and charge current densities of 1 and 0.5 mA cm<sup>-2</sup>, respectively, and between 3.7 and 2.0 V. The discharge rate was C/2: (●) lithium manganese oxide synthesised with carbon, and (□) the same material but synthesised without carbon.

in a solution of FeSO<sub>4</sub> and sulfuric acid after the firing step, has revealed that the carbon is still present. Measurement of the electronic conductivity carried out on pellets of the spinel prepared with and without carbon yielded identical results suggesting that the added carbon does not enhance electronic contact between the particles. None of the above factors is, therefore, responsible for the improved performance on cycling [4,6,12]. It has been known since the first report of lithium insertion into LiMn<sub>2</sub>O<sub>4</sub> that this is a two-phase reaction involving the formation of tetragonal Li<sub>2</sub>Mn<sub>2</sub>O<sub>4</sub>. As the degree of lithium intercalation increases, a greater proportion of the cubic, LiMn<sub>2</sub>O<sub>4</sub>, phase is converted to the tetragonal structure. Several authors have suggested that the 6.5% increase in volume on converting from the cubic to the tetragonal spinel is likely to result in a loss of particle contact on cycling and that this may be the origin of the greater capacity fade noted for cycling the 3 V spinel compared with cycling spinels over the 4 V plateau. The latter process is associated with the removal of lithium from LiMn<sub>2</sub>O<sub>4</sub> and its reinsertion; although this also involves a two-phase process, at least in part, the differences between the phases are more minor than are the differences between cubic and tetragonal spinel.

In order to examine conversion of the cathode between the cubic and tetragonal structures on cycling and to identify any differences with and without carbon, we have collected powder XRD data on the cathodes at different stages of cycling. Several cathodes were investigated each was subjected to cycling under identical conditions. The cathodes differed only in that half were fabricated using LiMn<sub>2</sub>O<sub>4.1</sub> prepared with carbon and half were fabricated from the spinel without carbon. Results from one cathode of each type are presented and discussed. XRD patterns were collected for both cathodes prior to cycling and indicated the presence of single-phase cubic material. The cathodes were then inserted into their respective cells and subjected to 50 cycles at a charge and discharge current of 0.75 mA cm<sup>-2</sup> between potential limits of 3.7 and 2.0 V. The 50th cycle was carried out at a somewhat lower current density of 0.25 mA cm<sup>-1</sup> between the same voltage limits. The cathodes were then removed from the cells at the end of discharge on the 50th cycle, powder XRD patterns were collected and the cathodes then returned to their respective cells. Cycling was continued at 0.75 mA cm<sup>-2</sup> and XRD patterns collected at the end of discharge on the 100th cycle. In this case a cycle at lower current was not employed. The critical XRD data are presented in Fig. 2. The broad and high background at low angles is due to the Mylar film used to seal the cathodes from the atmosphere during data collection. As a result of the low synthesis temperature, the peaks from the spinel are broad and somewhat low in intensity. Nevertheless, it is evident after 50 cycles that the powder XRD patterns for cathodes with and without carbon are identical, both displaying peaks associated with the tetragonal, lithium intercalated, spinel. In contrast, XRD patterns collected after discharge on the 100th cycle reveal a significant difference between the two cathode materials. The cathode fabricated without carbon consists of a mixture of cubic and tetragonal spinel phases whereas the materials synthesised with carbon added during the solution step is a single-phase, tetragonal, product. In a separate experiment carried out under identical conditions the cathodes with and without carbon were examined at the end of charge after 50 and 100 cycles and only cubic material was observed in all cases.

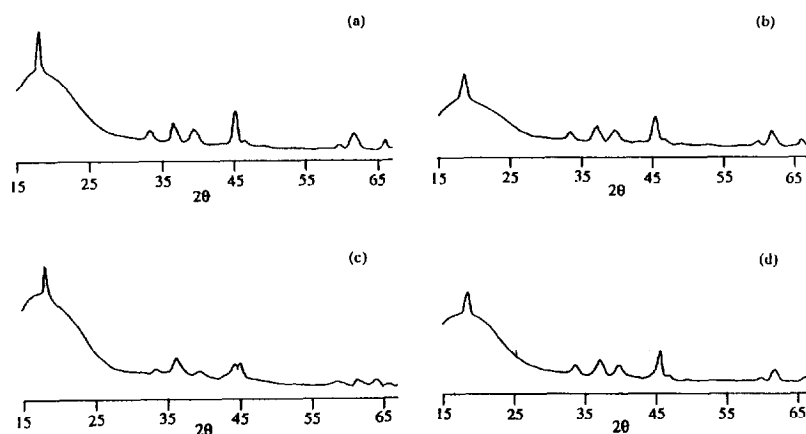


Fig. 2. Powder XRD patterns for the electrodes synthesised: (a) without; (b) with carbon after 50 cycles; (c) without, and (d) with carbon after 100 cycles. High background at low angles is due to material used to seal samples from air.

These results confirm that the capacity fade on cycling is due to the inability of the composite cathodes to transform completely between the cubic structure of the fully charged material and the tetragonal, fully discharged state. This probably results from the loss of contact between particles accompanying their contraction upon recharge from the tetragonal to the cubic phase. However, it is evident that recharging is always possible since no tetragonal material is observed in the fully charged electrodes. The loss of capacity must therefore arise from isolation occurring at or near the state of full charge, at which point, of course, the degree of particle contraction is at a maximum. Subsequent discharge can then occur only for those particles which are in simultaneous contact with the electrolyte and the rest of the electrode (the latter to maintain an electronic pathway to the current collector). Previous studies by Nohma et al. [15] examined only the phases present at the end of charge and as a result such studies did not reveal the important structural origin of the capacity fade. The second and more important conclusion to be drawn from the XRD results is that the small amount of carbon added to the solution during synthesis enables a more complete conversion of the entire powdered cathode from the cubic to the tetragonal phase thus enhancing the capacity retention compared with materials prepared without carbon. The detailed mechanism by which carbon achieves this is not yet fully understood. It may be that finely divided carbon between the particles ensures a more flexible composite cathode better able to accommodate the volume changes on cycling.

### 3.2. Layered $\text{LiMnO}_2$

Lithium manganese oxides do not, in general, favour the formation of low dimensional structures, instead they readily form three-dimensional close packed solids. In solid-state chemistry layered structures form in response to incompatible size or bonding requirements, the layered compounds can avoid otherwise intolerable stresses in the structure. Such a situation pertains with the ternary oxides composed of the larger alkali cations and the first row transition metal ions. The relative size of sodium in an octahedral oxygen site (1.02 Å) compared with manganese in the same environment (0.58 Å) and the more ionic nature of the Na–O bond helps to stabilise the layered structure [16]. By first forming sodium manganese oxide phases then ion exchanging lithium for sodium, kinetically stable but thermodynamically metastable

lithium manganese oxides with a layered structure may be prepared. Many inorganic solids with desirable ionic and electronic properties belong to the class of thermodynamically metastable compounds.

We have demonstrated the efficacy of this approach by synthesising  $\text{NaMnO}_2$  and then replacing sodium with lithium forming  $\text{LiMnO}_2$  with the structure of  $\text{LiCoO}_2$ . The layered structure has been verified by refinement using powder neutron diffraction data. The Rietveld method was employed as implemented in the program TF12LS based on the Cambridge Crystallographic Subroutine Library [17]. A final weighted profile  $R$  factor,  $R_{\text{wp}}$ , of 2.06% for the layered structure was obtained ( $R_{\text{expected}} = 0.60\%$ ). Attempts to fit a model based on tetragonal spinel,  $\text{Li}_2\text{Mn}_2\text{O}_4$ , yielded a significantly inferior fit,  $R_{\text{wp}} = 4.79\%$ . The final atomic parameters and other crystallographic data are given in Table 1. Further details concerning the structure refinement may be found in Ref. [18]. The  $\text{LiMnO}_2$  stoichiometry was confirmed by atomic absorption analysis. The presence of the Jahn–Teller active  $\text{Mn}^{3+}$  necessarily distorts the structure from the ideal rhombohedral space group  $R\bar{3}m$  of  $\text{LiCoO}_2$  to the monoclinic space group  $C2/m$  in order to accommodate a tetragonally distorted  $\text{MnO}_6$  octahedron. XRD data collected on de-intercalated  $\text{Li}_{1-x}\text{MnO}_2$  suggests that around  $(1-x) \approx 0.5$ , the structure is rhombohedral, consistent with reduction in the proportion of the Jahn–Teller active  $\text{Mn}^{3+}$  ion to 50%.

Only preliminary electrochemical studies have been carried out to date. We have established that the composite cathodes are stable up to at least 4.4 V in 1 M  $\text{LiClO}_4$  in rigorously distilled propylene carbonate. A charging curve for a three-electrode cell utilising this electrolyte is shown in Fig. 3. Charging was carried out at  $10 \mu\text{A cm}^{-2}$  and a total capacity of  $270 \text{ mAh g}^{-1}$  was obtained corresponding to the removal of 0.95 Li per formula unit. Charging at a higher current density of  $0.5 \text{ mA cm}^{-2}$  still delivers a capacity of  $200 \text{ mAh g}^{-1}$  up to the 4.3 V limit. Results of cycling the composite cathode at  $0.5 \text{ mA cm}^{-2}$  between potential limits of 3.4 and 4.3 V are shown in Fig. 4. There is a significant reduction in capacity even on the discharge immediately following the first charge, thereafter the capacity fade is more modest. While the initial capacity is encouraging, the cycling results are not so at this stage. Further work is in progress to understand how the structural changes accompanying the Jahn–Teller distortion occur and what influence this might have on the cycleability. It is important to recall that the early

Table 1  
Structural parameters for layered  $\text{LiMnO}_2$  <sup>a</sup>

Atom	Wyckoff symbol	x	y	z	$B_{\text{eq}}$	Site occupancy
Li1/Mn1	2d	0	0.5	0.5	2.4(2)	0.91/0.09(4)
Li2/Mn2	2a	0	0	0.0	0.72(6)	0.10/0.90(3)
O1	4i	0.2723(3)	0	0.7706(2)	0.68(4)	1

<sup>a</sup> Monoclinic, space group  $C2/m$  (no. 12);  $a = 5.4387(7)$  Å;  $b = 2.80857(4)$  Å;  $c = 5.3878(6)$  Å,  $\beta = 116.006(3)^\circ$ .  $\chi^2 = 11.83$ ;  $R_{\text{exp}} = 0.60\%$ ;  $R_{\text{p}} = 1.86\%$ ;  $R_{\text{wp}} = 2.06\%$ ;  $R_1 = 3.98\%$ .

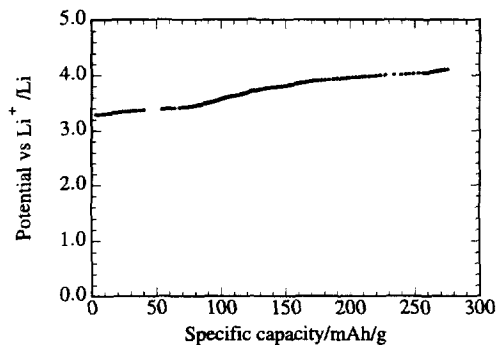


Fig. 3. Variation of electrode potential with capacity on charging at a current density of  $10 \mu\text{A cm}^{-2}$ .

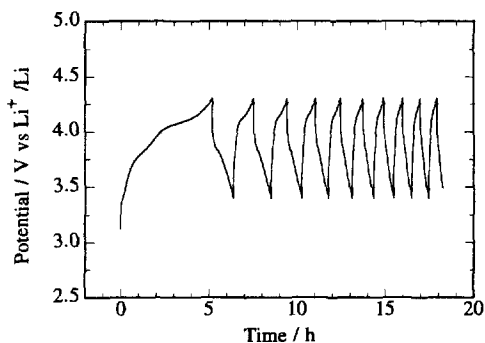


Fig. 4. Cycling of the  $\text{LiMnO}_2$  electrode at a current density of  $0.5 \text{ mA cm}^{-2}$  and between voltage limits of 3.4 to 4.3 V vs.  $\text{Li}^+/\text{Li}$ .

$\text{LiMn}_2\text{O}_4$  spinel materials exhibited an unacceptably large capacity fade on cycling. However, later optimisation has yielded materials with excellent cycleability. Whether ultimately commercially attractive or not the synthesis of layered, anhydrous and stoichiometric  $\text{LiMnO}_2$  with a structure analogous to  $\text{LiCoO}_2$  should lead to scientifically fertile studies in the future.

## Acknowledgements

PGB is indebted to the EPSRC for financial support under the EPSRC/DTI LINK Scheme and to NEDO.

## References

- [1] P.G. Bruce, *Proc. R. Soc. Trans. A*, (1996) in press.
- [2] J.N. Reimers, E.W. Fuller, E. Rossen and J.R. Dahn, *J. Electrochem. Soc.*, **140** (1993) 3396.
- [3] D. Guyomard and J.M. Tarascon, *J. Electrochem. Soc.*, **139** (1992) 937.
- [4] H. Huang and P.G. Bruce, *J. Electrochem. Soc.*, **141** (1994) L76.
- [5] H. Huang and P.G. Bruce, *J. Electrochem. Soc.*, **141** (1994) L106.
- [6] H. Huang and P.G. Bruce, *J. Power Sources*, **54** (1995) 52.
- [7] M.M. Thackeray, W.I.F. David, P.G. Bruce and J.B. Goodenough, *Mater. Res. Bull.*, **18** (1983) 461.
- [8] M.M. Thackeray, A. de Kock, M.H. Rossouw, D.C. Liles, R. Bittihn and D. Hodge, *J. Electrochem. Soc.*, **139** (1992) 363.
- [9] J.M. Tarascon and D. Guyomard, *Electrochim. Acta*, **38** (1993) 1221.
- [10] G. Pistoia and G. Wang, *Solid State Ionics*, **66** (1993) 135.
- [11] R.J. Gummow and M. M Thackeray, *J. Electrochem. Soc.*, **141** (1994) 1178.
- [12] (a) H. Huang and P.G. Bruce, *Proc. Int. Workshop on Advanced Batteries, Osaka, Japan, 1995*, p. 37; (b) Lithium Manganese Oxide using Carbon, *UK9305440.1*, Mar. 1993; (c) Lithiated Manganese Oxide using  $\text{Li}_2\text{CO}_3$ , *UK9305457.5*, Mar. 1993; (d) Lithium Manganese Oxide, *Int. Patent No. PCT/GB94/00545* (Sept. 1995).
- [13] F. Leroux, D. Guyomard and Y. Piffard, *Solid State Ionics*, **80** (1995) 299-306.
- [14] S. Bach, J.P. Pereira-Ramos, N. Baffier and R. Messina, *Electrochim. Acta*, **36** (1991) 1595.
- [15] T. Nohma, T. Saito, N. Furukawa and H. Ikeda, *J. Power Sources*, **26** (1989) 389.
- [16] R.D. Shannon, *Acta Crystallogr. A*, **32** (1976) 751.
- [17] J.C. Matthewman, P. Thompson and P.J. Brown, *J. Appl. Crystallogr.*, **15** (1982) 167.
- [18] A.R. Armstrong and P.G. Bruce, *Nature*, **381** (1996) 499.